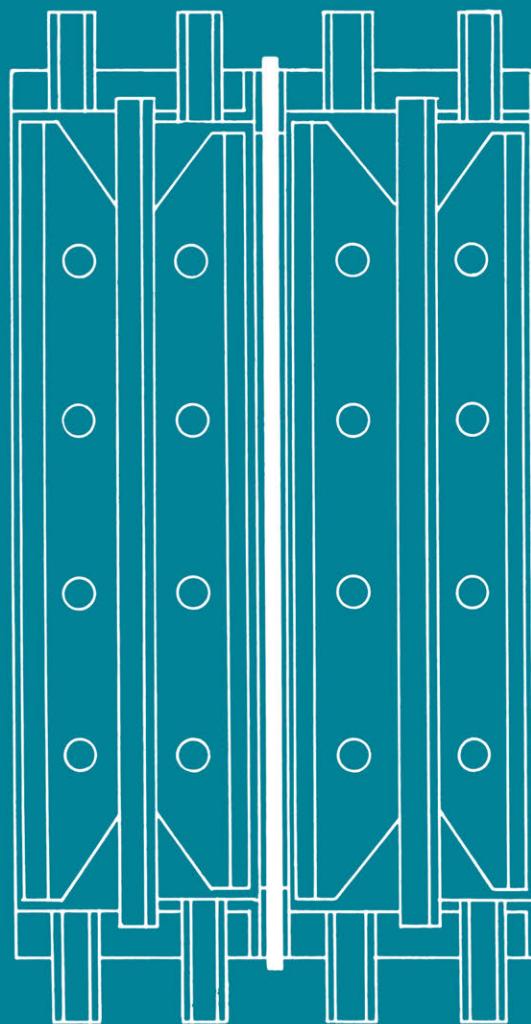


# INDUSTRIAL ELECTROCHEMISTRY



DEREK PLETCHER

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# **Industrial Electrochemistry**

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D E R E K P L E T C H E R

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To Gill, Linda and Ian

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## Preface

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Electrochemistry is clearly an important component of the technology of many quite diverse industries. Moreover, the future for electrochemical technology is bright and there is a general expectation that new applications of electrochemistry will become economic as the world responds to the challenge of more expensive energy, of the need to develop new materials and to exploit different chemical feedstocks and of the necessity to protect the environment.

In this situation, the present rather fragmentary state of electrochemical technology is disappointing. While there are many similarities in the underlying principles and even the practices of the electrochemically based industries, they are often not fully appreciated. Certainly, the R and D programmes in many industries are in the hands of those with little formal training and whose experience of and interest in other branches of electrochemistry is very limited. Moreover, the academic world has done little to help. Electrode processes are, too often, totally ignored in courses to both scientists and engineers and certainly electrochemical technology is almost never taught as a unified subject with an appropriate balance between fundamentals, engineering and applications. Overall, it is not surprising that the various strands have not interwoven and that scientists and engineers do not have a proper appreciation of the importance of electrochemical technology.

In the first half of 1979 I conducted a survey into the research and development needs of the various industries in Britain using electrochemical technology. The discussions I held with companies and academic institutions re-emphasized the need to seek to unify the various aspects of electrochemical technology into a single subject. The contacts developed also gave me a unique opportunity to assess the present state of the various industries and to collect the information on which this book is based. Certainly, I became fascinated by the breadth and scope of applied electrochemistry, in particular by the exciting advances of recent years, and felt prompted to write this book.

I have sought to apply a uniform approach to each group of industrial application applications and throughout I have attempted to emphasize and explain present attitudes and the current state of the various technologies. On the other hand, I should emphasize that I have never set out to discuss patent cells or devices or to compare the technologies of competing companies since it seems to me that such a discussion is only of interest to the potential customer. Also, I have resisted the

temptation to discuss the many potential applications of electrochemistry where it is a matter of conjecture whether they will be economically or socially viable.

Hence I have set out to produce a readable account of real industrial electrochemistry which I hope might be useful to the student who is considering a career in electrochemistry and interesting to those already engaged in R and D in one branch of the subject and who would benefit from some knowledge of other topics within electrochemical technology.

I would like to express my gratitude to the many who have contributed to the appearance of this book. The most obvious are those who have kindly persuaded their companies to release photographs to illustrate the text. There are, however, many other friends and colleagues who have helped with specific information and references and even more, both inside and outside the Electrochemistry Group in Southampton, who by discussions over a long period of time have stimulated my interest in various topics. Perhaps the many will forgive me if I make special mention of Professor Martin Fleischmann and Dr Gordon Lewis. It is traditional to thank the typist but in my case I owe a particular debt to Mrs Kate Welfare for her improvements made during typing and her endless patience during the several revisions. Finally, I must thank my family, particularly my wife but also my parents and children, for their continuous support and understanding during my many absences from their lives.

September 1981

Derek Pletcher

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# List of Symbols

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The following is a list of symbols used repetitively throughout the text.

$C$	Capacitance; also capacity
$C_i$	Concentration of species $i$
$C_i^\sigma$	Concentration of species $i$ at the electrode surface
$C_i^\infty$	Concentration of species $i$ in the bulk solution
$D_i$	Diffusion coefficient of species $i$
$d_e$	Equivalent diameter of a cell
$E$	Potential applied to or measured at an electrode versus a reference electrode
$E_e$	Equilibrium potential (also termed the reversible potential) for an electrode process measured versus a reference electrode
$E_e^A$	Equilibrium potential of the anode reaction versus a reference electrode
$E_e^C$	Equilibrium potential of the cathode reaction versus a reference electrode
$E_e^\ominus$	Standard electrode potential for an electrode reaction versus a reference electrode
$E_{\text{CELL}}$	Potential of a cell, i.e. $E^A - E^C$
$E_{\text{CORR}}$	Corrosion potential
$E_{\text{pzc}}$	Potential of zero charge versus a reference electrode
$F$	The Faraday
$\Delta G$	Free energy change in a reaction per mole
$I$	Measured or applied current density
$I_L$	Limiting current density (commonly the mass-transport-limited current density)
$I_0$	Exchange current density
$\overline{I}$	Partial cathodic current density
$\tilde{I}$	Partial anodic current density
$I_{\text{CORR}}$	Corrosion current density
$k$	Rate constant for a chemical process
$\overrightarrow{k}$	Rate constant for a cathodic process
$\overleftarrow{k}$	Rate constant for an anodic process
$k_0$	Rate constant for an electron transfer reaction at $E = 0$

$k_0^\ominus$	Standard rate constant for an electrode process
$l$	Characteristic length in a cell
$M$	Molecular weight
$m$	Number of moles of electroactive species
$N$	Number of nuclei
$n$	Number of electrons transferred per molecule of electroactive species in the electrode reaction
$Q$	Charge passed in an electrolysis
$q$	Charge density
$R$	Resistance; also the gas constant
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$T$	Temperature
$t$	Time
$\bar{u}$	Flow velocity
$V$	Cell voltage
$x$	Distance from an electrode surface
$\alpha$	Transfer coefficient
$\beta$	Inverse of the slope of a $\log I$ vs $E$ plot
$\delta$	Thickness of a boundary or diffusion layer
$\eta$	Overpotential
$\eta_A$	Overpotential at the anode
$\eta_C$	Overpotential at the cathode
$\theta$	Material yield; also surface coverage
$\mu$	Viscosity
$\rho$	Density
$\sigma$	Surface force energy per mole
$\phi_M$	Absolute potential at electrode surface
$\phi_S$	Absolute potential of the bulk solution phase
$\phi_2$	Absolute potential at the plane of closest approach of cations
$\phi$	Current efficiency
$\omega$	Rotation rate

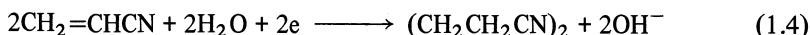
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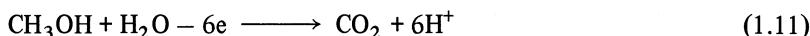
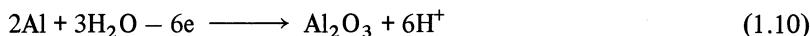
# 1 Fundamental Concepts

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An electrochemical reaction is a heterogeneous chemical process involving the transfer of charge to or from an electrode, generally a metal or semiconductor. The charge transfer may be a cathodic process in which an otherwise stable species is reduced by the transfer of electrons from an electrode. Examples of such reactions important in electrochemical technology include

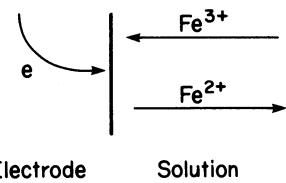


Conversely, the charge transfer may be an anodic process where an otherwise stable species is oxidized by the removal of electrons to the electrode and relevant examples would be

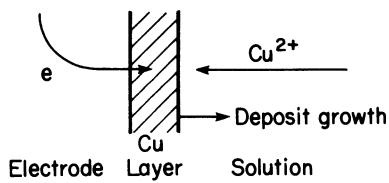


Some typical cathodic and anodic processes are also shown schematically in Fig. 1.1.

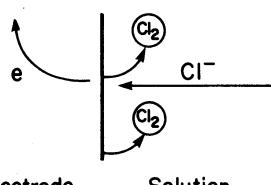
Of course, electrochemistry is only possible in a cell which contains both an anode and a cathode and, owing to the need to maintain an overall charge balance, the amount of reduction at the cathode and oxidation at the anode must be equal. The total chemical change in the cell is determined by adding the two individual electrode reactions; thus the chemical change in a lead/acid battery is obtained by



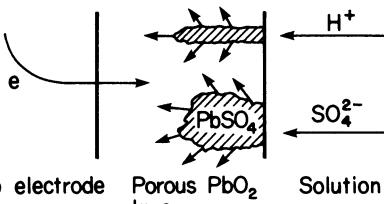
(a) Simple electron transfer,  
e.g.  $\text{Fe}^{3+} + \text{e} \rightarrow \text{Fe}^{2+}$



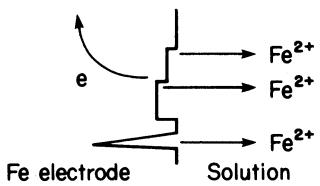
(b) Metal deposition, e.g. Cu



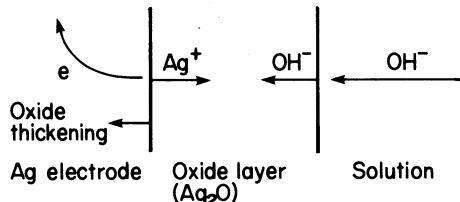
(c) Gas evolution, e.g.  $\text{Cl}_2$



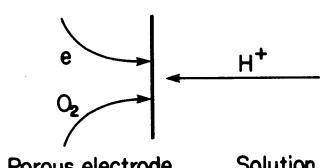
(d) Surface film transformation,  
e.g.  $\text{PbO}_2 \rightarrow \text{PbSO}_4$



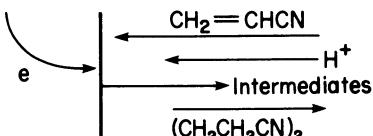
(e) Corrosion, e.g. Fe in active regime



(f) Oxide formation, e.g.  $\text{Ag}_2\text{O}$



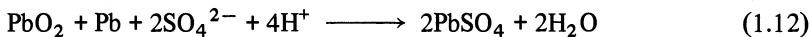
(g) Gas reduction in porous gas diffusion electrode, e.g.  $\text{O}_2$



(h) Electron transfer with coupled chemistry,  
e.g.  $\text{CH}_2=\text{CH}-\text{CN} \rightarrow (\text{CH}_2\text{CH}_2\text{CN})_2$

Figure 1.1 Schematic representations of some common types of electrode processes. For simplicity, ions of the background electrolyte (numerically in large excess) and counter ions are not shown.

adding reactions (1.5) and (1.9), i.e.



and that in a water electrolyser by adding reactions (1.1) and (1.6), i.e.



Moreover for any electrochemical reaction to occur in the cell, electrons must pass through the circuit interconnecting the two electrodes. Hence the current  $I$  is a convenient measure of the rate of the cell reaction while the charge  $Q$  passed during a period  $t$  indicates the total amount of reaction which has taken place; indeed, the charge required to convert  $m$  moles of starting material to product in a  $ne$  electrode reaction is readily calculated using Faraday's law, i.e.

$$Q = \int_0^t I dt = mnF \quad (1.14)$$

When the two electrodes in a cell are interconnected by an external circuit, however, the cell reaction will not necessarily take place. It will only occur spontaneously if the free-energy change associated with the overall cell reaction is negative and even then its rate, i.e. the current, will depend on the kinetics of the two electrode reactions. The free-energy change for reaction (1.12) is, indeed, negative and a cell based on electrode reactions (1.5) and (1.9) may therefore be used as a battery. Its effectiveness as a secondary battery depends on cell potential (related to the magnitude of the free-energy change for (1.12)), the current that may be drawn from the cell (the kinetics of the electrode reactions) and the ability to recharge the cell (to reverse reaction (1.12) by applying an external potential and to obtain the Pb and  $\text{PbO}_2$  in a suitable physical form for further discharge). On the other hand the free energy of reaction (1.13) is positive and hence to electrolyse water it is necessary to supply energy by applying an external potential. The potential required will depend on the magnitude of the free-energy change and also on the kinetics of the two electrode reactions.

It will already be clear that to understand the way in which the various experimental parameters can affect the performance of electrochemical cells and, in particular, the behaviour of the two electrode reactions, it will be necessary to have a knowledge of the thermodynamics and kinetics of electrode reactions. Thus the purpose of this chapter is to develop the concepts and equations which will be used in electrochemical technology.

First, however, we need to recognize the nature of electrode reactions. Perhaps the simplest electrode reaction is one which interconverts, at an inert surface, two species O and R which are completely stable and soluble in the electrolysis medium containing an excess of electrolyte which is electroininactive:



Even in this case the electrode reaction is a sequence of more basic steps; to maintain a current it is essential to supply reactant to and to remove the product

## 4 Industrial Electrochemistry

from the electrode surface, as well as for the electron transfer reaction at the surface to occur. Hence, for example, in experimental conditions where O is reduced to R, the electrode reaction must have three steps



and since the rate of reduction or cathodic current is determined by the rate of the overall sequence, it must be dependent on the rate of the slowest step. Thus to understand the characteristics of such an electrode reaction, we need to know about both mass transport and electron transfer.

An examination of reactions (1.1)–(1.11) at the beginning of this chapter quickly shows that electrode reactions of interest in electrochemical technology are seldom that simple. They involve multiple electron transfers and at least three additional types of basic steps also occur.

### (a) Chemical reactions

The species formed by electron transfer may not be stable in the electrolysis medium: it may only be an intermediate which undergoes chemical change to form the observed product. In favourable conditions there may be a single reaction pathway leading to one product but with reactive intermediates it is common for there to be competitive reactions leading to a mixture of products. In general the chemical reaction may be a homogeneous process occurring as the species R is transported away from the surface or a heterogeneous process occurring while the species R is adsorbed on the surface (see below). Processes (1.4) and (1.11) are examples where such following chemical reactions are important.

Less frequently it is found that the electroactive species O is not the major species in bulk solution but is only formed by a chemical process, i.e. the electrode reaction is disturbing an equilibrium in homogeneous solution. An example is the reduction of acetic acid to hydrogen which proceeds via dissociation prior to electron transfer.

### (b) Adsorption

Sequence (1.16)–(1.18) assumes that electron transfer occurs at the electrode surface but without formation of a bond between the surface and either O or R. This may not be the case and for the reaction to proceed it may be necessary for reactants, intermediates or product to be adsorbed on the electrode.

Moreover adsorption has other important roles in electrochemical technology. In electrocatalysis, e.g. reaction (1.1) at Pt, adsorption of intermediates is a key step since their presence on the surface provides alternative lower energy pathways

(see later). Also adsorption of species not directly involved in the electron transfer process is used to modify the net electrode reaction, e.g. additives used for the modification of electroplates and in the inhibition of corrosion.

*(c) Phase formation*

The electrode reaction may involve the formation of a new phase (e.g. the electrodeposition of metals in plating, refining and winning or bubble formation when the product is a gas) or the transformation of one solid phase to another (e.g. reaction (1.5)). The formation of a new phase is itself a multistep process requiring both nucleation and subsequent growth, and crystal growth may involve both surface diffusion and lattice growth.

Since electrode reactions commonly involve the transfer of several electrons, the complications (a)–(c) can occur sandwiched between as well as preceding or following electron transfer. Moreover very complex situations do arise. Thus, for example, reaction (1.5) is likely to involve electron transfer, diffusion, chemical reactions (protonation and hydration equilibria as well as sulphation), phase transformation and adsorbed intermediates! In this chapter, however, we shall take the approach of considering each fundamental type of process in turn. The equations that will arise must be regarded as idealistic and simplistic but will generally be sufficient for us to understand most cells in industrial practice provided we can recognize which of the fundamental steps in the overall electrode processes predominantly determine the cell characteristics.

## 1.1 ELECTRON TRANSFER

We shall discuss the electrode reaction



occurring in the cell shown schematically in Fig. 1.2. It contains two electrodes, a small and inert working electrode (WE) and a large platinum electrode, both in aqueous acid (1 M) but separated by a glass frit. Hydrogen gas is bubbled over the surface of the platinum so that this electrode is effectively a normal hydrogen electrode (NHE) whose potential is by convention taken to be 0.0 V. The solution in the working electrode compartment is deoxygenated and contains low concentrations,  $C_{\text{O}}^{\infty}$  and  $C_{\text{R}}^{\infty}$  of the electroactive species O and R respectively. The relative areas of the two electrodes are chosen so that the NHE is never polarized (its potential remains at zero even when current is passed), so that the characteristics of the cell are determined solely by the behaviour at the WE. Moreover low concentrations of O and R are used so that the  $IR$  drop through the solution between the electrodes is never significant.

As with any chemical process, it is necessary to consider both the thermodynamics and the kinetics of the electrode process. If we connect the two electrodes and monitor the cell potential while allowing no current to flow, the potential of the working electrode will eventually reach a steady-state value indicating that the cell

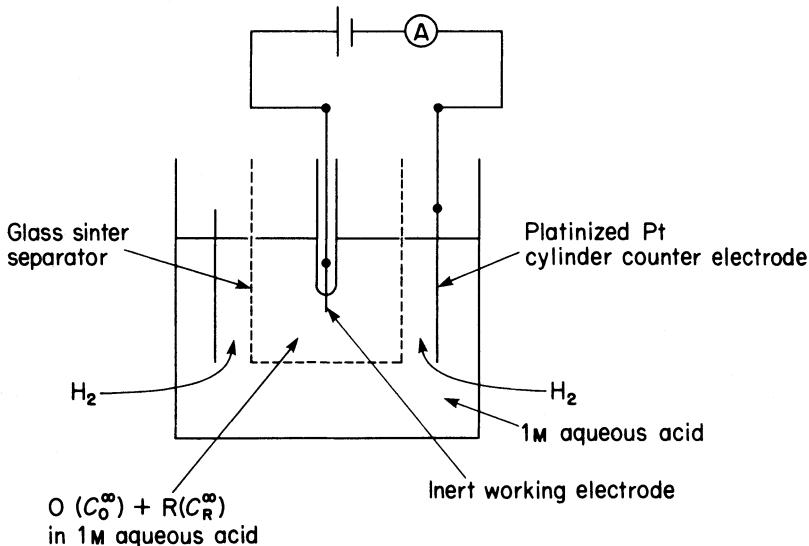


Figure 1.2 Hypothetical electrochemical cell used in the development of equations describing the thermodynamics and kinetics of electron transfer.

is in equilibrium. The potential of the WE is then given by a purely thermodynamic equation, the Nernst equation

$$E_e = E_{e^\ominus} + \frac{RT}{nF} \ln \left( \frac{C_O^\sigma}{C_R^\sigma} \right) \quad (1.20)$$

where the equilibrium (or reversible) potential is related to the standard potential  $E_{e^\ominus}$  of the couple O/R and the surface concentrations  $C_O^\sigma$  and  $C_R^\sigma$  of O and R. Clearly the standard potential is the particular equilibrium potential when the surface concentrations of O and R are equal. In the experiment outlined above, no current has passed through the cell and therefore the surface concentrations were identical to those prepared in the bulk solution. Hence we may write

$$E_{\text{CELL}} = E_{\text{WE}} - E_{\text{NHE}} = E_{\text{WE}} - 0$$

or

$$E_{\text{CELL}} = E_{e^\ominus} + \frac{RT}{nF} \ln \left( \frac{C_O^\infty}{C_R^\infty} \right) \quad (1.21)$$

While no current is flowing and there is no net chemical change in the cell, there must be a dynamic equilibrium at the surface of the WE, i.e. the reduction of O and oxidation of R are both occurring but the processes are of equal rate

$$\vec{I} = \tilde{I} = I_0 \quad (1.22)$$

where  $I_0$  is an important kinetic characteristic of an electron transfer process known as the exchange current density.

If the potential of the WE is made more negative than  $E_e$ , equation (1.20) requires that to re-establish equilibrium, the surface concentrations of O and R must change. In fact a decrease in the ratio  $C_O^\sigma/C_R^\sigma$  is necessary and this can only be brought about by the conversion of O to R by the passage of a cathodic current. Conversely if the potential of the WE is made more positive than  $E_e$ , an anodic current should be observed.

These simple predictions about the  $I-E$  behaviour of the cell in Fig. 1.2 are based only on thermodynamics and it is also essential to consider the kinetics of electron transfer. The rate of reduction of O depends only on a rate constant and the surface concentration of O, i.e. the concentration at the site where electron transfer is occurring:

$$\text{Rate of reduction of O} = \vec{k} C_O^\sigma \quad (1.23)$$

and therefore the reduction current density is given by

$$\vec{I} = nF\vec{k}C_O^\sigma \quad (1.24)$$

But the rate constant for a heterogeneous electron transfer process has a particular property; it is dependent on the potential field close to the surface driving the movement of electrons and hence on the applied electrode potential  $E$ . We shall assume, as is found experimentally, that the dependence is of the form

$$\vec{k} = \vec{k}_0 \exp \left[ - \left( \frac{\alpha nF}{RT} E \right) \right] \quad (1.25)$$

therefore

$$\vec{I} = nF\vec{k}_0 C_O^\sigma \exp \left[ - \left( \frac{\alpha nF}{RT} E \right) \right] \quad (1.26)$$

$\alpha$  is known as the transfer coefficient. It has a value between 0 and 1, commonly close to 0.5.

The corresponding equations for the oxidation of R, which occurs simultaneously with the reduction of O, are

$$\text{Rate of oxidation} = \vec{k} C_R^\sigma \quad (1.27)$$

$$\vec{I} = nF\vec{k}C_R^\sigma \quad (1.28)$$

$$\vec{k} = \vec{k}_0 \exp \left[ \frac{(1-\alpha)nF}{RT} E \right] \quad (1.29)$$

and

$$\vec{I} = nF\vec{k}_0 C_R^\sigma \exp \left[ \frac{(1-\alpha)nF}{RT} E \right] \quad (1.30)$$

The observed current density at any potential is given by

$$I = \vec{I} - \bar{I}$$

or

$$I = nF \left\{ \vec{k}_0 C_O^\sigma \exp \left[ - \left( \frac{\alpha nF}{RT} E \right) \right] - \vec{k}_0 C_R^\sigma \exp \left[ \left( \frac{(1-\alpha)nF}{RT} E \right) \right] \right\} \quad (1.31)$$

We have already noted that at the equilibrium potential  $E_e$ , there is no net current and we may therefore write

$$I_0 = \vec{I} = \vec{I} = nF \vec{k}_0 C_O^\sigma \exp \left[ - \left( \frac{\alpha nF}{RT} E_e \right) \right] = nF \vec{k}_0 C_R^\sigma \exp \left[ \left( \frac{(1-\alpha)nF}{RT} E_e \right) \right] \quad (1.32)$$

at this potential. If we now define a new parameter, the overpotential, defined by

$$\eta = E - E_e \quad (1.33)$$

which may be regarded as the potential of the WE using the equilibrium potential of the O/R couple as the reference state, manipulation of (1.31), (1.32) and (1.33) allows us to obtain the simpler and more fundamentally important equation

$$I = I_0 \left\{ \exp \left[ - \left( \frac{\alpha nF}{RT} \eta \right) \right] - \exp \left[ \left( \frac{(1-\alpha)nF}{RT} \eta \right) \right] \right\} \quad (1.34)$$

This equation, known as the Butler–Volmer equation, states that we may calculate the form of the  $I$ – $E$  relationship for any solution of O and R if we know

- (1) The standard potential  $E_e^\ominus$  for the couple O/R.
- (2) The exchange current  $I_0$ .
- (3) The transfer coefficient  $\alpha$ .

Moreover it clearly indicates that at high negative overpotentials, i.e. at potentials more negative than the equilibrium potential by say 100 mV, the cathodic current will increase exponentially as the potential is made more negative (the second term is negligible compared with the first). Conversely, very positive to the equilibrium potential the anodic current will increase exponentially with increasing potential, i.e. at high cathodic overpotentials  $\vec{I} \gg \vec{I}$

$$I = \vec{I} = I_0 \exp \left[ - \left( \frac{\alpha nF}{RT} \eta \right) \right] \quad (1.35)$$

or

$$\log I = \log I_0 - \frac{\alpha nF}{2.3RT} \eta \quad (1.36)$$

and at high anodic overpotentials  $\vec{I} \gg \vec{I}$  and

$$I = \vec{I} = I_0 \exp \left[ \left( \frac{(1-\alpha)nF}{RT} \eta \right) \right] \quad (1.37)$$

or

$$\log I = \log I_0 + \frac{(1-\alpha)nF}{2.3RT} \eta \quad (1.38)$$

Equations (1.36) and (1.38) are the Tafel equations, and lead to an experimental method of determining  $I_0$  and  $\alpha$ . The  $I-E$  data for a solution of O and R (note that  $E_e$ ,  $\eta$  and  $I_0$  all depend on  $C_O^\sigma$  and  $C_R^\sigma$ ) are replotted as  $\log |I|$  versus  $\eta$ , and  $I_0$  and  $\alpha$  may be obtained from the intercepts and slopes respectively of the linear portions of the graph (see Fig. 1.3). At low overpotentials the mathematical approximation is no longer appropriate and the resulting deviation from linearity may be seen in the figure. Indeed for very low overpotentials,  $\eta < 10$  mV, a different approximate  $I-\eta$  relationship may be deduced. Expanding the exponentials as series and noting that for low values of the argument, second- and higher-order terms will be negligible, one obtains

$$I = I_0 \left( 1 - \frac{\alpha nF}{RT} \eta \dots \right) - I_0 \left( 1 + \frac{(1-\alpha)nF}{RT} \eta \dots \right)$$

or

$$I = \frac{-I_0 nF}{RT} \eta \quad (1.39)$$

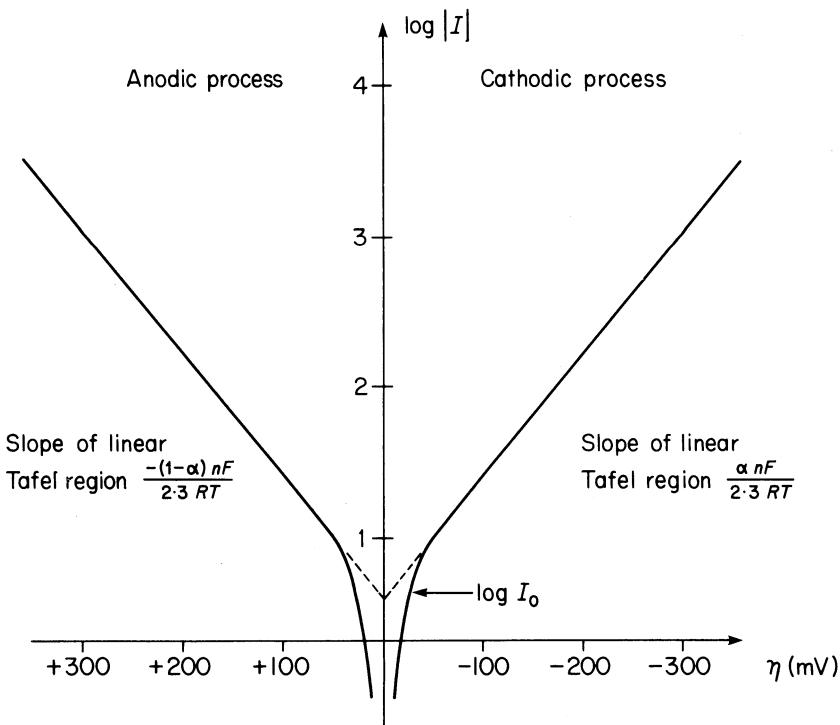


Figure 1.3 Experimental determination of  $I_0$  and  $\alpha$  using the Tafel equations, equations (1.36) and (1.38).

## 10 Industrial Electrochemistry

and over the restricted range of potentials close to the equilibrium potentials, the  $I-\eta$  relationship should be linear with a slope giving the exchange current density.

The exchange current density depends on the concentration of O and R in solution and hence it is often convenient to define a kinetic parameter without such a dependence. It is usual to use the standard rate constant  $k_0^\ominus$ , the rate constant at the standard electrode potential. It may be calculated from the exchange current for any solution using the equation

$$I_0 = nFk_0^\ominus(C_O^\infty)^{1-\alpha}(C_R^\infty)^\alpha \quad (1.40)$$

It should also be noted that, in practice, it is not always possible to estimate kinetic parameters from  $I-E$  data. Some redox couples O/R have kinetic parameters such that the rate of electron transfer is, under all experimental conditions, fast compared with the prevailing rate of mass transport; in such circumstances the electron transfer at the surface will appear to be in equilibrium and the ratio of surface concentrations  $C_O^\infty/C_R^\infty$  can be calculated from the Nernst equation. Such electrode reactions are called by electrochemists reversible. On the other hand, irreversible reactions are those where the electron transfer process is not in equilibrium and the surface concentrations must be calculated from the Tafel equation. The  $I-E$  response of reversible and irreversible processes are quite different (see Fig. 1.10 later) and as implied above the distinction depends on the value of the standard rate constant  $k_0^\ominus$  for the couple. For a steady-state experiment in an unstirred solution, it will be found that

$$k_0^\ominus < 5 \times 10^{-3} \text{ cm s}^{-1} \quad \text{irreversible process}$$

$$k_0^\ominus > 2 \times 10^{-2} \text{ cm s}^{-1} \quad \text{reversible process}$$

So far the treatment of electron transfer is somewhat pragmatic and gives little insight into the factors which determine their properties. To remedy this to some extent, one should first look at Fig. 1.4 which shows the energy level diagram for a particular but typical simple electrode reaction

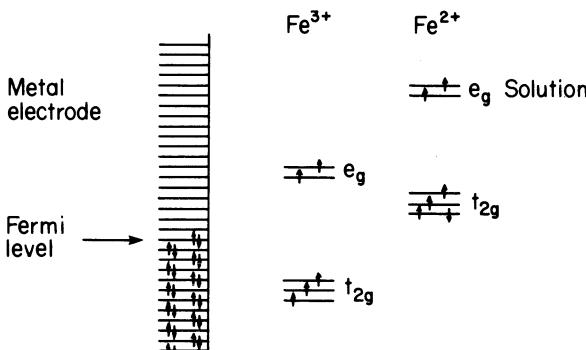


Figure 1.4 Energy level diagram for the electrons in the metal and on the ions in solution.

In the inert metal electrode (which only acts as a sink or source of electrons) the electronic energy levels are close together and the valence electrons may be considered to be in orbitals delocalized over the whole metal lattice. The effect of changing the electrode potential is to pump electrons into or away from the metal and hence to vary the highest filled orbital, known as the Fermi level; as the potential is made more negative, the number of filled orbitals increases, making the transfer of electrons from the electrode to the ferric ions in solution more likely. The energy levels for the ferrous and ferric ions in solution are, however, discrete (only the d-electrons need be considered) and those for the ferric ion lie lower than those for the ferrous ion because of less electronic repulsion. Thermodynamic predictions about oxidation or reduction will depend on the relative energy levels in the electrode and for the species in solution taking into account the potential and concentrations of the species.

Our understanding of the factors which control the kinetics of electrode reactions can be increased by applying transition state theory to the heterogeneous process occurring in a potential gradient. In general the theory is based on the concept that the rate of reaction is determined by an activation barrier in free energy, i.e. the rate constant is given by the equation

$$k = Z \exp\left(-\frac{\Delta G_{\ddagger}}{RT}\right) \quad (1.42)$$

where  $Z$  is the frequency factor and  $\Delta G_{\ddagger}$  the energy of activation. In electrochemistry we must consider how a potential difference,  $\phi_M - \phi_S$ , between the metal and the solution can be taken into account. Figure 1.5 shows the free-energy curves for the initial and final states of the electrochemical reduction at two overpotentials. Variation of the overpotential will cause  $\phi_M - \phi_S$  to change and because O and R (in general) and the electrons are charged species their free energies will depend on the electric potentials in the phases where they reside:

$$G_O = G_O' + Z_O F \phi_S - nF \phi_M \quad (1.43)$$

$$G_R = G_R' + Z_R F \phi_S \quad (1.44)$$

where  $G_O$  and  $G_R$  are the free energies of the initial and final states of the electrode reaction with a potential difference across the interface,  $G_O'$  and  $G_R'$  are the free energies in the absence of field and  $Z_O$  and  $Z_R$  are the charges on O and R respectively. Making the overpotential more negative makes the solution more positive and destabilizes O and R (assuming they are positively charged), although since the charges on O and R must be different their potential energy curves will be shifted to different extents by the change in overpotential. It is apparent from Fig. 1.5 that the free energy  $G_{\ddagger}$  of the transition state is less sensitive than  $G_O$  and  $G_R$  to a change in  $\phi_M - \phi_S$ . Hence

$$G_{\ddagger} = \text{constant} + \alpha nF(\phi_M - \phi_S) \quad (1.45)$$

a statement which is equivalent to noting that only a fraction of an applied overpotential will affect the rate of an electrode reaction. The cathodic current is

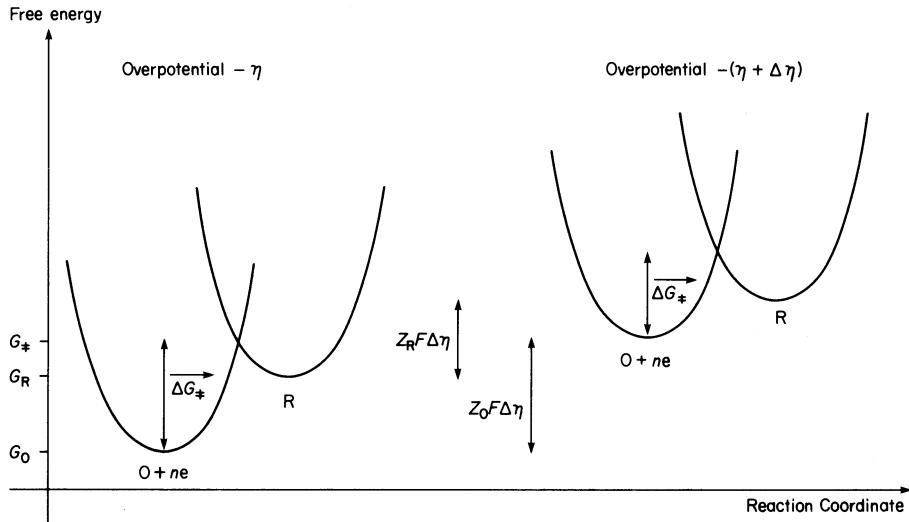


Figure 1.5 Free-energy curves for the initial state ( $O + ne$ ) and the final state ( $R$ ) of a simple  $ne$  transfer reaction at two overpotentials. Note that (a) the additional overpotential  $-\Delta\eta$  destabilizes both  $O$  and  $R$  if both are positively charged –  $O$  is more positively charged and is destabilized to a greater extent – and (b)  $\Delta\vec{G}_\ddagger$  decreases by less than  $nF\Delta\eta$ , in fact  $\alpha nF\Delta\eta$ .

therefore given by

$$I = nFZC_O^\sigma \exp\left(-\frac{\text{constant} + \alpha nF(\phi_M - \phi_S)}{RT}\right) \quad (1.46)$$

which will lead to a Tafel-type equation. It will also be found that the fraction  $\alpha$  is equivalent to the transfer coefficient of equation (1.25) and the Tafel equation (1.36).

The application of transition state theory to electrode processes emphasizes that the standard rate constant will be determined by an activation energy and that the activated complex will have a structure intermediate between those of  $O$  and  $R$ . It is therefore reasonable to postulate that the activation energy depends on the extent of rearrangement of the solvent shell or ligands or changes in molecular geometry necessary when reducing  $O$  to  $R$ . Indeed such correlations are observed and the standard rate constant is found to be low when

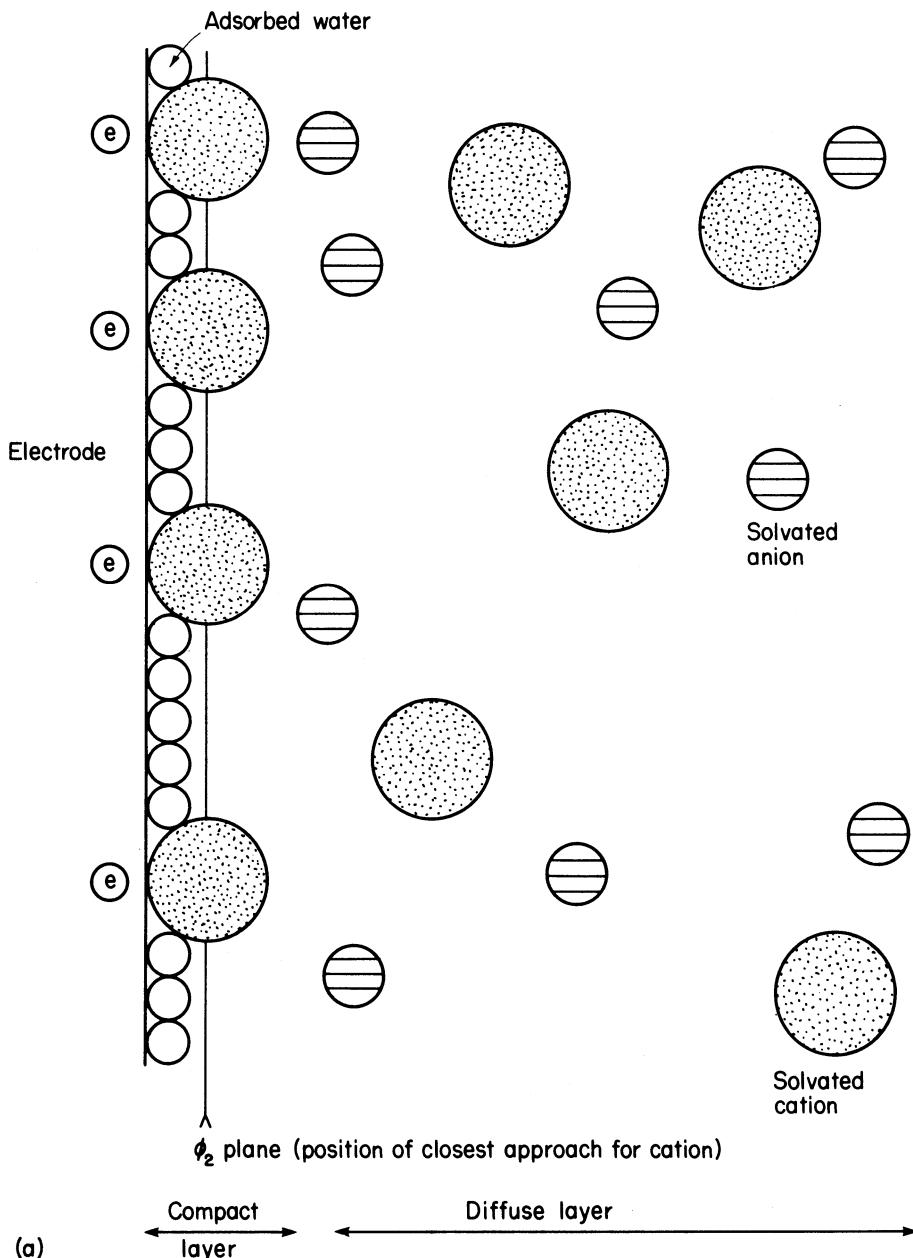
- (a) The species  $O$  and  $R$  have different geometries,
- (b) The coordination number of a transition metal in  $O$  and  $R$  are different, or
- (c) The rate of ligand substitution is low.

The data in Table 1.1 illustrate these trends. First it should be noted that the standard rate constant for apparently simple one-electron reactions range from  $10^{-7}$  to  $10 \text{ cm s}^{-1}$ . Where the inner coordination sphere of transition-metal

Table 1.1 Standard electrode potentials and kinetic characteristics for some simple electrode reactions

Couple	Electrode + medium	$E_e^\ominus$ (V vs SCE)	$k_0^\ominus$ (cm s <sup>-1</sup> )	$\alpha$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}/\text{Cr}(\text{H}_2\text{O})_6^{2+}$	Hg, 0.1 M HClO <sub>4</sub>	-0.72	$2 \times 10^{-5}$	0.45
$\text{Fe}(\text{H}_2\text{O})_6^{3+}/\text{Fe}(\text{H}_2\text{O})_6^{2+}$	Pt, 1 M HClO <sub>4</sub>	+0.50	$5 \times 10^{-3}$	0.42
$\text{Co}(\text{H}_2\text{O})_6^{3+}/\text{Co}(\text{H}_2\text{O})_6^{2+}$	Pt, 5.6 M HClO <sub>4</sub>	+1.84	$2 \times 10^{-7}$	0.47
$\text{Ce}(\text{H}_2\text{O})_6^{4+}/\text{Ce}(\text{H}_2\text{O})_6^{3+}$	Pt, 1 M HClO <sub>4</sub>	+1.47	$2 \times 10^{-5}$	0.52
$\text{Eu}(\text{H}_2\text{O})_6^{3+}/\text{Eu}(\text{H}_2\text{O})_6^{2+}$	Hg, 1 M NaClO <sub>4</sub> pH 3	-0.63	$3 \times 10^{-4}$	0.58
$\text{Cr}(\text{CN})_6^{3-}/\text{Cr}(\text{CN})_6^{4-}$	Hg, 1 M KCN	-	0.22	0.45
$\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$	Pt, 1 M KCl	+0.20	$9 \times 10^{-2}$	0.50
Anthracene/anion radical	Hg, DMF, 0.1 M Bu <sub>4</sub> NI	-1.95	4	0.52
Naphthalene/anion radical	Hg, DMF, 0.1 M Bu <sub>4</sub> NI	-2.49	1	0.56
Cyclooctatetraene/anion radical	Hg, DMF, 0.1 M Bu <sub>4</sub> NI	-1.62	$9 \times 10^{-3}$	0.36
Sym-Dibenzocyclooctatetraene/anion radical	Hg, DMF, 0.1 M Bu <sub>4</sub> NClO <sub>4</sub>	-1.94	$4 \times 10^{-3}$	0.70

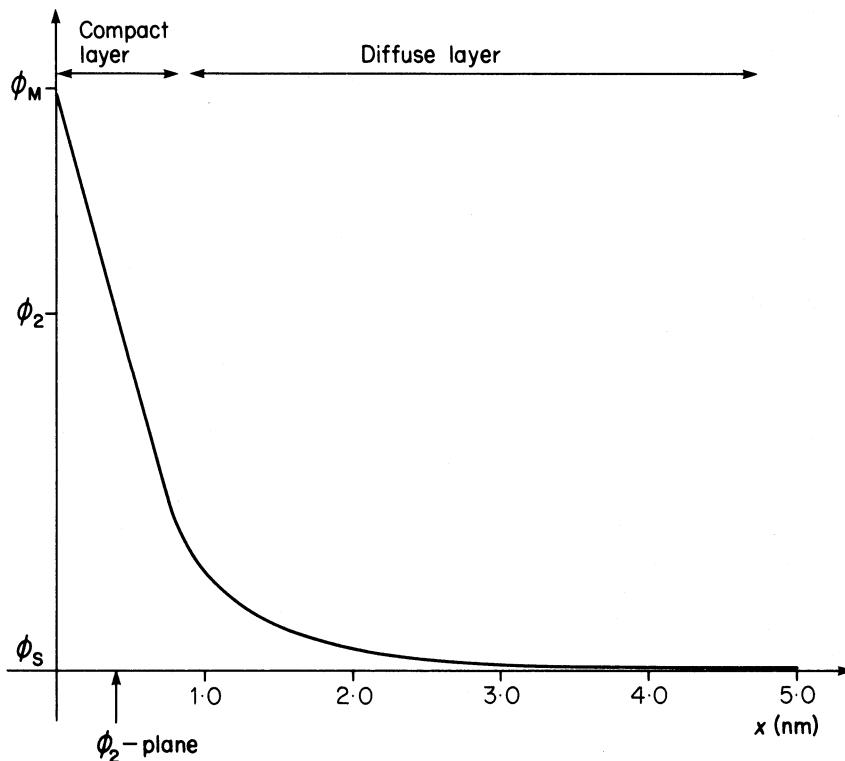
complexes undergoes little change on electron transfer (e.g. ferrocyanide) the rate constant is relatively high while, in general, for the aquo complexes it is much lower (cf. outer-sphere vs inner-sphere homogeneous electron transfer), particularly with the cobalt and chromium species which are substitution-inert. In the case of the hydrocarbons the rate constants are very high when both the neutral compound



and the anion radical are planar but lower when, as for the cyclooctatetraene derivatives, the reduction requires a change in geometry; here between a tub neutral molecule and a planar anion radical.

Strictly the interpretation of kinetic parameters requires a more sophisticated model of the interface which takes into account the presence of an electrical double layer (ions are attracted to the surface by the charge on the electrode). Figure 1.6(a) shows the generally accepted view of the electrode/solution interphase; the charged electrode (in the figure the electrode is polarized negatively) attracts a layer of highly organized cations (both electroactive species and base electrolyte cations since the interaction is purely electrostatic), the inner or compact layer, and outside this layer there is a further larger layer, the diffuse layer, where the degree of organization is intermediate between the compact layer and that in the bulk solution. The double layer causes the potential difference,  $\phi_M - \phi_S$ , to be smeared out over several molecular dimensions (see Fig. 1.6(b)). The kinetic parameters

— Potential



(b)

Figure 1.6 (a) Structure of the double layer at the electrode/solution interface. Note the highly ordered structure of the compact layer; the diffuse layer is less ordered but is not the random arrangement of the solution away from the interface. (b) Potential field resulting from this model.

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should be corrected for (a) the effect of the smeared-out potential field on the driving force for electron transfer (from the model in the figure, it can be seen that the species O is, at best, at the plane of closest approach to the electrode and at the centre of the species the potential available to drive the reaction is only  $\phi_2 - \phi_S$ , less than  $\phi_M - \phi_S$ ); (b) if O is charged its concentration at the plane of closest approach differs from that in bulk solution because of the potential field. A detailed treatment of these ‘double-layer corrections’ is available in the texts recommended at the end of this chapter.

The last twenty-five years have seen several attempts to develop a statistical-mechanical theory of electron transfer. These treatments, however, do not predict the simple linear  $\log I$  vs  $E$  relationship of the Tafel equation which seems adequate for almost all experimental investigations and therefore will not be considered here.

### 1.2 MASS TRANSPORT

In general, in electrochemical systems, it is necessary to consider three modes of mass transport; namely diffusion, migration and convection.

#### (a) Diffusion

Diffusion is the movement of a species down a concentration gradient and it occurs whenever there is a chemical change at a surface. An electrode reaction converts starting material to product ( $O \rightarrow R$ ) and hence close to the electrode surface there is a boundary layer (up to  $10^{-2}$  cm thick) in which the concentrations of O and R are a function of distance from the electrode surface; the concentration of O is lower at the surface than in the bulk while the opposite is the case for R and hence O will diffuse towards and R away from the electrode

#### (b) Migration

Migration is the movement of charged species due to a potential gradient and it is the mechanism by which charge passes through the electrolyte; the current of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes (both cations to the cathode and anions to the anode). It is, however, not necessarily an important form of mass transport for the electroactive species even if it is charged. The forces leading to migration are purely electrostatic and hence do not discriminate between types of ions. As a result, if the electrolysis is carried out with a large excess of an inert electrolyte in the solution, this carries most of the charge, and little of the electroactive species O is transported by migration (i.e. the transport number of O is low).

#### (c) Convection

Convection is the movement of a species due to mechanical forces. It can be eliminated, at least on a short timescale (it is difficult to eliminate natural convection arising from density differences on a longer timescale, i.e. longer than 10 s) by carrying out the electrolysis in a thermostat in the absence of stirring or vibration.

In industrial practice it is much more common to stir or agitate the electrolyte or to flow the electrolyte through the cell. These are all forms of forced convection and, when present, it is always the predominant form of mass transfer.

The treatment of mass transport, more than any other aspect of the subject, highlights the differences between electroanalytical experiments and industrial-scale electrolyses. In the former there is great concern to ensure that the mass transport conditions may be described precisely by mathematical equations (which moreover are solvable) since this is essential to obtain reliable mechanistic and quantitative kinetic information. In an industrial cell the need is only to promote the desired effect and this permits the use of a much wider range of mass transport conditions.

### 1.2.1 Mass transport in electroanalytical experiments

The investigation of the mechanism and kinetics of electrode processes is normally undertaken with solutions containing a large excess of base electrolyte (i.e. the migration of electroactive species is unimportant), but two types of experiment are common

- (1) Using unstirred solutions
- (2) Using a form of forced convection which may be described exactly; by far the most important system is the rotating disc electrode.

In both, the experiment is carried out so that we may assume that mass transport in only one dimension, that perpendicular to the electrode surface, is important.

Fick's laws of diffusion describe the mass transport in type (1) experiments. The electron transfer process, O  $\rightarrow$  R, at the surface will lead to a boundary layer where the concentration of O is lower and that of R is higher than in the bulk. In this situation, Fick's first law states that the flux of any species  $i$  through a plane parallel to the electrode surface (see Fig. 1.7(a)) is given by

$$\text{Flux} = -D_i \frac{dC_i}{dx} \quad (1.47)$$

where  $D_i$  is its diffusion coefficient. The second law discusses the change in concentration of  $i$  with time due to diffusion. At a point at the centre of an element of solution bounded by two planes parallel to the electrode (see Fig. 1.7(b)), the concentration will change because diffusion is occurring both into and out of the element. This leads to the equation

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad (1.48)$$

Integration of equation (1.48) with initial and boundary conditions appropriate to the particular experiment is the basis of the theory of instrumental methods such as chronopotentiometry, chronoamperometry and cyclic voltammetry. The first law applied at the electrode surface,  $x = 0$ , is used to relate the current to the chemical

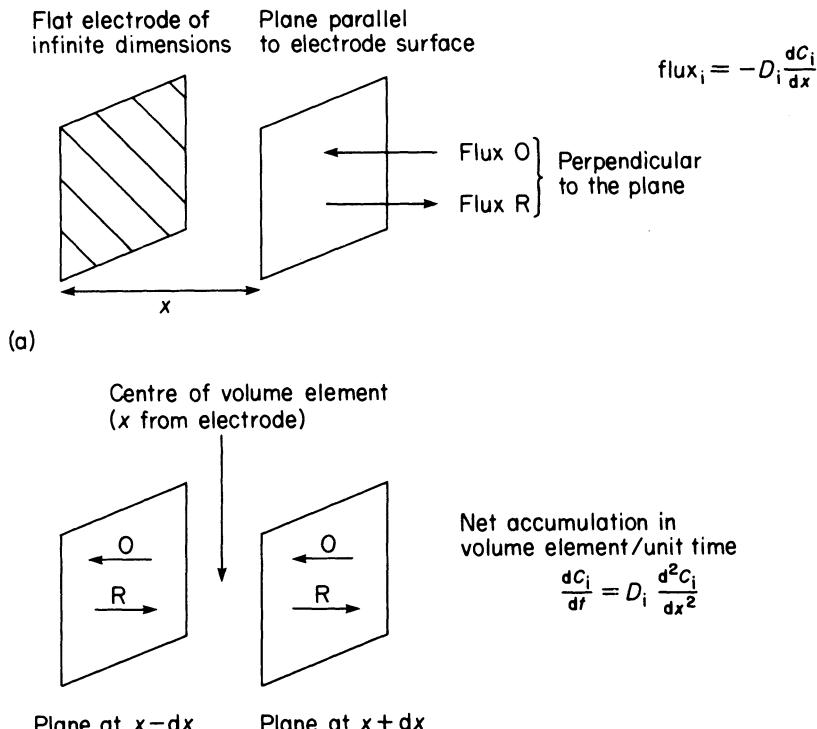


Figure 1.7 Model used for the description of the diffusion of the electroactive species, O, and product, R, during an electroanalytical experiment. (a) Fick's first law, (b) Fick's second law.

change at the electrode by equating the flux of O and R with the flux of electrons:

$$\frac{I}{nF} = -D_O \left( \frac{\partial C_O}{\partial x} \right)_{x=0} \quad (1.49a)$$

or

$$\frac{I}{nF} = D_R \left( \frac{\partial C_R}{\partial x} \right)_{x=0} \quad (1.49b)$$

A rotating disc acts as a pump, pulling solution up to the disc and throwing it out across the shroud (see Fig. 1.8); hence in experiments with a rotating disc electrode concentration changes will arise due to both diffusion and convection. If the radius of the disc is small compared with that of the shroud we can assume that access of the solution to all the electrode surface is uniform and again write an expression in one dimension

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - V_x \frac{\partial C_i}{\partial x} \quad (1.50)$$

diffusion      convection

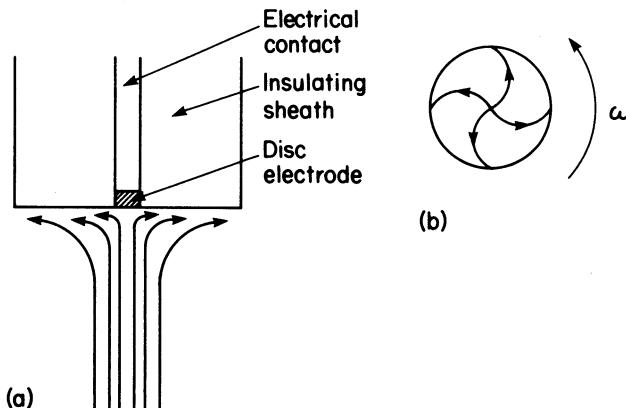


Figure 1.8 Convection resulting from a rotating disc electrode. Streamlines from (a) side view and (b) below the disc, i.e. view from direction of disc.

where  $V_x$  is the velocity of solution movement perpendicular to the disc. A solution of this problem depends on knowing the relationship between  $V_x$  and  $x$  and other parameters, particularly the rotation rate of the disc,  $\omega$ . The relationship

$$V_x \propto \omega^{3/2} x^2 \quad (1.51)$$

comes from fluid mechanics, see below.

Because of the dependence of  $V_x$  on  $x$ , it is possible and convenient to define a boundary layer thickness  $\delta$ , inside which diffusion is the principal mode of mass transport. Using this concept the steady-state concentration profiles for a solution of O and R are shown in Fig. 1.9. With a rotating disc electrode, the diffusion layer thickness is determined by the rotation of the disc; for an electrode in unstirred

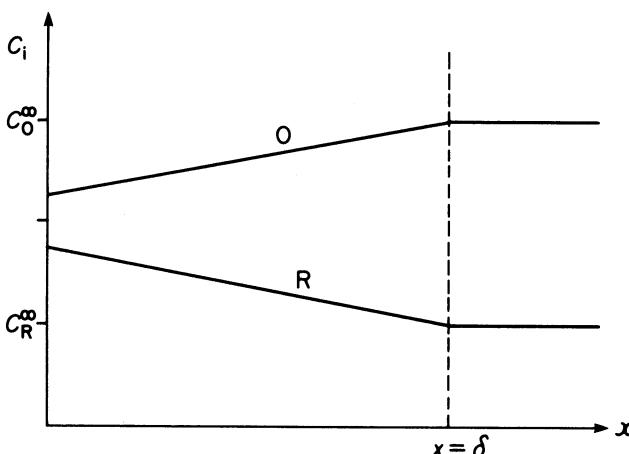


Figure 1.9 Steady-state concentration profiles for the electrode process  $O + ne \rightarrow R$ ; solution contains  $C_O^\infty = 3C_R^\infty$ .

solution a slightly less well defined layer results from natural convection. The  $C_i$  vs  $x$  plots inside the boundary layer are linear since diffusion is the physical process which seeks to minimize differences in concentration at all points. Hence the steady-state current is given by

$$\begin{aligned} I &= -nFD \left( \frac{dC_O}{dx} \right)_{x=0} \\ &= -nFD \frac{C_O^\sigma - C_O^\infty}{\delta} \end{aligned} \quad (1.52)$$

The surface concentration  $C_O^\sigma$  is, of course, a function of potential but the 'diffusion-limited current' corresponds to the maximum flux, i.e. the potential where  $C_O^\sigma = 0$

$$I_L = \frac{nFD C_O^\infty}{\delta} \quad (1.53)$$

It is now possible to understand the complete steady-state  $I-E$  characteristic sketched in Fig. 1.10. As the potential is made more negative than the equilibrium value, the reduction of  $O \rightarrow R$  will commence and then increase in rate as the overpotential becomes larger causing the surface concentration  $C_O^\sigma$  to decrease. As the rate of the electron transfer process increases it must eventually be fast compared with the maximum rate of mass transport and the surface concentration will then become zero. Diffusion is then the rate-determining step (of sequence (1.16)–(1.18)) and the current becomes independent of potential with the value given by equation (1.53). A similar argument applies to the oxidation reaction although the limiting current is about one-third of the plateau reduction current because of the ratio  $C_O^\infty/C_R^\infty$  employed. Figure 1.10 shows the  $I-E$  curves for both the reversible and the irreversible cases. In the former, the  $I-E$  response arises directly from equation (1.20) while for an irreversible couple we need an overpotential to drive both the oxidation and reduction processes, see equations (1.35) and (1.37).

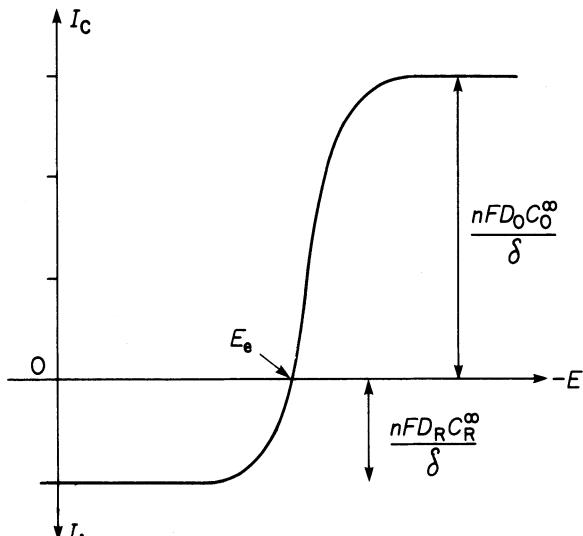
### 1.2.2 Mass transport in industrial electrolysis

In industrial practice, it is possible to find examples of cells which use unstirred solutions (e.g. electrorefining, batteries), stirred or agitated solutions (e.g. electroplating) and flowing electrolytes (e.g. synthesis, water treatment). Moreover, it is unusual for the flow of solution and the current path, which depends on cell geometry, to be parallel and the electrode may not be equivalent to a flat plate (e.g. bed electrodes, cathodes for plating); as a result, we must write our mass transport expressions in three dimensions. Nor is it always possible to assume that migration of the electroactive species is unimportant.

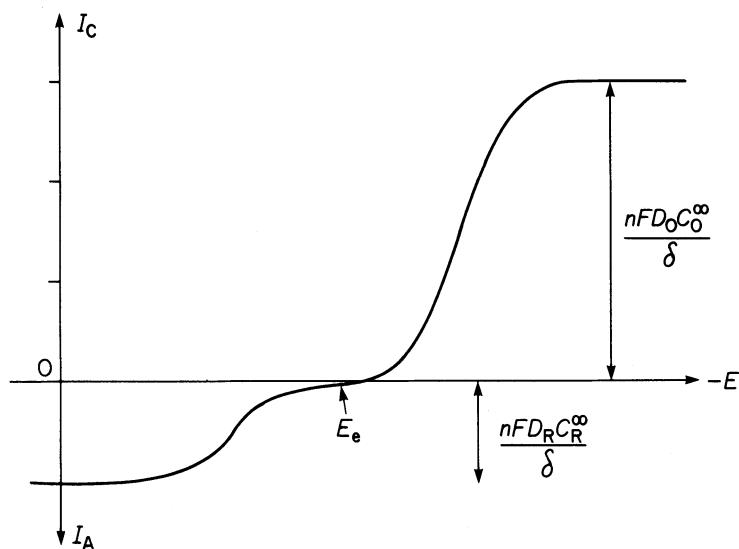
Thus the most general forms of the mass transport equations are

$$(Flux)_i = -D_i \text{ grad } C_i - U_i C_i \text{ grad } \psi + C_i V \quad (1.54)$$

diffusion	migration	convection
-----------	-----------	------------



(a)



(b)

Figure 1.10 Complete  $I-E$  curves for a reaction  $O + ne \rightleftharpoons R$  where the solution contains  $C_O^\infty = 3C_R^\infty$ . (a) Reversible electron transfer. (b) Irreversible electron transfer.

where  $U_i$  is the mobility of species  $i$  and  $\psi$  the potential field strength, and

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - U_i \operatorname{grad} \psi \operatorname{grad} C_i - V \operatorname{grad} C_i \quad (1.55)$$

These equations may be written in the most convenient coordinates for the cell and electrode geometry but as an example, equation (1.55) in cartesian coordinates becomes

$$\begin{aligned} \frac{\partial C_i}{\partial t} = & D_i \left[ \frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right] - U_i \left[ \frac{\partial \psi}{\partial x} \frac{\partial C_i}{\partial x} + \frac{\partial \psi}{\partial y} \frac{\partial C_i}{\partial y} + \frac{\partial \psi}{\partial z} \frac{\partial C_i}{\partial z} \right] \\ & - \left[ V_x \frac{\partial C_i}{\partial x} + V_y \frac{\partial C_i}{\partial y} + V_z \frac{\partial C_i}{\partial z} \right] \end{aligned} \quad (1.56)$$

Clearly such expressions are intractable and we need to consider limiting cases or to use other approaches.

Fluid mechanics is the study of the motion of flowing or stirred fluids, i.e. liquids or gases. In electrochemical technology it has two different applications: (a) to describe the movement of electrolyte solutions in a cell since this will be a principal driving force for mass transport to the electrodes and (b) to ensure the proper design of the pipes, valves and junctions which join the cell to the rest of the plant. Quantitative fluid mechanics is based upon the continuity equations which state that all points in space, mass, momentum and, for inviscid flow (i.e. fluids where no viscous forces operate), energy must be conserved. Because of the very complex nature of flow in most electrolyzers, this section will deal mainly with the qualitative concepts.

We shall consider first the flow of solution over a flat plate. In such systems, two forces will be acting upon the fluid. The first is the cause of the flow (that generated by a pump or a solution head) and is known as the inertial force. The second opposes the flow and results from viscous forces at the interface between the plate and the solution. Suppose we assume that the solution may be divided into elements, then the viscous force will initially cause that element next to the stationary plate to be retarded and later each element will be slowed down by that closer to the plate. Hence as the solution flows over the plate, a boundary layer of more slowly moving solution will develop, as shown in Fig. 1.11. In an electrolytic cell, the flat plate would normally be the electrode and therefore the formation of such boundary layers has particular importance. The electrode reaction takes place in the boundary layer in the presence of velocity gradients.

With such a flat plate, the boundary layer will increase in thickness indefinitely, if slowly (see Fig. 1.11(c)). On the other hand, if the flow is in a restricted channel, e.g. a circular tube or a parallel-plate cell, the boundary layers at the two walls must merge at some point and beyond, a steady-state situation or 'fully developed laminar

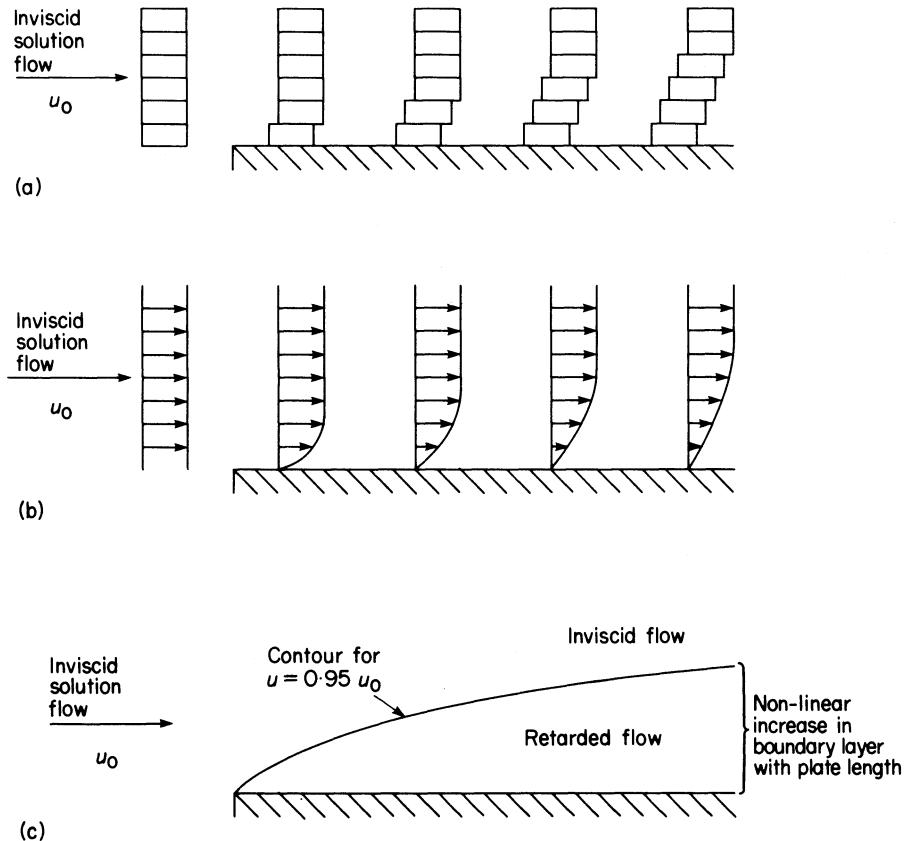


Figure 1.11 *Three different representations of the development of a boundary layer over a flat plate, e.g. an electrode.*

flow' will result (see Fig. 1.12). Mass transport studies in electrolytic cells are usually carried out in cells with an entry length without electrodes so that the boundary layer thickness is uniform over the current-carrying surface.

It can already be seen that the development and scale of the boundary layer will be dependent on the relative importance of the inertial and viscous forces. For this reason, the ratio inertial/viscous forces is given a name, the Reynolds number (*Re*), and it may be calculated from the formula

$$Re = \rho l \bar{u} / \mu \quad (1.57)$$

where  $\rho$  is the density of the solution,  $\mu$  its viscosity,  $\bar{u}$  a mean flow velocity and  $l$  a characteristic length (in the example above, the length of the plate). Indeed, the boundary layer develops in the way discussed only below a critical value of Reynolds number where the viscous damping is sufficient to suppress any

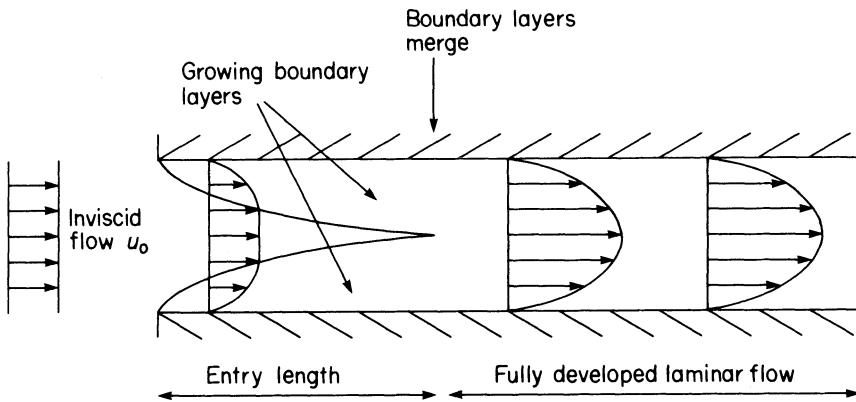


Figure 1.12 *Development of boundary layer for solution flowing down a tube.*

perturbations which arise. At higher Reynolds number, the viscous damping is no longer predominant and turbulence commences; in effect, the high rates of shear induce rotation of the solution and small eddies are formed. This may be clearly shown by experiments where dye is injected into a solution flowing down a glass tube (Fig. 1.13). Any obstacles to fluid flow or roughness in the channel wall will cause the commencement of turbulence at lower Reynolds number.

Turbulence in electrolytic cells is usually advantageous since the eddies both increase mass transport of the electroactive species to the electrode surface and promote the exchange of species between the bulk solution and the boundary layer, minimizing local pH and other concentration changes due to the electrode reaction. Indeed, it is not uncommon to introduce bars or other structural features into the cell to act as turbulence promoters.

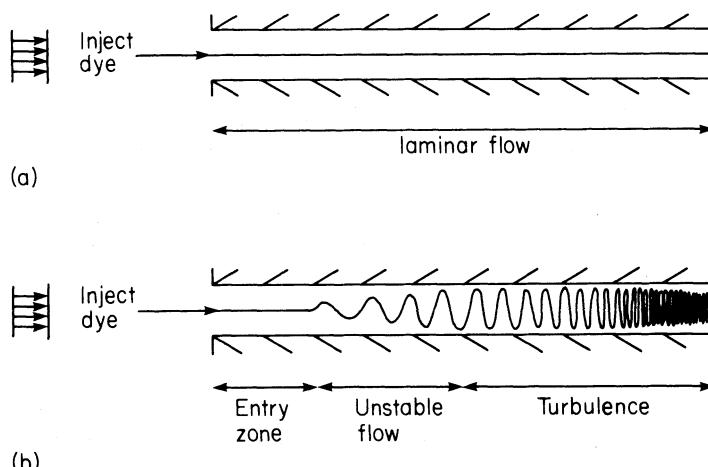


Figure 1.13 *Solution flow down a tube as shown by dye technique: (a) Reynolds number  $Re < 2000$ ; (b) Reynolds number  $Re > 3000$ .*

It will be seen in the next and subsequent chapters that a wide variety of cell geometries (e.g. parallel plates, concentric cylinders, Swiss roll), types of electrode (e.g. plates, beds, porous, expanded metals and gauzes) and flow patterns are used in industrial electrochemistry. In most the flow is too complex to warrant a detailed fluid-mechanical calculation. Rather the normal approach to mass transport in electrolytic cells is to treat the cell as a unified whole and to seek expressions in terms of space-averaged quantities which permit some insight into the mass transport conditions within the cell.

Once again, considering the simplified problem of flow over a flat plate, it is possible to derive an expression

$$Sh = 0.646 Re^{1/2} Sc^{1/3} \quad (1.58)$$

Here the Sherwood number ( $Sh$ ) is a measure of the rate of mass transport, which is usually calculated from the limiting current density  $I_L$  for the plate electrode (i.e. the potential of the plate is held at a value where all the electroactive species reaching the surface undergo the electrode reaction) using the relationship

$$Sh = \frac{I_L L}{n F C_O^\infty D} \quad (1.59)$$

where  $L$  is the length of the plate. The Reynolds number, as was discussed above, compares the relative magnitudes of the inertial forces to the viscous forces in the cell. The Schmidt number ( $Sc$ ) defined by

$$Sc = \mu / \rho D \quad (1.60)$$

compares the rate of transport by convection to that by diffusion.

In general, mass transport in electrolytic cells with flow may be discussed in terms of the expression

$$Sh = K Re^n Sc^m \quad (1.61)$$

where the constants  $K$ ,  $n$  and  $m$  may be obtained from experimental measurements of  $I_L$  under various flow conditions. For each reactor it will be necessary to define certain average parameters. For example, if one considers a parallel-plate cell where the rectangular anode and cathode are inset in the walls of a flow channel in a position where one has fully developed laminar flow (see Fig. 1.14), the appropriate equation is

$$Sh = 1.85 Re^{1/3} Sc^{1/3} \left( \frac{d_e}{L} \right)^{1/3} \quad (1.62)$$

where  $Re = \rho \bar{u} d_e / \mu$ ,  $Sc = \mu / \rho D$  and  $Sh = I_L d_e / n F C_O^\infty D$  and  $d_e$  is the equivalent diameter defined by

$$d_e = \frac{4bh}{2b + 2h} \quad (1.63)$$

Of course, this expression is only applicable in the absence of turbulence and

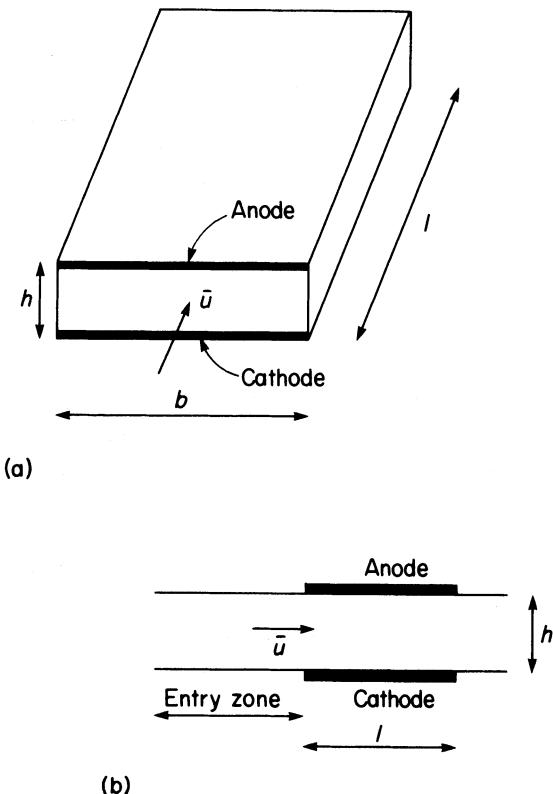


Figure 1.14 *Parallel-plate cell without separator but with fully developed laminar flow. Critical cell dimensions are  $b/h > 6$  and  $10 < l/d_e < 40$ .* (a) *View along cell at the beginning of the electrodes.* (b) *View across cell.*

hence, above a critical value of Reynolds number where turbulence is observed, for the parallel-plate cell  $Re > 2000$ , a different expression must be used:

$$Sh = 0.023 Re^{0.8} Sc^{1/3} \quad (1.64)$$

### 1.3 ADSORPTION

The electrochemistry of many industrial processes is totally dependent on the ability of the electroactive species, reaction intermediates, product or, indeed, species apparently not involved in the electron transfer process to adsorb on the electrode surface, i.e. to form some type of bond with the electrode material. The role of the adsorbed species is to accelerate or to decrease reaction rates and in extreme situations this may lead to a total change in the dominant pathway and hence in the products of electrolysis. Important examples of the application of adsorption in electrochemical technology would include electrocatalysis, the

inhibition of corrosion and the control of electroplating by organic additives, and the variation of product selectivity in organic electrosynthesis.

Adsorption results from a wide variety of interactions between the adsorbing species and the electrode surface. In some cases, the forces are merely electrostatic (e.g. the adsorption of cations and anions on a surface of opposite charge) or due to charge–dipole interactions (e.g. the adsorption of amines, thiourea or aromatic hydrocarbons), while in others the adsorbing species may form a covalent bond with the electrode surface, e.g. the adsorption of hydrogen atoms



or the dissociative adsorption of methanol



which is considered to be the first step in the complete anodic oxidation of methanol to carbon dioxide. Moreover one sees great variations in the strengths of the bonds between the electrode and the adsorbate and in the extent of reversibility of the adsorption process.

### 1.3.1 Adsorption equilibria in the absence of electron transfer

The extent of adsorption is formally described by  $\theta$ , the surface coverage or fraction of surface covered. In the absence of electron transfer processes, the value for any species will be determined by two factors, the affinity or otherwise of the species for both the electrode and the solution and the ability of all other species in the solution to adsorb. Hence the surface coverage is determined by competition between the electrode and the solution and between several species for sites on the electrode surface. Adsorption is therefore, even in the simplest of situations, a displacement reaction, the adsorbate displacing molecules of solvent or ions of the base electrolyte.

As a result, the coverage by a neutral adsorbate will generally be a maximum where the interaction of the solvent and the electrolyte with the electrode is a minimum. This occurs at the point of zero charge (p.z.c.), a characteristic of the electrode/solution interface and the potential where the surface charge is such that no charged species are attracted to the surface. When the adsorbate is charged or is a dipole that will show a preferred orientation in the potential field, adsorption occurs on the appropriate side of the p.z.c.

Clearly the surface coverage will depend on the nature and concentration of the adsorbate as well as on the electrode potential (surface charge density), electrode material, solvent, electrolyte, pH, temperature and other possible adsorbates in solution.

The adsorption isotherms describe the dependence of the surface coverage on the concentration of adsorbate in solution and on the free energy of adsorption, the latter quantity being determined by (a) vertical interactions between the species and the surface,  $\Delta G_{\text{ADS}}^\ominus$ , and (b) lateral interactions between adjacent adsorbed

species. It is normal to visualize the former as the interaction between an isolated adsorbed molecule and the surface, i.e. at zero coverage, and the latter as related to deviations from ideality in the two-dimensional adsorbed layer, i.e. factors which cause  $\Delta G_{\text{ADS}}^{\ominus}$  to deviate from the standard state. The extent and method of taking into account the second type of interaction gives rise to a number of isotherms.

The simplest isotherms arise if one assumes that only a monolayer of adsorbate is possible, that all sites on the electrode surface are equivalent and that there are no interactions between neighbouring molecules of adsorbate. At low coverages, the ideal isotherm

$$\theta = \beta C^{\infty} \quad (1.67)$$

where

$$\beta = \exp\left(-\frac{\Delta G_{\text{ADS}}^{\ominus}}{RT}\right) \quad (1.68)$$

may be used. The Langmuir isotherm relates to a wider range of coverages since it takes into account the fact that only the fraction  $(1 - \theta)$  of the surface is available for adsorption at any time and it is defined by the equation

$$\frac{\theta}{1 - \theta} = \beta C^{\infty} \quad (1.69)$$

In the Frumkin isotherm, interaction between adsorbed species is considered; the free energy of adsorption is considered to increase linearly with the coverage, i.e.

$$\Delta G_{\text{ADS}} = \Delta G_{\text{ADS}}^{\ominus} + r\theta \quad (1.70)$$

which leads to the equation

$$\frac{\theta}{1 - \theta} \exp\left(\frac{r\theta}{RT}\right) = \beta C^{\infty} \quad (1.71)$$

In practice the choice between these and other isotherms is made by analysis of experimental data.

The free energy of adsorption must depend on the electrode potential (see above), and the model whereby the adsorption process consists of the displacement of solvent adjacent to the electrode by a material of different permittivity leads to a quadratic dependence of the free energy of adsorption on potential, i.e.

$$\Delta G_{\text{ADS}} = (\Delta G_{\text{ADS}}^{\ominus})_{\text{pzc}} + h(E - E_{\text{pzc}})^2 \quad (1.72)$$

At a mercury electrode, the surface coverage is traditionally deduced from measurement of the surface tension. A more general procedure involves the measurement of the electrode capacitance  $C$  (using an AC modulation technique)

$$C = \partial q / \partial E \quad (1.73)$$

since this can readily be measured rapidly as a function of potential and solution

parameters, even with solid electrodes. The surface charge density is a function of both potential and coverage but the capacitance can be split into two terms, the high-frequency capacitance and the adsorption pseudocapacitance by taking measurements at a series of frequencies, i.e. since

$$\begin{aligned} dq &= \left( \frac{\partial q}{\partial E} \right)_{\theta} \partial E + \left( \frac{\partial q}{\partial \theta} \right)_E \partial \theta \\ C = \frac{\partial q}{\partial E} &= \left( \frac{\partial q}{\partial E} \right)_{\theta} + \left( \frac{\partial q}{\partial \theta} \right)_E \frac{\partial \theta}{\partial E} \\ &= C_{\text{hf}} + C_{\theta} \end{aligned} \quad (1.74)$$

The adsorption pseudocapacitance is dominated by the term  $\partial \theta / \partial E$  and hence a plot of  $C_{\theta}$  versus  $E$  gives information about the coverage directly. Figure 1.15 shows a set of  $C_{\theta}$ – $E$  plots for a pentanol solution at a mercury electrode. The peaks are due to adsorption/desorption processes, so, for example, from the 0.1 M solution, the alcohol adsorbs in the potential range between –0.1 V and –1.1 V.

All the above models of adsorption, however, assume that all sites on the electrode surface are equivalent. With solid electrodes this is never entirely true; on an atomic scale, the surface cannot be flat and unless the electrode is a single crystal a variety of lattice orientations will be exposed to the solution. Hence, the surface is likely to contain a number of different types of sites, each with a characteristic  $\Delta G_{\text{ADS}}^{\ominus}$ . Indeed, it is because adsorbates interact first at sites where the free energy of adsorption is most negative that organic additives may be used to control metal deposition; adsorption occurs at lattice imperfections, e.g. screw

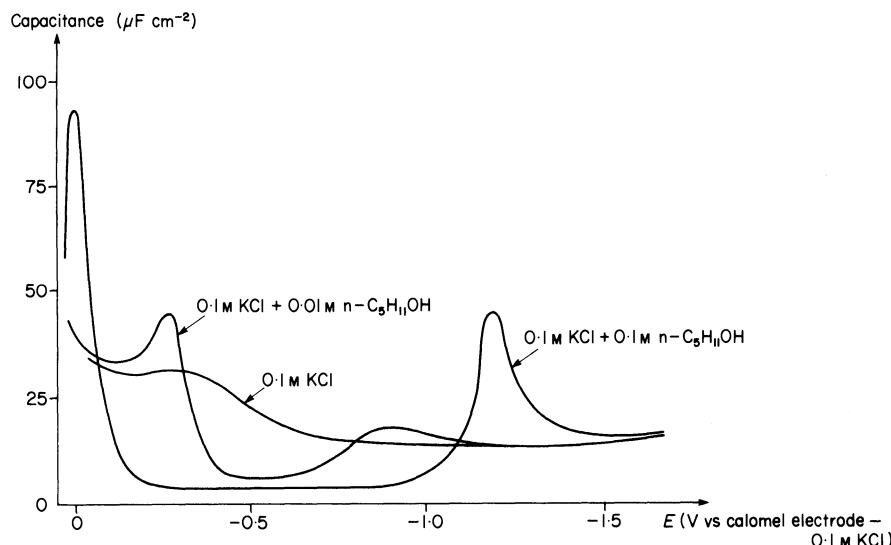


Figure 1.15 Capacitance–potential curves for *n*-pentanol in 0.1 M KCl at a Hg drop electrode.

dislocations, where otherwise the rate of deposition would be most rapid, creating an uneven thickness of the electroplated layer.

### 1.3.2 The effect of a neutral adsorbate on an electron transfer process

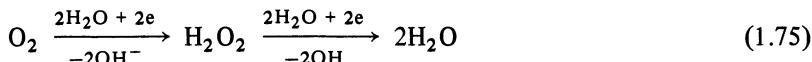
The presence of an organic molecule capable of adsorbing on the electrode surface will, in general, cause a decrease in the rate of electron transfer for a couple O/R. The explanation will depend on the most appropriate model for the electron transfer process.

Thus if electron transfer occurs while an adsorbate layer remains on the electrode surface, the oxidation or reduction must occur by the transfer of an electron over a far greater distance. Figure 1.6 showed the potential distribution on a molecular scale close to the electrode and it was noted that only the potential difference  $\phi_2 - \phi_S$  (not  $\phi_M - \phi_S$ ) was available to drive electron transfer; the adsorbate layer will cause a substantial decrease in the  $\phi_2$  potential. In the limit, the presence of adsorbate may totally prevent electron transfer and then only a fraction  $(1 - \theta)$  of the electrode is available for the O/R couple. An alternative model would require displacement of adsorbate by O or R before electron transfer can occur and the extent of such a process will depend on  $\Delta G_{ADS}^\ominus$ . Finally the adsorbate may also be able to act as a ligand for O and R and complex formation at the electrode surface may increase or decrease the kinetic parameters for electron transfer.

These are the roles of additives for corrosion inhibition and the modification of electrodeposits. For electrode reactions where the overall sequence includes chemical steps, however, the role of the adsorbate layer may be quite different. Rather it may be to create an environment which is more favourable than the bulk solution for a particular reaction. For example, the proton availability may be different; it is not unusual for an adsorbate layer to be relatively aprotic compared with an aqueous electrolyte and such modifications of electrode processes have been used in the following.

#### (a) *The reduction of oxygen*

Normally the reduction of oxygen at a mercury cathode in aqueous solution occurs in two steps



but in basic medium in the presence of sufficient triphenylphosphine oxide to form a monolayer on the mercury surface, a reversible one-electron reduction is observed and the product is the superoxide ion, i.e.



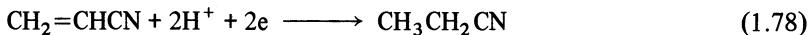
This is thought to be due to the aprotic conditions which prevail at the site of electron transfer and the superoxide ion is able to escape the electrode before it is protonated.

(b) *The hydrodimerization of acrylonitrile*

In the electrolytic preparation of adiponitrile



it is necessary to have tetraalkylammonium ions in the system to avoid the predominant formation of propionitrile



The organic cation is again thought to modify the electrode reaction by creating an aprotic layer on the cathode surface where the anion radical resulting from the 1e reduction of acrylonitrile does not immediately protonate.

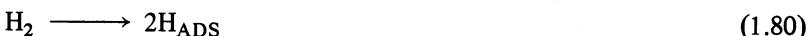
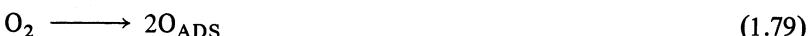
### 1.3.3 Adsorption in the presence of a faradaic current

When the electroactive species or an intermediate adsorbs on the electrode surface, the adsorption process usually becomes an integral part of the charge transfer process and therefore cannot be studied without the interference of a faradaic current. In this situation, surface coverages cannot be measured directly and the role of an adsorbate must be inferred from a kinetic investigation. Tafel slopes and reaction orders will deviate substantially from those for a simple electron transfer process when an adsorbed intermediate is involved. Moreover the kinetic parameters, exchange current or standard rate constant, are likely to become functions of the electrode material and even the final products may change. These factors will be discussed further in the section on electrocatalysis (Section 1.4).

In a few cases it is possible to take data for the coverage by the electroactive species at potentials prior to the onset of electron transfer and to extrapolate such data into the potential region where oxidation or reduction occurs. In any case, the concept of competition between species for sites on the electrode surface, the form of the isotherms and the qualitative variation in the coverage with potential are likely to remain valid. Hence the earlier discussion remains a useful guide even when there is a faradaic current.

### 1.3.4 Dissociative adsorption

The adsorption of some molecules occurs by a more complex process where bonds are broken and the fragments adsorb at different sites on the electrode surface. In the case of small molecules such as oxygen or hydrogen this may remain a relatively simple process



although the bond energies of such diatomic gases are high and few materials will have all the characteristics essential to make these steps effective in the catalysis of oxygen reduction or hydrogen oxidation. With organic molecules, however, the adsorption process, e.g.



may be much more complex and involve a number of bond-breaking processes. The overall reaction is unlikely to be reversible and coverages by each species will be determined by kinetic rather than thermodynamic factors. Even so such dissociative adsorption processes are very important and are at the heart of the electrocatalysis necessary for fuel cells because the direct loss of an electron from potential fuels always requires a substantial overpotential.

The coverage by organic fragments cannot be described in terms of isotherms (since the adsorption is not an equilibrium process) and, indeed, it is usually difficult to identify with certainty the structure of the adsorbed species. The information available is generally deduced from measurement of the charges for

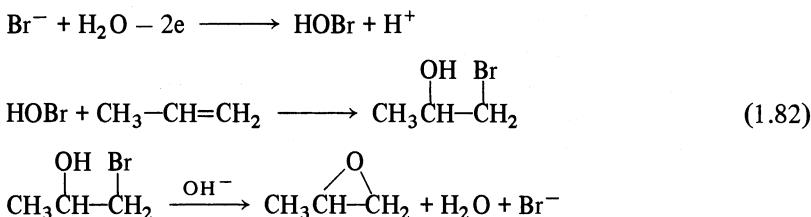
- (a) The adsorption process,  
(b) The complete oxidation of all fragments on the surface; this is measured by keeping or stepping the potential to a very positive value,  
(c) The adsorption of hydrogen in the presence and absence of the organic sorbate; the ratio indicates the fraction of the total surface covered by fragments,

though there is now an expectation that *in situ* vibrational spectroscopy might be used to obtain a more direct identification. The analysis of all such experimental data is complicated by the probable existence of a mixture of fragments on the surface and, in addition, the fractional coverage by each species may change with time. Indeed, this is the basis of the phenomenon of electrode poisoning — the poison is a fragment which is too strongly adsorbed and hence only oxidized very slowly. Thus although many metals are initially excellent catalysts for the complete oxidation of organic fuels to carbon dioxide, few maintain their activity for an extended period because of the accumulation of a poison either during the associative adsorption or the oxidation step (the oxidation of, for example,  $\text{—OH}_{\text{ADS}}$  will go through several other adsorbed fragments).

## 1.4 ELECTROCATALYSIS

Many electrode reactions only occur at a measurable rate at a very high overpotential, i.e. the exchange current is low. The art of electrocatalysis is to provide alternative reaction pathways which avoid the slow step and permit the reaction to be carried out with a high current close to the reversible potential, i.e. to increase the exchange current density.

In general, the catalyst may be an adsorbed or a solution-free species. Although many examples of the latter have been demonstrated in the laboratory, e.g. the oxidation of propylene oxide catalysed by bromide ion,



few, if any, have applied in industrial electrochemistry. On the other hand, electrocatalysis by adsorbed species is of considerable importance, e.g. for oxygen electrodes, hydrogen evolution and chlorine anodes, and it is on this aspect that we shall concentrate.

#### 1.4.1 The hydrogen evolution reaction

The hydrogen evolution reaction is historically very important since its study has contributed much towards our understanding of electrode reactions. It is also met in corrosion and as a cathode reaction in water electrolyzers, some chlorine cells and other oxidation processes.

In acid solution the overall reaction is



and in neutral and basic media



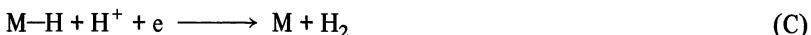
This discussion will assume an acidic medium although the modifications to include higher pH are obvious. In the absence of adsorbed intermediates, the reaction mechanism is likely to be



Admitting the possibility of an adsorbed hydrogen atom



as an intermediate changes both the thermodynamics and the kinetics of the hydrogen evolution reaction. First the formation of an adsorbed species changes the free energy of the electron transfer by an amount equal to the free energy of formation of the bond between the hydrogen atom and the surface. As a result reaction (1.87) can occur at a potential,  $\Delta G_{\text{ADS}}^\circ/F$ , less negative than that of reaction (1.85) (i.e. the stronger the bond, the larger the shift in reversible potential) and, indeed, reaction (1.87) does occur at potentials positive to the reversible potential of the  $\text{H}^+/\text{H}_2$  couple. Secondly, the existence of adsorbed hydrogen atoms makes possible alternative reaction routes and two mechanisms are considered important for the formation of hydrogen gas



where the adsorbed hydrogen is written in a way which emphasizes the importance of the electrode material in determining the properties of the surface bond.

It may be noted immediately that both mechanisms require the formation and then the cleavage of an M–H bond. Hence while a variation of the cathode so as to increase the free energy of adsorption will favour the formation of the adsorbed species, it will have the opposite effect on the second step in the overall process. As a result, it is to be expected that the maximum rate of hydrogen evolution will occur at intermediate values of  $\Delta G_{ADS}^\ominus$  which lead to a significant but not monolayer coverage by adsorbed hydrogen atoms. This is indeed observed and Fig. 1.16 shows a ‘volcano plot’ of exchange current density vs  $\Delta G_{ADS}^\ominus$  for a series of metal cathodes. Similar dependences of rate parameters on the free energy of adsorption of an intermediate are common in gas-phase catalysis.

Experimental investigations of hydrogen evolution at many cathodes have shown a wide variation in the Tafel slope, exchange current density and dependence of current on pH. This is typical of a reaction involving a specifically adsorbed intermediate. We shall therefore consider the values predicted by theory for mechanisms I and II.

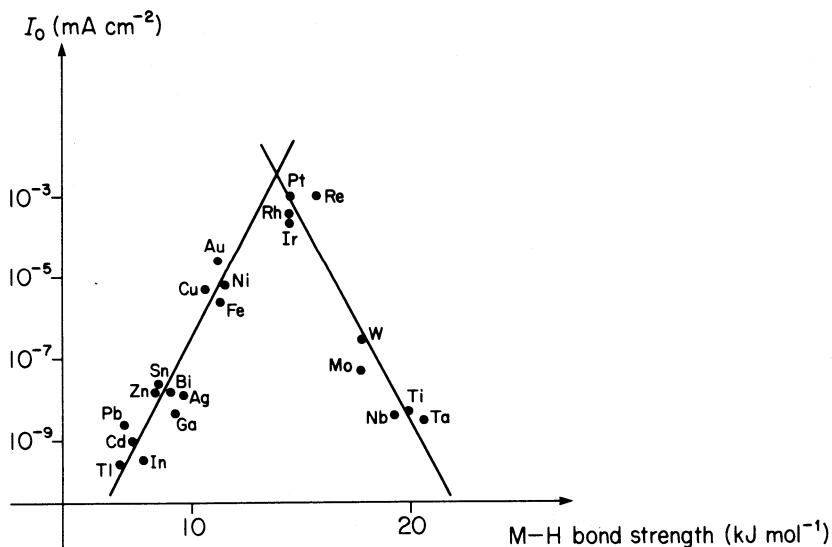


Figure 1.16 Dependence of exchange current density for the hydrogen evolution reaction on the strength of the metal–hydrogen bond formed in the electrode reaction. Data from Trasatti, S. (1972) J. Electroanal. Chem., 39, 163.

(i) *Step A as the slow step.* The formation of the adsorbed hydrogen atom as the first step is common to both mechanisms. Hence where this is the rate-determining step we cannot be certain of the overall mechanism. The rate of step A (and hence the rate of the overall sequence when it is the rate-determining step) may be written

$$\vec{V}_A = \vec{k}_A C_{H^+} (1 - \theta) \quad (1.88)$$

where  $\overrightarrow{k_A}$  is the rate constant for step A, which is potential-dependent since the reduction of a proton involves the transfer of an electron, and the rate of reaction  $\overleftarrow{V_A}$  also depends on the concentration of the electroactive species and on the fraction of surface free of adsorbed hydrogen atoms and therefore available for the reaction. If step B or C is always fast compared with step A,  $\theta$  must be small and  $(1 - \theta) \rightarrow 1$ . Hence the current density for this mechanism may be written

$$\begin{aligned} I &= F\overrightarrow{k_A}C_{H^+} \\ &= Fk_A C_{H^+} \exp\left(-\frac{\alpha_A F}{RT} \eta_A\right) \end{aligned} \quad (1.89)$$

and

$$\log I = \log Fk_A + \log C_{H^+} - \frac{\alpha_A F}{2.3RT} \eta_A \quad (1.90)$$

It can be seen that the current is first-order with respect to proton and assuming the transfer coefficient  $\alpha_A = 0.5$ , the Tafel slope,  $\partial \log I / \partial \eta_A$  or  $\partial \log I / \partial E$ , is  $(120 \text{ mV})^{-1}$ .

(ii) *Mechanism I, rate-determining step – reaction B.* In this case the current is given by

$$I = 2Fk_B\theta^2 \quad (1.91)$$

where  $k_B$  is a chemical rate constant. At potentials close to the equilibrium potential,  $\theta$  may be obtained by noting that  $\overrightarrow{V_A} \gg \overrightarrow{V_B}$  and  $\overleftarrow{V_A} \gtrapprox \overrightarrow{V_B}$  and using the quasi-equilibrium assumption for the discharge step, i.e.  $\overleftarrow{V_A} = \overrightarrow{V_A}$  or

$$\overrightarrow{k_A}C_{H^+}(1 - \theta) = \overleftarrow{k_A}\theta$$

and hence

$$k_A C_{H^+}(1 - \theta) \exp\left(-\frac{\alpha_A F}{RT} \eta_A\right) = k_A \theta \exp\left(\frac{(1 - \alpha_A)F}{RT} \eta_A\right) \quad (1.92)$$

which reduces to

$$\frac{\theta}{1 - \theta} = C_{H^+} \exp\left(-\frac{F}{RT} \eta_A\right)$$

or

$$\theta = \frac{C_{H^+} \exp[-(F/RT)\eta_A]}{1 + C_{H^+} \exp[-(F/RT)\eta_A]} \quad (1.93)$$

At very low overpotentials (remember the overpotential will be negative for a reduction),

$$C_{H^+} \exp\left(-\frac{F}{RT} \eta_A\right) < 1$$

and

$$\theta \simeq C_{\text{H}^+} \exp \left( -\frac{F}{RT} \eta_A \right) \quad (1.94)$$

and substitution into equation (1.91) gives

$$I = 2Fk_B C_{\text{H}^+}^2 \exp \left( -\frac{2F}{RT} \eta_A \right) \quad (1.95)$$

or

$$\log I = \log 2Fk_B + 2 \log C_{\text{H}^+} - \frac{2F}{2.3RT} \eta_A \quad (1.96)$$

For this mechanism the Tafel slope is therefore  $(30 \text{ mV})^{-1}$  and the current varies as the square of the proton concentration.

(iii) *Mechanism II, rate-determining step – reaction C.* The rate of reaction C is given by

$$\overrightarrow{V_C} = \overrightarrow{k_C} C_{\text{H}^+} \theta \quad (1.97)$$

since it depends on the concentration of protons and on the coverage of the surface by M–H;  $\overrightarrow{k_C}$  is again potential-dependent since reaction C involves the transfer of an electron. Two simple forms of rate expression may be obtained for low and high overpotentials.

At low overpotentials  $\overrightarrow{V_A} \gg \overrightarrow{V_C}$  and  $\overrightarrow{V_A} \gg \overrightarrow{V_C}$  and the coverage  $\theta$  may again be found by applying the quasi-equilibrium assumption to reaction A. By an identical argument to that above, the coverage will be given by equation (1.94). Hence the current for this mechanism will be given by

$$\begin{aligned} I &= 2Fk_C C_{\text{H}^+}^2 \exp \left( -\frac{F}{RT} \eta_A \right) \exp \left( -\frac{\alpha_C F}{RT} \eta_C \right) \\ &= 2mFk_C C_{\text{H}^+}^2 \exp \left( -\frac{(1 + \alpha_C)F}{RT} \eta_C \right) \end{aligned} \quad (1.98)$$

where  $m$  is a constant,  $\exp[-(F/RT)(E_C^0 - E_A^0)]$ , which arises because the overpotential scales for reactions A and C are not the same but differ by the difference in their equilibrium potentials ( $E_C^0$  and  $E_A^0$ ). Hence

$$\log I = \log 2mFk_C + 2 \log C_{\text{H}^+} - \frac{(1 + \alpha_C)F}{2.3RT} \eta_C \quad (1.99)$$

and the Tafel slope, assuming  $\alpha_C = 0.5$ , will be  $(40 \text{ mV})^{-1}$  and the current will depend on the square of the proton concentration.

At high overpotentials  $\overrightarrow{V_C} \gg \overrightarrow{V_A}$  and then  $\theta$  may be obtained by noting that  $\overrightarrow{V_A} \simeq \overrightarrow{V_C}$  or

$$k_A C_{\text{H}^+} (1 - \theta) \exp \left( -\frac{\alpha_A F}{RT} \eta_A \right) = k_C C_{\text{H}^+} \theta \exp \left( -\frac{\alpha_C F}{RT} \eta_C \right) \quad (1.100)$$

Then assuming  $\alpha_A = \alpha_C = \alpha$

$$\theta = \frac{m^\alpha k_A}{k_C + m^\alpha k_A} = K \quad (1.101)$$

and  $\theta$  is independent of potential;  $k_A$  and  $k_C$  are the rate constants at the equilibrium potentials for reactions A and C respectively. Here the rate expression is therefore

$$I = 2Fk_C C_{H^+} K \exp\left(-\frac{\alpha_C F}{RT} \eta_C\right) \quad (1.102)$$

or

$$\log I = \log 2Fk_C K + \log C_{H^+} - \frac{\alpha_C F}{2.3RT} \eta_C \quad (1.103)$$

and the reaction becomes first order in proton with a Tafel slope of  $(120 \text{ mV})^{-1}$ .

Table 1.2 summarizes the conclusions for the mechanisms which have been considered. While the mechanisms and rate-determining steps lead to several values for the reaction order and Tafel slope, the experimental observations will not be totally diagnostic because different mechanisms can lead to the same values. Moreover there are many more mechanistic possibilities than have been discussed here.

Table 1.2 Tafel slopes and reaction orders calculated for some mechanisms of the  $H_2$  evolution reaction

Mechanism	Rate-determining step	Overpotential range	Tafel slope	Reaction order in $H^+$
I or II	A	all	$(120 \text{ mV})^{-1}$	1
I	B	low	$(30 \text{ mV})^{-1}$	2
II	C	low	$(40 \text{ mV})^{-1}$	2
		high	$(120 \text{ mV})^{-1}$	1

From the viewpoint of electrochemical technology, however, the major point to be emphasized is that the choice of cathode material will have a substantial influence on the exchange current density and hence the cathode overpotential in any electrolysis cell. We shall consider the relevance of this overpotential to cell energetics in Chapter 2.

#### 1.4.2 Oxygen reduction

In almost all applications of the oxygen reduction reaction, it is desirable to select conditions where the complete  $4e^-$  reduction occurs, i.e. in acid solution



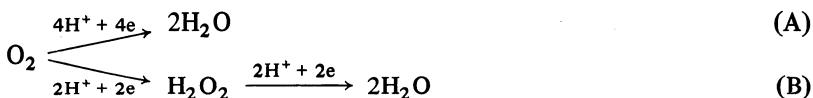
or in basic solution



and at pH 0 and 14, the standard potentials of reactions (1.104) and (1.105) are +1.23 V and 0.39 V (vs NHE) respectively.

Particularly in acid solution, relatively few cathode materials, capable of operating at these potentials, are available because most metals dissolve anodically at potentials well negative to the equilibrium potential for oxygen reduction. Moreover, even with the more noble metals which do not dissolve, the study of oxygen reduction is hampered by oxidation and/or reduction of their surface within the potential range of interest; this makes the experimental data for oxygen reduction less precise and perhaps also leads to a change in mechanism when the electrode surface changes from metal oxide to metal or vice versa. In this respect the oxygen evolution reaction is easier to study since it generally occurs on a fully oxidized anode surface and for such surfaces its study gives information relevant to its reverse reactions, providing the principle of microscopic reversibility may be applied.

In any case, the oxygen electrode is a complex system and the overall reaction in either direction requires the transfer of four electrons and four protons. As a result, it is possible to write a very large number of reaction mechanisms but they are essentially of two types



The first leads to water as the first identifiable product while in the other the reduction to water clearly occurs in two steps with hydrogen peroxide as an intermediate. Indeed, in some conditions the reaction stops at the hydrogen peroxide stage, e.g. at mercury oxygen is reduced in two well defined steps, separated by up to 1 V, and in this mechanism catalysts may well have the role of ensuring the rapid and total disproportionation of the hydrogen peroxide to oxygen and water. Route A implies the cleavage of the O—O bond by dissociative adsorption at an early stage in the reduction whereas in route B the first step is the reduction of oxygen to superoxide (or  $\text{HO}_2^+$  to  $\text{HO}_2^\cdot$ ). The two types of mechanism are most readily distinguished by an experiment with a rotating ring-disc electrode. Oxygen is reduced at a rotating disc of the active material and any hydrogen peroxide formed is monitored on a ring electrode surrounding the disc and separated from it by a thin layer of insulator; in general the disc and ring electrode may be controlled independently. At least fourteen reaction pathways for oxygen reduction have been considered and, taking into account the various possible rate-determining steps, the anodic and cathodic Tafel slopes for 53 mechanisms for the oxygen electrode system have been established. In these circumstances, reliable kinetic parameters can seldom be obtained. Certainly comparison between electrode materials, where the products and mechanisms may be different, is not possible.

Even so, the reduction of oxygen is clearly always a slow reaction and the best of the metals, platinum, required an overpotential of over 0.5 V for a reasonable current density. At other metals, e.g. Hg, and carbons, the overpotential may need to be of the order of 1.5 V.

Route A offers the best chance of effective electrocatalysis and is also necessary to ensure the full free-energy output from the 4e reduction and an approach to the equilibrium potential of 1.23 V. The O—O bond in oxygen is, however, strong and it is therefore not surprising that good catalysts have not proved easy to find. Recent research studies have concentrated on various mixed oxides (e.g. spinels, bronzes and perovskites) and transition-metal complexes (e.g. metal porphyrins). In general, such catalysts are mixed with or deposited onto a high-surface-area carbon and, even in this high-area form, it has to be admitted that they seldom approach the performance of the more active metal catalysts. The most promising materials are the oxide,  $\text{NiCo}_2\text{O}_4$ , and a dimeric, face-to-face porphyrin with two cobalt ions. Both these catalysts give electrodes where oxygen reduction occurs in the potential range +800 to +600 mV. This is comparable with the performance of massive precious metal; the best practical oxygen cathode, however, remains a high-surface-area platinum.

#### 1.4.3 The design of electrocatalytic electrodes

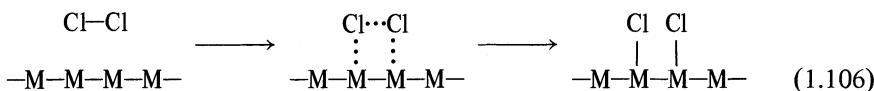
It is not sufficient for an electrode material to exhibit good catalytic properties under laboratory conditions. In an industrial process it is often essential for the electrode to catalyse specifically only one reaction; for example, it is a prerequisite for an anode for a chlorine cell to oxidize chloride ion at low overpotential but also it must not promote oxygen evolution since this is the thermodynamically preferred reaction (see Chapter 3). Furthermore it must be possible to design and construct an electrode from the catalyst material. Since modern catalysts may not be a metal, it may be necessary to mix them with an inert conductor and a binder and press them onto a supporting grid or to develop a technique for coating them onto an inert metal. In practice the electrode may be operated as a porous gas electrode or as a gas-evolving electrode and this will also place additional restraints on the design. Certainly under the electrolysis conditions the electrode structure must be physically stable, resistant to corrosion and the catalyst must maintain its activity over a long period of time, i.e. it must not poison.

What factors determine the activity of electrocatalysts and are likely to introduce specificity into an electrode reaction? At the present time, a complete answer to this question is not possible and we have certainly not reached the stage where it is possible to design electrocatalysts from theoretical considerations. On the other hand a number of general principles can be set out. Thus while metals, alloys, semiconductors (particularly oxides) and complexes have been shown to exhibit catalytic properties, invariably catalysts are based on transition metals and it seems that the design of a catalyst requires the placing of transition-metal ions or atoms in a matrix which serves to optimize their electronic configuration and position with respect to each other.

The dependence of electrocatalysis on adsorption has already been emphasized and therein lies the explanation of the success of transition metals as catalysts; they have unpaired d-electrons and unfilled d-orbitals which are available to form bonds with the adsorbate. The free energy of adsorption will, however, depend strongly on the number of unpaired electrons per atom and also on their energy levels.

Hence it is not surprising that activity varies with the transition metal and may be modified by alloying or placing in a non-metallic lattice. In the limit the lattice and the adsorbate may be considered as ligands in a metal complex. The observation that the rate of hydrogen evolution passes through a maximum when plotted versus free energy of adsorption is equally true of other electrocatalytic processes and hence the objective should be to tailor the electronic environment of the metal to obtain the free energy of adsorption which leads to the maximum current density.

In addition to electronic factors, the geometric arrangement of catalyst centres will also be important. All electrocatalytic reactions involve the formation or cleavage of bonds and it is likely that such processes will be substantially increased in rate if they can occur as concerted reactions, i.e. for example in the reduction of chlorine, the bond between the surface and the chlorine atoms forms at the same time as the Cl—Cl bond is broken:



Such mechanisms require the correct spacing of the adsorption sites. Here the sites are written as the metal atoms themselves but it is also possible that adsorption occurs at interstitial positions although the argument would remain the same. The adsorption of larger molecules may involve adsorption at more than one site and this will also require the appropriate site spacings.

The activity of electrocatalysts can further be enhanced by special sites on the surface and step, kink and edge sites, lattice vacancies, grain boundaries and dislocations have all been suggested to have a beneficial effect. This may be because they lead to sites with different free energies of adsorption or because they create unusual spacings or arrangements of potential adsorption sites.

To summarize the conclusions concerning catalyst design, we shall again look at oxygen reduction; how can we set out to find the most suitable catalysts? Certainly it is desirable to promote the dissociative adsorption of oxygen to give M—O bonds of intermediate strength so that the oxygen atom can readily be reduced to water (oxide). These processes will require the correct spacing of catalyst sites and the optimum electronic energy levels to ensure the appropriate free energy of adsorption. In addition it may be advantageous for the oxygen molecule to be able initially to form a  $\pi$ -complex at the surface and the final step may be assisted by polarization of the M—O bond. The various stages in the overall process may require different properties from the transition metal and one way of facilitating this is to use transition metals where the oxidation state may readily be altered. It must be said, however, that few catalysts lead to a lower overpotential than platinum metal and this will also be the case for the hydrogen electrode, the oxidation of ethylene,

methanol and carbon monoxide and chlorine evolution. Hence our search is largely limited to catalysts with a similar performance but which are cheaper. Present studies largely relate to non-stoichiometric oxides and metal complexes where inorganic chemistry would indicate that the oxide lattice or ligands may be tailored closely.

Once the catalyst is developed, it remains necessary to construct an electrode incorporating it. In electrocatalytic processes the real surface area of the electrode is important and the measured exchange current density can be increased by preparing a rough or otherwise high-area surface (this is in contrast to mass-transfer-controlled reactions where only the apparent geometric area matters provided that the surface-roughness is small compared with the diffusion layer thickness). Hence a variety of procedures for obtaining high-surface-area electrodes have been developed; these include spray coating, sputtering, thermal decomposition of solutions of a catalyst or a catalyst precursor and painting dispersions of the appropriate crystallite size. For example, satisfactory platinum electrodes have been manufactured with very low loadings of the active metal, e.g. a few milligrams per square centimetre of graphite.

When the reactant is a gas it is advantageous to minimize mass transport effects by employing a porous gas electrode. The electrode is manufactured by compressing catalyst, conducting powder (e.g. graphite) and perhaps a hydrophobic material (e.g. PTFE) onto a conducting grid and the gaseous reactant is passed over the back of the electrode so that the electrode reaction occurs at a three-phase interface between gas, solution and electrode material. When the product is a gas it is more common to use a shaped electrode (with 'louvres' or as a 'cheese grater') where the gas passes to the back of the electrode and away from the current path where it can increase cell resistance.

## 1.5 PHASE FORMATION IN ELECTRODE REACTIONS

Many of the electrode reactions of interest to electrochemical technology involve the formation of a new phase. This may be a metal resulting from the reduction of an ion in solution (as in electroplating or electrowinning), an oxide formed by corrosion (e.g. anodizing) or by oxidation of a solution free species (e.g.  $\text{PbO}_2$  from a nitrate bath), other metal salts from oxidation of an electrode (e.g.  $\text{PbSO}_4$  deposition from lead during the discharge of a lead/acid negative plate) or by the reduction of another phase (e.g.  $\text{PbSO}_4$  from the reduction of  $\text{PbO}_2$  in a lead/acid positive plate) or a gas (e.g. chlorine in a chlor-alkali cell or hydrogen and oxygen in a water electrolyser).

Such electrode reactions frequently have a unique feature; namely, the  $I-E$  characteristics before and after the formation of the new phase are quite different. For example, the  $I-E$  curves for a solution of copper ions at an inert electrode (e.g. carbon) and the same electrode covered with a thin layer of copper will be totally different, the latter being similar to a bulk copper cathode. Similarly the  $I-E$  curve for a recharging lead/acid positive electrode will change dramatically

once the lead sulphate layer contains microscopic centres of lead dioxide. This feature arises because the formation of a new phase requires nucleation, a process which is always inherently improbable and in electrochemistry generally only takes place at the cost of a substantial overpotential.

While nucleation phenomena are important in electrochemical technology, it must be recognized that for most of a process the nuclei will exist and the main reaction is expansion of the new lattice as the deposit thickens. Hence we need to consider two distinct situations; (i) the initial growth where a very thin layer or small centres of the deposit are created by nucleation and start to grow, and (ii) the subsequent growth to a macrophase.

### 1.5.1 Nucleation

The formation of a new phase is always difficult and always requires a high supersaturation for it to occur. For example, pure water can be supercooled very considerably before ice appears and the crystallization of organic compounds often takes some time. Indeed, in both cases true homogeneous nucleation is seldom observed because crystals prefer to form on the surface of the vessel or on dust particles (hence scratching with a glass rod to initiate crystallization). The explanation of the low rate of homogeneous nucleation lies in the high surface-to-volume ratio of small particles; although the bulk free-energy change must be negative for the new phase to be thermodynamically stable, the surface energy contribution is normally positive and dominant for small particles. For example, consider a hemispherical centre such as that shown in Fig. 1.17. The surface energies  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$  refer to the new phase/electrolyte solution, new phase/electrode and the electrode/electrolyte solution interfaces respectively. The free energy of formation of the nucleus of the new phase is

$$\Delta G_{\text{NUCL}} = -\frac{2}{3}\pi r^3 \frac{\rho nF}{M} \eta + 2\pi r^2 \sigma_1 + \pi r^2 (\sigma_2 - \sigma_3) \quad (1.107)$$

where  $\rho$  is the density of the nucleus and  $M$  the molecular weight of the phase.  $nF\eta$  is the bulk free energy per mole involved in forming the nucleus at an overpotential  $\eta$  (measured with respect to the equilibrium potential of the bulk phase). At each overpotential, it will be found that for small values of  $r$ , the second term on the

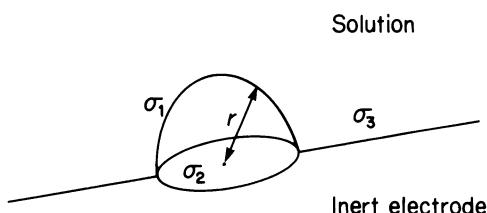


Figure 1.17 *Hemispherical nucleus of a new phase on a planar, inert electrode. The surface free energies between the phases,  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$ , are shown.*

right-hand side will predominate and  $\partial\Delta G_{\text{NUCL}}/\partial r$  will be positive so that the nucleus, if formed, will redissolve. Once the nucleus reaches a critical size, the other terms will have increased in importance sufficiently that  $\partial\Delta G_{\text{NUCL}}/\partial r$  will be negative and growth becomes spontaneous (see Fig. 1.18). In electrochemistry, nucleation may be forced by applying a large overpotential, i.e. ensuring that the first term predominates.

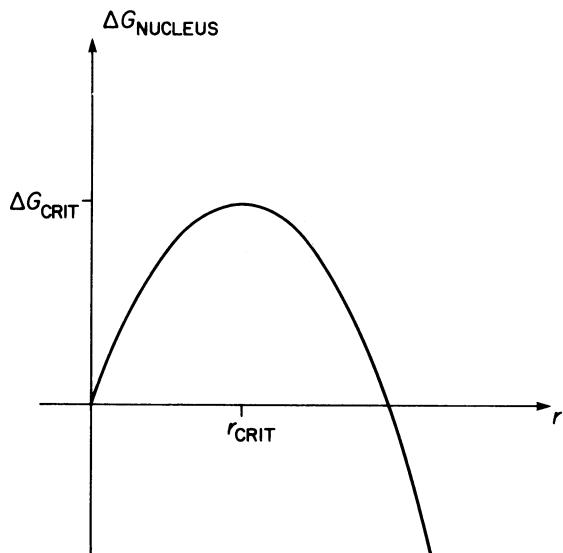


Figure 1.18 The dependence of the free energy of a nucleus on its size.

The total number  $N$  of nuclei growing will depend upon the time dependence of the nucleation process. This usually follows a first-order law

$$N = N_0 [1 - \exp(-At)] \quad (1.108)$$

where  $A$  is a nucleation constant. This has two limiting forms

$$N = N_0 \quad \text{when } At \gg 1 \quad (1.109)$$

which is called instantaneous nucleation and is most likely to occur at high overpotentials (see above) or

$$N = AN_0 t \quad \text{when } At \ll 1 \quad (1.110)$$

which is termed continuous nucleation.  $N_0$  is the total number of sites where nucleation can occur with the same probability (same  $\Delta G_{\text{NUCL}}$ ). This may not be the total number of sites on the electrode, however, since there may be preferred sites where nucleation is unusually easy, e.g. dislocations.

### 1.5.2 Growth of small centres

We shall again consider only the growth of hemispherical centres although similar equations can be derived for any shape of nuclei. Growth may be controlled either by kinetics or by mass transport. In the former case, the current at a fixed overpotential will depend only on the surface area  $S$  of a nucleus

$$I = nF\vec{k}S \quad (1.111)$$

but as the nucleus grows the surface will increase in area. The dependence of the surface area of a hemispherical nucleus on time is readily calculated, and substitution in (1.111) leads to

$$I = \frac{2nF\pi M^2 \vec{k}^3}{\rho^2} t^2 \quad (1.112)$$

This equation, however, gives only the current at a single nucleus and to obtain the observed  $I-t$  response we must combine equation (1.112) with the time dependence of nucleation, i.e. equation (1.109) or (1.110). Hence for instantaneous nucleation

$$I = \frac{2nF\pi M^2 \vec{k}^3 N_0}{\rho^2} t^2 \quad (1.113)$$

or for progressive nucleation

$$I = \frac{2nF\pi M^2 \vec{k}^3 A N_0}{\rho^2} t^3 \quad (1.114)$$

For diffusion-controlled growth of such hemispherical nuclei the corresponding equations (for short time only) are

$$I = \frac{nF\pi(2DC^\infty)^{3/2} M^{1/2} N_0}{\rho^{1/2}} t^{1/2} \quad (1.115)$$

for instantaneous nucleation and

$$I = \frac{4nF\pi(DC^\infty)^{3/2} M^{1/2} A N_0}{3\rho^{1/2}} t^{3/2} \quad (1.116)$$

for progressive nucleation.

It can be seen that each of these equations predicts that the current will increase with time and the observation of such behaviour in experiments is almost conclusive evidence for the involvement of a nucleation process. While the four equations (1.113)–(1.116) show the current to increase with a different power of time, the interpretation of  $I-t$  responses in terms of the kinetics of nucleation and the geometry of growth is not a simple matter because the various growth patterns (e.g. two-dimensional layer growth, conical nuclei) can lead to the same power of time. Such studies require electron microscopy to examine the size distribution of the nuclei (instantaneous nucleation should lead to all nuclei having an identical size) and experiments with very short prepulses at high overpotentials to enforce

instantaneous nucleation (and in systems where progressive nucleation occurs the prepulse will cause the power of  $t$  to be reduced by 1).

The above equations only apply to conditions where the growing nuclei are isolated from one another, i.e. early in the growth process. Once the centres start to overlap the current will not continue to increase at the same rate and, in general, the current will eventually reach a limiting value or pass through a maximum and start to fall.

### 1.5.3 Thickening of the deposit

In the deposition of a metal, the thickening of the layer is a relatively simple process. The metal ion,  $M^{n+}$ , will be transported through the electrolyte solution to the surface of the growing layer where it will be reduced to a metal adatom. The main question of interest is how this atom becomes incorporated into the metal lattice and how the structure of the deposit depends on the rate of formation of metal atoms, i.e. current density. These questions will be discussed in detail in the chapter on electroplating and, at this stage, we shall only note that, if the equilibrium lattice is to result, it will be necessary for the discharged atoms to diffuse across the surface to special sites (e.g. edge or kink sites or screw dislocations) where the lattice can reproduce itself in an orderly way. Certainly during this stage in the metal deposition process, the  $I-E$  characteristic will have the form of the Tafel equation — the current will increase exponentially with potential and be independent of time — and the phenomena occurring during nucleation and early stages of growth only affect the growth to the extent that they create the surface on which the later stages take place.

If the deposit is an oxide or an anodic film, the mechanism of the growth process is quite different and dependent on (a) whether the film is an electronic or an ionic conductor and (b) whether both components of the film come from the solution or, as is much more common, one lattice component is supplied by the solution and the other by the electrode.

In general, for an anodic film to grow on an electrode surface, an ion must be transported through the layer; if the mobile species is a cation, lattice growth occurs at the film/electrolyte interface, while if it is an anion the growth will occur at the electrode/film boundary. At ambient temperatures, the transport of an ion through a solid phase is a very slow process and hence this is likely always to be the rate-determining step. Two limiting growth laws, for high and low fields, are observed. In the latter case, it is assumed that the difference in electrochemical potential between two successive lattice positions is small compared with  $RT$  so that transport is essentially non-activated. The ion flux and hence the current is proportional to the electrochemical potential gradient in the film and at fixed potential this will depend only on the thickness  $x$  of the film. Therefore the rate of growth is given by

$$\frac{dx}{dt} = \frac{\alpha}{x} \quad (1.117)$$

where  $a$  is a constant and it can be seen by integration that the thickness of the film will increase with the square root of time. When a high field is necessary to bring about ionic transport, the elementary ionic jumps are activation-controlled and the current will increase exponentially with field strength, and as a result the thickness of the film varies with  $\log t$ . Electronically conducting layers behave very differently because they cannot support appreciable rates of ionic migration. Hence if they are coherent and protect the metal electrode completely from contact with the electrolyte solution, growth cannot occur.

## 1.6 ELECTROANALYTICAL TECHNIQUES

While a detailed discussion of instrumental methods is well beyond the scope of this book (the interested reader should consult the ‘further reading’ list at the end of this chapter), it is appropriate to acknowledge their contribution to electrochemical technology. They are largely responsible for the detailed information which is available about the electrode reactions used in commercial processes.

It is only twenty years since reliable instrumentation and convenient recording equipment made electroanalytical techniques, particularly those based on the control of electrode potential, routinely possible. Now the theoretical basis of such methods is well known; their application to the determination of reaction mechanisms is widespread and the equations and/or dimensionless plots necessary to obtain quantitative kinetic data are available in the literature. Table 1.3 describes some of the more widely used electroanalytical methods and lists those applications to which the methods are particularly advantageous.

We shall only use the example of cyclic voltammetry to illustrate the use of these modern techniques. In a cyclic voltammetric experiment, the potential of a small working electrode is varied linearly with time from an initial potential  $E_i$  to a second potential  $E_r$ , where the direction of the scan is reversed and the potential is swept back to  $E_i$ . The current is recorded and presented as a plot of  $I$  vs  $E$ . The potential limits,  $E_i$  and  $E_r$ , are selected to maximize the information which may be obtained and the experiment is carried out at a series of potential scan rates, usually in the range  $0.01 - 1000 \text{ V s}^{-1}$ ; changing the potential scan rate is equivalent to examining the electrode reaction on a different timescale.

Figure 1.19 shows cyclic voltammograms for some types of reactions which are most common; it can be seen that the voltammograms have quite characteristic shapes. While it is, indeed, the total  $I-E$  response which is characteristic of a particular mechanism, Table 1.4 lists some properties which are used to recognize reaction mechanisms.

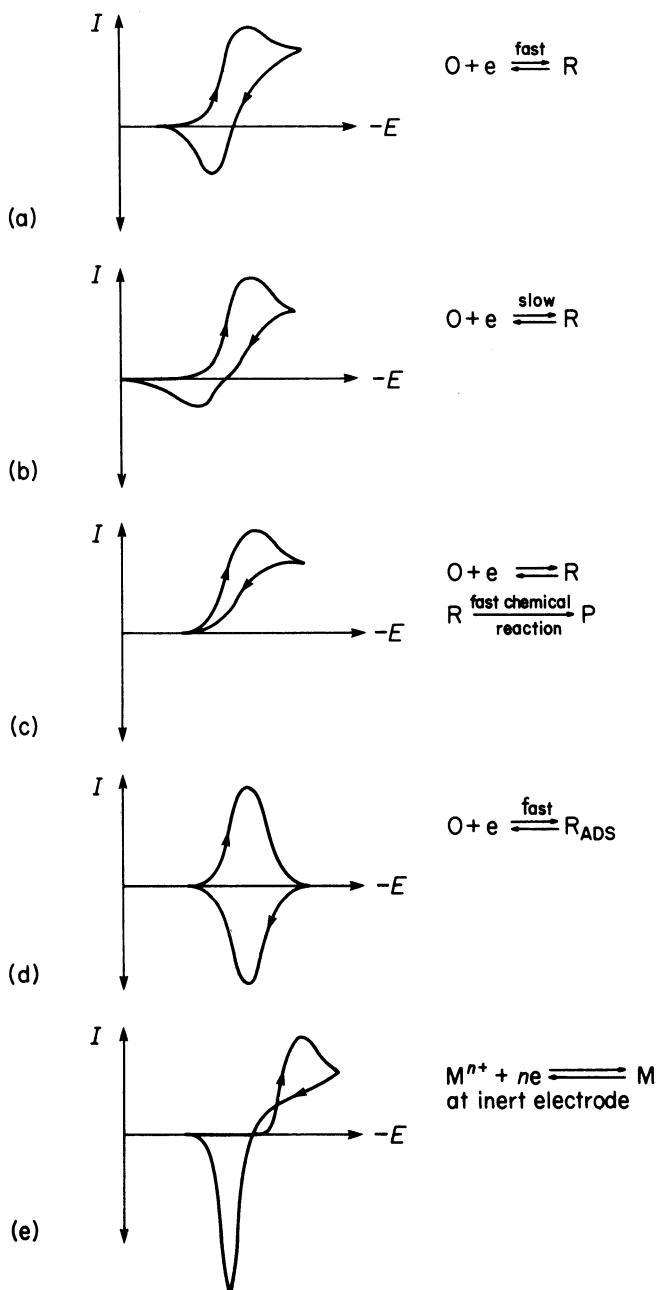


Figure 1.19 Cyclic voltammograms for several types of electrode process.

Table 1.3 Some widely used analytical methods

Technique	Experiment	Main variables	Measurements taken	Particular applications
Steady state	Vary potential (in steps or using slow linear potential sweep) and record steady-state current	Concentration of electroactive species, pH*	Tafel slopes. Exchange currents. $\frac{\partial I}{\partial C}$ ; $\frac{\partial I}{\partial (\text{pH})}$	Study of mechanism of complex reactions
Cyclic voltammetry	Scan potential between two limits linearly with time and cyclically. Record $I-E$ response	Potential scan rate $v$ . Potential limits	Peak potentials and currents as a function of $v$ . Monitor appearance of additional peaks	Qualitative study of mechanism. Coupled chemical reactions. Electron transfer. Measurement of capacitance
Chronopotentiometry	Step current from zero to constant value. Measure potential as a function of time	Current density	Transition times. Analysis of transient shape	Transport processes. Nucleation
Chronoamperometry	Step potential and measure $I-t$ response	Potentials. Timescale of measurement	Analysis of transient shape	Transport processes. Phase growth. Precise kinetics on systems of known mechanism
Chronocoulometry	Step potential and measure charge $Q$ as a function of time	Potentials. Timescale of measurement	Analysis of transient shape	Adsorption. Kinetics of electron transfer

AC impedance	Modulate electrode reaction about equilibrium with small AC current. Measure potential response and use correlation method to find in-phase and 90° out-of-phase signals	Frequency of AC input	Plot out-of-phase vs in-phase components at each frequency (Argand diagram)	Kinetics of electron transfer. Phase formation
AC voltammetry	Superimpose small-amplitude AC voltage on slow linear potential sweep. Measure AC current as a function of potential	Frequency amplitude of AC potential modulation	Measure peak potentials, peak shapes and compare forward and reverse potential sweeps. Correlate to find in-phase and out-of-phase components of response	Capacitance. Kinetics of electron transfer. Coupled chemical reactions
Coulometry	Carry out complete oxidation or reduction of electroactive species (using large electrode). Record $I$ and $Q$ as functions of time	Potential. Solution conditions	Charge for complete reaction ( $n$ value from Faraday's law). Analysis of electrolyte, electrode surface after electrolysis	Define electrode reaction; $n$ value and products
Rotating disc	Measurement of $I-E$ response as a function of rotation rate $\omega$	Rotation rate	Analysis of $I-\omega$ data at each potential	Transport processes. Electron transfer
Rotating ring-disc	Measurement of $I-E$ response of ring electrode as a function of potential (or current) at central disc electrode and rotation rate	Rotation rate. Experiment (controlled $I$ , $E$ or $I-t$ or $E-t$ ) at disc electrode. Potential of ring electrode	Analysis of $I_{\text{ring}}-\omega$ , $I_{\text{disc}}-\omega$ data, etc.	Coupled chemical reactions. Separation of solution free and adsorbed intermediates.
Spectroelectrochemistry	Measurement of spectroscopic response to electrochemical experiment	Nature of electrochemical experiment (controlled $I$ , $E$ or programmed $I-t$ or $E-t$ ). Nature of spectroscopy; visible, UV, IR, Raman, ESR	Analysis of spectra and absorbance time in addition to electrochemical read-out	Mechanism, particularly identification of intermediates both adsorbed and solution free. Kinetics

\* These also apply to all other techniques.

Table 1.4 Cyclic voltammetry – diagnostic criteria for four illustrative mechanisms.  $E_p \equiv$  peak potential,  $E_{p/2} \equiv$  half peak potential,  $\Delta E_p = E_p^f - E_p^b$ ,  $I_p$  = peak current density; superscripts f, b = forward and back reactions

	$E_p$ (V)	$\Delta E_p$ (mV)	$E_p - E_{p/2}$ (mV)	$I_p^f$	$I_p^b/I_p^f$
(a) $O + ne \xrightleftharpoons[n]{\text{fast}} R$	$E^\Theta - \frac{0.029}{n}$	$60/n$	$60/n$	$I_p \propto \nu^{1/2}$	1.0
(b) $O + ne \xrightleftharpoons[k_\Theta, \alpha]{\text{slow}} R$	Function $k_\Theta^\Theta, \alpha$ Shifts neg with $\nu$ $\frac{\partial E_p}{\partial \nu} = \frac{0.5RT}{anF}$ mV	Increases with $\nu, k_\Theta^\Theta, \alpha$ Function of $\nu, k_\Theta^\Theta, \alpha$	48/an	$I_p \propto \nu^{1/2}$	approx. 1.0
(c) $O + ne \xrightleftharpoons[k]{\text{fast}} R \longrightarrow P$	Function of $k$ . Shifts neg with $\nu$ $\frac{\partial E_p}{\partial \nu} = 30/n$ mV	Function of $k$ . Shifts neg with $\nu$	–	$I_p \propto \nu^{1/2}$	< 1.0
P electroinactive				Function of $k, \nu$	
(d) $O + ne \xrightarrow{\text{fast}} R_{ADS}$	$E^\Theta$	0	–	$I_p \propto \nu$	1.0
				Note $Q_f = Q_b$ and Gaussian shape of peak	

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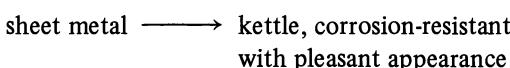
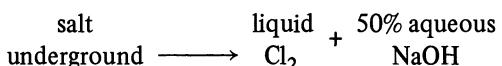
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## 2 Electrochemical Engineering

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Industry exists to manufacture the needs of society and, while operating within a legal and social structure, it seeks to maximize its profits. In general, therefore, it will wish to use the cheapest feedstocks and sources of energy (taking into account their projected cost and availability during the expected lifetime of the plant) and by low-cost technology convert them into the desired product. The role of the engineer is to transform the ideas of science into an industrial-scale plant; he must select between the various possible process routes and design the plant for the optimum financial return while recognizing society's concern about the environment and safety (although the cynical would say that these factors, too, are translated into costs for meeting legal specifications for effluents, insurance, etc.). Hence one cannot discuss industrial processes without constant reference to economics. Moreover, not all processes will have the same objective; some will be designed to produce a high-quality product that will command a high price, while others will manufacture to a lower specification because the product is used internally in the company or can be sold in large volume albeit at a lower profit per unit. Nor are circumstances the same in all companies; some will have feedstocks available as a result of other processes when the internal price may be below the market price. Also the cost of transport and energy, particularly electric power, is widely dependent on the site of the plant.

Some possible routes for the manufacture of certain products will contain an electrolytic step. The electrolytic route will, however, only be chosen if accountants can be convinced that, in economic terms, it is the best. Furthermore, it must be recognized that commonly the electrolysis will be one stage in a complex sequence and the economic assessment must consider the overall process, e.g.



rather than the electrolytic step, i.e. the brine electrolysis, the cathodic hydro-dimerization of acrylonitrile, and the electroplating of chromium, in isolation.

Hence one must seek to optimize the total process and it will sometimes be found advantageous to the total process to run the electrolysis under conditions which are non-optimum for the cell if considered alone. For example, a separator may be included in the cell solely to permit simple isolation of pure anode and cathode products although the separator will increase cell resistance (hence energy consumption) and the complexity of the cell design.

The design and operation of electrolytic processes is the province of the electrochemical engineer. It is convenient for him to concentrate on the electrolysis cell and, indeed, its design is a complex business requiring an understanding of potential and current distribution, electrolyte flow patterns, electrode kinetics, etc., and the consideration of the cost and performance of cell components (e.g. electrodes, separators, rectifiers). The cell, however, must fit into the overall process and hence it is normal to develop 'figures of merit' which indicate cell performance and permit a discussion of its interaction with other parts of the process.

The figures of merit should also aid the selection of cell design; for example, the optimum cell for (a) an energy-intensive electrolysis, e.g.  $\text{Cl}_2$  or Al production, (b) a process requiring extensive work-up and recovery of products, e.g. an organic synthesis, (c) an effluent treatment where large volumes of dilute solutions must be handled or (d) a process which consumes little charge but where the electrodes must be readily removed, e.g. electroplating or anodizing, will each be quite different.

Hence in this chapter we will first consider briefly the factors involved in costing an electrolytic process and discuss the various figures of merit. Then cell components and the principles of cell design will be discussed.

## 2.1 COSTING AN ELECTROLYTIC PROCESS

To a company who are deciding whether to build a new chemical plant, an important factor will be the percentage return on investment defined by the equation

$$\begin{aligned} \% \text{ return on capital} &= \frac{\text{profit}}{\text{capital investment}} \times 100 \\ &= \frac{\text{sales value} - \text{total product cost}}{\text{capital invested}} \times 100 \end{aligned} \quad (2.1)$$

since this will allow them to compare the effectiveness of using their money for the chemical plant with, for example, investing the money in a bank or starting other business activities. In the circumstances of 1980, the return would need to be at least 15–25% to make a new plant likely.

The capital,  $C$ , invested is the total sum of money required initially to set up the plant and it is estimated from

$$C = C_F + C_W + C_L \quad (2.2)$$

(a)  $C_F$  is the fixed capital or the cost of buying and installing the plant. For an electrolytic process this will include the cell houses, cells and rectifiers, all auxiliary unit processes (e.g. distillation, crystallization, liquefaction of gaseous products, effluent treatment) and a computer system to control and continuously optimize the overall process. Clearly,  $C_F$  is minimized by designing a plant with a high manufacturing rate. (b)  $C_W$  is the working capital, i.e. the cost of buying all the chemicals to start up the process. In the case of an electrowinning plant, for example, the cost of the metal to fill the cells with a concentrated solution of its ion is substantial. (c)  $C_L$  is the land capital, i.e. the cost of buying the land. This is minimized by packing the units as closely as safety considerations will permit and by building upwards rather than outwards.

The total product cost is computed for each working year and when it is estimated the following items must be considered:

(a) *Direct costs* – the cost of raw materials, utilities (effluent treatment, water and energy for heating, pumping, etc., as well as electrolysis, labour, maintenance and replacement of components (in electrolyses), particularly electrodes and membranes) and royalties if the company needs to license patent rights in respect to the process.

(b) *Plant overhead costs* – the cost of insurance, administration, safety, medical services, canteen and recreational facilities for the workforce, quality-control laboratories.

(c) *Marketing and distribution costs* – the product must be advertised, sold and transported to the customer.

(d) *Research and development costs* – the process must repay the expenditure involved in its development and perhaps also support an R and D programme to improve its performance, e.g. to develop better electrodes or to run pilot plants under modified process conditions.

(e) *Depreciation* – during the working life of the plant, the capital cost of the plant must be recovered. This is usually done by charging a depreciation  $D$ , each year. The simplest procedure for calculating  $D$  is by the equation

$$D = \frac{C - C_S}{N} \quad (2.3)$$

where  $C_S$  is the total scrap value of the plant and land and  $N$  years is the projected lifetime of the plant. It is normal to be very cautious in the evaluation of both the scrap value and the life of the plant despite the probability that the value of the land and chemical inventory ( $C_L + C_W$ ) will increase with time. Moreover, many plants are running for many years after their capital investment has been fully recovered and this is a big disincentive to the introduction of replacement technology; the absence of depreciation in the total product costs often leads to a situation where old technology can compete with apparently better processes.

Many of the items in (a)–(e) above would be difficult to estimate from first principles and the total product cost is more likely to be computed from an

equation such as

$$\text{Total product cost} = \frac{\text{raw materials} + \text{utilities} + x \cdot \text{labour} + y \cdot C_F + D}{z}$$
(2.4)

where  $x$ ,  $y$  and  $z$  are empirical factors (typical values  $x = 1.15$ ,  $y = 0.01$ ,  $z = 0.68$ ) which are based on experience and recognize, for example, that the cost of canteen and recreational facilities is related to the labour cost and the cost of component replacement is related to the fixed capital.

In order to compute the capital required to build the plant or the total product cost, the first step will be to estimate the volume of the product which can be sold since this will determine the size of the plant. The chemical engineer will then be in a position to begin the detailed design of a possible plant; he will commence the task by drawing up a detailed flow sheet (Fig. 2.1). The purposes of the flow sheet

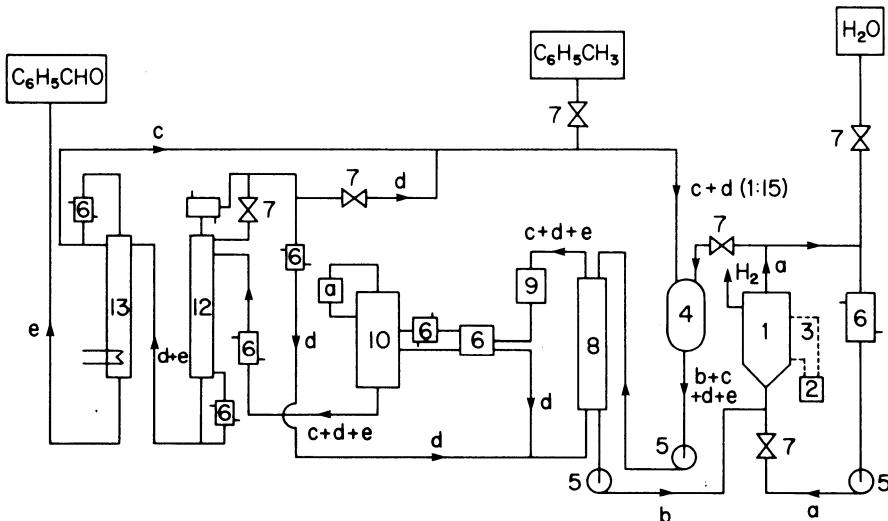


Figure 2.1 Preliminary flow sheet for a 2000 ton  $\text{yr}^{-1}$  benzaldehyde plant using electrolytic oxidation of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  in  $\text{HClO}_4$  and two-phase chemical oxidation, i.e. aqueous  $\text{Ce}^{4+}$  with toluene in hexane, in a second reactor. From Kramer, K., Robertson, P. M. and Ibl, N. (1980) J. Appl. Electrochem., **10**, 29. Key: 1, electrolysis cells (proposed 31 undivided tubular cells, radius 91.4 cm, height 86.4 cm;  $I = 113 \text{ mA cm}^{-2}$ ); 2, rectifier; 3, bus-bars; 4, chemical reactor (proposed  $5 \times 20 \text{ m}^3$  reactors); 5, pump; 6, heat exchanger; 7, valve; 8, extraction column (with hexane); 9, electrolyte stripper; 10, solvent extractor using heat pump principle with compressor(s); 11, distillation column to remove remaining hexane; 12, condenser; 13, distillation to separate toluene and benzaldehyde. Process streams: a, aqueous  $\text{HClO}_4$  with  $\text{Ce}^{4+} + \text{Ce}^{3+}$ ; b, aqueous  $\text{HClO}_4$  with  $\text{Ce}^{3+}$ ; c, toluene; d, hexane; e, benzaldehyde.

will be:

- (1) To allow an accurate evaluation of the number of unit processes (e.g. cells, pumps, distillation columns, crystallizers, compressors, solvent extractors, heating devices, heat exchangers, filters) which will be necessary;
- (2) To permit an estimate of the size of each unit process — this will require detailed performance data;
- (3) To allow a preliminary mass and energy balance and hence to show up useful waste heat which might be used elsewhere in the process, identify byproducts which might be sold and improve the process economics, etc;
- (4) To identify problems where further R and D might significantly improve the process and define the additional data required to optimize the overall process.

When complete, the flow sheet can be used for a preliminary economic evaluation of the process. If this shows that the process is promising, then the outstanding problems will be tackled and a pilot plant will be built to confirm the conclusions. Then as more data become available the flow sheet will be refined until the company has the confidence in the process to commence building the plant. Even after the plant is running, however, improvement of the process technology will continue and larger processes will be supported by an active pilot-plant facility which will seek to define the optimum working parameters for the overall process for the various economic and market conditions which are likely to arise. Also an R and D programme will aim to improve the weaker points in the process and the pilot plant will again test and adapt the conclusions. Hence for a larger process, modification to improve the financial return is a continuous procedure.

## 2.2 FIGURES OF MERIT

While the percentage return on investment will be the final criterion for the assessment of a process, it is for the scientist or engineer a very intractable parameter. It is more convenient to those involved in electrochemical technology, therefore, to develop other criteria or ‘figures of merit’ which pertain more closely to the electrolysis process and allow it to be treated as another unit process in the overall scheme.

It can be seen by perusing the later chapter headings in this book that the applications of electrochemistry are extremely diverse. Hence it is not surprising that the importance of and, in the limit, the relevance to the different applications of the various figures of merit will vary substantially. Moreover, it will commonly be found that it is not possible to optimize all the figures of merit; a change in reactor design or electrolysis parameters to improve one figure of merit will be detrimental to another. Then it is necessary to trade off the importance of the figures of merit to find the overall economic optimum.

### 2.2.1 Material yield

The material yield  $\theta$  is defined by

$$\theta = \frac{\text{moles of starting material converted to product}}{\text{moles of starting material consumed}} \times 100 \quad (2.5)$$

and it clearly determines the annual consumption of raw material for the desired tonnage of product. In addition, however, the material yield is important because, for  $\theta < 100\%$ , it will be necessary either to accept the lower price normally associated with an impure material or to introduce additional unit processes for purifying the product and handling the byproduct. The latter will inevitably increase the fixed capital.

Material yield is sometimes also discussed in terms of selectivity where

$$\text{Selectivity} = \frac{\text{moles of desired product}}{\Sigma \text{ moles of all products}} \quad (2.6)$$

### 2.2.2 Current efficiency

The current efficiency  $\phi$  is the yield based on the charge passed during the electrolysis, i.e. electricity is such an important 'reactant' in an electrolytic process that it derives its own figure of merit. It is defined as

$$\phi = \frac{\text{charge used in forming product}}{\text{total charge consumed}} \times 100 \quad (2.7)$$

where the charge used in forming the product is calculated using Faraday's law. A value of  $\phi$  below 100% indicates either that to some extent the back reaction occurs in the cell or, more likely, that byproducts are being formed. These may, however, arise by electrolysis of the solvent or the background electrolyte rather than the starting material, e.g. hydrogen from electrolysis of water during many metal depositions or oxygen in chlorine from oxidation of water will lead to current efficiencies below 100% for such metal-plating processes and chlorine respectively. Hence a value of  $\phi$  below 100% need not be associated with a material yield less than 100%.

### 2.2.3 Percentage conversion per pass

In general, this is the percentage of starting material consumed on each pass through the reactor. Since electrolysis is a heterogeneous process, the percentage conversion per pass depends on the ratio of the active electrode area to the cell volume and to the flow rate of the electrolyte. A high conversion per pass is desirable if, for example, the starting material is not to be recycled (e.g. an effluent treatment) or the product must be extracted during each cycle (e.g. product unstable). This is obtainable with most existing cell designs only when a slow flow rate is used which leads to a long residence time and poor mass transport conditions.

Hence a cell with a high conversion per pass at a high flow rate is often a desirable goal and certainly provides a driving force for designing cells with a high surface area per unit volume.

### 2.2.4 Product quality

Product quality often cannot be defined quantitatively. In some processes, however, product quality and its reproducibility are paramount. Examples would include surface finishing, where it is of overriding importance that the surface has the desired appearance or properties, and drug manufacture, where the absence of even trace amounts of some impurities can be critical.

### 2.2.5 Energy consumption

The energy consumption (or the energy yield) states the electric power required to make unit weight of the product and it is normally quoted in kilowatt-hours per kilogram ( $\text{kWh kg}^{-1}$ ) or kilowatt-hours per ton ( $\text{kWh ton}^{-1}$ ). It will be seen that it is a function of both the electrolysis conditions and the cell design. The energy consumption (in  $\text{kWh kg}^{-1}$ ) is given by the equation

$$\text{Energy consumption} = \frac{nFV}{3.6 \times 10^4 \phi M} \quad (2.8)$$

where  $M$  is the molecular weight in kilograms. It can be seen that the energy consumption does not depend directly on current density (because the passage of current is essential to the conversion of starting material to product – the charge to form one mole of product is determined by Faraday's law) but really only on the cell voltage and the current efficiency. Hence the energy consumption can be minimized only by selecting the electrolysis conditions so that the current is used solely for the reaction of interest and by making the cell voltage as low as is practicable. The cell voltage is a complex quantity made up of a number of terms, i.e.

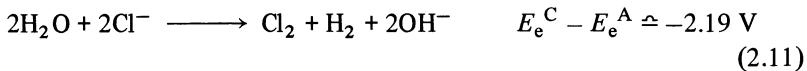
$$V = E_e^C - E_e^A - |\eta_A| - |\eta_C| - IR_{\text{CELL}} - IR_{\text{CIRCUIT}} \quad (2.9)$$

$E_e^A$  and  $E_e^C$  are the equilibrium potentials for the anode and the cathode reactions respectively so that  $(E_e^C - E_e^A)$  may be calculated from the free-energy change for the overall cell reaction by

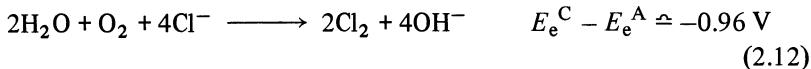
$$\Delta G = -nF(E_e^C - E_e^A) \quad (2.10)$$

Electrochemical technology, with the exception of batteries and other power sources, is concerned with carrying out reactions where the free energy is positive (i.e.  $E_e^C - E_e^A$  is negative) and, indeed, an advantage of electrolytic methods is that they may be used to drive very unfavourable reactions, e.g. the electrolysis of molten NaCl to sodium metal and chlorine. In electrolytic processes the over-potentials and  $IR$  terms represent energy inefficiencies and hence will make the cell voltage a larger negative value.  $(E_e^C - E_e^A)$  is the fraction of the cell voltage which cannot be avoided. It may only be reduced by changing the overall cell reaction and

in some circumstances this is possible by changing the counterelectrode reaction. For example, in present diaphragm or membrane chlor-alkali cells, the cathode reaction is the reduction of water so that the cell reaction is



but an attractive alternative would be to use an oxygen cathode. The cell reaction would then be



and although the free-energy changes for reactions (2.11) and (2.12) are both positive, clearly from a thermodynamic viewpoint the energy required by reaction (2.12) is much less.

In equation (2.9)  $\eta_A$  and  $\eta_C$  are the anode and cathode overpotentials respectively. In general, these overpotentials can contain a contribution from the electron transfer process and from mass transport. An industrial cell is normally operated under conditions where the contribution from the second term is small. Hence rearranging equation (1.36) or (1.38) it can be seen, that, for a simple electron transfer reaction, the overpotential is given by the expression

$$|\eta| = \frac{2.3RT}{\alpha nF} (\log I - \log I_0) \quad (2.13)$$

In other words, the overpotential will depend on the transfer coefficient and on the exchange current density. For more complex processes

$$|\eta| = \beta(\log I - \log I_0) \quad (2.14)$$

and it is the measured Tafel slope rather than  $2.3RT/\alpha nF$  which is important. In practice, the overpotential will increase by 30–250 mV, depending on Tafel slope, for each decade increase in current and the major factor determining the magnitude of the overpotential will be the exchange current density, i.e. the kinetics of the electrode process. This will depend on the electrolysis conditions (electrolyte, pH, temperature), and particularly the electrode material (see Section 1.4). It has to be borne in mind, however, that the requirement for the electrode material is even more specific; it must catalyse the reaction of interest but not others, for example the electrolysis of water which is commonly the thermodynamically preferred reaction. Thus, the anode in the chlor-alkali cell must catalyse chlorine but not oxygen evolution and the cathode in the synthesis of adiponitrile must allow acrylonitrile reduction but not hydrogen evolution.

The design of cells with minimum resistances is the first problem of electrochemical engineering. Clearly the cell resistance  $R_{\text{CELL}}$  is decreased by making the inter-electrode gap smaller and using a highly conducting electrolyte (molten salts and water with a high concentration of electrolyte are particularly favourable media in this respect). Moreover, any separators will cause a substantial increase in cell resistance although they may be essential for a good current and material yield or

for safety reasons. The final term in equation (2.9) recognizes that there will be a potential drop in the bus-bars which carry the current, in the various connectors and in the other parts of the electrical circuit, and the total potential drop in the cell house must be apportioned between the cells.

Cell performance with regard to energy is also discussed in terms of an energy efficiency defined by

$$\begin{aligned} \text{Energy efficiency} &= \frac{\text{ideal energy yield}}{\text{real energy yield}} \times 100 \\ &= \frac{\phi(E_e^C - E_e^A)}{V} \end{aligned} \quad (2.15)$$

## 2.2.6 Space time yield

The space time yield is a measure of the rate of production per unit volume of reactor and is normally quoted in units such as mol dm<sup>-3</sup> h<sup>-1</sup>. The space time yield is proportional to the effective current through the cell per unit volume of reactor and hence on the current density (overpotential, concentration of electroactive species and the mass transport regime), current efficiency and the active surface area of electrode per unit volume.

The need to design a cell with a high active surface area per unit volume of electrolyser is the second problem of electrochemical engineering. In heterogeneous catalysis where the requirement is only to have a high surface area of catalyst the problem is relatively simple, but in electrolytic cells there is the additional restriction that for the reaction to occur the local potential must be suitable. Moreover, for the desired situation of a uniform rate of reaction over the whole electrode area, the current and hence the potential must be the same over all the electrode surface. This will only be the case if all the electrode surface is geometrically equivalent with respect to the other electrode. For example, Fig. 2.2 shows four electrode geometries. In (a) the parallel-plate cell and (b) the rotating-cylinder cell, the current distribution will be uniform (provided the electrode operates at low  $\eta$  so that the electroactive species is not markedly depleted as the solution flows through the cell). On the other hand, in cells (c) and (d) the current distribution cannot be even. In cell (c) the backs of the electrodes are not insulated (cf. cell (a)) and clearly the back and the front of the electrodes are not equivalent; the additional *IR* drop will ensure that little current flows through the backs of the electrodes (although the situation would change totally if auxiliary electrodes were placed facing the backs of the electrodes). In cell (d) the non-uniformity of the current distribution will be less dramatic but less current will flow through the depressions than at the tips of the projections because the electrode surface in the depressions is further from the other electrode.

Hence electrode geometry is paramount in obtaining the high surface area per unit volume essential to a good space time yield. Indeed, it is perhaps not surprising that in comparison with other chemical reactors, electrolytic cells have poor space time yields; the expectation for chemical reactors is a space time yield of

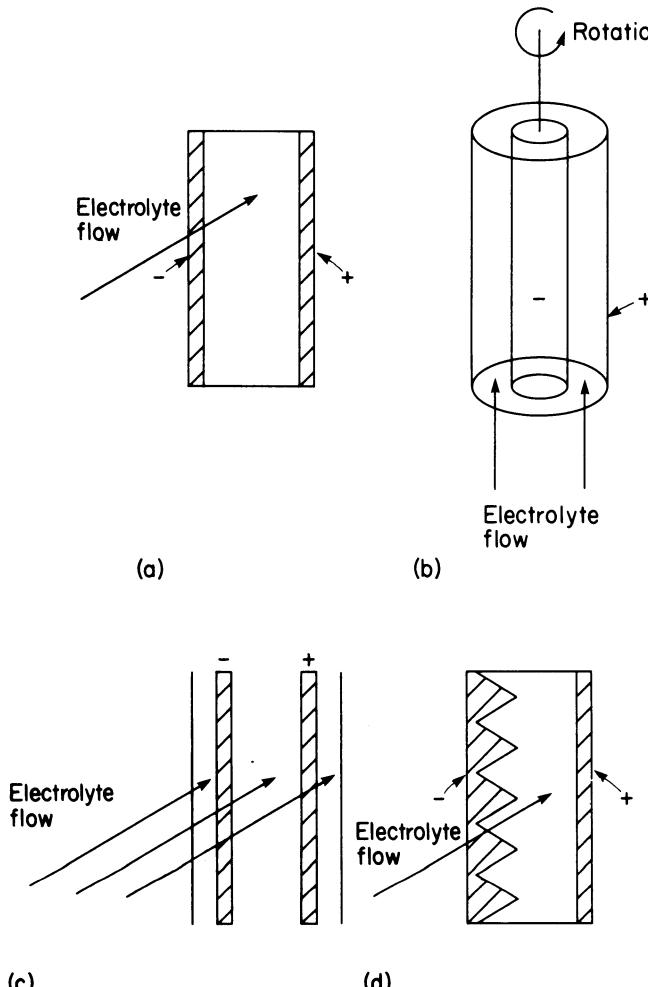


Figure 2.2 Elementary cell geometries: (a) parallel-plate cell, (b) rotating cylinder in tube cell, (c) two plates in reactor cell, and (d) plate cell with non-parallel electrodes.

$0.2\text{--}1.0 \text{ kg h}^{-1} \text{ dm}^{-3}$  while that, for example, for a typical copper electrowinning cell is only  $0.08 \text{ kg h}^{-1} \text{ dm}^{-3}$ . As a result, much academic electrochemical engineering has sought to increase this figure of merit by revolutionary changes in cell design, e.g. the introduction of fluidized bed electrodes.

It should also be noted that it is not possible to optimize both the space time yield and energy yield. The former requires the use of the highest possible current density which is certain to affect the energy consumption adversely because of the increased  $IR_{\text{cell}}$  term in equation (2.9).

### 2.2.7 Cost and lifetime of cell

While this is another figure of merit which, away from totally specific circumstances is difficult to quantify, it is clear that the initial cost, performance and lifetime of all cell components will affect the design of the electrolysis cell. For example, the benefit of catalytic electrodes will depend on the initial cost and their lifetime, which in turn will depend on current density; certainly the saving in electricity consumption during the lifetime of the electrodes must exceed the difference in cost between the catalytic and poorer electrode materials. Because of the inconvenience and cost of failure of components such as electrodes and separators, cells are usually taken off stream on a routine cycle and the components replaced or, at least, inspected closely; hence, ease of maintenance is another important factor in cell design.

Also, in selecting materials for the construction of cells it must be remembered that the concentrated electrolyte solutions used for electrolysis are corrosive and even pumps, pipework and cell bodies must be selected with corrosion resistance in mind.

## 2.3 ELECTROLYSIS PARAMETERS

As was discussed above, each of the figures of merit depends on a number of experimental variables. Hence, the overall cell performance will be determined by a complex interplay of these factors and it seems appropriate at this stage to summarize the various parameters which may be used to optimize an electrolytic process. The main electrolysis parameters are as follows.

(i) *Electrode potential.* The electrode potential determines which electron transfer reactions can occur and also their absolute (and relative) rates (i.e. current densities). In many processes the potential, or current density, is a major factor controlling the current efficiency, the space time yield and the product quality.

(ii) *Electrode materials and structure.* The ideal electrode material for most processes should be totally stable in the electrolysis medium but permit the desired reaction with a high current efficiency and at low overpotential. In a few processes, the anode reaction is the dissolution of a metal (e.g. plating or refining) and then this reaction should occur with the same current efficiency as the cathodic deposition so as to maintain the electrolyte composition constant but again at low overpotential.

In practice, we remain far from meeting these apparently trivial requirements: so-called ‘inert’ electrodes have a finite lifetime due to corrosion and physical wear while it is common, even normal, to accept an overpotential of several hundred millivolts. Only in the chlor-alkali process and, to a lesser extent, in water electrolysis has significant progress towards improved electrode materials been made. Generalizations concerning electrode materials are probably unwise and the choice of electrodes for particular industrial processes will be discussed in

Table 2.1 Common electrode materials.

Cathodes	Anodes
Hg, Pb, Cu, Ni	Pt, Pt/Ti, Ir/Ti
Graphite and other forms of C sometimes treated thermally or with organics to modify porosity, density, corrosion resistance	Graphite or other forms of C (treated, cathodes) Pb in acid sulphate media $\text{PbO}_2$ on Ti or Nb
Steels	Ni in alkaline media
Coating of low $\text{H}_2$ overpotential materials on steel, e.g. Ni, Ni/Al, Ni/Zn	Dimensionally stable anode (DSA), i.e. $\text{RuO}_2$ on Ti Other oxide coatings, e.g. $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ , $\text{IrO}_2$ , on Ti Magnetite $\text{Fe}_3\text{O}_4$

subsequent chapters; Table 2.1, however, lists some common anode and cathode materials.

The present trend is away from massive electrodes. The better materials are frequently expensive and it is therefore more common for the active material to be a coating on a cheaper, inert substrate (titanium, niobium or tantalum for anodes, steel for cathodes). Dispersed electrodes where the catalyst is pressed with a conducting powder (carbon), perhaps with additives (e.g. PTFE to decrease wetting) have also been discussed in Chapter 1. The coated electrodes are produced by several techniques including plating, spraying, vacuum sputtering and pyrolysis of solutions containing one or more metal ions. In addition to cheapness, these electrodes have the attraction that they have high real surface areas, i.e. they are microrough, and can be produced with different structures, e.g. various crystallite sizes, in order to improve activity.

The form of the electrode is also modified to meet the needs of particular processes. Thus, for example, electrodes are commonly constructed from meshes, expanded metal and related materials in order to maximize surface area, reduce cost and weight and also enhance the release of gaseous products. It will also be seen in the later discussion of cell design that various types of particulate bed electrodes have been proposed and the possibilities for porous gas electrodes, which reduce mass transport restrictions for gaseous reactants, must also be considered.

(iii) *The concentration of electroactive species.* The concentration of the electroactive species is the major parameter that determines the maximum feasible current density and hence the optimum space time yield. Normally this current is proportional to concentration and hence in most systems the concentration of electroactive species will be as high as possible.

(iv) *Electrolysis medium.* The properties of the electrolysis medium will be determined by the choice of solvent, electrolytes and pH and perhaps also complexing agents, additives (i.e. species present in relatively low concentration to modify the properties of the electrode/electrolyte interface) and reagents present to react with intermediates produced in the electrode reaction. The concentration of each constituent will also be important.

Although the last twenty-five years have seen much academic research on electrochemistry in non-aqueous solvents, its impact on industrial processes has been small because of the lower conductivity of such solvents and doubts concerning their long-term stability under electrolysis conditions. Certainly, water with a high concentration of electrolyte is the medium of choice for an industrial electrolytic process, with molten salts a second best if their use is essential to a process. Some of the achievements in aprotic solvents (e.g. acetonitrile, dimethyl-formamide, propylene carbonate) are, however, impressive (e.g. non-aqueous batteries, electroplating baths and as media for certain organic syntheses) and electrochemical engineers continue to seek cell designs where their use in industry is more likely.

The other constituents of the electrolysis medium are chosen on the basis of cost and their effectiveness in meeting the needs of a particular process. Their selection will be discussed in many subsequent chapters.

(v) *Temperature and pressure.* Electrolysis at elevated or reduced pressures is generally to be avoided because of the complexity of cell design; in practice, the examples of electrochemistry away from atmospheric pressure are limited to special water electrolyzers and battery systems.

On the other hand, temperature is a parameter employed frequently. Particularly, temperatures above ambient are used because of the beneficial effect on the kinetics of all steps in an electrode process. The diffusion coefficient, the exchange current density and the rate of chemical reactions are all increased.

(vi) *Mass transport regimes.* The mass transport regimes used in industrial processes range from natural convection and diffusion in unstirred electrolytes to highly turbulent conditions produced by rapid stirring or pumping or using turbulence promoters such as a bed of particles. A high Reynolds number is commonly favourable since it increases mass transport and hence both increases the current density at any potential and leads to a greater uniformity of concentration in the reaction layer adjacent to the electrode surface. All forms of pumping and stirring, however, cost money and in undivided cells can produce problems of interaction of anode and cathode products, e.g. aluminium electrolysis.

(vii) *Cell design.* The design of the cell will affect all the figures of merit for an electrolytic process. Cell design will be considered in detail in the next section but it should be noted here that the principal factors determining the electrolysis performance will be the presence or absence of a separator and its type (porous diaphragm or ion-selective membrane), the mass transport regime, the arrangement

of the electrodes and hence the anode–cathode gap and potential distribution at both electrodes and the materials of construction.

## 2.4 PRINCIPLES OF CELL DESIGN

### 2.4.1 Classical chemical reaction engineering

Chemical engineering recognizes three broad types of reactor (see Fig. 2.3). These are now described.

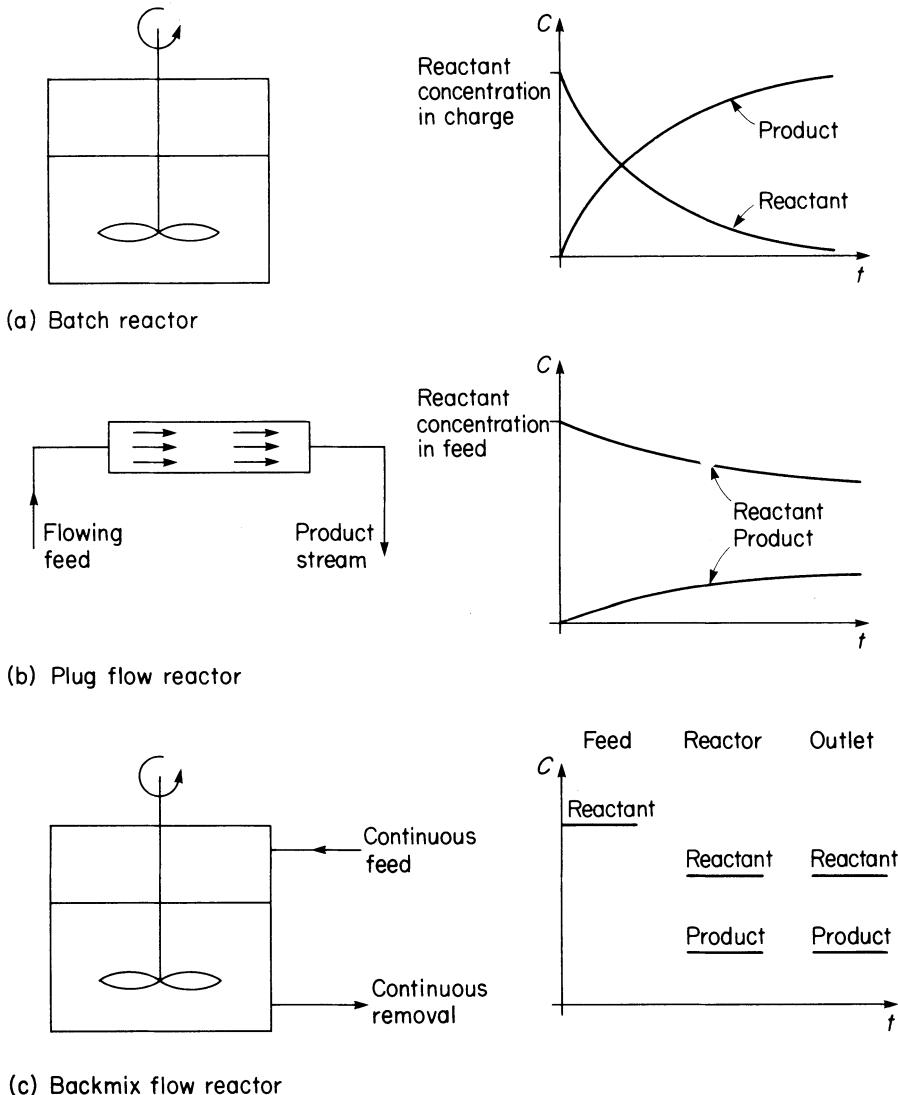


Figure 2.3 The three fundamental ideal types of chemical reactors and their characteristic reactant/time and product/time curves.

(a) *The batch reactor*

Here the reactor is charged with the reactants which are then well mixed and left for a period for the reaction to occur to some predetermined extent. The resulting solution is then discharged from the reactor and worked up to isolate the product. The concentration of reactants and product will change smoothly with time (in a way dependent on the reaction kinetics) but the composition is uniform throughout the reactor volume and the residence time is well defined, i.e. the same as the reaction time.

Batch processing is clearly labour-intensive and only suited to small-scale operation.

(b) *The plug flow reactor*

This is a continuous and steady-state reactor. The reactant mixture is flowed through the reactor, e.g. a tube filled with catalyst, and the product is extracted from the mixture leaving the reactor. Ideally, a plug flow reactor is characterized by a flow of fluid where no element overtakes or mixes with that preceding or following it; hence it is equivalent to a train passing through a tunnel with the carriages proceeding in a perfectly orderly manner. The composition of the mixture changes with distance through the reactor and the residence time is the same for all species.

(c) *The backmix reactor*

This system consists of a well stirred tank so that the composition throughout the reactor is uniform but reactant is added continuously and a product stream is removed at the same rate. The exit stream will have the same composition as the fluid in the reactor.

Using the concept of mass balance (see Fig. 2.4), it is possible to derive quantities which may be used to compare reactors and conditions and to calculate

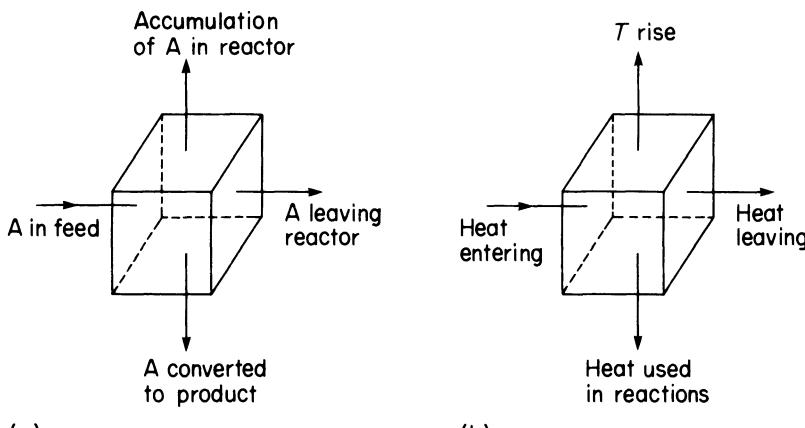


Figure 2.4 *Concepts of (a) the mass balance of A and (b) heat balance as applied to a chemical reactor.*

the size of reactor for a particular production rate. The space time  $\tau$  is defined as the time to process one reactor volume and space velocity  $S$  is the number of reactor volumes processed per unit time.

$$\tau = \frac{1}{S} = \frac{C_A^0 V}{f_A^0} \quad (2.16)$$

where  $C_A^0$  is the concentration of A in the feed and  $f_A^0$  the feed flow rate in moles per unit time;  $V$  is the volume of the reactor.

For example, for a plug flow reactor (see Fig. 2.5), the mass balance equation is

$$\text{moles of A in feed} = \text{moles of A in product stream} + \text{moles of A reacted} \quad (2.17)$$

and applying this mass balance equation to a typical volume element  $dV$  in the reactor one obtains

$$-f_A^0 dx_A = r_A dV \quad (2.18)$$

where  $r_A$  is the rate of disappearance of A (e.g. for a first-order reaction,  $kC_A$ ) and the other symbols are defined on the figure. The rate of reaction varies along the reactor (clearly  $C_A$  decreases) and hence the expression must be integrated, i.e.

$$\int_0^V \frac{dV}{f_A^0} = - \int_0^{x_A^f} \frac{dx_A}{r_A}$$

or

$$\frac{V}{f_A^0} = - \int_0^{x_A^f} \frac{dx_A}{r_A} \quad (2.19)$$

and

$$\tau = \frac{1}{S} = \frac{C_A^0 V}{f_A^0} = -C_A^0 \int_0^{x_A^f} \frac{dx_A}{r_A} \quad (2.20)$$

Equations such as (2.19) or (2.20) are known as design equations. Equation (2.19) allows the estimation of reactor volume necessary for a given feed rate and conversion,  $x_A^f$ , while (2.20) permits the calculation of space time or space velocity.

Similar derivations for the other types of reactor show that the reactor volume necessary for a particular conversion will be the same for a plug flow reactor or a batch reactor but the corresponding backmix reactor would need to be much larger,

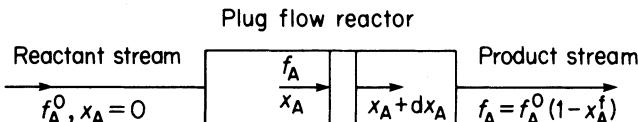


Figure 2.5 *Plug flow reactor*.  $f_A^0$  (moles per unit time) is the feed rate of the reactant A and  $x_A$  is the fraction of A converted to product.

the factor depending on the conversion and the reaction order. In other words, for a fixed reactor volume, the conversion obtained with a plug flow reactor will be much higher (by a factor 2–100) than that with a backmix reactor. This is understandable because soon after entry into a plug flow reactor the concentration of reactant and therefore the reaction rate is high whereas in a backmix reactor, the reactant is immediately diluted by the whole reactor volume.

In practice the reactor system may be more complex. It is possible to introduce partial or complete recycle of the outlet stream, to consider the use of multistage set-ups with reactors in series or parallel or to introduce feed or heat management between stages. The principles for the discussion of such systems are, however, the same.

The three ideal reactor types and the more complex systems are all to be met in electrochemical technology. There are, however, some additional factors which are only relevant to electrolytic processes and these will be reviewed in the next section, prior to the discussion of cell design.

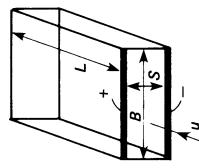
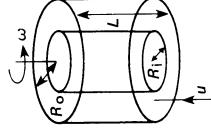
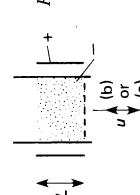
#### 2.4.2 The additional technology of electrolytic processes

In earlier sections, the similarities between the design and characterization of electrolysis cells and other chemical reactors and the need to integrate the cell with the other unit processes in the plant has been emphasized. On the other hand, there are some notable differences which need to be recognized. For example, in a comparison of an electrolysis cell with a reactor for a more familiar heterogeneous process, gas-phase catalysis, there are two outstanding differences. First, mass transport processes in the liquid phase are always very slow in comparison with those in the gas phase. This will cause both mass transport limitations on the rate of chemical changes in the reactor and the creation of reaction layers at the solid/fluid interface to be much more troublesome to the electrochemical engineer. Secondly, while in both types of reactor it is desirable to maximize the surface area per unit volume, the designer of an electrolytic cell has to concern himself with the problems of non-uniform current distributions since the electrode surface will only be active if there is an appropriate local potential difference; it was noted above that the geometric arrangement of anode and cathode is the key factor.

It is the purpose of this section to review these problems and then to discuss those technological features of a cell house which are unique to electrolytic processes.

(i) *Mass transport effects in electrolytic reactors.* It is normal to characterize as a function of flow rate and cell and/or electrode dimensions, the mass transport regime within a reactor. This is generally done in terms of average parameters derived from measurements of the total cell current when the cell voltage is such that all the electroactive species reaching the surface are oxidized or reduced. These experimental data are cast onto equations in terms of dimensionless parameters which indicate the relative importance of inertial/viscous forces and convection/diffusion, etc. (see Chapter 1), and some typical equations for common electrode geometries are given in Table 2.2.

Table 2.2 Average mass transfer correlation equations for some simplified electrode geometries.\*

Cell	Conditions	Correlation equation	Definitions
1. Vertical parallel plate			
(a) Natural convection, $u = 0$	$Gr \times Sc < 10^{12}$	$Sh = 0.45 Gr^{0.25} Sc^{0.25}$	
(b) Fully developed laminar flow	$Re < 2000, B > S, L/d_e < 35$ $Re > 2000, L/d_e > 10$	$Sh = 1.85 Re^{0.33} Sc^{0.33} (d_e/L)^{0.33}$ $Sh = 0.023 Re^{0.8} Sc^{0.33}$	$d_e = 2BS/(B + S)$
			
2. Concentric cylinders			
(a) Fully developed laminar flow, $\omega = 0$	$Re < 2000$ , inner electrode	$Sh = 1.61 \phi Re^{0.33} Sc^{0.33} (d_e/L)^{0.33}$	$\phi = \frac{r - 1}{r} \left( \frac{0.5 + [r^2/(1 - r^2)] \ln r}{1 + [(1 + r^2)/(1 - r^2)] \ln r} \right)$ $r = R_i/R_o$
			
	$Re > 2000$ , inner electrode	$Sh = 0.023 Re^{0.8} Sc^{0.33}$	$d_e = 2(R_o - R_i)$
	$100 < Re < 1.6 \times 10^5$	$K = 0.079 (R_i \omega) Re^{-0.3} Sc^{-0.64}$	$Re = \frac{2R_i^2 \rho \omega}{\mu}$ $d_e = 2R_i$
(b) Rotating cylinder, no external pumping			
3. Bed electrodes			
(a) Packed	$Re > 35$	$Sh = 1.52 Re^{0.55} Sc^{0.33}$	$d_e = \text{ave particle diameter}$
			
(b) Fluidized	$u$ or (a)	$Sh = \frac{(1 - \epsilon)^{0.5}}{\epsilon} Re^{0.5} Sc^{0.33}$	$d_e = \text{ave particle diameter}$ $\epsilon = \text{bed voidage}$

\* The dimensionless parameters, the Reynolds number  $Re$ , the Grashof number  $Gr$ , the Schmidt number  $Sc$  and the Sherwood number  $Sh$  are defined

$$Re = \frac{ud_e}{\nu} \quad Gr = \frac{g \Delta \rho L^3}{\nu^2 p} \quad Sc = \frac{\nu}{D} \quad Sh = \frac{K d_e}{D}$$

where  $u$  = flow velocity,  $d_e$  = characteristic length parameter,  $\nu$  = kinematic viscosity,  $\Delta \rho$  = difference in density between solution at electrode surface and the bulk,  $\rho$  = bulk solution density,  $D$  = diffusion coefficient, and  $K$  = average mass transfer coefficient.

Such equations do not, however, characterize completely the mass transport conditions since in many cell designs there will be local variations from the average behaviour. Such variations may be investigated by dividing the electrode into a number of sections and measuring, separately, the current on each section. The local current can then be plotted as a function of position and flow conditions. Further information about the mass transfer conditions in flow cells may be deduced by the analysis of marker experiments; in such experiments, a well defined pulse of a dye or an ion (formed by anodic dissolution of a metal) is introduced at the inlet to the reactor. The solution with the marker is allowed to pass through the cell (with no current flowing) and the concentration of marker as a function of time is monitored at the outlet. Ideally, for plug flow, the marker concentration vs time at the outlet should have the same shape as that at the inlet. In practice, some solution will be slowed down by its proximity to solid surfaces (see Chapter 1) during the passage of the solution through the cell and this leads to dispersion of marker pulse (see Fig. 2.6). Analysis of the response at the outlet gives information about flow conditions in the cell.

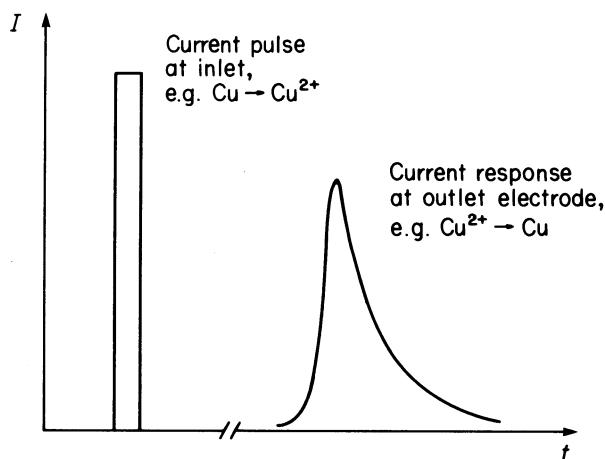


Figure 2.6 *Electrochemical version of the marker experiment to investigate the dispersion of electrolyte through the reactor.*

The electrochemical engineer's interest in mass transport relates to three different aspects of cell performance:

- The desire for a uniform current density over all the electrode surface,
- The advantage to be gained from a high current density,
- The need in certain processes to maintain the composition of the reaction layer at the electrode close to that in the bulk solution.

Hence, in general, the cell designer will be concerned with concentration variations in two directions, that parallel to the electrolyte flow and that perpendicular to the electrode surface. Figure 2.7 uses the example of an electrode

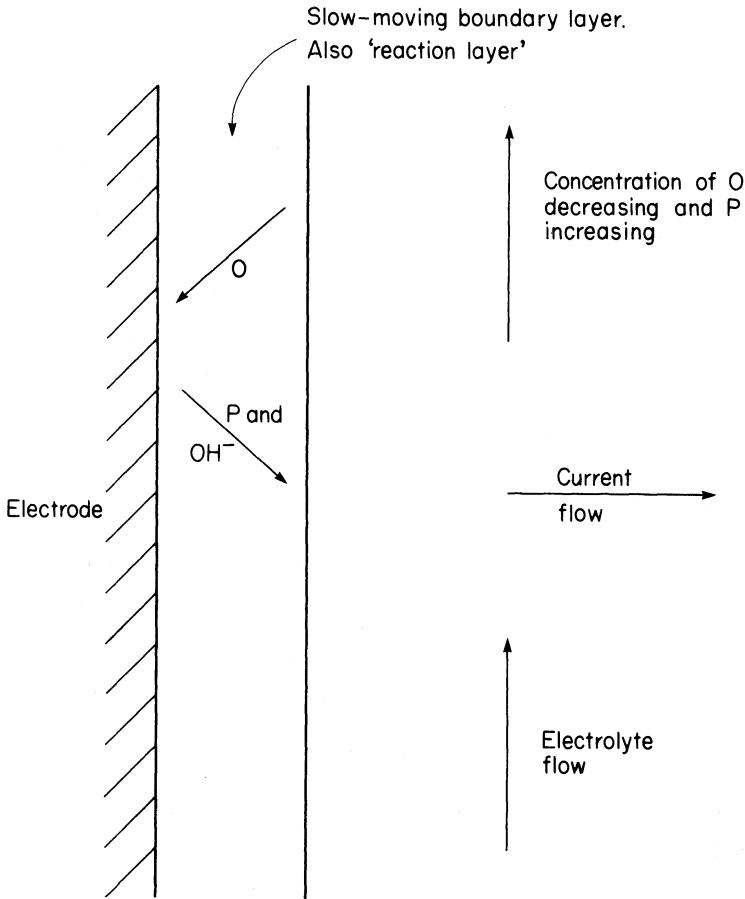


Figure 2.7 Concentration variations in a parallel-plate cell for the case where the electron transfer  $O + e \rightarrow R$  is followed by the coupled chemical reaction  $2R + 2H_2O \rightarrow P + 2OH^-$  in a neutral electrolyte.

in a parallel-plate cell. As the solution flows up the electrode, the electrode reaction is occurring and hence the concentration of the electroactive species must decrease. Whether this depletion is significant will depend on the electrode potential (and hence on the ratio of  $I$  to  $I_L$ ), on the length of the electrode, on the flow rate and the ratio of electrode area to electrolyte volume. There must also be a layer next to the electrode surface where there is a concentration gradient in the electroactive species. The variation of the concentration within this reaction layer and its thickness will again depend on the ratio  $I/I_L$  via the surface concentration and the Reynolds number respectively. In some electrolyses, particularly those involving complex chemistry, there will be concentration gradients in reagents other than the electroactive species within the reaction layer (where almost all the chemistry will occur because of the relatively high concentration of intermediates). For example,

in electrolyzers for the production of hypochlorite from sea water, a problem can arise at the cathode. The electrode reaction is hydrogen evolution but it also generates hydroxide ion and, unless there is efficient mixing between the reaction layer and the main body of electrolyte, the pH of the solution will rise to a value where the magnesium in the sea water precipitates as magnesium hydroxide. The maintenance of uniform conditions in the reaction layer is greatly assisted by turbulence, since the small eddies enter the reaction layer, or tangential shear forces.

Fluid mechanics is also important in the design of electrolytic plant in other ways. First, the pipework between cells and between the cells and other units must be designed to minimize pumping costs. This requires the correct choice for the diameter of the pipework and the avoidance of unnecessary pressure drops caused by obstructions or restrictions, incorrectly designed entries, sharp turns or rapid changes in pipe diameter. More importantly, however, the electrochemical engineer must pay particular attention to the fluid entry into the cell and ensure that there are no dead zones and that the flow becomes uniform as quickly as possible. This requires the correct design of the distributor.

(ii) *Current distribution.* The objective of cell design is normally to obtain a uniform potential distribution and often also a uniform current distribution. The current distribution is a function of the local concentration of electroactive species (see the last section) as well as the potential distribution.

The potential distribution will depend on the relative positions of the anode and cathode. The reason for this may not be obvious since, if the electrode is made of a highly conducting metal, it must have an equipotential surface. But while in Chapter 1 the kinetics of electron transfer were discussed in terms of overpotential, it was pointed out that the current, in fact, is determined by the potential differences between the metal and the solution, i.e.  $\phi_M - \phi_S$  (or more correctly  $\phi_2 - \phi_S$ ), and  $\phi_M - \phi_S$  (as is  $\phi_2 - \phi_S$ ) is a potential difference in the solution phase. The potential field in the solution depends on the arrangement of electrodes, the solution resistivity  $\rho_S$ , and the applied voltage between the electrodes. Indeed, overpotential is usually used in kinetic equations only because of its ease of measurement and since it is proportional to  $\phi_M - \phi_S$ .

The primary current distribution is calculated assuming that the current density is low so that there is no significant overpotential and no depletion of the electroactive species over the electrode surface. The variation of the solution potential  $\phi_S$  is found by solving, analytically or numerically, Laplace's equation

$$\frac{\partial^2 \phi_S}{\partial x^2} + \frac{\partial^2 \phi_S}{\partial y^2} + \frac{\partial^2 \phi_S}{\partial z^2} = 0 \quad (2.21)$$

with boundary conditions appropriate to the electrode geometry. From a map of  $\phi_S$  immediately adjacent to the electrode surface the variation in  $\phi_M - \phi_S$  and hence current density can be calculated.

As was shown in Fig. 2.2, the primary current distribution is only uniform when all points on the electrode surface are strictly equivalent and the current density is low. This is possible only with two reactor designs, a parallel-plate reactor having

electrodes of equal area and occupying opposite walls and a concentric-cylinder reactor. For all other electrode arrangements there will be a variation of potential and current density over the surface. An example is shown in Fig. 2.8 where the broken lines join equipotential points and the current density is inversely proportional to the length of the arrowed lines. The highest current density is between the points closest together on the two electrodes and almost no current flows on the reverse side of the anode.

Such simple calculations do not correspond to the real conditions in electrolytic cells; in the electrolysis cell there will be a significant current and hence there is likely to be a substantial overpotential associated with electron transfer. The calculation must now consider the way in which the local current density will affect  $\phi_M - \phi_S$  and hence  $\phi_S$  in the electrolyte. The result is the secondary current distribution and, in general, it shows that the variation in current over the electrode surface is not as great as indicated by the primary current distribution. The tertiary current distribution also takes into account the variation of current density when there are significant changes in the concentration of electroactive species across the

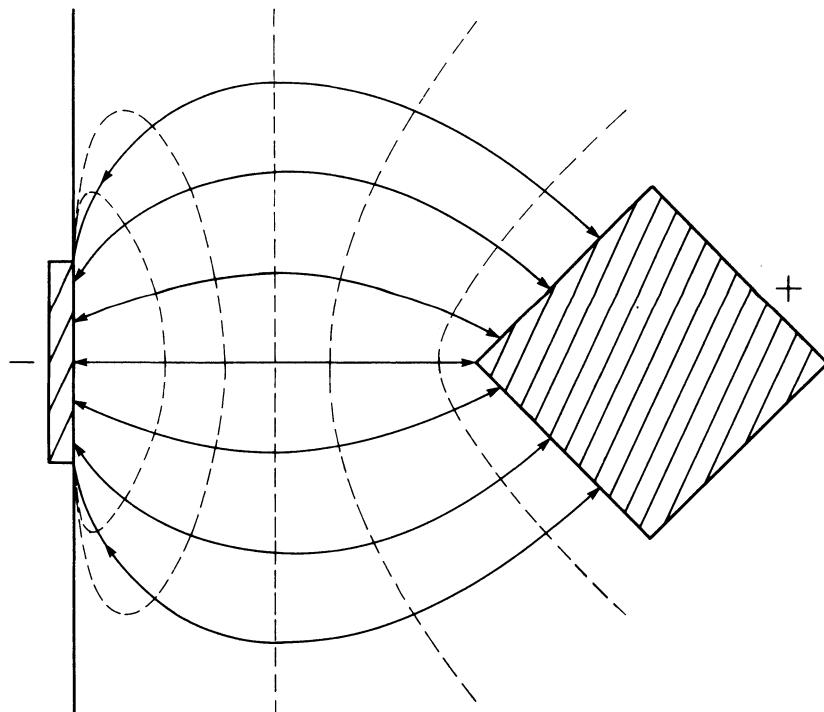


Figure 2.8 Current distribution for the electrode geometry shown. The broken lines show equipotential contours. The current density is inversely proportional to the length of the arrows. Note that almost no current will flow on the anode surface away from the cathode.

surface; the largest variation must occur when the overpotential is so high that the current is mass-transfer-controlled.

As an example, Fig. 2.9 is a sketch of the various current distributions for a parallel-plate cell with electrodes of length  $L$  and of infinite width, and with fully developed laminar flow. The primary current distribution shows the current to be uniform over most of the electrode but with a considerable edge effect at  $x = 0$  and  $x = L$ ; the current goes to a very high value at these ends. The secondary distribution is similar but is even closer to the ideal while the limiting tertiary distribution shows that in these conditions the current density drops sharply along the electrode.

The conclusion for practical cell design is clear — the electrode geometry must be simple. The exceptions to this rule will be when the current distribution is not important (e.g. in low-current devices for removing dilute metal ion from solution) or when by necessity one electrode must have a complex shape, e.g. electroplating or electrochemical machining. In the latter case it is often necessary to use auxiliary counterelectrodes, shields of insulating materials to guide the current paths or counterelectrodes of very carefully designed shape in order to obtain an even current distribution.

(iii) *Special cell house technology.* Electric power, whether generated in a slave power station on site or bought from a national grid, almost always becomes available as high-voltage alternating current. It must therefore first be rectified and transformed

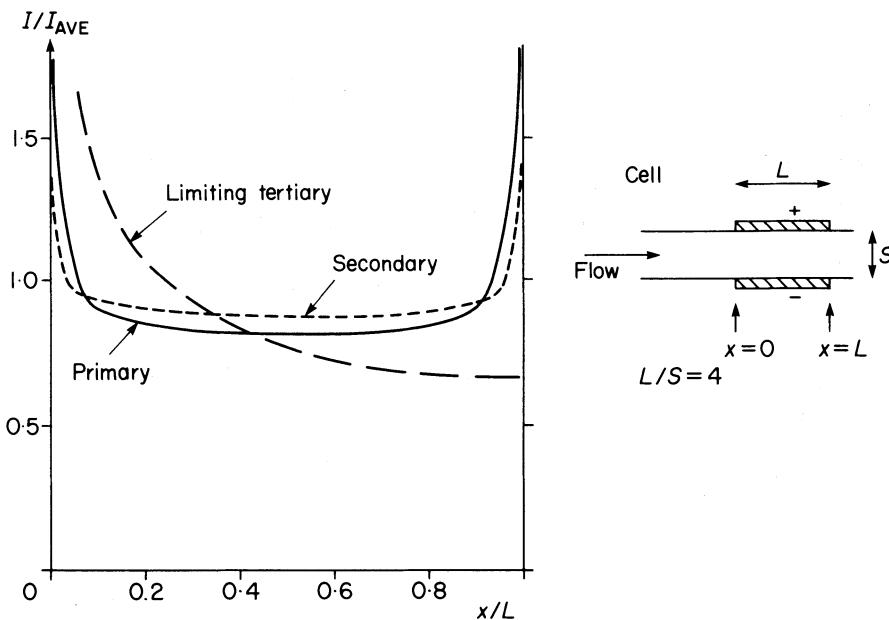


Figure 2.9 *Current distributions for a parallel-plate reactor with fully developed laminar flow: (a) primary current distribution, (b) secondary current distribution and (c) limiting tertiary current distribution.*

to give DC current at the required voltage and then be transmitted around the cell house with the minimum energy loss. The developments in rectification which occurred during the 1950s allowed substantial advances in electrolytic processes. Before this period, rectifiers were very bulky and gave the highest conversion efficiencies, then only about 85–90%, for high voltages and low currents. The silicon semiconductor rectifiers were much more compact and for the first time permitted economically the production of high currents at lower voltages; even at 200 V the efficiency was above 95%. As a result silicon rectifiers are universally used and now rectification and transmission is cheapest in the range 200–700 V. Cell rooms are arranged electrically so that the voltage requirement falls within this range; a common arrangement is for the cells to be connected in series so that the total voltage requirement is about 450 V; the centre of the cell stack is earthed and the two ends are at +225 V and –225 V, larger voltages being avoided for safety reasons. The current requirement will depend on the scale of the process and the size of the cells but at this time it is not unusual for the plant to use  $(1-5) \times 10^5$  A.

The transmission of power around the cell room once it is at the appropriate voltage and current also requires thought. The current is transmitted along bus-bars, normally constructed from copper or aluminium because of their exceptional conductivity, and the dimensions of the bus-bars are carefully calculated because of the considerable investment in the metal. Moreover, the connectors to the cells must be designed to avoid energy loss even at the very high currents and there must be switches which permit individual cells to be isolated for maintenance without disturbing the rest of the cell house.

Physically the arrangement of cells is also important. The plant must be electrically and chemically safe and, although it is common for each cell to have a number of pipes for electrolyte feed and effluent and for gaseous products, the connections must again be made so that individual cells may be isolated for cleaning, maintenance and the replacement of cell components. In larger plants, the high currents create a substantial magnetic field and it is therefore necessary to lay out the cells to minimize this field.

When a cell or cell stack contains more than two electrodes, there are two ways of making the electrical connection; the cell may be monopolar (Fig. 2.10(a)) or bipolar (Fig. 2.10(b)). In the monopolar cell there is an external electrical contact to each electrode and the cell voltage is applied between each cathode and anode. It can be seen that in the cell shown, anodes and cathodes alternate and both faces of each central electrode are active, with the same polarity. Monopolar connection requires a low-voltage, high-current supply. Bipolar connection requires only two external electrical contacts to the two end electrodes and it recognizes that the cell reaction will occur wherever there is an appropriate potential difference. The voltage field caused by the bipolar connection is shown in Fig. 2.11 and demonstrates how the six electrodes of the cell in Fig. 2.10(b) can lead to five electrolysis cells. The voltage distributes itself between the end electrodes with the electrical contacts, most of the potential drop occurring in the solution phase because of the high conductivity of the metal electrodes. Hence if the total applied voltage is sufficient to drive current through the structure, then a potential

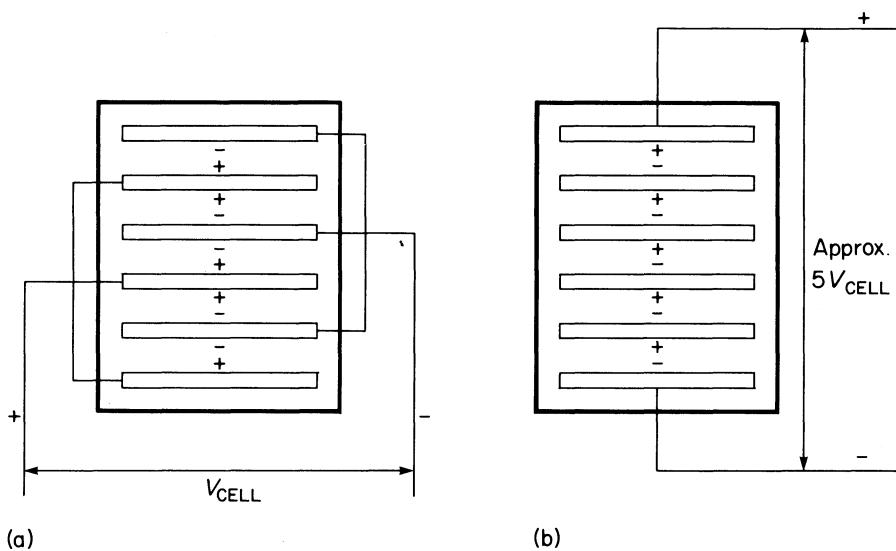


Figure 2.10 *Electrical connection in multi-electrode cells: (a) monopolar and (b) bipolar*

difference equivalent to one monopolar cell voltage will exist between electrodes 1 and 2, 2 and 3, etc. In the bipolar cell, the opposite face of each electrode will have different polarities. In addition to simplicity of electrical connection, the bipolar cell has the advantage that it produces the equivalent amount of product to monopolar cells using a lower current and a higher voltage (note that, effectively, the current is used many times) and this can be a more economic way of using power.

With bipolar connection, however, an additional problem can arise if the cell body is metal or there is an electrolyte path between neighbouring cells, e.g. common feeds or exhausts. This is the electrical leakage current – also known as the bypass or shunt current. The electrical leakage current is a current not between the electrodes of the same cell but between electrodes in neighbouring cells; this arises because in a bipolar cell there is a voltage difference between such electrodes and current can flow if there is a current path. A leakage current not only causes a loss in current efficiency (which can be 4%), but it can also lead to corrosion, since cathodes will have ‘anodic’ zones, and to products which are impure (and may be safety hazards, e.g. H<sub>2</sub> in Cl<sub>2</sub>). The leakage current can best be avoided by using an insulating cell body and introducing a break, e.g. a weir, or a barrier, such as an insulating paddle, into the electrolyte flow.

Much greater sophistication in process control has become possible with the advent of cheaper computers. They have made it possible both to monitor routinely characteristics from each cell (and hence to locate problem cells) and to vary control parameters ( $V$ ,  $I$ , feed rates) to optimum values for the prevailing conditions,

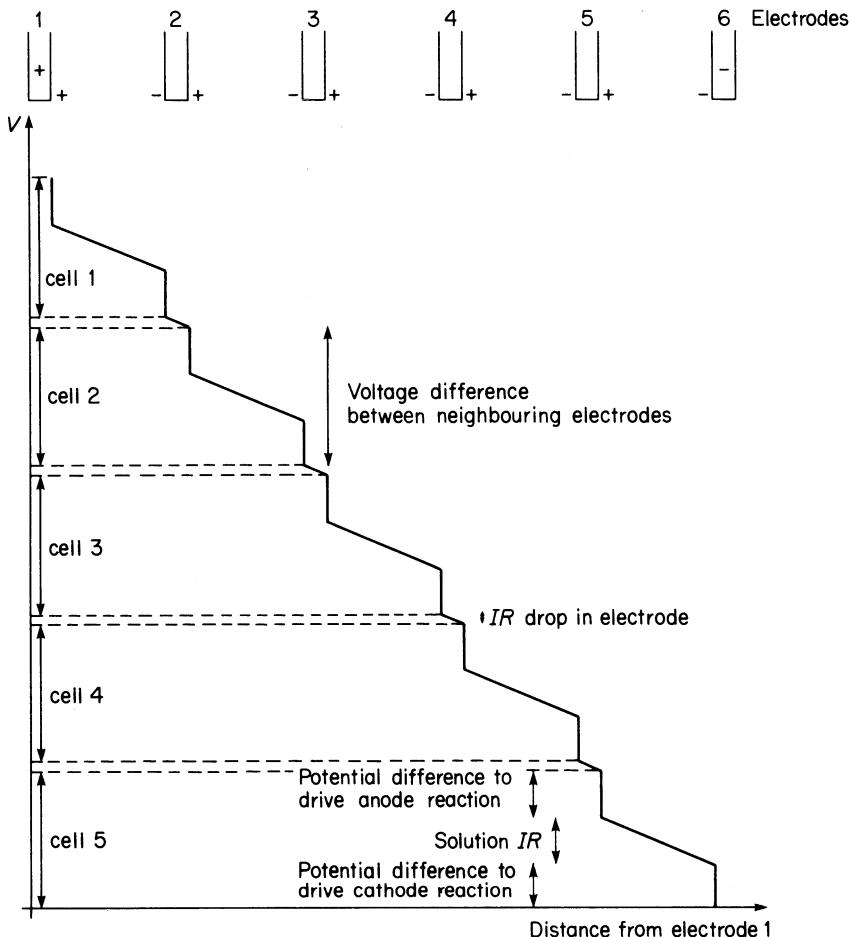


Figure 2.11 Voltage distribution across bipolar cell.

e.g. cost of power, feed composition. Certainly, in the UK where power is cheaper at night it is routine practice to increase current for this period.

The electrodes and the separator are the only components in an electrolytic cell which are not to be found in other chemical reactors. Electrode materials have been discussed thoroughly in earlier sections but some comments should be made about separators. In the first place it is clear that a cell should only have a separator if one is entirely necessary. Besides their cost, the inclusion of a separator restricts the electrode geometry and mass transport conditions which are possible, increases the cell resistance substantially and certainly makes the cell design more complex; the separator must be gasketed to avoid leaks, there must be separate anolyte and catholyte chambers and therefore twice the number of pipe connections to the cell.

In many electrolyses, a separator is, however, unavoidable and two types of material have been used for the purpose:

(a) A porous material (e.g. asbestos, porous plastics, a glass frit, porcelain and other porous pottery) which acts purely as a physical barrier, slowing down transport between the anode and cathode compartments. Such materials do not distinguish between species; all will pass through the separator in time if there is a concentration gradient.

(b) Ion-selective membranes (e.g. Nafion, Flemion, sodium- $\beta$ -alumina). These materials are highly selective, permitting the transport only of either cations or anions and perhaps solvent. Indeed, the cation exchange materials can show considerable selectivity between positively charged ions and likewise the anion exchange membranes between negatively charged ions. Recent years have seen great advances in membrane materials both in terms of such selectivity and in reducing their resistance. Their cost, however, remains high.

The question of materials for electrolysis cells has also been mentioned. It should be emphasized again, however, that concentrated solutions of electrolytes in water can be highly corrosive media. This restricts the choice of materials of construction and in later chapters there will be many examples of cell bodies made from unusual materials such as concrete, asbestos, alumina, carbon and nickel as well as more normal structural materials, e.g. steel, polymers.

## 2.5 TYPICAL CELL DESIGNS

While in a discussion of fundamental electrochemistry the unity of the subject matter is very clear, this is not always the case when dealing with electrochemical technology. Nowhere is this more evident than in a discussion of cell design. The cells used for the different industrial applications of electrochemistry look quite different, ranging from the rectangular open tanks common in electroplating, through the highly optimized parallel-plate cells used in the chlor-alkali industry, to the complex designs used in metal-ion removal from effluent or organic electro-synthesis; for electrochemical machining or grinding there is no cell in the sense of a reactor body. This should not be unexpected because in the different applications the relative importance of the various figures of merit will be quite different. Thus in electroplating, the quality of the product is of key importance and energy efficiency almost unconsidered because the charge used in plating is so small. On the other hand in the large, power-intensive processes such as chlor-alkali or aluminium production, energy yield and space time yield are the important figures; in organic synthesis selectivity must be added.

Despite this diversity there are clearly some general rules in cell design; these would include the following:

(1) The cell design should aim to meet the process requirements in the simplest (and cheapest) way. Hence separators and even solution flow or stirring should be avoided if at all possible.

(2) The cell must integrate directly into the overall process and if other operations (e.g. gas separation, solvent extraction) can be carried out in the cell this must be advantageous.

(3) When electrolyte flow or stirring is to be used, the transport regime must be considered at an early stage. The mixing can be augmented by baffles, beds of particles and other turbulence promoters.

(4) There should be a uniform potential distribution over the electrode surface. Depending on the application this may be achieved by simple electrode geometry or using counterelectrodes of complex shape, maybe combined with auxiliary electrodes and non-conducting shields to direct the current path.

(5) The anode–cathode gap should be small.

(6) All materials of construction must be compatible with the electrolyte and the electrolysis products.

The section will discuss some typical examples of these principles of cell design and each subsequent chapter will deal with cell design in the more specific context of the particular application.

### 2.5.1 Tank cells

The tank cell is the classical batch or semi-batch (reactants added and products removed at intervals) reactor of electrochemical technology. The battery is perhaps the best example of a batch reactor; the electrodes, electrolyte and electroactive species are sealed into the cell during manufacture and the ‘reactor’ is either discarded or recharged when the stored energy has been used. Electroplating is also often a batch process carried out in an open rectangular tank; the items to be plated are placed in the tank together with the soluble anodes and, depending on the complexity of the cathode shape, various degrees of care will be taken with the anode–cathode geometry and the placing of auxiliary anodes and/or shields. Moreover tank cells operated in a semi-batch manner are used in electrolytic processes, for example in aluminium extraction, fluorine generation and water electrolysis. For aluminium extraction, the choice of a tank cell is determined by the extremely aggressive nature of the cryolite electrolysis medium and the materials problem which it poses. The same is largely true for the acidic fluoride melt used for fluorine generation, but in water electrolyzers the selection of a tank design is more because of the simple construction and cheap materials which may be used.

In the usual Hall–Héroult aluminium cell, the electrodes are horizontal, the cathode being the molten metal and the anode being carbon blocks mounted from the top of the cell so as to give parallel-plate electrode geometry. In most tank cells, however, the electrodes are vertical and made from sheet, gauze or expanded metal. The cell is arranged with parallel lines of alternate anodes and cathodes, the electrodes extending across and to the full depth of the tank. The anode–cathode gap is made as small as possible to maximize the space time yield and to reduce the energy consumption. In fact, the minimum inter-electrode gap is usually determined by a practical limitation, e.g. the need to prevent shorts in electrowinning cells or the need to separate anode and cathode gases in a fluorine cell. In some cells, e.g.

some water electrolyzers (Fig. 2.12) and lead/acid batteries, there is a separator (asbestos sheet and porous plastic respectively), although this is not usually sealed so as to prevent the passage of liquid around the outside; the asbestos diaphragm in a water electrolyzer is only to prevent mixing of the oxygen and hydrogen while allowing the inter-electrode gap to be quite small. It is unusual in tank cells to induce convection by mechanical means although gas bubbles evolved at electrodes stir the electrolyte strongly. Moreover the electrical connection may be monopolar or bipolar.

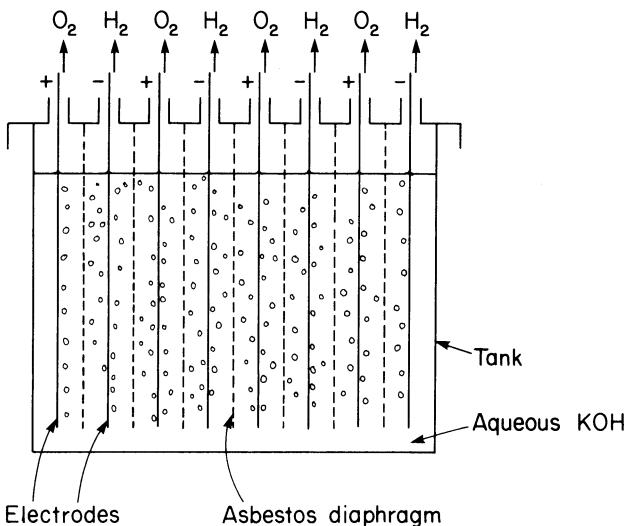


Figure 2.12 *Schematic diagram of a monopolar, tank water electrolyser.*

The great advantage of the tank cell is the simplicity of construction and the wide range of materials which can be used for the manufacture of the simple components required. It is, however, limited in space time yield and unsuited to large-scale operation or to a process where control of the mass transport conditions is necessary.

### 2.5.2 Flow cells

Most industrial flow cells are based on the parallel-plate electrode configuration and again the electrodes may be horizontal or vertical.

The most common cell with horizontal electrodes is the mercury cell from the chlor-alkali industry (see Chapter 3). The mercury cathode flows down the slightly sloping base plate of the cell and many rectangular dimensionally stable anodes (DSA) (of gauze or expanded-metal-type structure to allow the chlorine gas to rise with only minimum restriction) are mounted from the top of the cell so that they cover the surface area of the mercury and give an inter-electrode gap of a few centimetres (see Fig. 2.13). The cell may be as big as  $70\text{ m}^2$ . The brine is, however,

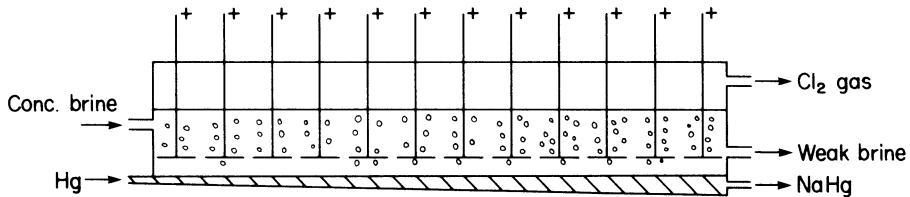


Figure 2.13 *Mercury cell for the production of chlorine and caustic soda.*

flowed through the cell at a relatively low velocity and because of the considerable mixing caused by the evolving chlorine gas the cell shows intermediate behaviour between a plug flow and a backmix reactor.

With vertical electrodes the cell is usually constructed in a plate-and-frame arrangement and mounted on a filter press. The electrodes, electrolyte chambers, insulating plates to separate cells electrically and, where used, membranes or separators are constructed individually and mounted with suitable gasketing materials between each component; the filter press is then used to seal the cells with up to 100 cells in each unit (see Fig. 2.14). It is difficult to manufacture the cells with an area greater than 1 m<sup>2</sup>. Again the electrical connection may be bipolar instead of monopolar (effectively by removing the intercell insulation) and in a series of cells the electrolyte feeds to the cells may be connected so that the cells are in series or parallel so far as the electrolyte is concerned.

In plate-and-frame cells it is normal to reduce the inter-electrode gap to 0.5–5.0 cm and the electrolyte flow rates are often high. The electrolyte entry ports must

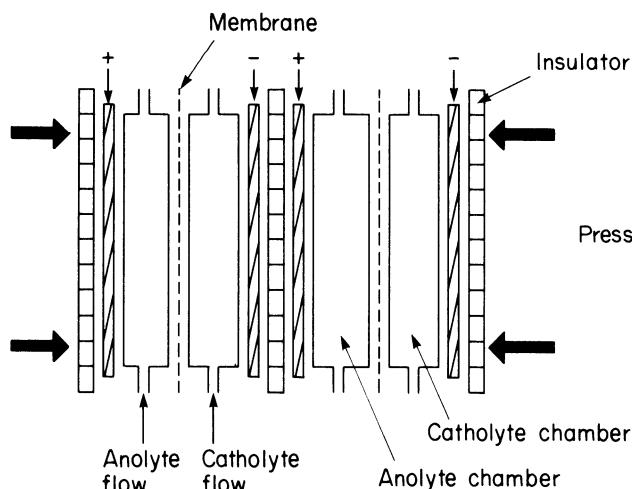


Figure 2.14 *Two of a group of monopolar plate-and-frame cells. Typically these are mounted in a filter press with suitable gasket materials between each component to prevent leaks.*

be designed to give a uniform distribution of electrolyte into the cell and the flow within the cell can be made more turbulent with promoters or directed across the electrode with baffles as in Fig. 2.15. The flow within such cells approximates to plug flow although there is always some dispersion because of the slowly moving phase along the cell wall.

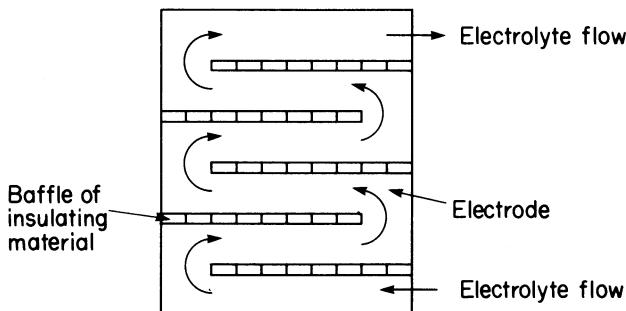


Figure 2.15 *Direction of electrolyte flow across electrode surface with baffles. This increases contact time and increases the plug flow nature of the flow.*

Diaphragm cells used in chlor-alkali production are also effectively a parallel-plate flow reactor but they are constructed in a very different way; they will be discussed in the next chapter. While the potential distribution in a parallel-plate cell is good and the mixing conditions can be made to meet most requirements, the space time yield leaves much to be desired and it is often difficult to reduce the inter-electrode gap sufficiently to give the required space time yield and energy efficiency. These problems have led to the development of many novel cell designs; at the present time they remain laboratory or pilot-plant concepts but it is to be expected that some will eventually have an impact on the industrial scene.

Figure 2.16 shows the capillary gap cell first developed in order to reduce the energy consumption for an organic electrosynthesis in a poorly conducting organic solvent. The cell is cylindrical and the electrodes are a stack of discs kept apart by insulating spacers, 1 mm thick. The cell is bipolar and the electrolyte is pumped through the inter-electrode gaps from the centre outwards. Several modifications have been proposed, for example the pump cell. In this cell, there is again a stack of discs but all the discs except the end ones are mounted on a central spindle which can be rotated so that the cell also acts as a pump; the spaces between the discs are about 1 mm. Figure 2.17 shows a pump cell with a single rotating electrode. Despite the superficial similarities between the capillary gap cell and the pump cell, the mass transport conditions are quite different. The pump cell permits higher Reynolds number in the thin gaps between the electrodes and, although in both cells the electrolyte must decelerate as it flows radially outwards, in the pump cell the tangential shear increases. The net effect in the pump cell is for the rate of mass transport to increase continuously as the fluid moves outwards; in contrast in the capillary gap cell it reaches a maximum value then declines. Hence the current

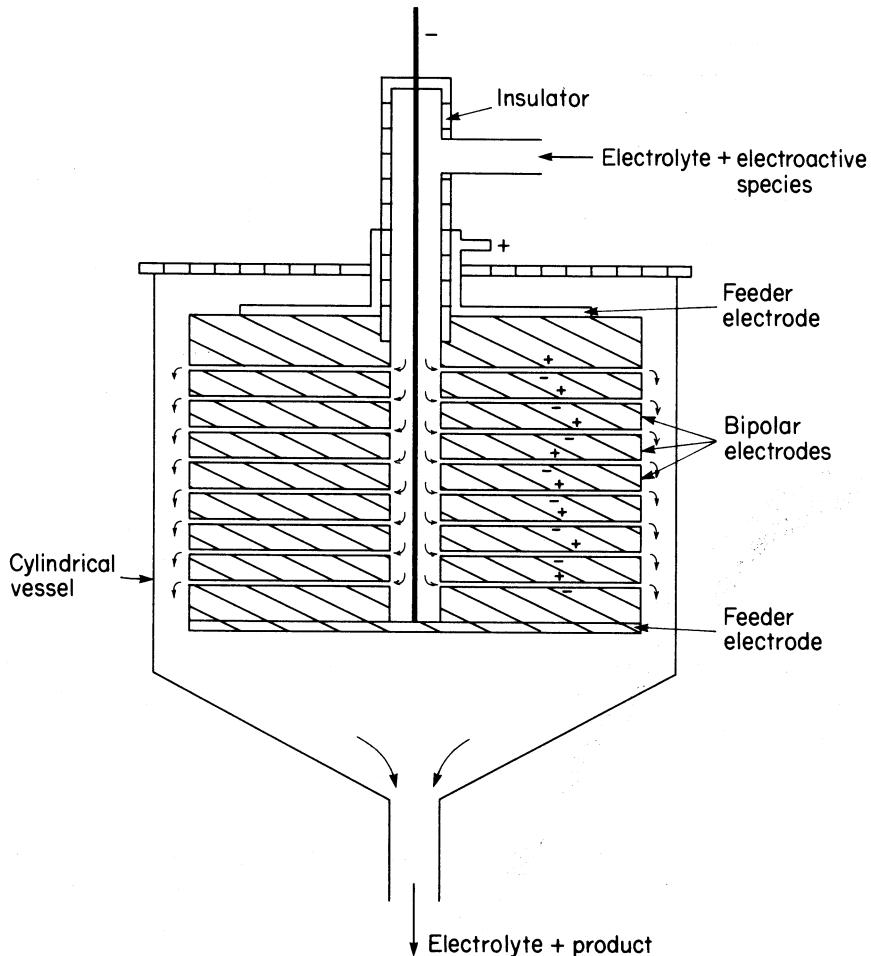


Figure 2.16 Bipolar capillary gap cell. The electrodes are a stack of closely spaced discs. From Beck, F. and Guthke, H. (1969) Chem.-Ing.-Tech., 41, 943.

density in the pump cell is higher. Moreover, as the rotational speed increases, the pump cell behaves increasingly as a plug flow reactor in the radial direction but with the tangential shear producing intense mixing across the gap.

Similar cells based on cylindrical geometry have been proposed. In the stationary version, the electrolyte is pumped through a thin gap between two electrodes formed by the inside of a pipe and a concentric central cylinder. When the central electrode is rotated the cell is again self-pumping and the rotating cylinder cell has many of the attractions of the pump cell. It has been manufactured commercially for the removal of metal ions from dilute solutions. The cylinder cells have a poor space time yield compared with their disc counterparts but have the advantage that they may be modified to include a separator.

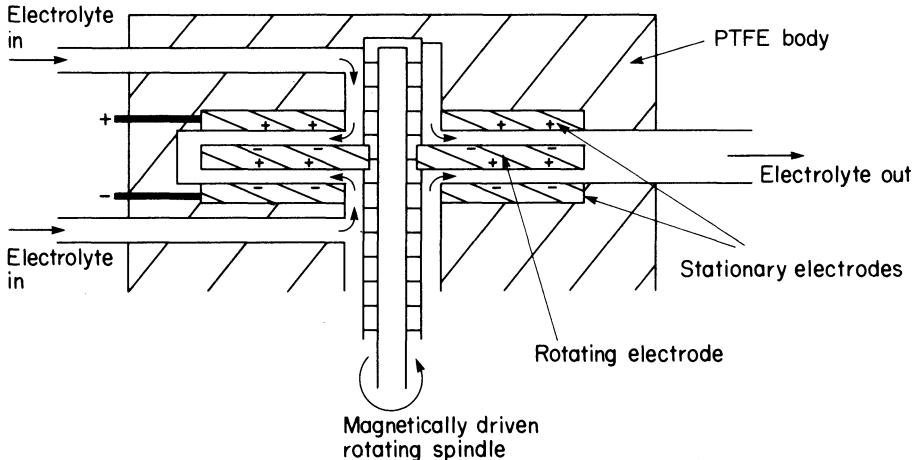
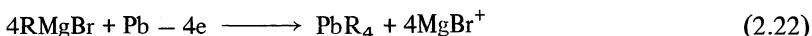


Figure 2.17 *The rotating electrolyser with a single rotating electrode. The electrolyte inlets and outlet are mounted tangentially.* From Janson, R. E. W., Marshall, R. J. and Rizzo, J. E. J. (1978) *J. Appl. Electrochem.*, 8, 281.

Cells based on particulate beds have been studied intensively. Indeed, the cell for the production of lead alkyls by the oxidation of Grignard reagents on a lead anode in an ether mixture



is based on a packed bed of lead shot. The cell case is a steel pipe, diameter 5 cm and length 75 cm, which also acts as the cathode, and the anode is a packed bed of lead shot inside the pipe and separated from the steel by a porous polypropylene diaphragm and a spacer (see Fig. 2.18(a)). A number of such steel pipe cells are mounted in parallel in a shell-and-tube reactor arrangement which can be cooled and into which reactants are added from the top. The attraction of this cell design for the lead alkyl process is the simple addition of the consumable anode in the form of shot. It will be clear from the earlier discussion, however, that the current distribution in this cell cannot be uniform and only the lead surface closest to the cathode will be active. In fact, the centre of the bed is totally inactive and it is possible to use a lead rod there as a feeder electrode, i.e. electrical contact, to the bed.

When the electrolyte flow is upwards through an unrestrained, particulate bed, the particles will fluidize and then one has a fluidized bed electrode. Several designs have been investigated and three are shown in Fig. 2.19. The cells differ in geometry, direction of the current path relative to the solution flow and in one the absence of a separator. Both membrane and porous diaphragms, even cloth, have been used as separators and cell (a) is probably the most convenient design. The advantages claimed for the fluidized bed electrode include a very high surface area per unit volume and a high mass transport rate. These combine to give a high conversion per

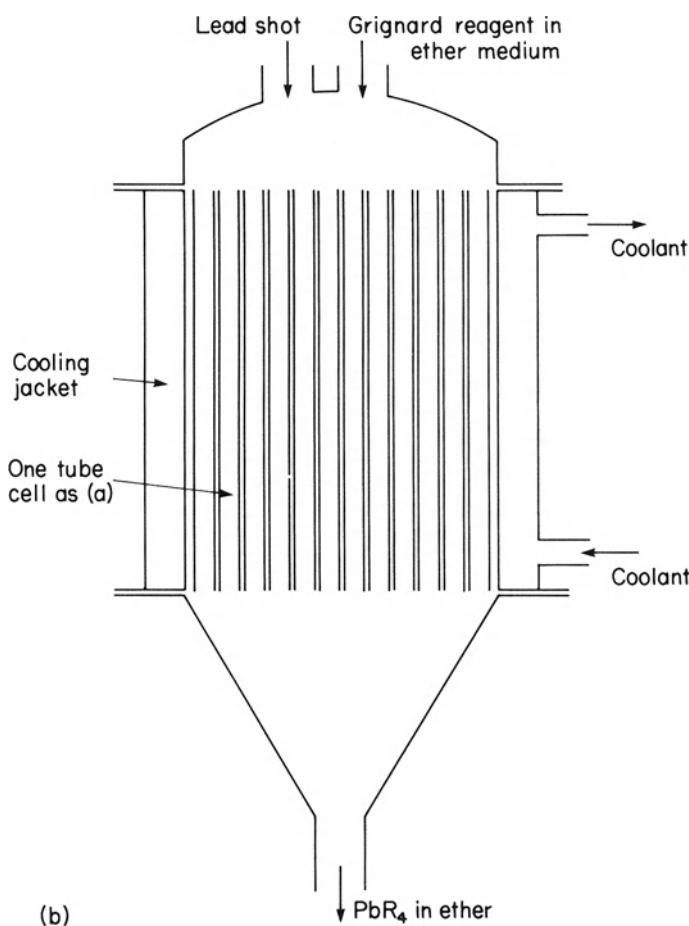
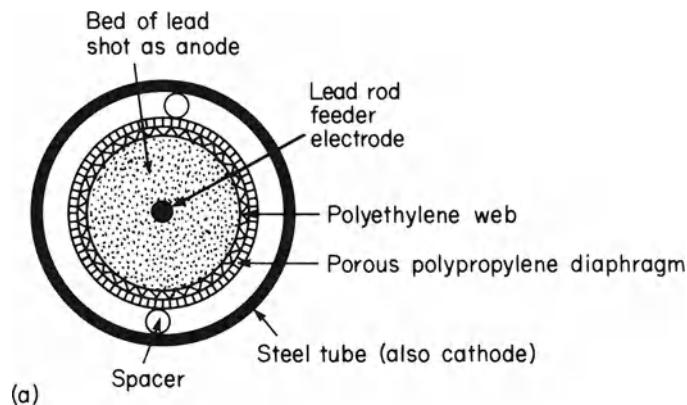


Figure 2.18 Principle of the shell-and-tube reactor used for the electrolytic oxidation of Grignard reagents to lead alkyls at a bed of lead shot. (a) Single tube cell, (b) complete reactor.

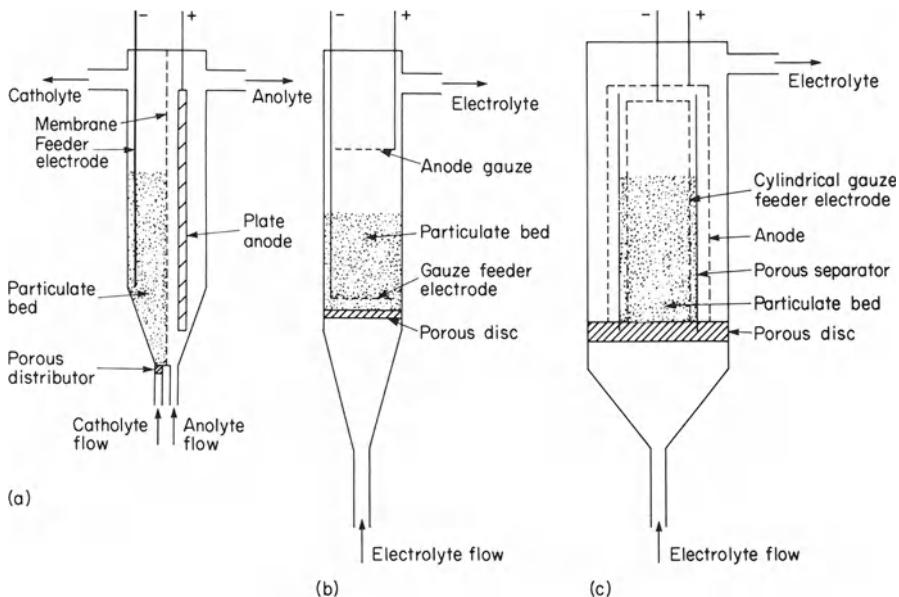


Figure 2.19 *Cells with fluidized bed cathodes. (a) Rectangular cell – current path perpendicular to electrolyte flow. (b) Cylindrical cell without separator – current path parallel to electrolyte flow. (c) Cylindrical cell with separator – current path perpendicular to electrolyte flow.*

pass and a high space time yield even for a low current density. Thus the cells have the ability to process very dilute solutions (< 0.1%) and, in particular, this aspect has been exploited for metal recovery from effluents and process stream conditioning. The fluidized bed electrode, however, suffers problems with respect to potential distribution; this can be complex and depends on the dimensions of the bed, the positioning of the feeder electrode(s) and counterelectrode(s), bed expansion and the solution composition. It is even possible to have ‘anodic regions’ within a fluidized bed cathode. Also with all but the most dilute solutions, massive metal deposition can occur close to the separator or feeder electrodes and this causes agglomeration of the bed. Recently several companies have attempted to exploit cells for metal recovery and effluent treatment and this has led to cells with more uniform potential distribution and improved performance. These will be discussed in Chapter 11, but the future of fluidized bed electrodes in electrochemical technology remains uncertain.

### 2.5.3 Other cell arrangements

Although flow cells have great advantages over tank cells in terms of both current density and control of the mass transport regime, they commonly suffer from the problem that the conversion per pass is low. For this reason it is common to run

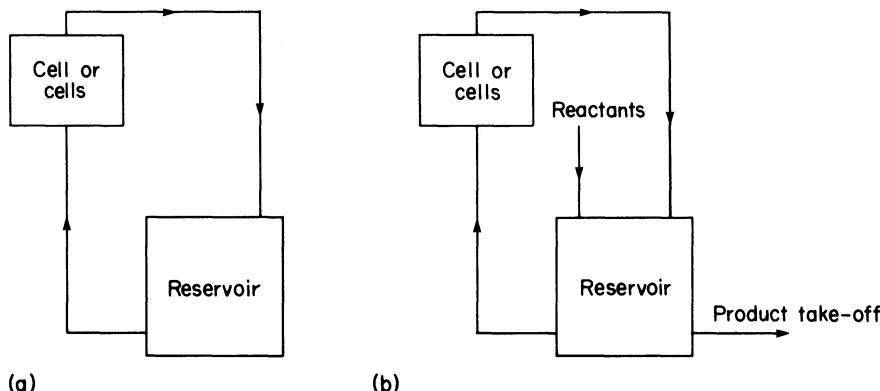


Figure 2.20 Common flow arrangements in electrochemical processes: (a) batch recycle process; (b) backmix reactor with cycle.

such cells with an electrolyte reservoir and to recirculate the electrolyte repeatedly through a cell or group of cells and back to the reservoir. If the system is run batchwise it is known as a batch recycle process (Fig. 2.20(a)). If, however, reactant is added to, and solution removed from, the reservoir continuously then the process is equivalent to a backmix reactor (Fig. 2.20(b)).

An alternative is to use a cascade of cells where the conversion is increased by passing the electrolyte through a series of cells. This approach has the advantage that the reactors and/or electrolysis conditions need not be the same throughout the cascade. For example, the current density can be decreased as the electroactive species is depleted.

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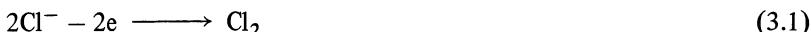
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### 3 The Chlor-alkali Industry

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The electrolysis of aqueous sodium chloride, normally brine obtained directly from natural salt deposits, to yield chlorine, sodium hydroxide and hydrogen is the largest of the electrolytic industries. In the USA, the annual production of chlorine is of the order of  $10^7$  tons while in the UK it is about  $1.7 \times 10^6$  tons.

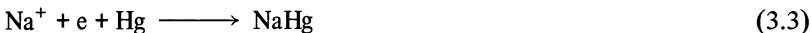
The electrode reactions are, at the anode,



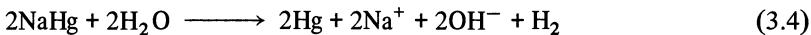
and at the cathode, effectively,



although it will be seen later that in a mercury cell the cathode reaction is



and the sodium amalgam is decomposed in a separate reactor to give the desired product



Both chlorine and sodium hydroxide (normally traded as a 50% aqueous solution) must be considered to be main products and which is in greater demand varies with time; their major uses are summarized in Table 3.1. The hydrogen is also used, where possible as a chemical (e.g. for the hydrogenation of fats), otherwise as a fuel for the power station which is inevitably on site at most chlor-alkali facilities because of their large demand for electricity.

The chlor-alkali industry is of particular interest to the student of electrochemical technology, not only because of its size but also because three different types of electrolytic processes based on mercury, diaphragm and membrane cells exist side by side and each must be considered when new plant is to be installed. Moreover, although it is a mature industry, the first electrolytic cells having been introduced in the 1890s, the last twenty-five years have seen extensive and notable advances in the technology resulting both from scientific innovation and the economic and social pressures for energy conservation, pollution control and higher safety standards.

Table 3.1 Major uses of chlorine and caustic soda (sodium hydroxide).\*

*Chlorine*

Manufacture of polyvinylchloride (17)  
 Preparation of chlorinated organic solvents, e.g. methylene chloride, chloroform, carbon tetrachloride, per- and trichloroethylene, 1,1,1-trichloroethane (18)  
 Preparation of propylene oxide (10)  
 Synthesis of other organic compounds, e.g. chlorobenzenes, alkyl chlorides (particularly methyl chloride for lead alkyls), herbicides (10)  
 Preparation of fluorocarbons (7)  
 Pulp and paper manufacture (13)  
 Preparation of inorganic compounds, e.g. sodium hypochlorite, titanium tetrachloride, iodine chlorides (10)  
 Water treatment (5)

*Caustic soda*

Synthesis of many organic compounds (39)  
 Manufacture of textiles and rayon (7)  
 Soap and detergent production (4)  
 Oil refining (6)  
 Paper and pulp manufacture (15)  
 Aluminium extraction (7)  
 Manufacture of inorganic compounds, e.g. sodium cyanide, sodium salts (11)

\* Figures in brackets are percentage of production (taken from Harke, C. J. and Renner, J. (1978) *J. Electrochem. Soc.*, **125**, 455c).

### 3.1 GENERAL CONCEPTS OF BRINE ELECTROLYSIS

A discussion of the electrolytic production of chlorine and sodium hydroxide requires an understanding of the very large scale of the industry. The annual tonnages produced in the USA and the UK are given above and it might further be noted that the US production requires 0.2 square miles of anode and  $3.3 \times 10^7$  megawatt hours of electric power! Hence without, at this stage, a discussion of the economics of the processes, the importance of the following cannot be over-emphasized.

- (a) Simple and cheap cell design.
- (b) High current densities to minimize capital investment in plant.
- (c) Cell components which are reliable, readily available and have a long lifetime.
- (d) Good current efficiency and material yields for both the anode and cathode reactions. Parasitic reactions not only lower the energy consumption and increase the use of materials but also lead to impurities in the products.
- (e) Low power consumption ( $\text{kWh ton}^{-1}$ ). This is determined by the current efficiency and the cell voltage. The latter was discussed in the last chapter and it was shown that the cell voltage is made up of a number of terms, i.e.

$$V = E_e^C - E_c^A - |\eta_A| - |\eta_C| - IR_{\text{CELL}} - IR_{\text{CIRCUIT}} \quad (3.5)$$

and a good energy efficiency will only be obtained if attention is paid to minimizing each component voltage.

Table 3.2 lists the reversible potentials for the four electrode reactions which must be considered in brine electrolysis. The data are given for the pH's which prevail at the anodes and cathodes in the various cells. Chloride ion is always oxidized in slightly acid solution to prevent hydrolysis of chlorine to hypochlorite while the pH at the cathode will, with the exception of the mercury cell, be at least 14. Two factors emerge immediately. First, in a mercury cell where the electrode reactions are A and D, the term  $(E_e^C - E_e^A)$  of equation (3.5) is  $-3.25\text{ V}$ , a value much larger than the corresponding minimum cell voltage for a diaphragm or membrane cell,  $-2.20\text{ V}$ , where the electrode reactions are A and C (if an oxygen cathode were introduced, the electrode reactions would be A and B(ii) and the cell voltage would fall further to  $-0.97\text{ V}$ ). Hence a mercury cell is only competitive because some of the other terms in equation (3.5) are favourable (e.g. since a mercury cell does not require a separator between the electrodes,  $R_{\text{CELL}}$  is lower) and because it has other advantages which will become apparent later. Secondly, it can be seen that kinetics play an important role in a chlor-alkali cell; not only is it desirable for the overpotentials for the required anode and cathode reactions,  $\eta_A$  and  $\eta_C$ , to be low but it is also necessary for other reactions to be hindered. Thus a mercury cell is only possible because the hydrogen evolution overpotential is very large at both mercury and sodium amalgam and sodium amalgam can therefore be formed without hydrogen evolution; indeed it is essential that reaction C does not take place even to a minor extent since even a low percentage of hydrogen in the chlorine from the cell would be a potentially explosive mixture. Moreover, at the anode of all the cells there is a need to suppress oxygen evolution. The reversible potentials for reactions A and B(i) would suggest that only oxygen would be evolved at the anode, but fortunately under controlled conditions the oxygen overpotential is high enough for chlorine to be produced in almost quantitative yields.

Table 3.2 Reversible potentials for reactions relevant to chlorine/caustic soda production. pH's are those applicable to the various cell technologies.

Reaction	pH	$E_e$ (V vs NHE)
A. $2\text{Cl}^- - 2\text{e} \longrightarrow \text{Cl}_2$	4	+1.36
B.(i) $2\text{H}_2\text{O} - 4\text{e} \longrightarrow \text{O}_2 + 4\text{H}^+$	4	+0.99
(ii) $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \longrightarrow 4\text{OH}^-$		+0.39
C. $2\text{H}_2\text{O} + 2\text{e} \longrightarrow \text{H}_2 + 2\text{OH}^-$	14	-0.84
D. $\text{Na}^+ + \text{Hg} + \text{e} \longrightarrow \text{NaHg}$	4	-1.89

## 3.2 MODERN TECHNOLOGICAL DEVELOPMENTS

### 3.2.1 Electrode materials

It was noted above that one should seek electrode materials where the overpotential for chlorine evolution is as low as possible but where there is a considerable oxygen overpotential. In addition, for diaphragm and membrane cells there is the requirement for cathodes with a low hydrogen overpotential. Catalysis of hydrogen evolution was discussed in Chapter 1 and it was shown that strong catalysis is promoted by metals where the free energy of adsorption of hydrogen atoms has an intermediate value. This allows mechanisms such as



which can bypass the need for the direct formation of hydrogen species in solution, reactions which have large activation energies and hence only occur at high overpotentials. On metals where the metal–hydrogen bond is too strong, reaction (3.7) becomes slower and again an overpotential becomes necessary. Presumably similar criteria can be applied to a chlorine anode although oxide rather than metal surfaces are commonly the preferred catalyst (in any case most metals are oxide covered at the potential where chlorine is formed).

Where surface intermediates are important, the apparent current density will depend on the real surface area, i.e. the roughness of the electrode surface, and some of the catalysis observed with many materials may be partly due to a very high surface area. Other properties, particularly stability, are essential in a potential electrode material, since a chlor-alkali cell will be expected to run for months or even years without extensive renovation or replacement of components.

Throughout most of the history of chlor-alkali processes the anode material has been graphite or some related form of carbon. The overpotential for chlorine evolution was as high as 500 mV and the wear rate 5–7 lb per ton of  $\text{Cl}_2$ . There was some attempt to replace these by a dispersed form of a precious metal, e.g. Pt or Pt/Ir on a titanium base, and indeed these did reduce the overpotential to about 100 mV. These anodes were, however, expensive and not entirely stable, platinum in the concentrated chloride medium being lost at the rate of 0.2–0.4 g per ton of  $\text{Cl}_2$ . Hence the development in the early 1960s of materials which have become known as dimensionally stable anodes (DSA) was a major advance. These materials are titanium-based with a coating of ruthenium dioxide containing other transition-metal oxides, e.g.  $\text{Co}_3\text{O}_4$ . They are both excellent catalysts, the chlorine overpotential being as low as 5–40 mV, and extremely inert, their service life being several years. Largely for reasons associated with patent rights, other companies have since developed anodes, for example based on  $\text{PdO}_2$  or  $\text{M}_x\text{Co}_{3-x}\text{O}_4$  ( $0 < x < 1$ , M = Cu, Mg or Zn), which have similar properties. All such oxide electrodes, however, need to be used under carefully controlled conditions. For example with some DSA, decreasing the temperature or carrying out the electrolysis with sulphate ion in solution can lead to oxygen contamination of the chlorine. The

replacement of carbon by DSA or related anodes in chlor-alkali cells is now almost complete and this change alone has reduced the energy requirement by 8–15% (the cell voltage is decreased by 0.45 V in 2.5–5 V).

The cathode in diaphragm and membrane cells has been steel where the hydrogen overpotential is about 400 mV. Coatings of nickel alloys are now available which decrease this overpotential to 150–200 mV and there are expectations that improvements in the catalytic coating will reduce it further to 20–50 mV. Such cathode coatings will again substantially improve the energy consumption of the industry.

In addition to the material of the electrode, its physical structure can also be important. At electrodes where gas is evolved, the design must permit rapid bubble release, otherwise the bubbles will contribute an additional *IR* loss. Hence it is common to employ expanded metal or plates with louvres (see Fig. 3.1) to release gas in the desired direction. The design of such structures, however, must ensure that there is no *IR* drop in the electrode itself and this may require the inclusion of additional current-carrying bars.

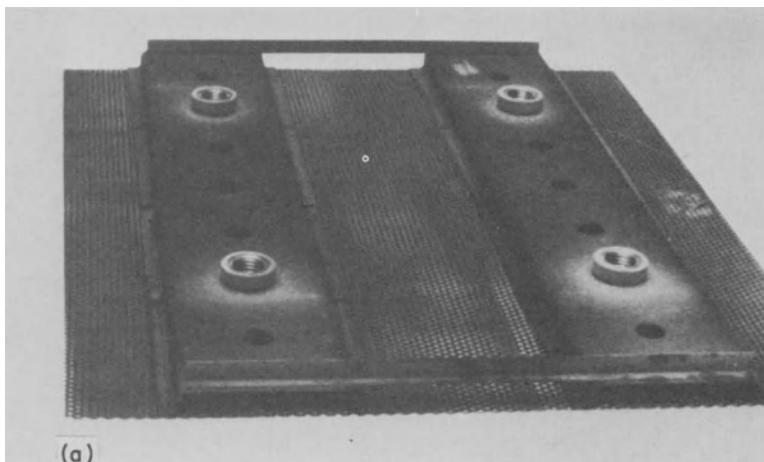
### 3.2.2 Membranes

The perfect separator in a chlor-alkali cell (a) would pass only sodium ions without allowing the transport of chloride ion from anolyte to catholyte (leads to  $\text{Cl}^-$  contamination of the  $\text{NaOH}$ ) or hydroxide ion from catholyte to anolyte (causes  $\text{O}_2$  contamination of the  $\text{Cl}_2$ ), (b) would have a low resistance, and (c) would be stable to wet chlorine and 50% sodium hydroxide over a long period of time. Moreover these properties should be maintained even when the catholyte is 50% sodium hydroxide as ideally it would be when leaving the cell.

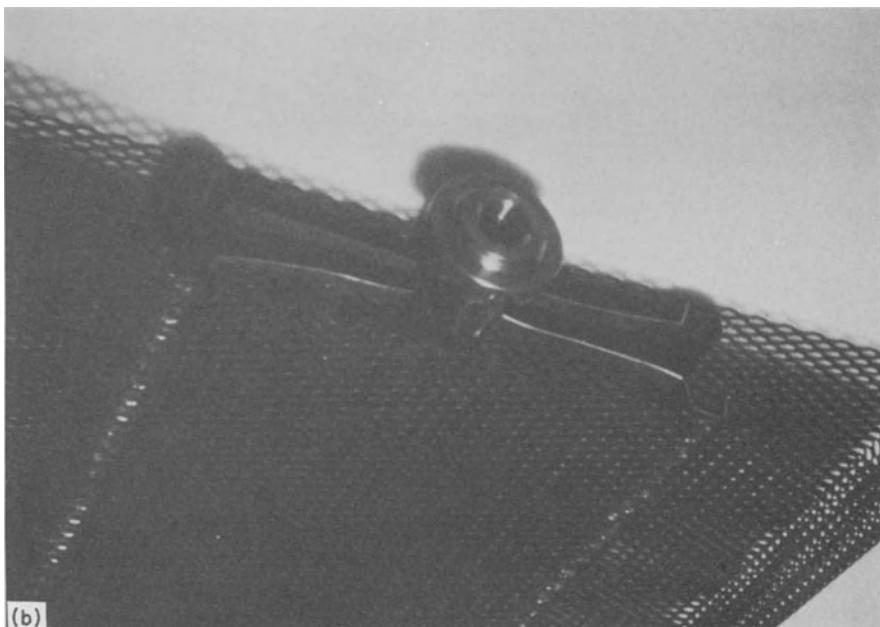
A diaphragm is porous and cannot discriminate between species. All will diffuse through its pores where there is a concentration difference. For this reason the caustic soda produced in a diaphragm cell is always contaminated with chloride ion and the catholyte leaving the cell cannot contain more than 10% sodium hydroxide since otherwise hydroxide ion diffusion to the anode becomes significant and oxygen as well as chlorine is evolved. Thus prior to sale, the sodium hydroxide produced in a diaphragm cell must be concentrated by evaporation to a 50% solution.

On the other hand, cation exchange membranes are theoretically capable of meeting all the criteria set out above. It is, however, only in the last ten years that membranes with properties approaching those required have become available and they have been the basis for the development of membrane cell technology. The membranes are all perfluorinated polymers with side chains including acidic groups, and Fig. 3.2 shows the basic building blocks for two polymers, Nafion and Flemion, which are used as membranes for chlor-alkali cells, i.e. as thin sheets usually reinforced by a plastic net. The properties of the membrane can be modified by variation of equivalent weight, the pretreatment and the addition of copolymers.

The development of membranes for chlor-alkali cells is, however, a continuing activity and two problems remain to be resolved: (i)  $\text{OH}^-$  transport becomes



(a)



(b)

Figure 3.1 Modern anodes for chlorine cells: (a) horizontal DSA for mercury cell; (b) vertical DSA for diaphragm cell. Photographs supplied by Diamond Shamrock Corp.

important when the cell contains very concentrated caustic soda and this effect limits the concentration which may be produced directly in the cell; with the strong acid membrane, the limit is below 20% and with the weak acid membrane 40%.

(ii) The sodium ion conductivity of the membranes restricts the maximum current density to about  $600 \text{ mA cm}^{-2}$  without a severe voltage penalty.

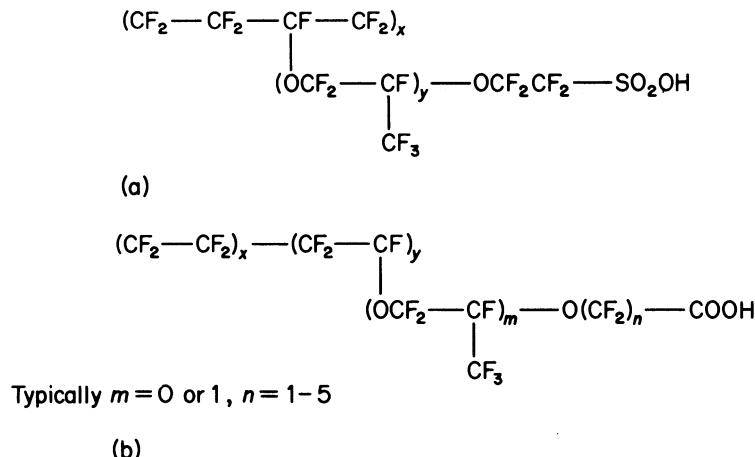


Figure 3.2 *Chemical structure of perfluoropolymers for ion-permeable membranes:*

(a) Nafion manufactured by E. I. du Pont; (b) Flemion manufactured by Asahi Glass Co. Ltd.

### 3.2.3 Engineering and control equipment

As in all chemical engineering, a major trend has been towards the complete utilization of all raw materials and energy and, for example, all heat from exothermic reactions or Joule heating is used elsewhere in the plant. Moreover the plants have had to change in order to comply with the legal requirement to monitor and control emissions of possible pollutants; in the chlor-alkali industry the major concerns have been mercury and chlorine itself. Normally both the atmosphere and the effluent will be monitored for Hg and Cl<sub>2</sub> and the hazards have been much reduced.

Certainly this industry has not been immune to the tendency to build larger plants and to intensify the operation of chemical processes. In particular, current densities have been increased and cell rooms have become larger. This has required the design of very heavy current and switch gear; mercury cells operate at up to 500 000 A. The cell room will thus require equipment to operate at this rating and to rectify grid AC to DC. Perhaps the first step in the modern era was the introduction of silicon rectifiers which improved the conversion efficiency from 86 to 99%; they can produce DC current at 240 V and it is normal to arrange the cell room so that the centre of a series of cells is earthed and there is a 240 V drop on either side of the earth making the total voltage drop available in the cell room 480 V. Subsequently the electronics revolution has had a substantial impact on the organization and control of a chlor-alkali plant. It is now possible to measure and record on a computer data from each cell, flow and reactor. The aim is to detect problems as they arise and to have a measure of automatic control, e.g. of anode–cathode gaps in a mercury cell.

The computer has a second and larger control function. The optimum conditions in the cell room are not time-invariant. For example, in the UK the cost of power

from the national grid is less at off-peak times, at nights and weekends, and at these times it will be economic to run the cell room on a high load and current density. On the other hand when power is expensive the load should be reduced, and the computer is programmed to make these changes automatically.

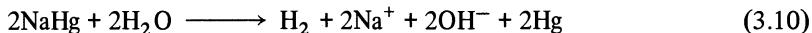
### 3.3 CHLORINE CELL TECHNOLOGIES

#### 3.3.1 Mercury cells

In a mercury cell the electrode reactions are



and the sodium amalgam is hydrolysed



in the presence of a catalyst in a separate reactor known as the denuder. The reversible cell potential is  $-3.08$  V and provided the anodes are DSA the overpotentials associated with the electrode reactions are very low. The normal cell voltage is about  $4.50$  V and the additional voltage is required to drive the current through the mercury–DSA gap, the electrodes and the cell connections and bus-bars.

A typical mercury cell is shown in Figs 3.3 and 3.4. It consists of a large, shallow trough, dimensions  $15\text{ m} \times 2\text{ m} \times 0.3\text{ m}$ , with a steel base which slopes slightly from end to end so that the mercury can flow along the bottom of the cell. The coated, expanded titanium DSA anodes (see Fig. 3.1), each of approximate dimensions  $30\text{ cm} \times 30\text{ cm}$ , enter the cell from the top and are arranged parallel to the mercury surface with an anode–cathode gap of about  $1\text{ cm}$ . The cell will have about 250

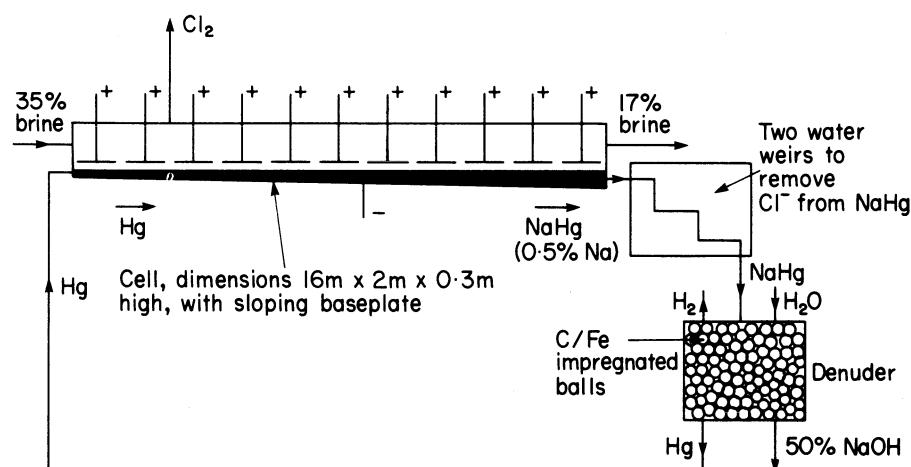


Figure 3.3 Sketch of mercury cell design and coupled Hg circuit.

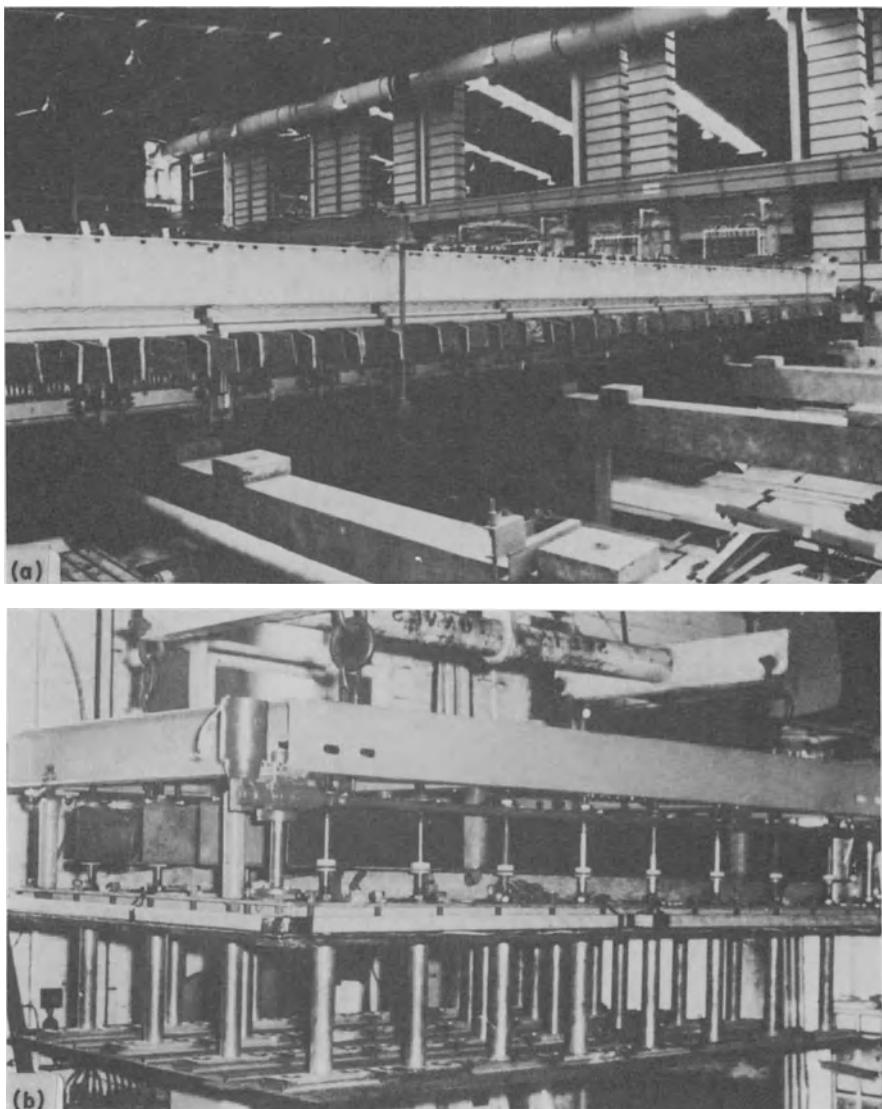


Figure 3.4 *Mercury cell under construction. (a) Side view of cell trough. (b) Anode assembly being moved into position. The assembly has 32 anodes and there are ten such assemblies per cell. Photographs supplied by ICI Ltd, Mond Division.*

such anodes so that most of the mercury is covered by anode; the cell approximates to a horizontal parallel-plate configuration. The brine, concentration 35% and temperature 60°C, flows through the cell and leaves at 17% either to be recycled through the salt deposit or after treatment to be discharged. The chlorine gas leaves the cell at the top while the sodium amalgam (approximately 0.5% sodium) leaves

at the base, passes through two washing weirs to remove all sodium chloride and enters the denuder.

The denuder is a cylindrical reaction vessel packed with graphite balls impregnated with a transition metal (e.g. Fe or Ni) to catalyse the amalgam decomposition. The sodium amalgam and a controlled volume of pure water flow down the graphite and react. It was noted above that the sodium amalgam/water reaction is kinetically hindered; on the other hand the reaction occurs rapidly in the denuder and is highly exothermic, because the transition metal provides an alternative surface to mercury for the hydrogen evolution reaction. The reaction in the denuder thus occurs by a type of corrosion mechanism, i.e. the reactions



occur on different parts of the impregnated graphite surface but at equal rates so that no net current flows. The hydrogen gas leaves from the top of the denuder, and the mercury for recirculation to the cell and the 50% aqueous sodium hydroxide separate at the bottom. Hence it can be seen that the process produces pure 50% caustic soda directly.

A typical cell room (Fig. 3.5) consists of a large number of cells in electrical series so as to make use of the available 480 V, i.e. about 100 cells. Mercury cells operate at current density in the range 0.8–1.4 A cm<sup>-2</sup> so that the total cell current will vary between 180 000 and 315 000 A and the cell room power requirement is 80–160 MW.

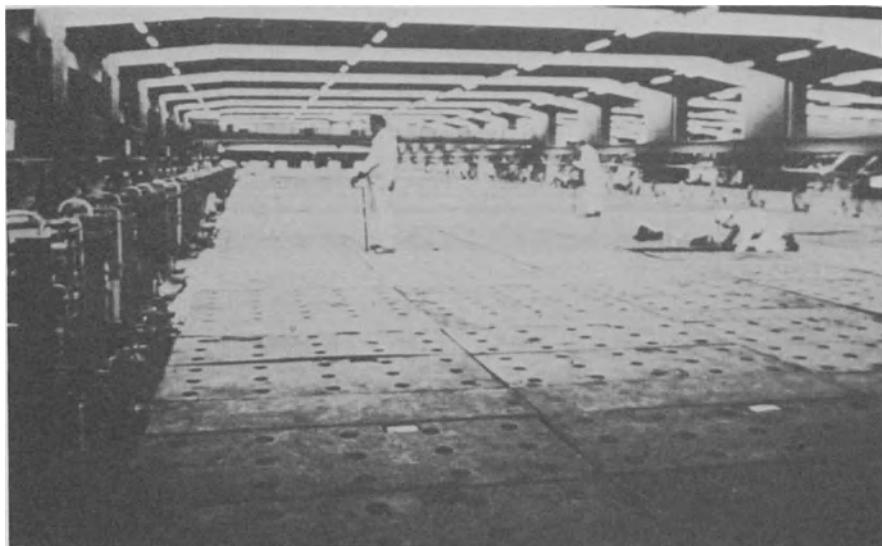


Figure 3.5 General view of a mercury cell room, with 106 cells each 25 m<sup>2</sup> and a current rating of 225 kA. Photograph supplied by ICI Ltd, Mond Division.

It may also be noted that the cell room will be somewhat larger than a soccer pitch and be capable of producing about a quarter of a million tons of chlorine each year.

Many of the world's major chlor-alkali companies have developed their own mercury cells and the designs will differ in the way they seek to obtain the maximum electrode area and in the arrangement of the auxiliary equipment. The development of the cells during almost a century of electrolytic chlorine and caustic soda production and the variation in the cells recently available are described in the texts at the end of the chapter.

The cell room is only part of the plant necessary for conversion of brine into chlorine and caustic soda and the complete process is shown diagrammatically in Fig. 3.6. Most chlor-alkali plants are sited above or close to a salt dome and the brine is made by pumping water through the salt deposit. The resulting solution is not, however, pure sodium chloride and prior to electrolysis the group II metals must be removed since they give rise to a phenomenon known as thick mercury or mercury butter where solid amalgam is formed in the mercury, leading to shorts and possible damage to the anode coatings. The purification process is usually by precipitation of the group II metals as hydroxides by increasing the pH with sodium hydroxide although ion exchange methods are also available. The brine is then acidified, to avoid hydrolysis of the chlorine, heated to 60° using heat from the denuder and passed to the cell. After electrolysis and decomposition of the sodium amalgam in the denuder all three products, chlorine, hydrogen and sodium hydroxide, must be filtered and transformed to forms required for sale. The sodium hydroxide is sold as 50% solution or pellets, and the chlorine is compressed and liquefied for storage and transport or used directly in an adjacent chemical plant. The hydrogen gas is used, if possible, as a chemical feedstock or sold as compressed gas; otherwise it is burnt as a fuel in the power station. The effluent brine must also be treated to remove residual chlorine and to reduce the mercury level to the legally required level. Whether it is then recycled to the salt deposits or allowed to enter natural waterways will probably depend on the proximity of the bore holes into the salt dome.

### 3.3.2 Diaphragm cells

A diaphragm cell has a separator based on asbestos with various polymers added to improve its performance and the electrode reactions generate chlorine and sodium hydroxide directly (reactions A and C of Table 3.2).

The principle of a diaphragm cell is sketched in Fig. 3.7. The asbestos is deposited directly onto a steel gauze which also acts as the cathode. The anode is placed close to the diaphragm and the 30% brine is passed through the anode compartment, commonly formed between two sections of diaphragm (as in the figure). The chlorine and the hydrogen plus sodium hydroxide are formed on opposite sides of the asbestos and are readily collected separately. The anodes will nowadays be DSA and in the most modern cells the steel cathode will also be coated with a catalyst to minimize the overpotential for hydrogen evolution.

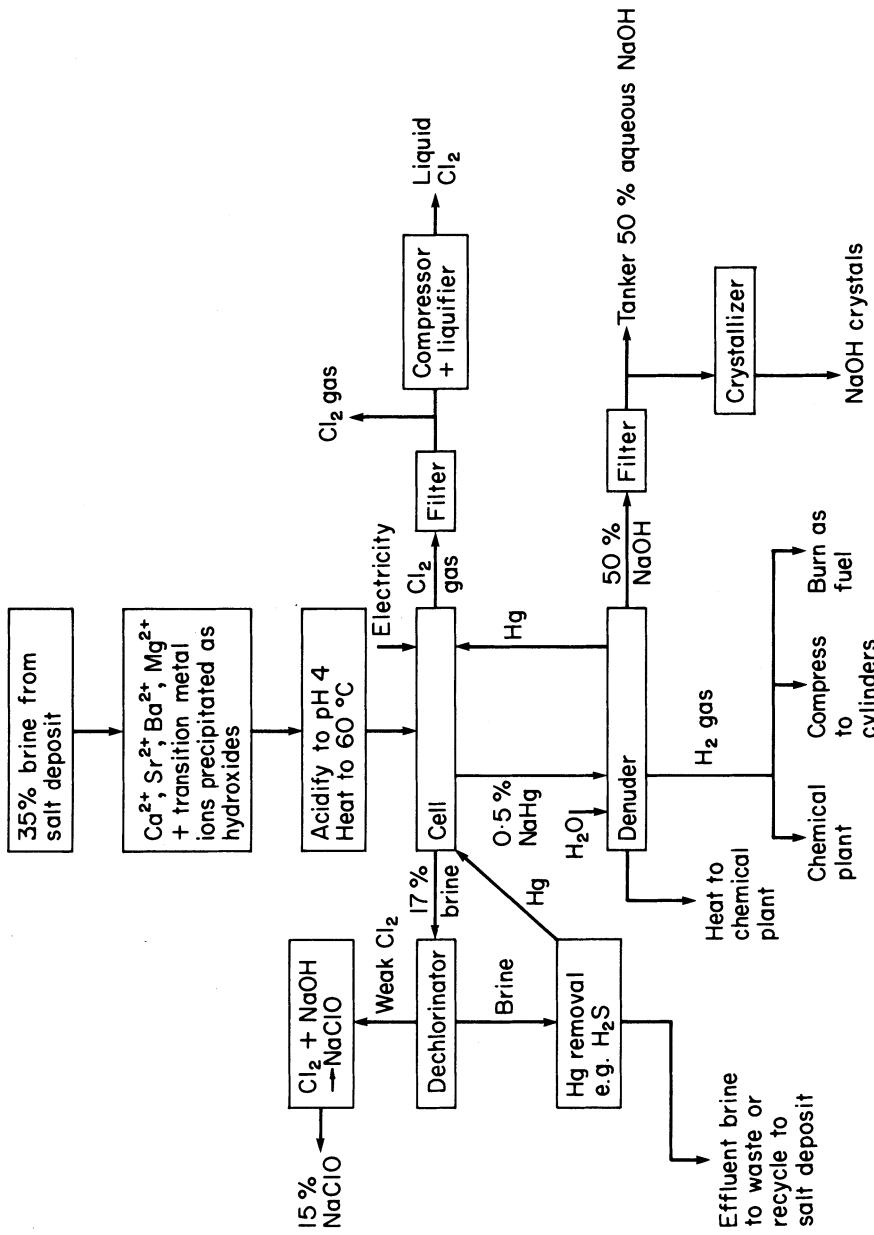


Figure 3.6 Complete mercury cell process for the conversion of salt deposits into chlorine and 50% caustic soda.

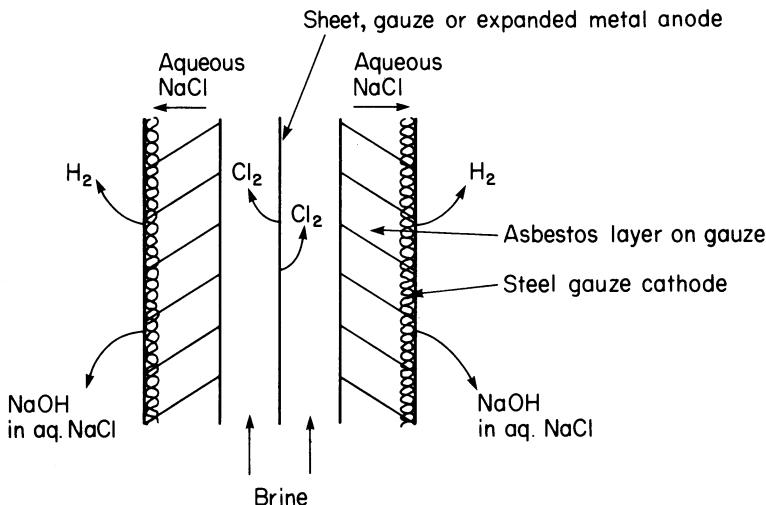


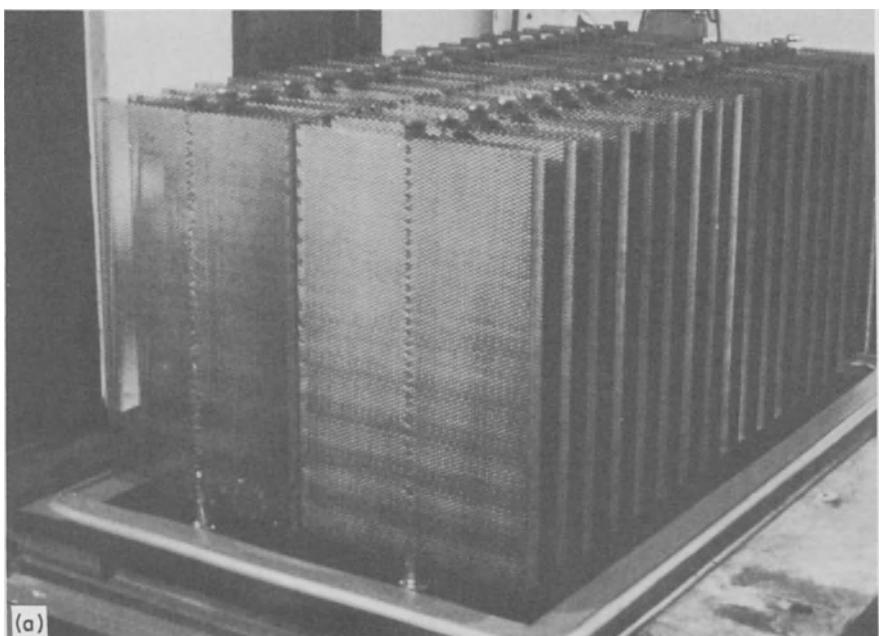
Figure 3.7 Principle of the diaphragm cell.

The use of an asbestos diaphragm has several problems associated with it:

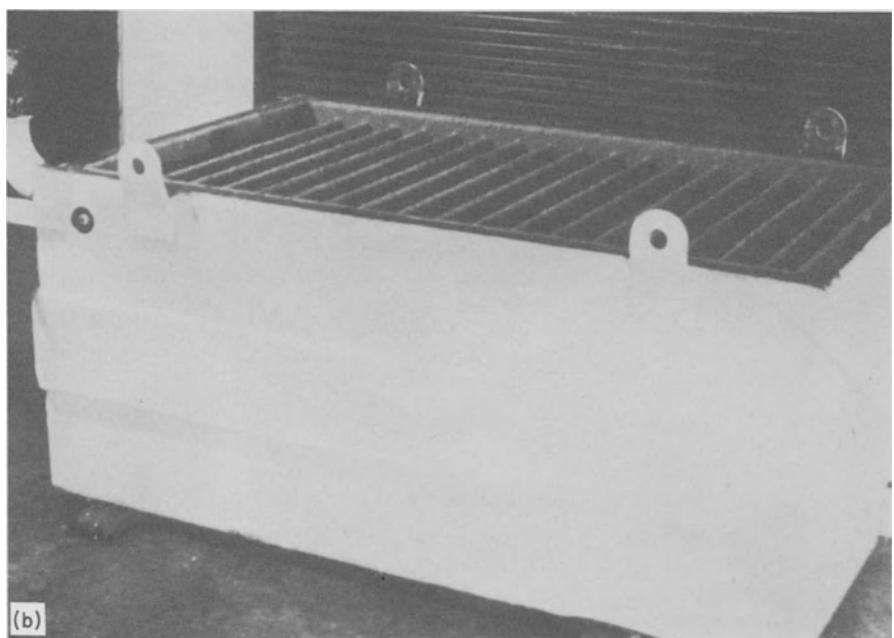
(1) First, it is purely a physical barrier and all ions and other species are equally able to diffuse through it when there is a concentration gradient. While sodium ions are transported rapidly through the diaphragm from anolyte to cathode by both diffusion and migration, chloride ion also passes into the catholyte so that the caustic soda is bound to contain a high percentage of chloride ion. Moreover the concentration of hydroxide ion formed at the cathode must be restricted to below 10%, otherwise diffusion of hydroxide ion into the anolyte becomes significant. This leads to loss of chlorine by hydrolysis to hypochlorite and formation of oxygen at the anode and hence contamination of the chlorine.

The limitation of the caustic soda concentration to 10% means that an additional step must be introduced into the process. To increase the concentration to the 50% solution normally traded, water must be evaporated and this requires additional energy and plant. The evaporation stage does, however, reduce the problem from chloride contamination since on cooling much of the sodium chloride crystallizes out from the 50% sodium hydroxide solution. Even so, the chloride level remains about 1% and this is not an acceptable level for all the applications of sodium hydroxide.

(2) The *IR* drop in the diaphragm is considerable. While the reversible potential for the cell is about  $-2.2\text{ V}$ , diaphragm cells operate in the range  $-3.2$  to  $-3.8\text{ V}$  and much of the additional voltage is associated with the asbestos. Moreover the *IR* drop in the cell increases with time because of the deposition of calcium and magnesium hydroxides in the pores of the diaphragm and to minimize this effect, very highly purified brine must be used. The brine purification process must be more rigorous than for mercury cells.



(a)



(b)

Figure 3.8 The (a) anode and (b) cathode assemblies for a chlor-alkali diaphragm cell. Photographs supplied by Diamond Shamrock Corp.

(3) The asbestos does not last indefinitely and its lifetime is the factor determining the operation of the cell and its design. The diaphragm must be replaced every few months and the cell design must permit the washing off of old asbestos and its replacement by new. The cell must be readily dismantled and reassembled and the change of diaphragm is carried out on a routine cycle. Recently, diaphragm performance has been improved by addition of various polymers to the asbestos base.

The optimum current density for diaphragm cells is a relatively low value, in the range 150–300 mA cm<sup>-2</sup>. Hence in designing the cell there is an overriding need to

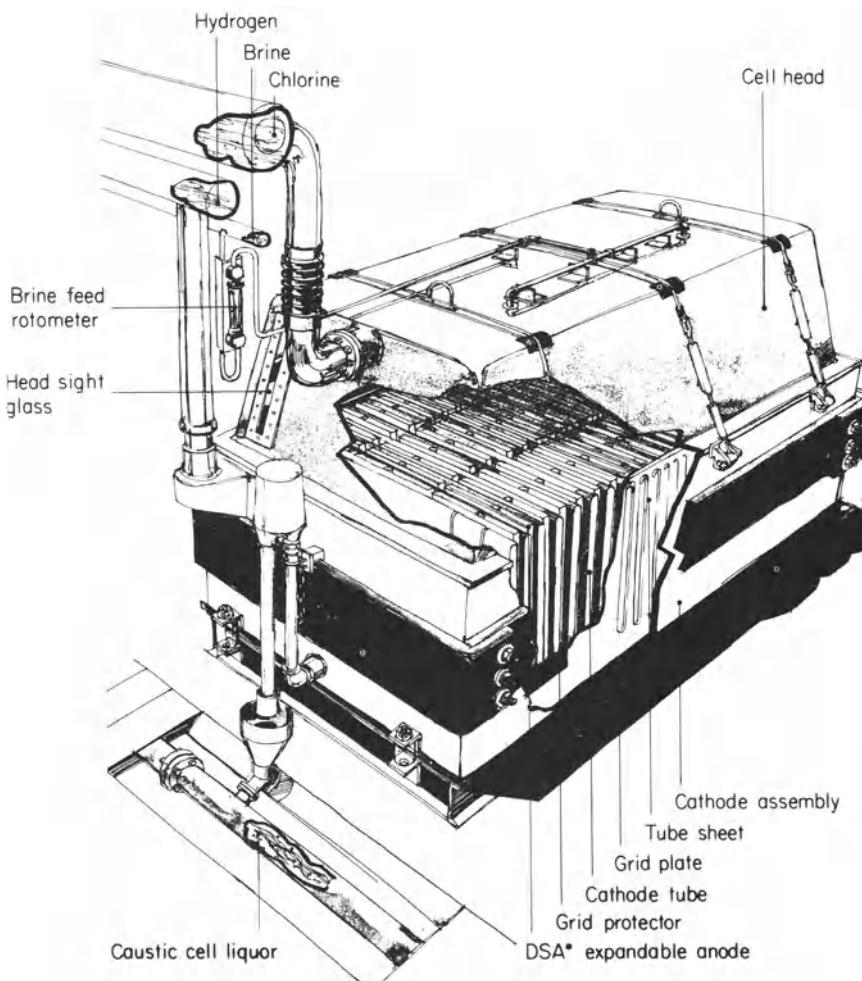


Figure 3.9 Cutaway diagram of complete diaphragm cell, type MDC 55. Diagram supplied by Diamond Shamrock Corp.

arrange for the maximum electrode area per unit volume to the cell. With this in mind a number of electrode configurations have been developed and one is illustrated in Figs 3.8 and 3.9.

The photographs show a Diamond Shamrock MDC 55 cell. It is designed on the 'toast rack' principle where a number of DSA anodes are bolted to the cell base (Fig. 3.8(a)) and the cathode assembly (Fig. 3.8(b)) is designed so that each anode is totally surrounded by cathode when it is lifted into place. It is dropped down from above over the fixed anodes. The cell is then completed (Fig. 3.9) by attachment of electrical connections, electrolyte feeds and product take-off pipes. The cathode assembly shown in Fig. 3.8(b) has seventeen cathode 'tubes' which extend from one side of the cell body to the other. The body of each tube (see Fig. 3.10) and the internal faces of the cell sides are constructed from steel mesh (maybe covered by nickel cathode catalyst) and the asbestos-based diaphragm is deposited onto the mesh by dipping the whole cathode assembly into an asbestos slurry. The caustic soda and hydrogen are collected from inside the tubes. The MDC 55 cell produces approximately 5 tons of  $\text{Cl}_2$  per day and has the dimensions 3 m x 1.6 m x 2 m. Its dry weight is almost 7 tons.

Table 3.3 shows the voltage distribution in some recent Diamond Shamrock diaphragm cells and the values emphasize the improvements provided by changes

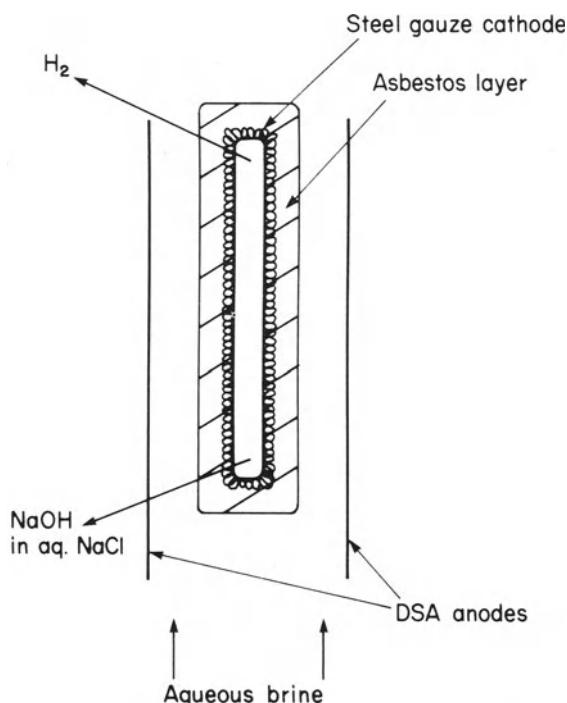


Figure 3.10 Cathode tubes in diaphragm cell.

Table 3.3 Potential distribution in recent diaphragm cells,  $I = 250 \text{ mA cm}^{-2}$ .

Cell type	$E^{\text{C}} - E^{\text{A}}$ (V)	$IR_{\text{SOLN}}$ (V)	$IR_{\text{DIAPHRAGM}}$ (V)	$IR_{\text{CIRCUIT}}$ (V)	Cell voltage (V)
1. DSA box anode, steel cathode + standard asbestos diaphragm	-2.48	-0.53	-0.71	-0.27	-3.99
2. DSA expanded anode, steel cathode + polymer modified diaphragm	-2.48	-0.27	-0.46	-0.27	-3.48
3. DSA expanded anode, Ni catalyst coated cathode + polymer modified diaphragm	-2.36	-0.27	-0.46	-0.27	-3.36

Data taken from Diamond Shamrock leaflet, *Modified Diaphragm Cells*.

in diaphragm composition and cathode catalyst. The diaphragm life has been increased to over one year but this remains the component determining the cell service routine since the anode and cathode catalyst coatings have an estimated lifetime of 5–8 years and 15–20 years respectively.

### 3.3.3 Membrane cells

The electrode reactions in a membrane cell are the same as those in a diaphragm cell but the separator is now a cation-permeable membrane. The development of membrane cells has been the result of the availability in the last decade of much improved membranes, and this is a highly promising area of continually developing technology.

Because of the ability of the membrane to discriminate between cations and anions and to a lesser extent between sodium ions and protons, the cell is, in principle, able directly to produce 50% sodium hydroxide free of chloride ion. The membranes presently available do not quite have the necessary resistance to hydroxide ion transport and this limits the sodium hydroxide concentration which may be produced directly to 20–40%, and hence an evaporation step is still necessary. The energy consumed in evaporation to produce a 50% NaOH solution is, however, obviously much less than in the case of diaphragm cells. The chloride ion level is, however, very low and hence in both these regards membrane cells are significantly better than diaphragm cells. Moreover the optimum current density for a membrane cell is twice that for a diaphragm cell at about  $500 \text{ mA cm}^{-2}$  without any significant increase in the cell voltage, –3.1 to –3.8 V.

The change from an asbestos diaphragm to a thin sheet of membrane necessitates a total change in cell engineering. Membrane cells are generally made from a series of frames in a filter press arrangement, each frame being an anolyte and a catholyte compartment. Figure 3.11 shows the design of such a membrane cell. The electrodes are vertical, and placed as close as possible to the membrane. Also they are constructed with slits or louvres or from expanded metal in such a way that the gases formed in the electrode reactions are directed to the back of the electrodes and do not collect in the current path (this would increase the *IR* drop in the cell). The anode and cathode compartments are fed with 35% brine and dilute caustic soda respectively. A complete filter press stack of cells is illustrated in Fig. 3.12 and contains 80 cells capable of producing 10 000 tons of chlorine each year. The plate-and-frame construction is well suited to bipolar electrical connection and indeed the figure shows bipolar cells; the cell current is 10 000 A and the stack requires a total voltage around 300 V.

It can be seen that membrane cells still have a production capability which is small compared with mercury cells, the limitation being the size of membrane sheet which can be manufactured and handled. In addition it should be recognized that the pipework for electrolyte feeds and product take-off is more numerous and much more complex than for diaphragm or mercury cells and there remains a lack of experience of and confidence in the long-term performance of the membranes.

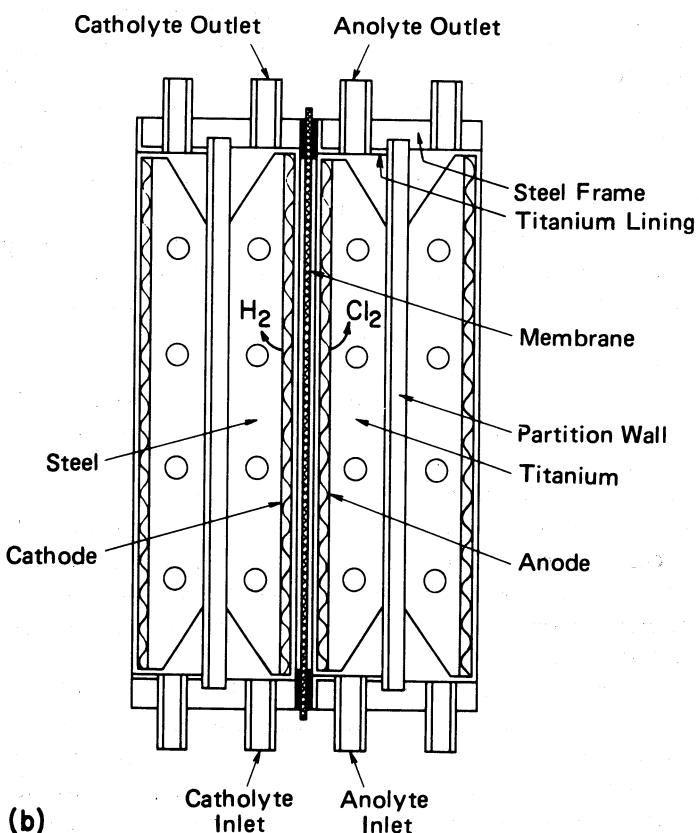
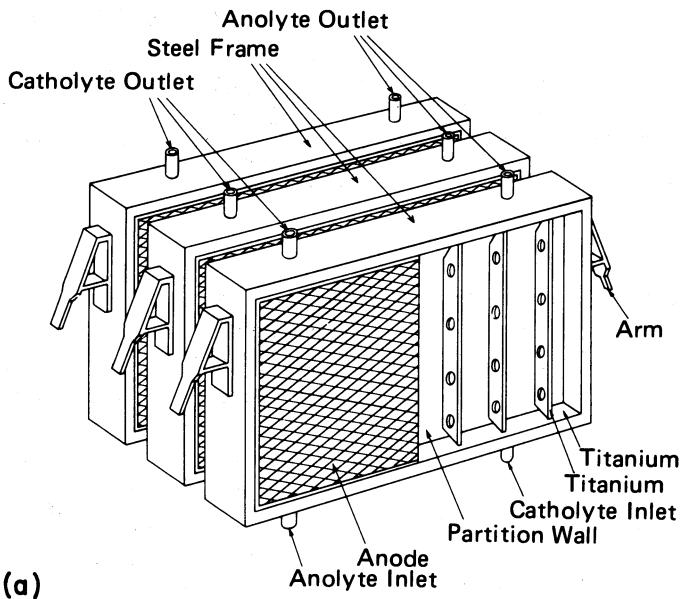


Figure 3.11 Schematic diagram of the construction of the Asahi Chemical Co. membrane cell.

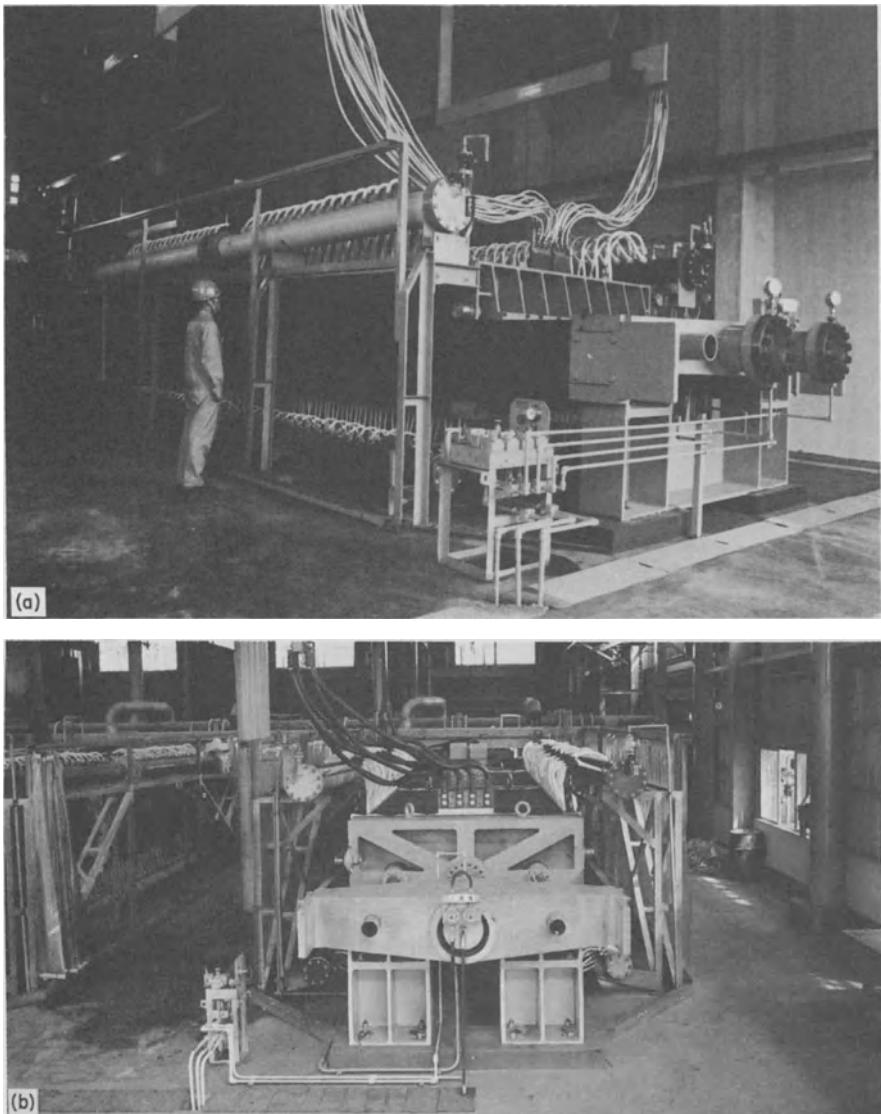


Figure 3.12 Two views of a filter press membrane cell. Photographs supplied by Asahi Chemical Co.

On the other hand, membrane cells look particularly attractive for small-scale chlor-alkali plants. This market is expanding as the social pressures to restrict the transport of chlorine increases and the ability to vary the number of cells in the filter press allows a uniform approach to the construction of a 25 ton  $\text{yr}^{-1}$  plant for the pretreatment of cooling water in power stations and a 10 000 ton  $\text{yr}^{-1}$  plant for a paper mill at a remote site. Chlor-alkali plants at large paper mills are

particularly attractive since papermaking requires both chlorine and sodium hydroxide and the hydrogen may be used as fuel.

### 3.3.4 A comparison

A comparison of the relative merits of the three electrolytic routes for the production of chlorine and caustic soda must be based on economics, although there are social factors which must also be taken into account. It is the intention here to discuss the factors determining the economics of the processes only in qualitative terms because the uncertainties in a more exact calculation are too great. It might be noted, however, that recent published calculations would indicate that the costs of chlorine and caustic soda produced by the processes are very similar and this must be the case since mercury, diaphragm and membrane cells are all currently operated and all are still considered when new plant is to be purchased. The important data to be used in the comparison are summarized in Table 3.4.

#### (a) *The initial cost of the plant*

This will include the purchase of the cells, control equipment and all the ancillary equipment for purifying the brine, liquefaction of the gases, concentration of the caustic soda to a 50% solution, effluent treatment, etc.

In electrochemical processes, the current density determines the size and number of cells necessary for the required annual production and hence is a key factor determining the cost of the cell rooms. It has been recorded in the preceding sections and is noted in Table 3.4 that the normal working current density for a mercury cell is very much higher than for a membrane or diaphragm cell, and the effect of this parameter combined with the easier scale-up of such cells may be seen in the comparison of the annual production rates. Further factors favouring mercury cells are the absence of the need for an evaporation stage to produce 50% caustic soda and the less stringent requirements for brine purity; mercury cells can tolerate higher concentrations of calcium and magnesium. On the other hand in order to meet legal requirements, mercury cell facilities must have plant to treat the effluent for the removal of mercury, and the presence of large quantities of mercury increases monitoring requirements in the plant. Finally the cost of the mercury and pumping it are not negligible!

#### (b) *Operating costs*

These include the cost of labour, the cost of replacing components and the rent and rates on the area of land. A comparison of the latter is very unfavourable to diaphragm cells where almost twice as much land is necessary because of the low current density and the need for evaporation plant. Membrane and mercury cells have similar land requirements because the former are packed together closely in a filter press and to some extent the electrodes scale vertically. All the processes are largely automated and hence the difference in labour costs is likely to arise because of a variable incidence of component and pipework failure. Certainly the need to replace diaphragms on a routine cycle increases the labour costs for the diaphragm cell process.

Table 3.4      Typical data for recent commercial chlor-alkali cells.

	Mercury cell	Diaphragm cell	Membrane cell
Cell voltage (V)	-4.4	-3.45	-3.5
Current density ( $\text{A cm}^{-2}$ )	1.0	0.2	0.45
Current efficiency for $\text{Cl}_2$ (%)	97	96	93
Energy consumption (kWh per ton of NaOH)			
(a) Electrolysis only	3150	2550	2700
(b) Electrolysis + evaporation to 50% NaOH	3150	3260	2920
Purity $\text{Cl}_2$ (%)	99.2	98	99.3
Purity $\text{H}_2$ (%)	99.9	99.9	99.9
$\text{O}_2$ in $\text{Cl}_2$ (%)	0.1	1 – 2	0.3
$\text{Cl}^-$ in 50% NaOH (%)	0.003	1 – 1.2	0.005
Need for evaporation to 50% NaOH	no	yes	currently no
Hg pollution problem	maybe	no	
Production rate/single cell (tons NaOH per year)	5000	1000	100
Land area ( $\text{m}^2$ ) for plant for $10^5$ tons NaOH per year	3000	5300	2700

(c) *Value added during the process*

This depends on both the cost of the raw materials and the value of the products. The raw materials for all three processes are similar but differences in the purity of the products will affect the price which may be obtained for them. The diaphragm cell process again comes a poor third since the caustic soda is high in chloride ion and the chlorine contains a higher content of oxygen. Hence the diaphragm cell becomes much more favourable if the caustic soda is not to be sold on the open market and if the internal use can tolerate the chloride ion impurity, even using it as a 10% solution, direct from the cell, thus avoiding the need to concentrate.

(d) *The cost of energy*

Figure 3.13 shows current density–cell voltage plots for cells of all three technologies, the full lines indicating the normal operating regions. The plots are all linear and this indicates the total predominance of the  $IR_{CELL}$  term in equation (3.5). The cell voltage is, however, only important so far as it determines the energy consumption of the cell and Fig. 3.14 therefore shows the relationship between energy consumption and current density; both the energy consumed in the

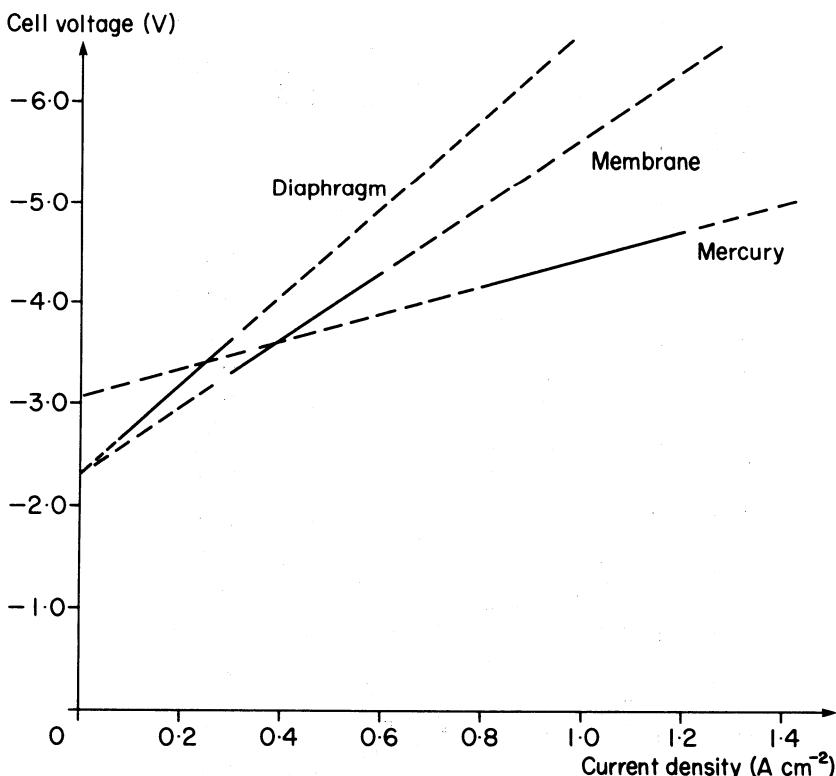


Figure 3.13 *Cell voltage vs current density plots for the three types of chlor-alkali cell. The full lines indicate the normal operating regions.*

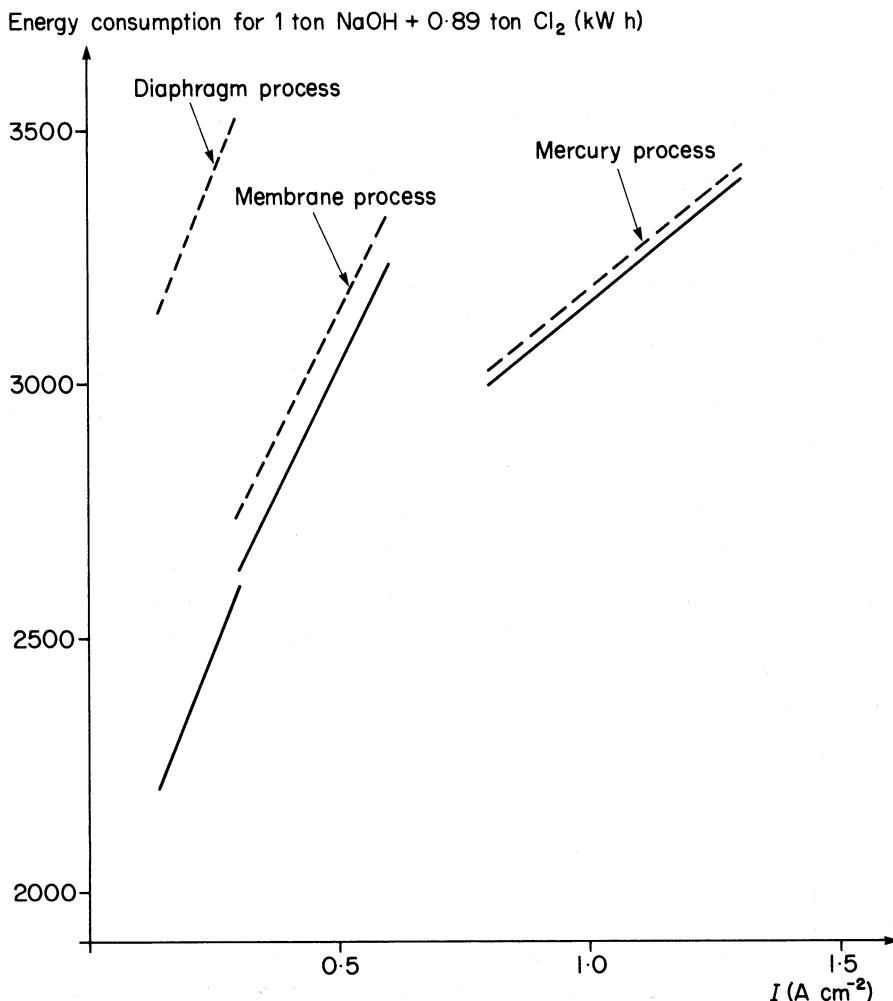


Figure 3.14 Comparison of the energy consumption in the three cell technologies for chlor-alkali production. Full lines represent electrolysis only; broken lines represent total energy consumption including evaporation and heating the electrolyte.

electrolysis and the total energy to form chlorine and 50% aqueous sodium hydroxide are included, the latter being the normal for comparison.

In seeking the conditions for operating the cell, both the absolute energy consumption and the slope of the lines, essentially the cell resistance, are important since there will be a trade-off between energy consumption and the rate of production (i.e. current density) when the total cost is taken into account; the slopes indicate the additional energy which must be consumed to permit a faster production rate. It is the low resistance of the mercury cell which allows the use of high current densities without an unreasonable voltage penalty.

It will be seen that the energy consumptions of the three cells are similar. This is because to the present time it has always been considered worthwhile to increase current density (i.e. production rate) rather than conserve energy as cell technology has been improved. This decision may change as electric power becomes more expensive and it is conceivable that current densities might even be reduced to decrease the energy requirement.

(e) *The choice*

The choice of cell technologies has not been made on the basis of an economic assessment alone. It is clear from the above that the mercury cell, despite being the oldest of the technologies, has many substantial advantages. It has, however, come under strong pressure because of the fear of mercury pollution. Following several deaths due to mercury poisoning at Minimata in Japan during the 1950s the dangers of the industrial use of mercury became fully recognized. Two responses to the problem of potential mercury poisoning are possible: to control carefully the use of mercury in the plant and to ensure that effluent does not contain harmful amounts of the heavy metal, or to discontinue completely the use of mercury. The USA and Japan opted to replace mercury cells as rapidly as possible (see Table 3.5), while in Europe the tendency has been to control the cell room environment, to perform continuous health checks (mercury in blood levels) on the workers and to carry out careful effluent treatment to remove mercury. It is claimed that in the UK the mercury in effluent from chlor-alkali plants does not significantly increase the mercury level of the local water environment. This diversity of action largely resulted from a difference in the market response to chloride-contaminated caustic soda; European customers insisted on the continued supply of chloride-free sodium hydroxide.

The move to diaphragm cell technology may well be an intermediate step. Diaphragm cells already seem to compare unfavourably with membrane cells and there is the expectation that substantial improvements in membranes and the associated technology are yet to come, e.g. it is hoped to produce membranes which permit the production of 50% sodium hydroxide directly and to design larger cells. Hence the predominance of diaphragm cells in the USA results from an early change from mercury cells; the change occurred later in Japan and after membrane cells became viable. Moreover, membrane cells may well meet all the

Table 3.5 Chlor-alkali industries\* according to production method

	Mercury	Diaphragm	Membrane
UK	95	5	0
Europe (EEC)	75	24	1
Japan	17	50	33
USA	22	78	0
Canada	29	67	4

\* The figures are for the late 1970s.

requirements of the European market and they would then be expected to displace mercury cells as cell houses become obsolete. The past twenty-five years has seen continuous change and much improvement (with regard to energy consumption, pollution control, etc.) in the chlor-alkali industry based on achievements in developing low-overpotential anodes and cathodes, membranes and new control strategies. Perhaps the next major innovation will be the development of oxygen cathodes, i.e. cathodes where the reaction is the reduction of oxygen rather than water; this could reduce the energy consumption by a further 30% but would only be feasible in a membrane cell. Thus in thirty years time, membrane cells may well be the only commercial chlor-alkali technology.

### 3.4 THE PRODUCTION OF POTASSIUM HYDROXIDE

Caustic potash is considerably more expensive than caustic soda because the feedstock is refined, crystalline potassium chloride. Hence it is only used when it has a particular advantage, and the production of potassium hydroxide is only 2–3% that of sodium hydroxide. Potassium hydroxide can be produced by each of the electrolytic routes described in Section 3.3 above; the only major difference is that the potassium chloride electrolyte is always recycled, the solution leaving the cell being resaturated and passed back to the cell.

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## 4 Metal Extraction and Refining

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This chapter will describe those electrolytic processes that are used in the manufacture of metals from their ores, i.e. electrowinning, and for the purification of metals, i.e. electrorefining.

The extraction of a metal from its ore will always include a reduction step from whichever oxidation state is most stable in our oxygen-rich natural environment to the zero oxidation state. In principle this reduction can almost always be accomplished by electrolysis and, indeed, many metals are, at least on a small scale, isolated by an electrolytic route. Commonly, however, routes based on carbon or sodium reduction are preferred for economic reasons. On a large scale, electrolysis is only used for the manufacture of the very electropositive elements, aluminium, sodium, lithium and magnesium, where the electrolysis medium is a molten salt, and for elements where the chemical route has environmental problems or the electrolytic route has advantages in terms of the purity of the metal. This latter group includes particularly copper, zinc and perhaps nickel. Cobalt, chromium, manganese, gallium, rare earths, tantalum and niobium are examples of other metals where electrolysis has been used, at least on a small scale, for their extraction. Large electrolytic plants for metal extraction are heavy consumers of electric power and it is therefore common for them to be sited close to cheap sources of electricity, e.g. near hydroelectric power stations.

In electrorefining the objective is to remove unwanted elements from impure metals. The impure material will be the anode and the process seeks to lead to the deposition of pure metal at the cathode, the other metals being left as anode sludge (i.e. solids) or as ions in the electrolyte solution. Where very pure metal is essential (e.g. copper for some conduction and electronics applications), the electrorefining process may be part of the overall extraction procedure but it is more common for electrorefining to be employed to assist the recycling of metals. Recycling metals is increasingly necessary as the world reserves become depleted and electrorefining is a powerful process for the separation of the complex mixtures found in scrap. Many metals are now electrorefined but perhaps the most important are copper, tin, lead, nickel, cobalt, aluminium, silver and gold.

## 4.1 ELECTROWINNING

### 4.1.1 Aluminium extraction

In terms of scale of production (around  $2 \times 10^7$  ton yr $^{-1}$  worldwide) aluminium electrolysis is second in importance only to the chlor-alkali industry. This is because aluminium is both light and strong and therefore suitable for many engineering and construction applications, may readily and cheaply be treated by anodizing (see Chapter 7) to retard corrosion and is the principal alternative to copper as a conductor of electricity. Moreover, the known reserves of aluminium ores are relatively high.

Aluminium is normally produced from the ore, bauxite, a hydrated aluminium oxide containing silica and other metal oxides, particularly iron. It is converted to a pure alumina using the equilibrium



The ore is first treated with caustic soda under pressure. The aluminium largely dissolves as the aluminate, the iron oxide is insoluble and the silica also remains in the form of a sodium aluminium silicate, which leads to a loss of aluminium. Hence the best bauxites are those low in silica. After filtration, the hydrated aluminium oxide is reprecipitated by seeding and the caustic soda solution may be re-used. The alumina is washed and then heated at 1200°C to remove water. The final step in the production of aluminium metal has to be electrolytic since the reduction of alumina with carbon is only possible at very high temperatures and the reverse reaction occurs on cooling. Moreover, because of the chemistry of aluminium, the electrolysis medium cannot be water; in fact almost all commercial production of aluminium during the last ninety years has used an electrolysis in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ).

The process is based on the observation made during the nineteenth century by Hall in the USA and Héroult in France that, whereas alumina melts at 2020°C to give a non-conducting liquid, it will dissolve to the extent of 15 wt % in molten cryolite at 1030°C to give a conducting medium. The high solubility results from the near equality of size of fluorine and oxygen atoms in the aluminium complexes in the melt and hence the ready formation of oxyfluoride ions on addition of the oxide to the cryolite. Indeed the aluminium is probably present as a mixture of several related species although the exact chemistry of the system is not known and it is therefore difficult to write complete electrode reactions. Clearly, however, the cathode reaction is the reduction of an aluminium (III) species to the metal which is molten at the electrolysis temperature; the cathode is effectively a pool of liquid aluminium. Ideally the anode reaction would be the oxidation of oxide ion to oxygen but it is difficult to find an anode material inert in the electrolysis conditions. Hence the electrolysis has always been run with consumable carbon anodes so that the overall cell reaction is



The carbon anode is consumed in a stoichiometric amount but the free energy for

this reaction is 340 kJ per mole of Al (at 1000°C) compared with 640 kJ per mole of Al for the reaction



the overall cell reaction if oxygen was evolved at the anode. In consequence the sacrifice of the carbon anode leads to a cell voltage and energy consumption which will be much reduced. Thus the reversible cell voltage is  $-1.18\text{ V}$  compared with  $-2.21\text{ V}$ .

A cell for the Hall–Héroult process is shown in Fig. 4.1, and a block diagram of the whole process is shown in Fig. 4.2. Cell design is determined largely by the need to contain molten cryolite at high temperatures and to withstand attack by molten aluminium and also by sodium and fluorine formed as minor products at the cathode and anode respectively. Hence the cell is a strong steel box lined first with alumina to act as a refractory, thermal insulator and then with carbon. In fact the base of the tank is lined with prebaked carbon blocks which are inlaid with steel bars to reduce their electrical resistance and which act as current carriers to the molten aluminium cathode. The sides are lined with partially graphitized anthracite in coal tar pitch. The process is then run so that there remains a layer of solid cryolite and alumina at the sides of the cell and a solid crust on the surface. This acts as a further barrier to corrosion and also to reduce the heat loss from the cell. The cell also has facilities for the periodic addition of alumina through the crust and for the removal of aluminium metal by suction. It is hooded with an extractor

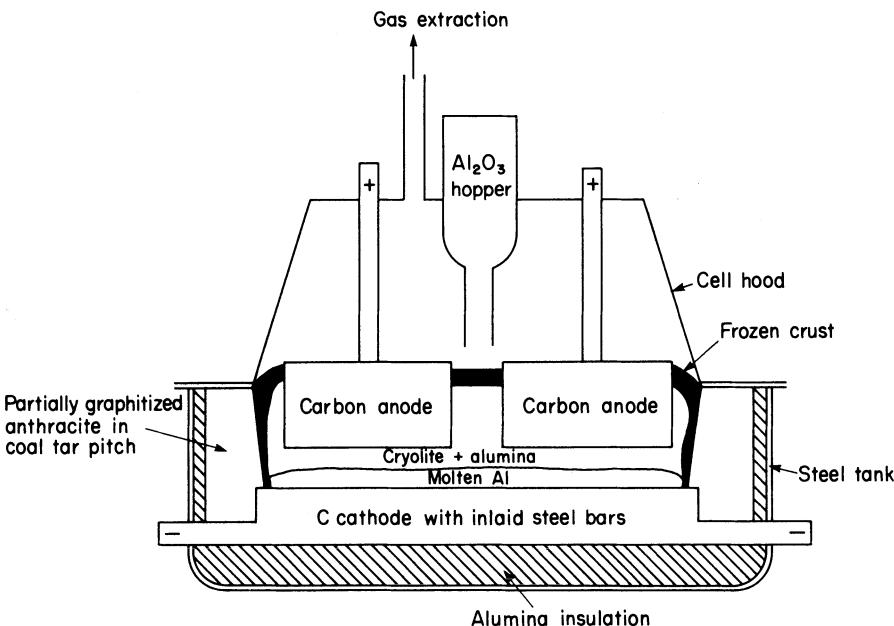


Figure 4.1 *Cell for the Hall–Héroult process for the extraction of aluminium.*

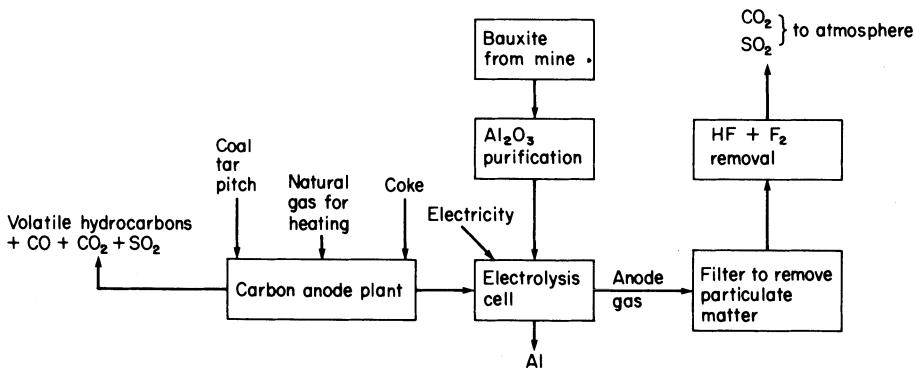


Figure 4.2 The steps in the Hall–Héroult process for the extraction of aluminium.

to vent the anode gases, mainly carbon dioxide, but also containing carbon monoxide from the unwanted back chemical reaction



and particulate matter and sometimes fluorine or hydrogen fluoride. Reaction (4.4), of course, reduces the current efficiency for the electrolysis.

The carbon anodes are manufactured from a carbon source such as anthracite and a pitch binder mix. Two types have been used:

- (1) Prebaked carbon blocks of dimensions approximately 80 cm × 100 cm × 50 cm deep.
- (2) Self-baking anodes (known as Soderberg anodes), usually one per cell and therefore of much larger dimensions. Such anodes are fed at the top with the ground carbon and pitch binder and this bakes *in situ* as it gradually descends into the molten electrolyte to form a hard, dense material which acts as the anode surface.

In both cases the anode is consumed and therefore must be lowered regularly (approximately 2 cm day<sup>-1</sup>) to maintain a constant anode–cathode gap. Soderberg anodes were common in the late 1940s and the 1950s because they removed the anode manufacturing step and hence made the overall process cheaper to operate. Prebaked anodes were used in earlier cells and are again almost universally employed because they give a better energy performance and lead to less difficult environmental problems; the *in situ* baking causes fumes which are more difficult to control.

Except for the anodes, cell design has changed little since the introduction of the process in the last century. The cells have got bigger, however, as the materials and construction techniques have improved, and typically a cell will now be 3 m × 8 m × 70 cm deep with eighteen prebaked anodes. The inter-electrode gap must be rather wide, about 5 cm, (a) to prevent shorting because the small difference in density between the melt (2.1 g cm<sup>-3</sup>) and the molten aluminium

( $2.3 \text{ g cm}^{-3}$ ) leads to an unstable cathode/electrolyte interface and (b) to minimize the chemical reaction of the electrolysis products (equation (4.4)) which causes loss in current efficiency.

While the electrolyte is essentially molten cryolite, certain additions are made and a typical electrolysis medium also contains excess aluminium trifluoride (4–6%) and calcium fluoride (4–6%). These additives increase the conductivity of the medium and lower the melting point of the cryolite to 960–980°C. A reduction in the operating temperature has the advantages of decreasing energy consumption and lowering the extent of reaction (4.4) (by about 1% per 10°C). On the other hand, by both decreasing the operating temperature and diluting the cryolite, the additives cause a decrease in the solubility of the alumina and this limits their total concentration.

Alumina must be added to the cell periodically and this is done through a hopper and it is first necessary to break the surface crust. In the normal electrolysis conditions, i.e. cryolite with calcium fluoride and excess aluminium fluoride and an operating temperature of 970°C, the alumina is only soluble to 6 wt %. During electrolysis its concentration drops and if it is allowed to fall below about 2% the electrolysis cell undergoes a sudden and major operational failure known as an ‘anode effect’. The cell voltage increases rapidly from 4.5 V to 40–60 V, and this is thought to be due to an insulating gas film, fluorine or carbon tetrafluoride, across the anode surface. To return the cell to its normal operating conditions, alumina must be added and the bath stirred to remove the gas film. The anode effect is, however, not regarded as totally unhelpful since sparking across the gas film burns off macroscale surface roughness to produce a better anode and provides a simple, if exotic, *in situ* analysis of alumina concentration in the electrolyte. Overfeeding of the cell causes problems by precipitation of alumina on the molten aluminium cathode. Hence it is common to permit an anode effect to occur at regular intervals.

A typical cell house will contain about 200 cells arranged in series on two lines, each  $3 \text{ m} \times 8 \text{ m}$  cell having a total anode area of  $15 \text{ m}^2$ . The optimum current density is around  $1 \text{ A cm}^{-2}$ , giving a total cell current of 150 kA and this requires a cell voltage of –4.0 to –4.5 V. The cell voltage, of course, depends on alumina concentration since this determines the concentration of electroactive species at both electrodes. It drops to just below 4 V after addition of alumina to 6% and rises to about 4.5 V before the onset of an anode effect. All cell houses have a strong magnetic field due to the large currents used and it is particularly important to take this into account in the design of aluminium electrolyzers because of the turbulence the magnetic field can produce at the aluminium/electrolyte interface due to the small difference in their densities. Hence the cells are arranged in the cell house to produce the minimum magnetic field.

Reaction (4.3) always leads to some loss in current efficiency and in most cells the aluminium current efficiency is only 85–90%. From these data the energy requirement may be estimated to be 14 000–16 000 kWh per ton of aluminium and we can also calculate that the cell house described would produce  $70\,000 \text{ ton yr}^{-1}$ .

It can be seen that the energy consumption of the aluminium electrolyser is very high (cf. 3000 kWh per ton of  $\text{Cl}_2$ ). This is partly because the production of

aluminium requires  $3 \text{ F mol}^{-1}$  and partly because of its low atomic weight, but also because of very substantial inefficiencies in the cell. Table 4.1 shows how the cell voltage is made up. The reversible potential is calculated from thermodynamic data and it can be seen that it represents only a small fraction of the observed cell voltage. Similar calculations for a cell where the reaction (4.3) occurs, i.e. where the anode reaction is oxygen evolution and the electrode is inert, show that the reversible potential would be  $-2.21 \text{ V}$ . An anode which is stable in the molten salt and able to evolve oxygen at low overpotentials would, however, be advantageous since it would remove the need to manufacture carbon anodes and hence remove considerable environmental problems. Moreover the penalty of a higher reversible potential may be more than outweighed if the anode overpotential and resistance were less than those shown in Table 4.1.

Table 4.1 Estimate of voltage distribution in the Hall–Héroult cell.

	Voltage (V)
Reversible cell potential	-1.2
Overvoltages – anode	-0.5
cathode	0.0
<i>IR</i> drop in electrodes – anode	-0.5
cathode	-0.6
<i>IR</i> drop in the electrolyte	-1.5
Total cell voltage	-4.3

In view of the high temperature it is to be expected that the kinetics of the electrode reactions will be rapid and this is certainly the case at the cathode. A substantial overpotential has been found at the anode but it must be remembered that the oxidation of an oxyanion at carbon to give carbon dioxide is probably an unknown reaction at room temperature.

The *IR* drops in the cell are large. Those in the electrodes arise because of their size and the relatively low conductivity of carbon, particularly the form used in this electrolysis; the carbon cathode has inlaid steel bars to decrease its resistance. The substantial electrolyte *IR* drop is due to the need for a large (5 cm) inter-electrode gap. This overpotential is, however, used to some extent since it gives rise to heat which maintains the electrolyte in a molten state.

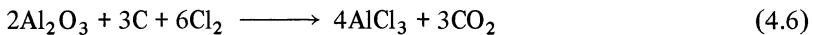
If the energy required to maintain the cell at  $970^\circ\text{C}$  is taken into account, the energy efficiency of the process is only 33%. Even this relatively poor performance has only been achieved as a result of a careful examination of the physical chemistry of the electrolyte and electrodes and of the cell technology. Moreover, the process has several environmental problems associated with both the curing of

the carbon anodes and the anode gases, which must be treated to remove both fluoride and particulate matter. Hence it is not surprising that considerable effort has gone into developing an alternative technology.

While some of this effort has gone into inert anodes, the major emphasis has been to develop a process in a chloride medium. Much of the work has been unsuccessful, but Alcoa in the USA have recently had some success and now operate a small plant based on a chloride electrolysis. The cell reaction is



and the electrolysis is carried out at C electrodes in a 3:2 mixture of sodium and lithium chloride containing 2–15% aluminium trichloride. The temperature is 700°C, almost 300°C below that for the Hall–Héroult process but above the melting point of aluminium (this greatly simplifies the process). The process requires the prior conversion of alumina to aluminium trichloride by the chemical reaction



The cell for the electrolysis consists of a bipolar stack of horizontal carbon anodes with an inter-electrode gap of 1.5 cm. The electrodes and electrolyte flow is designed to ensure the minimum contact between the electrolysis products since the molten aluminium and gaseous chlorine would otherwise react rapidly. The aluminium falls to a pool below the electrodes while the chlorine is pumped out the top of the cell to be used in the reaction with alumina. A simplified cell is shown in Fig. 4.3. It may be noted that the overall process again uses carbon in at least stoichiometric quantities although now in a chemical step. Overall the process run at 1 A cm<sup>-2</sup> has an energy efficiency which is currently claimed to be about 10% better than that for the Hall–Héroult process.

Aluminium is regarded as a strategic material, i.e. it is essential for military applications. Bauxite is, however, not found in large quantities in the developed Western world; rather it comes from Africa, South America, Australia and Asia and is transported in the form of purified alumina. On the other hand, aluminium is the most abundant metal in the Earth's crust and is found everywhere, although in a less concentrated form than in bauxite, in common clays. Hence a further objective of R and D activity is to develop processes for the extraction of aluminium metal from clay.

Aluminium production will always be a highly energy-intensive industry. Table 4.2 shows a breakdown of the costs in a typical Hall–Héroult plant and it can be seen that electric power is the second largest item. Hence the importance of energy conservation cannot be overemphasized.

#### 4.1.2 Sodium, magnesium and lithium manufacture

These metals are all produced by electrolysis of a mixture of molten metal chlorides; the electrolyte composition is selected to minimize the process temperature and to ensure that it is the desired metal that is discharged at the cathode. The estimated annual world production of sodium and magnesium is a few hundred thousand tons while that for lithium is only a few thousand tons. The

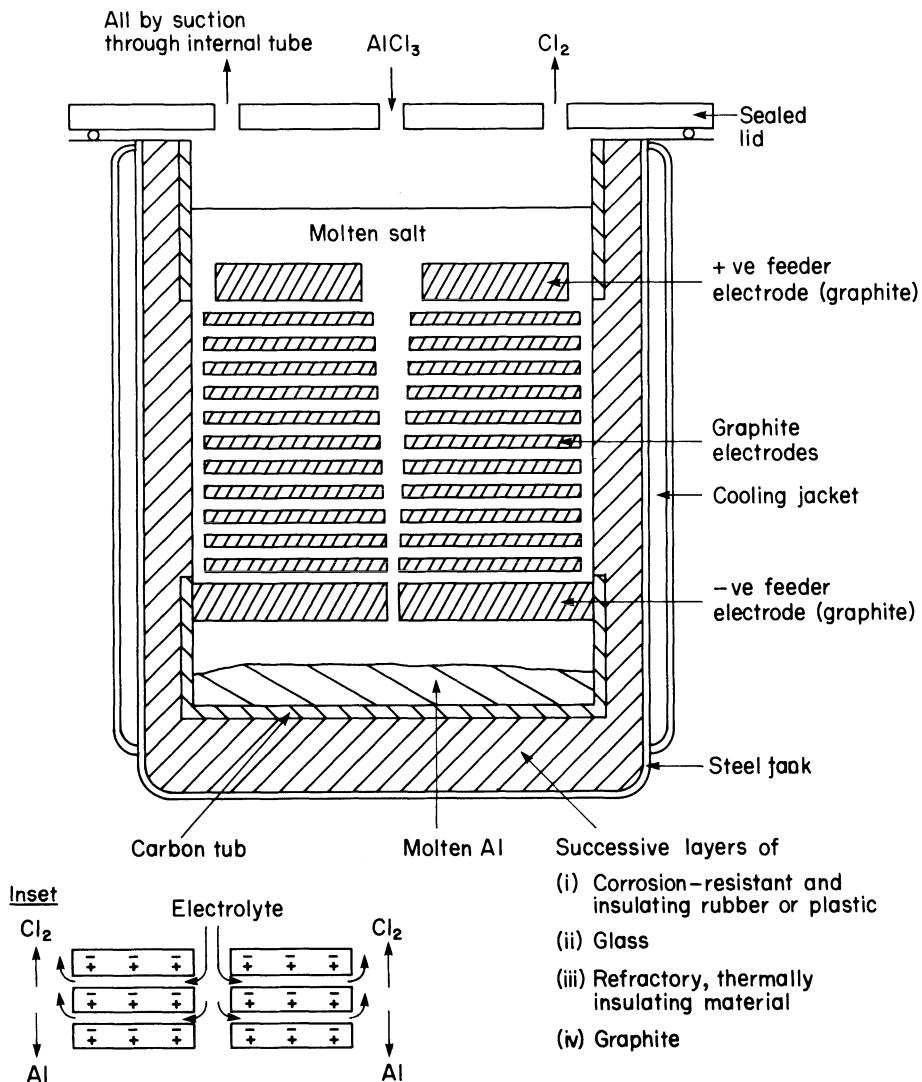


Figure 4.3 Cell for aluminium extraction by the Alcoa chloride process.

major uses are: (a) sodium — manufacture of lead alkyls, isolation of titanium metal, production of several organic and inorganic substances; (b) magnesium — organic synthesis, metal alloys; (c) lithium — polymer initiation, organic synthesis, batteries.

The general technology may be illustrated by the example of sodium production in the Down's cell. The electrolyte is a molten mixture of sodium chloride (40%) and calcium chloride (60 wt %) requiring a process temperature of about 600°C. The principle of cell design is shown in Fig. 4.4, although more

Table 4.2 Cost breakdown for aluminium metal production.

	Fraction of total cost (%)
Alumina	30
Anodes	7
Other materials	7
Electricity	23
Labour	16
Capital cost	17

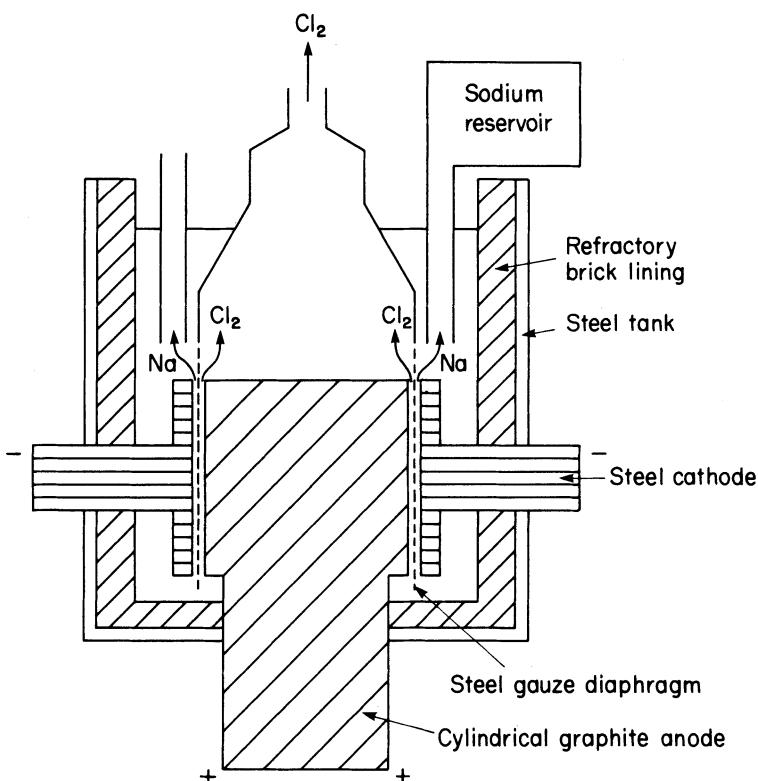
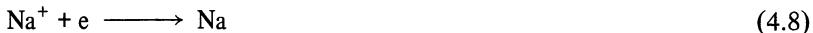


Figure 4.4 Down's cell for the extraction of sodium metal by molten  $\text{NaCl}/\text{CaCl}_2$  electrolysis.

modern cells have four anodes and cathodes in each cell. The design and materials of construction are again determined by the electrolysis medium. The electrode reactions are simple; at the cylindrical graphite anode



and at the steel cathode surrounding the anode



Some separation of the products is necessary to prevent the back reaction and a steel gauze diaphragm ensures that the chlorine gas and the liquid sodium are guided to different collection reservoirs. The sodium is much less dense than the melt and readily rises up a pipe into a reservoir; indeed, this is the basis of its separation from the small quantity of calcium which also forms at the cathode. The calcium is more dense and sinks back into the electrolyte where the equilibrium



ensures that its concentration remains constant and low. The operation of the cell is controlled by the rate of anode corrosion; in the presence of some trace water or oxide ions in the molten chloride medium, the graphite anode is oxidized to carbon monoxide and carbon dioxide, and hence precautions are necessary to minimize the rate of loss of graphite.

Down's cells operate at about  $1 \text{ A cm}^{-2}$  with a cell voltage of  $-7 \text{ V}$ . This compares with a reversible cell voltage of approximately  $-3.6 \text{ V}$ , the difference being almost entirely  $IR$  in the electrolyte and the electrodes since overpotentials for the electrode reactions will be small at the operating temperature. The current efficiency is about 80%, indicating that significant back reaction occurs, and the energy consumption is in the range  $9000\text{--}10\,000 \text{ kWh ton}^{-1}$ .

#### 4.1.3 Hydrometallurgical processes

Hydrometallurgical processes may be used when the metal ion is readily reduced to the parent metal and hence the electrolytic reduction may be carried out in aqueous solution. Such chemistry, however, implies that other routes from the ore to the metal must be possible and, indeed, smelting techniques are always applicable. Hence the choice between smelting and electrolysis will depend on the quality and type of ore available and local economic factors, particularly the cost of various forms of energy.

Copper and zinc are the principal metals extracted by electrolysis in aqueous solution; the total world production of both approaches  $10^7 \text{ ton yr}^{-1}$  although the electrolytic route accounts for only 10% of the copper and 50% of the zinc produced. Moreover the large electrolytic plants are limited to sites in Africa, Australia and Canada where hydroelectric power is available close to the mines. Cobalt, nickel, chromium, manganese, cadmium, gallium, thallium, indium, silver and gold have also been reported to have been extracted by a hydrometallurgical process but, since these metals are only produced in a low tonnage, the electrolytic processes are on a small scale.

The electrolysis is the final step in a complex procedure. Usually the electrolysis medium is sulphuric acid and the electrode reactions are



and



The complete extraction process will have the following stages:

(a) Mining the ore, which is commonly a sulphide or an oxide or a mixture of both and will contain several metal ions.

(b) If the ore is a sulphide, it is roasted in air to convert it to an oxide



which is then leached with acid, normally sulphuric acid to give an acidic metal sulphate solution



The first step inevitably produces large quantities of sulphur dioxide and hence environmental problems. In addition, it is energy-intensive particularly if the metal to be isolated is not the major constituent and large quantities of crude ore must be heated. For these reasons, oxide ores which may be leached directly are preferred although their supply is usually insufficient for the demand. To reduce the energy requirement in the roasting process, the crude ore is sometimes purified, e.g. by flotation, and completely different approaches to metal removal from the ore, e.g. direct electrolytic leaching



have been considered;

(c) The acidic metal sulphate solution is purified and all metal ions which are reduced more readily than the element of interest must be removed. The principal methods of purification are:

- (i) Precipitation with hydroxide or sulphide ion.
- (ii) Solvent extraction. Chelating agents are used to make the metal ions soluble in an organic solvent. Much recent research effort has gone into designing chelating agents which are highly selective for single transition-metal ions.
- (iii) Cementation, i.e. the solution is passed through a reactor containing a more electropositive metal in powdered form so that the reaction



can occur.

- (d) The electrolysis.
- (e) The liquor from the electrolysis cells may contain a relatively high percentage of elements which were originally minor constituents (e.g. As in liquor

from Cu cells) and such elements are often extracted. In any case the effluent liquors must be treated to remove transition-metal and heavy-metal ions before they are discharged into the environment.

The technology of these electrowinning processes is very simple. The cells are open concrete tanks lined with rubber or plastic and the lines of anode and cathode plates are placed alternately with a separation of 5–15 cm; the cells are connected monopolar and one arrangement is shown in Fig. 4.5. The anodes are lead alloy sheets which in the sulphate medium form a lead dioxide coating; the metal additions to the lead (e.g. silver) are to catalyse oxygen evolution and therefore reduce the anodic overpotential. The starter sheets for the cathodes are aluminium or titanium and the metal is deposited until there is a layer 3–5 cm thick, at which point the cathodes are removed from the cell. The metal is then stripped from the starter sheets and these are re-used. The electrodes are typically 0.3–0.5 m<sup>2</sup> in area but the anodes are always larger than the cathodes to prevent deposition edge effects and hence obtain an even deposit. The electrolyte is flowed slowly through the cells and there is often no attempt to introduce convection since this can lead to contamination of the cathode deposits by solids which form in the cell. On the other hand, air sparging of the cathode surface (i.e. passing air through a series of nozzles below the cathode) can increase the current density by a factor of 5–10.

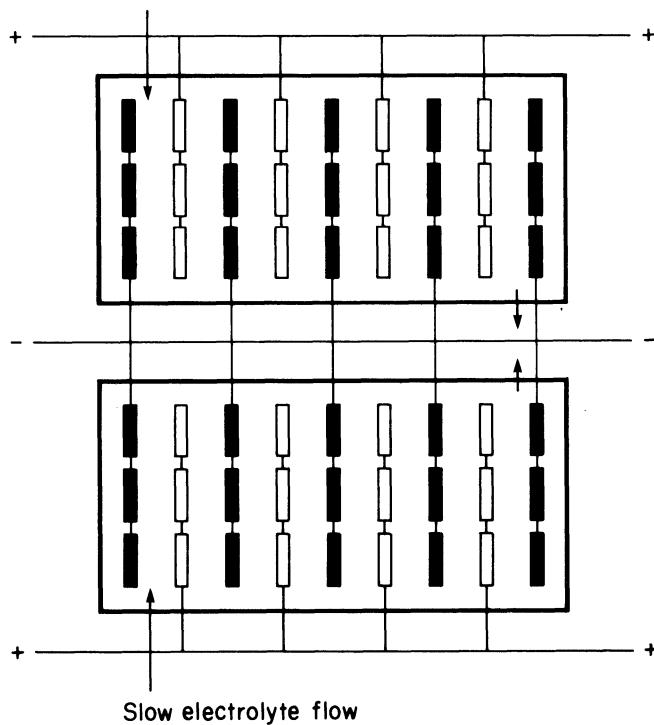


Figure 4.5 Layout of copper electrowinning cell house.

For copper winning the electrolyte feed is sulphuric acid (2 M) with copper sulphate (0.5–1.0 M) together with various additives (e.g. glue, thiourea, gelatin) in low concentrations to improve the quality of the copper deposit by increasing crystallinity and avoiding dendrites and gas occlusions (see Chapter 7). The operating conditions depend critically on the impurity content of the electrolyte but typically these would be electrolyte temperature 40–60°C, current density 15–150 mA cm<sup>-2</sup>, cell voltage –1.9 to –2.5 V and current efficiency 80–96%. Commonly the purity of the copper deposit exceeds 99.5% and the energy consumption is in the range 1900–2500 kWh per ton of copper. Thus for a production rate of 10<sup>4</sup> ton yr<sup>-1</sup> a cell house might contain twelve tanks each with 100 sets of parallel anode and cathode pairs and a total cathode area of 100 m<sup>2</sup>.

For zinc the electrolyte is sulphuric acid and zinc sulphate (0.5–1.0 M) and the usual additives are silicate or animal glue. The current density is 30–75 mA cm<sup>-2</sup>, requiring a cell voltage of about 3.3 V and an energy requirement of 3000–3500 kWh ton<sup>-1</sup>.

The present cell houses are designed for ease of operation and the absence of shorts and it is clear that they have a number of shortcomings, namely:

(a) The cells are not designed for energy efficiency. The inter-electrode gaps are large and the oxygen overpotential at the anode is considerable.

(b) The productivity of the cell house is poor; the low current density and the cell design combine to give a low space time yield. Not only does this lead to large cell rooms but also to large quantities of metal being tied up in the cell house; the residence time of a metal atom may be up to a month, and this represents a considerable investment at present prices.

(c) The concentration of the metal ion must be high. The leaching of low-grade ores leads to dilute solutions which must be concentrated, and it would be advantageous to have cells which could handle such leach solutions directly.

These have led to efforts to develop cell technology based on concepts different from the parallel-plate design and in particular various forms of three-dimensional electrodes. For example, cells with fluidized or spouted bed cathodes have been studied in the laboratory and operated on a large pilot-plant scale. Such cells are discussed in Chapters 2 and 11. Particulate electrodes lead to very high rates of mass transport of metal ions to the particle surface and in any case their surface area per unit volume is high; it is possible, therefore, to process dilute solutions (e.g. 1 g l<sup>-1</sup> Cu<sup>2+</sup>) with high efficiency in a single pass and with a high apparent current density. Particulate electrodes, however, have difficulties. First, there has to be a potential and hence current distribution along the direction of current flow. Secondly, the bed tends to coalesce during electrowinning, particularly on a long timescale and with concentrated metal ion solution; this destroys the favourable properties of such electrodes. Hence at the present time, cells with particulate electrodes are considered more likely to have an impact in metal recovery from effluents than in large-tonnage electrowinning.

## 4.2 ELECTROREFINING

In an electrorefining process, the anode is the impure metal and the impurities must be lost during the passage of the metal from the anode to the cathode during electrolysis, i.e. the electrode reactions are, at the anode



and at the cathode



Electrorefining is a much more common process than electrowinning and such plants occur throughout the world on scales between 1000–100 000 ton yr<sup>-1</sup>.

Usually they are part of a larger operation to separate and recover pure metals from both scrap and primary ores. Therefore, the process must be designed to handle a variable-quality metal feed and lead to a concentration of all the metals present in a form which can be treated further. Electrorefining leads to metal of the highest purity.

Although electrorefining processes using a molten salt electrolyte are used, e.g. see aluminium refining later, and indeed are the subject of further development because of the possibilities they offer for increasing current densities and refining via lower oxidation states not stable in water (e.g. refining of copper via Cu<sup>+</sup> would almost halve the energy requirement), aqueous processes presently predominate.

### 4.2.1 Aqueous electrorefining

The conditions used for the refining of five metals are summarized in Table 4.3. The electrolyte and other conditions must be selected so that both the anodic dissolution and the deposition of the metal occur with high efficiency while none of the impurity metals can transfer from the anode to the cathode. Certainly there must be no passivation of the anode (see Chapter 9) and the objective is to obtain a good-quality, often highly crystalline, deposit at the cathode. Where necessary, additives are added to the electrolyte to enforce the correct behaviour at both electrodes. Chloride ion is a common addition to enhance the dissolution process and, where essential, organic additives are used to modify the cathode deposit. Since, however, organic compounds can be occluded to some extent and reduce the purity of the metal, their use is avoided when possible.

The process for electrorefining copper is typical of those carried out in aqueous solution. The electrolyte is copper sulphate (0.7 M) and sulphuric acid (2 M) and the way in which the purification of the copper occurs can be seen by considering the metals likely to be found as impurities:

(a) Ag, Au and Pt are more noble than copper and therefore will not dissolve anodically. They will be found as metals in the anode slime.

(b) Sn, Bi and Sb dissolve anodically but will precipitate in the electrolyte as oxides or hydroxides which will again be found in the anode slime.

Table 4.3 Parameters for electrorefining processes.

Metal	Electrolyte (g 1 <sup>-1</sup> )	$I$ (mA cm <sup>-2</sup> )	Cell voltage (V)	$T$ (°C)	Current efficiency	Impurity metals	
						Slime	Solution
Cu	CuSO <sub>4</sub> (100–140) H <sub>2</sub> SO <sub>4</sub> (180–250)	10–20	0.15–0.30	60	95	Ag, Au, Ni, Pb, Sb	Ni, As, Fe, Co
Ni	NiSO <sub>4</sub> (140–160) NaCl (90) H <sub>3</sub> BO <sub>3</sub> (10–20)	15–20	1.5–3.0	60	98	Ag, Au, Pt	Cu, Co
Co	CoSO <sub>4</sub> (150–160) Na <sub>2</sub> SO <sub>4</sub> (120–140) NaCl (15–20) H <sub>3</sub> BO <sub>3</sub> (10–20)	15–20	1.5–3.0	60	75–85	—	Ni, Cu
Pb	Pb <sup>2+</sup> (60–80) H <sub>2</sub> SiF <sub>6</sub> (50–100)	15–25	0.3–0.6	30–50	95	Bi, Ag, Au, Sb	—
Sn	Na <sub>2</sub> SnO <sub>3</sub> (40–80) NaOH (8–20)	5–15	0.3–0.6	20–60	65	Pb, Sb	—

(c) Pb is oxidized anodically but will form insoluble lead sulphate in this electrolyte. Again this will fall to the slime in the base of the cell.

(d) As, Fe, Ni, Co and Zn all dissolve anodically and in the sulphate medium form species which are soluble in the electrolyte. The species formed, however, only reduce at potentials more negative than that at which the copper deposits and therefore remain in the electrolytes.

Hence the impurities accumulate in either the electrolyte or the cell slime and these can be processed further to recover the significant metals.

The electrolytic cells are generally of a very simple open tank and parallel-plate electrode design, similar to that described above for copper winning except that the anodes are now of the impure copper. The copper anodes must have the correct size and geometry (i.e. flat plates larger than the starter sheets of aluminium, titanium or steel for the cathodes to avoid heavy edge deposits) and have a homogeneous composition. The flow rate of the electrolyte through the cells is low so that the slime drops to the base of the cell and does not come into contact with the cathode.

Figure 4.6 summarizes the total process. Normally the sludge removal is by filtration of the electrolyte although in some cases (e.g. Pb) the sludge collects on the anode which periodically must be removed from the cell and scraped. Before recycle, the electrolyte must be purified and the concentration of metal ion, electrolytes and addition agents adjusted to the correct values. The purification process normally involves cementation or precipitation (by addition of hydroxide or sulphide ion or by change of oxidation state, e.g. Sn(II)  $\rightarrow$  Sn(IV) $\downarrow$ ). The exact procedure will depend on the level and type of impurities in the electrolyte.

It can be seen from the data in Table 4.3 that in order to obtain the pure metals at the cathode, the current density is always low. On the other hand, with the exception of tin the current efficiencies are good and the cell voltages can be low. In electrorefining the cathode reaction is the reverse of that at the anode and therefore, in the ideal case, the cell voltage is only required to drive the current

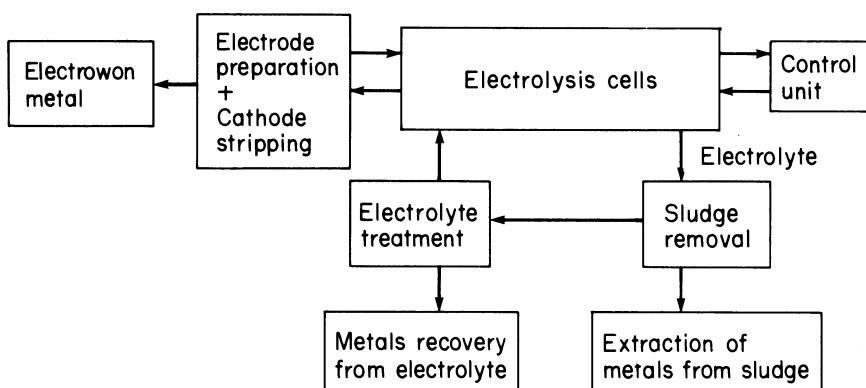


Figure 4.6 Hydrometallurgical process including an electrolysis step for the refining of a metal and the recovery of the minor elements.

through the electrolyte. In practice there may also be overpotentials associated with the anode and cathode reactions, and in the cases of nickel and cobalt these are considerable because the  $M/M^{2+}$  couples are very irreversible. The energy consumptions are relatively low, in the range 200–1500 kWh per ton of metal, and to the present time this has led to the use of cells with relatively large inter-electrode gaps (5–15 cm) which minimizes the labour costs for checking cells to prevent shorts and to handle electrode changes. The low current densities contribute to the low energy consumption (the  $IR$  term is small) but causes the cell houses to be large and, more importantly, the weight of metal tied up in the cell house to be large – the residence time of the metal in the cell is normally 21–28 days – and this is expensive. Hence increased current densities without loss in purity of the refined metal would be advantageous.

#### 4.2.2 Molten salt electrorefining

The principal metal refined in a molten salt medium is aluminium. Something approaching 2% of the total aluminium produced is refined by a process based on the principle illustrated in Fig. 4.7. The density of the impure aluminium is increased by the addition of copper (25–30%) and that of a cryolite melt by the addition of barium fluoride so that three distinct layers, pure aluminium, melt and aluminium/copper, are formed in the cell. On electrolysis the aluminium is transferred from the anode of impure aluminium to the top layer while the major impurities (i) Na, Mg, Ca and Sr are oxidized from the anode pool to the melt but do not reduce at the cathode and therefore accumulate in the melt, and (ii) Fe, Si, Mn, Zn (and Cu) are oxidized less readily than aluminium and hence remain in the anode pool. The aluminium obtained is very pure, being in the range 99.99–99.999%.

Molten salt processes for refining metals as diverse as lead, beryllium, magnesium, molybdenum and uranium have been described but are probably never used commercially.

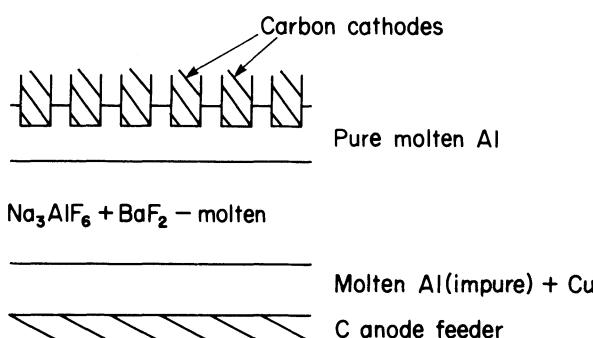


Figure 4.7 Principle of the molten salt refining process for aluminium.

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## 5 Other Inorganic Electrolytic processes

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In this chapter, the electrolytic preparation of inorganic compounds other than chlorine, alkalis and metals will be discussed. The processes are, in general, low tonnage but have an established position in industrial practice. The compounds prepared by electrolytic processes are the strong oxidizing agents, e.g.  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{F}_2$ , metal oxides which are particularly active when prepared anodically, e.g.  $\text{MnO}_2$  and  $\text{Cu}_2\text{O}$ , and hydrogen and/or oxygen by water electrolysis.

### 5.1 FLUORINE

Electrolysis is the only method for the isolation of the element fluorine. Although the reaction was first described in the mid-nineteenth century, the first commercial production of fluorine was not until 1946 in the USA and 1948 in Europe. The process was first developed to produce the fluorine required for  $^{238}\text{U}$  enrichment; the enrichment of  $^{238}\text{U}$  is based on a diffusional separation of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  and one step in the conversion of uranium ores to  $\text{UF}_6$  is the oxidation of  $\text{UF}_4$  either by elemental  $\text{F}_2$  or by  $\text{ClF}_3$ . The nuclear industry remains a major producer of fluorine for this purpose but on a smaller scale fluorine is also used in the chemical industry for the production of  $\text{SF}_6$  (a gaseous dielectric which is non-toxic and non-inflammable) and fluorinated organic compounds. The total world production of fluorine is probably between 10 000 and 20 000 ton  $\text{yr}^{-1}$ .

All commercial electrolyses employ an electrolyte which is close in composition to the eutectic  $\text{KF}_2\text{HF}$  (melting point 82°C), because of the low vapour pressure of hydrogen fluoride above such melts. In the electrolysis, the overall cell reaction is



and hence the composition changes with time. Normally the hydrogen fluoride content is kept in the range 38–42% by periodic addition and the electrolysis is operated at 90°–110°C.

The aggressive and acidic nature of the electrolysis medium and the chemical reactivity of fluorine limit the choice of materials and determine the simple and sealed cell design based on a mild steel tank, with a volume of the order of 1 m<sup>3</sup>.

The anodes are carbon blocks and the cathodes are the tank and/or mild steel coils also used for water cooling of the electrolyte. In a cell under normal operating conditions a separator is not essential provided the anode–cathode gap is more than a critical distance, commonly about 4 cm. The product gases, fluorine and hydrogen, must be kept apart and this is achieved with a nickel or monel skirt which dips into the electrolyte surface and directs the anode and cathode gases into different collection vessels. A typical cell will have 20–40 anode blocks and will operate at a total current of 1000–10 000 A.

Because of corrosion, it is not possible to use a metal anode and hence, in practice, the choice of material is limited to a carbon. Even with carbon, however, a careful choice of type and grade is necessary since the properties of the carbon will determine the current efficiency, energy efficiency and the lifetime of the electrodes. The behaviour of the anode is dominated by a phenomenon known as ‘polarization’; in this context ‘polarization’ is not just a relatively small over-potential caused by slow kinetics. Rather it is an increase in cell voltage, maybe of several volts, and it is thought to arise because of non-wetting of the anode by the electrolyte. The fluorine gas is consequently not released from the surface and collects as a barrier to electron transfer. In the limit, ‘polarization’ becomes an ‘anode effect’ and the cell voltage increases to maybe 40–60 V, when sparking across the gas layer and incandescence are observed (see also Al extraction). The cause of the non-wetting of the surface by the electrolyte is probably a layer of  $(CF)_n$  formed *in situ* by reaction of the anode carbon with fluorine.

Clearly polarization must be minimized and two approaches are used. In the first a fairly permeable carbon is chosen for the anode. The objective is to allow the fluorine gas to enter the pores without their flooding with electrolyte. Then the fluorine leaves the cell by passing through the pores in the electrode, which also assists the separation from hydrogen formed at the cathode, and contact between the carbon and the electrolyte is maintained. The second approach is to use a hard non-porous carbon and additives to control polarization. These may be  $Na^+$ ,  $Li^+$  or  $Al^{3+}$  or more effectively nickel in a higher oxidation state. The latter forms in the electrolyte anyway, because of corrosion of the skirt used to separate the anode and cathode gases. Water, in addition to leading to oxygen in the fluorine, also promotes polarization and it is therefore normal to specify hydrogen fluoride with a very low water content. Moreover when a new cell is set up it is often necessary to pre-electrolyse with a low current density to remove most of the water. Another impurity to be avoided is sulphate since this leads to erosion of the anode. Certainly, the period between servicing of the cell is determined either by disintegration of the anode or by corrosion of the anode contact and downtime is a constant problem with fluorine cells.

The fluorine leaving the cell contains a high percentage of hydrogen fluoride and this is removed by passing the gas over trays of powdered sodium fluoride. The hydrogen fluoride may be recovered and recycled back to the cell by periodic heating.

Although polarization can be controlled to some extent, it is never fully overcome and this, combined with the anode–cathode gap of about 5 cm necessary

to avoid reaction between the electrolysis products, causes the cell voltage to be  $-10$  to  $-14$  V for the working current density of  $100\text{--}200\text{ mA cm}^{-2}$ . This compares with the calculated reversible cell voltage of  $-1.8$  V so it is clear that fluorine manufacture cannot be described as energy-efficient! The total energy consumption for a cell with a 95% current efficiency (i.e. with a small amount of back chemical reaction between  $\text{F}_2$  and  $\text{H}_2$ ) is about 15 000 kWh per ton of fluorine, a very high figure and only possible because of the high sale price of this halogen.

## 5.2 WATER ELECTROLYSIS

Water electrolysis is a route to both very pure hydrogen and very pure oxygen, although in most applications it is the hydrogen which is considered the principal product. The overall cell reaction is



which from thermodynamic considerations requires, at room temperature, a potential of  $-1.23$  V at all pH. The reversible potentials for both hydrogen evolution and oxygen formation shift by 60 mV per pH unit towards negative potentials as the pH is increased.

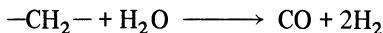
Water electrolysis plants are used for the production of hydrogen for use as a chemical for the hydrogenation of organic molecules (particularly in the food industry), in the manufacture of semiconductors, in the production of high-purity metals and even in the synthesis of ammonia. Generally, however, for large quantities of hydrogen it is an expensive route compared with separation of CO and  $\text{H}_2$  from synthesis gas produced by coal gasification



or the degradation of natural gas or light oils, e.g.



and/or



Therefore water electrolysis is only used where high purity is essential (e.g. for foodstuffs or where catalyst poisoning is a problem) and/or cheap hydroelectric power is available. Moreover it should be remembered that hydrogen is a byproduct in the chlor-alkali industry.

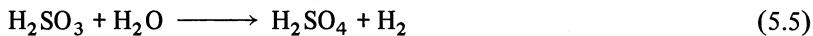
However, even if the economics of large-scale water electrolysis are not always favourable, the process on a small scale finds many diverse applications because of the convenience of obtaining high-purity gases at a controllable rate. These would include the supply of oxygen and/or hydrogen to industry at remote sites, hydrogen for atmospheres in power stations, gases to laboratories and oxygen to

life-support systems in submarines and spacecraft. Hence water electrolysis plants range from one designed to produce  $2 \times 10^3 \text{ cm}^3 \text{ H}_2$  per hour for a gas-liquid chromatograph detector to one to produce  $10^{10} \text{ cm}^3 \text{ H}_2$  per hour for a synthetic ammonia plant.

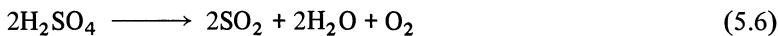
Water electrolysis has also been used as a method of producing heavy water. Kinetic factors determine that hydrogen is evolved more rapidly than deuterium (by a factor of 2–10) and hence the deuterium concentrates in the electrolyte. The natural abundance of deuterium in water is, however, only 150 p.p.m. and hence much electrolysis is necessary to produce a significant percentage of heavy water. In practice, it is best achieved by using a cascade of cells through which the water passes as it becomes enriched. This would now only be an economic procedure if cheap electricity was available and the hydrogen gas could be used fruitfully.

A much larger exploitation of water electrolysis as part of the ‘hydrogen economy’ has been predicted. In such a society, hydrogen would be produced using ‘cheap’ electricity from nuclear power stations or solar collectors and be used as a method of storing and transporting energy; at urban sites, fuel cells would be used to reconvert the hydrogen to electricity. To the present time, the ‘cheap’ electric power is not available and there remain problems with the energy efficiency of both the water electrolyser and the fuel cell.

In this connection, several recent research programmes have sought to reduce the electricity consumed in water electrolysis by supplying some of the energy required to split water either thermally or photochemically. An example of the former is the following scheme for the production of hydrogen; the electrolysis step is



a reaction theoretically requiring a cell voltage of only 0.17 V. The sulphuric acid is then decomposed thermally at  $875^\circ\text{C}$  and the resulting sulphur dioxide dissolved in water to give further sulphurous acid, i.e.



The cell, however, requires a separator since sulphurous acid would otherwise reduce to sulphur at the cathode. There are also problems at the anode since, with presently available electrode materials, the oxidation of sulphurous acid to sulphuric acid requires an overpotential of several hundred millivolts. Hence, the advantage compared with direct water electrolysis is yet to be realized. Currently, the most promising examples of photochemically assisted water electrolysis are photovoltaic cells which use a semiconductor electrode. For example, it is possible to construct a cell with an anode made from an optically transparent material covered with a thin layer of an n-type semiconductor, an aqueous electrolyte and a cathode which has a low overpotential for hydrogen evolution. When light is shone on the anode, photons of energy greater than the energy gap of the semiconductor will excite electrons from the filled levels to the conduction band leaving a hole in the filled

bands



In the potential field, the electron and hole can separate, the electron passing through the external circuit to the cathode and the hole moving to the surface of the anode where the reaction



can take place; hydrogen evolution occurs at the cathode so that overall the absorbed photons lead to oxygen and hydrogen. Indeed in these systems all the energy for water splitting may be supplied photochemically and then the cell behaves as a fuel cell, i.e. it is a power source rather than requiring the input of electrical energy. The most successful cell to date has an n-type GaAs anode with surface states modified by adsorption of a Ru<sup>III</sup> complex onto the surface and a polyselenide electrolyte; this system gives a solar to electrical efficiency of 12%.

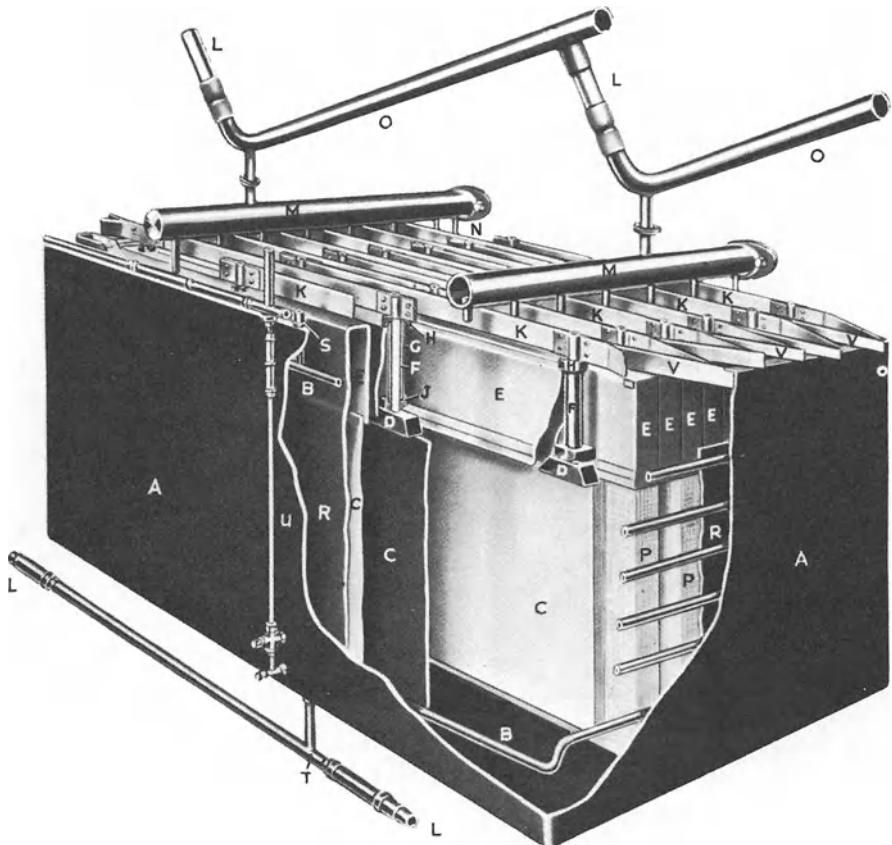
### 5.2.1 Commercial water electrolyzers

Three types of water electrolyser based on a tank cell, a filter press design and the use of elevated pressure are presently manufactured in various sizes to meet the various markets described above. In addition, a solid electrolyte cell is expected to become available by the mid-1980s. All these cells are described below.

The cells currently available have a number of common features largely because each design aims principally to minimize the cell voltage and to avoid problems from corrosion. In older cell designs the cathode was steel and the anode was nickel; now more care is taken to reduce the overpotentials at both electrodes. It has long been realized that platinized platinum was a superior material for both electrodes but it was too expensive. It took longer to develop economic alternatives but now the anode is more likely to be nickel plated onto steel in conditions to give a high surface deposit and the anode coating may also contain precious metals to enhance further the rate of oxygen evolution. The cathodes are also catalytic coatings, e.g. high-surface-area nickel alloys, and both electrodes are shaped to enhance gas release and to direct the gasses away from the current path. The electrolysis is conducted at 80° to reduce the electrode overpotentials.

The electrolyte is potassium hydroxide or sodium hydroxide because the alkaline medium causes less corrosion problems with the cheaper structural and

Figure 5.1 *The Knowles water electrolysis cell. Key: A, steel cell tank; B, temperature control tubes; C, electrodes; D, leads; E, gas collection bells; F, insulating sleeves; G, sealing and safety tubes; H, J, insulating caps (top, bottom); K, copper connections; M, gas take-off pipes; N, drain tubes; O, S-pipes; P, asbestos diaphragms surrounding anodes; R, skirting; S, T, temperature control mains; U, feed water main; V, inter-cell connections. Diagram supplied by International Electrolytic Plant Co. Ltd.*



SECTIONAL VIEW OF KNOWLES CELL

AA	Cell Tank.	KK	Copper Connections.
BB	Temperature Control Tubes.	MM	Gas Offtake Pipes.
CC	Electrodes.	NN	Drain Tubes.
DD	Electrode Leads.	OO	S Pipes.
EE	Gas Collecting Bells.	PP	Asbestos Diaphragms.
FF	Insulating Sleeves.	RR	Skirting.
GG	Sealing and Safety Tubes.	SS, TT	Temperature Control Mains.
HH	Insulating Caps (Top).	UU	Feed Water Main.
JJ	Insulating Caps (Bottom).	VV	Inter Cell Connections.

electrode materials. Their concentration is 20–25% since such values give close to the optimum conductivity at the operating temperature. It is also necessary to use very pure water since it is consumed during the electrolysis causing impurities to accumulate; in particular, chloride ion, a common impurity in water, causes pitting of the passive films formed on the metal surfaces in alkali (see Chapter 9).

The separator is almost invariably asbestos, often with a nickel gauze support. It should be remembered that the only role of the separator in a water electrolyser is to keep the gaseous products apart. It was noted above that the equilibrium potential for the cell is –1.23 V. In fact no discernible gas evolution is observed until the cell voltage is –1.65 to –1.70 V, and for the operating current densities of 100–600 mA cm<sup>–2</sup> the cell voltage is generally in the range –1.9 to –2.6 V, giving an energy efficiency of 45–65%.

The great advantage of the tank cell is its simplicity and reliability although its space time yield is poor compared with the other designs – it also takes up a lot of floor space although it does not require a gas/liquid separator or electrolyte circulation as do the filter press cells. Figure 5.1 shows a typical cell design. The cell consists of a rectangular tank with the electrodes, alternately anodes and cathodes, made of rigid metal, closely spaced and placed parallel. The hydrogen and oxygen are kept separate by surrounding the anodes with a sleeve of pure asbestos cloth open at its lower end. The gas from each electrode is collected by a bell at the top of the electrode from where it passes to the hydrogen or oxygen off-take pipe. Each anode and cathode in the cell is connected to a common electrical contact so that the voltage between each anode and cathode is 1.9–2.3 V. Cells are connected in series so that the total voltage drop is that of the rectifier output (100–500 V). The Knowles cell is manufactured in sizes which range from 4 ft × 6 ft × 0.8 ft to 4 ft × 6 ft × 8 ft or 500 A to 12 000 A or 0.2–5.0 m<sup>3</sup> h<sup>–1</sup>. They produce gases with purities above 99.5% with an energy consumption of 4.15 kWh m<sup>–3</sup> hydrogen (these are the normal units for hydrogen – a lot of Faradays are required to produce a ton of H<sub>2</sub>) or an energy efficiency of approximately 60%. Figure 5.2 shows an installation of such cells.

Filter press cells are structurally more complex and require electrolyte circulation and gas/electrolyte separators external to the cell but they give enhanced space time yields. Figure 5.3 shows the design of a typical filter press bipolar unit which again is manufactured with various sizes to give hydrogen delivery rates between 0.3 and 4.80 m<sup>3</sup> h<sup>–1</sup>. The important components are anodes and cathodes based on perforated steel (perforated so that much of the evolving gas passes to the back of these electrodes) placed very close to either side of an asbestos diaphragm strengthened with nickel gauze. The other cell components ensure stable and leak-free operation and effective circulation of the electrolyte. The increase in hydrogen delivery rate may be achieved by increasing both the area of the diaphragm and electrodes and the number of cells in the filter press stack. The unit shown in Fig. 5.4 operates at a cell voltage of 2.1 V per cell and a current density of 200 mA cm<sup>–2</sup>. The energy efficiency is therefore 58%.

The elevated-pressure cells operate at about 30 atmospheres. In such cells, the bubbles of gas are reduced in size, decreasing the *IR* drop between the electrodes,

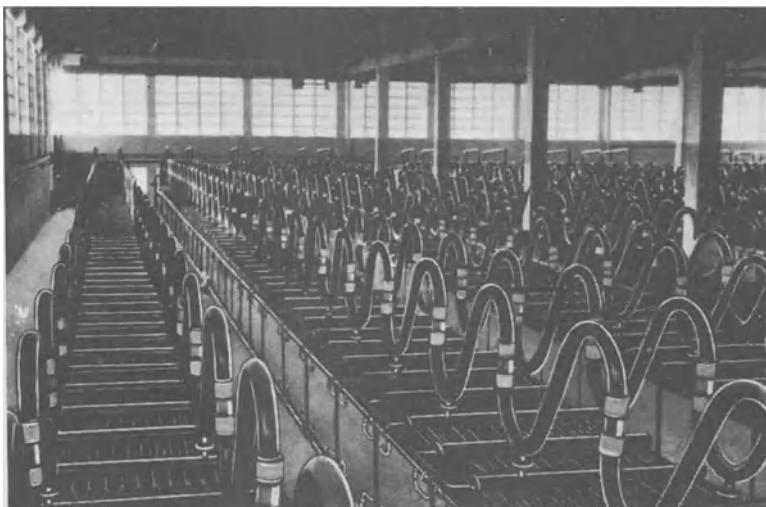


Figure 5.2 *Electrolytic hydrogen plant. Photograph supplied by International Electrolytic Plant Co. Ltd.*

and it is also possible to place the electrodes closer to the membrane. The energy efficiency is, however, not significantly better than the ambient-pressure cells and the design and manufacture is more difficult. The design is normally based on a filter press cell.

The General Electric solid electrolyte water electrolyser is presently only available as small units but the development of very large units is well under way. It is based on quite different technology from the cells discussed above and the basic design is sketched in Fig. 5.5. The electrolyte is a Nafion membrane (thickness 0.2–3.0 mm) again based on an aliphatic perfluorocarbon sulphonic acid polymer but in this case with a structure which permits proton conduction. The electrodes are fluorocarbon bonded fuel cell type structures embedded onto the surface of the membrane to form an integral membrane plus electrode structure, while screens in contact with the electrodes act as current collectors. The gases are released through the screen and a porous carbon layer. In operation, pure water at 80°C is fed to the anode where it is oxidized to oxygen and protons; the latter pass through the electrolyte and are reduced at the cathode. In fact, excess water is circulated through the anode compartment to take away the waste heat. The cell can be operated at a current density of  $1\text{--}2 \text{ A cm}^{-2}$ , a value much higher than the conventional alkaline electrolyzers. Moreover, it can be seen from the performance plots of Fig. 5.6 that the cell voltage is also lower. Table 5.1 shows the estimated magnitudes of the terms making up the cell voltage and the data again emphasize the importance of developing better oxygen catalysts. The present electrode compositions have not been fully disclosed but it is believed that the cathode is a PTFE/graphite-based porous structure with precious metal (probably Pt) catalyst, loading  $0.1\text{--}0.25 \text{ mg cm}^{-2}$ , and the anode has a similar base but with ruthenium dioxide mixed with transition-metal additives as the catalyst.

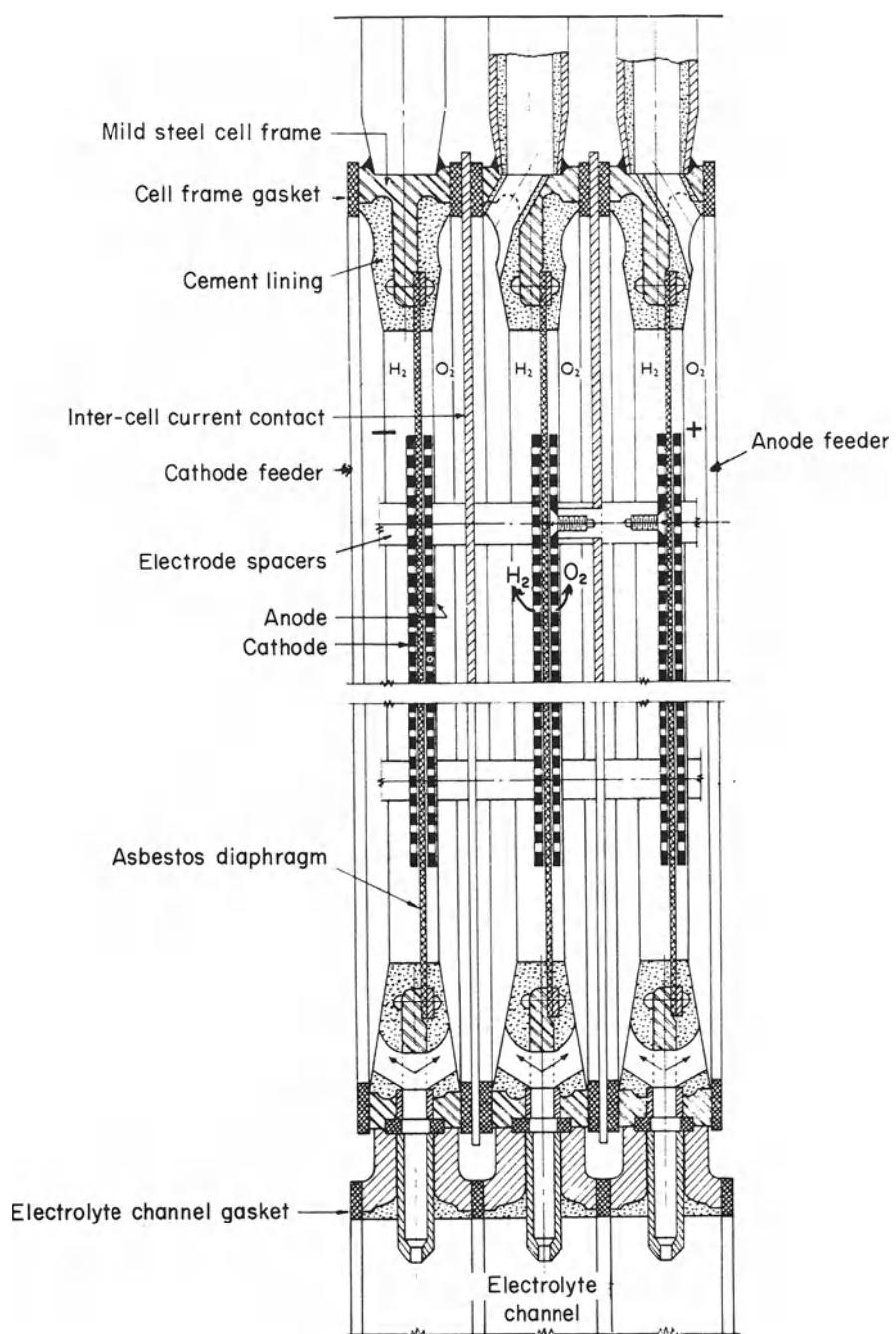


Figure 5.3 *CJB bipolar filter press type water electrolyser.*

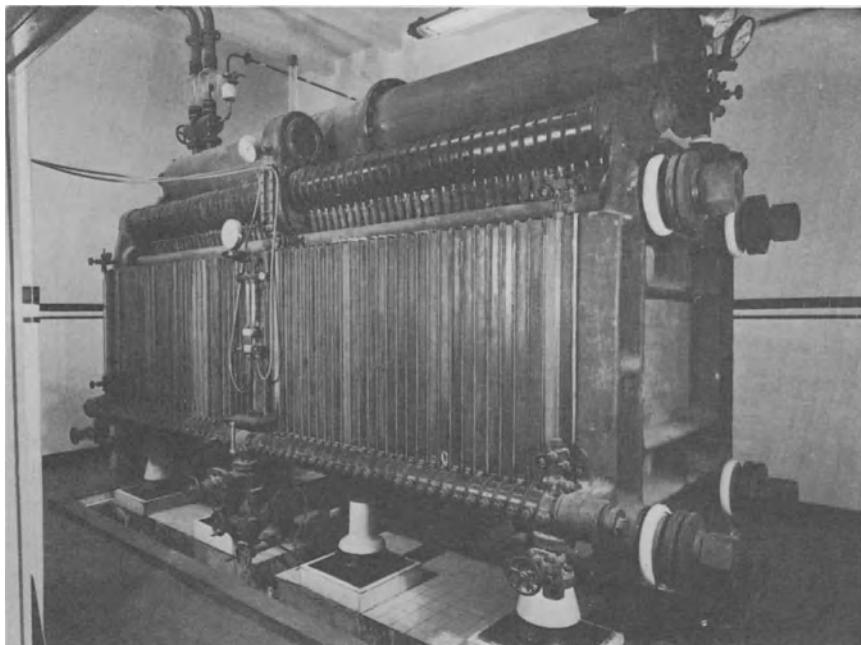


Figure 5.4 A CJB B60 type filter press water electrolyser. This unit has 60 cells and the capability to produce  $81 \text{ m}^3 \text{ h}^{-1}$  (bipolar cell current 3000 A). Photograph supplied by CJB Developments Ltd.

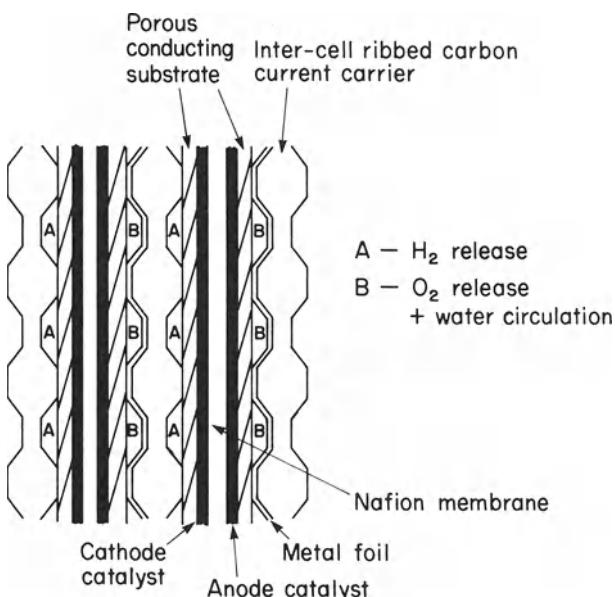


Figure 5.5 View from above of two of a bipolar stack of solid electrolyte water electrolyser cells.

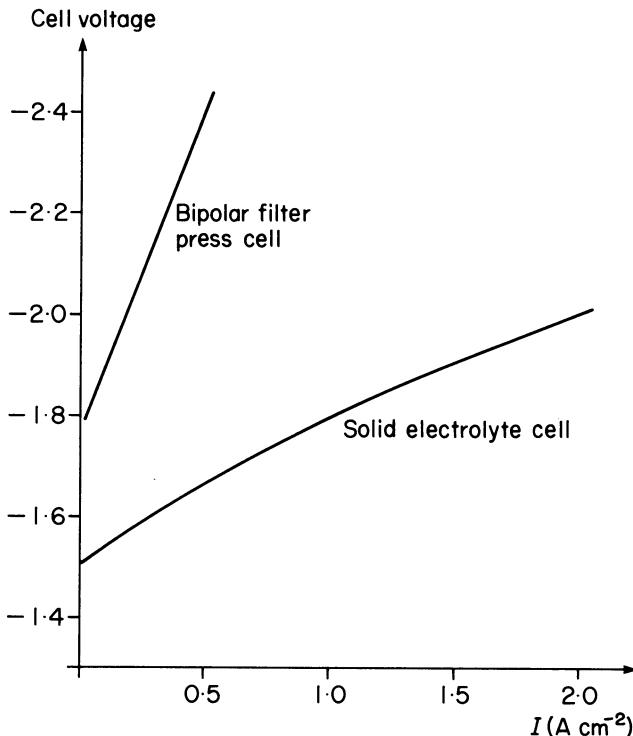


Figure 5.6 Comparison of I-V characteristics for a solid electrolyte and conventional bipolar filter press cell. Temperature 80°C.

Table 5.1 Estimated voltage distribution in a solid electrolyte water electrolyser at 80°C and an operating current density of 1.08  $\text{A cm}^{-2}$ .

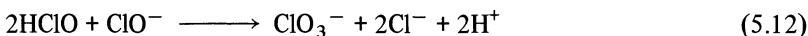
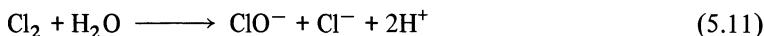
Reversible cell voltage, at 80°C (V)	-1.18
Anode overpotential (V)	-0.30
Cathode overpotential (V)	-0.02
Solid electrolyte resistance, $IR$ (V)	-0.27
Contact resistances, $IR$ (V)	-0.03

Pilot units with 1  $\text{m}^2$  electrodes and series of cells with bipolar connections are now operating. Such units have great advantages of space time yield and energy consumption and it is to be hoped that the present problems of cost can be overcome. There would be a further large advantage to be gained from increasing the electrolysis temperature to 150°C. This would also be the case with alkaline electrolyzers and, once the materials problems are solved, it is likely that the next generation of cells will all operate at such temperatures.

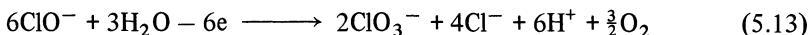
### 5.3 SODIUM CHLORATE

Sodium chlorate is used in papermaking, where demand for it is increasing, in the textile industry and as a cheap, if unselective, weedkiller. There are many electrolytic plants for its production, usually on the 1000–10 000 ton yr<sup>-1</sup> scale. and because of the proximity of both wood and hydroelectric power it is common in Scandinavia, USA, Japan and Canada for the plant to be close to the paper mill.

The electrolytic formation of chlorate is dependent on complex chemistry coupled to a simple electron transfer process, i.e.



There is a second route to the formation of chlorate which involves the direct anodic oxidation of hypochlorite. This has the stoichiometry



and is, if possible, to be avoided since chlorate formed by this route consumes 9 F mol<sup>-1</sup> whereas that resulting from reaction (5.12) has consumed only 6 F mol<sup>-1</sup> ClO<sub>3</sub><sup>-</sup>; the additional 3 F are lost as oxygen formation. Hence the energy consumption can be optimized by using a cell with a high Reynolds number and turbulence so that the hypochlorite is removed from the anode surface before reaction (5.13) can occur. Since reaction (5.12) is rather slow, the process is best carried out with a circulating system with a reservoir tank where reaction (5.12) can go to completion before the electrolyte re-enters the cell. With such process design, the hypochlorite concentration in the cell does not build up; not only is the further oxidation of hypochlorite avoided but a separator to stop its reduction at the cathode becomes unnecessary and the cathode reaction may be used to maintain the pH of the electrolyte constant (one proton/electron transferred is formed at the anode and removed at the cathode). Careful control of the pH is essential because the hydrolysis of chlorine requires a pH above 6 while the disproportionation of hypochlorite requires some of the anion to be in the protonated form.

Hence the electrolysis is carried out in an undivided cell, in practice often a bipolar stack of parallel electrodes (to increase the space time yield). The cathodic faces are steel and the anodic parts are graphite or platinized titanium or a similar precious-metal coating. As in the chlorine cell, the graphite anodes have a higher overpotential and are also lost at the rate of 4–8 kg per ton of ClO<sub>3</sub><sup>-</sup> during electrolysis. The electrolyte is circulated rapidly through the cell but is held in a reservoir for the disproportionation to go to completion; once formed, the chlorate is totally stable and the electrolyte may be recirculated to obtain maximum chloride consumption. In general, the electrolyte is initially NaCl (3.3 M) plus NaClO<sub>3</sub> (3 M) and the electrolysis is terminated when the chlorate concentration reaches 5.5 M. Typical current densities are for Pt/Ti 200–300 mA cm<sup>-2</sup> or for graphite 20–80 mA cm<sup>-2</sup> and the cell voltage normally falls in the range –3 to

–4 V. With a current efficiency of 80–95%, the energy consumption is 5000–6500 kWh ton<sup>–1</sup>.

Other alkali-metal chlorates are produced by analogous technology while sodium and potassium bromate are produced electrolytically starting both from bromide ion and bromine solutions. The production of bromate is, however, a very small-scale process and the cells have not been optimized to any extent; for example while cells with lead dioxide and platinized titanium have been described, some plants still use solid platinum electrodes! The mechanism of bromate formation is identical to that described for chlorate by reactions (5.10)–(5.13); the kinetics are, however, different. The hydrolysis of bromine is slower than chlorine but the disproportionation step is much faster (by a factor of 100) and it is therefore advisable to use a more alkaline electrolyte, about pH 11.

#### 5.4 PERACIDS AND THEIR SALTS

Electrolysis is used to manufacture sodium, potassium or ammonium salts of several peracids including persulphates, perchlorates, periodates and perborates by anodic oxidation of sulphate, chloride, iodate and borax respectively and, indeed, electrolysis is the only commercial route to several of these anions. All are now very small-scale processes although in the past persulphate has been a medium tonnage process because it was an intermediate in the manufacture of hydrogen peroxide; now hydrogen peroxide is produced via the chemical autoxidation of anthraquinone which requires only 10–20% of the energy consumed in the electrolytic process and also is capable of producing 37% aqueous solutions directly (cf. electrolytic method only 5%). Presently the only interest in the electrolytic production of hydrogen peroxide is the possibility of producing strongly alkaline solutions by the reduction of oxygen.

The electrochemical formation of all these peroxyanions requires a high positive potential and to facilitate such conditions it is normal to use an acidic medium and either a Pt or PbO<sub>2</sub> anode. Because platinum is often superior it is usual to use a platinized titanium, tantalum or niobium surface or a thin platinum foil spread on a base-metal support.

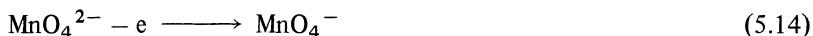
The largest of these processes remains those for ammonium and sodium persulphate and there are several plants operating on the 2000–10 000 ton yr<sup>–1</sup> scale. The process involves the oxidation of the sulphate in a sulphuric acid medium at a Pt-based anode and the medium must be free of heavy-metal ions which catalyse the decomposition of persulphate. The current density is high, about 1 A cm<sup>–2</sup> and the current efficiency 60–80%. Two cell technologies are used: one uses a cell with an asbestos diaphragm while the other is an undivided concentric tube cell. To avoid reduction of the persulphate at the cathode, the conversion per pass is kept low and the persulphate is crystallized between passes through the cell.

Perchlorate is always made as the sodium salt and potassium and ammonium perchlorate is then prepared by double decomposition. The electrolyte is sodium chloride (300–700 g l<sup>–1</sup>) at a pH between 0 and 1 and sodium perchlorate is also often present in the cell feed to ease isolation of the product. The anode is

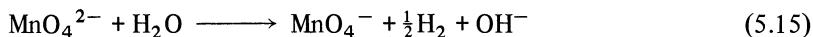
platinized titanium or platinum-covered base metal and the cathode is steel or another cheap metal; a separator is not necessary as the reduction of perchlorate is strongly kinetically hindered and the cathode reaction is hydrogen evolution. Energy consumptions reported lie in the range 2400–3500 kWh ton<sup>-1</sup>. The energy efficiencies are as low as 20–40%, suggesting that cell designs could well be improved.

## 5.5 POTASSIUM PERMANGANATE

Potassium permanganate is widely used as an oxidizing agent, especially for oxidation in the fine organic chemicals industry. World production is about 40 000 ton yr<sup>-1</sup>, by far the largest plant being 15 000 ton yr<sup>-1</sup> sited in the USA. The electrochemical step is the oxidation of manganate



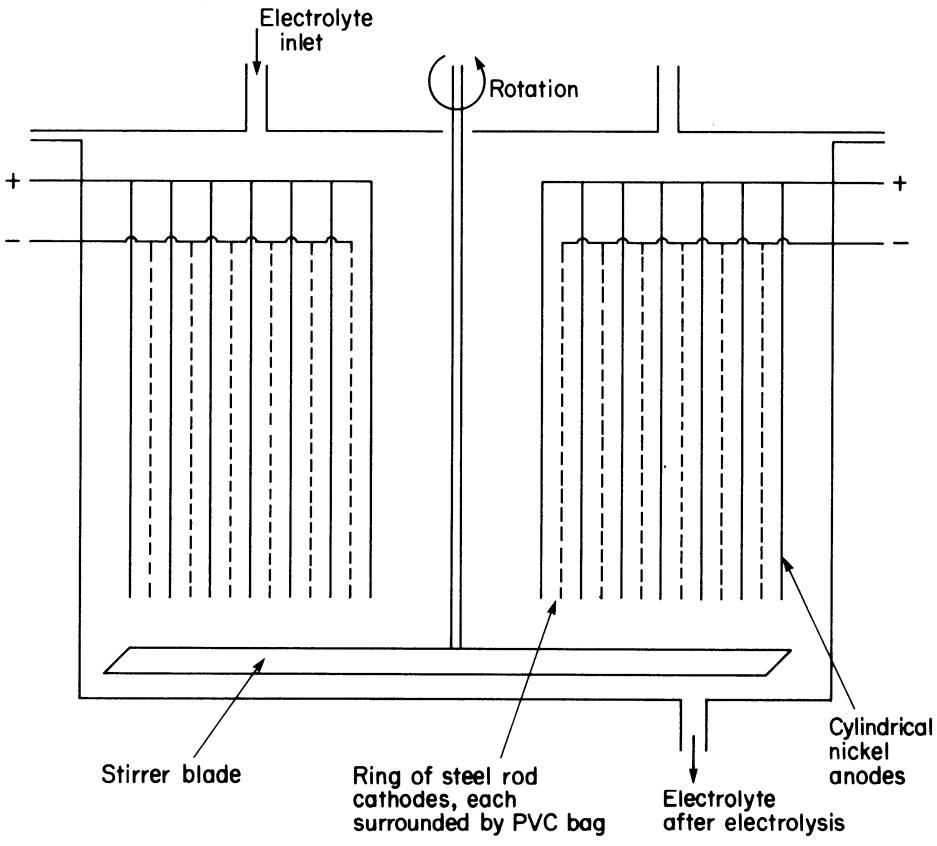
which is carried out in a strongly alkaline aqueous medium; the cathode reaction is always hydrogen evolution. Hence the overall cell reaction is



The starting point for the manufacture of permanganate is pyrolusite ore which contains about 60% manganese dioxide. The ore is ground and suspended in 50–80% potassium hydroxide and oxidized by air to the manganese(VI) state, either in the liquid phase or by evaporating the solution and roasting the resulting solids in air-filled rotary kilns. In either case, the oxidation is carried out in two stages and the conditions must be carefully controlled in order to obtain a pure manganate solution.

The electrochemical oxidation is carried out with an electrolyte which is caustic potash (1–4 M) and potassium manganate (100–250 g l<sup>-1</sup>) at 60°C at an anode made from nickel or monel (Ni/Cu). The cathode is iron or steel. The anode reaction requires an unusually low current density between 5 and 150 mA cm<sup>-2</sup> but usually at the lower end of this range. Even so some oxygen evolution occurs and the current yields are between 60 and 90%; the material yield generally exceeds 90%.

With such a low current density, there is a premium on packing the maximum electrode area into the cell volume in order to obtain an acceptable space time yield. There are, however, several types of cell design used in the manufacture of permanganate. The early and smaller processes are based on batch cells. Figure 5.7 shows an example of such a cell used in Germany. The cell body is a cylindrical rubber vessel jacketed to allow steam heating or water cooling and it is fitted with a stirrer; a series of concentric nickel sheet tubes (anodes) alternate with a ring of steel rod cathodes, each surrounded by a porous polyvinylchloride bag to decrease the transport of permanganate to the cathode. The electrical connection is monopolar with 2.5 V applied between anode and cathode and the anode current density is 10 mA cm<sup>-2</sup>. The cell is charged with a solution containing potassium hydroxide (2 M) and potassium manganate (250 g l<sup>-1</sup>) and the electrolysis is

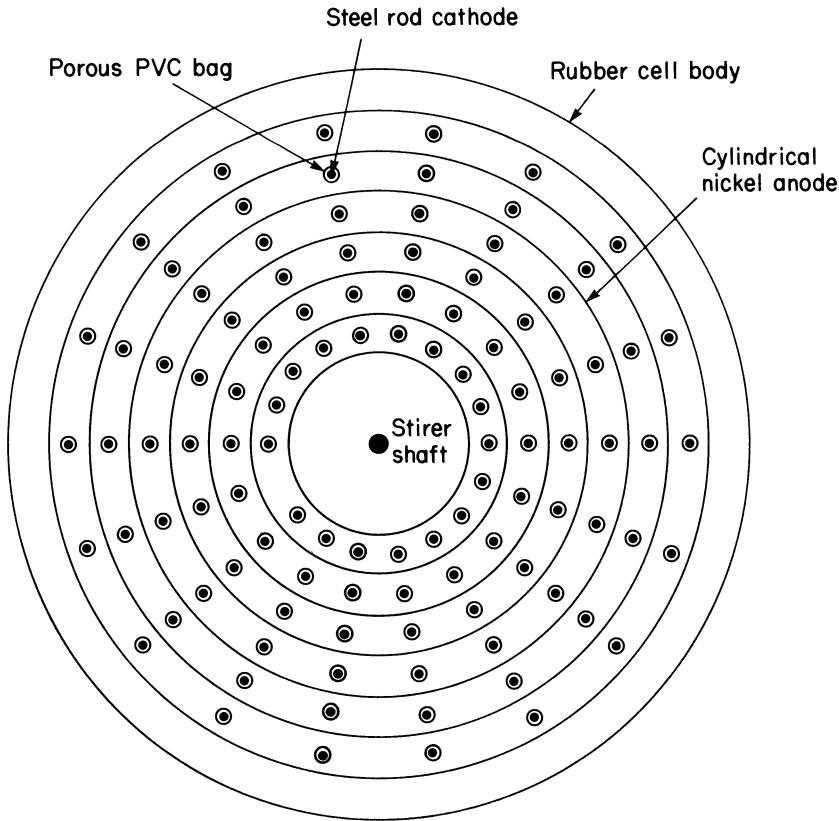


(a)

Figure 5.7 *Batch cell for the production of potassium permanganate (Neue Bitterfelder cell): (a) side view and (b) view from above.*

continued until the manganate concentration has dropped to about 10% of the original level. The current efficiency is 80% with an energy consumption of 600 kWh ton<sup>-1</sup>.

The larger-scale American process is continuous and fully automated. The electrolysis unit is arranged as a bipolar filter press containing three groups of twenty cells. The electrolyte feed to the three groups of cells is parallel but within each of the groups there are openings for electrolyte flow between the individual cells so that the feed passes serially through the twenty cells (see Fig. 5.8(a)). Each of the bipolar electrodes (Fig. 5.8(b)) is manufactured on a steel baseplate. On the anode side is welded a monel gauze (about 8 mesh) while onto the cathode side is welded a steel sheet with small perpendicular projections. The space between the projections is filled with an insulator, e.g. polystyrene, so that only the ends of the projections are in electrical contact with the solution. This gives a cathode of low surface area compared with that of the anode (1:150) but one where the active area is uniformly distributed over the face opposite the anode. Such low-surface-area

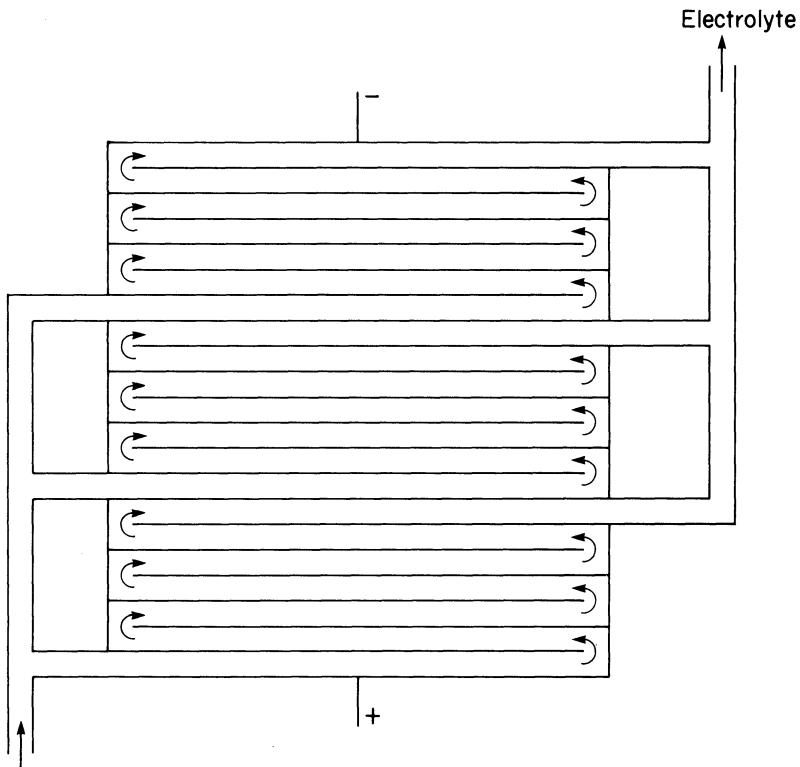


(b)

counterelectrodes avoid the use of a separator because, even if the reduction of permanganate is diffusion-controlled, the flux of permanganate is totally insufficient to maintain the essential, very high current density and most of the cathode current therefore must go into hydrogen evolution. There is a penalty in the cell voltage for this trick, however, since both the cathode overpotential and the cell resistance must be increased. The edges of the electrodes are insulated and the spacing between the electrodes is 22 mm.

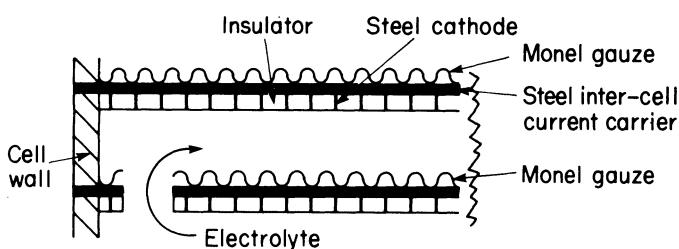
The electrolyte is pumped through the cell with a high Reynolds number since turbulence minimizes the crystallization of the product in the cells. The electrolyte feed contains potassium hydroxide ( $120\text{--}150\text{ g l}^{-1}$ ), potassium manganate ( $50\text{--}60\text{ g l}^{-1}$ ) and potassium permanganate ( $30\text{--}35\text{ g l}^{-1}$ ) and in the effluent from the cell the permanganate concentration has almost doubled. The current efficiency is about 90% so the effluent also contains oxygen and hydrogen (from the cathode) and to assist the escape of gas the cell unit is at a slight angle.

In this cell the current density is  $8.5\text{--}10\text{ mA cm}^{-2}$  at the anode and the cathode



Electrolyte  
feed

(a)



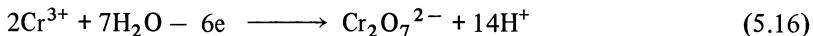
(b)

Figure 5.8 *Electrolysis cell used by the Carus Chemical Co. for the production of potassium permanganate. (a) Electrolyte flow pattern. (b) Design of bipolar electrodes.*

current density is  $1.3\text{--}1.5 \text{ A cm}^{-2}$  with an undivided cell voltage of  $-2.3$  to  $-2.8 \text{ V}$ . The total voltage across the 60-cell stack is  $140\text{--}170 \text{ V}$  with a cell current of  $1200\text{--}1400 \text{ A}$ . The energy consumption is  $500 \text{ kWh ton}^{-1}$  although the energy required for pumping must, in this process, be high.

## 5.6 POTASSIUM DICHROMATE AND CHROMIC ACID

The oxidation of chromic ion



in acidic media has been used for the manufacture of potassium dichromate but more commonly the reaction has been used to regenerate spent chromic acid solutions from the oxidation of organic compounds (e.g. anthracene, pyrene, montan wax), etching and polishing baths and for conditioning chromium plating baths. As part of processes for the indirect oxidation of organic compounds, several such chromic acid electrolyses operate on a  $1000 \text{ ton yr}^{-1}$  scale; in the other applications the scale is always small.

Invariably the electrolysis medium contains sulphuric acid but the concentrations of both the acid and the chromium(III) vary widely depending on the source of the solution; from the oxidation of organic compounds, a typical solution may contain  $1 \text{ M Cr(III)}$  and  $3 \text{ M H}_2\text{SO}_4$ , while from a plating bath to be conditioned, the chromium(III) may be as dilute as  $0.02 \text{ M}$  with  $0.005 \text{ M H}_2\text{SO}_4$  and a large excess of chromium(VI).

The only anode material where it is possible to obtain a high current efficiency is lead dioxide and, although it is subject to slow corrosion in the electrolysis conditions, lead dioxide formed *in situ* on lead or a lead alloy, e.g. Pb/5% Sb, is the only practical choice as anode material. The oxidation of chromium(III) to chromium(VI) at a lead dioxide anode requires a high positive potential, so it is always likely that some oxygen evolution will occur as a competing reaction. With concentrated solutions of chromium(III), it is possible early in the electrolysis to obtain current efficiencies above 95% with a current density of  $50\text{--}200 \text{ mA cm}^{-2}$ . The current efficiency drops as the chromium(III) concentration diminishes and with solutions containing very low concentrations of chromium(III) and less acid a figure of 30–50% at  $30 \text{ mA cm}^{-2}$  is more likely. It is also well known that organic molecules in the anolyte poison the lead dioxide surface causing oxygen evolution to occur at a dramatically enhanced rate. Hence solutions from organic reactions must be scrubbed before they are passed to the electrolysis cell.

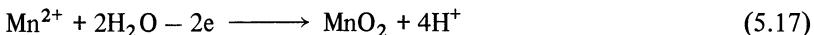
The old design of cell is based on a lead-lined tank filled with aqueous sulphuric acid, and the spent chromic acid solution in porous ceramic pots was placed in the tank. The anodes were lead rods dipped into the ceramic pots and the cathode was the lining to the tank. The plant was obviously operated totally as a batch process. More modern and economic cells are now available; they are based on a bipolar filter press concept with lead alloy anodes, steel cathodes and a Nafion proton-conducting membrane. The energy consumption and space time yields with such

cells are clearly likely to be superior, although reliable figures are not available. Moreover such cells can be operated as continuous or semi-continuous processes.

## 5.7 MANGANESE DIOXIDE

The performance of Leclanché and related batteries depends critically on the source or method of manufacture of the manganese dioxide because the activity and properties of the oxide vary with crystallite size, density of lattice imperfections and the extent of hydration. The manganese dioxide produced by the anodic oxidation of manganese(II) in solution is particularly active although it is also more expensive, perhaps by a factor of four compared with natural pyrolusite. As a result, electrolytic manganese dioxide is manufactured largely to be used in high-quality Leclanché cells or alkaline manganese batteries. More recently it has been recognized that the higher activity of electrolytic manganese dioxide extends to its chemical reactions with other species, especially if the manganese dioxide is used directly after its preparation. Hence electrolytic manganese dioxide is increasingly considered as an oxidizing agent in the fine chemicals and pharmaceutical industries. Over the last twenty years, the manufacture of manganese dioxide by electrolysis has expanded rapidly and the current world annual production probably exceeds 100 000 tons; most of the capacity is in Japan.

The manganese dioxide is formed by the electrode reaction



and deposits onto an inert anode such as graphite, lead or titanium. In fact, this reaction is complex, involving hydrolysis and disproportionation of an adsorbed manganese species, and its rate is limited by the kinetics of these chemical processes. Hence the current density is always low. The counterelectrode reaction is hydrogen evolution and an undivided cell may be used as the manganese dioxide remains on the anode surface. A typical electrolysis medium will be manganese sulphate (0.5–1.2 M) in aqueous sulphuric acid (0.5–1.0 M) at 90–100°C and the electrolysis will be carried out at 7–12 mA cm<sup>-2</sup>, requiring a cell voltage of –2.2 to –3.0 V. Current yields of manganese dioxide are reported to be 75–95%. The cells are similar to those described earlier for copper winning and aqueous refining; they are based on an open tank with parallel and alternating lines of anodes and cathodes. The manganese dioxide layer is allowed to grow until it is 20–30 mm thick before the anodes are removed and the deposit removed mechanically. The manganese dioxide for batteries is dried at 80°C.

Such cells do not permit continuous operation and have a very low space time yield. This has led to the study of cells where the MnO<sub>2</sub> is formed as a slurry in the anolyte in which case the manganese dioxide may be formed in a flow system, e.g. a filter press cell. Usually such systems use a lower temperature and a higher pH but, although successful in the laboratory, are probably not yet used in commercial practice.

## 5.8 CUPROUS OXIDE

Cuprous oxide is also manufactured electrolytically but on a much smaller scale. Around the world, there are several plants producing 200–500 ton yr<sup>-1</sup>. In this case the oxide results from direct oxidation of the metal in an alkaline medium



The electrolyte also contains chloride ion as a pitting agent to prevent passivation of the anode surface (see Chapter 9).

## FURTHER READING

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## 6 Organic Electrosynthesis

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In this chapter we shall consider the role of electrolysis in the preparation of organic compounds. Modern society requires the chemical industry to produce a very wide range of compounds; in 1975 in the USA, over 200 organic chemicals were made on a scale exceeding 10 000 ton yr<sup>-1</sup> and many thousands more are produced on a smaller scale. Most of these chemicals are prepared via multistep syntheses starting with feedstocks arising from crude oil, coal or plant extracts and the reactions will frequently involve oxidation and reduction. Electrode reactions would seem an obvious way to carry out such processes and, indeed, on a laboratory scale almost all organic reactions involving electron transfer have an electrochemical analogue. In addition, electrode reactions sometimes permit chemistry not possible in homogeneous solutions.

However, one must face the fact that, although there have been organic electrolytic processes throughout this century, their number has always been small and electrochemistry has yet to make a major impact on the chemical industry. At the present time the number of commercial processes is increasing slowly and there are reasons to expect this trend to continue: (i) Many inorganic redox reagents, e.g. Na, K, Zn, Cl<sub>2</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, are themselves prepared electrolytically and the replacement of such reagents in organic synthesis by direct electrode reactions would reduce the number of steps in the synthesis. (ii) Compared with many chemical oxidations and reductions, electrode reactions are non-polluting and non-hazardous. Of common redox reagents in industry, metal powders (Zn, Fe) are pyrophoric and produce large volumes of aqueous effluent containing the corresponding ions, permanganate produces manganese dioxide which presents a disposal problem and chlorine, bromine, sodium and potassium all present serious hazards. (iii) Electricity is the most versatile of reagents and can be produced from many raw materials; electrolytic processes may become particularly attractive if the goal of cheap electric power from nuclear or solar energy becomes a reality.

On the other hand, what are the problems which presently prevent the widespread commercial exploitation of organic electrosynthesis? First we must recognize that organic electrosynthetic processes are *chemically* much more complex than any other processes considered in this book. Usually the overall electrode reaction is not simple electron transfer, but is a sequence of electron transfers and coupled chemical processes either on the electrode surface or in

homogeneous solutions close to the electrode surface. Phrasing this another way, the electron transfer processes simply produce organic intermediates (e.g. carbanions, radicals, carbenium ions, ion radicals) which all too frequently have a range of reactions available to them. It is for this reason that electrochemists have often failed to produce the promised selectivity in organic products by controlling the electrode potential. Controlling the electrode potential only ensures selectivity in the electron transfer process and hence the intermediates formed – to obtain overall selectivity we must also direct the chemical reactions of the intermediates by tailoring and controlling the reaction environment. Unfortunately this is not a trivial problem since the chemistry is occurring in a reaction layer close to the electrode and the electrode reaction itself is causing changes in this layer (e.g. by varying pH or the concentration of another reactant) and a non-uniform reaction environment (i.e. the concentration of some species must be a function of distance from the electrode surface). We still have much to learn about the control of organic electrode processes although it is clear that the parameters available to us include:

- (a) Electrode potential
- (b) Electrode material
- (c) Solvent and electrolyte
- (d) pH, concentration of electroactive species and all species capable of reacting with intermediates in the electrode process
- (e) Temperature and pressure
- (f) Cell design, particularly the presence or absence of a separator and the mass transport regime which will largely determine the reaction layer conditions.

Furthermore, the combination of electrochemistry and organic chemistry will almost always require compromise since the former is best suited to water containing high concentrations of electrolyte while the latter generally are better carried out in an organic medium.

Organic electrosynthetic processes have also suffered from a failure to develop the cell components and the technology essential for successful operation. The reason is economic. One or even a few processes on a small or medium scale does not justify the development of optimum electrodes, membranes, etc., and in any case organic processes require the use of diverse media and conditions. As a result organic processes have often been constructed with inappropriate, although the best available, cell components and hence have been run with technology far from the optimum and this has undoubtedly affected their performance and reputation.

In this chapter we shall consider first the largest-scale industrial process, the Monsanto hydrodimerization of acrylonitrile to adiponitrile, and then go on to discuss the other processes presently used or likely to be introduced in the near future.

## 6.1 THE HYDRODIMERIZATION OF ACRYLONITRILE

Nylon 66 (Fig. 6.1) is a polymer manufactured by the condensation of adipic acid with hexamethylenediamine and in the USA alone in excess of  $10^6$  ton  $\text{yr}^{-1}$  are

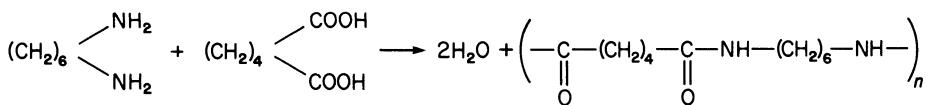
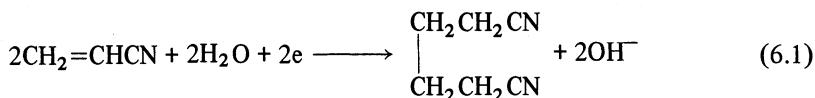


Figure 6.1 Synthesis of nylon 66.

manufactured. Adiponitrile is a convenient intermediate in the production of both adipic acid and the hexamethylenediamine.

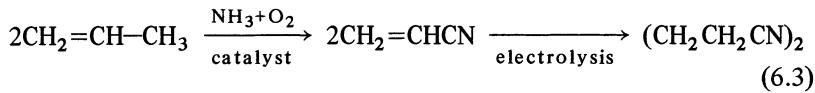
The electrochemical process for adiponitrile involves the cathodic hydro-dimerization of acrylonitrile



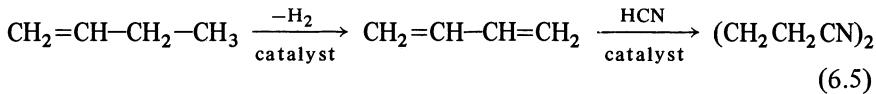
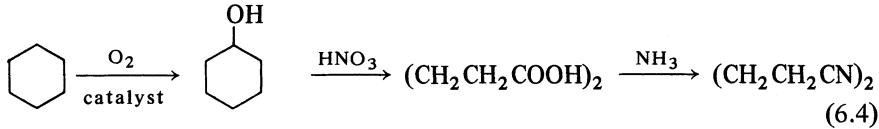
and the anode reaction is generally oxygen evolution



This electrolysis is the second step in the conversion of propylene, available from oil, to adiponitrile; the first is the oxy-amidation of propylene which is carried out catalytically. Hence the complete process sequence is



Other chemical routes to adiponitrile are available, namely

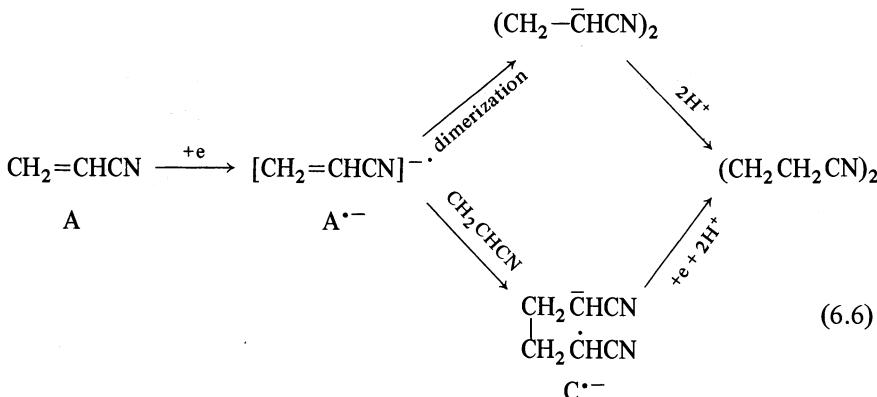


but the nitric acid oxidation is difficult to control and the route (6.3) has the advantage that the feedstocks, propylene, ammonia and air, are cheaper than the larger hydrocarbons or hydrogen cyanide used in routes (6.4) and (6.5). The route from butadiene is, however, also used on a very large scale.

### 6.1.1 Basic chemistry

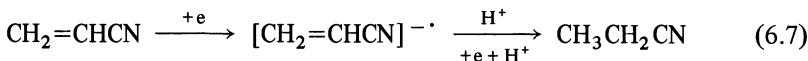
The hydrodimerization of acrylonitrile is only one of many possible chemical reactions in the catholyte and, indeed, several have been observed during electrolysis. The first step in the hydrodimerization is the reduction of acrylonitrile to its anion radical, and to form adiponitrile dimerization and protonation must

somehow occur, e.g. by

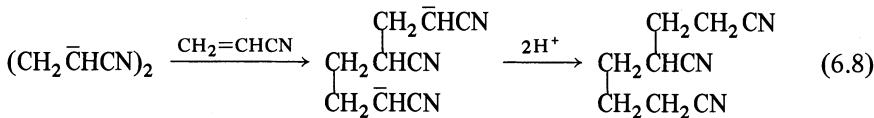


(for more detailed discussion of the mechanism see later).

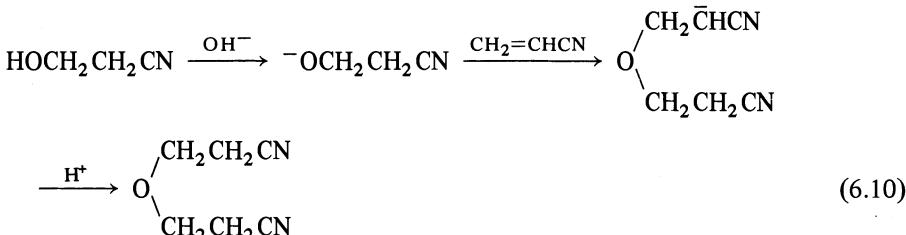
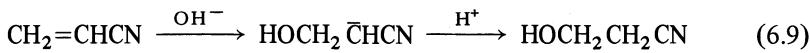
If the anion radical,  $\text{A}^{\cdot-}$ , protonates rapidly or the reaction leading from  $\text{C}_3$  to  $\text{C}_6$  molecules is not fast, then propionitrile will be formed



while if the  $\text{C}_6$  anions are not rapidly protonated, attack on further neutral acrylonitrile molecules may occur and this will lead to trimers or polymers, e.g.



The desired cathode reaction consumes protons and hence the reaction layer close to the electrode surface will tend to become basic. If this increase in basicity is not controlled, further reactions are likely, namely



The occurrence of reactions (6.7), (6.8), (6.9) or (6.10) leads to a decrease in the organic efficiency (selectivity) while reactions (6.7) and (6.8) also cause a decrease in current efficiency. Moreover, the reduction of acrylonitrile occurs at quite negative potentials ( $-1.9$  V vs SCE) and therefore hydrogen evolution is

another reaction likely to decrease the current efficiency



Experiments show that good organic and current efficiencies for adiponitrile are only obtained under a restricted range of conditions; the concentration of acrylonitrile must be high and the proton-donating ability of the reaction layer must be controlled carefully. Indeed with low concentration of acrylonitrile (< 1%), propionitrile is the major product and reactions (6.7)–(6.11) all occur if the reaction layer pH is incorrect.

In order to obtain high yields of adiponitrile, the early studies also showed that it was necessary to use a tetraalkylammonium salt as the electrolyte; although acrylonitrile reduced in the presence of only inorganic cations, the product was again propionitrile. The tetraalkylammonium cations adsorb on the electrode surface and it was suggested that their role was to form a water-deficient layer on the cathode surface which avoids the immediate protonation of the acrylonitrile anion radical as it is formed. These salts have the additional advantage that they assist the dissolution of the high concentration of acrylonitrile in a water-containing medium.

### 6.1.2 The early Monsanto process

The main features of the cell for the Monsanto process brought on stream in 1965 are shown in Fig. 6.2. The following points should be noted:

- (a) The catholyte stream contains a very high concentration of acrylonitrile considered essential to obtain a high yield of adiponitrile and also a high concentration of an organic electrolyte so that the activated olefin and water mix to give a homogeneous solution. In fact tetraethylammonium ethylsulphate was selected as the electrolyte after studies of the selectivity of the reaction and the conductivity of the catholyte with a series of related salts.
- (b) The cathode material must have a high hydrogen overpotential and, indeed, a decrease in yield with time during early operation of the process was traced to nickel as an impurity in a feedstock depositing on the cathode. While several metals gave reasonable yields of adiponitrile, lead was considered the best.
- (c) Organic components of the catholyte decomposed anodically and it was therefore necessary to use a separator. A cation-permeable membrane suitable for the electrolysis conditions was found but the process predates the modern developments in membrane technology (see Chapter 3) and for many years its performance was a difficulty in the operation of the process.
- (d) It was decided to use the simplest anode reaction, oxygen evolution. The membrane conducted protons and hence sulphuric acid was a natural choice for the anolyte. The anode was a lead/silver alloy, the silver reducing the oxygen overpotential and increasing the corrosion resistance.
- (e) To avoid the formation of substantial amounts of  $\beta$ -hydroxypropionitrile and *bis*-dicyanoethylether by reactions (6.9) and (6.10) it is necessary to remove rapidly the hydroxide ion from the reaction layer and this requires high mass transport rates in the cell. This was achieved using a fast catholyte flow rate

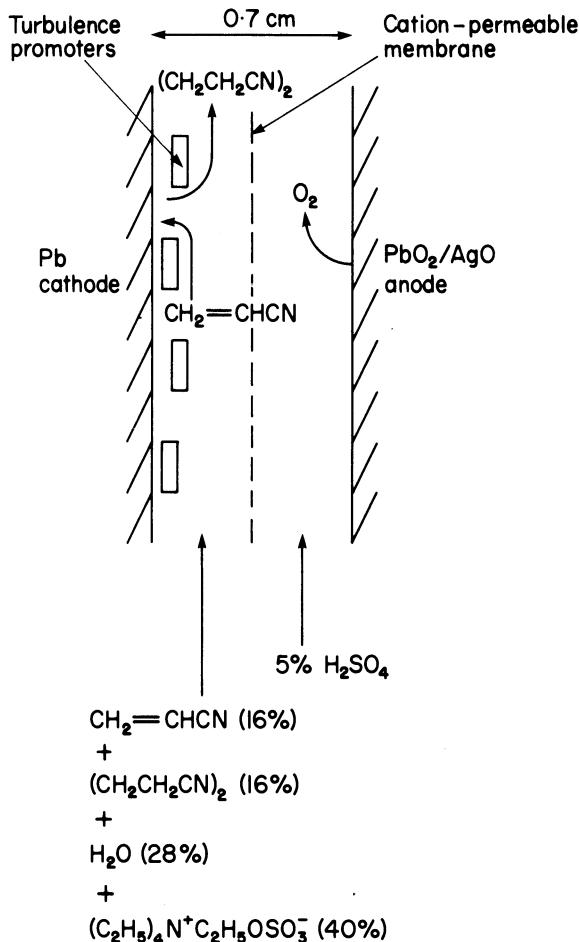


Figure 6.2 The early Monsanto process for the hydrodimerization of acrylonitrile.

$(1-3 \text{ m s}^{-1})$  and fastening polyethylene strips to the cathode to act as turbulence promoters. In these conditions the yield of adiponitrile was in excess of 90% with propionitrile and acrylonitrile oligomers as the major byproducts.

The electrolysis was carried out in stacks of 24 cells in parallel in a filter press (Fig. 6.3). Each cell (Fig. 6.4) consisted of a cathode spacer, lead cathode, catholyte distribution block, membrane, anolyte distribution block and lead dioxide anode and will have its own catholyte and anolyte streams with compositions shown in Fig. 6.2. The catholyte distribution block includes turbulence promoters and the cell was designed to minimize the cathode-membrane gap (0.8–3.2 mm) because of the poor conductivity of the catholyte required to obtain the high selectivity for adiponitrile. The electrical connection was bipolar with 300 V applied across the stack, i.e. about 12 V per cell, which gives a cathode current density in the range  $0.4-0.6 \text{ A cm}^{-2}$ . The total cell current was 2870 A.

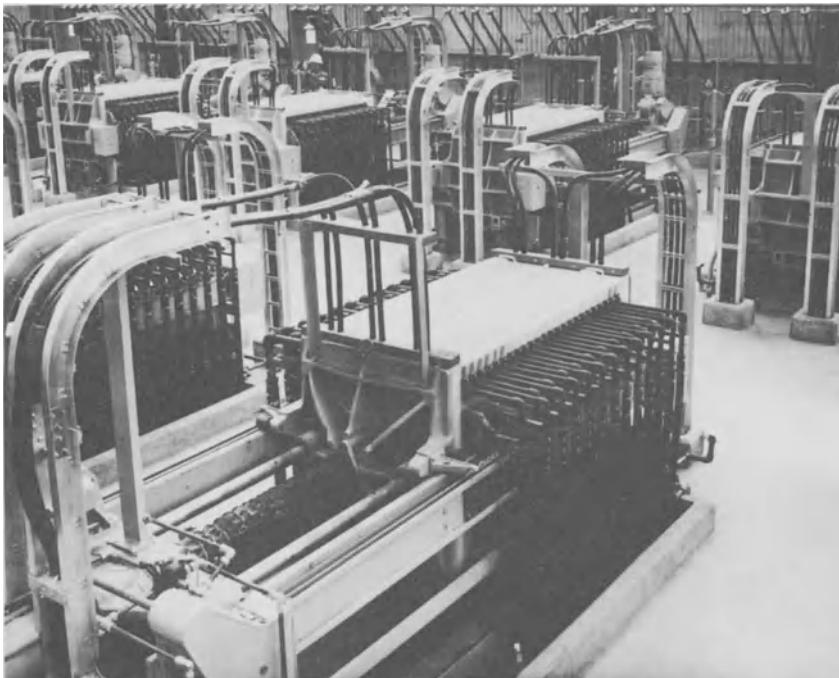
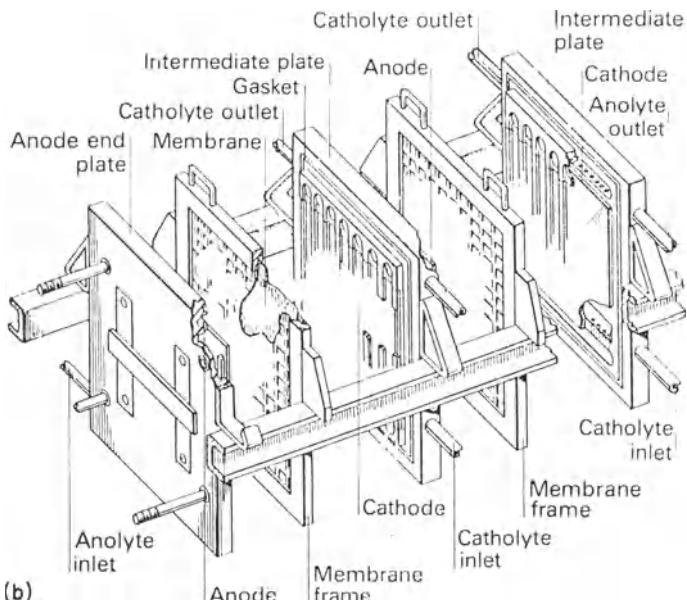
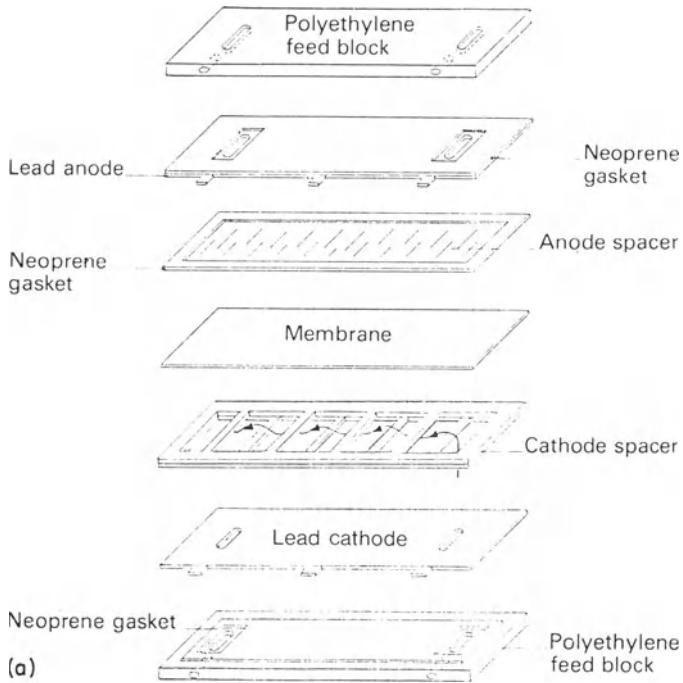


Figure 6.3 *Monsanto adiponitrile synthesis cell house at Decatur, Alabama. The cell stacks are placed in a filter press arrangement. Photograph supplied by Monsanto Corp.*

Owing to the high catholyte flow rate necessary to avoid side reactions the conversion of acrylonitrile to adiponitrile per pass of the catholyte through the cell is only 0.2%. Hence the catholyte streams in each stack were coupled to a reservoir tank and the catholyte was continuously recirculated through the cell stack. A fraction of the solution in the reservoir passed into an extraction plant and hence the reservoir combined with the cell stack operated in the same way as a continuous stirred tank reactor.

The extraction plant was quite complex since it is essential to the economics of the process to recover the quaternary ammonium salt as well as to isolate pure adiponitrile and unreacted acrylonitrile. The sidestream from the catholyte reservoir was cooled and the adiponitrile and unreacted acrylonitrile extracted with further acrylonitrile in a sieve tray column. The organic phase from this unit was countercurrently extracted with water to recover the quaternary ammonium salt and the acrylonitrile was then removed by distillation. The final stage is the vacuum distillation of the adiponitrile. The total process is shown in Fig. 6.5.

In the 1965 plant for producing 14 500 ton  $\text{yr}^{-1}$  of adiponitrile there were 16 stacks of 24 cells, arranged so that four cell stacks were connected to each catholyte reservoir. The energy requirement for the electrolysis step alone is of the order of 6700 kWh per ton of adiponitrile. While the process was economically



**Figure 6.4 Construction of cells for the filter press stack. Early Monsanto process.**

*(a) Preliminary laboratory cell. (b) Detailed design of the commercial cell.*

*Figure supplied by Monsanto Corp.*

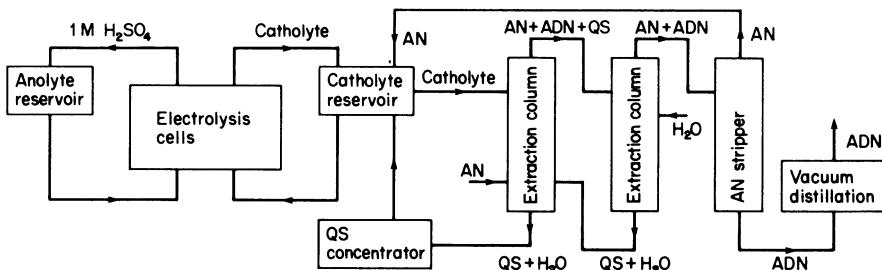


Figure 6.5 *Flow sheet for Monsanto hydrodimerization of acrylonitrile to adiponitrile. AN, acrylonitrile; ADN, adiponitrile; QS, tetraethylammonium ethylsulphate.*

comparable with other processes for adiponitrile, it had obvious shortcomings:

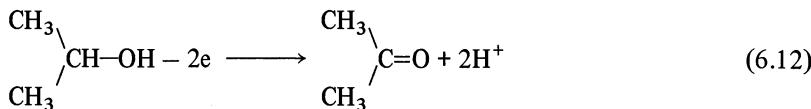
- (1) The high energy consumption resulting from the large cell voltage. This may be attributed to the low conductivity of the catholyte (note high acrylonitrile and low water contents) and to the use of a membrane; since the reversible cell potential is unlikely to exceed 3 V, 75% of the cell voltage is *IR* drop.
- (2) The use of large quantities of an expensive quaternary ammonium salt which must be recovered during extraction.
- (3) The complex cell design necessitated by the use of a membrane, separate anolyte and catholyte feeds, turbulence promoters and high flow rates.

As a result, several groups have, during the last fifteen years, sought to modify the process and, indeed, improvements have been made; these are described in the next section. In recent years a new process has been introduced by Monsanto and the details disclosed to date are discussed in Section 6.1.4.

### 6.1.3 Developments from the early Monsanto process

Asahi Chemical Industries in Japan in the early 1970s introduced a commercial process which also uses a divided cell with a lead cathode. The catholyte stream, however, contains two phases, acrylonitrile and 12% tetrabutylammonium bisulphate in water. As a result the aqueous phase contains about 7% acrylonitrile and the product adiponitrile extracts into the organic phase in the cell. The catholyte has a lower pH and hence the major byproduct is propionitrile. This technology therefore uses less tetraalkylammonium salt and leads to a lower cell voltage as well as reducing the number of extraction stages.

The early attempts to use an undivided cell were based on the addition of an organic anode depolarizer such as isopropanol. It was thought that the reaction



would occur more readily than oxidation of acrylonitrile or tetraalkylammonium

ions at a lead dioxide anode and would, in addition, form protons at the rate required to maintain a constant pH in the electrolyte. This proved to be the case although the current efficiency for reaction (6.12) was only about 70% because further oxidation of the acetone to carbon dioxide and other products also occurred. A typical electrolyte composition was acrylonitrile (55%), isopropanol (28%), water (16%) and a tetraalkylammonium salt (1%), the isopropanol also acting as a co-solvent, and a yield of adiponitrile exceeding 90% could again be obtained. The absence of a membrane certainly reduced the cell voltage and energy consumptions below 3000 kWh per ton of adiponitrile were claimed (less than half that used by the 1965 Monsanto process). The major byproducts were derived from isopropoxide in reactions analogous to (6.9).

BASF in Germany considered the use of the capillary gap cell (see Fig. 2.16 in Chapter 2) for this electrolysis. The cell consists of a stack of carbon discs closely spaced by 0.2 mm thick strips of an insulator. The electrolyte is pumped through the inter-electrode gaps and a voltage is applied to endplates so that a bipolar cell is formed. The cell design is compact, simple and cheap compared with a filter press cell and the tetraalkylammonium concentration could be reduced to below 0.5% without loss of yield and with an energy consumption below 3000 kWh ton<sup>-1</sup>.

These studies together showed that it was possible to run the process effectively with low acrylonitrile and tetraalkylammonium ion concentrations. In such circumstances the anode depolarizer would seem unnecessary and, indeed, Phillips have run a pilot plant with an undivided cell, lead cathode and steel anode, and a very simple electrolyte consisting of dipotassium hydrogen phosphate (1.5 M), acrylonitrile (6%) and a tetrabutylammonium salt (0.03%) in water; the anode reaction is again oxygen evolution. The yield of adiponitrile is over 90% and the major byproducts were propionitrile and trimer.

Hence it is clear that considerable advances on the technology employed by Monsanto in 1965 are possible: improvements to cell design allow reductions in energy consumption and increases in space time yield, and careful control of the electrolyte permits operation without a separator and with only a low concentration of tetraalkylammonium ion.

#### 6.1.4 The new Monsanto process

For some years, Monsanto have had a programme of research with the objective of developing a second-generation acrylonitrile hydrodimerization process based on an undivided cell and combining less complex conditions with simpler cell design to give both lower capital costs and a reduced energy consumption. It has recently been disclosed that this programme has led to new technology which has been used in recent expansions of adiponitrile production in both the USA and the UK. Monsanto production of adiponitrile by electrolysis now exceeds 200 000 ton yr<sup>-1</sup>.

The new process employs an emulsion of acrylonitrile and 10–15% disodium hydrogen phosphate in water containing a low concentration of a quaternary ammonium salt (0.4%). Thus the concentration of acrylonitrile in the aqueous phase is 7% (i.e. saturated) and the adiponitrile will extract into the organic phase. The quaternary ammonium salt now used is hexamethylene-bis(ethyldibutyl-

ammonium) ( $\text{C}_2\text{H}_5(\text{C}_4\text{H}_9)_2\text{N}^+(\text{CH}_2)_6\text{N}^+(\text{C}_4\text{H}_9)_2\text{C}_2\text{H}_5$ ) phosphate because it is found to give a slightly higher yield of product and is easier than simpler quaternary ammonium salts to extract with water from the organic phase. In the undivided cell and this medium, the choice of anode was a major problem. Lead dioxide degraded the acrylonitrile while all precious metals and transition metals were found to corrode. Such anode corrosion is a problem not only because it means that electrodes must be replaced but more importantly because it leads to a build-up of metal ions in the electrolyte, subsequent deposition on the cathode and catalysis of hydrogen evolution. In consequence the current efficiency for adiponitrile formation decreases with time. In the end the difficulty has been overcome using a carbon steel as the anode and minimizing its corrosion rate with additives which are borax (2%) and EDTA (0.5%). These additives reduce anode corrosion by over 95% and also produce mildly corrosive conditions at the cathode preventing the deposition of transition metals on the cathode surface and also bringing about a slow but continuous renewal of the cathode surface. In the absence of EDTA, hydrogen evolution at the cathode increases over a 24–48 h period until it consumes 10–15% of the charge passing; in the presence of EDTA hydrogen evolution remains less than 5% of charge consumed.

The cell design is very simple. It consists of a bipolar stack of 50–200 rectangular carbon steel sheets whose cathode faces are electroplated with cadmium to a thickness of 0.1–0.2 mm; the anode–cathode gap is fixed at about 2 mm by

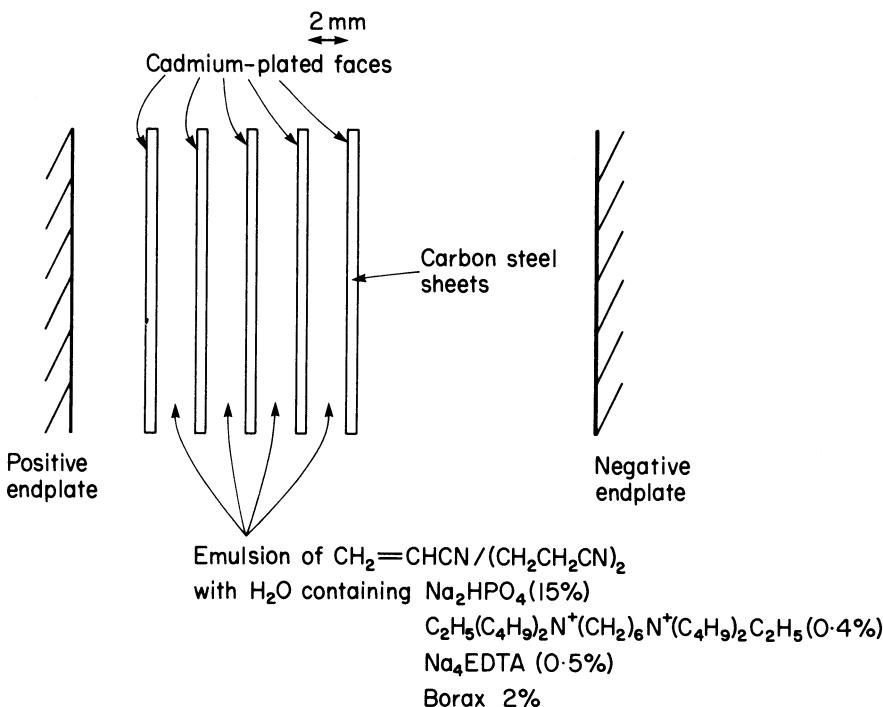


Figure 6.6 *The new Monsanto process for the hydrodimerization of acrylonitrile.*

insulating plastic spacers. The electrolyte is fed uniformly across the parallel electrode chambers at a flow velocity of  $1\text{--}2 \text{ m s}^{-1}$ . The process is summarized diagrammatically in Fig. 6.6. The emulsion is recycled through the cell from a reservoir and a fraction of the organic phase is removed continuously from the reservoir for extraction of product; the organic phase in equilibrium with the aqueous electrolyte contains 55–60% adiponitrile and 25–30% acrylonitrile. A fraction of the aqueous electrolyte is also treated continuously to prevent the continuous build-up of organic byproducts and metal ions from the corrosion of the cadmium and steel.

The two Monsanto processes are compared in Table 6.1. First, it must be recognized that the undivided cell stack is very much cheaper than the complex plate-and-frame divided cell (in fact, the cost is less than 10%). This reduces the capital cost of the plant to such an extent that when both the capital and energy costs are taken into account, the optimum current density is lower for the undivided cell (although this obviously implies that more cells must be built). Secondly, it is clear from the table that the absence of a membrane, the reduction in the inter-electrode gap and the increase in the electrolyte conductivity combine to have a dramatic effect on the cell voltage. The change from  $-11.65 \text{ V}$  to  $-3.84 \text{ V}$  reduced energy consumption by almost two-thirds. Moreover the continuous extraction of the product in the cell greatly simplifies the adiponitrile isolation procedures. Clearly the undivided cell process is a very significant advance.

### 6.1.5 Reaction mechanism

The complete study of the mechanism of the hydrodimerization of acrylonitrile is beyond the capability of the instrumental methods presently available. This is for three principal reasons: (i) The concentration of electroactive species generally

Table 6.1 Comparison of the Monsanto 1965 divided cell process with the recent Monsanto undivided cell process.

	Divided cell	Undivided cell
Adiponitrile selectivity (%)	92	88
Inter-electrode gap (cm)	0.7	0.18
Electrolyte resistivity ( $\Omega \text{ cm}$ )	38*	12
Electrolyte flow velocity ( $\text{m s}^{-1}$ )	2	1–1.5
Current density ( $\text{A cm}^{-2}$ )	0.45	0.20
Voltage distribution (V)		
Estimated reversible cell voltage	-2.50	-2.50
Overpotentials	-1.22	-0.87
Electrolyte <i>IR</i>	-6.24	-0.47
Membrane <i>IR</i>	-1.69	—
Total	-11.65	-3.84
Energy consumption ( $\text{kWh ton}^{-1}$ )	6700	2500

\* Catholyte.

employed in electroanalytical experiments to investigate the mechanism and kinetics of electron transfer and coupled chemical reactions is generally below  $10^{-2}$  M. In this concentration range the reduction of acrylonitrile is always a 2e reaction leading to propionitrile and hence conclusions from such electroanalytical experiments can have no relevance to the hydrodimerization of acrylonitrile to adiponitrite. (ii) There are many possible reaction mechanisms for the conversion of acrylonitrile to adiponitrite. The reaction pathways are illustrated in Fig. 6.7 and in each there are several possible rate-determining steps. (iii) None of the intermediates have a half life sufficient to allow direct detection, i.e. all  $\tau_{1/2} < 10^{-5}$  s. Even so some comments on the mechanism are, however, possible and desirable.

First, we should consider the role of the tetraalkylammonium ion in the hydrodimerization reaction. Certainly the ions are essential to the process; in their absence (but with for example a lithium or sodium salt as the electrolyte) the reduction of acrylonitrile leads only to propionitrile and a critical concentration of  $R_4N^+$  is necessary to obtain a good yield of adiponitrite. This critical concentration decreases along the series  $(CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_4H_9)_4N^+$  and with the latter can be as low at 0.01%. It may also be noted that the presence of these ions suppresses hydrogen evolution and there is evidence that they adsorb on the cathode surface. This led to the proposal that the adsorption of the tetraalkylammonium ion produces a layer at the electrode surface which is relatively aprotic. In this layer anionic coupling can occur because protonation is slow compared with that in the bulk solution.

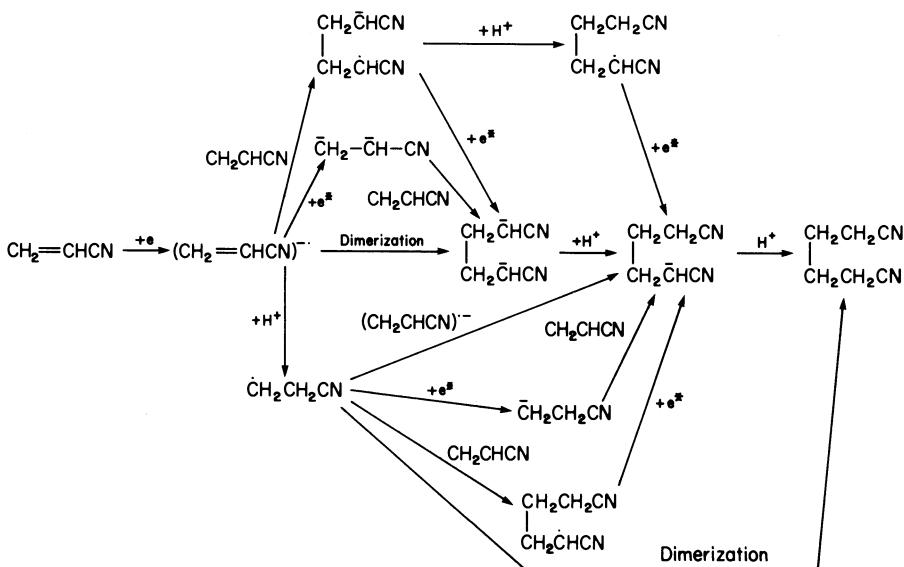
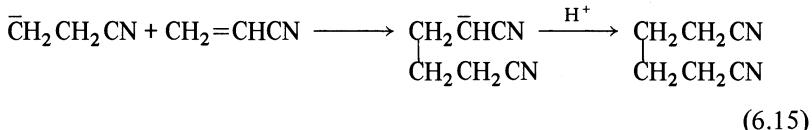


Figure 6.7 Possible reaction pathways for the hydrodimerization of acrylonitrile to adiponitrite. The asterisk \* indicates that electron transfer can be from the cathode or from  $[CH_2CHCN]^-$  in homogeneous solution.

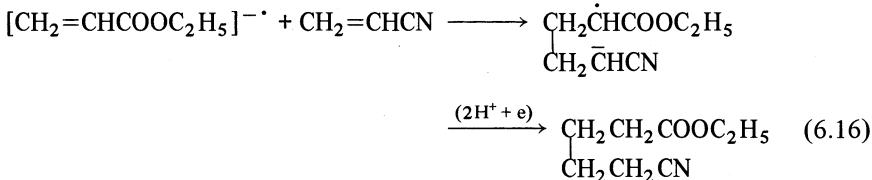
A study of the dependence of the steady-state  $I-E$  curves on the reaction conditions gives some mechanistic information. In mixtures of acetonitrile, water, acrylonitrile and tetraalkylammonium tosylate, a Tafel slope of  $(120 \text{ mV})^{-1}$  was observed and it was found that the current was proportional to the concentrations of both acrylonitrile and water. This would indicate a rate-determining step



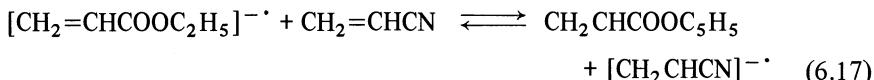
perhaps followed by the fast steps



In other attempts to define the mechanism of the hydrodimerization, many investigators have studied reactions which might be considered analogous but using olefins with two or more substituents (e.g. methylcinnamate, diethylfumarate) chosen so as to stabilize the anion radical formed in the initial electron transfer reaction. With such olefins the mechanism of hydrodimerization may be investigated successfully using cyclic voltammetry or a rotating ring-disc electrode. The balance of the evidence favours a radical ion–radical ion coupling process to form the dimeric product. This conclusion is clearly not compatible with that from the steady-state investigations with acrylonitrile. Moreover, it has been shown possible to form mixed hydrodimers by electrolysis of two different activated olefins, e.g. ethylacrylate and acrylonitrile, at a potential where only one of the olefins may be reduced. This might be taken to indicate coupling by attack of an anionic intermediate on another molecule of olefin, e.g.



although a radical ion–radical ion coupling cannot be ruled out if the electron transfer

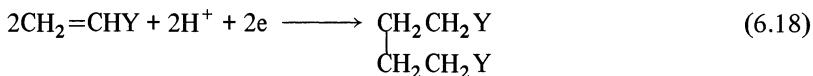


is possible in solution. This will be the case provided the standard potentials for the olefin/radical ion couples are not too different. The mechanism may well, however, vary with the structure of the olefin, particularly when structural features substantially change the stability of the reactive intermediates. Hence it may be inappropriate to seek similarities between the mechanism of the hydrodimerization

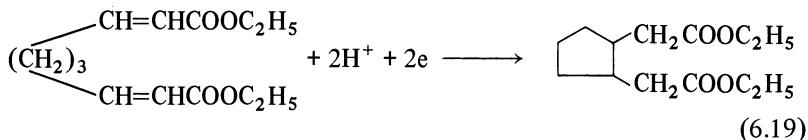
of acrylonitrile and that for more substituted olefins. The high selectivity of the hydrodimerization of acrylonitrile clearly indicates, however, that the reaction occurs by a single reaction pathway and that all competitive routes are unfavourable.

### 6.1.6 Other hydrodimerization reactions

While the hydrodimerization of acrylonitrile to adiponitrile is the only one to have been exploited commercially, it should be recognized that, using the conditions described above, hydrodimerization is a general reaction for activated olefins, i.e. olefins with an electron-withdrawing group on the double bond. The reaction



has been reported to give yields in excess of 60% (without extensive optimization). The reaction is also possible with polysubstituted olefins and particularly good yields are obtained when the coupling is intramolecular to give a cyclic product, e.g.



Mixed coupling of two different olefins was mentioned in the previous section. Synthetically, however, it is not a particularly satisfactory procedure since it is never possible to obtain the mixed hydrodimer without the two simple hydrodimers. Highest yields (< 60%) are obtained in conditions where only one olefin is reducible but the other is present in a large excess.

## 6.2 OTHER INDUSTRIAL PROCESSES

While the hydrodimerization of acrylonitrile to adiponitrile has been the most successful commercial organic process, a few other organic compounds are known to be prepared by electrolysis on an industrial scale. Many more possible processes have been examined on a pilot-plant scale and some of these may also have been extended to commercial operation. In addition, the literature describing laboratory-scale organic electrosynthesis is now very extensive.

The known commercial processes and a selection of the reactions which have been run on a pilot-plant scale are listed in Table 6.2. It can be seen that the processes cover a very wide range of chemistry including oxidation and reduction of functional groups, hydrogenation, dimerization and substitution. Moreover the processes make use of both direct and indirect electrode reactions. In the latter an inorganic redox reagent is used as a catalyst or ‘electron carrier’, i.e. the inorganic species is oxidized or reduced at the electrode to give an oxidation state which

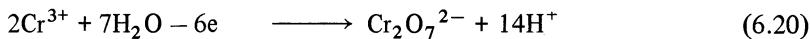
reacts with the organic reactant away from the electrode surface. Redox couples which are commonly considered for use in electrode reactions include for oxidations  $\text{Ce}^{3+}/\text{Ce}^{4+}$ ,  $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Mn}^{2+}/\text{MnO}_2$ ,  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ,  $\text{Br}^-/\text{Br}_2$  and  $\text{Cl}^-/\text{ClO}^-$  and for reductions  $\text{Sn}^{4+}/\text{Sn}^{2+}$ ,  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and  $\text{Ti}^{4+}/\text{Ti}^{3+}$ .

On the other hand there are a number of similarities in the processes. It can be seen that, in contrast to academic studies of recent years, reactions in aqueous media predominate. This is largely because the state of the art in cell design still does not allow electrolysis with a competitive energy efficiency except in highly conducting media, i.e. aqueous media with high electrolyte concentration. Hence the successful reactions are those where:

- (a) The chemistry can be carried out with high selectivity in a largely aqueous medium.
- (b) The electroactive species has considerable solubility in the medium. This is essential to obtain a reasonable current density and hence space time yield. To obtain a current density of  $100\text{--}500 \text{ mA cm}^{-2}$ , a solution 1–10% in the electroactive species is necessary.
- (c) A cheap electrode material, e.g. Pb, Ni or Cu, may be used.
- (d) The products are readily isolated from the electrolysis medium.
- (e) The competitive chemical processes require difficult reaction conditions, toxic reagents or produce large volumes of effluents or unwanted solids.

Thus many of the direct electrolytic processes were developed to replace metal (normally Zn or Fe)/acid reductions and oxidations with permanganate or dichromate and involve Pb electrodes and a highly water-soluble starting material, e.g. nitrogen-containing bases. The exceptions to these generalizations are the oxidations using benzene and propylene as raw materials which are carried out with two phases in the anolyte and the production of lead alkyls. This last process employs conditions which are not well suited to electrochemistry, but it was developed as the result of an intensive R and D programme because of the complexity of the rival chemical processes.

The indirect electrolytic processes still employ redox reagents but because they are continuously recycled the effluent problem is greatly reduced. The conversion of anthracene to anthraquinone is a typical example of such a process. A concentrated solution of chromium(III) in aqueous sulphuric acid is partially oxidized to dichromate at a Pb (i.e. Pb covered *in situ* by  $\text{PbO}_2$ ) anode



and the dichromate is then reacted with anthracene

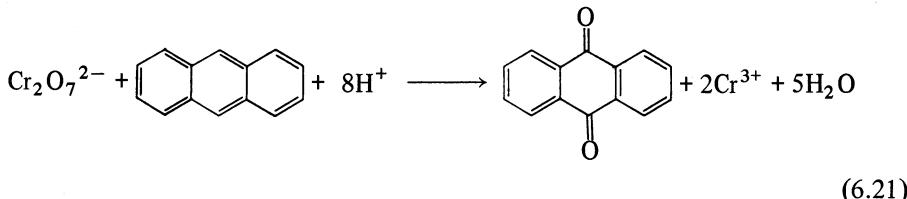


Table 6.2 (a) Commercial electroorganic processes.

Product	Feedstock	Type of process	
1. $(\text{CH}_2\text{CH}_2\text{CN})_2$	$\text{CH}_2=\text{CHCN}$	Cathodic hydrodimerization	
2. $\text{Pb}(\text{CH}_3)_4$ and $\text{Pb}(\text{C}_2\text{H}_5)_4$	$\text{CH}_3\text{MgCl}$ or $\text{C}_2\text{H}_5\text{MgCl}$	Oxidation at a Pb anode in a mixed ether solvent	
3. $\text{C}_8\text{F}_{17}\text{COF}$ $\text{C}_3\text{F}_7\text{COF}$	$\text{C}_8\text{H}_{17}\text{COOH}$ $\text{C}_3\text{H}_7\text{COOH}$	Perfluorination at a Ni anode in HF medium	
4.			Reductions at a Pb cathode in mixed aqueous/organic solvent containing sulphuric acid
5.			Indirect oxidations via chromic acid
Purified montan wax	Crude montan wax		
6. Dialdehyde starch	Starch	Functional group oxidation – indirect via periodate	
7. Sorbitol	Glucose	Reduction of functional group at Pb cathode in aqueous buffer	
8. Gluconic acid	Glucose	Indirect oxidation via hypobromite	
9.		Indirect oxidation via $\text{Br}_2$ in methanol	

Table 6.2 (b) Extensive pilot plants

Product	Feedstock	Type of process
1.		Reduction at a Cu cathode in very acid medium to promote rearrangement of phenylhydroxylamine
2.		Reduction at a Pb or Hg cathode in aqueous/organic solvents, pH 1–6
3.		Reduction at a Pb cathode in aqueous solution
4.		Reduction in aqueous acid
5.		Reduction at Hg in aqueous solution
6.		Kolbe oxidation in methanol; Pt anode
7. $\text{C}_2\text{H}_5\text{COCH}_3$	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	Oxidation following hydration in $\text{H}_2\text{SO}_4$
8.		Indirect oxidation via $\text{Cr}_2\text{O}_7^{2-}$
9.		Oxidation at Pb in $\text{H}_2\text{SO}_4$
10.		Indirect oxidation via $\text{MnO}_2$
11.	$\text{CH}_3\text{CH}=\text{CH}_2$	Indirect oxidation via hypohalite
12.		Oxidation at Pb in $\text{H}_2\text{SO}_4$

the chromium(III) being re-formed in this chemical reaction. It is normal for the electrolysis and the chemical process to be carried out in separate reactors because the current efficiency for the inorganic electrode reactions are often greatly diminished by the presence of low concentrations of soluble organic compounds. Indeed in such cases the solution of spent redox reagent is generally treated to remove organic material, for example by passing through a column of activated carbon, before it is recycled through the electrolysis cell. Furthermore, the chemical reaction is commonly a two-phase process since this minimizes the contamination problem and also permits straightforward extraction of the product. Certainly the oxidation of anthracene is carried out in a separate reactor and is a reaction between aqueous chromic acid and solid hydrocarbon; the product anthraquinone is also insoluble.

Indirect electrolytic processes therefore have the advantages:

- (1) The inorganic electrode reaction is often efficient at relatively high current densities and the cell can be designed to run at low cell voltages and hence energy requirement.
- (2) It is possible to use our considerable background of homogeneous chemistry and chemical reactor design to ensure high selectivity in the reaction of the organic substance, while the coupled electrolysis removes the need to purchase redox reagent and minimizes the volume of effluent to be handled.
- (3) When the reaction can be carried out between two phases, the extraction of the product is particularly straightforward and it does not interact with the electrolysis step.

On the other hand, it is clear that the space time yield of the process must suffer and the investment costs must increase because of the need to have a chemical reactor (and perhaps an electrolyte scrubber) as well as an electrolysis cell. Hence the designer will always wish to combine the cell and reactor as closely as the chemistry will allow.

In general the future for electroorganic processes must be bright. The expectations are that we shall see a substantial increase in the number of processes for the production of low-tonnage organic compounds such as pharmaceuticals, dyestuffs, agricultural and fine chemicals. The major stumbling blocks to such progress are undoubtedly the unavailability of cell technology and cell components with the desired properties and inexperience in the design, assessment and running of such processes in the chemical industry. In the longer term, the prospects for the production of high-tonnage chemicals are probably dependent on solar or nuclear power making electricity significantly cheaper than other forms of energy, on chemists showing that electrode reactions can accomplish synthesis from feedstocks such as CO, CO<sub>2</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH which cannot be carried out by other methods or on significant advances in electrochemical technology. An example of the latter would be processes which used both the anode and cathode reactions for useful chemistry. In contrast to a chlor-alkali cell, it is normal in an organic process to use only the anode or the cathode synthetically and only to evolve oxygen or hydrogen at the counterelectrode (but perhaps thereby controlling the pH of the

electrolysis medium). Moreover the counterelectrode reaction is not always designed to minimize the cell voltage and thus it is not surprising that organic electrolytic processes are not always energy efficient. The economics of many processes would change dramatically if both the anode and cathode reactions were used to make desirable products without incurring other severe problems.

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# 7 Metal Finishing

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Metal finishing is the name given to a range of processes carried out to modify the surface properties of a metal, for example by the deposition of a layer of another metal or a polymer, or by formation of an oxide film. The origins of the industry lay in the desire to enhance the value of metal articles by improving their appearance, but in modern times the importance of metal finishing for purely decorative reasons has decreased. The trend is now towards surface treatments which will impart corrosion resistance or particular physical or mechanical properties to the surface (e.g. conductivity, heat or wear resistance, lubrication or solderability) and hence to make possible the use of cheaper substrate metals or plastics covered to give them essential metallic surface properties.

A large fraction of the metal objects which we see in everyday life (e.g. car components, kitchen utensils, cans for food, screws and metal window frames) have undergone a metal finishing process. Moreover similar processes are an essential part of modern engineering and of the manufacture of electronic components (e.g. circuit boards, capacitors and contacts). As a result, the practice of metal finishing extends to many electronics, engineering and metal processing companies as well as to both large and small specialist firms, producing a particularly diverse industry. In general, however, the industry tends to be labour intensive and dependent on personal experience, and certainly the plant has not reached a state of great sophistication.

Not all surface finishing is carried out using electrochemical methods, but electroplating, anodizing and related processes together with electrophoretic painting represent a large portion of the industry.

## 7.1 ELECTROPLATING

Electroplating is the process of electrochemically depositing a layer of metal onto a surface. The object to be plated is made the cathode in an electrolyte bath containing the metal ion,  $M^{n+}$ , so that the reaction at the cathode is



Where possible the anode reaction is the dissolution of the same metal



and the electrolysis conditions are controlled in such a way that the current efficiencies of reactions (7.1) and (7.2) are the same and hence the concentration of  $M^{n+}$  in the bath remains constant. In a few cases, the metal ion has to be added as a salt and then an inert anode, usually lead dioxide, is employed; the anode reaction is then oxygen evolution. For a successful electroplating process, the correct pretreatment of the cathode and careful selection of the anode material, plating bath, current density and other electrolysis conditions are essential. All these factors will be discussed below.

It is common to electroplate:

- (a) Single metals; the most important are Sn, Cu, Ni, Cr, Zn, Cd, Pb, Ag, Au and Pt.
- (b) Alloys; including Cu/Zn, Cu/Sn, Pb/Sn, Sn/Ni, Ni/Co and Ni/Cr.
- (c) Composites; i.e. metals containing solids such as PTFE or WC<sub>2</sub>.

### 7.1.1 Requirements of electroplating processes

The objective of an electroplating process is to prepare a deposit which adheres well to the substrate and which has the required mechanical, chemical and physical properties. Moreover it is of overriding importance that the deposit properties meet their specification on all occasions, i.e. the process is reproducible. On the other hand, many metals may, by modification of the bath and plating conditions, be deposited with different properties. It is for this reason that it is not possible to define a single set of conditions for electroplating each metal; the bath, current density, temperature, etc., will depend to some extent on the deposit properties required.

Because of the importance of reproducibility in the deposit, it is important that the plating bath is stable for a long period of time. It is also necessary that the quality of deposit is maintained over a range of operating conditions since some variation in concentrations and current density are, periodically, bound to occur particularly when different objects are to be plated. Tolerance of the bath to mishandling during operation on the factory floor is an additional advantage.

It is clearly desirable that the deposit has an even thickness over the whole of the surface to be electroplated. This requires the potential to be the same at all points over the surface of the cathode and this is impossible to attain when the object to be plated has a complex shape. To some extent the evenness of the deposit can be improved by introducing auxiliary anodes (usually platinized titanium electrodes where the reaction is oxygen evolution) at various positions in the electrolyte, the objective being to increase the cathode current density at points where it would otherwise be very low, i.e. at points on the cathode furthest from the normal anodes (e.g. in holes or recesses in the object being plated). The problem with this approach, however, is that a totally new cell geometry is necessary for each new plating job and in any case its success is limited. Hence, in general, we are dependent

on the properties of the plating bath to give a good, even deposit of metal. The ability of a plating bath to give an even deposit is measured by its throwing power which may be determined in the Haring–Blum cell (Fig. 7.1). Two cathodes are placed at markedly different distances from a single anode and electroplating is carried out. The weight of metal plated on the two cathodes,  $W_1$  and  $W_2$  respectively, will be different because the  $IR$  drops in the two electrode gaps are not the same; electrode 1 must be at a lower overpotential and hence less metal will deposit at this cathode. Several formulae have been used to express throwing power but that proposed by Field has some general acceptance. The Field formula is

$$\text{Throwing power} = \frac{(K - M) \times 100}{K + M - 2} \quad (7.3)$$

where  $K = x_1/x_2$  and  $M = W_2/W_1$ , an equation designed to give throwing powers between +100 (very good) and –100 (very poor).

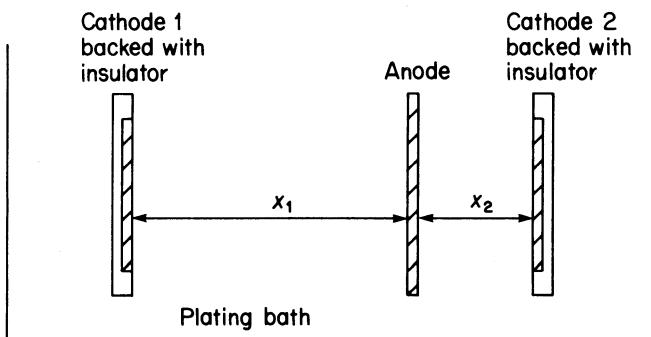


Figure 7.1 *The Haring–Blum cell for the determination of the throwing power of a plating bath.*

Factors which determine the throwing power of an electroplating bath include:

- (a) Conductivity of the electrolyte – a high conductivity will minimize the  $IR$  drops in the bath which cause differences in potential over a complex cathode surface and therefore causes the rate of deposition to be more uniform.
- (b) The Tafel slope for the deposition reaction – it will be seen from the curves in Fig. 7.2(a) that for any variation of potential the difference in deposition rate will be smaller when the Tafel slope is high (curve (ii)). Experimentally it is generally found that Tafel slopes are higher when complexing agents and additives, which adsorb on the cathode, are present in solution. Some additives known as levellers and brighteners have the role of ensuring an even deposit on a microscale; their mode of action will be discussed later.
- (c) Competing electrode reactions – the throwing power can be enhanced by the occurrence of other reactions, e.g. hydrogen evolution, at the same time as metal deposition. In the situation shown in Fig. 7.2(b), hydrogen evolution will occur only at points on the surface where the potential is high. The current for

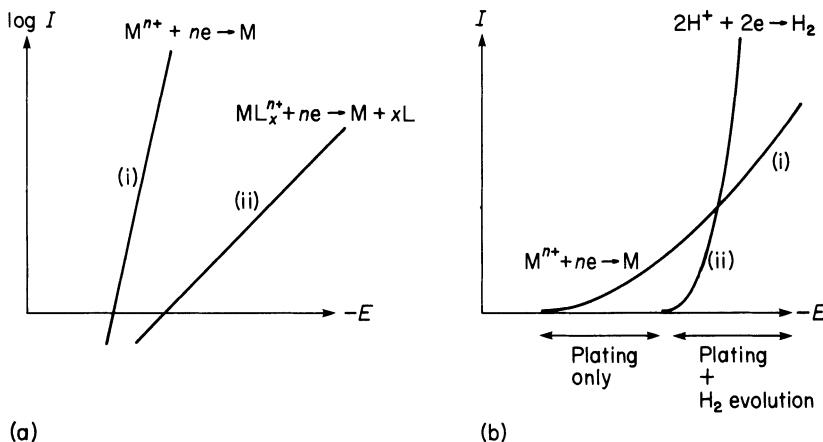


Figure 7.2 (a) Tafel plots showing the common effects of the addition of a complexing agent to a plating bath on the reduction of the metal ion. (b) I–E plots for a metal ion and proton reduction in a plating bath.

hydrogen evolution will then contribute to the *IR* drop without leading to metal deposition. Hence it causes a reduction in the local overpotential, and leads to a more even deposit.

It can be seen that the main process parameters which affect the throwing power are the composition of the plating bath (i.e. total electrolyte concentration, complexing agents, pH, additives), temperature and current density.

From the viewpoint of energy efficiency it is attractive for the electrodeposition process to have a high current efficiency and the plating cell to be designed to have a low anode–cathode voltage. In practice the energy used in the electrolysis itself is commonly low compared with that required to heat the bath and to prepare the surface prior to plating. Moreover, the charge consumed during plating is low,  $1\text{--}10 \text{ C cm}^{-2}$  for a  $10 \mu\text{m}$  layer and the value added during the process may be very high. Hence energy efficiency is not as important as in the large-scale electrolytic processes and this accounts for the relatively simple cells employed. In fact, however, the electroplating of many metals is carried out with a very high current efficiency, the exception being chromium deposition when the efficiency is in the range 5–20%.

It is, of course, unavoidable that electroplating processes employ solutions containing high concentrations of heavy-metal and transition-metal ions. There is, however, an increasing awareness that the environment must be protected and that particularly toxic solutions should be avoided. Thus all large electroplating facilities will have a plant for the removal of metal ions and other toxic species before effluent water is discharged. Moreover the trend is towards recovery of the metal in a useful form (see Chapter 11) and it is a long-term aim of the industry to employ plating baths which avoid the most toxic chemicals such as chromium(VI) and

cyanide ion, and some concern is even expressed about the toxicity of the organic additives used to improve the product quality.

### 7.1.2 The mechanism of the electrodeposition of metals

In discussing the mechanism by which an electroplate is formed it must first be recognized that the deposition process has two distinct phases. At the start of the plating process, the deposition of the metal will occur on an electrode surface of a different material, that of the object to be plated. Hence the first step will be the formation of nuclei of the new phase and their growth into crystals with the characteristic lattice of the electroplating metal. Then, once the electrode is fully covered by a few atomic layers of this metal one is dealing with a  $M/M^{n+}$  electrode and the thickening of the layer into a macroscopic deposit. In terms of time or charge, the plating process consists almost entirely of the latter process, but the initial stages are also important since they determine the structure of the primary layer (such factors as the shape and number of growing crystallites) and thereby influence the structure of the final electroplate and its properties.

Nucleation and the early stages of phase growth were discussed briefly in Chapter 1. It was noted that nucleation was always an improbable event and is achieved at an electrode surface by the application of a large overpotential. The density of nucleation is dependent on the plating bath and is extremely sensitive to the electrode potential (therefore also, of course, the current density). The growth of the nuclei once formed occurs quite rapidly at comparatively low overpotentials, and in a constant-current situation the potential will decrease substantially once nucleation has occurred.

The growth of the crystals occurs by incorporation of the individual metal atoms into the crystal lattice. The newly incorporated metal atom is only likely to be stable when it enters the lattice at a site where it interacts with several other atoms already in the lattice. Of the sites which are possible in a perfect crystal lattice (Fig. 7.3), incorporation will be most favourable at a kink site (where the atom can interact with three neighbours) although some incorporation will also take place at edge sites (two neighbours); adatoms (one neighbour) are likely to redissolve

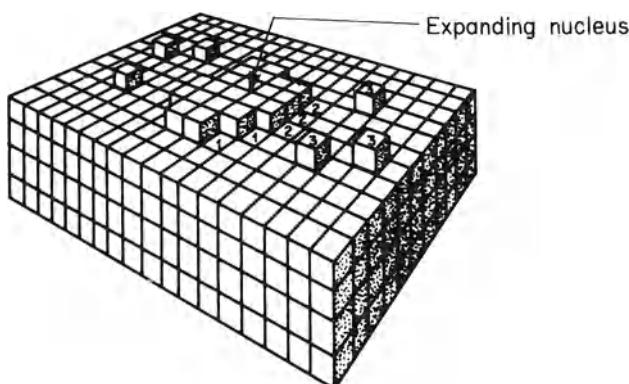


Figure 7.3 *Types of site on a perfect crystal: 1, kink site; 2, edge site; 3, adatom.*

although a very small number will expand into new nuclei. Clearly the overall phase growth is a sequence of at least three steps:

- (a) Mass transport (this may be diffusion, convection or migration) of the metal-bearing species to the electrode surface;
- (b) Electron transfer to form an adatom;
- (c) Diffusion of the adatom across the surface into a position in the lattice.

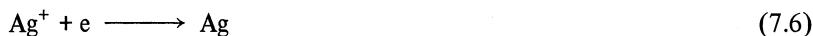
The structure of the growing layer will largely be determined by the relative rates of processes (b) and (c) and, in a plating process, the current density employed. At low current density, the surface diffusion is fast compared with electron transfer and the adatom is likely to end up in a favoured position in the lattice. At higher current densities, surface diffusion is no longer fast compared with electron transfer and further nuclei must form; the layer will be less ordered.

In Chapter 1 it was also shown that nucleation and the early stages of growth can be studied using potential step methods and analysis of the rising  $I-t$  transients which result; the number and kinetics of formation of nuclei (e.g. progressive or instantaneous?) can be deduced and it is also possible to gain insight into the nature and geometry of growth of the centres (e.g. is the growth limited to a single monolayer, does it occur layer by layer, or does three-dimensional growth take place? If three-dimensional, do the centres grow as cones or hemispheres? Is the reaction kinetically or diffusion controlled?) and the way the centres eventually overlap.

During most of the electroplating process, however, this primary metal layer is thickening from a few atomic layers to the desired thickness, perhaps 1–10  $\mu\text{m}$ . In this period the metal deposition reaction occurs effectively at an electrode of the electrodeposited metal. The rate of this process may generally be estimated by an equation of the type

$$i = nFk\vec{C}_{M^{n+}} \exp\left(-\frac{\alpha nF}{RT} \eta\right) \quad (7.4)$$

although this does not necessarily infer that the electrode reaction is simple. In many cases the electroplating reaction will involve the reduction of a complexed metal species and then the electrode reaction may involve chemical predissociation steps, e.g.



Moreover, some reactions, e.g. chromium plating, must be regarded as very complex processes whose mechanism is still not fully understood. The plating bath for chromium metal always contains chromium(VI) when the solvent is water and while the reduction to chromium(III) occurs to some extent, chromium(III) does not reduce to the metal. Hence chromic ions are not intermediates in the reduction of chromium(VI) to metal. Moreover, there is evidence that both sulphate ions and chromium(III) catalyse the deposition and this has led to the proposal that species

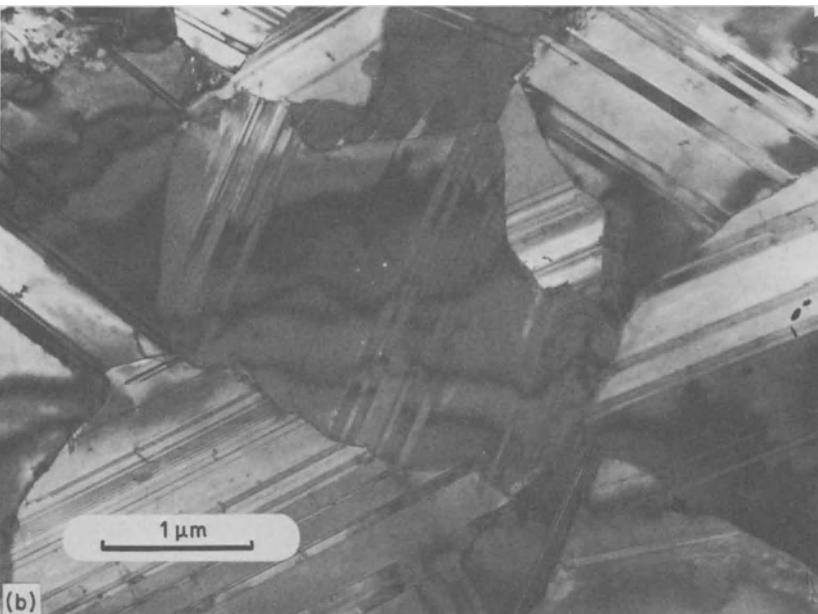
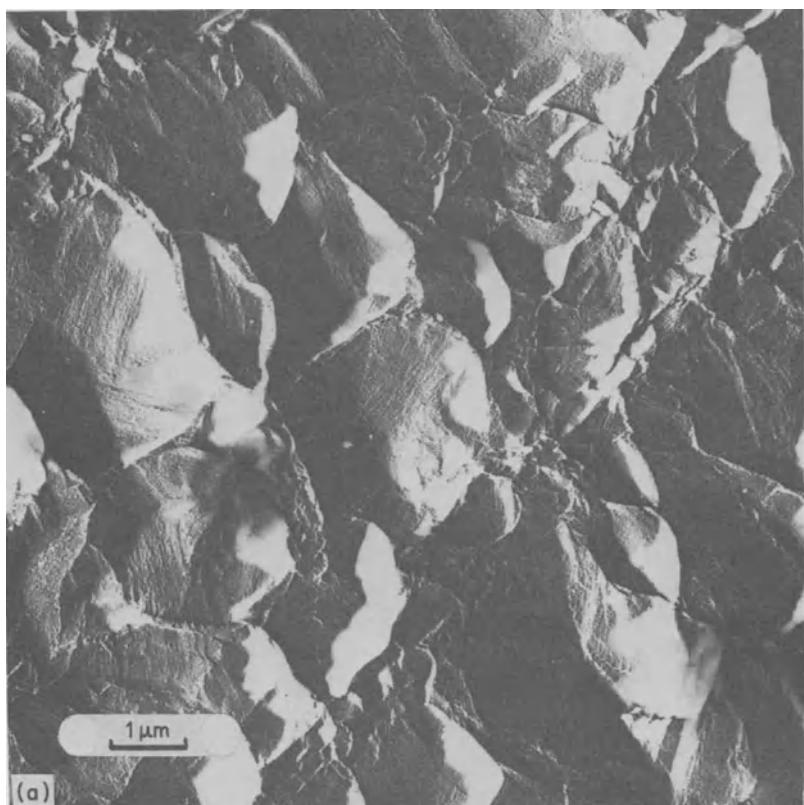
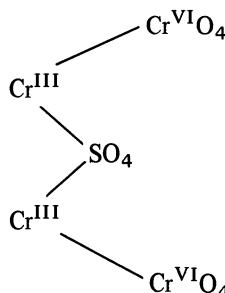


Figure 7.4 (a) Scanning electron micrograph and (b) transmission electron micrograph of nickel plated from a  $\text{NiSO}_4/\text{NiCl}_2/\text{H}_3\text{BO}_3$  bath. Photographs supplied by Dr J. K. Dennis, University of Aston, Birmingham.

of the type



are intermediates at the electrode surface.

Electrochemical experiments tell us little about the thickening process. Rather information about thick deposits comes from empirical studies and from techniques such as optical microscopy, scanning and transmission electron microscopy (see Fig. 7.4) and electron diffraction. On the other hand, the structure and properties of the deposit are totally determined by electrochemical parameters combined with the properties of the plating bath. Electrodeposits are almost invariably polycrystalline with many grain boundaries and imperfections such as screw dislocations (Fig. 7.5). Screw dislocations provide an edge which does not grow out; rather it rotates around the centre to form a pyramid of stacked rows of edges, the radius of curvature of the emerging dislocation controlling the step spacing on the pyramid.

Again during the thickening stage a key parameter is the current density. At low current densities, the surface diffusion process is fast compared with electron transfer and both the crystal lattice and structures such as screw dislocations can be well formed and may be observed by electron microscopy. The predominant orientations of surface planes can also be determined using electron diffraction.

As the current density is increased, surface diffusion is no longer fast compared with the discharge process and adatoms no longer reach their equilibrium position

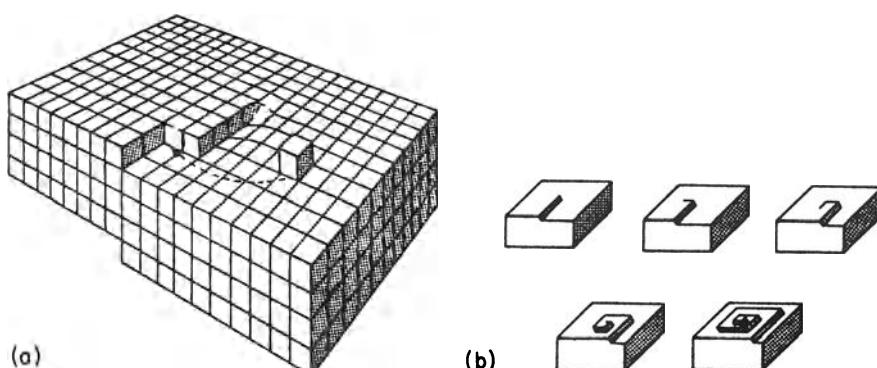


Figure 7.5 A screw dislocation and its propagation leading to a spiral feature. Note that as the screw dislocation extends, the kink site is never lost.

in the lattice. Furthermore, at the increased overpotential, nucleation of additional growth centres remains a more frequent event. Hence the lattice formed will be less ordered and macroscale features, steps, ridges and polycrystalline block growth (see Fig. 7.6), become more likely. With further increase in current density, outward growth of the layer becomes of increasing importance and problems arising from mass transport control in solution can arise. For example, dendrite (or whisker growth) can occur and once this form of growth commences, it predominates totally because of the enhanced rate of mass transport to the tip (spherical diffusion

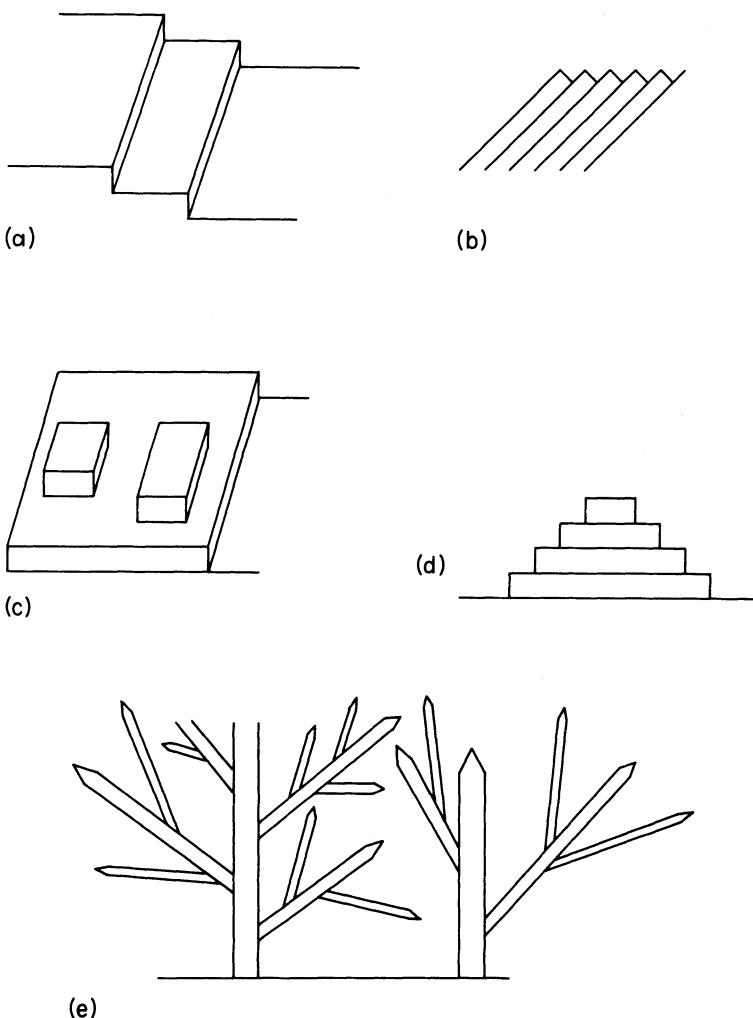


Figure 7.6 *Schematic representation of various growth forms observed in metal deposition: (a) layer growth, (b) ridge growth, (c) block growth, (d) pyramidal growth, and (e) dendritic growth.*

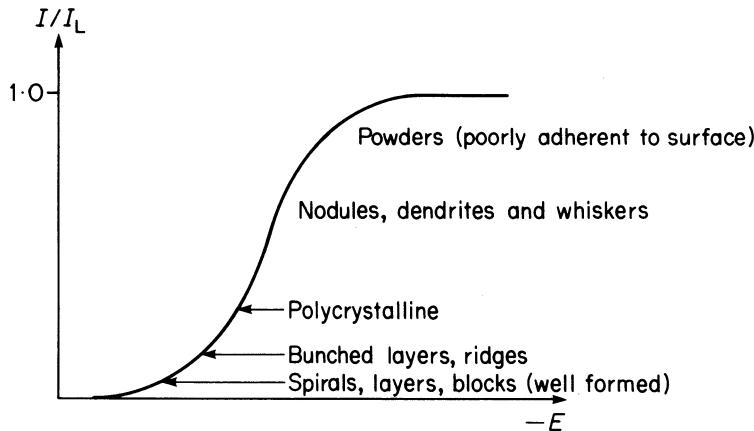


Figure 7.7 *The variation of the characteristic growth modes on the normalized current density ( $I/I_L$ ).*

to the microscaled tip) and because the  $IR$  drop to the tip is also a minimum as it is the closest point to the anode. In the completely mass transport controlled potential region, the deposit becomes a powdered texture.

The way the structure depends on current density is summarized in Fig. 7.7. The above discussion should not, however, be taken to imply that the best electro-deposits are necessarily formed at the lowest current density; the correct conditions must be sought experimentally. Even when a perfect lattice is grown on a substrate with similar lattice dimensions (epitaxial growth), a good adhesive deposit is not always obtained. In many applications, the most durable deposits are often the even, polycrystalline type.

### 7.1.3 Anodes

The performance of the anode is of considerable importance in determining the success of an electroplating process.

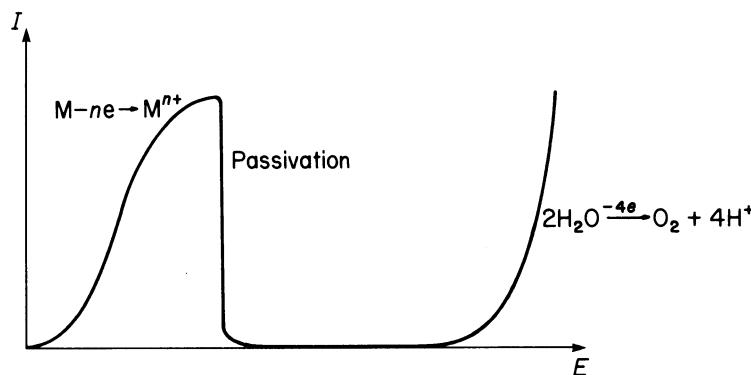


Figure 7.8 *Typical  $I$ – $E$  curve for an anode in an electroplating bath.*

Where possible the anode is made from the same metal as that being plated at the cathode and the conditions are selected so that the concentration of the metal ion in solution remains constant. This requires the anode and cathode current efficiencies to be matched (usually with values approaching 100%) over the whole service life of the anode. In particular the electrolytes in the plating bath must be chosen so that the anode does not passivate. A common type of polarization curve for the dissolution of a metal is shown in Fig. 7.8. In the active region, the electrode reaction is the desired metal dissolution but, on increasing the current density or the overpotential above a critical value, the surface becomes covered with an oxide film which passivates the anode, i.e. causes the current for the corrosion reaction to drop to a low level. In a constant-current electrolysis the potential of the anode will shift into the transpassive region where oxygen evolution is a major component of the current. Hence in a plating process, it is essential to maintain the anode potential in the active region. This may be ensured by using a large anode surface area and hence maintaining a suitably low current density at the anode (the anode is frequently in the form of small pellets to increase surface area). Additions of complexing agents, which prevent passivation, or halide ions, which generally cause sufficient pitting of the oxide film for dissolution to continue, are made to many baths. The metal must also dissolve to form the correct oxidation state. Thus in acid solution, tin may dissolve as tin(II) or tin(IV) but only the former may be reduced to the metal at a potential positive to the hydrogen evolution reaction and therefore the current density must be controlled to form only tin(II).

The anodes are designed to produce the minimum of anode sludge which may contain the metal as oxide or hydroxide or even the metal itself if physical disintegration of the anode accompanies dissolution. In addition, impurity elements in the anode which do not dissolve, collect in the sludge. The mode of fabrication and the purity of the anode metal affects its performance, particularly with regard to physical disintegration and rolled metal is frequently better than case metal. For several metals, particular forms have been developed for electroplating anodes; examples are nickel carbonyl and S-nickel pellets which combine a high surface area with smooth dissolution and a minimum of sludge.

Chromium passivates strongly in acid sulphate media. Hence an inert anode is always employed in chromium plating. It is generally a lead alloy which immediately covers with lead dioxide on positive polarization in the electrolyte. The alloying elements are tin, antimony and silver which are added to the lead to improve its mechanical properties and to reduce the overpotential for oxygen evolution.

In addition to the main anodes, auxiliary anodes of Pt/Ti are sometimes also used to improve the current distribution at the cathode.

#### 7.1.4 The plating bath

The plating bath is normally a complex mixture of salts of the metal being plated, electrolytes and various additives to ensure that the electroplate has the desired

properties and quality. In this section we shall consider the role of each of the components.

(a) *The metal ion*

The metal to be plated is present in solution either as the simple hydrated ion or as a complex but always in high concentration, typically 1.0–3.0 M. This high concentration is essential because, while it is necessary to use a reasonable current density, the quality of the plate suffers badly if the deposition occurs under conditions where the electrode reaction is even partially mass-transfer-controlled (see Fig. 7.7). A non-complexing medium is frequently used for rapid plating on objects of simple shape while complexing media are employed when a high throwing power is of importance.

(b) *Electrolytes*

Electrolytes are also added in high concentration to give the bath maximum conductivity. They also have the role of controlling the pH and buffering the solution particularly if hydrogen or oxygen is evolved at the cathode or anode respectively, since these reactions will tend to change the pH. An increase in pH may lead to deposition of metal hydroxides or a decrease of H<sub>2</sub> evolution.

(c) *Complexing agents*

Complexing agents are used to make the deposition potential more negative when it is necessary to prevent a spontaneous chemical reaction between the cathode and the plating ion, e.g. plating copper onto iron or steel



This chemical reaction would lead to a very poor copper deposit so a complexing agent is added to make the potential of the Cu<sup>2+</sup>/Cu couple negative to that for the Fe/Fe<sup>2+</sup> couple; reaction (7.7) is then no longer thermodynamically favourable. Complexing agents are also used to modify the Tafel slope for the metal ion reduction and hence to improve the throwing power of the bath. The most common complexing agents in electroplating are cyanide, hydroxide and, more recently, sulphamate ion.

Complexing agents also have a role at dissolving anodes; they can prevent passivation and therefore loss of current efficiency in the corrosion reaction and it is for this reason that a low concentration of chloride ion is a common constituent of many baths.

(d) *Organic additives*

A wide range of organic molecules are added in relatively low concentration to the electroplating bath to modify the structure, morphology and properties of the cathode deposit. Their development has been almost totally empirical and details of their mode of operation are seldom known. Indeed it is not always clear whether their effect is due to the additive itself or to decomposition products formed in electrode reactions. Several generalizations concerning their operation are, however, possible.

Certainly additives are usually capable of adsorption on the cathode surface and in some cases organic matter is occluded into the deposit, especially when the plated metal has a high surface energy (high melting point). Many additives also increase the deposition overpotential and change the Tafel slope. This may be due to the need for electron transfer to occur through the adsorbed layer or due to complex formation at the electrode surface.

While the additives may affect more than one property of the deposit, and there is clear evidence that when several additives are present in the electrolyte their effect is synergistic, they are often considered in the following classification:

(i) *Brighteners*. For a deposit to be bright the microscopic roughness of the deposit must be low compared with the wavelength of the incident light so that it is reflected rather than scattered. Brighteners are commonly used in relatively high concentration ( $\text{g l}^{-1}$ ) and may result in substantial organic matter in the deposit. They usually cause the formation of an even, fine-grained deposit and hence may act by modification of the nucleation process.

For nickel deposition from a Watts bath (a weakly acidic bath containing sulphate and chloride), two types of brightener are recognized. The first are aromatic sulphones or sulphonates and they lead to bright deposits without lustre and also reduce stress. The second are molecules containing  $-\text{C}\equiv\text{N}$ ,  $>\text{N}-\text{C}=\text{S}$  or  $>\text{C}=\text{O}$  entities, e.g. thiourea and coumarin, which produce deposits with a high lustre but also raise the stress and brittleness in the metal. In practice both types are used in combination. The aromatic sulphonates are also brighteners for tin or copper.

(ii) *Levellers*. These produce a level deposit on a more macroscopic scale and act by adsorption at points where otherwise there would be rapid deposition of metal. Thus adsorption of additives occurs preferentially at dislocations because of a higher free energy of adsorption and at peaks because the rate of their diffusion to such points is enhanced; the adsorbed additive will reduce the rate of electron transfer.

(iii) *Structure modifiers*. These additives change the structure of the deposit and maybe even the preferred orientation or the type of lattice. Some are used to optimize particular deposit properties and others to adjust the stress in the deposit (stress is due to lattice misfit). The latter are often called stress relievers.

(iv) *Wetting agents*. These are added to accelerate the release of hydrogen gas bubbles from the surface. In their absence, the hydrogen which is often evolved in a parallel reaction to metal deposition can become occluded in the deposit causing, for example, hydrogen embrittlement.

### 7.1.5 Typical electroplating processes

Some of the many applications of electroplated metals are shown in Table 7.1. Each will require somewhat different deposit thickness and characteristics and

Table 7.1 Some applications of electroplated metals.

Electrodeposited metal	Application
Tin	Protective coating for steel cans used for food packaging, etc. Electrical contacts for soldering
Nickel	Protection and decoration of household items. Protection and repair of engineering components. Undercoat for Cr plating. Protection of chemical plant
Copper	Contacts and circuitry in the electronics industry. Undercoat for Ni and Cr plating. Decoration of consumer goods
Chromium	Decoration and protection of household items, car components, screws, etc., usually on Ni or Cu undercoat. Wear-resistance surfaces in tools, machine parts and valves
Cadmium and zinc	Corrosion protection of steel- and iron-based alloys
Silver and gold	Decoration. Mirrors and reflectors. Electrical contacts

hence a different bath formulation and electrolysis conditions. Table 7.2 therefore sets out some typical plating conditions for six metals which are extensively electroplated. For several metals there is a choice of an acidic, non-complexing bath which is used for rapid plating of simple shapes, e.g. flat surfaces and wires, and a complexing medium which gives a lower plating rate but the additional throwing power essential for intricate surfaces. Moreover for several parameters only a range is given since the value will depend on the deposit properties sought.

From Table 7.2 it can be seen that most plating processes operate at a current density between 10 and 70 mA cm<sup>-2</sup>, a value which is low compared with that for the preparative electrolytic processes. Since, in general, the thickness of the deposit required will range between 0.01 and 100 µm, depending on the application, the electroplating procedure will only last from a few seconds to thirty minutes. The current density for silver deposition is particularly low while those for nickel in sulphamate media and tin in the chloride/fluoride bath are markedly higher. The value for chromium is deceptive because of the low current efficiency; most of the current is hydrogen evolution. For most metals, the table also shows that the current efficiencies are good and that the use of additives and temperatures slightly above ambient is normal.

The plating of some alloys is also possible although the limitations are greater and the control of the conditions is more critical. It is essential to use a complexing bath selected to make the deposition potentials of the components of the alloy the same although the *I-E* curves for the individual metals are not always a good guide

Table 7.2 Some typical electroplating conditions.

Metal	Electrolyte (g l <sup>-1</sup> )	T (°C)	I (mA cm <sup>-2</sup> )	Current efficiency (%)	Additives	Anode	Applications
Cu	(a) CuSO <sub>4</sub> (200–250) H <sub>2</sub> SO <sub>4</sub> (25–50)	20–40	20–50	95–99	Dextrin, gelatin, S-containing brighteners	P-containing rolled Cu	Not suitable for iron and iron alloy substrates. High <i>I</i> but low throwing power. Additives essential
	(b) CuCN (40–50) KCN (20–30) K <sub>2</sub> CO <sub>3</sub> (10)	40–70	10–40	60–90	Na <sub>2</sub> SO <sub>3</sub>	O <sub>2</sub> -free, high- conductivity Cu	Good throwing power, deposits adhere well and are bright. Used as undercoat. Cyanide decomposes at anode
Ni	(a) NiSO <sub>4</sub> (250) NiCl <sub>2</sub> (45) H <sub>3</sub> BO <sub>3</sub> (30) pH 4–5	40–70	20–50	95	Coumarin, saccharin, benzenesulphonamide, acetylene derivatives	Ni pellets or pieces	H <sub>2</sub> evolved with deposition. Additives depend on purpose of deposit. Medium throwing power
	(b) Ni sulphamate (600) NiCl <sub>2</sub> (5) H <sub>3</sub> BO <sub>3</sub> (40) pH 4	50–60	50–400	98	Not essential. Naphthalene-1,3,6- trisulphonic acid	Ni pellets or pieces	Good throwing power. Some H <sub>2</sub> . With additives, mirror finish at 400 mA cm <sup>-2</sup>
Ag	KAg(CN) <sub>2</sub> (40–60) KCN (80–100) K <sub>2</sub> CO <sub>3</sub> (10)	20–30	3–10	99	S-containing brighteners	Ag	Good throwing power. Functional or decorative

Sn	(a) $\text{SnSO}_4$ (40–60) $\text{H}_2\text{SO}_4$ (100–200)	20–30	10–30	90–95	Phenol, cresol	Sn	Poor throwing power. Additives essential
	(b) $\text{Na}_2\text{SnO}_3$ (50–100) $\text{NaOH}$ (8–18)	60–80	15–20	70		Sn (control)	Good throwing power but uses twice charge ( $\text{Sn}^{\text{IV}}$ rather than $\text{Sn}^{\text{II}}$ )
	(c) $\text{SnCl}_2$ (75) $\text{NaF}$ (37) $\text{KF}$ (50) $\text{NaCl}$ (45) pH 2.5	65	50–200	90	$\text{SCN}^-$ , disulphono- naphthalimic acid	Sn	Reasonable throwing power. More stable than (a). Rarely used
Zn	(a) $\text{NH}_4\text{ZnCl}_3$ (200–300) $\text{NH}_4\text{Cl}$ (30–50) pH 5	25	10–40	98	Dextrin, organic additives	Zn	Poor throwing power. Additives essential
	(b) $\text{ZnO}$ (20–40) $\text{NaCN}$ (60–120) $\text{NaOH}$ (60–100)	15–30	10–50	70–90	Glycerin, organic additives	Zn	Good throwing power
	(c) $\text{ZnO}$ (6–10) $\text{NaOH}$ (70–100)	20–40	10–30	60–80	Organic additives	Zn	Medium throwing power. Non-toxic. Additives essential
Cr	(a) $\text{CrO}_3$ (450) $\text{H}_2\text{SO}_4$ (4)	45–60	100–200	8–12	Complex fluorides to increase efficiency	$\text{Pb}/\text{Sb}$ or $\text{Pb}/\text{Sn}$ coated with $\text{PbO}_2$	Need to reoxidize $\text{Cr}^{3+}$ formed. Decorative finish.
	(b) $\text{CrO}_3$ (200) $\text{H}_2\text{SO}_4$ (2)	40–55	100–200	10–15	$\text{Pb}/\text{Sb}$ or $\text{Pb}/\text{Sn}$ coated with $\text{PbO}_2$	Poor throwing power Hard, wear-resistant deposit	

Table 7.3 Typical conditions for plating alloys

Alloy	Electrolyte (g l <sup>-1</sup> )	T (°C)	I (mA cm <sup>-2</sup> )	Current efficiency (%)	Anode	Comments
70% Cu/30% Zn (brass)	K <sub>2</sub> Cu(CN) <sub>3</sub> (45) K <sub>2</sub> Zn(CN) <sub>4</sub> (50) KCN (12)	40–50	5–10	60–80	Brass	Additives essential. Close control of bath + plating conditions essential
	Sodium tartrate (60)					
40% Sn/60% Cu (bronze)	K <sub>2</sub> Cu(CN) <sub>3</sub> (40) Na <sub>2</sub> SnO <sub>3</sub> (45) NaOH (12) KCN (14)	60–70	20–50	70–90	Bronze or mixture of Sn and Cu anodes	Additives essential
65% Sn/35% Ni	NiCl <sub>2</sub> (250) SnCl <sub>2</sub> (50) NH <sub>4</sub> F.HF (40) NH <sub>4</sub> OH (30)	60–70	10–30	97	Separate Ni and Sn plates	Good throwing power. Deposit composition not dependent on electrolysis conditions over a wide range
80% Ni/20% Fe	NiSO <sub>4</sub> (300) FeSO <sub>4</sub> (20) H <sub>3</sub> BO <sub>3</sub> (45) NaCl (30) pH 3–4	50–70	20–50	90	Ni + Fe as pieces	Close control of [Ni <sup>2+</sup> ]/[Fe <sup>2+</sup> ] in bath essential

for suitable baths. The alloy deposited clearly depends on the electrolyte, bath temperature, current density and the ratio of the metal ions in solution. The latter is often critical, the exceptions being deposits which are intermetallic compounds, e.g. SnNi, although the deposit composition is not the same as that of the solution. Also the current densities are towards the low end of the metal plating range and many of the alloys do not dissolve anodically so that it is necessary to use anodes of both metals. The conditions for plating four alloys are summarized in Table 7.3.

The plating of composites is a recent development but one which is likely to be of increasing importance because it is found that the occlusion of solid particles into the metal deposit can greatly enhance the wear resistance and friction properties of the deposits. Solids such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{WC}_2$ , TiC and PTFE present in solution as particles 0.5–5.0  $\mu\text{m}$  in diameter are entrapped in a deposit by rapid electroplating. They are usually present in 2–10 vol. %.

### 7.1.6 The overall plating process

To obtain a good electrodeposit it is essential for the surface to be correctly prepared. A typical procedure will have the following steps:

- (a) Cleaning with organic solvents and/or aqueous alkali. In some situations the aqueous cleaning is assisted by making the surface cathodic ( $30\text{--}100 \text{ mA cm}^{-2}$ ) at  $60\text{--}80^\circ\text{C}$ ; this has the effect of increasing the pH locally at the surface and catalysing the hydrolysis of fats while the hydrogen evolved also removes organics by electrofloatation (see Chapter 11).
- (b) Where the surface is covered by oxides as a result of corrosion, it is cleaned by immersion in acid; again electrochemical enhancement is possible by making the surface anodic ( $\sim 100 \text{ mA cm}^{-2}$ ).
- (c) Rinsing with water.
- (d) Electroplating.
- (e) Rinsing and drying.
- (f) Quality control.

Where the surface is particularly bad, these steps may be preceded by an abrasive or ultrasonic clean.

Three approaches are used for electroplating depending on the scale of operation and the size of the articles to be handled. In large-scale plants which carry out the same job repetitively, the articles or components to be plated are mounted on a jig specifically designed for the job and already including any essential auxiliary anodes (Fig. 7.9). The jig is then moved from tank to tank automatically and according to a preset programme to complete the cleaning and preparation of the surface, the electroplating and testing. This type of process is known as line plating. In vat plating, the process is not automated and the electroplating is carried out manually by shifting the jig between tanks containing the solutions for each step in the process.

When very small objects such as screws, nuts and bolts are to be plated this is usually carried out by barrel plating. They are loaded by weight into a perforated

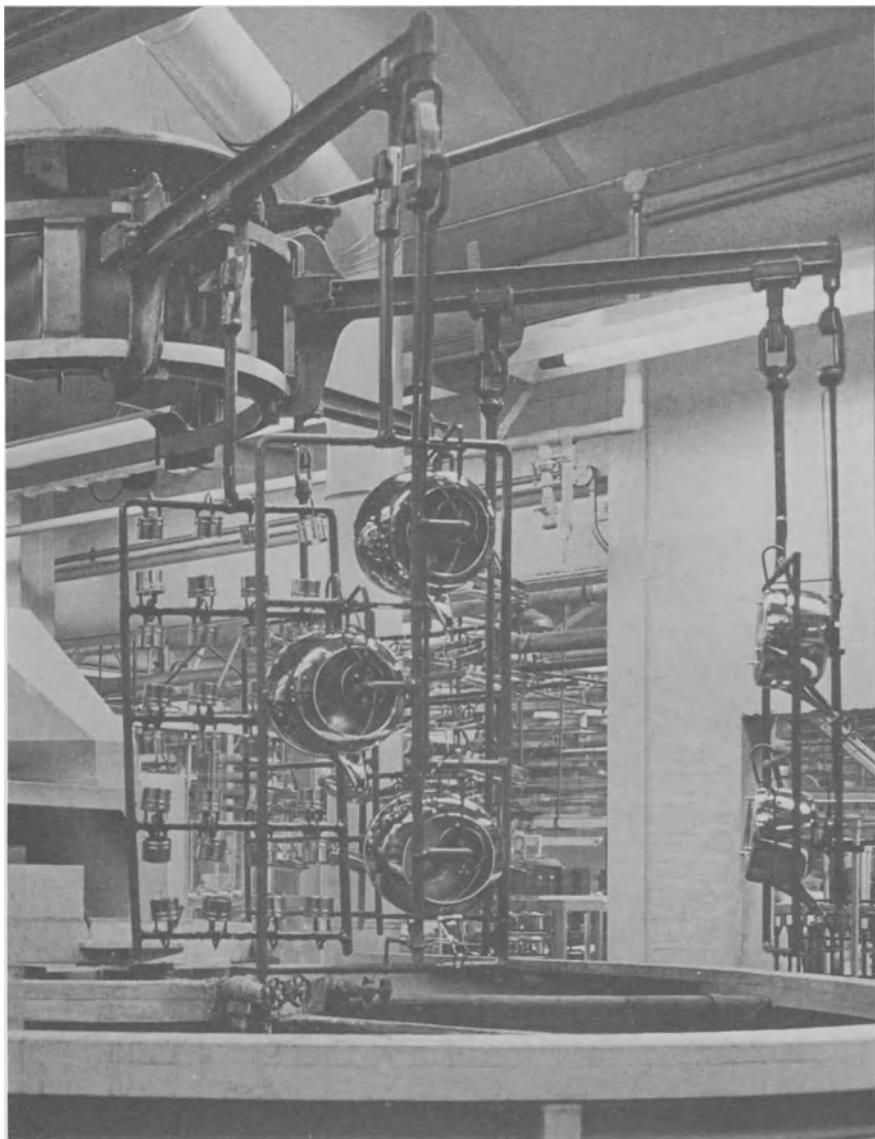


Figure 7.9 *Jig for nickel plating the interior and exterior of kettle bodies. Note the Pt/Ti auxiliary anodes inside the kettles. Photograph supplied by W. Canning Materials Ltd.*

barrel made either from metal, when it also acts as the cathode connection, or from plastic, when cathode contacts are placed inside the barrel. The barrel is then rotated slowly (5–20 revolutions per minute) in the various solutions, and in the plating step an even deposit is obtained by the rotation of the drum causing the articles to have a random orientation with respect to the anode. Barrel plating is

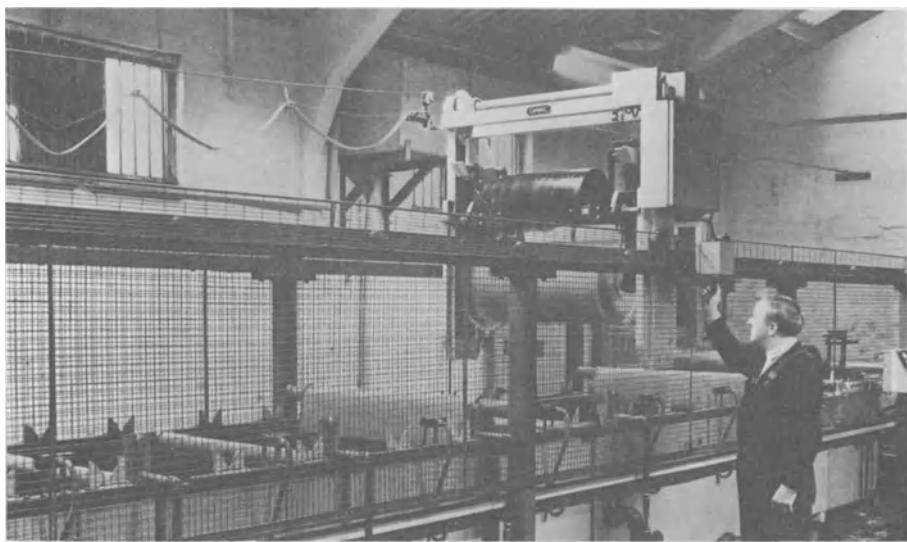


Figure 7.10 *Semi-automatic barrel plating plant. Polyethylene barrel filled with screws being moved from washing tank to electroplating bath.*

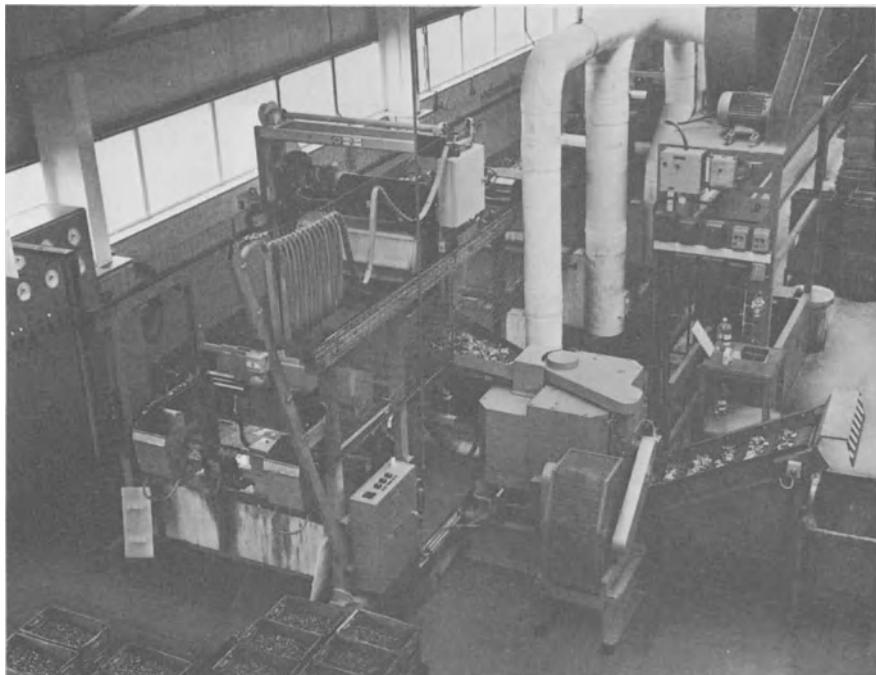


Figure 7.11 *Fully automated barrel plating bath, showing components passing from the plating line to a drying oven.*

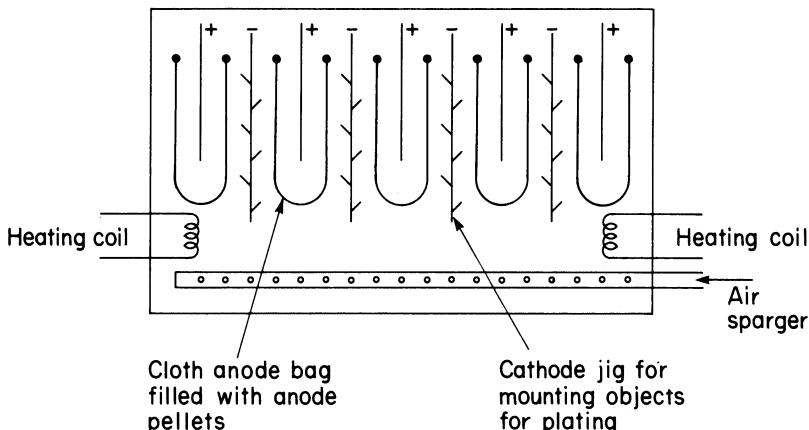


Figure 7.12 *Schematic diagram of an electroplating tank.*

carried out in both semi- and full automated plating lines (see Fig. 7.10 and 7.11).

The electroplating step is normally carried out in a simple rectangular tank of volume between 100 and 2000 litres (Fig. 7.12). They should be lagged and have provision for heating the electrolyte. It is also frequently advantageous to introduce convection into the plating tank and, where oxygen does not interfere with the metal deposition, bubbling air through the electrode is the cheapest procedure. The jigs are mounted in the tank with anodes, in bags of cotton or plastic to retain anode sludge, placed symmetrically about the cathode jig; the positioning of the jigs, main anodes and auxiliary anodes may be based on experience or a detailed computer optimization depending on the cost of the product and the scale of the operation.

In larger facilities, the tanks will have a loop for continuous filtering of the electrolyte and the bath temperature, pH and current will be monitored. The concentration of metal ions will be determined by external analysis on a regular basis. The most modern plants will also have an effluent control plant to deal with liquids resulting from washing and spillages and sludges removed from the tanks. The heavy metals are still commonly precipitated with caustic soda and the solids then allowed to settle, although the modern trend is towards direct electrolytic metal recovery from the effluent (see Chapter 11). The control units for the electroplating baths operate at a current between 100 and 10 000 A and a voltage of -8 to -12 V.

## 7.2 ANODIZING

Anodizing is the process of forming a surface oxide film by electrochemical oxidation. It is used as a surface finishing technique particularly for aluminium but also for titanium, copper and steel, and for the manufacture of electrolytic capacitors based on aluminium, tantalum and niobium.

### 7.2.1 The protection of aluminium

Aluminium is a very important metal. It is light, has a high conductivity and mechanical strength and is widespread in nature. Its extraction is, however, difficult and energy-intensive and it is, therefore, fortunate that there is a simple and cheap way of surface finishing aluminium which gives it both corrosion resistance and a pleasant appearance, i.e. anodizing. Indeed, as a finished product, aluminium compares well with steel as regards energy consumption per ton. Maybe 5–10% of the aluminium produced is anodized prior to sale for use in the construction of buildings, for household articles and for power transmission.

For these applications, aluminium is anodized in an acid electrolyte, usually 10% sulphuric acid although chromic acid and oxalic acid are also employed. The latter at low current density gives excellent results and is used for aluminium which is to be coloured. Chromic acid is preferred for the anodizing of complex shapes where thorough rinsing of the surface after oxidation is a problem; aluminium will corrode in sulphuric acid but not in chromic acid.

Anodizing is carried out in simple tanks very similar to those used for electroplating and the cathodes are steel or copper; the temperature is 20–25°C. The voltage is programmed to increase from 0 to –50 V so as to maintain an anode current density of 10–20 mA cm<sup>-2</sup>; the increasing voltage is required to force the aluminium oxide to continue to thicken to the 10–100 µm layer needed to impart good corrosion resistance. Throwing power is not a problem since once a partial layer of oxide is formed that area will passivate and further oxide will most readily

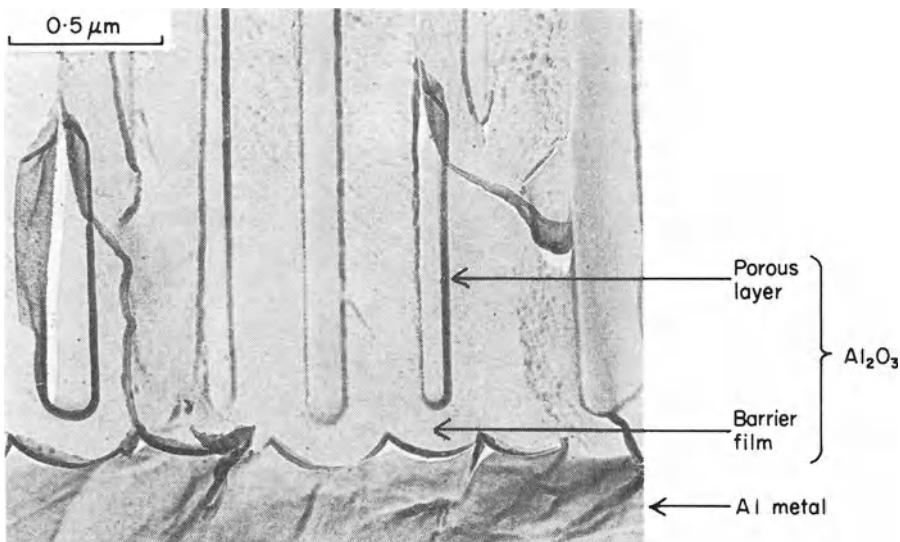


Figure 7.13 Transmission electron micrograph of a carbon replica of a fracture section through an anodic film formed at Al for 70 min at 150 V in phosphoric acid (0.5 M). Photograph supplied by Dr G. E. Thompson, Corrosion and Protection Centre, UMIST.

be formed on the parts of the surface as yet uncovered. Formation of the 10–100 µm layer will take about one hour.

The aluminium oxide formed in this process has a complex form. It is partially hydrated and has a two-layer structure. At the surface of the metal there is a thin (perhaps 0.025 µm), compact boundary layer and then there is a porous overlayer. The latter has a very open structure and structural techniques (see Fig. 7.13) show it to consist of a collection of parallel tubes perpendicular to the surface. After the anodic oxidation the metal is dipped into a caustic soda solution to precipitate aluminium hydroxide in the pores and hence produce a more robust layer.

Aluminium can also be produced in a number of coloured finishes. Two types of method are used. In the first, an organic dye is adsorbed on the freshly anodized surface and it is then sealed with boiling water. In the second, a metal, either nickel or cobalt, is deposited into the pores using an AC current. The resulting colours are due to interference effects and a wide range of tints can be produced by variation of the plating time and conditions. The best results are obtained using a sequence of anodizing → metal plating → anodizing.

As with plating the aluminium must be prepared and cleaned prior to anodizing.

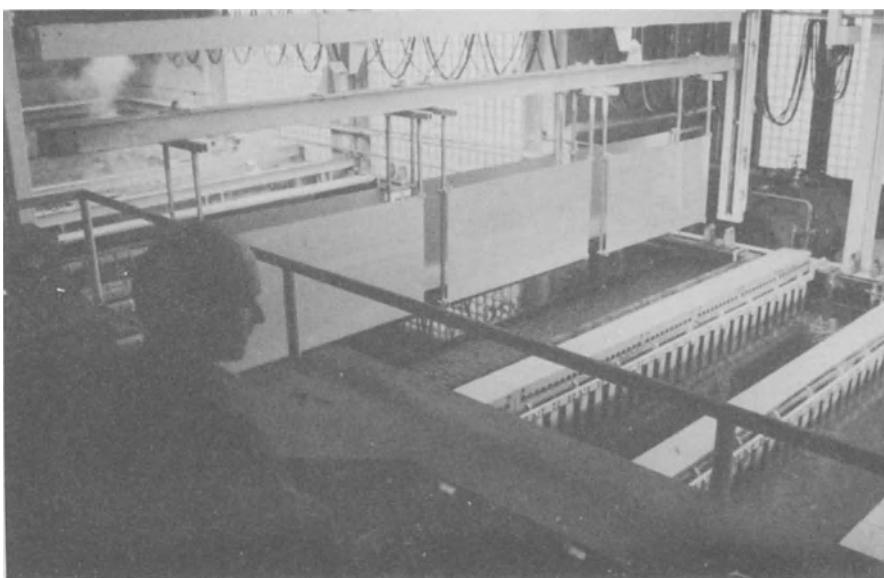


Figure 7.14 *The automated aluminium anodizing line at Alcan Benelux, Raeren, Belgium. Photograph supplied by the Aluminium Company of Canada.*

### 7.2.2 The manufacture of capacitors

For an electrolytic capacitor, the oxide requires very different properties from those discussed above. The oxide layer should be relatively thin but very compact so as to act as an effective barrier to electron transfer.

Thus, aluminium-based capacitors are manufactured by anodizing in a neutral medium, phosphate or borate, and a voltage source capable of an output of 500 V is required to thicken the layer to the 1 µm generally employed.

### 7.2.3 Electropolishing

Electropolishing is a process closely related to anodizing which is used to produce metal articles with a highly reflecting mirror finish. Again the most common metal to be electropolished is aluminium, but the procedure is also used for steel, brass, copper and nickel/silver alloy.

The article to be polished is made the anode with a current density in the range 100–800 mA cm<sup>-2</sup> in a bath of phosphoric acid at 60°C for a period of 5–10 min. The cathode material is not critical and may be steel, copper or lead. The mechanism of electropolishing is thought to involve both selective anodic dissolution (the potential distribution will favour corrosion of the surface at peaks rather than in troughs) and oxide film formation. The conditions are somewhat more forcing than those used in anodizing.

Electropolishing leads to extremely reflective surfaces which, unlike mechanically polished surfaces, are stress free. Before the process can be carried out successfully, however, the surface must already be smooth since macroroughness cannot be removed.

## 7.3 OTHER RELATED SURFACE FINISHING TECHNIQUES

Electrochemical variations of several other surface finishing methods are used to a limited extent and these will be considered in this section.

### 7.3.1 Electrochemical cleaning

This technique is used to remove grease and oil from metal surfaces. The medium is generally 5–10% caustic soda at 60–80°C and the surface is made cathodic (30–100 mA cm<sup>-2</sup>). The principles of operation include (i) a local increase in pH where the grease is sited and hence an increase in the rate of hydrolysis to water-soluble products, (ii) the evolution of hydrogen gas bubbles which rise to the surface and take organic particles with them, i.e. electroflotation.

### 7.3.2 Electrochemical pickling

In electrochemical pickling the objective is to remove rust and other oxides and sometimes to produce a uniform etch to produce adhesion of deposits. The surface is made anodic in an acid medium, e.g. H<sub>2</sub>SO<sub>4</sub> or FeCl<sub>3</sub>.

### 7.3.3 Phosphating and chromating

These processes produce a uniform layer of a passivating insoluble salt at the metal surface and are widely used as a preliminary treatment of steel, e.g. in car body manufacture. As the names suggest, the salts are either a phosphate or a chromate.

In some circumstances, the rate of formation of this layer is enhanced by carrying out the coating electrochemically with the surface as the anode. Commonly, however, the layer is sprayed on and dried.

#### 7.3.4 Metallidning

Metallidning is a deposition process carried out at elevated temperatures in a molten salt medium so that the deposited element diffuses into the lattice of the substrate. Elements of interest include nitrogen, boron, titanium and chromium, since the surfaces which result can be very hard and both wear and corrosion resistant. There have been extensive trials of electrochemical metallidning and it may be practised commercially to a limited extent.

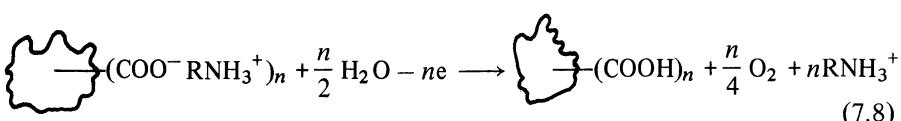
### 7.4 ELECTROPHORETIC PAINTING

An alternative approach to both the protection of surfaces from corrosion and the improvement of their appearance is to cover the surface with a crosslinked polymer containing solids and pigments, i.e. painting. Of course, most painting is carried out with a brush or a spray. When the surface to be covered is made of a conducting material, however, an electrochemical method known as electrophoretic painting becomes possible. In fact, paint for electrophoretic painting amounts to a few per cent of the total production, the major application being the undercoating of almost all car bodies.

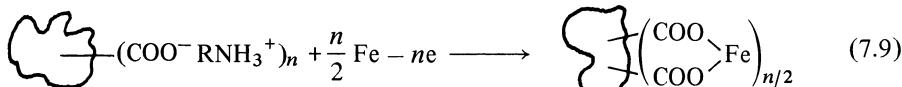
#### 7.4.1 Principles of electrophoretic painting

The medium for the electropainting process is water, sometimes containing a low percentage of an organic solvent such as cellosolve. The paint is a polymer containing (i) acidic or basic groups which may be solubilized usually to give micelles by the addition of base or acid respectively, (ii) some inorganic solids such as copper chromate, titanium dioxide or carbon black, and (iii) an organic pigment to give the desired colour; the bath contains in total about 10% solids. When a voltage is applied between two electrodes, deposition will occur at one of them; depending on the charge on the polymer, one will observe anodic or cathodic electrocoating. The following steps in the mechanism are important:

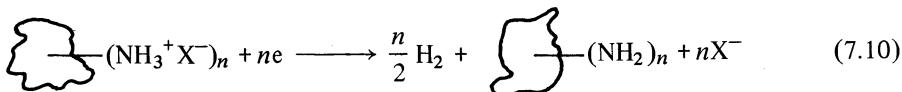
- (a) Migration of the charged micelles to the electrode of opposite polarity,
- (b) Neutralization of the charge at the electrodes. In anodic electrocoating, the major process will be of the type



although some corrosion of iron-based materials may also occur, i.e.



and there is also the possibility of neutralization of the micelles by the Kolbe reaction. In cathodic electrocoating the main reaction will be:



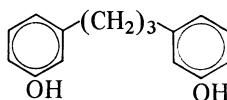
(c) Precipitation of the neutralized polymer with occlusion and adsorption of the inorganic solids and the organic pigments.

(d) Removal of water from the polymer layer by electroosmosis in the strong potential field across the non-conducting layer.

The product of the electrophoretic painting process is a paint layer which adheres strongly to the metal, contains over 90% solids and cures very rapidly on removal from the bath. Again, throwing power is not a problem because the deposit is non-conducting; deposition will naturally occur at uncovered surfaces and a high voltage is required to force the polymer layer to grow to the required thickness.

#### 7.4.2 Anodic versus cathodic electropainting

Commercial electropainting only dates from the early 1960s and the first processes to be introduced used anodic deposition. Some typical paint formulations would contain (i) polycarboxylic acids based on acrylic acid as monomer solubilized by an organic amine, (ii) alkyds, i.e. branched polyesters based on naturally occurring long-chain carboxylic acids and polyalcohols, e.g. glycerol, and (iii) epoxy resins based on phenols, e.g.



and ethyleneglycolchlorhydrin,  $\text{ClCH}_2-\text{CH}_2\text{OH}$ . The latter two will be dissolved using potassium hydroxide. The anodic process gives a good, reproducible finish but causes some corrosion of the underlying metal, see equation (7.6) above.

The cathodic process is, as yet, only used by a few US companies. There is no possibility that the electrode reaction will lead to corrosion and the throwing power of this version is even better than the anodic process. However, the paint formulations which are currently employed are complex and require some organic solvent. Moreover, the adhesion of the deposit requires improvement. Hence, although it would seem that in the long term cathodic processes will be expected to predominate, further development is necessary.

#### 7.4.3 Why electropaint?

The main advantage of electrophoretic painting processes are:

(a) The paints are water based, non-toxic and present no fire risk. Moreover, because the paints are relatively low concentration in solids and owing to the nature

of the process (tank vs spray), effluent disposal problems are a minimum.

(b) The throwing power is good and it is easily possible to obtain complete coverage of even the most complex surfaces, e.g. in deep recesses or the inside of a pipe.

(c) It is well suited for automation.

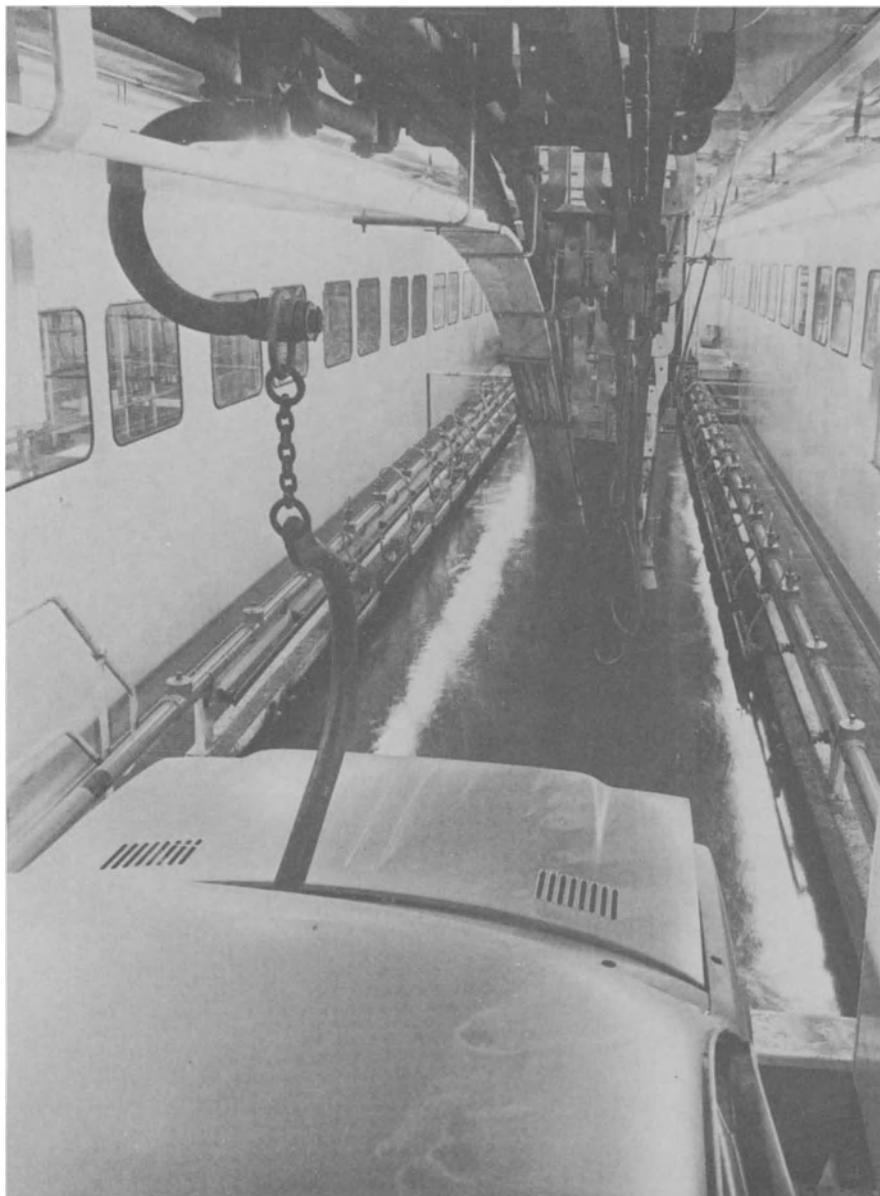


Figure 7.15 *A Metro car body about to enter an electrophoretic painting bath at BL's Longbridge Plant. Photograph supplied by ICI Ltd, Paints Division.*

On the other hand, it is obviously only possible to electropaint conducting surfaces and hence the process is limited to a single coat. Also, the colour range is more restricted than with conventional painting.

#### 7.4.4 The technology of electrophoretic painting

Two factors determine that the technology of electrophoretic painting is simple. First, the high throwing power which removes any need for good cell geometry and, secondly, the low charge and hence energy consumption compared with other steps in the overall surface treatment of steels. Hence, the anodic process uses a simple rectangular tank which also acts as the cathode. The cathodic process requires a more complex cell with steel or graphite anodes in anode boxes made of membranes. Both processes will lead to a dilution of the polymer as paint is deposited and it is, therefore, necessary to remove water. This is done continuously using ultrafiltration (i.e. pressure to force the water through a membrane). Plants for undercoating car bodies are usually fully automated and the car body will move slowly through the paint tank with the appropriate voltage applied between the car body and the tank wall (see Fig. 7.15).

Typically, a voltage of  $-200$  to  $-300$  V is used and the current at a stationary anode will drop from  $70 \text{ mA cm}^{-2}$  to  $5 \text{ mA cm}^{-2}$  in the steady state after a few seconds. It then takes 2–5 min to build up a paint layer of  $20 \pm 5 \mu\text{m}$ .

As in electroplating, the electrolysis step in electrophoretic painting is only one of a complex sequence which makes up the total surface protection sequence. Thus, for example, the steel in a car body will be treated as follows:

- (a) Degrease, clean and dry in oven.
- (b) Spray zinc phosphate and dry in oven.
- (c) Electropaint, cure in low-temperature oven.
- (d) Spray on top coat and cure in oven.

#### FURTHER READING

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6. Kuhn, A. T. (ed.) (1971) *Industrial Electrochemical Processes*, Elsevier, London.

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# 8 Metals Processing

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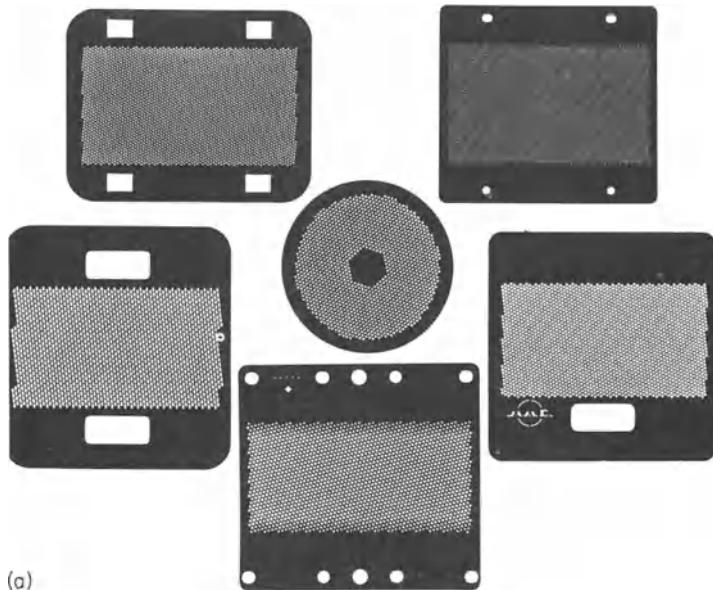
Several electrochemically based methods are employed in the metals processing industry because of their ability to manufacture metal articles or components which are difficult or impossible to produce by traditional mechanical workshop techniques. The most important methods are electroforming and a group used for the controlled removal of metal, i.e. electrochemical machining, grinding and deburring.

Because the principles of electrochemistry are foreign to an industry based on mechanical engineering and the electrolytes necessary for an electrochemical process cause corrosion in the workshop, these methods have generally been developed by specialist companies or sections. This has minimized their impact on the engineering industry as a whole and their full potential has yet to be realized.

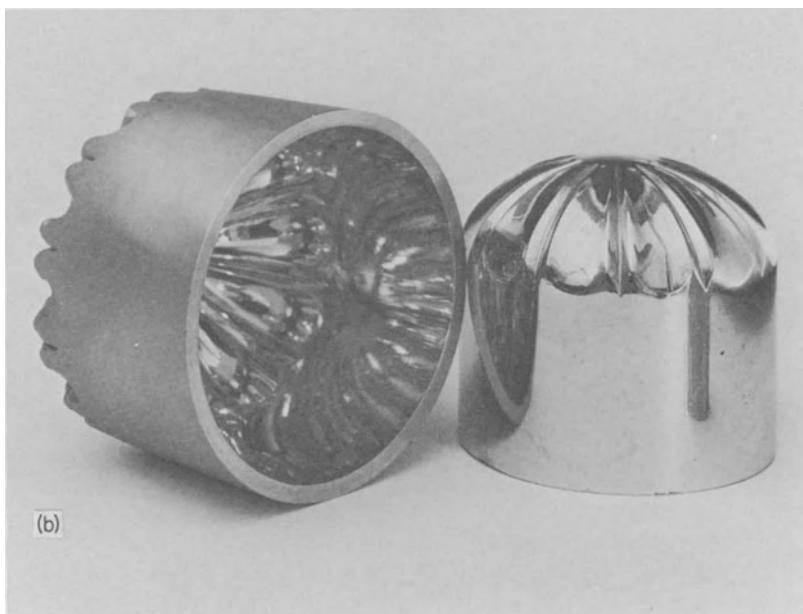
## 8.1 ELECTROFORMING

Electroforming is the complete manufacture of an article or component by electrodeposition. An early application of the method was the production of thin foils. Their cost when manufactured by conventional rolling is inversely proportional to thickness; in direct contrast the cost of producing the foil by electrodeposition is expected to increase with the weight of metal and therefore the thickness of the foil and it is therefore not surprising to find that it is economic to produce thin foil by electroforming. Now electroforming is used to produce a range of foils and gauzes, seamless perforated tubes (for printing materials) and endless plain or perforated bands as well as objects of more complex shape such as waveguides, record stampers, moulds and dyes. Figure 8.1 illustrates the complex shapes which may be electroformed.

As in the case of electroplating, the physical, chemical and mechanical properties of the electrodeposited metal must be controlled (in electroforming, the hardness, strength, stress and ductility will be of particular importance) and organic additives are used extensively for this purpose. It is necessary to have even greater control of the deposition bath and conditions. Moreover, in electroforming the weight of metal deposited greatly exceeds that in a plating process. The economics of the process are, therefore, determined to a greater extent by the current density, the



(a)



(b)

Figure 8.1 Examples of objects which are commercially electroformed: (a) electric razor foils and (b) a glass mould. Photographs supplied by Berec Components Ltd.

current efficiency and the cell design since these determine the rate of production and the energy requirement.

### 8.1.1 The electroforming process

The fundamental principles of electroforming are identical to those of electroplating and hence much of the discussion in the last chapter is again relevant. Rather than seeking an even deposit, however, the objective is to plate the metal in an uneven but controlled manner so as to produce the desired shape.

The metal is deposited onto a mandrel which for some products, e.g. gauzes, will be a mixture of conducting and non-conducting surfaces. For the forming of many products the mandrel will also be of a shape and size determined by the process designer who may further make use of other aids when producing complex shapes. These might include:

- (a) Shaped or conforming anodes.
- (b) Auxiliary anodes.
- (c) Non-conducting shields in the anode–mandrel gap to modify the local current density and hence the distribution of metal.
- (d) ‘Robber’ cathodes, i.e. cathodes which will not be part of the formed product and which act so as to reduce deposition at the part of the mandrel close to them. Their use will cause loss of both current and metal efficiency and hence should, whenever possible, be avoided.

It can be seen that the initial design of electroforming processes for complex shaped products will be difficult. Originally the electrodes and shields were designed and positioned on the basis of experience and ‘trial and error’. Now computer-aided design techniques have greatly shortened this approach and complex shapes can be formed reproducibly and to very close tolerances in a single stage.

It is clearly essential to separate the formed product from the mandrel without damage to the product and, if possible, to the mandrel since it can then be re-used. This is generally accomplished by using a cathode which is covered by a natural or chemically induced thick oxide layer. Suitable materials include titanium, chromium and steel. For some products, their shape predetermines that a permanent mandrel cannot be used. Non-permanent mandrels have to be constructed of a material which can be removed from the inside of the product and several techniques have been used. The non-permanent mandrel may be made from a low-melting-point metal (e.g. Zn, Al or their alloys), a metal which may be removed by chemically etching or a non-metallic material (e.g. perspex, PVC or epoxy resins) soluble in organic solvents and plated by electrodeless deposition with a layer of silver or copper to make it conducting.

Mandrels for perforated products and gauzes must be made so that the surface has the necessary arrangement of conducting and non-conducting zones. This is usually achieved by photoresist techniques. The prospective mandrel is covered with a thin layer of a liquid which may be hardened by a photochemical reaction and then exposed to the appropriate pattern of light of the required wavelength.

The remaining unreacted liquid is washed away to leave a metal surface partially covered by a resistive film. This patterned mandrel may then be modified by etching and machining.

### 8.1.2 Electroforming foil

The simplest electroforming process is that for manufacturing metal foil and the system is sketched in Fig. 8.2. The mandrel is a slowly rotating metal cylinder and the cell has a conforming anode so that the inter-electrode gap is constant. The anode may be dissolving pellets or rods or may be an inert electrode. The foil is separated from the mandrel by a knife system and is then passed through a roller system which keeps it taut.

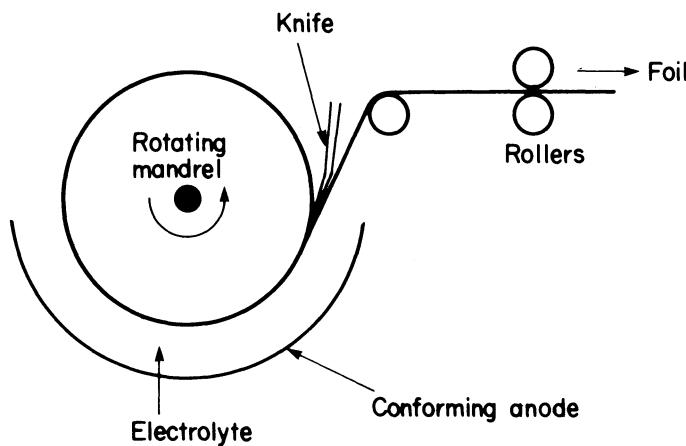


Figure 8.2 Principle of the process for electroforming metal foil.

The thickness of the foil will depend on the current density and the rotation rate of the drum. A system designed to produce nickel foil, 0.5 mm thick and employing a strongly stirred, concentrated sulphamate electrolyte so that a current density of  $0.5 \text{ A cm}^{-2}$  may be used will produce about  $1 \text{ m h}^{-1}$  of the foil. The width may be up to 1 m.

The process for mesh or gauze is similar except the mandrel must have the correct pattern of conducting and non-conducting zones.

### 8.1.3 Deposition baths for electroforming

The metal most used for electroforming is nickel, sometimes as an alloy with iron or cobalt, but the use of iron is increasing and copper is extensively used in the manufacture of components for the electronics industry. Electroforming with silver or gold is also carried out but only for the production of medals and in the jewellery trade.

For production on any scale, it is essential to have a plating bath which is capable of deposition at high current density without loss of throwing power or of quality of the product. The control of stress is particularly important in electro-forming because, if the metal is deposited with a high stress, the product will later change shape. It is the success of the concentrated sulphamate electrolyte for plating nickel at current densities in the range  $0.25\text{--}0.75\text{ A cm}^{-2}$  without stress in the deposit that has led to the predominance of nickel in forming processes. Additives are extensively used to obtain the properties of metal required and air agitation or stirring is universally used to increase the rate of transport of metal ions to the mandrel and hence the maximum current density.

As in electroplating, the deposition bath depends on the deposit characteristics necessary in the product and typical baths for three metals are shown in Table 8.1. Solution purity is particularly essential for electroforming.

Table 8.1 Typical electrodeposition baths for three metals

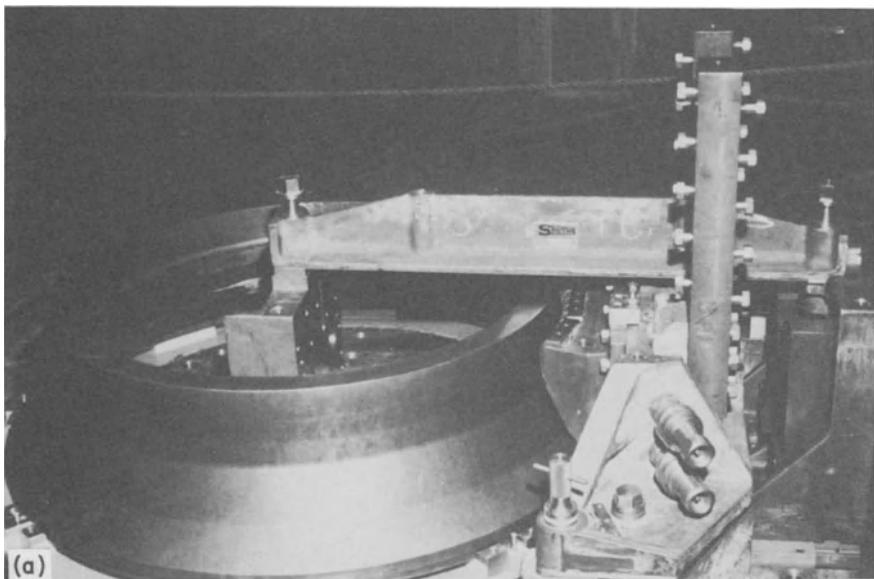
Metal	Bath	Maximum current density (mA cm $^{-2}$ )
Nickel	Standard Watts bath	85
	Conventional sulphamate	160
	Concentrated sulphamate	750
Copper	Cyanide	100
	Acid sulphate	100
	Pyrophosphate	40
	Fluoroborate	140
Iron	Acid chloride	150

### 8.1.4 Applications of electroforming in the printing industry

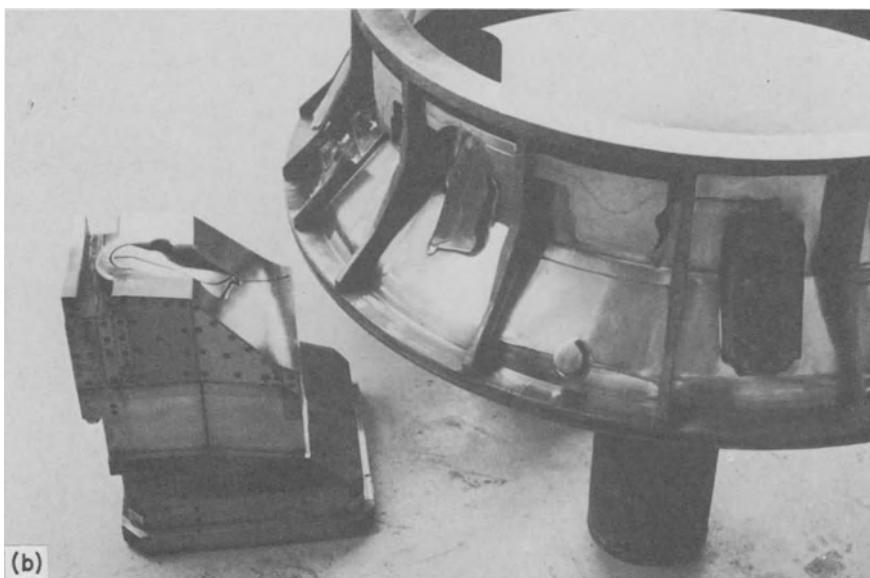
Another early application of electroforming which continues to be of importance is in the printing industry. It is used in a number of processes for forming or strengthening printing blocks. A typical procedure is that for the duplication of printing blocks in letterpress printing. An impression of the block is taken in plastic; this is then given a conducting surface by an electrodeless process and electroplated with nickel to form a plate  $20\text{ }\mu\text{m}$  thick which may be detached from the mould and given a backing of a Sn/Pb/Sb alloy to produce a block with the required rigidity. Other related processes use copper or tin/lead as the metal for the forming process.

## 8.2 ELECTROCHEMICAL MACHINING

In electrochemical machining, the removal of the metal to form a hole or other feature is by anodic dissolution (Fig. 8.3). Clearly for the process to have the

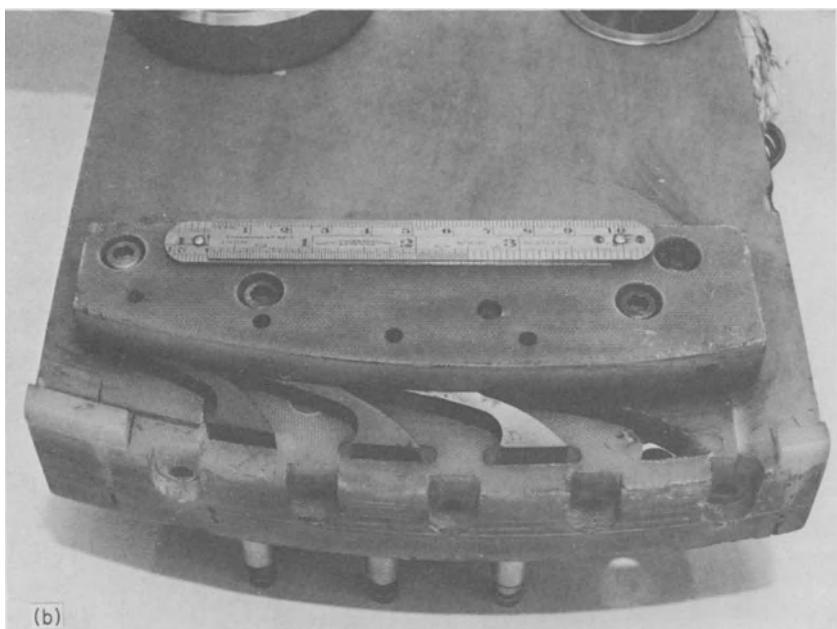
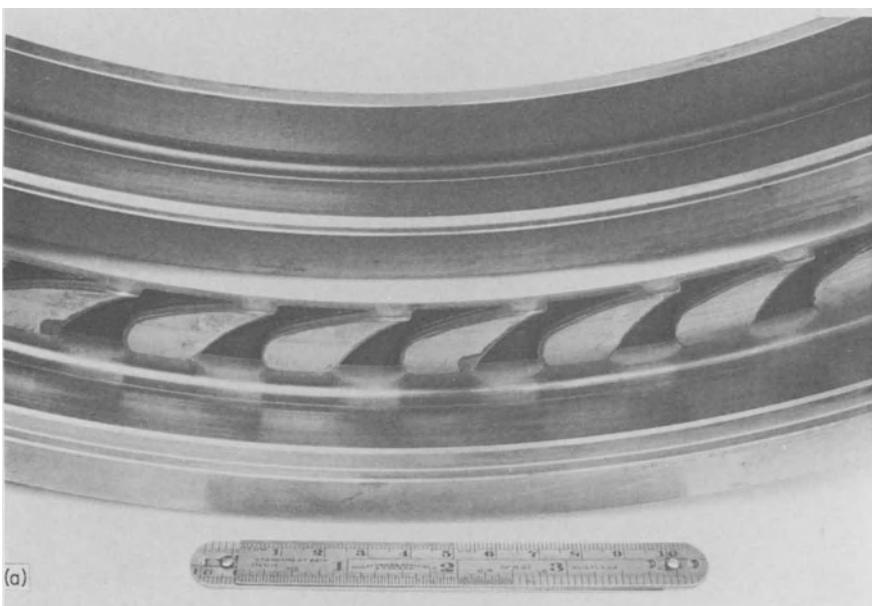


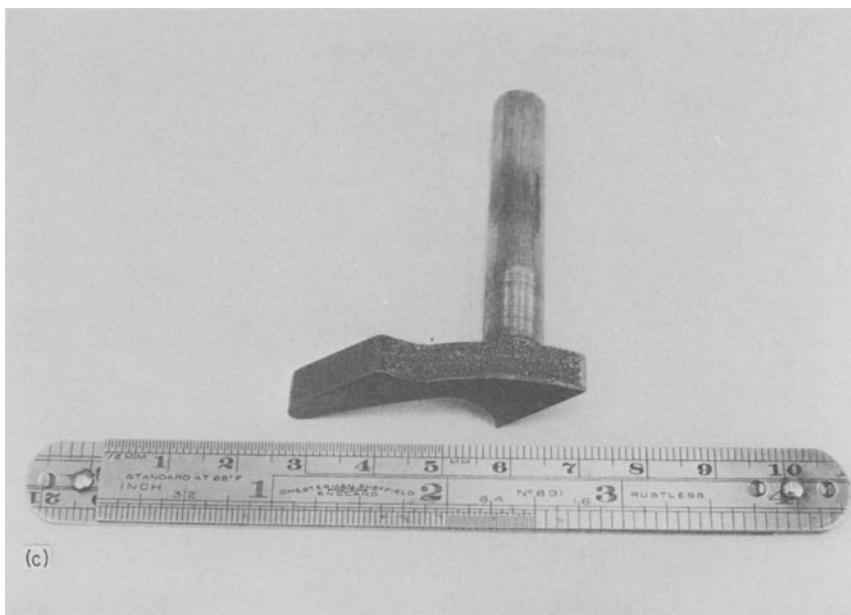
(a)



(b)

Figure 8.3 Aircraft engine casing (a) before and (b) after electrochemical machining. The cathode tool is also shown in (b). Photographs supplied by Rolls Royce Ltd, Aero Division.



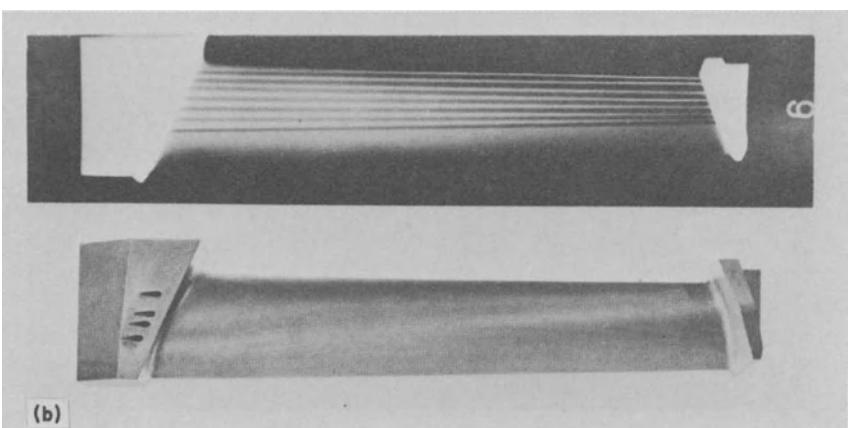
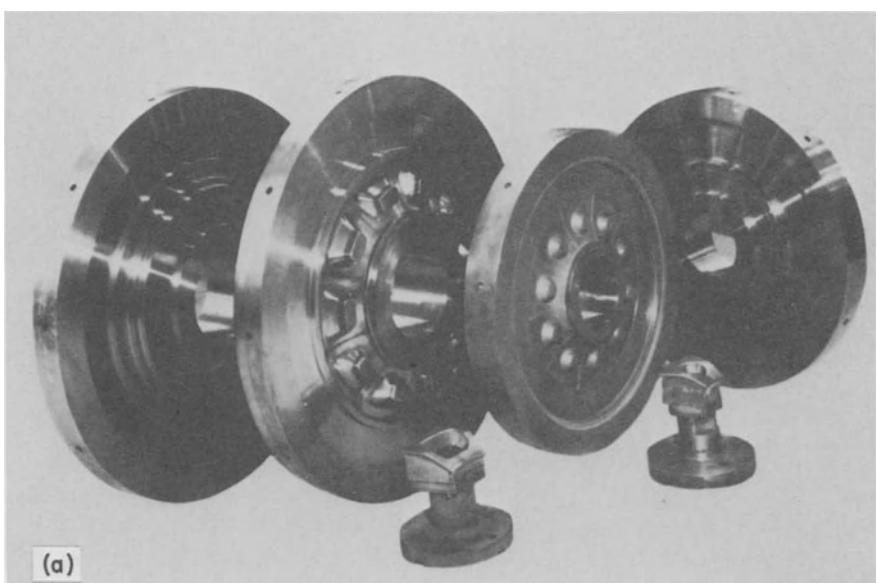


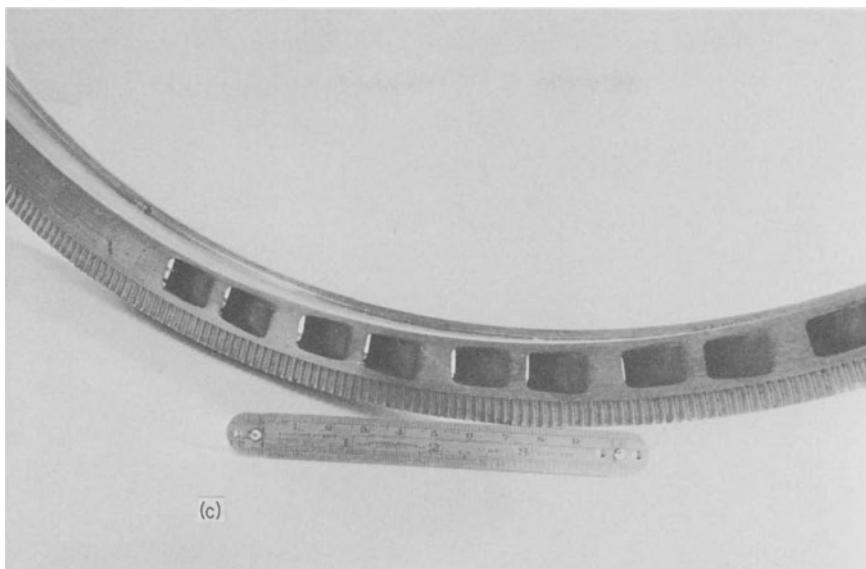
**Figure 8.4** *The electrochemical machining of air passageways in an aircraft engine component: (a) the final component, (b) the mask and electrode assembly and (c) the cathode tool. Photographs supplied by Rolls Royce Ltd, Aero Division.*

accuracy to be useful in engineering, the metal removal must occur under totally controlled conditions. This is possible to good tolerances but requires the design of a cathode, known as the tool, for each job.

Electrochemical machining is a recent innovation, the practice dating back less than twenty-five years. Much of the driving force for its development has come from the aerospace industry with its requirement to machine very hard alloys (e.g. those based on Ti and Fe/Co/Ni/Cr) to produce components able to perform a function reliably but also having minimum weight; this specification often leads to components of very complex shape. The alloys which must be employed cause problems in conventional machining because of the low rate of metal removal and the short tool life. Electrochemical machining is, however, based on different properties of the metal independent of its hardness and it is only necessary to find an electrolyte where the alloy will dissolve anodically without passivation when the rate of metal removal may be estimated from Faraday's law.

Furthermore, electrochemical machining has other attractive features (Figs. 8.4 and 8.5). It may be used to machine many complex features and complicated contoured shapes (e.g. fine holes, angled holes, non-round holes, engine casings and turbine components) in a single operation to close tolerances and good repeatability. It is also used to carry out sensitive operations such as the cutting of hypodermic





**Figure 8.5 Components manufactured by electrochemical machining:** (a) turbine discs (the cathode tools to form the complex features are also shown), (b) turbine blade with longitudinal cooling holes formed by machining (the holes are seen on the X-ray of the blade and (c) angled square holes for air cooling. Photographs supplied by Rolls Royce Ltd, Aero Division.

syringe needles without causing distortion. Moreover in contrast to conventional metal working, electrochemical machining leaves the metal without scratches, tears, unwanted sharp edges or burrs and the surface is almost without stress.

The main drawback to electrochemical machining lies in the need to design a tool (cathode) for each new job. Moreover the design process to obtain the correct current density distribution remains a skilled art rather than a science; it is often necessary to test the tool and to modify it by trial and error. In addition the need to use large volumes of electrolyte solutions does not fit in well to a mechanical workshop. However carefully they are handled, they lead to corrosion in the environment.

### 8.2.1 An electrochemical machining system

In the electrochemical cell the workpiece is the anode and the tool is the cathode. The electrolyte is fed through the tool at a rapid flow rate,  $9\text{--}60 \text{ m s}^{-1}$ , in such a way that the supply of electrolyte is uniform over the surface being machined. In practice the electrolyte flow pattern is as important as the arrangement of conducting surfaces on the tool in determining the current density distribution and both factors must be considered in the design of the tool.

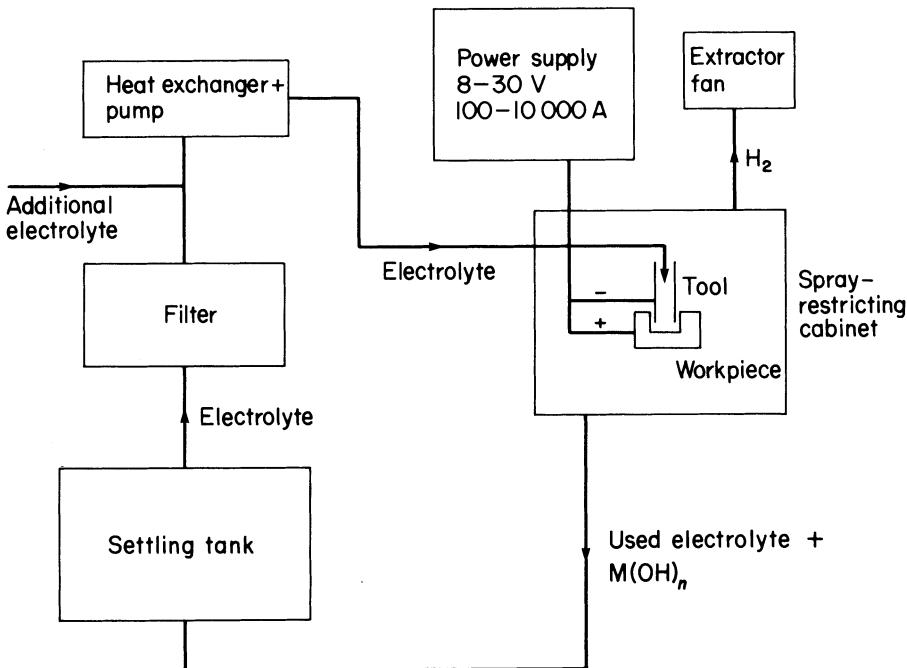


Figure 8.6 *The components of a system for electrochemical machining.*

Large volumes of electrolyte are required and hence it is normal to use an aqueous solution with a cheap electrolyte, i.e. NaCl or NaNO<sub>3</sub>, or where essential to obtain metal dissolution, NaBr or NaF; the workpiece must not passivate. The electrode reactions are, at the anode



and at the cathode



so that the metal ion will precipitate in the inter-electrode gap:



Thus the electrolyte leaving the gap will contain both solids and hydrogen gas. It is to sweep away these products and to remove the heat that a high electrolyte flow rate must be used.

Typically the control system should be capable of giving a total current of between 100 and 10 000 A at a voltage of –8 to –30 V and the machining process will use a high current density, in the range 5–400 A cm<sup>–2</sup>. The control system must also be capable of maintaining a constant, small (less than a few millimetres) gap between the workpiece and the tool and this will require the tool to move into the

workpiece as the machining proceeds. A circuit to detect sparking and shut down the electrolysis within 20 ms is also necessary if damage to the tool is to be avoided.

Electrochemical machining uses a large volume of electrolyte and produces large volumes of effluent. It is therefore normal to recycle the electrolyte. The scale of the system required is best seen by noting that the removal of 1 kg of steel produces 40 l of sludge containing about 20% solids. The electrolyte purification loop will contain a settling tank and filter as well as a heat exchanger, to remove excess heat, and a pump. There will also be a facility for continuous addition of new electrolyte since some is inevitably lost. The workshop environment must be protected from electrolyte spray and the hazards of hydrogen gas and hence the machining is carried out in an enclosed, spray-restricting cabinet with an extractor fan (similar to a fume cupboard).

The total system is shown in Figs 8.6 and 8.7 and it can be seen that the cell (tool + workpiece) is but a small part of the equipment necessary for electrochemical machining.

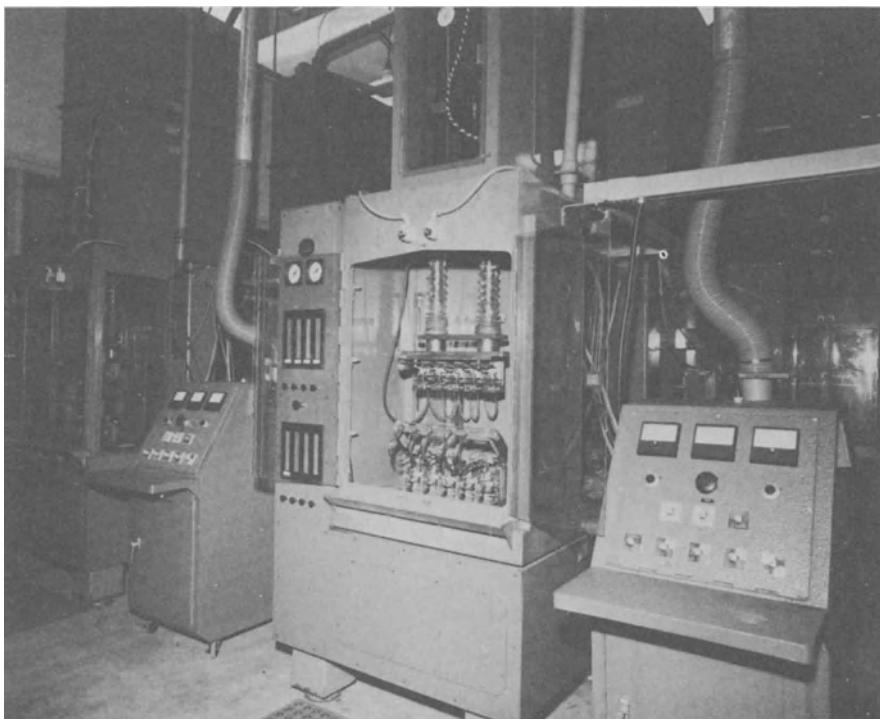


Figure 8.7 Spray cabinet and control unit for electrochemical machining the longitudinal holes into a turbine blade (see Fig. 8.5). Photograph supplied by Rolls Royce Ltd, Aero Division.

### 8.2.2 Tool design

It is the design of the tool that determines the current density distribution and hence the shape of the feature being machined although, in general, the tool will not be exactly the same shape as the feature.

The tool will be constructed of both conducting (copper, copper/tungsten alloy or steel) and non-conducting (epoxy resins and rubber materials) surfaces and the positioning of the holes for electrolyte entry will determine the electrolyte flow pattern between the workpiece and the tool. In order further to ensure even flow of electrolyte it is also common to use restrictors particularly when forming a feature in a flat surface.

Figure 8.8 illustrates the principles of tool design using the example of machining a square hole. The cathode is a thin square plate of copper with a diagonal electrolyte feed slot through which the electrolyte is pumped; the slot extends as far as possible into the corners of the tool and at both ends it broadens out slightly to a circular finish so that electrolyte flows right into the corners. The sides of the tool are insulated so that metal dissolution takes place only at the base of the hole; if the sides were conducting the hole would broaden towards the top. On the surface of the workpiece and around the tool, an electrolyte restrictor is placed to assist uniform electrolyte flow; this is particularly necessary at the start of the machining operation. Using a current density of  $10 \text{ A cm}^{-2}$ , the tool must be fed at  $0.3 \text{ mm min}^{-1}$ .

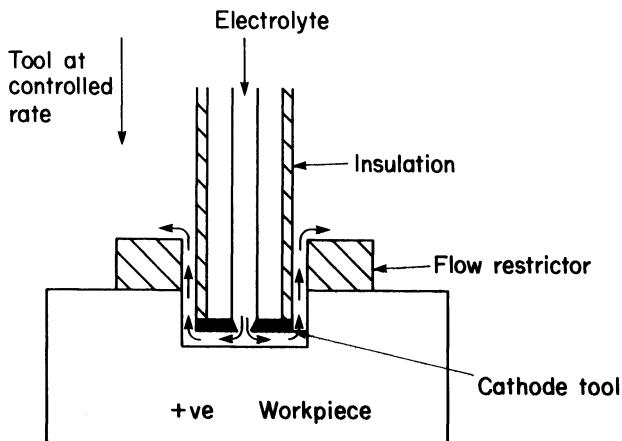
### 8.2.3 Electrochemical grinding

This modification of electrochemical machining has been widely used for grinding carbide tools since conventional methods can produce burrs, poor-quality finish and even cracking and it is also used to grind stainless steel and titanium honeycomb material and other surfaces.

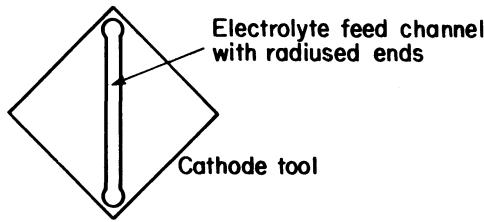
In electrochemical grinding (see Fig. 8.9) the tool is a rotating and conducting circular stone or wheel composed of diamond abrasive bonded to copper. The electrolyte is pumped, more slowly than in machining, over the whole surface of the wheel which is moved slowly across the surface of the workpiece with a gap as low as  $0.025 \text{ mm}$ . The workpiece is again the anode and the wheel is the cathode. The process is operated at  $50\text{--}3000 \text{ A cm}^{-2}$  and requires a source with a voltage of  $-4$  to  $-8 \text{ V}$ . In addition all the ancillary equipment shown in Fig. 8.6 for electrochemical machining will again be required but generally on a smaller scale. In electrochemical grinding (Fig. 8.10) it is thought that perhaps 90% of the metal removal is due to electrolysis while the balance is due to the abrasive action of the grinding wheel.

### 8.2.4 Electrochemical deburring

Electrochemical deburring is another modification of electrochemical machining carried out with smaller-scale ancillary and control equipment. It is used essentially to remove sharp corners and other imperfections and hence to finish metal components which have been manufactured by mechanical machining; its



(a)



(b)

Figure 8.8 Cathode tool for electrochemical machining of a square hole: (a) side view and (b) view from below.

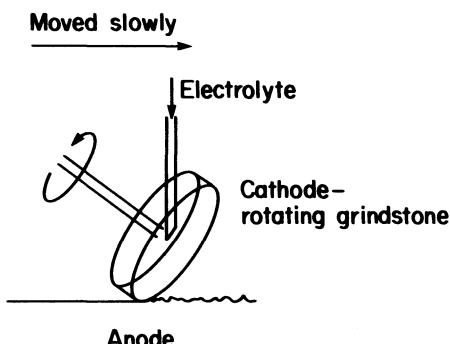


Figure 8.9 Principle of electrochemical grinding.

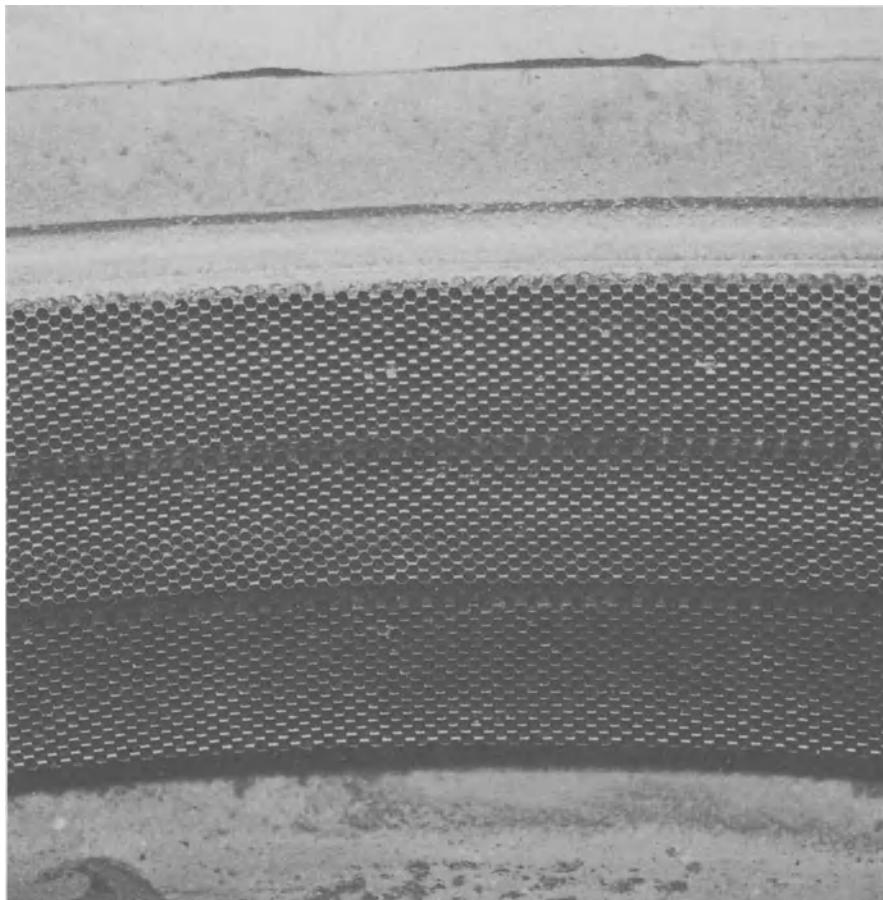


Figure 8.10 *Aero engine component constructed partly from a nickel alloy honeycomb cell structure (cell size 2 mm). The top surface is smoothed using electrochemical grinding. Photograph supplied by Rolls Royce Ltd, Aero Division.*

applications are particularly in the manufacture of components for engineering and include the finishing of pistons, power steering shafts, connecting rods and fuel injector nozzles. It requires the design of only a simple cathode tool and generally the currents do not exceed a few hundred amperes.

### 8.3 ELECTROCHEMICAL ETCHING

In the manufacture of printed circuit boards the plastic board is initially covered with a complete copper layer (typically 35 µm thick). Selected areas are then protected by photoresist or other insulation and the rest of the copper is etched

away. The direct anodic oxidation of the copper is difficult since the process must lead to a series of isolated copper areas to which it is difficult to maintain electrical contact. Hence, normal chemical etchants are used. Recently, however, a novel electrochemical process has been introduced. While it is effectively a form of 'low-power electrochemical machining', it is based on quite different principles. A slurry of high-surface-area graphite particles (15%) in sulphuric acid (10–15%) is charged positively by contact with a carbon or lead anode and is then pumped through nozzles onto the printed circuit board. The copper is etched by contact with the charged particles and the carbon particles are then returned to the anode for recharging. Moreover the copper ions formed in the etching process may be passed to the cell cathode and recovered as the metal. Hence the process has the following chemistry: at the anode



at the printed circuit board



at the cathode



and overall



and overall only transfers copper from the printed circuit board to the cathode for re-use.

The mechanism for storage of the charge on the carbon particles is not yet proven and in principle could be a mixture of double layer charging, reversible oxidation of surface redox systems or intercalation of sulphate species into the graphite lattice. The first is thought to be the major method because of the low potential used at the anode (< 1 V vs NHE). Even so it is possible to store 100 C per gram of carbon on the high-surface-area material used.

It is found that the etching rate increases with the conductivity and storage capacity of the carbon, particle surface area and concentration, spraying pressure and temperature, and the process is also catalysed by the presence in solution of a soluble redox species. Hence the process solution generally contains 30 g l<sup>-1</sup> of ferric sulphate.

Figure 8.11 shows the principal components of the process. In the cell, both of the surfaces of the plate anode are used and the steel cathodes are separated from the anode by a cupric-ion-conducting cation exchange membrane. The anode current density is 20–100 mA cm<sup>-2</sup> and the cell voltage is –2 to –4 V. In addition to the etching chamber, the circuit contains a porous graphite tube for bleeding off a clear solution to the anode compartments and a tower for purifying the electrolyte. Electrodes of 1 m<sup>2</sup> area will permit the etching of approximately 2 m<sup>2</sup> of printed circuit board (70% removal of 35 µm copper layer on both sides of the board).

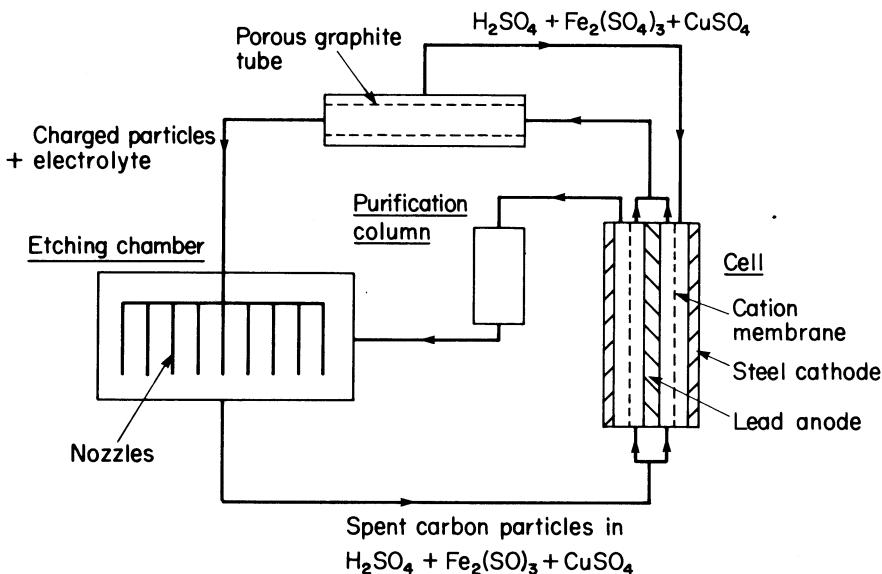


Figure 8.11 *Schematic diagram of electrochemical etching process for the manufacture of printed circuit boards.*

## FURTHER READING

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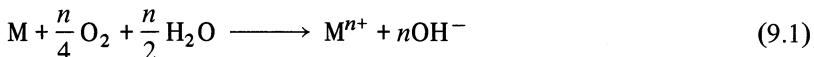
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## 9 Corrosion Control

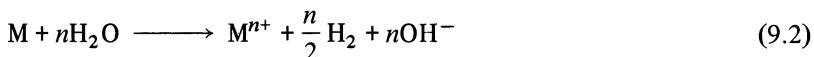
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At first sight it may be surprising to find a chapter on corrosion in a book on industrial electrochemistry. Corrosion is, however, essentially an electrochemical phenomenon and the importance to society of its control needs little emphasis; wherever metals are used, for example in cars, for household goods, in building, in oil rigs or in chemical plant, corrosion must be considered and is likely to determine the useful life of the component. More importantly though, based on an understanding of the electrochemical mechanism of corrosion, it is possible to devise methods which decrease its rate — stopping corrosion completely is an unreachable goal. Hence this chapter will first discuss the mechanism of corrosion and then describe some electrochemical methods for corrosion control which are widely used.

Corrosion is the spontaneous dissolution of a metal by the reactions



and/or



In fact, however, these reactions do not occur by direct interactions of the metal with oxygen or water but rather by two electrode processes occurring simultaneously on the surface of the metal, i.e.



with either



or



These equations imply that the rate of corrosion will depend on the presence of water, the concentration of oxygen and the pH and composition of the aqueous

electrolyte in contact with the metal as well as temperature and the nature of the metal itself.

Many surfaces will be homogeneous, i.e. metals or alloys in a uniform environment, and the anodic and cathodic reactions will occur randomly over the whole surface, although maybe at particular sites, e.g. lattice imperfections. Since metals are good electronic conductors, however, this need not be the only situation where corrosion occurs. For example, where two metals are in contact or one metal is in contact with two quite different environments, e.g. a leg of a North Sea oil platform passing through the sea water into the sea bed, there may be well defined anodic and cathodic areas and electrons pass through the metal from one to the other. Indeed, it will be seen that such situations often lead to the worst corrosion problems and are a major cause of component failure.

On the other hand, although electrons may move around the metal, the metal cannot accumulate a net charge and hence the currents for the anodic and cathodic processes must be equal and the metal will take up a potential where the current for reaction (9.3) is the same as for reactions (9.4) and/or (9.5).

## 9.1 THE THERMODYNAMICS OF CORROSION

Thermodynamic data for the reactions involved in corrosion (i.e. the reactions of the metal with water (or protons) and oxidizing agents, particularly oxygen) are commonly presented in the form of a Pourbaix diagram. Figure 9.1 shows a typical Pourbaix diagram, that for nickel at 25°C. The diagrams are an economical way of summarizing data both for the equilibrium potentials for the different redox couples of the metal as a function of pH and for the various hydrolysis and proton exchange reactions of each oxidation state. Hence they show the most stable species at each pH and potential and also the conditions where change becomes thermodynamically favourable. For example at each pH, it shows the potential where, kinetics permitting, oxidation will occur and it indicates the nature of the species which will be formed (in equation (9.3)  $M^{n+}$  should be taken to mean any species in the  $n+$  oxidation state). The potentials for the reduction of oxygen and the evolution of hydrogen as a function of pH are also shown as lines on the diagrams.

The free energy of reactions (9.1) and (9.2) will be negative if the potentials for reactions (9.4) and (9.5) respectively are more positive than for reaction (9.3). Hence corrosion is possible at pH where the lines for oxygen reduction or hydrogen evolution lie above the line for the  $M/M^{n+}$  couple. Using the Pourbaix diagram of Fig. 9.1, we can make the following predictions about the behaviour of nickel.

(a) At all pH the reaction between oxygen and nickel should be spontaneous (indeed this is true for almost all metals). Below pH 8, the product should be solution free  $(Ni(H_2O)_6)^{2+}$  but above this critical value an insoluble oxide  $Ni_3O_4$  should be formed.

(b) Only in acid media is the dissolution of nickel to give hydrogen thermodynamically favourable and hence nickel cannot corrode in oxygen free solutions with a pH above 7.

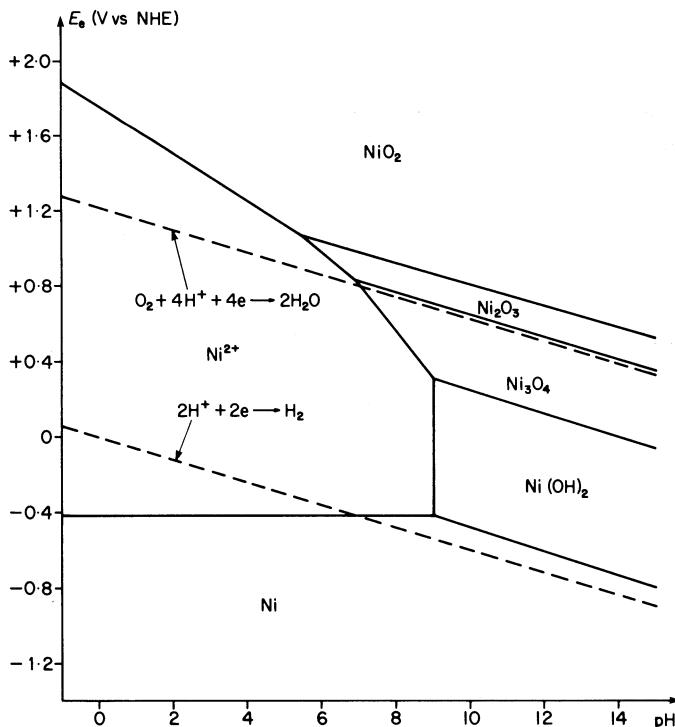


Figure 9.1 Pourbaix diagram for nickel in aqueous medium at 25°C. Values of  $E_\phi$  are calculated for  $10^{-6}$  M Ni<sup>II</sup> in solution.

It must again be emphasized that Pourbaix diagrams are based solely on thermodynamic data and it will be shown in the next section that when kinetics are taken into account the picture changes dramatically. Indeed the stability of metals to corrosion must be determined by experiment.

## 9.2 THE KINETICS OF CORROSION REACTIONS

Consideration of the Pourbaix diagrams for the metals familiar in everyday life will lead to the conclusion that the metals have little stability; almost all the metals should react with oxygen and many should also dissolve to give hydrogen, particularly in acid solution. Fortunately, many metals corrode only very slowly in a normal environment and hence it is clear that kinetic factors are often totally predominant in determining the stability of metals. This should not be surprising since it was shown in Chapter 1 that both oxygen reduction and hydrogen evolution can be slow processes and their rate varies greatly with the metal of the cathode. In fact, the kinetics of metal dissolution reactions also vary and it is also necessary to consider passivation (see later).

Figure 9.2 shows an  $I-E$  curve recorded for a metal, M, in an oxygen-free aqueous electrolyte. Suitable analytical experiments have confirmed that the cathodic current is due to hydrogen evolution and that the anodic current is due to metal dissolution. At open circuit or if a lump of the metal is dropped into the same aqueous solution, the metal must take up the corrosion potential,  $E_{\text{CORR}}$ , the potential where no net current flows because the anodic and cathodic partial currents are equal, i.e.

$$I_{M/M^{n+}} = I_{H_2O/H_2} = I_{\text{CORR}} \quad (9.6)$$

The partial current  $I_{\text{CORR}}$  is called the corrosion current and the rate of corrosion estimated from this current and Faraday's law should be the same as that from weight loss experiments where the rate of metal dissolution is determined by weighing a sample of metal before and after standing in the electrolyte for a period. It should be noted that the corrosion potential is a so-called, mixed potential since it is determined by the kinetics of two electron transfer couples,  $M/M^{n+}$  and  $H_2O/H_2$  (cf. the equilibrium potential for a single couple, Chapter 1).

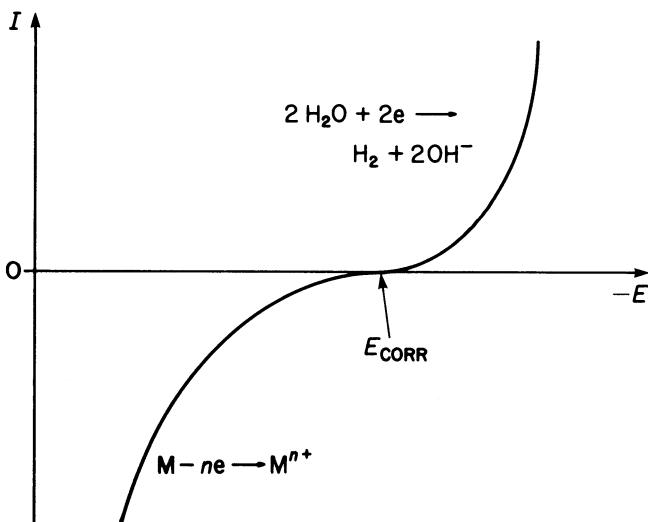


Figure 9.2  $I-E$  curve for an electrode, prepared from metal M, in an aqueous deoxygenated electrolyte.

To understand more quantitatively the dependence of the corrosion potential and current on the kinetic parameters of the two electrode processes (9.3) and (9.5), the  $I-E$  data of Fig. 9.2 should be replotted in a semi-logarithmic form, i.e. as a Tafel plot (Fig. 9.3). A linear Tafel line will only be observed in the potential range where a single electrode process predominates. However, these Tafel lines can be extrapolated to the corrosion potential and if necessary (as in the figure) also to the calculated equilibrium potentials for the  $H_2O/H_2$  and  $M/M^{n+}$  couples where the exchange currents are  $I_0^H$  and  $I_0^M$  respectively. The equations for the two

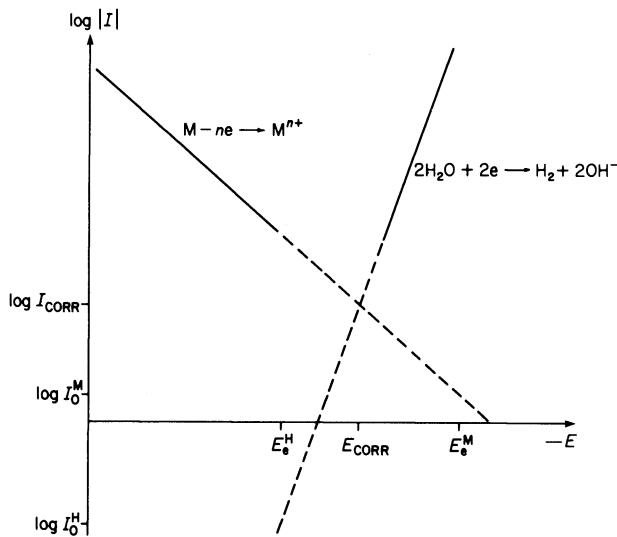


Figure 9.3 Steady-state I-E data in the form of a Tafel plot for a metal in deoxygenated aqueous solution. Definition of the corrosion current and the corrosion potential. The reversible potentials,  $E_e^H$  and  $E_e^M$ , and the exchange currents,  $I_0^H$  and  $I_0^M$ , for the two fundamental reactions are also shown.

Tafel lines are

$$E - E_e^H = -\beta_H (\log I - \log I_0^H) \quad (9.7)$$

and

$$E - E_e^M = \beta_M (\log I - \log I_0^M) \quad (9.8)$$

where  $1/\beta_H$  and  $1/\beta_M$  are the Tafel slopes. For both the anodic and cathodic processes,  $I = I_{\text{CORR}}$  at  $E = E_{\text{CORR}}$ ; substituting this information into equations (9.7) and (9.8), one obtains a pair of simultaneous equations which may be solved to give

$$I_{\text{CORR}} = (I_0^M)^{\beta_1} (I_0^H)^{\beta_2} \exp\left(\frac{2.3(E_e^H - E_e^M)}{\beta_H + \beta_M}\right) \quad (9.9)$$

where  $\beta_1 = \beta_M/(\beta_M + \beta_H)$  and  $\beta_2 = \beta_H/(\beta_M + \beta_H)$  and

$$E_{\text{CORR}} = \frac{\beta_M E_e^H + \beta_H E_e^M}{\beta_H + \beta_M} + \frac{\beta_H \beta_M}{2.3(\beta_H + \beta_M)} \log\left(\frac{I_0^H}{I_0^M}\right) \quad (9.10)$$

It can be seen that the corrosion current and potential depend on both the equilibrium potentials for the hydrogen evolution reaction and metal dissolution calculated from the Nernst equation, and the kinetic parameters, the exchange currents and the Tafel slopes. Table 9.1 shows the corrosion currents calculated for some typical values of these parameters; it is also important to note that even a

Table 9.1 Influence of the electrochemical parameters for hydrogen evolution and metal dissolution on the corrosion current in oxygen-free solution

$E_e^H - E_e^M$ (V)	$I_0^H$ (mA cm $^{-2}$ )	$I_0^M$ (mA cm $^{-2}$ )	$\beta_H$ (mV)	$\beta_M$ (mV)	$I_{CORR}$ (mA cm $^{-2}$ )
0.0	$10^{-6}$	$10^{-4}$	120	120	$10^{-5}$
0.5	$10^{-6}$	$10^{-4}$	120	120	$1.2 \times 10^{-3}$
1.5	$10^{-6}$	$10^{-4}$	120	120	17
0.5	$10^{-10}$	$10^{-4}$	120	120	$1.2 \times 10^{-5}$
0.5	$10^{-10}$	$10^{-8}$	120	120	$1.2 \times 10^{-7}$
0.5	$10^{-6}$	$10^{-4}$	120	60	$2.8 \times 10^{-3}$
0.5	$10^{-6}$	$10^{-4}$	30	120	$8.5 \times 10^{-2}$

corrosion current of  $10^{-3}$  mA cm $^{-2}$  corresponds to a metal loss rate of the order of  $10$  mg cm $^{-2}$  yr $^{-1}$ . Clearly the corrosion current has an appreciable dependence on both the reversible cell potential, ( $E_e^H - E_e^M$ ), and all the kinetic parameters. In most practical situations, the choice of metal is such that the reversible cell potential is seldom much in excess of  $0.5$  V. Even so, because of the large variations in exchange currents and mechanisms for the two electrode processes which are possible, the corrosion rate for different metals and environments can still vary by many orders of magnitude.

Equations (9.9) and (9.10) also emphasize the key role of pH in determining the rate of corrosion; it affects both the thermodynamic and kinetic terms. Both  $E_e^H$  and  $E_e^M$  may change with pH but shifts will have opposing effects on the rate of corrosion.  $E_e^H$  will always change by  $60$  mV per pH unit so as to decrease the reversible cell potential and hence the rate of corrosion with increasing pH.  $E_e^M$  will only vary with pH if the oxidation of the metal leads to an oxide or hydroxide (e.g. nickel above pH 9; see Fig. 9.1) and hence the effect of pH depends on the metal and the pH range. Where a shift in  $E_e^M$  with pH occurs, the effect will be to make the potential more negative with increasing pH and thus to increase ( $E_e^H - E_e^M$ ). This will increase the corrosion current. The exchange currents, particularly that for hydrogen evolution, are very sensitive to pH and it is also possible that the mechanisms for hydrogen evolution and metal dissolution, and in consequence the Tafel slopes, will be a function of pH.

So far, the quantitative discussion of corrosion has only dealt with deoxygenated solutions. In the real world, this is a very unusual environment; oxygen is almost always present. How does the presence of oxygen change our discussion of corrosion? In fact, two situations must be considered.

(a) When there is a plentiful supply of oxygen to maintain the corrosion current, the argument will be similar to the above except that the cathode reaction is the reduction of oxygen. The corrosion current and potential are then determined by the intercept of the Tafel lines for oxygen reduction and metal oxidation (see Fig. 9.4) and since  $E_e^{O_2}$  is more positive than  $E_e^H$  by  $1.23$  V the thermodynamic

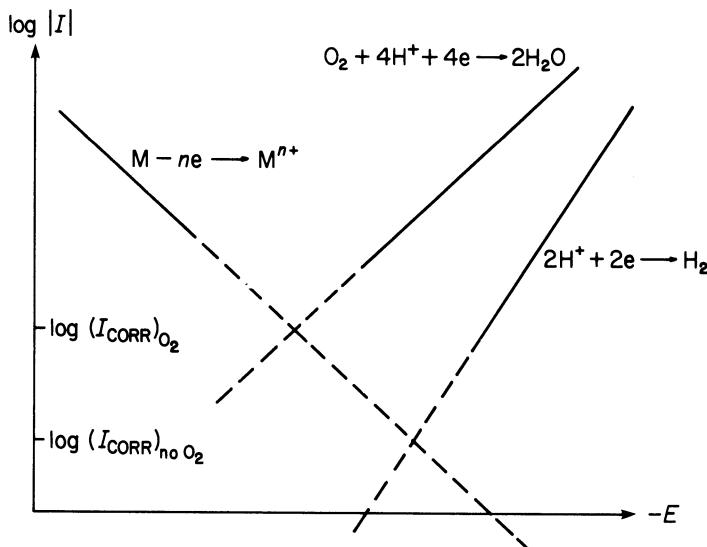
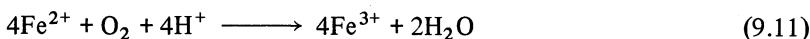


Figure 9.4 Tafel plots for the reactions involved in corrosion in a deoxygenated solution and in an oxygen-rich medium. The presence of oxygen substantially increases the rate of corrosion.

driving force for corrosion, ( $E_e^{O_2} - E_e^M$ ), will be larger and the rate of corrosion would be expected to be higher; an equation analogous to (9.9) will again give the corrosion current. To some extent, the rate of corrosion is commonly less than expected because of the extremely low exchange current for oxygen at many surfaces. Even so, corrosion normally becomes more of a problem in the presence of oxygen.

Corrosion, in the presence of a high concentration of oxygen but at a metal where the exchange current for oxygen reduction is low, is also enhanced by the presence in solution of redox couples with an equilibrium potential in the range 0 to +1.23 V (at pH 0). For example in the presence of ferrous ions, the cathodic reaction in the corrosion process can be a part of the catalytic cycle



i.e. oxygen reduction is catalysed by such ions, effectively causing an increase in the exchange current for oxygen reduction.

(b) In the presence of a lower concentration of oxygen, the corrosion current may be controlled by the rate of mass transport of the oxygen to the metal surface and the corrosion potential will occur at the intercept of the oxygen plateau with the Tafel line for metal dissolution. The  $\log I$  versus  $E$  curves for this simple situation are illustrated in Fig. 9.5. It is also possible for the cathodic current to be

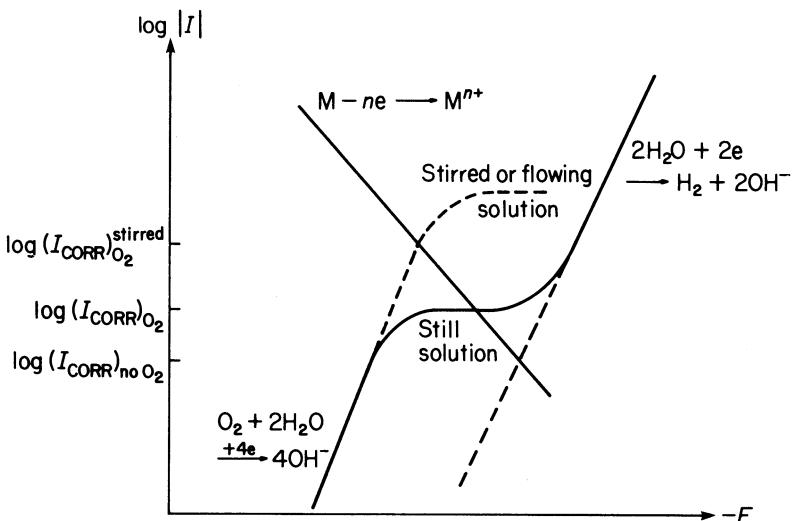


Figure 9.5 Corrosion in an electrolyte solution with a low concentration of oxygen and the effect of convection.

the sum of the limiting current for oxygen reduction and a contribution from hydrogen evolution.

In such systems the rate of corrosion will depend on the mass transport regime in the solution. Increasing the rate of transport of oxygen to the surface must increase the rate of corrosion.

### 9.3 PASSIVATION

When metals are placed in a solution of an oxidizing agent, it is common to find that corrosion does not occur although the oxidation of the metal is thermodynamically very favourable. Indeed, this phenomenon was first observed over one-hundred years ago when it was found that iron dissolved in dilute, but not in concentrated nitric acid; it was suggested that in concentrated nitric acid, a thin layer of a non-porous and insoluble oxide film was formed. This protection by a surface film is termed passivation and explains the apparent stability of metals such as Al, Cr, Ni and Pt in damp air.

Passivation is also observed in electrochemical experiments. Figure 9.6 shows an  $I-E$  curve resulting from a potential sweep experiment commenced at a potential where the metal is immune from corrosion. At some potential the metal will begin to oxidize and initially the product is likely to be a soluble metal ion. Throughout this active region the current will increase with overpotential and at least during the early part of the rising  $I-E$  region this increase will be exponential. As the potential is made more positive, however, a critical potential is reached where the rate of dissolution drops sharply (often by several orders of magnitude), and from the Fladé potential the current remains almost constant at a low value until a new

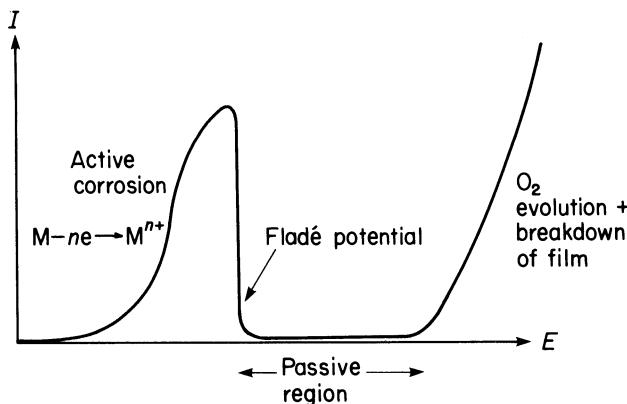


Figure 9.6 I–E curve for a metal which passivates.

process, probably oxygen evolution, is observed at very positive potentials. The potential range where only a low current is observed is the passive region. Natural passivation therefore occurs if, in the solution, there is a species, e.g. oxygen or a redox reagent, capable of taking the surface potential into the passive region (the surface potential is calculated from the Nernst equation for the redox reagent couple).

While it is certain that in the passive region, the metal is covered by an adherent and non-porous film (usually thought to be 1–15 nm thick), the exact nature of this layer and its mechanism of formation remain a subject of controversy. The simplest model for the formation of the film would note that as the current increases through the active region, the surface concentration of  $M^{n+}$  will also increase and at some point the solubility product for a metal species, e.g.  $M(OH)_n$ , must be exceeded and a precipitate must result. The mechanism, however, cannot always be this straightforward since a surface layer often forms prior to passivation. This suggests that the surface layer is only passivating if it has certain properties. Thus the Fladé potential may correspond to a change in film composition, e.g. oxidation, which causes a change in properties. This may be a reduction in porosity although it has been proposed that the change is from ionic to electronic conduction – if there is no mechanism for ions to travel through the film, corrosion must stop since the film cannot thicken.

Whether and how readily passivation occurs will depend on both the metal and the solution environment. Even when passivation is observed, however, there is a further phenomenon which must sometimes be considered. This is pitting, a process which causes an increase in current in the passive region and which in its severest form causes complete breakdown of the passive film. It is commonest in media containing halide ion. The term derives from characteristic circular holes which appear in the passive film but their mechanism of formation is not well understood. Generally pitting becomes worse with increasing halide ion concentration and as the potential is made more positive (see Fig. 9.7) and it is thought likely that the pits

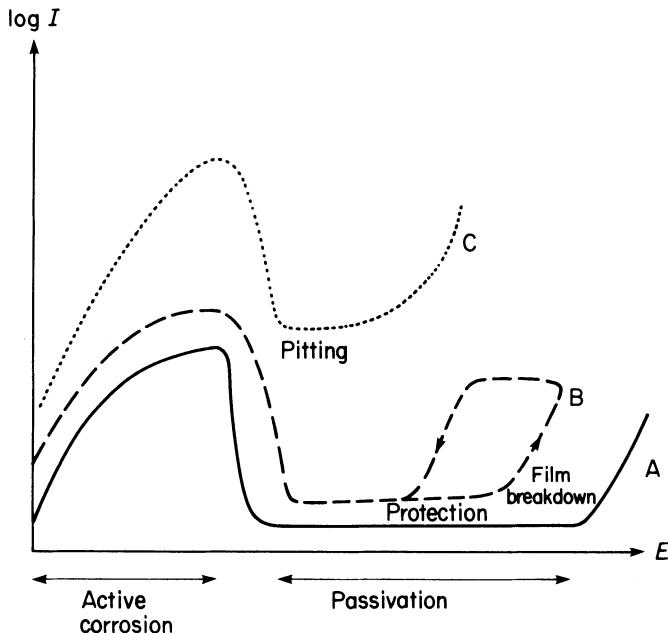


Figure 9.7 *Corrosion of nickel in acid solution. Concentration of chloride ion: curve A, 0; curve B,  $10^{-2}$  M; curve C,  $10^{-1}$  M.*

arise by transport of the anion through the passive film and corrosion from beneath. This is said to create acid spots which locally dissolve the passive film and set up a situation akin to crevice corrosion (see next section) where the metal dissolves rapidly. Solutions containing ions which promote pitting are particular corrosion hazards.

#### 9.4 CORROSION PROBLEMS IN PRACTICE

So far the discussion has been limited to a consideration of homogeneous metals in a uniform environment where corrosion will occur at the same rate over the whole surface. This situation seldom constitutes a major corrosion hazard. The corrosion engineer is generally much more concerned with situations where corrosion is accelerated because it is limited to particular sites. There are several mechanisms whereby this can occur.

Many hazardous corrosion situations arise because of differential aeration. To understand differential aeration one should first consider two pieces of the same metal placed in media identical except for their oxygen concentration. For example, as in Fig. 9.8, one is placed in unstirred solution below an air atmosphere and the other is placed in a solution saturated with oxygen by a stream of gas. The metal samples will take up different potentials and corrode at different rates; that in the oxygen-saturated solution must be more positive and the corrosion current will be

higher (see Figs 9.4 and 9.5). How does the situation change if the two pieces of metal are joined by a wire contact? Provided the metal remains in the active corrosion region and the resistance of the medium is not very high, the two pieces must take up the same potential and therefore the rate of corrosion becomes uniform over both surfaces. The corrosion potential will take up an intermediate value between that of the two isolated pieces of metal. In order to allow an even corrosion rate, however, electrons must flow through the contact from the metal in the oxygen-deficient solution to the metal in the oxygen-rich solution and ions must move through the environment so as to maintain neutrality. Hence if the resistance of the medium between two pieces of metal is not negligible there will be an *IR* drop and the rate of corrosion at the two pieces of metal will not totally equalize. In practice this occurs on large metal structures particularly in poorly conducting media, e.g. an underground pipe, but in this situation the highest rate of corrosion is always in the oxygen-rich region.

The real problem of differential aeration is when it is combined with passivation. In the presence of a sufficient supply of oxygen, many metals will passivate. Consider again the experiment in Fig. 9.8 with the contact closed; it is possible for the piece of metal in the oxygen-rich medium to take up a potential in the passive region and corrosion will then stop. If the film is an electronic conductor, however, oxygen reduction can continue to occur and in order for the metal oxidation and oxygen reduction currents to balance, the rate of corrosion at the metal in the oxygen-deficient solution must increase. The corrosion rate will become even higher if the piece of metal in the oxygen-rich solution is larger than the other where corrosion is occurring – the total current for oxygen reduction and metal corrosion must still balance.

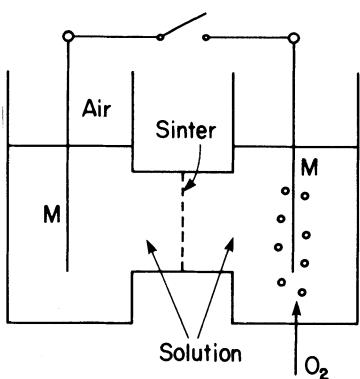


Figure 9.8 *Electrochemical cell to discuss the effect of differential aeration.*

There are many examples of the way in which differential aeration combines with passivation to produce difficult corrosion problems. Figure 9.9 illustrates the case of crevice corrosion. The outer flat surface receives a plentiful supply of oxygen and hence passivates to produce a large protected area where oxygen reduction can

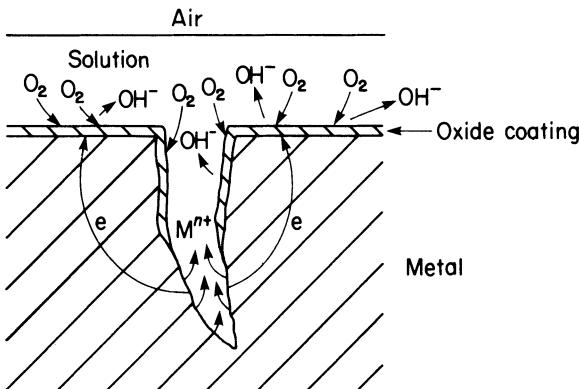


Figure 9.9 Schematic explanation of accelerated corrosion inside a crevice. The oxide acts as the cathode and only the bare metal at the bottom of the crevice acts as the anode.

occur. Only the inner part of the crevice is free of the film and it is in this small area that the metal oxidation is localized. Hence, once crevice corrosion has commenced, the depth of the crevice increases very rapidly. An identical argument applies to corrosion between two metal plates (see Fig. 9.10) while a similar situation at scratches in paint on metals leads to severe peeling (Fig. 9.11). In the latter example, the oxygen supply is highest to the exposed metal at the centre of the scratch and it is there that passivation occurs; the anodic part of the corrosion process takes place beneath the paint causing it to lift and peel.

Localized corrosion can also occur when two different metals are in contact. For example, for different applications iron is protected by a layer of zinc or tin. The former is the better choice although it is potentially more prone to corrosion than tin. If a scratch or hole is formed in a tin layer, the corrosion of the underlying iron is rapid; again oxygen reduction can occur over the whole tin surface while the anodic oxidation is limited to an exposed area of iron. On the other hand, zinc is more electropositive than iron so even if the top layer is damaged, the iron does not

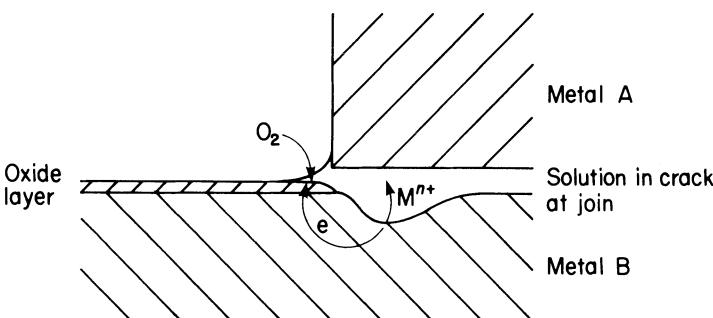


Figure 9.10 Corrosion between two metal plates.

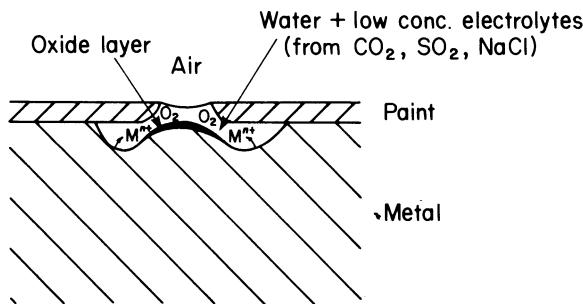


Figure 9.11 Corrosion due to a paint scratch.

corrode. The iron is protected at the expense of the zinc (see Fig. 9.12). Tinplate is used largely for packaging foods because tin ions are non-toxic.

All situations when two different metals are in contact are potential corrosion hazards. It is always likely that one of the metals will dissolve more rapidly and a corrosion cell will be set up. This metal will become anodic while the more stable metal will become cathodic; as a result all the metal loss will occur from the more susceptible metal.

The exact mechanism of stress cracking corrosion is unknown but it is thought to be related to hydrogen embrittlement and to be another phenomenon whose intensity is due to the effect being localized. It was seen in the earlier discussion that in many corrosion situations the cathodic part of the process is hydrogen

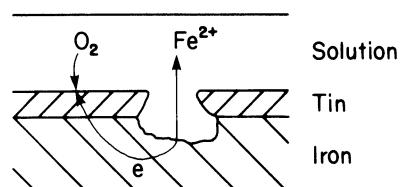
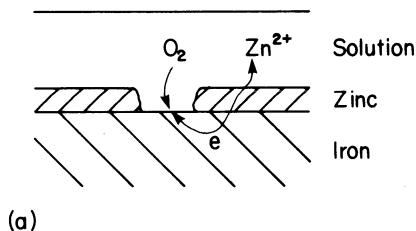


Figure 9.12 Corrosion at damaged layers of (a) zinc and (b) tin coatings on iron or steel.

evolution. We know from Chapter 1, however, that a mechanism of hydrogen formation will at many metals involve adsorbed hydrogen atoms. Also hydrogen atoms are small and it is not surprising that they are able to enter the lattice of some metals; the classic example is palladium but it is also found with iron and alloys based on iron. Of course, during proton or water reduction, hydrogen gas evolution is the dominant process but a small percentage of the hydrogen enters the lattice. Moreover, hydrogen absorption into the lattice is usually quite reversible up to a critical percentage; beyond this limit, however, the lattice is forced to change its structure with a consequent loss of mechanical strength and changes in other properties occur. Normally, the limit is only reached under conditions which by corrosion standards are quite extreme (e.g. at a current density well above the corrosion current), but it is found that the hydrogen tends to collect in areas in the metal where there is stress. Hence the role of stress is to concentrate the hydrogen and this creates the conditions for hydrogen embrittlement and component failure. This may not be the only result of the hydrogen collecting in areas of stress; the build-up of hydrogen pressure in fissures and cracks may cause them to expand and, when they reach the surface, the conditions are ripe for crevice corrosion. Certainly stress cracking corrosion has led to sudden and catastrophic failure of components and has been a frequent cause of plane crashes, etc.

We must recognize that there are two quite different situations where corrosion arises. In atmospheric corrosion, the electrolyte is normally a thin film or small pool of water rendered slightly conducting by  $\text{CO}_2$ ,  $\text{SO}_2$  or  $\text{H}_2\text{S}$  absorbed from the atmosphere (hence its pH will not be extreme and the electrolyte will only be dilute) but it will contain a high concentration of oxygen. It is also necessary, however, to restrict corrosion in containers (for foods, paints, oil, etc.) and in pipes and reactors carrying all types of plant streams. In general these streams will be less rich in oxygen but may contain concentrated electrolytes, be at any pH, contain redox species (which may be corrosion catalysts) and be based on non-aqueous solvents rather than water. It will be clear that these latter situations may produce even more difficult corrosion problems than are met in atmospheric oxidation and certainly each stream must be considered individually.

## 9.5 ELECTROCHEMICAL MEASURES AGAINST CORROSION

The recognition that corrosion, with the exception of physical erosion, has an electrochemical mechanism, should allow one to devise measures to reduce the rate at which corrosion occurs. Of course, this expectation has been confirmed in practice and it is the purpose of this section to review the principal procedures based on electrochemical concepts.

### 9.5.1 Methods based on impressed current

In many earlier chapters, the key to the success of an application of electrochemistry has been the ability to control the potential of a metal surface, either with a potentiostat or, more likely, by passing a calculated and controlled current density.

Clearly this concept can be applied to reducing the rate of corrosion by fixing the potential of the surface to a value where the current for metal oxidation is very low. The complete  $\log |I|$  versus  $E$  characteristic for a metal in a medium where it passivates at positive potentials is shown in Fig. 9.13; it suggests two potential regions where the potential could usefully be held, at negative potentials or in the passive region. The former is known as cathodic protection and, in principle, can give an extremely low rate of corrosion. The second is known as anodic protection and its effectiveness depends on the passivation current density.

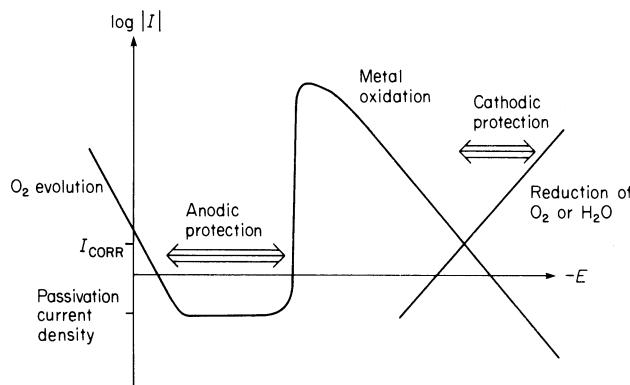
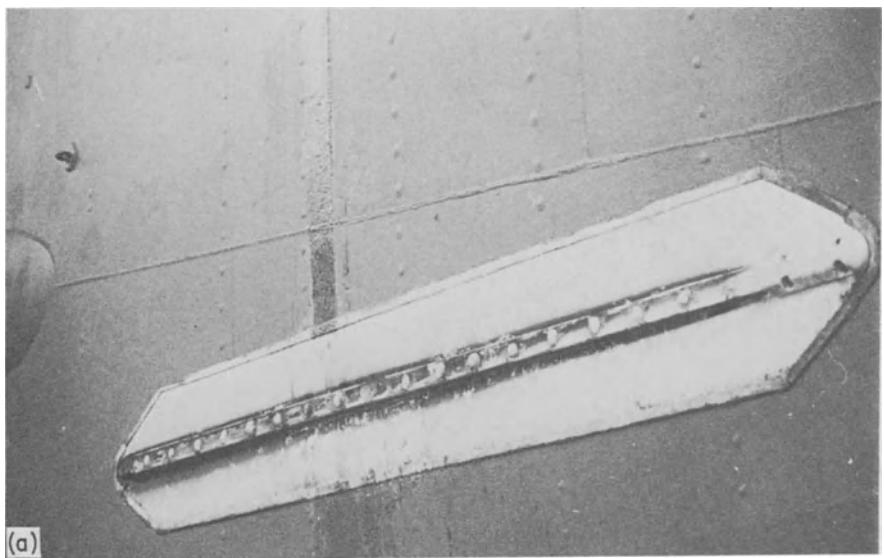


Figure 9.13 Complete  $\log |I|$  vs  $E$  characteristic for a metal to show the potential zones for anodic and cathodic protection.

For cathodic protection, it is necessary to place an inert anode as counter-electrode in the environment close to the surface to be protected. The cathodic current density through the surface must then be higher than the corrosion current density. Indeed, theoretically it would be possible to hold the potential at a value where the metal is thermodynamically immune from corrosion. In practice, however, this is likely to be too expensive. The continuous passage of current requires the consumption of power ( $IVt$  kWh) and, particularly if the medium between the protected surface and the anode is not highly conducting, the use of anything but a very low current will entail an unacceptably high energy consumption. Moreover, if the electrode process initiated by the cathodic current is hydrogen evolution, the likelihood of hydrogen embrittlement is greatly increased by a higher current density.

Anodic protection is best carried out using a crude potentiostat to hold the potential in the passive region but it will again require the placing of counter-electrodes in the environment. It has the advantage, however, that there is no possibility of hydrogen damage and that the current, and hence energy consumption, can be low.

Both these forms of protection, based on an imposed current, require careful positioning of the counterelectrode to ensure that the whole surface is protected. For anodic protection this only requires that all the surface has a potential within





**Figure 9.14** Cathodic protection with an impressed current. (a) Lead/silver anode for the protection of a ship's hull. Note that the anode is insulated from the hull and surrounded by a non-conducting shield to improve the potential distribution over the hull. The anodes will be placed at intervals around the hull. (b) Anode cans for the protection of an underground pipeline (some distance away). The anode cans contain a Fe/Si rod surrounded by coke breeze (to increase anode area). (c) Monitor and controlled power supply for a ship's corrosion protection system. Photographs supplied by Corrintec UK Ltd.

the passive region. But for cathodic protection, the requirement for a uniform potential distribution can be more stringent, since an additional overpotential of 30–120 mV at some parts of the surface may produce hydrogen embrittlement in these areas. These methods are unlikely to be appropriate for very large objects, e.g. pipelines, and for complex shapes, e.g. oilrigs, it would be necessary to have a network of counterelectrodes. Moreover, since it is the resistance of the medium between the 'electrodes' which will determine the energy consumption and potential distribution, these approaches to protection are likely to be most effective if the environment for the surface to be protected is a conducting solution.

### 9.5.2 Corrosion inhibitors

An approach which is attractive for the protection of metals in contact with aqueous solutions, particularly where the solution is part of a closed system (e.g. cooling and heating systems), is that based on corrosion inhibitors. These are organic or inorganic species, which slow down corrosion when added to the solution in low concentration.

There are several mechanisms whereby inhibition occurs. A major group of inhibitors function by adsorption on the metal surface. The adsorption must occur in the region of the corrosion potential and decrease the rate of either or both the anodic and the cathodic reactions by one of the mechanisms discussed in Chapter 1. Figure 9.15 illustrates the case where an additive inhibits only the anodic dissolution of the metal. It can be seen, however, that the decrease in the rate of metal oxidation decreases the corrosion current and hence the rate of metal loss. Inhibitors which operate mainly on the metal dissolution process would include aromatic and aliphatic amines, various sulphur compounds and carbonyl molecules; phosphorus, arsenic and antimony compounds have a greater effect on the hydrogen evolution reaction. Additions to the metal can have a similar effect; for example phosphorus is added to some steels to inhibit H<sub>2</sub> evolution.

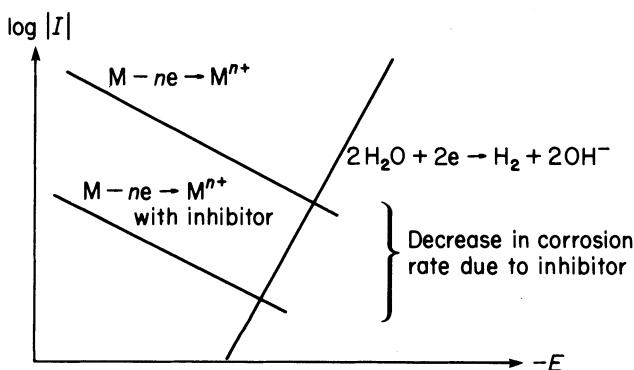


Figure 9.15 Curves of  $\log I$  vs  $-E$  showing the mode of action of an inhibitor (in fact, an anodic inhibitor) on the corrosion rate.

A second group of inhibitors promote the appearance of a precipitate on the metal surface and maybe catalyse the formation of a passivating layer. Examples would include phosphate and bicarbonate; the oxidation of the metal leads to an ion and commonly the phosphate and carbonate salts of multivalent ions are quite insoluble. Other inhibitors are redox reagents which are able to shift the potential of the surface into the region where cathodic or anodic protection takes place, e.g. dichromate will often lead to passivation of a surface.

### 9.5.3 Sacrificial anodes

It is also possible to protect a surface by placing in electrical contact with it a metal which is more readily oxidized. The principle is explained in Fig. 9.16 where it can be seen that the dissolution of the auxiliary metal will cause the equilibrium potential to shift to a more negative value. While both metals have almost the same potential (there will be an *IR* drop between sites), the auxiliary metal will function as an anode while the surface to be protected will become cathodic. It is apparent

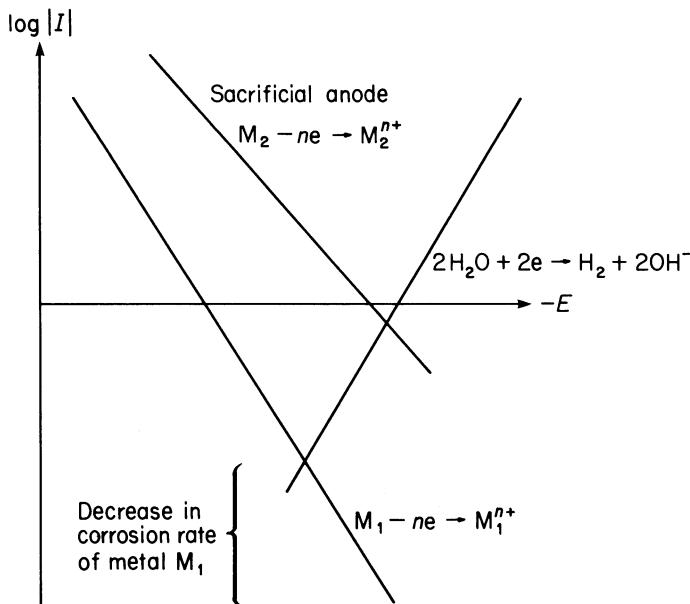


Figure 9.16 Curves of  $\log I$  vs  $E$  showing the mechanism of a sacrificial anode made of metal  $M_2$  on a surface of metal  $M_1$ .

that the overall rate of metal loss will increase but it is the auxiliary metal that dissolves; the rate of metal loss from the protected surface decreases — hence the term *sacrificial anode*.

The use of a sacrificial anode is electrochemically equivalent to cathodic protection since it causes the potential of the surface to become more negative. Hence it must produce the same risks of hydrogen embrittlement. It is, however, a convenient procedure for reducing corrosion and has been widely used for protecting such metal structures as ships hulls, oilrigs and pipelines. On large structures the anodes must be placed at intervals to ensure that the whole surface is protected. This is because, in practice, there will be an *IR* drop caused by the need for ions to move between the anodic and cathodic zones and this must be provided by the sacrificial anode being at a more negative potential than indicated in the figure. In a poorly conducting medium the anodes must be closer together.

Traditionally, sacrificial anodes are made of zinc or magnesium although it is now increasingly common to use aluminium alloys because of their low density and the low equivalent weight of aluminium. It may be noted that if aluminium, or indeed magnesium, were to dissolve anywhere near their equilibrium potentials and the metals remained in the active state, the simple argument of Fig. 9.16 would suggest that they would be unsuitable as sacrificial anodes; the anodes would dissolve too rapidly and much hydrogen would evolve from the protected surface. This does not happen because both metals passivate readily and as sacrificial anodes they are probably in a state of controlled and partial passivation (which will vary with the

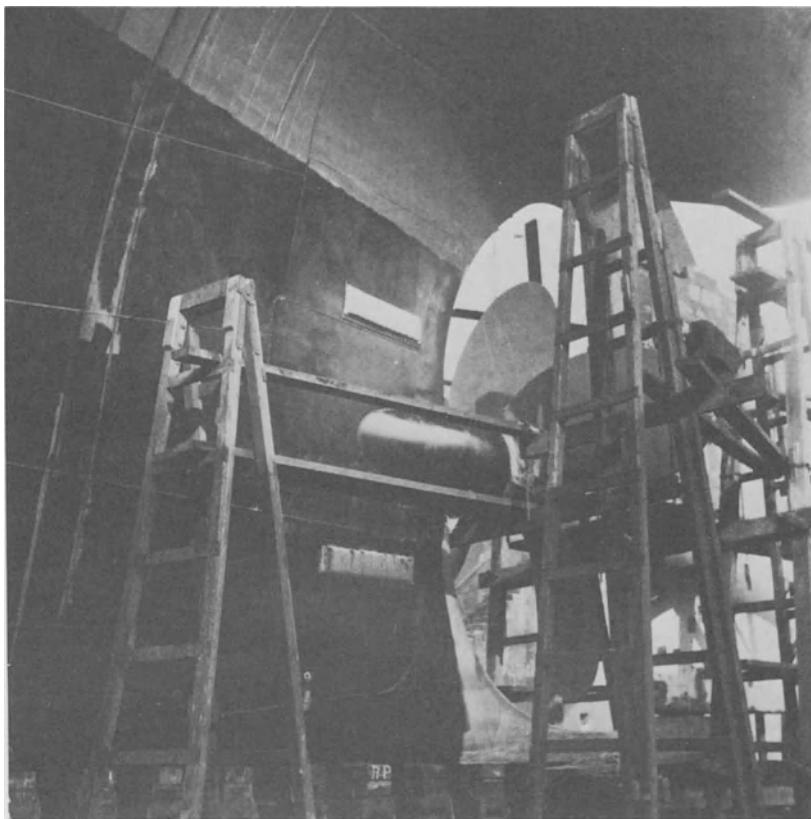


Figure 9.17 *Sacrificial anodes of Alcan 420 alloy placed above and below the propeller shaft of a tanker to protect the hull from corrosion. Photograph supplied by the Aluminium Company of Canada.*

medium). Indeed, aluminium itself cannot be used in this application because it passivates totally and the role of the alloying element (usually Mg, Hg, or Tl in 1–5% content) is to catalyse dissolution.

#### 9.5.4 Protective coatings

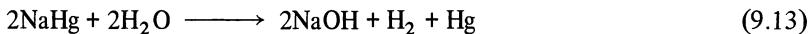
A wide variety of protective coatings are applied to metal surfaces to reduce corrosion. Indeed, much plating (see Chapter 7) has this objective and metals including Sn, Zn, Ni and Cr are widely used to protect cheaper metals. In addition, metals are anodized, phosphated and chromated as well as painted.

The major problem with protective coatings is the rapid, localized corrosion which can occur when the coating is damaged, and several examples (e.g. scratched paint, tinplate) were given in Section 9.4.

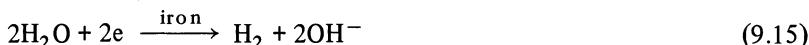
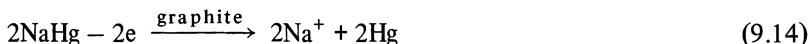
## 9.6 A CORROSION MECHANISM FOR CHEMICAL REACTIONS

The recognition that corrosion occurs by a mechanism involving two concurrent electron transfer processes at the same surface has implications elsewhere in chemistry. Perhaps this is a mechanism which should be considered for other chemical reactions.

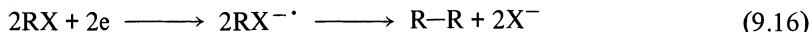
It has already been proposed in Chapter 3 that the catalysis of the sodium amalgam/water reaction



by graphite impregnated with iron occurs by a corrosion mechanism, i.e.



and similar mechanisms could be written for catalytic hydrogenations, oxidations with molecular oxygen at solid/liquid interfaces and reductions with metals. The many reductions carried out with, for example, iron, zinc and sodium can all be written as taking place by a mechanism where the key step is transfer of an electron from a delocalized electronic level rather than from a particular metal atom; the metal dissolves in a separate reaction, possibly elsewhere on the surface. For example, the reaction of sodium with an alkyl halide may well occur by the two concurrent electron transfer reactions



A further example is electrodeless plating, where metals such as nickel and copper are plated from solutions containing their ions and a reducing agent (e.g. formaldehyde, hypophosphite, hydrazine); again, the reduction of the cupric or nickel ion and the oxidation of the reducing agent occur at different sites on the metals.

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## 10 Batteries and Fuel Cells

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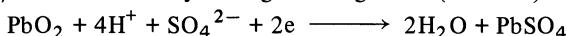
A battery is a device which can store chemical energy and, on demand, convert it into electrical energy to drive an external circuit. The importance of batteries to modern life surely requires no emphasis. Even so, there may be a tendency to overlook their diversity and the scale on which they are used; for example, in size they range from a fraction of a cubic centimetre for a hearing aid battery, to many cubic decimetres for some industrial and military versions, and in the western world we manufacture 4–10 batteries per year per head of population.

The electrical energy results from a spontaneous chemical change (i.e. a redox reaction with a negative free energy) within the battery. The redox reagents must not react directly but are consumed at different sites in the battery, at the anode and the cathode, and it is this which causes electrons to flow through the external circuit between the battery terminals. The electrochemistry of the three battery systems that are by far the most widely manufactured is summarized in Table 10.1. In practice, a battery is always designed and manufactured for a particular duty, e.g. to power a torch, to start a car engine, to supply emergency power for a hospital or a computer. For each application, a set of battery characteristics will be essential and these will, in turn, place requirements on the electrode reactions and determine the design of the cell. Figure 10.1 is a schematic diagram of a battery which recognizes that, in general, the electroactive species and the products of the electrode reactions are solids. The performance of the battery will depend on the cell geometry and on the design and composition of all the components labelled in the figure in addition to the choice of electrode reactions and their kinetics. The multitude of battery specifications is met by the manufacture of a number of battery systems (see later) but also by the production of the same system in various sizes. For example, a lead/acid battery for a car is typically 50 A h while for industrial use it may exceed 1000 A h. The range of Leclanché cells manufactured by Berec Ltd is illustrated in Fig. 10.2.

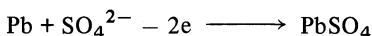
Hence in this chapter, battery characteristics and their relationship to the thermodynamics and kinetics of the electrode reactions and to cell design will first be discussed. Later some battery specifications, the evaluation of battery performance and the design, manufacture and performance of some practical batteries will be described. The discussion will include both batteries presently manufactured and those under development.

Table 10.1 Electrochemistry of the three most common battery systems.

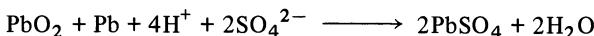
(i) *Lead/acid* Chemistry during discharge: +ve (cathode)



-ve (anode)



overall reaction



Electrolyte: aqueous  $\text{H}_2\text{SO}_4$ .

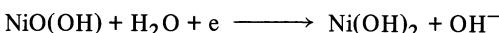
Current collectors: both Pb.

Reversible cell potential = 2.05 V.

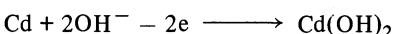
$$\Delta G = -394 \text{ kJ mol}^{-1}$$

Applications: cars, standby supplies, industrial, traction.

(ii) *Nickel/cadmium* Chemistry during discharge: +ve (cathode)



-ve (anode)



overall reaction



Electrolyte: aqueous KOH.

Current collectors: Ni and Cd.

Reversible cell potential = 1.48 V.

$$\Delta G = -283 \text{ kJ mol}^{-1}$$

Applications: standby supplies, industrial, plane engine starting, railway lighting.

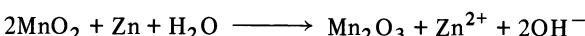
(iii) *Zinc/carbon* Chemistry during discharge: +ve (cathode)



-ve (anode)



overall reaction



Electrolyte: moist  $\text{NH}_4\text{Cl}/\text{ZnCl}_2/\text{MnO}_2/\text{C}$  powder.

Current collectors: graphite and Zn.

Reversible cell potential = 1.55 V

$$\Delta G = -257 \text{ kJ mol}^{-1}$$

Applications: small (but not miniature) portable power sources (torches, radios, toys).

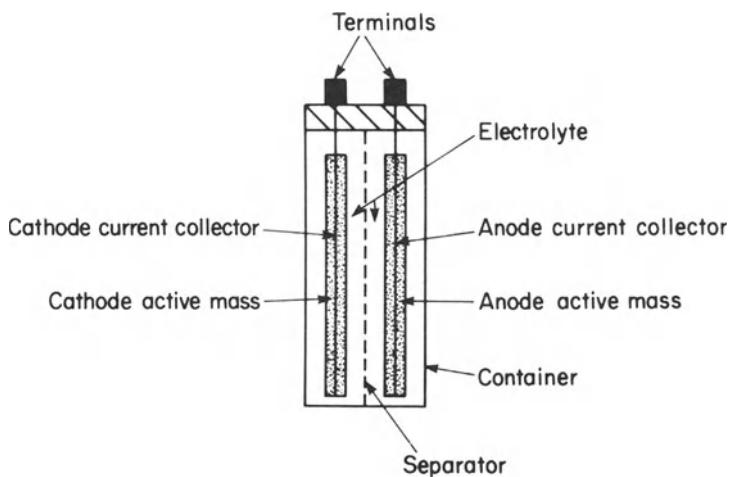


Figure 10.1 *Schematic diagram of a battery showing the principal components.*



Figure 10.2 *The Ever Ready range of Leclanché cells. Photograph supplied by Berec Ltd.*

In the final section of this chapter, fuel cells will be considered briefly. In principle, a fuel cell differs from a battery only in that the reactants are fed from outside the cell but the nature of the electrode reactions requires totally different technology based on catalytic, gas diffusion electrodes. Fuel cells were conceived as a method of converting primary fuels, particularly hydrocarbons, and oxygen into electrical energy in a way that would avoid the well known Carnot inefficiencies of conventional power generation based on burning the fuel. It has, however, proved impossible to obtain meaningful cell potentials and current densities because of the poor performance of the available electrocatalysts, and at the present time fuel cells would only be considered for very specialist applications. Moreover, the anode fuel is more likely to be hydrogen, methanol or carbon monoxide.

## 10.1 BATTERY CHARACTERISTICS

A certain performance is necessary for a battery to perform satisfactorily in any duty and we therefore need to define characteristics which may be measured and used to judge whether a battery is suitable for a particular application. Moreover in some cases, e.g. a car traction battery, no battery system presently available has all the essential properties. Hence it is important to understand how the characteristics depend on the choice of electrode reactions and on the design of the cell. It will also be clear that the various battery characteristics are not independent of each other and commonly a change of design to improve one will have an adverse effect on another.

(i) *Voltage.* The terminal voltage of the battery will depend on the free-energy change in the overall cell reaction and hence the choice of electrode reactions, the kinetics of the electrode reactions and the cell resistance, i.e.

$$V = E_e^C - E_e^A - |\eta_A| - |\eta_C| - IR_{\text{CELL}} \quad (10.1)$$

This equation has been used in other chapters but, in contrast to its application in electrolytic processes, the battery designers' concern is to make the voltage as high as possible.

Clearly the voltage will decrease as the current drawn from the battery is increased since  $\eta_A$ ,  $\eta_C$  and the  $IR$  term will all increase with current density. The cell voltage, excluding the  $IR_{\text{CELL}}$  of a practical battery, can be estimated from  $I-E$  data for the anode and cathode processes (see Fig. 10.3).

In principle, the polarization at each electrode may have a contribution from charge transfer, mass transport, nucleation and passivation overpotentials. The major contribution will normally be from the charge transfer overpotential since mass transport control has a catastrophic effect on the battery voltage (see Fig. 10.3) and one would not normally design a battery to operate in such conditions. Examples of nucleation and passivation overpotentials do occur. The former occur when the electrode reaction requires the formation of a new phase although the nucleation overpotential is normally a transitory phenomenon since, once nuclei of the new phase are present in numbers, the overpotential will disappear. The

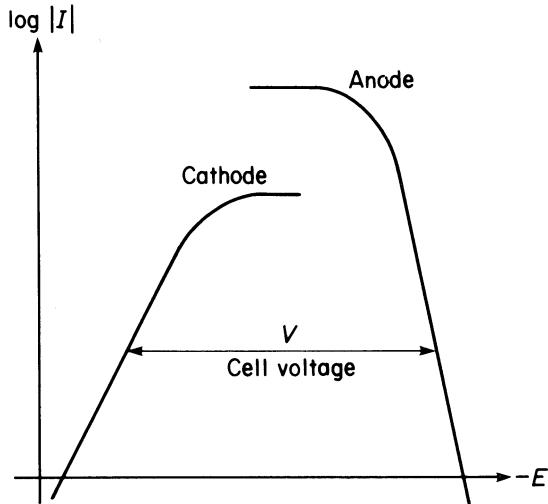


Figure 10.3 Plot of  $\log |I|$  vs  $E$  (vs a reference electrode) for the cathode and anode of a battery.

nucleation overpotential therefore occurs as a dip on the discharge curve at the commencement of discharge (see Fig. 10.4); such a dip is seen in the discharge curve of Zn/HgO cells since the cathode reaction requires formation of mercury nuclei on the graphite powder current collector. Passivation can contribute a substantial overpotential, as for example in the Mg/AgCl sea water battery; this is a reserve battery stored dry and activated by addition of sea water. The magnesium anode does not take up the potential of the  $Mg/Mg^{2+}$  couple because it corrodes with the

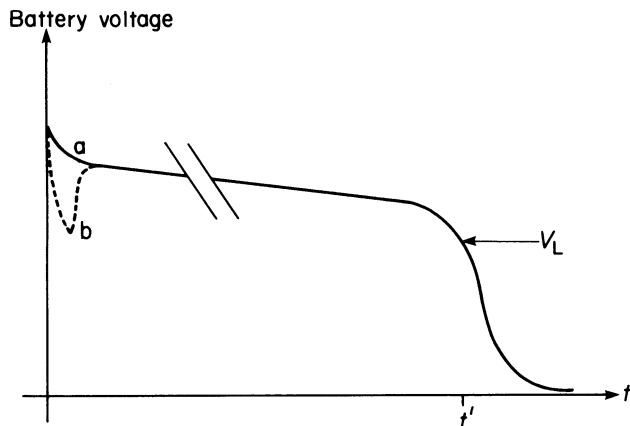


Figure 10.4 Discharge curves at constant current  $I$  for (a) a simple battery and (b) a battery where one electrode reaction has a nucleation overpotential.  $t'$  is the time for the battery voltage to reach a limiting value where the cell is no longer useful. The capacity of the battery is then  $I t'$ .

formation of a passive layer in the sea water medium. The polarization due to the passive layer can exceed 1 V although this can be reduced by alloying the magnesium. Lithium anodes in aprotic medium, increasingly common because of their high theoretical energy density, also suffer to some extent from passivation effects; in this case, however, the passivation overpotential generally decreases when the battery is operating.

Generally a high cell potential is sought and this is favoured by (a) the selection of electrode reactions which lead to an overall cell reaction with a high negative free-energy change, (b) electrode reactions without large overpotentials in the range of current to be drawn from the cell, i.e. the electrode reactions should be fast, and (c) the design of the cell with a low resistance, i.e. with a high-conductivity electrolyte, low-resistance separator and small inter-electrode gap.

(ii) *Current.* Current is a measure of the rate at which the battery is discharging. Current and voltage are, of course, always interlinked (see Fig. 10.3) but the ability to deliver a high current without an excessive voltage penalty is dependent on rapid electron transfer reactions and correct design of the active material to ensure a plentiful supply of electroactive species to the site where electron transfer is occurring. The active material generally behaves as a porous electrode but it should be noted that its composition and structure can change during discharge, e.g.  $\text{PbO}_2$  to  $\text{PbSO}_4$  during discharge of the lead/acid positive. This involves the conversion of an electronically conducting species to a very poor conductor and hence the current which can be drawn from the cell may depend on the state of charge and on the rate at which it has been discharged; both factors will determine the distribution of the  $\text{PbSO}_4$  in the porous structure.

(iii) *Capacity.* The capacity is the charge that may be obtained from the battery; it is usually quoted in ampere hours and clearly depends on the size of the battery. The nominal capacity of each electrode may be calculated from the weight  $W$  of active material via Faraday's law, i.e.

$$C = \frac{WnF}{M} \quad (10.2)$$

where  $M$  is the molecular weight of the active material. The capacity of the battery will be determined by the electrode of lowest capacity.

The practical capacity of each electrode, and hence of the battery, will depend on how much of the active materials can actually be consumed during discharge and this must be determined by experiment. Certainly the capacity will depend on the discharge conditions, e.g. current, and it is measured by monitoring voltage vs time during a fixed current discharge (see Fig. 10.4). The capacity is then  $It'$  where  $t'$  is the time at the fixed current  $I$  for the voltage to reach a value where the battery is no longer useful. The positive electrode of a lead/acid battery is an example where the practical capacity is well below the theoretical value. The cause is the formation of poorly conducting  $\text{PbSO}_4$  in the discharge reaction which can form a barrier

between the electroactive  $\text{PbO}_2$  and the current collector and prevent continuation of the reduction.

(iv) *Electricity storage density.* This is a measure of the charge per unit weight stored in the battery, i.e. it is the capacity per unit weight. Hence it is measured as in Fig. 10.4 but it applies to the whole battery, and hence the weight is that of the complete battery including electrolyte, current collectors, terminals, the case, etc.

Therefore, a high storage density depends on good battery design (minimizing the weight of all subsidiary elements) and also the correct selection of electrode reactions. The popularity in recent years of lithium anodes is partly due to the low weight of a mole of the metal while aluminium gives an even lower value of  $M/n$ , see equation (10.2).

(v) *Energy density.* Energy density is the energy obtainable per unit weight of battery ( $\text{kWh kg}^{-1}$ ) and is defined by

$$\text{Energy density} = \frac{It' V_{\text{AVE}}}{W} \quad (10.3)$$

Hence it is measured by determining the capacity (see Fig. 10.4) and noting the average potential during discharge and the total weight of the battery. It depends on the cell voltage (i.e. the choice of electrode reactions) and the factors which determine the storage density.

(vi) *Power density.* Some battery applications require a defined capability to deliver power ( $IV$ ) per unit weight of battery. This is the power density. The requirement may be for a continuous power density above a certain value or for a high value for a short period (i.e. pulse capability). The power density will decrease during discharge.

(vii) *Discharge rate.* The discharge rate is, as is current, a measure of the rate at which charge is drawn from the cell. It is normally quoted as the  $C/n$  or  $n$ -hour rate, which is the current to discharge the nominal capacity  $C$  of the battery in  $n$  hours.

(viii) *Cycle life.* Primary batteries are designed only for a single discharge but a secondary battery is expected to be capable of repetitive charge/discharge cycles. The cycle life is the number of charge/discharge cycles that are possible before failure occurs.

For a secondary battery, it is essential for the discharge/charge cycle to reform the active material in a suitable state for further discharge. The active material must have the correct chemical composition, morphology and distribution in the cell (with respect to current collectors). The cycle life will often depend strongly on the depth of each discharge, attempts to discharge totally the battery often being particularly damaging to the electrodes. The most common forms of failure include corrosion of the current collectors or contacts, shedding of the active material from the plates, shorting due to dendrites growing between the electrodes or changes in

morphology. The battery may show a gradual decline of performance as it is cycled or the failure can occasionally be quite sudden.

(ix) *Energy efficiency.* With secondary batteries for energy storage on a large scale, the energy efficiency (%) defined by

$$\text{Energy efficiency} = \frac{\text{energy released on discharge}}{\text{energy required for charge}} \times 100 \quad (10.4)$$

will be important. This will depend on the current efficiency of the electrode processes and the overpotentials involved in both discharge and charge reactions as well as the battery resistance. Again it will depend on the rate of charge and discharge.

(x) *Behaviour on overcharge.* With secondary batteries, it is not always possible to stop charging at exactly the correct moment. If the battery is overcharged, new electrode reactions must occur, e.g. electrolysis of water, and it is important that these reactions do not represent a hazard, e.g. the possibility of fires or explosion, or damage to the active material.

(xi) *Shelf life.* It is essential for most batteries to be stored, sometimes for many years, without self-discharge (i.e. reaction between the anode and cathode active materials or between either and the solvent or electrolyte) or corrosion causing significant loss of performance.

(xii) *Tolerance to service conditions.* The battery duty may require that it provides power continuously, intermittently or at an irregular rate. It may also be expected to perform its duty or be stored under a range of conditions. For example, a car battery in the USA must operate between temperatures of  $-30$  to  $+50^{\circ}\text{C}$  if it is to be successful in the extreme conditions of winter and summer. The battery may also have to be tolerant to various types of misuse, including occasional shorting, vibration and shock.

(xiii) *Reliability.* This is the ability to perform to specification reproducibly and without failure. It will normally be expressed as a failure rate within a given period.

(xiv) *Economic factors.* Two factors must be considered, the cost of manufacture and the cost of servicing during the working life of the battery. Clearly the components of the battery must be cheap enough for the final product to be competitive (although not all batteries need be cheap – it again depends on the application) and the raw materials must be available on the scale required. In duties which require long service lives, the extent and cost of maintaining the batteries in prime condition will, however, also be important in determining the choice of battery system.

## 10.2 BATTERY SPECIFICATIONS

It has already been noted that a battery is always manufactured for a specific duty. On the other hand, batteries are used to provide a wide variety of power requirements and, prior to the design of a battery system, it is essential to write an accurate specification. In this section three examples will be discussed.

Table 10.2 shows a specification for a car traction battery. A battery to power a car will clearly require a substantial power and energy output and by necessity will contribute substantially to the weight and volume of the vehicle. Hence the emphasis is on energy and power density in order to minimize the weight and volume of the battery. Moreover the capacity must be large to permit an acceptable range and, of course, the battery must be rechargeable. Moreover, unlike the duty of present car batteries, the battery is likely to be almost fully discharged on a regular basis to obtain the maximum range. Hence the specification must ask for a large number of charge/discharge cycles to deep discharge (this is much more difficult than cycling, say, to 50% discharge). Energy efficiency is also important since any value below 100% will represent a proportionate increase in running costs. The other specifications recognize the way in which a car is used — it must cruise at an acceptable speed, periodically accelerate and be driven intermittently with periods parked or garaged (a few minutes to several weeks) and be able to operate over a wide range of climatic conditions. It may also be involved in accidents, when the battery must present no additional hazards. To give confidence to the driver, a high reliability and a measurement of the state of charge of the battery will additionally

Table 10.2 A specification for a car traction battery.

Voltage	90–400 V
Capacity	10–20 kA h
Size	0.1–0.5 m <sup>3</sup>
Cycle life	> 600 deep discharge cycles
Energy density	> 50 Wh kg <sup>-1</sup>
Power density	
constant	> 20 W kg <sup>-1</sup>
for 20 s period	> 100 W kg <sup>-1</sup>
Energy efficiency	> 60%
Temperature	253–313 K
Vibration	> 5g
Shock	> 30g
Usage	Intermittent with uneven demand during use. Must store and withstand overcharge
Maintenance	Low
Reliability	Very high
Cost	Battery cost + power for charging equivalent to petrol cost over mileage during battery life. Say \$600–1500
Market	Many millions per year

be necessary. At the present time, no system can meet this specification, but the potential market is so large that such a battery remains a very active research goal. Possibilities include improved lead/acid, nickel/zinc, nickel/iron, sodium/sulphur, lithium/iron sulphide and aluminium/air (see later).

The requirements for a heart pacemaker power supply are quite different (see Table 10.3). A primary cell will suffice and it need only have a power output of a few microwatts ( $\mu\text{W}$ ) but this must be supplied continuously for several years without maintenance and with absolute reliability. It must also be compatible with the body and operate at  $37.4^\circ\text{C}$ . Lithium/iodine cells are presently used for this application.

Table 10.3 Specification for heart pacemaker battery.

Voltage	1–3 V
Capacity	0.5 A h
Size	Few $\text{cm}^3$
Cycle life	Primary
Power density	1–5 $\text{mW kg}^{-1}$
Temperature	310 K
Usage	Almost constant demand for many years
Maintenance	None
Reliability	Extremely high
Cost	Relatively unimportant
Market	$10^5$ per year

The final specification (Table 10.4) is for an emergency power supply for a computer memory; this is again a relatively small battery and the prime need is a long shelf life and the ability to work promptly on demand. Possible batteries would include secondary Ni/Cd or sealed Pb/acid or a long-life primary cell such as HgO/Cd or certain lithium cells.

Table 10.4 Specification for standby supply to volatile computer memories.

Voltage	1–3 V
Capacity	0.1–0.5 A h
Size	Few $\text{cm}^3$
Cycle life	Some advantage in ability to recharge; never deeply discharged
Power density	1–4 $\text{W kg}^{-1}$
Temperature	273–313 K
Usage	Long shelf life. Operational for a few milliseconds to hours at infrequent intervals (to cover mains failure or deliberate disconnection)
Maintenance	Low
Reliability	High
Cost	Relatively unimportant
Market	Few millions per year

### 10.3 EVALUATION OF BATTERY PERFORMANCE

It is important to evaluate the performance of a battery, i.e. to determine the characteristics described in Section 10.1, in conditions which relate closely to those where it will be used. Traditional methods would include measurement of capacity, energy density and power density and for secondary batteries the determination of cycle life and energy efficiency during:

- (a) Discharge into fixed resistances – this is the test which is least critical of the battery. It is necessary to monitor both voltage and current as a function of time.
- (b) Discharge (and charge) at constant currents – this permits simple and direct measurement of capacity, cycle life, etc.
- (c) Discharge (and charge) at constant voltages – this method gives the maximum power output directly and allows the determination of the capacity at fixed voltage.
- (d) Discharge at constant wattages – this most closely imitates the duty of many batteries to power instrumentation but it is the most difficult test to carry out; it requires complex electronic equipment. For this reason it is often easier to test the battery with the instrumentation that it is designed to power.

With developments in computers and electronic instrumentation it is now possible to automate battery testing. Such evaluation facilities are also capable of much more complex test procedures. It is, for example, common to test using a variable current, voltage or wattage demand which seeks to imitate more closely the battery duty. Thus car traction batteries are evaluated using a standard, programme cycle defined by the US Department of Energy. It represents the demands on the battery during a typical day in urban driving conditions i.e. start–stop driving at 30–50 m.p.h., regular acceleration, parking and recharge overnight.

A complete test programme must consider many other factors including:

- (a) The effect of ambient conditions, particularly temperature and pressure, both during duty and storage, on performance. The length of shelf life before use must also be varied.
- (b) The effect of mechanical shock, acceleration and perhaps radiation.
- (c) The dangers arising from various types of misuse including overcharge, spillage of the electrolyte, damage by fire.
- (d) The eventual recycle or disposal of cell components in the battery.

Table 10.5 shows a comparison of some primary and secondary batteries, the data being obtained for R20 size ( $50 \text{ cm}^3$ ) by constant current discharge at the 100 h rate (i.e.  $C/100$  rate). It can be seen that while there is a wide variation of performance, the primary cells do, in general, give higher capacities and energy densities. Moreover, they are much cheaper, by at least a factor of ten.

The Leclanché cell (Zn/C) has the advantage of cheapness although it can be seen that other primaries have a considerable advantage in terms of performance, particularly the cells with a lithium anode or an air cathode, and the reasons for this can readily be understood. It was noted above that the performance depends on

Table 10.5 Performance data for R20 size ( $50 \text{ cm}^3$ ) batteries during discharge at  $100 \text{ h}$  rate at  $20^\circ\text{C}$ .

Battery	Average voltage (V)	Capacity (A h)	Weight (g)	Energy density ( $\text{Wh kg}^{-1}$ )
<b>(i) Primary systems</b>				
Zn/C	1.2	6	90	80
Mg/C	1.5	8	100	120
Alkaline MnO <sub>2</sub>	1.2	10	120	100
Zn/HgO	1.2	12	170	85
Zn/air	1.3	22	85	340
Li/SOCl <sub>2</sub>	3.4	12	100	410
Li/MnO <sub>2</sub>	2.9	10	100	290
<b>(ii) Secondary systems</b>				
Sintered plate Ni/Cd	1.25	4	150	33
Spiral wound Pb/acid	2.1	2.7	185	30
Zn/AgO	1.5	5	105	70

the mode of discharge. As an example, it may be noted that the Zn/C battery gives higher performance on intermittent discharge; the capacity increases to about  $10 \text{ A h}$ .

## 10.4 BATTERY COMPONENTS

### 10.4.1 The container

The battery case must be resistant to corrosion from both inside and outside and hence it must be stable to chemical attack by the electrolyte, active materials and the environment at the operating temperature. In addition it must have the required mechanical strength, be cheap and light and there must be a simple method of sealing.

For alkaline batteries the case is generally a steel, while for systems with an acid electrolyte, polypropylene is rapidly replacing materials such as hard rubber. For a few batteries the case also acts as one of the active materials, e.g. the zinc can in a Leclanché cell.

### 10.4.2 Separators

Again the separator must be chemically stable to the electrolyte and to the active materials at the temperature of operation. It is also necessary for the membrane to have the correct qualities of wettability, selectivity, resistivity and flexibility for the particular battery system. The cost is very variable; in lead/acid batteries the target would be pence per square metre while for some Ni/Cd batteries £1 per square metre may be acceptable.

In practice, a wide range of materials are used as battery separators. Even with one system, different materials may be used for batteries designed for different discharge rates or, indeed, manufactured by different companies. An example of the former is the Ni/Cd battery; for high-discharge-rate pocket plate cells the separator is generally only a series of thin plastic pins, while for sintered plate cells it will be 1–3 layers of nylon or cellulose-based felt reinforced for vented cells by a membrane (to act as an oxygen barrier). The most common materials are microporous (pore size 0.01–10 µm) or macroporous (30–70 µm pores) polymer sheets a fraction of a millimetre thick; these generally have a porosity of 50–80% and a resistance of 0.05–0.5 Ω cm<sup>2</sup>. An example is the microporous polyethylene material normally used for lead/acid car starter batteries. With more expensive systems, ion exchange membranes are considered and the sodium-β-alumina developed for the sodium/sulphur battery is an example.

#### 10.4.3 Current collectors

In order for the battery to have an acceptable capacity, the active material is almost always a thick layer of porous, particulate paste and the electronic conductivity of this material is seldom very high. Hence it is necessary to have a current collector, which is usually a metal grid or sheet, to provide a conducting path through the paste and thereby minimize the resistance of the battery. The current collector also acts as a physical support for the active mass which otherwise would be a very brittle structure.

In early batteries, the current collector was generally a plate or a closely spaced grid. These, however, contributed substantially to the total battery weight and have proved to be not always essential; certainly the current collector is now designed to minimize weight, e.g. by using very thin metal sheet or expanded metal. In some cases even less metal is necessary. In the lead/acid negative the paste always contains sufficient lead to make a current collector superfluous and the modern design is more of a contact to the external circuit. In contrast the positive electrode paste is poorly conducting and a close grid is essential. In some pastes, e.g. the Leclanché electrolyte, a carbon powder is added to improve conductivity to the central carbon rod current collector.

Clearly, the current collector must be stable to chemical attack by both electrolyte and active material and this limits the choice of material, e.g. lead is the only widely used material in a lead/acid battery. Corrosion of the collector and shedding of the active paste are the two major causes of battery failure.

#### 10.4.4 Electrolyte

The selection of the electrolyte is determined by the electrode reactions and its concentration is also important. This will control the plate potentials, the electrolyte resistance and viscosity and, by its effect on the rate of diffusion, the differences in concentrations of species between the inside and the outside of the pores of the active paste.

Temperature has a large effect on electrolyte properties and both viscosity and resistance increase by more than an order of magnitude as the temperature drops from ambient to  $-30^{\circ}\text{C}$ . This largely accounts for the poorer performance of the battery at lower temperatures.

The weight of the electrolyte is a major contribution to that of the complete battery and hence must be minimized. In any case the electrode spacings should be small to minimize battery resistance.

#### 10.4.5 Active materials

For a battery with a reasonable discharge rate and capacity, the electroactive species must be readily available at the sites of electron transfer and be present in large quantities. In most batteries these necessities are provided by using solid reactants, and at least in secondary batteries the product of the electrode process is also a solid; the anion of the electrolyte and sometimes the proton are also participants in the chemical change during the charge or discharge process. Hence if the change is to be accomplished at a reasonable rate, intimate contact and a high-area surface between the solid reactants and the electrolyte are essential. This is accomplished by using the electroactive materials in the form of a paste on the current collector.

Such structures are known as porous electrodes and they behave quite differently from the effectively planar electrodes used in most other areas of applied electrochemistry. The porous electrode is a mass of particulate reactants (sometimes with additives) with many random and tortuous electrolyte channels between. Real porous electrodes cannot be modelled but their behaviour can be understood qualitatively using a simplified model shown in Fig. 10.5; in fact, there are two distinct situations which arise. In the first (Fig. 10.5(a)) the electroactive species is a good electronic conductor, e.g. a metal or lead dioxide; here the electrode reaction will occur initially on the face of the porous electrode in contact with the electrolyte but at the same time, and probably contributing more to the total current, the

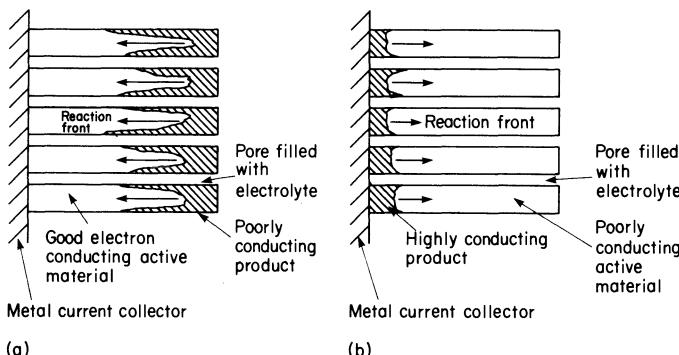


Figure 10.5 *Simple models for a porous electrode in a battery. (a) Active material highly conducting, e.g. a metal or  $\text{PbO}_2$ . (b) Active material poorly conducting, e.g.  $\text{PbSO}_4$ .*

reaction will occur inside the pore; not, however, along the whole depth of the pore because of the *IR* drop in solution. The potential and current distribution will depend on both the kinetics of electron transfer and the resistance of the electrolyte phase. A quantitative treatment of the straight, circular pore approximation allows a calculation of the penetration depth (the distance down the pore where reaction occurs to a significant extent) and it is found to increase linearly with electrolyte conductivity and the radius of the pore but to be inversely proportional to the exchange current density. It should also be noted that the active mass and its structure changes during discharge (and, of course, charge). For example, in the lead/acid negative electrode, the lead is oxidized to lead sulphate and this change causes an increase in volume of the active mass and the interconversion of a good electronic conductor to a bad one. Since this change will occur at the highest rate, initially at the pore/electrolyte interface, a consequence is pore blocking and a loss of capacity compared with that calculated from the weight of active material. In pore blocking, the non-conducting material seals the head of the pore, preventing contact between the electrolyte and active material down the pore.

During recharge, a different situation can arise (see Fig. 10.5(b)). Here the active mass in the discharged state would largely be poorly conducting material, e.g.  $\text{PbSO}_4$  in the lead/acid positive electrode. Now the electrolyte is more conducting than the solid structure and it is perhaps more helpful to discuss a ‘porous electrolyte’. The behaviour of such electrodes should be quite different. Certainly the oxidation of lead sulphate to lead dioxide must occur first at the current collector/paste interface and the reaction zone will move out through the paste towards the electrolyte. This is in sharp contrast to the case where the porous paste is conducting; then the reaction occurs initially at the electrolyte side and the reaction zone will tend to move through the paste towards the current collector.

The electroactive species at the negative electrode is generally a metal. For secondary batteries, the porous metal electrode is usually prepared by electrochemical reduction of a paste containing the metal ion, e.g.  $\text{PbO}/\text{PbSO}_4$  for the lead/acid and  $\text{ZnO}/\text{Zn}/\text{KOH}$  for the zinc electrode. The preparation is carried out *in situ* in the battery in a process known as forming because the high-area metal would not be stable to oxidation by air. With many primary batteries the negative electrode can be a plate which develops porosity during discharge. The positive electrode paste can also be formed *in situ* (e.g.  $\text{PbO}_2$  from  $\text{PbO}/\text{PbSO}_4$ ,  $\text{NiO(OH)}$  from  $\text{Ni(OH)}_2$ ) or prepared by chemical oxidation (e.g.  $\text{CuO}$  from  $\text{Cu}$ ) or precipitation methods (e.g.  $\text{AgO}$  by addition of  $\text{KOH}$  to  $\text{AgNO}_3$ ).

In secondary batteries, metal electrodes are not area stable. During cycling an undesirable decrease in surface area occurs, i.e. ball up, and additives known as expanders are added to avoid this. For example, lignin sulphates and barium sulphate are added to the lead/acid negative. While their mode of action is not fully understood, it may be significant that  $\text{BaSO}_4$  is isomorphous with  $\text{PbSO}_4$  and therefore able to act as nuclei for  $\text{PbSO}_4$  formation during lead oxidation. On the other hand, positive electrodes are normally area stable and additives are not necessary.

Clearly the sizes of the particles and the pores, i.e. the porosity of the paste, are

important in determining the performance of the battery. In practice, porosity should be about 50%. Below this value, the utilization of the active material suffers due to pore blocking, and above it the mechanical stability becomes a problem. Hence there is a trade-off between capacity and cycle life.

The loading of the paste, the thickness of the porous layer, also affects performance (see Table 10.6). Thin plates improve capacity particularly at high discharge rates and also give a higher power density.

Table 10.6 Effect of paste loading on performance.

Battery	Capacity (A h)	
	10 min rate	30 h rate
13 plates 3/16 inch thick	40	152
26 plates 3/32 inch thick	67	182

## 10.5 PRESENT BATTERY SYSTEMS

### 10.5.1 Lead/acid batteries

While all are based on the same electrochemistry, the  $\text{PbO}_2/\text{PbSO}_4$  positive electrode and the  $\text{Pb}/\text{PbSO}_4$  negative electrode (see Table 10.1), a number of technologically quite different Pb/acid batteries are manufactured to obtain the various performances demanded by the many applications. Some of the more important types will be described here.

The most important market remains the car battery for starting, lighting and ignition (SLI), with approximately  $50 \times 10^6$  units per year being sold in the USA. Lead/acid batteries are, however, also used on a very large scale for traction (e.g. delivery vans, milk floats, fork-lift trucks, industrial trucks – there are more than 100 000 such vehicles in the UK) and for stationary back-up or emergency power supplies. More recently, small lead/acid cells to compete with high-quality primary cells and nickel/cadmium cells for instruments, radios, etc., have also become available.

#### (a) Car batteries

An SLI battery will be a 6 V or 12 V (three or six cells in series) battery with the following characteristics: (i) a capacity of 100 A h at the 20 h rate, (ii) a high pulse capability to permit engine starting, typically 400–450 A for 30 s without the voltage dropping below 7.2 V, (iii) the ability to provide a lower current for an extended period, e.g. 25 A for 3 h without the voltage dropping below 10.5 V, and (iv) multiple charge/discharge cycles although not necessarily to deep discharge.

Invariably, SLI car batteries are designed with each cell having parallel pasted electrodes and a separator, and Fig. 10.6 shows a cutaway diagram of a typical

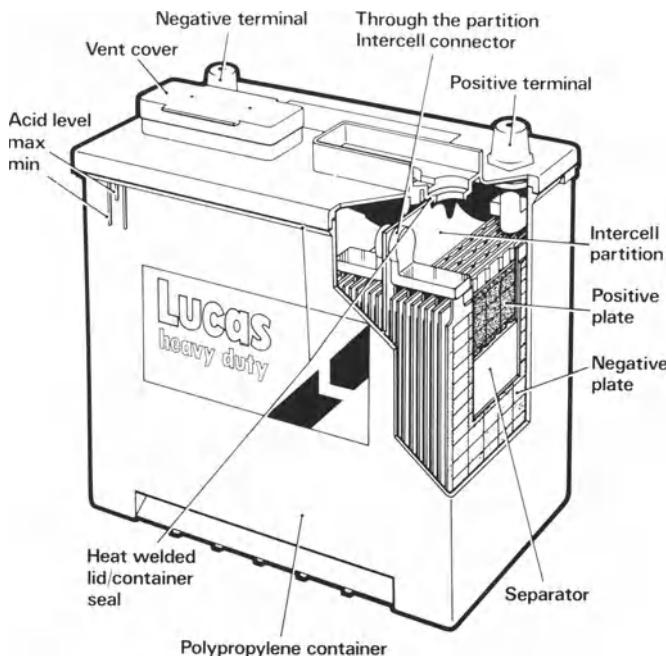


Figure 10.6 Cutaway drawing of an SLI lead/acid battery. Diagram supplied by Lucas Batteries Ltd.

battery. Conventionally, the current collectors are die cast grids (see Fig. 10.7), say 10 cm x 15 cm, made from an alloy of lead, usually Pb/5% Sb. The alloying element is present to improve the die casting and mechanical properties of the metal. More recently it has been found possible to reduce the weight of lead in the current collectors by using expanded metal. Moreover, with the negative electrode, the active mass always contains lead powder and is therefore relatively conducting. Hence it is found possible to use grids with greatly reduced amounts of lead (again see Fig. 10.7). Such changes in design of grid are not possible with the positive electrode because the paste has a lower conductivity and shedding of the active mass is also a common difficulty.

The electroactive pastes are prepared from pure lead. The massive lead is air oxidized under controlled conditions to give a powder mixture of lead oxide and lead (approximately 50:50). To the paste to be used for the negative electrode are added various additives, most commonly carbon powder (~ 0.25%), lignin sulphonates (~ 0.2%) and barium sulphate (~ 0.35%). The carbon improves the conductivity of the final plate while the latter compounds prevent the reduction in surface area of lead and other changes in morphology of the plate (i.e. they are expanders). Usually no additives are used in the positive electrode paste. The positive and negative pastes are then made by addition of aqueous sulphuric acid, and spread uniformly on the grids (the thickness of the final electrodes will be 0.1–0.5 cm). At this stage the electrodes are allowed to dry and stand for several

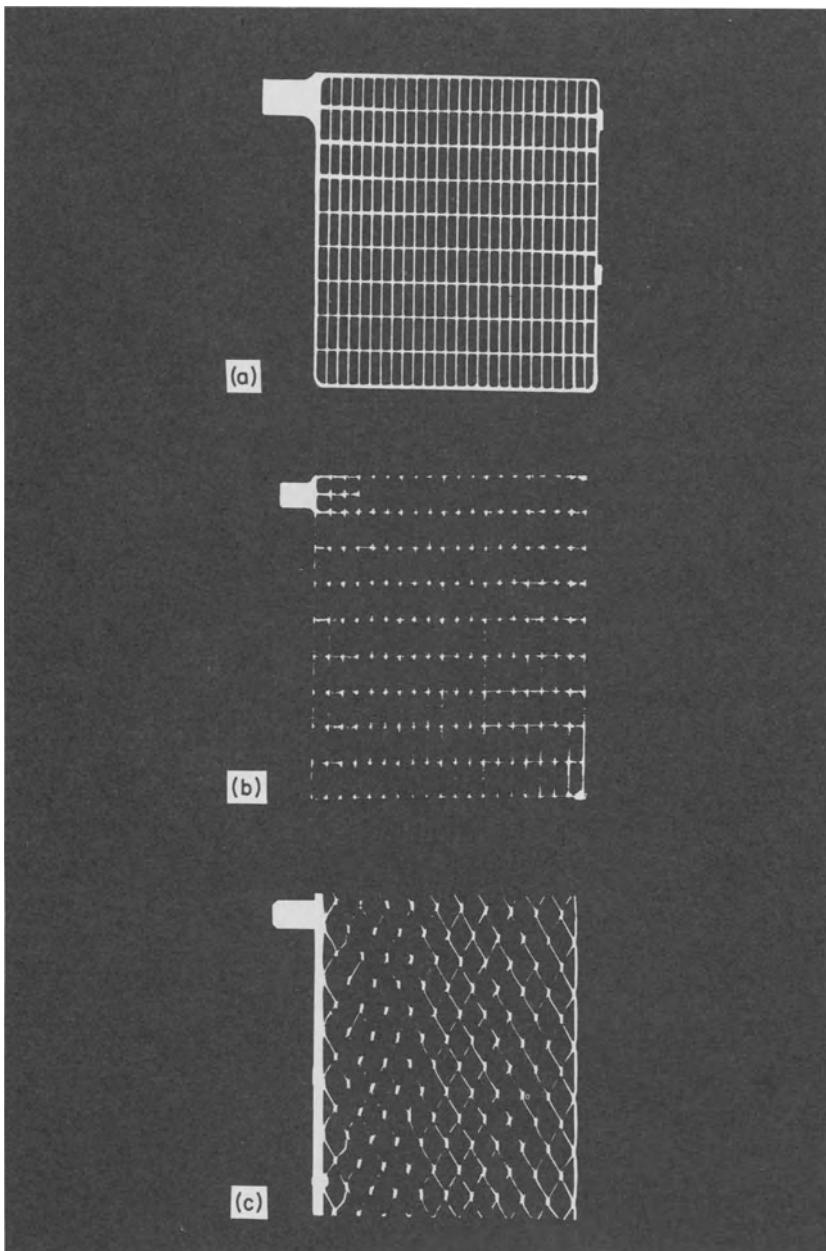
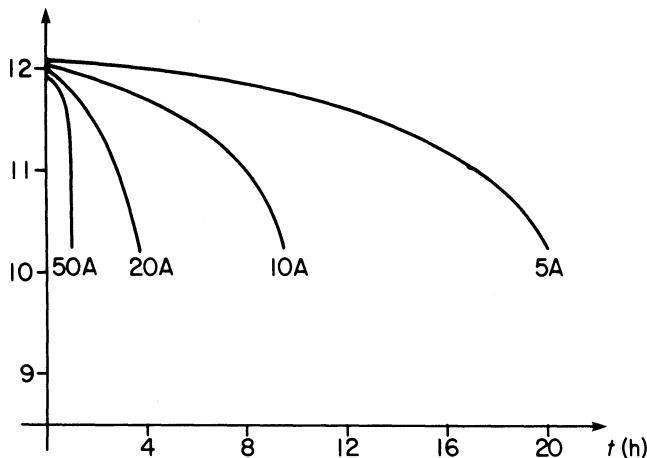


Figure 10.7 *The development of negative electrode grids, with reduced weight of lead, for the lead/acid battery: (a) and (b) cast grids, (c) expanded metal. Photograph supplied by Chloride Technical Ltd.*

days in air and the oxidation of the lead in the paste goes to completion. At this stage the electrode paste contains a mixture of  $\text{PbO}$  and  $\text{PbSO}_4$  and, in addition, the negative paste contains the additives. The pasted grids and the separators, usually microporous polyethylene or resin-impregnated paper, are placed in the battery container and the inter-cell connectors and terminals are welded into place. The battery is filled with sulphuric acid and sealed before the electrodes are charged slowly, e.g. at constant current at the 20 h rate.

#### Battery voltage (V)



#### Battery voltage (V)

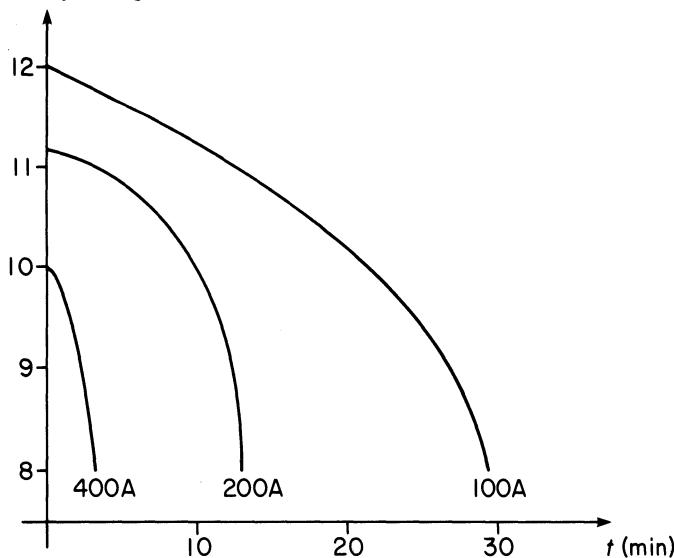


Figure 10.8 Constant current discharge curves for a 12 V, 100 A h SLI lead/acid battery at 25°C.

The design of lead/acid batteries develops continuously. The major changes in recent years have been to reduce the weight of the grids, to change the case from hard rubber to polypropylene and to improve slightly the use of active material, reducing that necessary in the battery. These combined have improved the energy density from 24 to 32 Wh kg<sup>-1</sup> without loss in other performance. The present trend is towards totally maintenance-free sealed batteries and this requires protection against overcharge; on overcharge water electrolysis will occur and oxygen and hydrogen will be formed. This increases the pressure inside the battery and the mixture of gases presents an explosion hazard. The approach is to build catalyst for the recombination of hydrogen and oxygen into the cell.

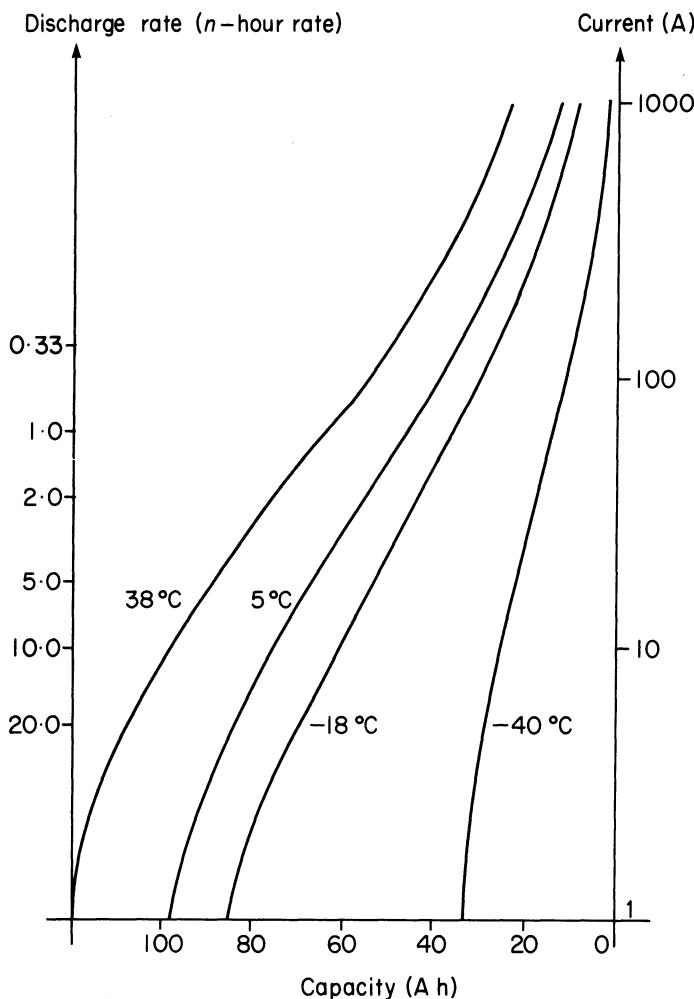


Figure 10.9 *The dependence of the capacity on the discharge rate for a 100 A h SLI battery.*

The performance of SLI batteries has been extensively characterized and data are available in several of the texts mentioned at the end of the chapter. For example, the capacity–discharge rate characteristics will be known as a function of temperature, plate thickness, type of separator and sulphuric acid concentration as will the variation of voltage and power as a function of current at various stages of charge. Figures 10.8 to 10.10 show some typical data.

(b) *Traction and industrial power supplies*

These batteries differ from the SLI type in that they often have a larger voltage, 48–96 V, and a higher capacity, obtained by using larger and thicker electrodes. They are also required to cycle to a much higher percentage of total discharge. The grids, therefore, must be more robust and care must be taken that the active material is available and is not shed during repeated cycling. The complete discharge of the electrodes may result in a volume increase of over 50% and this clearly presents a potential problem. In practice, shedding is a greater problem at the positive electrode and in this class of lead/acid battery it is normal to protect this electrode physically in some way.

Traction batteries are constructed with both the flat plate and the tubular positive plate design. The former are very similar to the SLI design except that they may be larger and more robustly constructed; the major addition is a second separator – a thick matted glass wool felt is placed against the positive plate to support the active material. The design of a tubular positive plate is shown in Fig. 10.11. Each plate consists of 15–23 tubes, diameter 8 mm, originally made from perforated India rubber but now from woven glass wool or a plastic. An example of the latter is the Chloride gauntlet type which is manufactured by stitching at intervals two layers of woven or non-woven, felt terylene cloth; tubular mandrels are placed in each ‘tube’ and the cloth is then impregnated with a

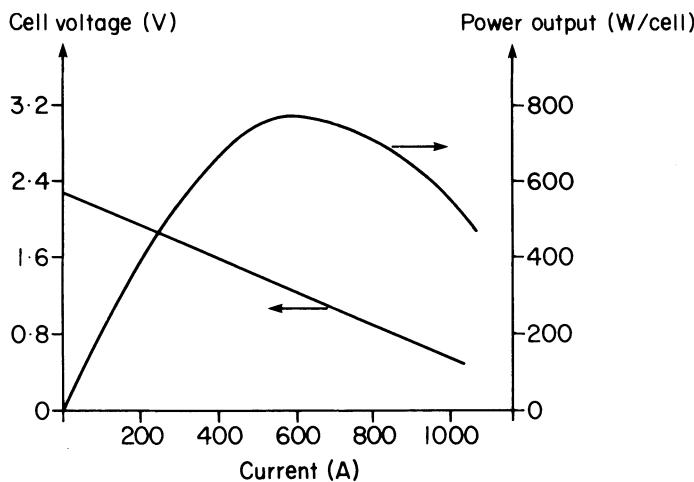


Figure 10.10 *Cell voltage and power output as functions of current for an SLI lead/acid battery.*

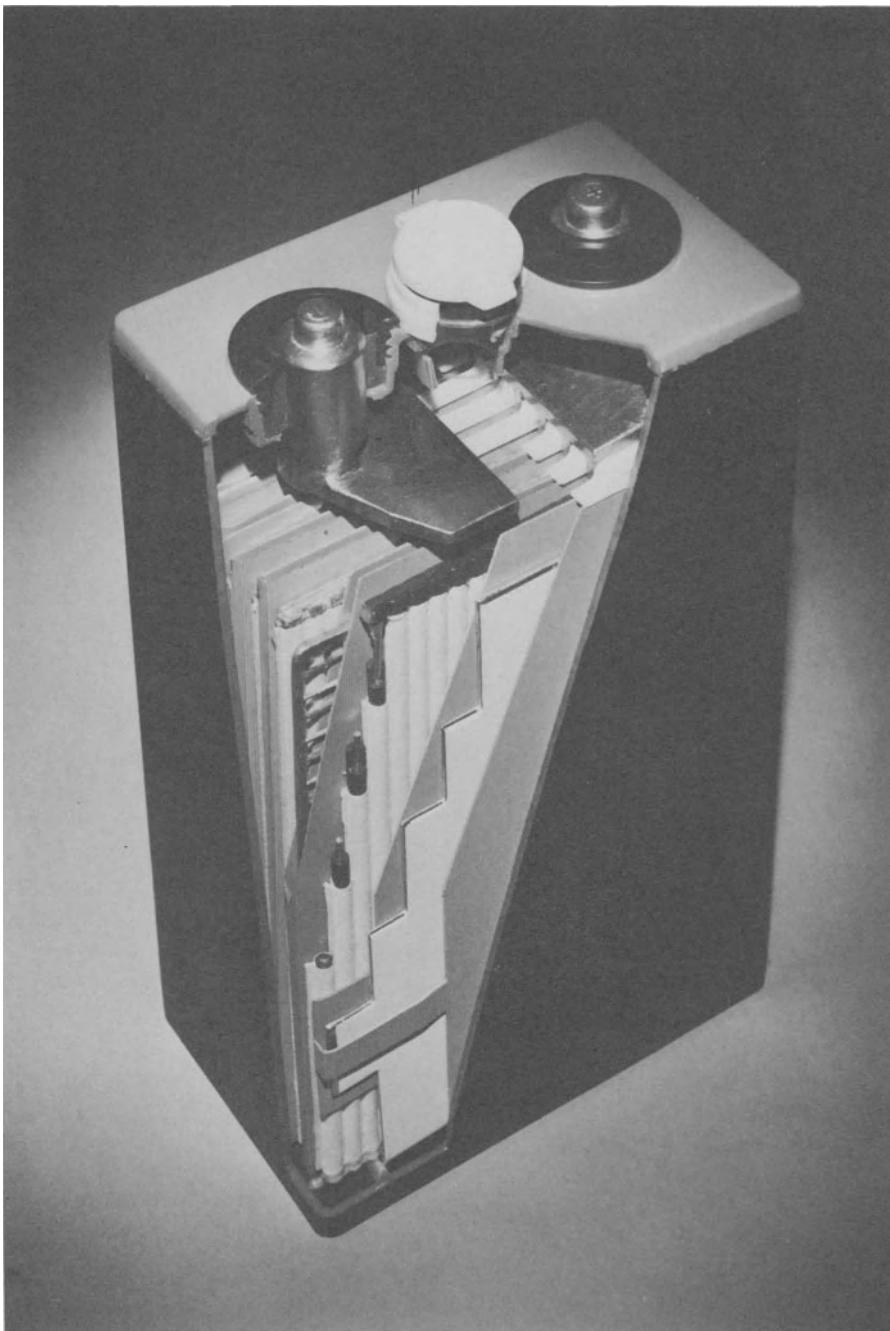


Figure 10.11 *Cut-away of a lead/acid motive power cell showing Gauntlet type non-woven terylene tubular plate positive electrodes (cf. Fig. 10.6). Photograph supplied by Chloride Technical Ltd.*

thermosetting resin to give it rigidity. The current collector is a Pb/Sb rod placed at the centre of each tube and the tubes are filled with positive paste. This is generally done by packing with dry oxide and then standing the plate in sulphuric acid. The negative plate is pasted, as the SLI battery, and the conventional separator is also present. The advantage of these tubular anode cells is that shedding of the positive active material is not possible and hence the cycle life is likely to be improved.

Energy densities for these larger batteries normally lie in the 20–30 Wh kg<sup>-1</sup> range although the contractors in the US Department of Energy car traction battery programme now claim values of 37–42 Wh kg<sup>-1</sup> for test Pb/acid units.

(c) *Stationary and standby power supplier*

Lead/acid batteries are used for many diverse remote and standby duties and hence are manufactured with a wide range of voltage and current capabilities and capacities. Pb/acid batteries do self-discharge slowly because of some reaction between the active materials and water; as a result the batteries are often on constant trickle charge.

Flat plate and tubular positive plate cells are produced for stationary duty, but where reliability is a prime consideration, Planté cells are used. In a Planté cell, the positive electrodes are manufactured by a quite different process. The oxide is formed by electrochemical oxidation (say, 10 mA cm<sup>-2</sup> for 20 h) of a lead baseplate or grid, often shaped to increase its surface area, in an electrolyte which contains sulphuric acid and an anion (perchlorate or nitrate) which forms a soluble Pb<sup>2+</sup> salt. This leads to a layer of thick porous oxide; the nitrate or perchlorate is present to prevent total passivation of the lead surface. The resulting plate, thickness 6–12 mm, is then reduced to form spongy lead metal, is washed thoroughly, and is recharged when in a fabricated cell. The active material formed in this way adheres to the base lead better than pasted materials and therefore cycles more reliably. Against this, there is less active material on each plate and, inevitably, the energy density of the battery will suffer; 7–12 Wh kg<sup>-1</sup> is typical.

(d) *Sealed cells without free electrolyte*

For many years, cells with electrolyte gelled by the addition of sodium silicate or sulphuric acid adsorbed onto a felted glass fibre mat or thick paper have been manufactured; such cells avoid the hazards of acid spillage and were sold mainly for aircraft or motorbikes. Now cylindrical lead/acid cells, typical capacity 2 A h and without free electrolyte, are produced to compete with small Ni/Cd and primary cells for the consumer market. These cells are spirally wound (as a Swiss roll) with electrodes of thin, pure lead sheet perforated to increase the amount of pasted active material adhering to the metal and an adsorbent glass fibre paper separator, packed into a metal can.

### 10.5.2 Nickel/cadmium batteries

The basic electrochemistry of the Ni/Cd battery was given in Table 10.1; once again, however, the equations are misleading in that the reactions, particularly at

the positive electrode, are not nearly as simple as indicated. In the nickel oxide paste, the oxidation state of the oxidized nickel species is uncertain and varies between +2 and +4, both the oxidized and reduced species exist in several crystal modifications and the important roles of water and potassium ions are not included in the equation.

Nickel/cadmium batteries are manufactured in very large numbers and there are two basic types, pocket plate cells and sintered plate cells. Pocket plate designs are known for their reliability and very long shelf life ( $> 20$  years) without any significant maintenance. Hence they are ideal for emergency power supplies and are also used for train lighting, switch gear and engine starting. Where there is direct overlap in applications with Pb/acid batteries, the Ni/Cd alternative often gives better performance but is also more expensive. Sintered plate cells give higher discharge rates and are capable of good performance at low temperatures; they are particularly attractive for many military applications.

#### (a) *Pocket plate batteries*

The active material for the positive electrode typically contains nickel hydroxide (80%), cobalt hydroxide (2%), graphite (18%) and maybe a trace of a barium compound. The graphite is present in two forms, powder and flake, to improve conductivity and the cobalt and barium compounds increase the percentage usage of the active material during discharge and also increases the cycle life. The nickel hydroxide is prepared by precipitation with caustic soda from aqueous nickel sulphate. The precipitate is filtered, dried, rewashed to ensure complete removal of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions and finally redried. The active material for the negative electrode is cadmium hydroxide (78%), iron (18%), nickel (1%) and graphite (1%) and is prepared by dry mixing; the iron, nickel and graphite are present to reduce ball up.

The electrodes are made from perforated, nickel-plated steel strip and the active material in the form of long briquettes. The process is illustrated in Fig. 10.12, the final stage being to compress the structure into a thin plate. The size of the final plate is determined by the number of strips interlocked together. Figure 10.13 shows the complete design of the battery, the electrodes being alternately positive and negative plates and the plates being kept apart by thin insulating rods. All the metal components are nickel plated and this cell is assembled in a plastic or steel case. The batteries are completed by filling with the electrolyte, 6 M KOH, and then charging.

Pocket plate batteries are manufactured with capacities between 10 and 1200 A h. Their chief advantage is their long life and their ability to deliver their capacity and maintain their voltage over a wide range of discharge rates and temperatures. They also retain charge over many months. The energy density is, however, only moderate, falling in the range 15–25 Wh kg<sup>-1</sup>.

#### (b) *Sintered plate batteries*

In these cells, the electrodes are manufactured from sintered metal, thickness 0.5–1 mm, and with a high porosity (80–85%) and surface area of 0.25–0.50 m<sup>2</sup> g<sup>-1</sup>.

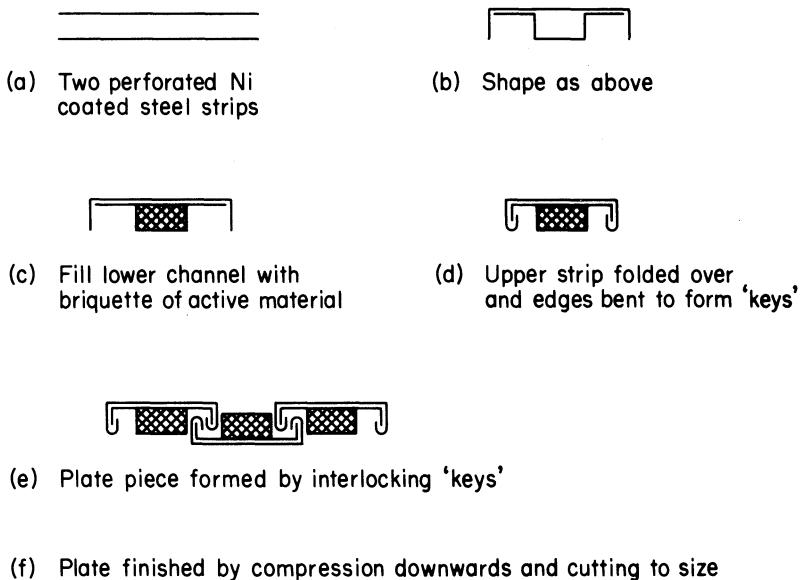
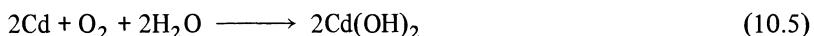


Figure 10.12 *Procedure for the manufacture of pocket plate electrodes for a Ni/Cd battery.*

The active material is impregnated into the sintered metal in a series of steps. The sintered metal is first dipped into a solution of the nickel or cadmium ions (usually present as nitrates) and a vacuum is used to draw the solution into all the pores. Then the sintered metal containing the solution is treated chemically, thermally or electrochemically to cause the ions to precipitate, nickel as the hydroxide and cadmium as a mixture of metal, oxide and/or hydroxide. The cycle is completed by washing and drying and then the complete procedure is repeated 3–10 times to obtain a high loading of active material. The solution for the positive electrode sometimes contains cobalt (< 10%) to help maintain capacity when the battery is cycled. The electrodes are generally charged after the cell is assembled.

In vented cells the sintered metal is cut to the final plate size and, after conduction tabs are welded, the cell is put together in a similar way to the pocket plate cells except that the separator is a thin sheet of low-resistance, small-pore plastic often with a second layer to prevent oxygen transport. These membranes may be cellophane and a non-woven polyamide respectively.

Sealed cells are made in three different designs where the sintered electrodes are vertical rectangular plates, horizontal discs (button cells) and spirally wound, cylindrical cells. In the sealed cells the problem of oxygen evolution during overcharge is overcome by using an excess of active material at the negative electrode and a separator which allows transport of any oxygen formed at the positive electrode (by oxidation of water) to the negative electrode. At the negative plate it reacts chemically with cadmium metal



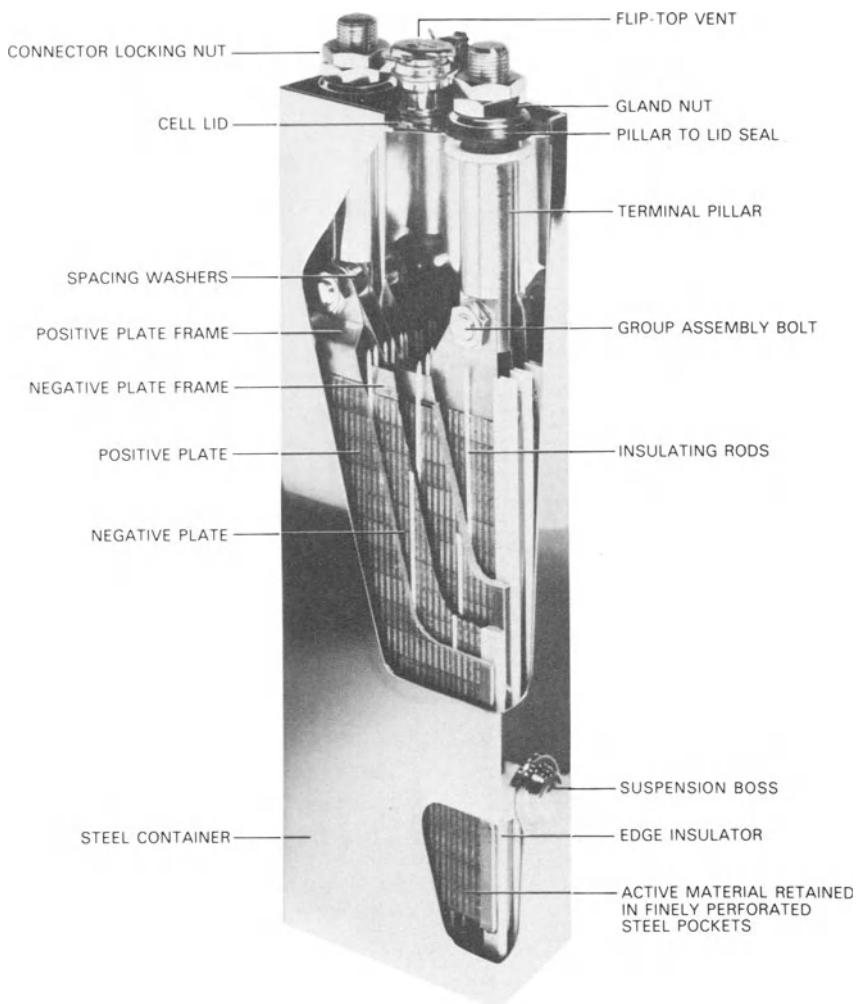


Figure 10.13 A cutaway diagram of a nickel/cadmium pocket plate battery. The battery shown has a nominal capacity of 100 A h. Photograph supplied by Chloride Alcad Ltd.

and this forms further material for the charging reaction. Hence the negative electrode never becomes fully charged. Suitable separator material can be non-woven polyamide or polypropylene.

Cells with rectangular electrodes are very similar to the battery in Fig. 10.13 except that the pins are replaced by a thin membrane, thus reducing the inter-plate gap and aiding the rapid discharge of the cell. Figures 10.14 and 10.15 show the designs of a spirally wound cylindrical cell and a button cell.

Sintered plate cells also made in a variety of sizes, i.e. rectangular plates

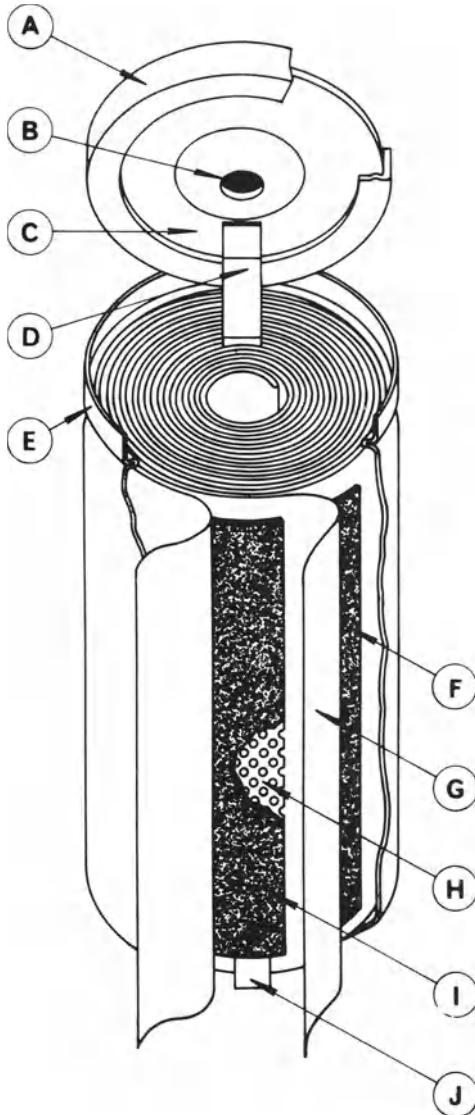
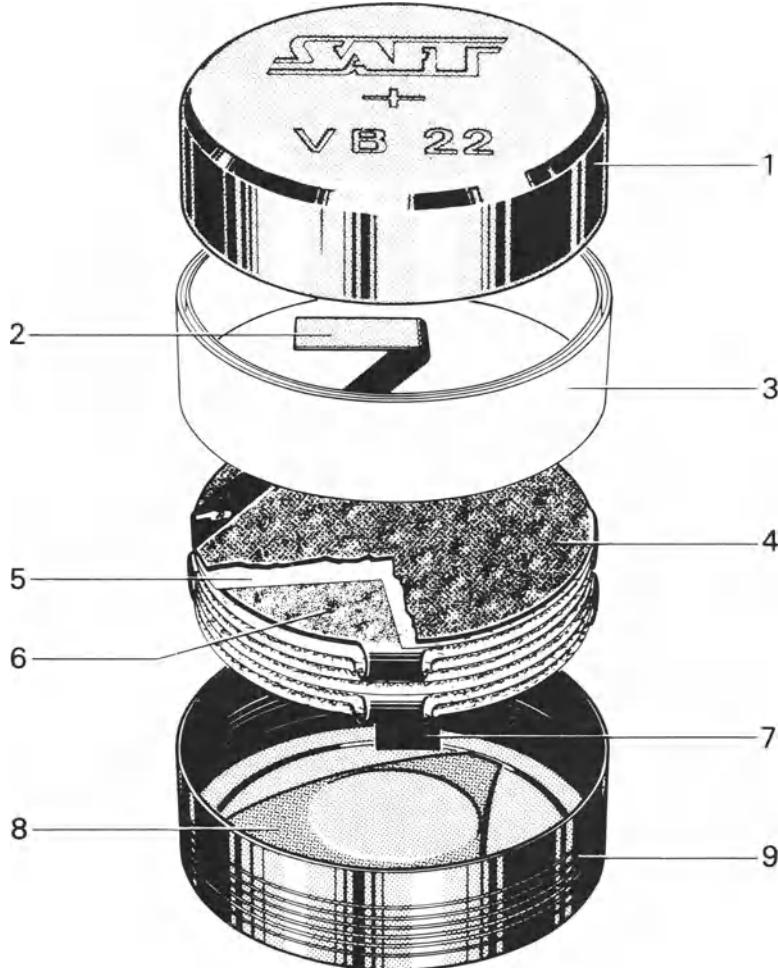


Figure 10.14 *The construction of a cylindrical nickel/cadmium battery. Key: A, seal; B, positive terminal; C, cell lid; D, connection to positive plate; E, cell case; F, positive plate; G, separator; H, sintered metal foil; I, negative paste; J, connection to negative plate. Diagram supplied by Berec Ltd.*

1–1000 A h, cylindrical cells 0.1–10 A h and button cells 0.04–1.75 A h. The energy density of sintered plate cells is considerably better than their pocket plate counterparts because the electrodes are closer together, and with the high porosity of the plates there is also more active material per unit volume; with a 100 A h cell



**Figure 10.15** Construction of a nickel/cadmium sintered plate button cell. Key: 1, positive cup; 2, positive connection; 3, insulating ring; 4, positive plate; 5, separator; 6, negative plate; 7, negative connection; 8, spring; 9, negative cup.  
Diagram supplied by SAFT Ltd.

an energy density of over  $50 \text{ Wh kg}^{-1}$  has been achieved. The major advantage is, however, their high discharge rated capability and even at the  $10C$  rate ( $1000 \text{ A}$  from a  $100 \text{ A h}$  cell) 75% of the rate capacity can be obtained. Moreover the sintered plate design has the ability to remain charged (70% after six months) and has good cycle characteristics; 1000–2000 cycles to 50% discharge is a reasonable expectation.

### 10.5.3 Leclanché cells

Unlike the Pb/acid and the Ni/Cd systems, Leclanché batteries cannot be recharged

effectively and hence are primary cells. Even so, Leclanché cells are produced in many shapes and sizes (Fig. 10.2) and the total world production probably exceeds  $10^{10}$  per year – they are truly the workhorses amongst consumer batteries. Their replacement by higher-performance or secondary batteries has frequently been predicted but the market has always held up because of their comparative cheapness. For example, a Leclanché cell is typically a twentieth of the cost of a Pb/acid battery or a fiftieth of that for a Ni/Cd battery to provide the equivalent power supply. Much of this cost difference lies in the materials of construction, but the battery also benefits from scale of manufacture since Leclanché cells are produced by fully automatic processes.

Despite the long history of manufacture, the dry Leclanché cell dating from the 1880s, its detailed electrochemistry is again far from understood. Indeed the open-circuit potential measured for the completed cell is frequently higher than that estimated on the basis of the equations in Table 10.1 or the more complex equation



and hence it is clear that they do not faithfully represent the reaction which occurs. Moreover the current/voltage characteristics depend on the source of the  $\text{MnO}_2$  and more directly the exact oxidation state of the manganese, the density of the lattice imperfections, the crystallite size and the extent of hydration.

Figures 10.16 and 10.17 illustrate two designs of Leclanché battery. The first

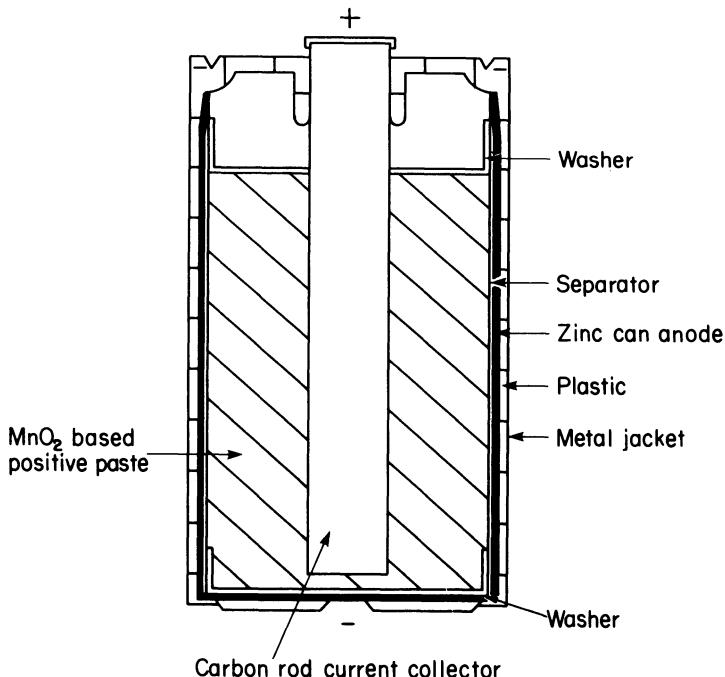


Figure 10.16 Construction of a cylindrical Leclanché battery.

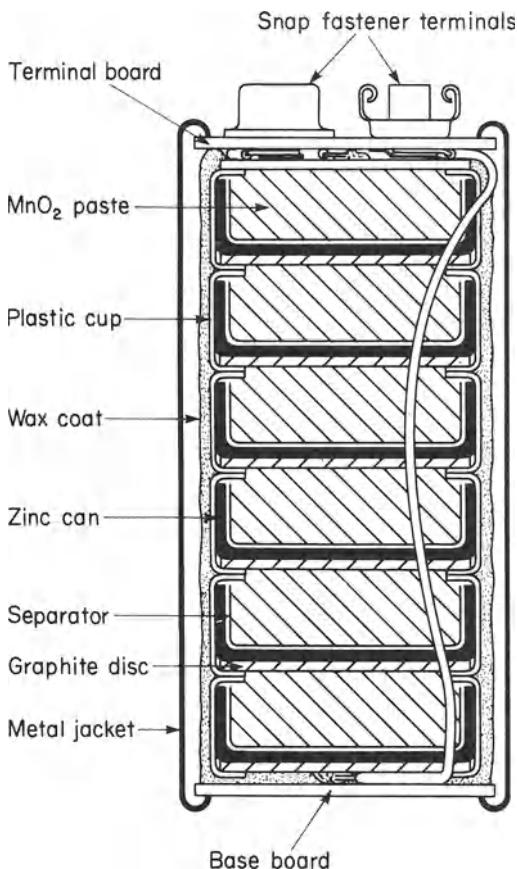


Figure 10.17 *Construction of a flat cell Leclanché battery.*

shows the traditional cylindrical design. The negative zinc electrode is a zinc lining to the metal can amalgamated with mercury to minimize hydrogen gas formation by reaction of the metal with water; the separator is a paper stiffened with cellulose or starch placed adjacent to the zinc can. The positive current collector is a carbon rod at the centre of the can, while most of the volume is taken up by the positive paste. This is a mixture of powdered manganese dioxide, ammonium chloride and acetylene black (carbon) to increase the conductivity; the pores are filled with an aqueous electrolyte ( $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ ) gelled by addition of starch. The can is totally sealed.

The second battery (Fig. 10.17) is a series of six cells with bipolar (or duplex) electrodes. Each cell has the same components as the first cell, i.e. zinc can, separator, positive paste and carbon current collector. The latter is not a carbon rod but the bottom face of the duplex electrode. The whole set of cells is sealed in wax. In both cells the zinc electrode rapidly develops porosity as the corrosion process occurs while the performance is largely determined by the quality of

manganese dioxide. Cells constructed from electrolytic manganese dioxide have a significantly better performance than those which use  $\text{MnO}_2$  from natural ores or prepared chemically.

Leclanché cells are produced with nominal capacities ranging from 0.05 to 500 A h, consumer batteries usually falling in the more restricted range of 1–10 A h. The practical capacity depends very much on the discharge regime. On constant discharge at high currents (0.1–1.0 A) only perhaps 25% of the rated capacity is obtained. On the other hand, when used only for a few hours per day, almost all the capacity is obtained with a current of 1–150 mA cm<sup>-2</sup> and these conditions correspond more closely to the normal applications of the battery. On drawing current the cell voltage always drops with time and, although it recovers on standing at open circuit (see Fig. 10.18), the absence of a stable voltage is a disadvantage. It may also be noted that the energy density, 70 Wh kg<sup>-1</sup>, is high compared with that for the secondary systems.

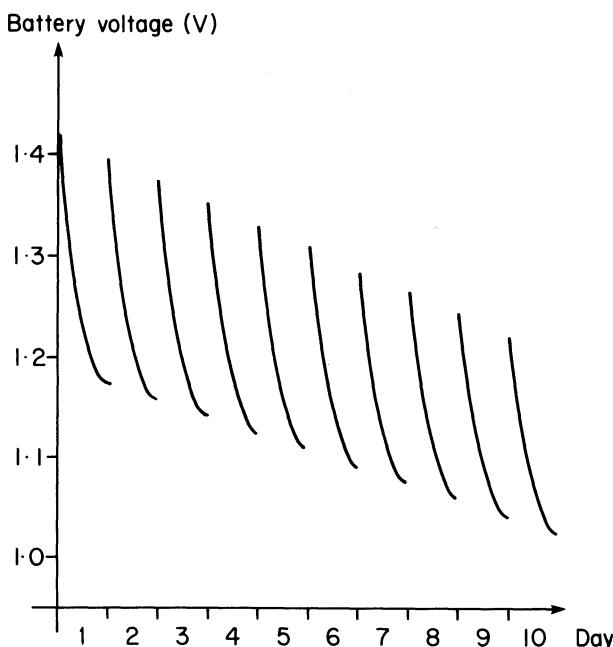


Figure 10.18 Discharge characteristics for a commercial Leclanché battery. The battery was discharged into a  $5\Omega$  resistance for 1 h each day.

#### 10.5.4 Other battery systems

Batteries based on a very wide range of electrode reactions are manufactured for military applications. The specifications for batteries in such applications are very diverse and suitable systems are produced in small numbers and often have no civilian market. Such batteries are well beyond the scope of this discussion but a few systems produced for more specialist civilian markets deserve some mention.

A number of batteries are based on modifications of the technology or the substitution of electrode reactions into either the Ni/Cd or Leclanché cells; the changes usually improve one characteristic of importance to a particular duty but usually only at an increased cost. In an alkaline manganese battery, the cathode is manganese dioxide and graphite in the form of compressed tablets, and the electrolyte is strongly alkaline. The cell reaction is



It is also normal to use the highest grade of manganese dioxide (inevitably more expensive) but in all respects the performance of such batteries is superior to the Leclanché cell. In the small (0.02–0.2 A h) button cells, the cathode active material is more commonly mercuric oxide + graphite or silver oxide + graphite pressed into pellets and the electrolyte is again aqueous potassium hydroxide (Fig. 10.19). The cell reactions are



and



and these cells have the advantage compared with those based on  $\text{MnO}_2$  that their voltage is constant during most of the discharge and their performance on continuous discharge is good. They are therefore suitable for watches and hearing-aid supplies.

Silver oxide/zinc can be manufactured in rechargeable cells with free potassium hydroxide electrolyte and pasted rectangular electrodes. Such cells are expensive but have a good energy density compared with Pb/acid or Ni/Cd ( $70 \text{ Wh kg}^{-1}$ ) and are also capable of high discharge rates for short periods. Other alkaline secondary batteries which have been manufactured include  $\text{NiO(OH)}/\text{Zn}$ ,  $\text{NiO(OH)}/\text{Fe}$  and  $\text{Ag}_2\text{O}/\text{Cd}$ .

Metal/air batteries have received considerable attention because one of the active materials does not contribute to the mass of the battery, and this gives the possibility of a very high energy density. The systems have not yet been totally successful even as primary cells because of polarization of the air cathode causing a substantial loss of cell voltage. Moreover, attempts to recharge such cells have met

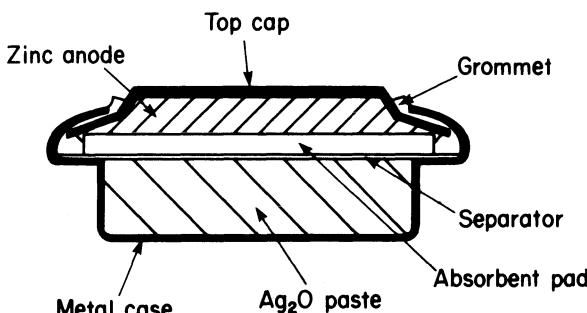


Figure 10.19 *Construction of a silver oxide/zinc button cell.*

problems at the negative metal electrode, e.g. with a zinc electrode the distribution of metal over the current collector changes with time. Commercially the most successful primary batteries have been based on Zn/air with a neutral or alkaline electrolyte. Aluminium/air, iron/air and lithium/air with an aqueous electrolyte now have supporters as traction batteries. Lithium (in strong hydroxide solution to prevent spontaneous dissolution) and aluminium combine low density with a low electrochemical equivalent and such metal/air cells could in theory give rise to very high energy densities, several kilowatt-hours per kilogram. Presently since aluminium can never be plated from aqueous media, it is envisaged that the aluminium would be recycled external to the battery; aluminium would be fed to the battery and would be oxidized to alumina or aluminium hydroxide, which would be collected in an electrolyte flow system outside the battery and returned to the smelter. In the long term, this battery looks particularly attractive for a car traction battery since the intractable problem of battery replacement or recharging on long journeys is avoided (more Al could be added) and the battery is based on room-temperature aqueous electrochemistry.

The greatest development of the last ten years has been the infiltration into the market of ambient-temperature lithium batteries with a non-aqueous electrolyte. Again, the attraction of such cells is their high energy density combined with a high cell voltage, 2.0–4.0 V. While they have been developed for many applications both primary and secondary, the greatest success has been with small primary cells for microelectronic circuitry.

There are many types of ambient-temperature lithium cells that are in or near to commercial production. While these cells have in common the dissolution of lithium as the negative electrode, there is a great variation in the other features of the cells. Three types of electrolytes have been used:

(a) An aprotic organic solvent containing a lithium salt. The organic solvents which have been investigated in detail include acetonitrile, propylene carbonate, dioxolane, methyl formate, tetrahydrofuran and mixtures of solvents, while the most popular electrolytes are lithium perchlorate, hexafluorophosphate, hexafluoroarsenate and thiocyanate.

(b) Thionyl chloride or sulphur dioxide, where the solvent is also the active species at the positive electrode. In thionyl chloride cells the electrolyte is lithium tetrachloroaluminate.

(c) A lithium-ion-conducting electrolyte such as a lithium iodide or lithium iodide + alumina (33 mol %). These cells are only able to discharge slowly, i.e. less than  $100 \mu\text{A cm}^{-2}$ , but in applications where they are required to provide only a low power, e.g. a heart pacemaker battery, the service life may be many years and such batteries also have a good shelf life. Lithium-ion-conducting polymers are another interesting possibility.

A great diversity of positive electrode reactions have also been described and/or used in commercial cells. These include the following:

(1) The reduction of an oxide, sulphide, or metal salt or an oxidizing agent, e.g.  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{CuS}$ ,  $\text{PbS}$ ,  $\text{PbI}_2$ ,  $\text{CuCl}_2$ ,  $\text{I}_2$  absorbed into a polymer.

- (2) The reduction of poly(carbon monofluoride)  $(CF)_n$ .
- (3) The reduction of the solvent, thionyl chloride or sulphur dioxide, at a carbon current collector.
- (4) The use of an intercalation compound, e.g.  $TiS_2$  or  $V_6O_{13}$ . In these materials the lithium passes into the lattice so that the cell reaction is



effectively the formation of a solid solution of lithium; the driving force for such reactions can be sufficient for an open-circuit potential of around 3 V.

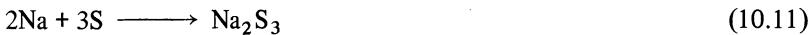
## 10.6 BATTERIES UNDER DEVELOPMENT

For many years, the batteries described in Section 10.5 underwent a slow evolutionary development. During the past twenty-five years, there has been a great spurt of research and development. The main driving forces have been the microelectronics revolution (which has led to a situation where power supplies are the largest part of a device or instrument) and the energy crisis. In particular the US response to the coming shortage of oil has been a Department of Energy programme with the dual objectives of developing batteries for energy storage (load levelling and solar-derived electric power) and for the electric car. It is particularly remarkable for the number of battery systems that have been studied. While many would argue that batteries are not the most likely way of solving the problems of energy storage or of personal and family transport, there can be no doubt that the programme has led to significant improvements in the presently manufactured secondary batteries and the demonstration of new battery systems with potentially greatly better characteristics.

This section will briefly describe the principles and problems of these new systems under development in the USA and elsewhere. Because of the early stage in their development, many of the problems lie in the compatibility of the materials of construction. There are often quite different approaches to finding a solution and to the design of the battery.

### 10.6.1 Sodium/sulphur batteries

The sodium/sulphur system is being discussed for load levelling and car traction and is believed to be close to commercial production in the UK as a traction battery for commercial vehicles. The overall cell reaction is usually written



which leads to an open-circuit potential of +2.1 V and a theoretical energy density of  $756 \text{ Wh kg}^{-1}$ . The cell is operated with a sodium-conducting solid electrolyte, in most cells sodium  $\beta$ -alumina although sodium-conducting glasses have also been investigated. The temperature of operation is 300–375°C so that the active materials are liquid and to increase the conductivity of the solid electrolyte.

The major problems with the cell are associated with safety, since if in any

circumstances the sodium and the sulphur come into contact a very exothermic reaction ensues, and with the low conductivity and high corrosiveness of the sodium polysulphides. These factors determine the cell design. A typical design, based on a sodium  $\beta$ -alumina tube (the easiest form to seal), is shown in Fig. 10.20. The outer tubular case is made of mild steel and the  $\beta$ -alumina tube fits inside with a small gap between. The positive electrode is molten sulphur, at all times except when 100% charged containing sodium sulphide, and this is placed inside the  $\beta$ -alumina tube so that it does not come into contact with and then corrode the outer case. The current collector is graphite felt which takes up all the volume inside the tube and there is also a central graphite rod which connects to the cell terminal. The negative current collector is the case and the molten sodium is stored below the cell and is only wicked up into the gap between the tube and the case as the sodium

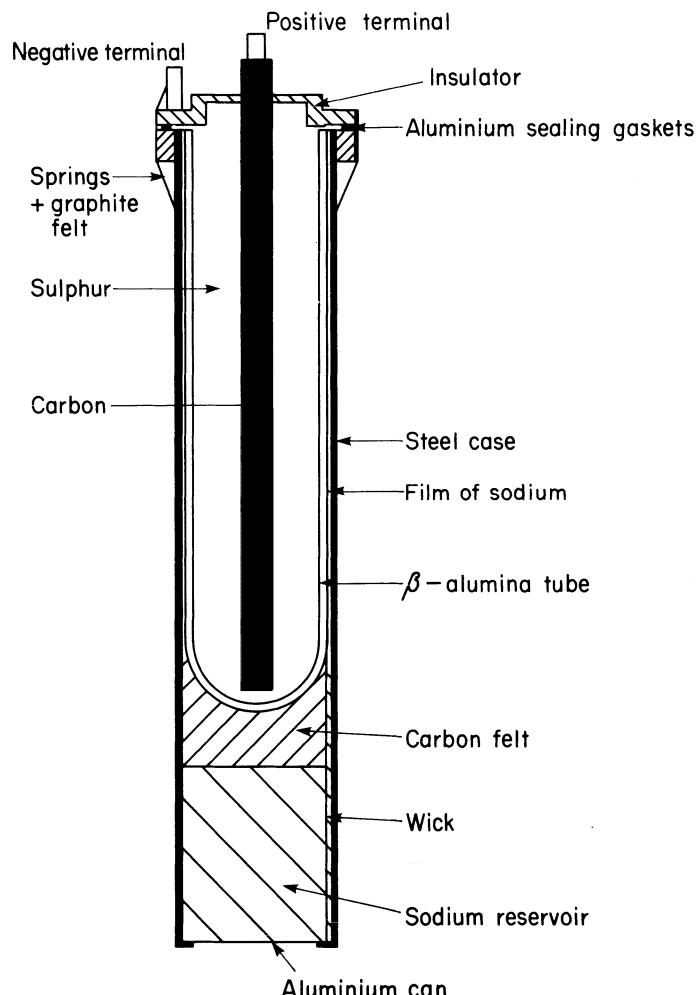


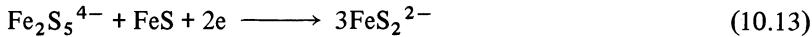
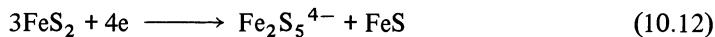
Figure 10.20 Construction of a 38 A h sodium/sulphur battery.

film there is consumed; this arrangement reduces problems from the sodium/sulphur reaction if the  $\beta$ -alumina tube cracks or, more commonly, sodium dendrites grow through faults in the  $\beta$ -alumina.

Such cells with a  $\beta$ -alumina tube 60 cm long and 3.5 cm diameter have been thoroughly tested. They have a capacity of about 150 A h and have been shown to maintain 80% capacity after more than 1000 charge/discharge cycles. The practical energy density lies in the range 100–150 Wh kg<sup>−1</sup> and they can maintain a peak power density (15 s) over 100 W kg<sup>−1</sup>. As with all high-temperature systems, thought must be given to heat management; although cells have been cooled and reheated, this cannot be advisable and hence batteries are insulated to allow the system to remain molten during reasonable storage periods. Even so, such batteries are probably best used in duties which are regular and without long off-periods.

### 10.6.2 Lithium/iron sulphide batteries

The second molten salt battery to have received detailed attention is the lithium/iron sulphide battery. During discharge, the negative electrode reaction is the dissolution of lithium from a lithium/aluminium alloy (10–20% Li), while the positive electrode reaction is the reduction of iron disulphide which occurs in stages

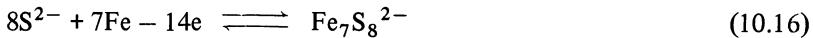


or the reduction of iron sulphide



The former gives a higher cell voltage but produces technological problems; corrosion of the current collector by iron disulphide always occurs unless it is made of molybdenum, an unacceptably expensive metal. Hence most practical cells have used iron sulphide as the active material and these batteries have now reached the stage of detailed engineering and testing on a laboratory scale.

Reaction (10.15) is not totally reversible and after the first discharge the positive electrode reaction is better represented by the equation



and the inability to reform iron sulphide causes a loss in capacity.

The electrolyte for the battery is a LiCl/KCl mixture with a temperature of 430–490°C. Batteries are constructed on the parallel-plate principle with alternate anodes and cathodes, and in each inter-electrode space there is a boron nitride cloth or felt separator. Commonly there is one extra negative plate because some lithium is lost during cycling. The plates, typically 5 mm thick, were initially prepared by cold compaction techniques, the active material being compressed into a fine metal honeycomb material which also acts as the current collector. The negative electrode was just the Li/Al alloy in an Fe lattice while the positive electrode was a mixture

of  $\text{FeS} + \text{LiS} + \text{CuS}$  (to improve use of active materials) in a nickel honeycomb. The positive electrode, when prepared in this way, tends to swell during discharge and the trend now is to assemble the cell in a half-charged state with the positive plate being produced by hot compression methods with carbon and molybdenum as additives instead of copper sulphide which has led to copper dendrite shorting.

In the present state of the art the energy density is about  $80 \text{ Wh kg}^{-1}$  and more than 300 cycles have been achieved; the peak power density is, however, rather low, indicating problems with the electrode kinetics. All these figures are likely to improve, however, as the programme proceeds.

### 10.6.3 Zinc/halogen batteries

Zinc/halogen batteries seem attractive since they are based on low-cost chemicals, on aqueous electrochemistry at almost ambient temperature and pressure and since the electrode reactions involved are fast. Moreover, they are capable of a high cell voltage and a good energy density. The problem has always been to store the halogens and this must almost certainly be done external to the cell so that the battery systems require storage and pumping as well as the cell; this makes their success dependent on the engineering.

In the zinc/chlorine cell, the chlorine is stored as chlorine hydrate,  $\text{Cl}_2 \cdot x\text{H}_2\text{O}$  ( $x = 6-10$ ), which precipitates as a solid below  $9.6^\circ\text{C}$ . During charge the electrolyte, aqueous zinc chloride, is cooled in a reservoir, while during discharge the reservoir is heated under controlled conditions. The cell itself, however, can be simple; the electrodes are graphite and can operate without catalyst and the cell can be constructed from PVC without a separator. There remain some problems with the morphology of zinc deposits.

In the zinc/bromine cell, the halogen is stored in the electrolyte as a polybromide (mainly  $\text{Br}_3^-$ ) and hence a separator is essential; Nafion cation exchange membrane has again been used. The electrolyte is aqueous zinc bromide with tetraalkyl-ammonium bromide to aid the bromine complex formation.

Engineering of the chlorine battery is well advanced but zinc/bromine cells exist only as small laboratory modules.

### 10.6.4 Some comments on the various battery systems

The US Department of Energy programme is divided into near-term batteries, advanced batteries and long-term batteries and has emphasized the development of systems which fulfil the requirements for car traction, load levelling and the storage of solar-derived energy. The state of the art at the end of 1979 with respect to some important performance characteristics is summarized in Table 10.7. It can be seen that efforts to modify the traditional battery systems ('near-term batteries') to meet the new challenges have met with some success. For example all the characteristics of the lead/acid battery show significant improvement compared with present commercial batteries – energy density 30 to  $40 \text{ Wh kg}^{-1}$ , power density 80 to  $100 \text{ W kg}^{-1}$ , cycle life to deep discharge 100 to 400 cycles. Even so,

Table 10.7 Comparison of data for batteries in the US DoE battery programme. December 1979.  
Theoretical values in parentheses.

	Open-circuit cell voltage (V)	Energy density (Wh kg <sup>-1</sup> )	Power density (W kg <sup>-1</sup> )	Cycles to deep discharge	Energy efficiency on cycle (%)
<i>Near term</i>					
Pb/acid	2.1	40 (170)	100	400	82
NiO(OH)/Zn	1.6	65 (380)	110	150	70
NiO(OH)/Fe	1.2	53 (390)	110	>1000	70
<i>Advanced</i>					
LiAl/FeS	1.2	80 (460)	80	350	80
Na/S	2.1	110 (760)	100	>600	80
<i>Long term</i>					
Al/air	2.7	— (4250)	—	0	—
Fe/air	1.2	84 (698)	74	—	—
Zn/Br <sub>2</sub>	1.8	65 (430)	—	—	70

such improvements are unlikely totally to change the future of batteries, and the Ni/Zn system has a serious weakness with respect to cycling.

The advanced batteries represent an attempt to select systems which have potentially a large advantage. For example the theoretical energy densities are shown in the table. While these have little meaning since they make no allowance for cell components other than the active materials and are never, in practice, approached, a high theoretical energy density (cf. Na/S with Pb/acid) gives potentiality for improvement. On the other hand, the systems selected present difficult materials problems and operate well above room temperature. Even so, without the many years of evolutionary development, these cells still show energy densities and cycle lives well above those of some of the traditional systems.

The long-term batteries are notable for a return to ambient-temperature, aqueous electrolyte cells. Particularly, the Al/air battery shows a huge theoretical energy density (10% of this value would be very acceptable!). The cells require fundamental advances in electrochemistry to be really successful (with the Al/air cell an improvement at both electrodes is necessary). Hence the trend is clear. A major problem is associated with power density and this highlights the need to improve electrode kinetics and the design of active materials to permit more rapid discharge.

## 10.7 FUEL CELLS

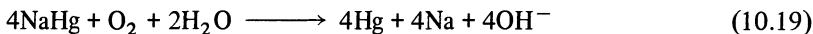
The original concept of the fuel cell was that primary fuels could be reacted with oxygen in an electrochemical cell, e.g.



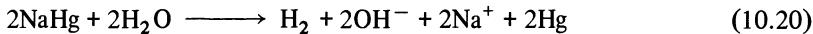
so as to convert, to electrical energy, the full free energy of oxidation of the fuel to carbon dioxide and water. Of course, for a reasonable energy efficiency both electrode reactions, (10.17) and (10.18), must occur close to their reversible potentials, and for the fuel cell to be useful this must be true at reasonably high current densities ( $> 100 \text{ mA cm}^{-2}$ ). The materials of construction must also be cheap and stable. Regrettably there remain problems at both electrodes. The need for better oxygen catalysts has been emphasized at several places in this book; with present materials the overpotential at the oxygen cathode is unlikely to be less than 400 mV. The anode reaction would cause worse problems. It is doubtful that conditions could be found for the complete oxidation of a fuel such as methane and certainly the catalytic activity would be low, permitting only very low current densities.

Hence an indirect approach has to be used. The primary fuel has to be converted to hydrogen or carbon monoxide before it is fed to the fuel cell. Although there are probably no commercial applications of fuel cells, the technology of several systems has reached an advanced state and fuel cells have been used as an integral part of the US space programme (i.e. where cost is unimportant). The following applications are regularly discussed.

- (a) To use a fuel cell with a battery as a hybrid car traction unit. The fuel cell would be used for power for cruising, while the battery provides peaks during starting and acceleration. The likely fuel would be 50% aqueous methanol which would be catalytically reformed in the gas phase at 190°C to give H<sub>2</sub> + CO<sub>2</sub>. The hybrid system greatly reduces the strain on the battery (it is no longer deeply discharged) and indefinitely increases the range of the vehicle.
- (b) Large-scale power generation. A 4.8 MW fuel cell operating on hydrogen from natural gas or coal is under test in New York City. An overall energy efficiency of 40% (cf. turbines 25–35%) is claimed.
- (c) Small-scale power generation at remote sites.
- (d) Energy recovery in the chemical industry, an application which might see fuel cells with unusual fuels. For example in the mercury cell process for Cl<sub>2</sub>/NaOH (Chapter 3), sodium amalgam is reacted with water at a catalytic surface in a denuder; the reaction is highly exothermic but the free energy of reaction is obtained only as low-grade heat. If on the other hand, the sodium amalgam was fed to an electrode in a cell where the other electrode reaction was oxygen reduction or hydrogen evolution, the free energy of the reactions



or



could be recovered as electrical energy. It should be noted that caustic soda is still obtained.

### 10.7.1 Phosphoric acid fuel cells

These cells operate only with hydrogen as the anode fuel and, moreover, the hydrogen must be pure since sulphur compounds and carbon monoxide adversely affect the performance of the Pt catalyst. Each cell consists of two teflon-bonded gas diffusion electrodes on a porous conducting support (see Fig. 10.21). At both anode and cathode the catalyst is platinum particles dispersed on carbon and a recent success has been a reduction in Pt loading from 10 mg cm<sup>-2</sup> to 0.75 mg cm<sup>-2</sup>. The electrolyte is concentrated phosphoric acid absorbed onto a solid matrix and the cell operates at 200°C to improve the electrode kinetics. The cells are then mounted in stacks to increase the power output.

At 200 mA cm<sup>-2</sup> the cell voltage is 0.67 V (cf. reversible cell potential 1.16 V) and most of the voltage loss occurs at the oxygen cathode.

These are the cells used in the 4.8 MW test fuel cell in New York.

### 10.7.2 Molten carbonate fuel cells

These cells operate at much higher temperature, which assists the kinetics of the electrode reactions. Also the anode is capable of using either hydrogen or carbon

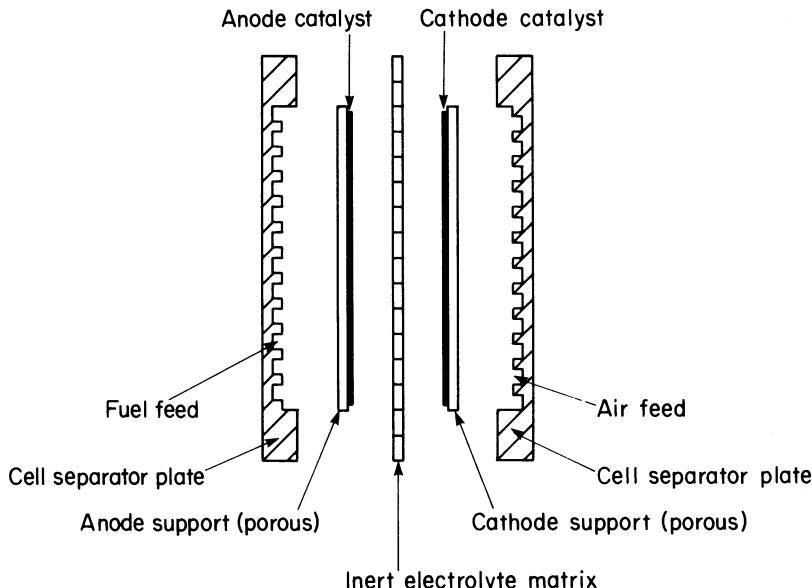
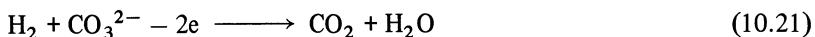


Figure 10.21 Sketch showing the basic structure of the phosphoric acid fuel cell.

monoxide as the fuel



while the reduction of oxygen in the molten carbonate medium is



so that the electrolyte must permit transport of carbon dioxide between the electrodes. The anode is porous nickel and the cathode is porous nickel oxide. The electrolyte (40%  $\text{LiAlO}_2$ , 28%  $\text{K}_2\text{CO}_3$  and 32%  $\text{Li}_2\text{CO}_3$ ) is absorbed into a porous inorganic matrix. The cell is operated at  $650^\circ\text{C}$ .

In this cell the voltage can be as high as +0.9 V with a current density of  $150 \text{ mA cm}^{-2}$ . This gives an overall energy efficiency, e.g. coal to electricity is in the range 40–45%. The major problem with this cell is the low tolerance of the electrode reactions to sulphur and chlorine. Power plants based on this fuel cell are due to be tested during the 1980s.

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## 11 Water Treatment and Environmental Protection

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There is now a great awareness of the dangers to ourselves and our environment of many effluents from industry and other activities of modern life. Certainly it is no longer acceptable to discharge, indiscriminately, gases into the atmosphere or liquids, solids and solutions into waterways or landfill sites. This is reflected by the legislation introduced by many governments which, for example, prescribes legal limits for toxic materials such as carbon monoxide in car exhausts, metal ions and cyanide ion in waste water from chemical plants and organic compounds in water from sewage works, chemical plants or food factories. For such laws to be enforced, methods must be available both for treating the effluent to meet the standards and for monitoring the effluent to ensure that the legal limits are not exceeded. Moreover, in many cases the legal requirements are becoming steadily harsher and the methods must therefore continue to develop. At the same time, with the increasing cost of raw materials and the threat of depletion of world reserves of many resources, it should become more attractive to re-use or recycle materials. Examples of this trend have been described in earlier chapters; in Chapter 6 indirect organosynthetic electrode reactions were considered and such processes consist essentially of recycling, electrolytically, traditional redox reagents. Also in Chapter 4 it was noted that electrorefining processes are commonly used to recycle metals.

The provision of water suitable for drinking is another essential to life. The quality of naturally available water varies greatly from site to site and in many places it may be necessary to remove bacteria, salts, heavy metal ions and organics; desalination and chlorination are the most common processes. Moreover, it is again advantageous to monitor the water quality continuously or, at least, routinely.

Hence effluent and water treatment is very big business, likely to expand and develop considerably in the future. While such processes have a variety of objectives, a common feature is the need to handle a highly variable feed. Typical are the local authority sewage works to be found in every town. Urban sewage is produced at the rate of about 200 litres per person per day and, although it varies with season and location, it will, on average, contain organic material equivalent to a biological oxygen demand (BOD) of  $400 \text{ mg l}^{-1}$ . To this is added a component of industrial

and commercial effluent, the nature of which will depend strongly on time and location, but the overall treatment process must aim always to reduce the BOD to below  $20\text{ mg l}^{-1}$ , to reduce suspended solids to below  $30\text{ mg l}^{-1}$  and to reduce to safe levels toxic and other undesirable species (e.g.  $\text{NO}_3^-$ , detergents).

What is the role of electrochemistry in water and effluent treatment? One answer would be, ‘relatively small’, since there are many competitive methods and on a large scale these are cheaper and use less energy. For example, Table 11.1 summarizes the main processes used in the three stages of treatment of urban sewage. The mechanical and biological methods are very effective on a large scale and the physical and chemical methods are used to overcome particular difficulties such as final sterilization, odour removal, the removal of inorganic chemicals and breaking oil or fat emulsions. Normally no electrochemical processes are used. On the other hand, there are particular water and effluent treatment problems where electrochemical solutions are advantageous. These will be discussed in this chapter and it will be seen that the electrochemical processes are based on quite diverse principles. In addition, although electroanalysis has never been very popular in the laboratory, electrochemical devices for on-line monitoring and fieldwork are more attractive. They can be small, have low power requirements easily met by a small battery and give a readout which can easily be read on a meter, be displayed digitally or be used to operate an alarm. Hence the principles of some of these devices will be discussed at the end of the chapter.

Table 11.1 Principal types of processes used in local authority sewage works.

Stage	BOD range ( $\text{mg l}^{-1}$ )	Mechanical or biological processes	Physical or chemical processes
Primary	$400 \rightarrow 250$	Communition, sedimentation, sludge digestion or incineration	Flocculation by chemical additives, flotation
Secondary	$250 \rightarrow 40$	Percolation through activated sludge filters, biological oxidation, nitrification	Flotation, coagulation by additives, precipitation (e.g. phosphate, fluoride, heavy metals), filtration
Tertiary	$40 \rightarrow <20$	Filtration, oxidation ponds, disinfection	Treatment with $\text{Cl}_2$ or $\text{O}_3$ , adsorption on high- surface-area carbons, osmosis, UV sterilization

## 11.1 METAL ION REMOVAL AND METAL RECOVERY

Electroplating, electrorefining and electrowinning (from ores) have been described in earlier chapters and all use electrolysis solutions where the concentration of metal ion is greater than  $50 \text{ g l}^{-1}$ . The processes described in this section aim to strip metal ions from dilute solutions, 1–1000 p.p.m, and in some cases there may not be a high concentration of inert electrolyte. The feeds to the cell may arise from plating or photography rinse waters, etching processes, chemical streams or naturally occurring waters close to ore-bearing deposits or mine workings.

At the outset it should be recognized that the driving forces for the installation of metal ion stripping processes may be quite diverse: namely (i) it may be necessary to comply with legislation barring the discharge of effluent into a river or the sea unless a metal ion concentration is below a proscribed limit; (ii) the local water authority may charge an excess for water from industrial sites to the community sewage installation which increases with the metal ion content; (iii) one may need to condition a process stream for recycle; and (iv) it may be worthwhile for the value of the metal recovered. Clearly if the metal recovered rapidly returns the investment in the new cell and also covers the running costs, the extraction process is likely to be attractive. This is most likely when the metal is silver or another precious metal although as their prices increase, other metals may be economically worthwhile to recover. Certainly a major advantage of electrochemical processes is that the metal can be recovered in its most valuable form. The competitive processes (i.e. precipitation of the metal ion as a hydroxide with caustic soda, solvent extraction and ion exchange) essentially only lead to another metal ion solution of increased concentration, while cementation leads to very impure metal. On the other hand, treatment with caustic soda is undoubtedly the cheapest of the various technologies, even if sometimes messy.

Cell systems for stripping metal ions from dilute solution must have a very high surface area and the design must promote a high rate of mass transport if the metal ion is to be stripped with an acceptable rate and current efficiency (therefore energy consumption). Moreover the cell may need to be capable of dealing with a variable feed in terms of metal ion concentration, complexing agents and other organic or inorganic species. Even so, a number of cell technologies are either available for licence or are in the late stages of development.

The Eco-cell process is based on a rotating cylinder cathode, which also acts as a pump, surrounded by an anion exchange membrane and a concentric anode. This cell geometry gives a uniform cathode potential and allows the cathode potential to be controlled by a crude potentiostat, thus avoiding a waste of charge and unnecessary power consumption and also introducing the possibility of separating a mixture of metal ions. The process is designed to convert the metal ions in solution to metal powder to be collected outside the cell and if necessary the cathode surface is scraped with a knife to facilitate removal of the powder. Figure 11.1 illustrates the complete process, and Figs 11.2 and 11.3 show the construction of the Eco-cell and the complete unit, respectively.

An acceptable rate of metal removal is obtained by designing the cell with a high

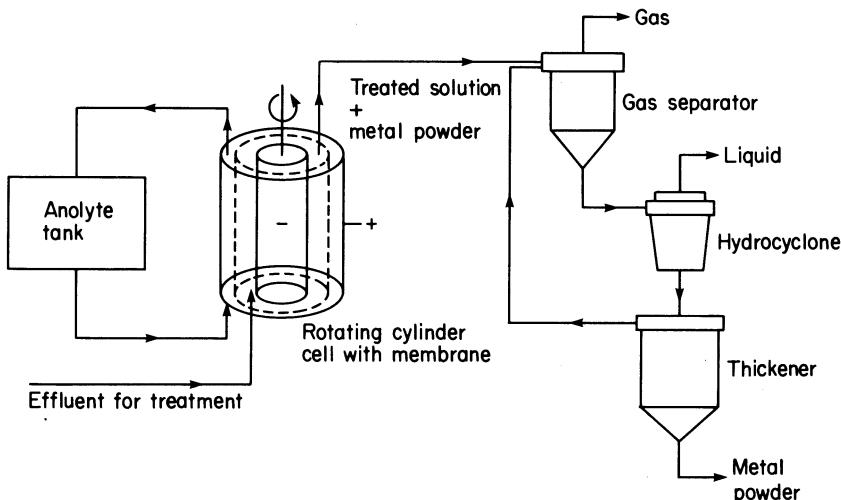


Figure 11.1 *Essential components for a typical Eco-cell plant for extracting metal ion as a metal powder.*

ratio of electrode surface area to catholyte volume and, more importantly, by using conditions which are highly turbulent. The turbulence is introduced by the rotation of the cathode, the peripheral velocity of this electrode being  $10\text{--}20\text{ m s}^{-1}$ , and is further enhanced by the roughness of the rotated surface resulting from the growing metal centres. These particles are very effective turbulence promoters and the mass transfer coefficient in such conditions can be more than fifty times that in the cell with a smooth rotating cathode. To ensure controlled hydrodynamics, in the larger cells the effluent enters and leaves the cell through manifolds placed along the diameter of the cell and parallel to the axis of rotation.

A typical 5 kA Eco-cell has a cathode drum of radius 0.37 m and height 0.74 m, and the cathode–membrane gap is about 1 cm. The cathode is rotated at 100–200 revolutions per minute. Such a cell can recover several kilograms per hour of copper powder from a 100–200 p.p.m.  $\text{Cu}^{2+}$  solution. For applications where complete stripping of the metal ion is advantageous, i.e. pollution control, it is necessary to operate a number of cells in series (see Fig. 11.4). It can be seen that the last two cells in the series are only responsible for the removal of 10% of the metal ion, while costing the same as the first two cells to install and operate. This clearly causes a high capital investment and running costs, but fortunately the same effect can be achieved in a single cell by dividing the catholyte compartment into several segments with baffles. For example the cell with dimensions given above but divided into twelve cathode compartments and operated at 1 kA can reduce the copper content of  $8\text{ m}^3\text{ h}^{-1}$  of solution from 100 p.p.m. to 1–2 p.p.m. This concept is described as the Eco-cascade-cell.

An Eco-plant operating in Denmark contains a 4 kA Eco-cell followed by a 1 kA Eco-cascade-cell and this treats  $200\text{ m}^3\text{ day}^{-1}$  of pigment effluent, reducing the  $\text{Cu}^{2+}$  concentration from 400 p.p.m. to 2–3 p.p.m. and recovering about 80 kg of

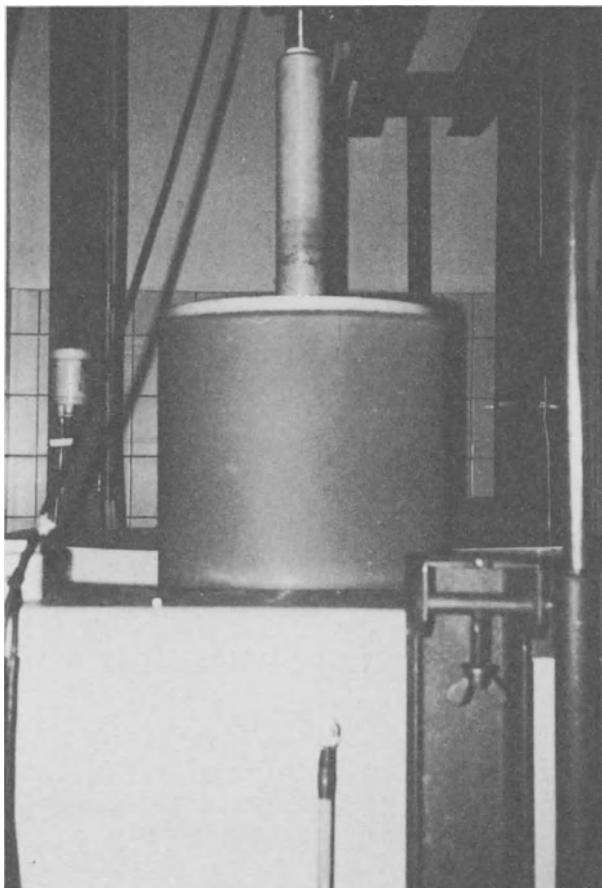


Figure 11.2 A 2 kA Eco-cell for the recovery of silver from photographic effluent.  
Photograph supplied by Ecological Engineering Ltd.

metal per day. Most developments have concentrated on copper-containing effluents but other metals should be recoverable with the Eco-cell.

In some cells, the turbulence of the electrolyte is produced by using a bed of small particles which create the essential small eddies in the catholyte. A simple and successful design is the Chemelec cell where a series of closely spaced gauzes or expanded metal electrodes, alternately anode and cathode, are separated by beds of non-conducting beads. The solution to be treated is pumped upwards through the cell so that the particulate bed becomes partially fluidized. The standard cell has the dimensions 0.5 m x 0.6 m x 0.7 m and contains six cathodes and seven anodes to give a total cathode area of 3.3 m<sup>2</sup>. Its main application has been in the treatment of wash waters from the electroplating industry where it is suitable for the recovery of copper, nickel, nickel/iron, zinc, cadmium, cobalt, gold and silver. At the normal operating current density of 5–30 mA cm<sup>-2</sup> it can recover metal at



Figure 11.3 *Mobile pilot plant containing a 500 A Eco-cell and a 250 A Eco-cascade-cell. Photograph supplied by Ecological Engineering Ltd.*

the rate of 70–400 g h<sup>-1</sup>. The Chemelec cell is, however, not able to treat solutions with very low concentration of metal; the limit of effective metal removal is about 50 p.p.m. It is therefore generally employed in the mode shown in Fig. 11.5 whereby the water in the first wash tank of the plating line is continuously cycled through the cell to maintain the metal ion at a relatively low level, say 100–250 p.p.m. This water can then be used for an extended period and the metal is recovered. The water in subsequent wash tanks will only be contaminated to a very small extent and may be discharged without treatment. The metal recovered may be stripped from the cathode or the cathode may be transferred to the electroplating bath and used directly as a dissolving anode. Figure 11.6 illustrates the Chemelec cell.

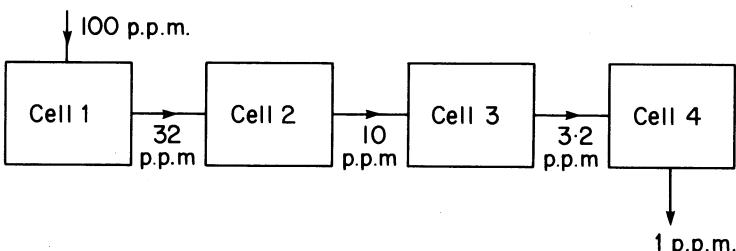


Figure 11.4 *Treatment of a 100 p.p.m. Cu<sup>2+</sup> solution by four 2 kA Eco-cells in series and operating under identical solutions.*

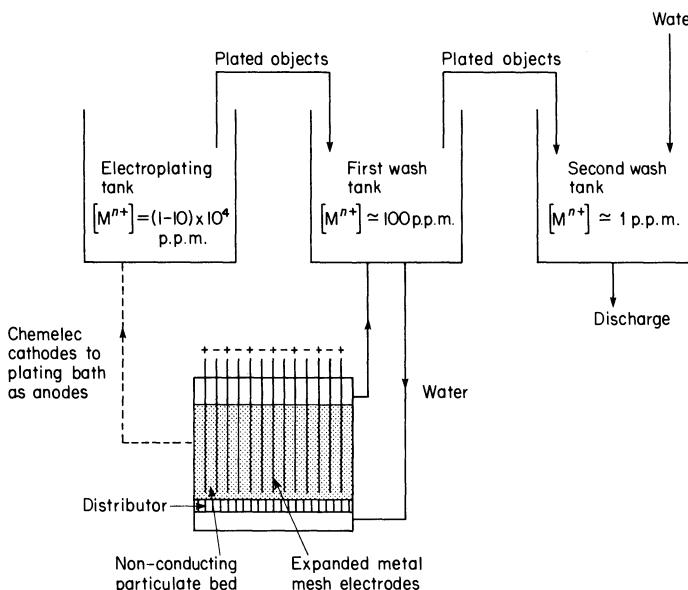
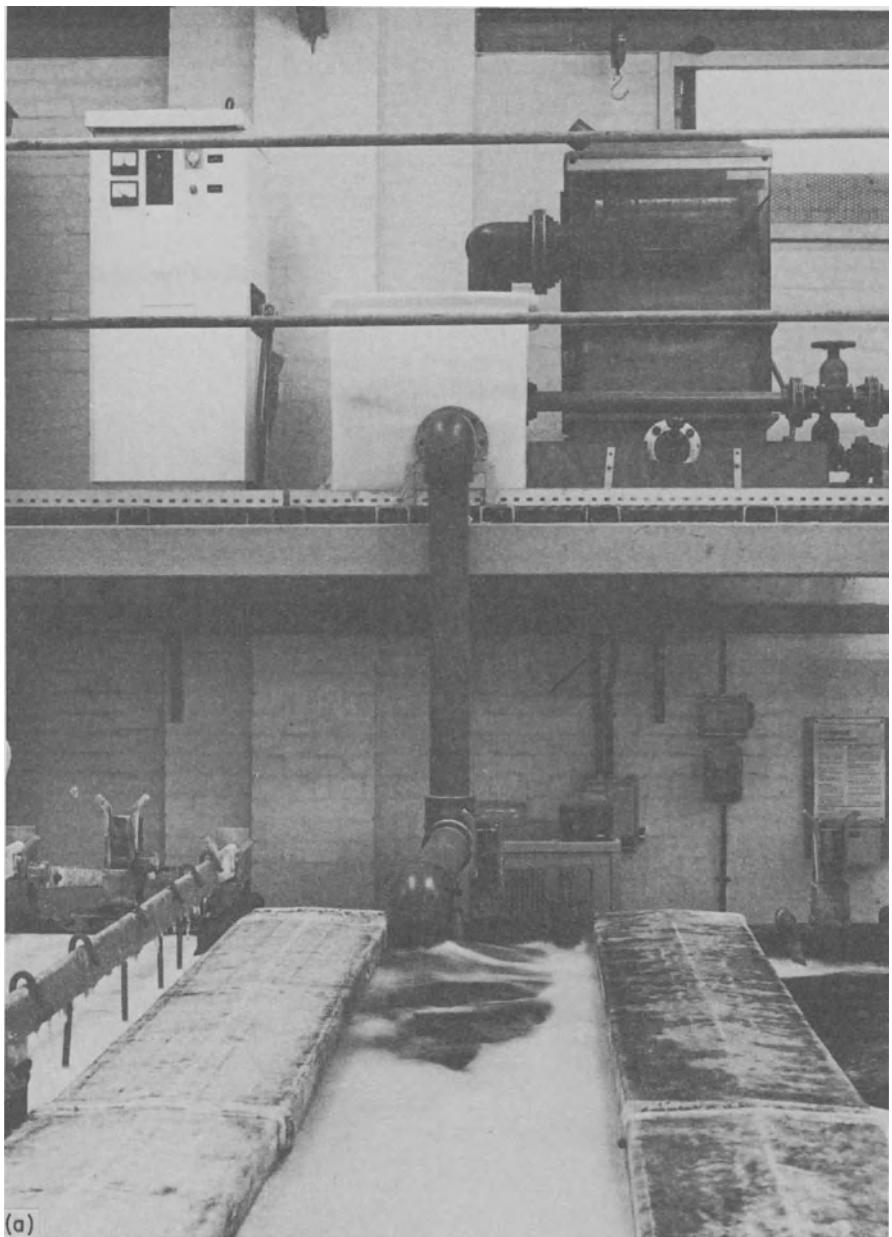


Figure 11.5 Common layout of Chemelec plant for treating wash waters from electroplating processes.

Akzo Zout Chemie have developed a process based on the fluidized bed cathode, i.e. where the cathode itself is the turbulence promoter. Such electrodes, because of their very high surface area per unit volume and effective introduction of turbulence, are capable of maintaining high apparent current densities and rate of metal removal. The main problem is the tendency for the particles of metal to agglomerate, especially if there are stagnant zones in the cell, and careful cell design is essential to avoid the rapid loss of performance which results. The design of the Akzo cell is shown in Fig. 11.7. The potential distribution within the fluidized electrode is made as uniform as possible by placing multiple anodes within the bed. Each anode is placed inside a tubular diaphragm and the anolyte and catholyte are controlled separately and may be different. The specially developed diaphragms have a high mechanical strength and resistance to chemical attack but a low hydrodynamic permeability and electrical resistance. Their surfaces are also very smooth to avoid the commencement of bed agglomeration at this interface.

A typical unit will be up to 0.5 m in diameter and the bed may be 1 m in height (plus 10–30% expansion on fluidization). The number of anodes will depend on the diameter of the cell. A 0.35 m diameter cell with seven anodes and operating at 1000–2000 A handles 10–20  $m^3 h^{-1}$  of solution. The bed is made of metal particles 0.5 mm in diameter and these are allowed to grow to 1 mm (a tenfold increase in weight); the particles gradually sink down the bed during the growth so that the process can be operated continuously by adding small particles at the top and removing the heaviest from the bottom of the bed.

Several examples of the application of this technology have been described; the



(a)

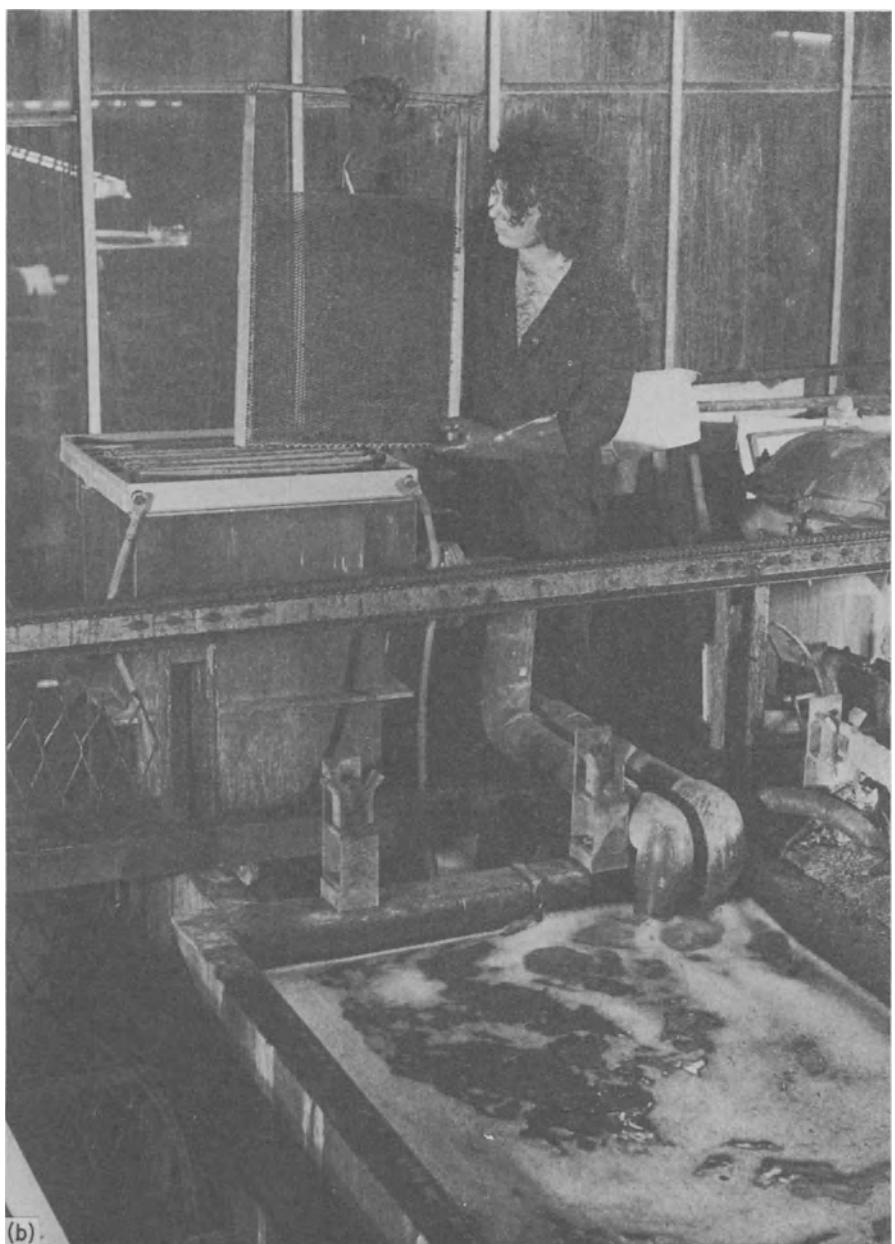


Figure 11.6 (a) Chemelec plant sited above a plating line. (b) Replacement of the electrodes in a Chemelec cell. Photographs supplied by the Electricity Research Council, Capenhurst.

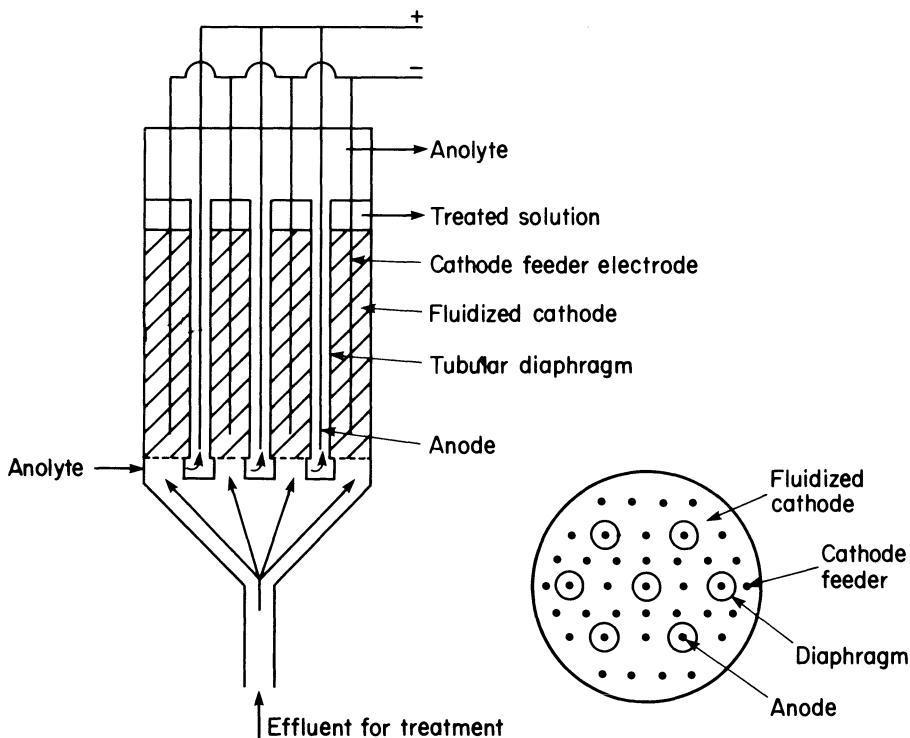


Figure 11.7 *The Akzo fluidized cathode cell for metal recovery from effluent.*

fluidized bed cells have been used (i) to remove copper from the effluent of a hydrocarbon chlorination process which contained both solids and chlorocarbons as well as copper(II) in an acidic chloride medium, the copper content being reduced from 100 to 1 p.p.m. with a 70% current efficiency, (ii) to strip mercuric ion from effluent resulting from the chlor-alkali mercury cell process, the concentration being reduced from 5 to 0.06 p.p.m., and (iii) to recover copper and cadmium and to purify a zinc electrolyte. Using sequential cells the copper and cadmium were removed to 0.1 p.p.m. and 1.0 p.p.m. with current efficiencies of 70% and 40% respectively. Moreover the purities of the metals were greater than 99% for copper and greater than 90% for cadmium.

New cell designs for metal stripping continue to be developed and may find commercial application. Their performance in terms of ability to remove metal ions is similar and indeed the difficulty with all cells lies in the chemistry when complexing agents may be present. Differences are, however, claimed in respect of investment cost and ease of both use and maintenance. Three new designs should be mentioned (see Fig. 11.8). In the first a circulating bed electrode is used since this type of electrode, although similar to a fluidized bed, is less prone to agglomeration; in such cells, the hydrodynamics within the catholyte compartment are controlled so that the particles of metal undergo a directed circulating

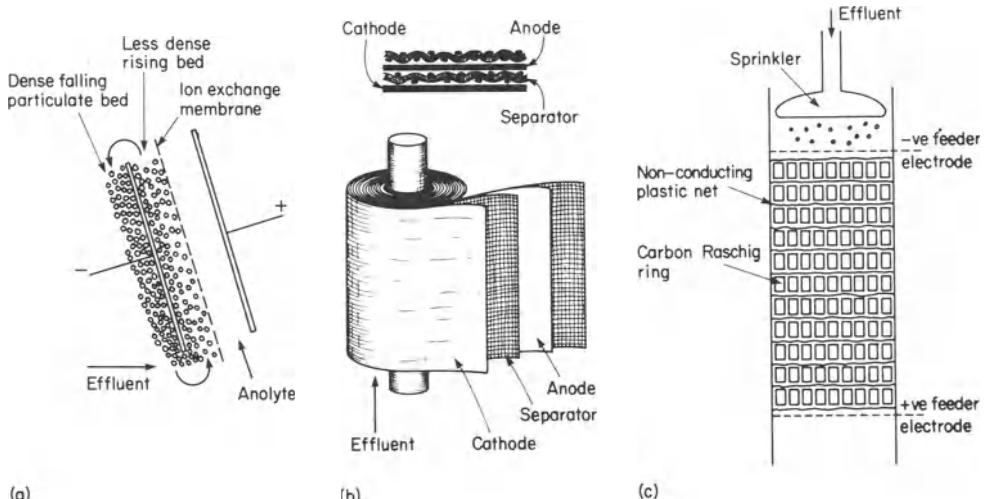


Figure 11.8 *Design concepts of three further cells for metal recovery from dilute solutions of metal ions. (a) Cell with circulating bed cathode. (b) The Swiss-roll cell. (c) The trickle tower cell*

movement, upwards in a low-density bed close to the diaphragm separating the anode compartment and downwards in a more dense stream at the back of the cathode compartment. The particles separate according to size if the electrolyte flow is stopped but otherwise the operation of the cell is similar to the fluidized bed cell described above. In the Swiss-roll cell, an anode plus separator plus cathode sandwich is rolled up to give a cell of high electrode area per unit volume. The electrodes may be sheets or gauzes (a cathode of several gauzes has been found to be particularly effective) while the separator ranges from a membrane to a simple cloth or insulating plastic net. The net acts as the best turbulence promoter and in this configuration the cell has been used to remove both zinc (cathodically) and cyanide (anodically) in a chloride medium (see next section). The bipolar trickle tower is based on a substantially different principle. The cell consists of a series of layers of carbon Raschig rings, each layer separated from its neighbours by an insulating net. When a voltage is applied between the feeder electrodes at each end of the stack, electrolytic cells form between each pair of adjacent layers. The solution to be treated is then trickled onto the top of the stack to give a very thin electrolyte film over the Raschig rings. Rapid diffusion in the thin film combined with an extremely high electrode area/solution volume ratio again lead to almost complete stripping of the metal ion in solution. The last two cell designs have the possible disadvantage that the metal formed is not readily removed from the cell. The normal procedure would be periodically to stop electrolysis and dissolve the metal chemically; effectively the cell is then a method of concentrating the metal ion although in many environments the concentrated solution may be re-usable directly.

Overall, with several attractive cell designs coming onto the market, the future of such electrolytic metal removal and recovery seems bright.

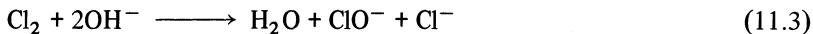
## 11.2 HYPOCHLORITE AND LOW-TONNAGE CHLORINE ELECTROLYSERS

The last few years have seen the introduction to the market of a number of small electrolysis cells for the generation of either hypochlorite or chlorine gas; in many applications either type of cell could, in principle, be employed and the choice will then depend on technological factors. In the water and effluent treatment industry, the common applications of on-site chlorine and hypochlorite cells will include the treatment of sewage (particularly at remote sites), the sterilization of water for food processes and hospital laundries, the treatment of water on board ships and for swimming pools, the treatment of cooling water at coastal power stations to prevent the growth of shellfish and seaweed in the pipes and the oxidation of cyanide ion in effluents. In addition the same cells are used to provide chlorine gas for power stations and to provide bleaching agents in the paper and textile industries.

Traditionally all these markets have been satisfied by liquid chlorine, tanked from the large chlor-alkali plants, but there is now the desire to avoid the potential hazards associated with the transport and storage of chlorine.

The low-tonnage chlorine electrolyzers are small versions of the membrane cells described in Chapter 3 although the anolyte will usually be a concentrated brine prepared from solid sodium chloride. Indeed, the development of membrane technology was a big boost to on-site chlorine generation since membrane cells, unlike mercury or diaphragm cells, are well suited to small-scale and intermittent production and units producing as little as a few kilograms per day are now available. The major disadvantage of such chlorine generators in the water treatment industry is the very high purity of brine which is necessary in membrane cells; particularly the  $Mg^{2+}$  level must be low and this makes a sea water feed possible only if the process is complicated by a purification unit.

At one time sodium hypochlorite was manufactured electrolytically on a substantial scale. Now it is regarded as a byproduct of the chlor-alkali industry; the tail gases containing only a low concentration of chlorine and resulting from dechlorination of the brine leaving the cell are reacted with caustic soda. On the other hand, there are many situations where low volumes of hypochlorite may be required on an irregular basis, and these can be satisfied by small electrolysis units. Such cells can be designed to operate with filtered sea water or with a neutral brine prepared from solid sodium chloride, and a wide range of designs have been described. Such cells do not need a separator since the hydroxide formed at the cathode is consumed by the hydrolysis of the chlorine, i.e. the cell chemistry is



Hence the simplest design is a closely spaced, bipolar stack of electrodes, although control of the hydrodynamics in the cell is essential to prevent cathodic reduction of the hypochlorite. Moreover when the anolyte feed is sea water, an additional

problem can arise due to the high pH close to the cathode. This is due to precipitation of group II metal hydroxides, particularly  $Mg(OH)_2$ , on the cathode surface and can only be prevented by designing the electrolyte chamber so that there are no dead spots in the flow where aggregation of the deposit can commence. For most applications, the electrolyte contains 0.01–1% hypochlorite as it leaves the cell.

For small-scale electrolysis units, energy consumption will be much less important than in a chlor-alkali process; ease of operation with a minimum of maintenance and replacement of components and the initial cost of the total unit will more often determine the choice of the cell. As a result, for example, while the cathode will generally be steel, a wide range of anode materials including graphite, lead dioxide and platinized titanium have been used as well as dimensionally stable anodes. Hence the quoted energy consumptions of hypochlorite cells lie in the range 4.5–7.0 kWh kg<sup>-1</sup>, considerably above those for a chlor-alkali cell. The current densities vary between 0.1 and 0.5 A cm<sup>-2</sup>.

### 11.3 ELECTRODIALYSIS

The principle of an electrodialysis cell is shown in Fig. 11.9. Anion and cation exchange membranes are arranged alternately in a stack and a potential field sufficient to force current through the stack is applied between two electrodes placed at each end of the stack. In order for current to pass between the electrodes, ions must be transported through each of the membranes and, by arranging the feeds to the various inter-membrane compartments, it is possible to force ionic salts to pass from the dilute stream to the concentrated stream. In fact, using a stack containing  $N$  pairs of anion + cation membranes, the passage of 1 Faraday of electricity will allow the transfer of  $N$  moles of salt.

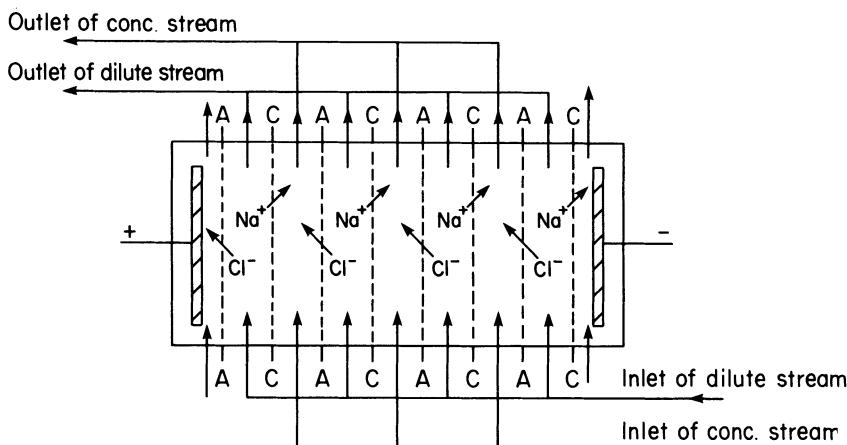


Figure 11.9 Principles of the electrodialysis plants. A = anion exchange membrane; C = cation exchange membrane.

Clearly electrodialysis can be used for concentrating ionic solutions, deionizing salt solutions and separating ionic and non-ionic species (Fig. 11.10). In the context of this chapter, electrodialysis has applications for the following:

(a) The desalination of potable water (Table 11.2). Typically sea water or well water is treated to reduce the total salt concentration from 1000–3000 p.p.m. to less than 500 p.p.m. In most cases the major ionic component is sodium chloride but this is not always so. For example, in some well water the chief salt is calcium sulphate.

(b) The recycling of transition-metal ions. For example, the rinse waters from nickel plating containing perhaps  $1\text{ g l}^{-1}$  nickel sulphate can be concentrated to  $60\text{ g l}^{-1}$  and recycled directly to the plating bath.

(c) Salt removal from effluent waters prior to re-use in industrial processes. Reduction in the concentration of ionic species is often necessary if the water is to be recycled through a chemical process (e.g. to reduce corrosion).

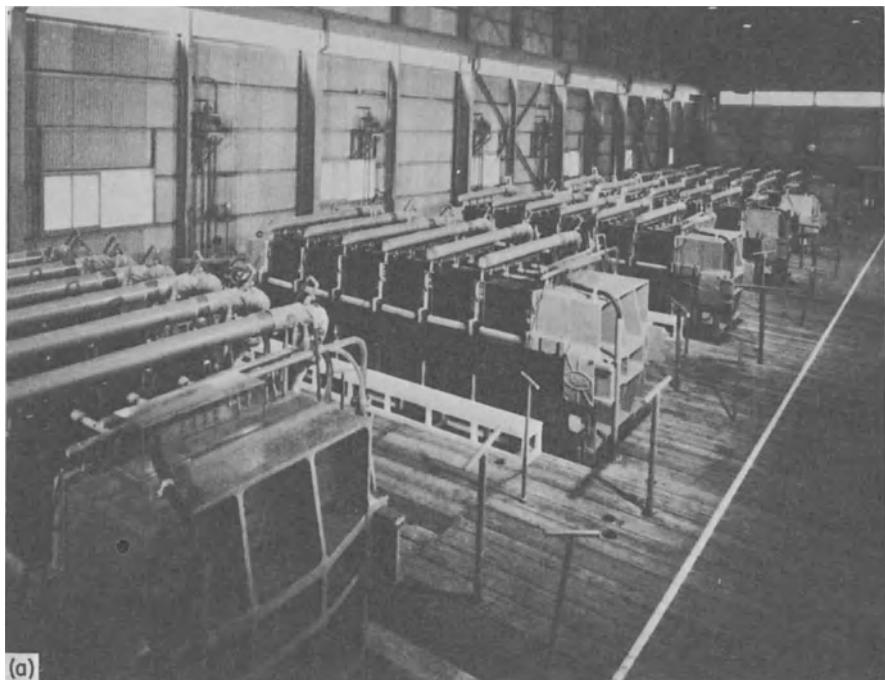
(d) Salt splitting, i.e. the recovery of acid and alkali from a neutral salt solution (e.g. the formation of  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$  from  $\text{Na}_2\text{SO}_4$ ). For this purpose it is essential to have one pair of electrodes for each pair of membranes; the acid is formed in the anode compartment, the alkali in the cathode compartment and the stream between the membranes is depleted in the neutral salt.

Electrodialysis has a number of other large-scale applications and these would include the manufacture of pure sodium chloride for table salt (in Japan, electrodialysis is the principal method, production exceeding  $10^6\text{ ton yr}^{-1}$ ), the demineralization of cows' milk (for baby food), cheese whey and sugar solutions, the removal of excess acid from fruit juice and the isolation of organic acids from reaction streams.

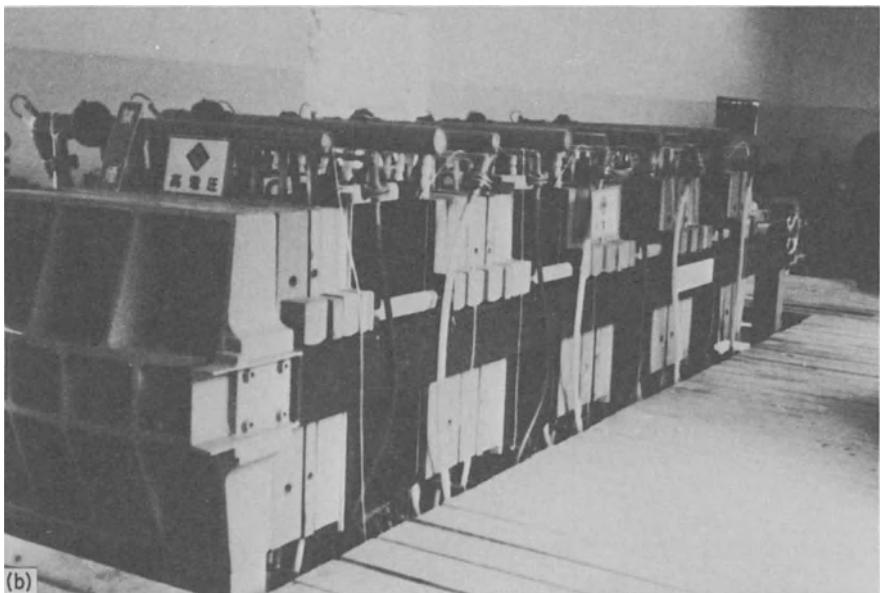
As in all electrochemical cells, the energy consumption of an electrodialysis cell is effectively determined by the cell voltage and the current efficiency. In electrodialysis, these quantities are, however, determined by quite different factors from electrolytic processes. The current efficiency is determined solely by the properties of the membrane (see below) and the faradaic processes occurring at the electrodes are unimportant except to the extent to which they introduce hazards or unwanted problems into the cell. In practice the cathode reaction is almost always hydrogen evolution and the anode reaction is the evolution of oxygen or in chloride media an oxygen/chlorine mixture. The cathode reaction, of course, increases the pH of the solution in this compartment and this can lead to precipitation of hydroxides if the feed is anything but very pure (e.g. sea water contains  $\text{Mg}^{2+}$  which precipitates as  $\text{Mg}(\text{OH})_2$  on the cathode; hence the catholyte is commonly acidified). The distribution of voltage in a cell containing  $N$  pairs of membranes is given by

$$V = E_e^C - E_e^A - |\eta_A| - |\eta_C| - NI(R_{\text{CATION MEMBRANE}} + R_{\text{ANION MEMBRANE}}) - NIR_{\text{DILUTE SOLN}} - (N - 1)IR_{\text{CONC. SOLN}} \quad (11.4)$$

and it will be apparent that the largest term will be the  $IR$  drop in the dilute streams, particularly towards the end of the process when the total ion concentration will be



(a)



(b)

Figure 11.10 Electrodialysis cells for (a) the concentration of sodium chloride in sea water and (b) the desalination of well water. Photographs supplied by Asahi Chemical Industry Co. Ltd.

Table 11.2 Data\* for three electrodialysis plants for the desalination of well water.

	Webster, USA	Shikine, Japan	Oshima, Japan
Capacity ( $\text{m}^3 \text{ day}^{-1}$ )			
(i) raw water	1660	227	1540
(ii) purified water	954	200	1340
Salinity of feed (p.p.m.)	1500–1800	1145	2900
Salinity of product (p.p.m.)	350	<500	<500
Major ionic species	$\text{CaSO}_4$	NaCl	NaCl
Operation	Continuous, four stacks in series	Batch, one stack	Continuous, one stack
Membrane pairs per stack	216	150	250
Membrane area ( $\text{m}^2$ )	$1.11 \times 1.11$	$1.11 \times 0.57$	$1.11 \times 1.11$
Power consumption ( $\text{kWh m}^{-3}$ )	1.4	1.3	1.0

\* Data from advertising literature, Asahi Chemical Industry Co. Ltd.

very low. Hence the cell must be designed to minimize this term, i.e. the gap between the membranes must be as small as possible (typically 0.7–1.5 mm). Particularly when  $N = 100$ –2000, the terms associated with the electrode reactions are negligible. Indeed, in electrodialysis, the selection of electrode material will be based on stability and cost rather than overpotentials; common electrode materials are Pt/Ti or Pt + Ir/Ti with steel considered as the cathode metal.

Clearly the performance of an electrodialysis cell is largely controlled by the properties of the membranes. Both the anion and cation membranes should have a low resistance and high chemical, mechanical and dimensional stability. But while immunity to chemical attack is essential, it should be noted that, with the exception of those adjacent to the electrodes, the membranes are not subjected to extreme pH conditions or the presence of strong oxidizing agents (cf. the membrane in a chlor-alkali cell). The requirement for high mechanical and dimensional stability arises because a large area of membrane and an even gap between neighbouring membranes are essential. In some applications it would be advantageous for the membrane to be selective to particular anions or cations, although in general it is only necessary for the transport number for anions in the anion exchange membrane and cations in the cation exchange membranes to be close to one.

Very large areas of membrane are used in an electrodialysis cell and hence they should be as cheap as possible. Thus while the perfluoropolymers have excellent properties, they are too expensive and the membranes used are copolymers of styrene and divinylbenzene. The cation-selective materials are activated by sulphonation while the anion-selective membranes are substituted with quaternary ammonium centres. To give the membranes the required mechanical and dimensional stability, the copolymerization reaction is initiated around a reinforcing mesh or within a porous polyethylene or thermoplastic sheet; the first method is generally preferred since it gives membranes of lowest resistance. The ratio of styrene to divinylbenzene determines the extent of crosslinking and hence, after activation, the amount of water absorbed into the polymer. The water creates channels across the membrane through which the ions can diffuse and the quantity of water controls the maximum size of ion which can be transported.

Such styrene/divinylbenzene copolymer membranes can be prepared with a wide variation of properties but the best anion exchange membranes give an anionic transport number greater than 0.98 (i.e. less than 2% of the current is carried by cations in the wrong direction) in typical operating conditions (the transport number will have some dependence on the concentrations of salt in the dilute and concentrated streams). The cationic transport number for the corresponding cation membrane is commonly lower, typically 0.90, and this controls the current efficiency of the process.

The maximum useful current density through the membrane is normally determined by a phenomenon known as polarization, in this context depletion of the transported ion at the membrane surface. This is a mass transport problem and it is therefore necessary to avoid stagnant layers at the membrane/solution interfaces by operating the cell at a high enough Reynolds number or with turbulence promoters. This will clearly be most necessary as the dilute stream

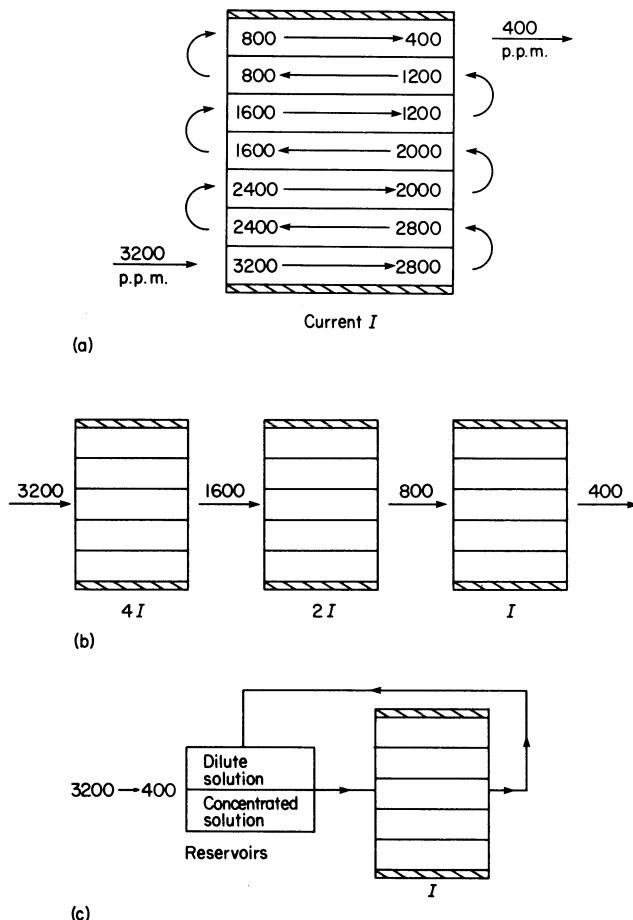
becomes depleted in ionic species. Electrodialysis cells are operated with a current density in the range 20–200 mA cm<sup>-2</sup>.

Membranes also suffer from a susceptibility to poisoning and fouling. Thus certain ions have such a high affinity for the active centres that they become irreversibly adsorbed. An example is Mn<sup>2+</sup> at cation exchange materials. This is poisoning and can only be controlled by removal of the offending ion before it contacts the membrane. Fouling is a similar but less serious problem caused by phenols, detergents and large organic acids (all common species in industrial effluents) at anion membranes; it can be minimized by controlling the pore structure of the membrane.

Electrodialysis cells are invariably mounted in a filter press and constructed on the plate-and-frame principle. The membranes are typically 0.5–2.0 m<sup>2</sup> and very thin to minimize their resistance. Hence they are supported by inert polymer separators placed in each space between membranes. These separators also serve to maintain the membranes a fixed distance apart, 0.5–2.0 mm, to guide the electrolyte flow and to act as turbulence promoters. The number of membrane pairs will depend on the volume of solution to be processed, the total ion concentration in the feed and the level of ions desired in the solution leaving the cell. For the desalination of water, 100–300 membrane pairs are typical, while for the recovery of solid salt, the units may have 1000–2000 pairs. The operation of the cells is dependent on very good gasketing to prevent leaks, particularly from the concentrated to the dilute stream, and the design must permit a good, even solution flow through the cells. The hydraulic pressure must be the same on either side of each membrane and fairly uniform to each membrane gap. It is also necessary to prevent significant current leakage between adjacent membrane gaps through the common solution feeds since this will contribute to the current inefficiency.

A critical path length through the cell, dependent on the current density and flow rate, will be necessary to achieve the desired amount of ion transport from the dilute to the concentrated stream. Several strategies for the solution flow are possible (see Fig. 11.11) but all designs must recognize that the current through each membrane in the stack is always the same, i.e. the transfer of ions at each membrane will be the same. Hence, for example, in the case shown where 400 p.p.m. salt is removed for each pass through the cell, the ion concentration cannot be reduced below 400 p.p.m. Further reduction in this concentration would require passage through a further cell where the current density is lower and, say, 100 p.p.m. per pass is removed. The choice between flow patterns shown will be based on the volume of solution to be treated and other local conditions. With each flow pattern, the path length can, however, be increased by using the separator between each of the pairs of membranes to direct the solution in a labyrinth pattern across the cell.

The energy consumption in electrodialysis plants is very dependent on local factors and the objectives of the process but for modern plant it normally lies in the range 1.0–2.0 kWh per litre of solution treated. The number of electrodialysis plants is presently on the increase. The competitive processes for the concentration



**Figure 11.11** *Three flow patterns for electrodialysis cells to reduce salt concentration from 3200 p.p.m. to 400 p.p.m. The relative currents in each stack are shown. (a) Eight pairs of membranes in series in one stack. (b) Three stacks in series, each stack with N pairs of membranes. (c) Batch process with recycle through one stack.*

of ionic solutions and for desalination are evaporation and reverse osmosis (another process based on membranes but using pressure to push solvent through the membrane). Electrodialysis is likely to be the process of choice where the ion concentration of the dilute stream is relatively low, the scale of operation is large and the cost of electric power is low.

#### 11.4 ELECTROLYTIC METHODS OF PHASE SEPARATION

A recurrent problem in effluent treatment is the separation of solid suspensions and emulsions or colloidal particles of oil or other organic compounds in water;

such separation is essential to lower the BOD of the effluent to an acceptable level before the water is discharged. Such effluents arise in the oil industry, from engineering, printing and paint workshops, in the food processing industry, in paper mills and in fibre and glass manufacture. The traditional approach to the solution of these problems is to allow the effluent to stand in holding tanks until separation into two phases occurs. Such methods can be expensive when large volumes of liquid have to be stored for extended periods of time. Hence it has become common (a) to add flocculating agents, commonly highly charged inorganic ions ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ), to the mixture, (b) to use dissolved air flotation. Flocculating agents, however, represent an additional cost and can constitute an environmental hazard so that their addition requires a reliable dosing procedure and their concentration must be monitored. In method (b) small bubbles of air are allowed to rise through the effluent and float the suspended matter to the surface where it can be removed by a scraper or a paddle into a collection hopper. This method requires a source of compressed air and a well designed sparger to give a uniform supply of very small air bubbles throughout the tank. There are electrochemical versions of both (a) and (b) which are attractive in some circumstances.

In electroflootation, the gases are generated electrolytically in a cell such as that shown schematically in Fig. 11.12. A pair of closely spaced (0.2–2.0 cm), horizontal gauze or expanded metal electrodes are placed towards the base of the tank and cover the whole tank area. The water containing suspended liquid or solid organic particles is flowed slowly (convection should be minimized) into the top of the cell and the gas bubbles rising through the water capture the organic matter and lift it to the surface. The resulting scum, a much more concentrated form of the organic, is skimmed off for disposal and the purified water leaves the base of the tank.

It is generally considered that the mechanism is, as in dissolved air flotation, purely mechanical; as the bubbles of gas rise, they capture the organic particles and carry them upwards. In electroflootation it is also possible that there is an electrostatic contribution to the mechanism. If the gas bubbles leaving the

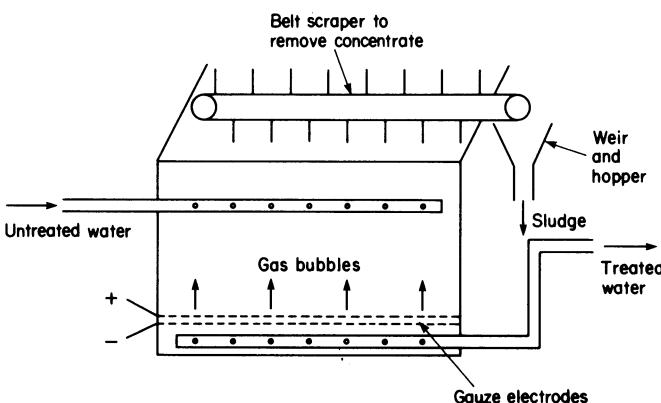


Figure 11.12 *Schematic drawing of the construction of an electroflootation cell.*

electrodes carry small charges, then they can neutralize the electrical charges known to exist on colloidal particles and cause them to coalesce.

In almost all applications of electroflootation the cell reaction is simple water electrolysis, so that the gases are oxygen and hydrogen. The size of the gas bubbles is critical in determining the efficiency of the separation process, and this is presumably a function of current density as well as the properties of the effluent and the electrode surfaces. Moreover, a major difficulty in the treatment of some effluents is the deposition of scale on the cathode surface and a consequent increase in the bubble size — the scale arises from the pH increase at the cathode surface leading to precipitation of magnesium and other metal hydroxides. The current density employed is low,  $0.1\text{--}10 \text{ mA cm}^{-2}$ , but even then and despite using a small inter-electrode gap the cell voltage may need to be as high at 5–10 V because the effluents, in general, contain little electrolyte. An overall energy consumption of  $0.2\text{--}0.4 \text{ kWh m}^{-3}$  of water is typical. This can be improved, and at the same time the problem of scaling can be overcome, by dosing the effluent with a low concentration of acid but this may be undesirable because of the cost and the influence on the environment after disposal.

Electroflootation cells vary in capacity between 1 and  $50 \text{ m}^3$ , the largest size giving the capability of dealing with up to  $150 \text{ m}^3$  of water per hour. In a typical specification the plant will reduce 1000 p.p.m. solids and 600 p.p.m. oils to 30 p.p.m. and 40 p.p.m. respectively. The components of the cell will be selected mainly for durability and low cost. The tank will be steel or a cheap plastic depending on size; the cathode will be a steel and the anode platinized titanium or lead dioxide on titanium.

Electroflootation is now an attractive process for smaller-scale operation although it is unlikely to challenge dissolved air flotation in its larger-scale applications in mineral ore concentration and oil/water separation in the petroleum industry. Certainly the number of electroflootation plants seems to be on the increase and, for example, there are now about twenty such plants in the UK.

In electroflocculation or electrocoagulation, the flocculating agent is introduced as a result of an electrode reaction and such processes permit a careful control of the amount of the reagent introduced into the effluent. Thus for example  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  can be introduced by using an aluminium or iron anode and it is also possible to use such an anode in an electroflootation cell. Also magnesium hydroxide, or even hydroxide ion produced at the cathode of chlorine or hypochlorite cells, can act as flocculating agents, again allowing the combination of coagulation with chlorination.

## 11.5 OTHER ELECTROCHEMICAL PROCESSES

Many other applications of electrochemistry in pollution control have been proposed and some of the more likely will be discussed briefly in this section.

The use of electrolysis for precise dosing has already been mentioned in the previous section; a major advantage is the ability to vary the dosing rate rapidly by controlling the current in the cell. This can be achieved particularly elegantly if a minicomputer is used to control a system combining, with the electrolysis cell, a fast response monitor to determine the dosing level required. An example is the

control of effluent pH — a glass electrode may be used to determine pH and a divided cell used to introduce  $\text{OH}^-$  or  $\text{H}^+$  by water electrolysis. An application might be in the chlor-alkali industry for readjusting the pH of the brine leaving the main cells from pH 4 to pH 7.

Anodic oxidation has long been discussed as a method of removing organic molecules from effluents. In most cases this is quite impracticable because the complete oxidation of organic species to carbon dioxide is not a facile reaction; it only takes place for some species and then only at a low rate in special conditions, e.g. at a platinized platinum electrode in concentrated acid or alkali at  $80^\circ\text{C}$ . Such conditions are clearly unsuitable for pollution control where it would be inappropriate to use large quantities of reagents, energy for heating or expensive electrodes. Moreover complete oxidation of large molecules requires the transfer of many electrons and inevitably a high energy consumption. Occasionally, however, a small transformation of molecular structure leads to a large reduction of toxicity, or complete oxidation is possible at a high-surface-area carbon or the species to be removed is an inorganic molecule requiring a 1e or 2e oxidation. Then anodic oxidation seems more feasible. Reversible electrochemical adsorption has also been considered as a method of removing large organic molecules; the electrode potential could be held at a value where the molecule adsorbs and periodically the electrode would be cleaned by changing the potential to a different region where the molecule desorbs. This would then only be a concentration procedure but it would consume little power.

Methods for the removal of low concentrations of species from effluent which involve either oxidation or adsorption will clearly require a cheap but high-surface-area electrode structure, and several carbon bed and carbon fibre electrode cells have been described. The latter are prepared from 5–15  $\mu\text{m}$  diameter carbon fibre which has a specific area of  $260 \text{ m}^{-2} \text{ g}^{-1}$  and hence permits a high throughput of effluent. Such a cell has been used for treatment of paper mill effluent and a 70% reduction of BOD with a 95% removal of highly toxic chlorinated phenols has been claimed.

In general, however, indirect oxidation by an electrogenerated oxidant seems a more promising technique. For example, while direct oxidation of cyanide ion is possible, the process is catalysed by the presence of chloride ion and most practical devices involve the intermediate formation of chlorine or hypochlorite; see above. While chlorine and hypochlorite are, at the present time, very widely used, there is some concern that they may themselves lead to toxic, chlorinated species in the environment. Hence there is interest in alternative oxidizing agents such as hydrogen peroxide and ozone; both could in principle be prepared on site in small electrolyzers, hydrogen peroxide by oxygen reduction or via the persulphate route (see Chapter 5) and ozone by oxidation of acidic water at low temperature. These are active research areas at the present time.

## 11.6 ELECTROANALYTICAL PROCEDURES

While all analysts are familiar with the principles of potentiometry and polarography and, indeed, most analytical laboratories will contain a pH meter and a polarograph, electrochemical methods are, in general, not very important in modern analysis. In

contrast, for trace metal ion analysis in water and effluent and, also, some other aspects of environmental analysis, electrochemical methods are particularly attractive. This is because (i) some methods, especially anodic stripping voltammetry, have a very high sensitivity for heavy metal ions and the lowest detection limit of  $10^{-10}$ – $10^{-12}$  M is well below that of other available methods; (ii) electrochemical methods are well suited for modification to on-line and/or portable devices for analysis in the field. Whether the analysis is based on current, conductivity or the response of an ion-selective electrode, both the cell and the control electronics are readily miniaturized and operate on low power. Hence this section considers the principles of the electroanalytical methods important in environmental and on-line analysis.

### 11.6.1 Polarography to anodic stripping voltammetry

DC polarography dates back almost sixty years to the discovery by Heyrovsky that highly reproducible  $I$ – $E$  curves could be obtained using a dropping mercury electrode (DME) as the working electrode. Thus in a polarographic analysis an  $I$ – $E$  curve is recorded using a slow linear potential scan and a DME with a droptime of 2–10 s; the  $I$ – $E$  curve will have the S-shape shown in Fig. 11.13. The half wave potential  $E_{1/2}$  can be used for qualitative analysis since it is a measure of how readily the electroactive species is reduced or oxidized and therefore is a reflection of its molecular structure. In addition, the measurement of the mass-transport-limited current  $I_L$  can be used for quantitative analysis.

Polarographic analysis has considerable generality since a very wide range of both organic and inorganic species are electroactive within the potential range of the DME. For the same reason, however, when analysing mixtures it is often difficult to obtain the necessary selectivity; the species to be determined must give a wave well separated from all others (in practice  $\Delta E_{1/2} > 200$  mV), and if other electroactive species are present in excess they must be more difficult to reduce (it is not possible to determine accurately a small change in a large current). The order of the reduction waves and the separation of the waves can only be varied using pH and/or complexing agents and these are often insufficient when dealing with mixtures of similar species. Polarography is also not a particularly sensitive technique.

These shortcomings led to modifications of the experiments to improve both the sensitivity and selectivity of analyses. It was found that the sensitivity could be improved by measuring the current under conditions of non-steady-state diffusion and increasing the ratio of the faradaic to the charging current. In pulse polarography this is achieved by constructing an  $I$ – $E$  curve point by point where each point is the current measured a short time, typically 40 ms, after a potential pulse has been applied during the final stages of the lifetime of a mercury drop. The selectivity could be improved by differentiating the  $I$ – $E$  curve since this led to separated peaks when  $\Delta E_{1/2} > 50$ – $80$  mV. The most successful technique is differential pulse polarography which employs a pulse profile which leads directly to a differentiated curve while giving the increased response due to non-steady-state diffusion. These modified polarographic methods are illustrated in Fig. 11.13 and compared in Table 11.3.

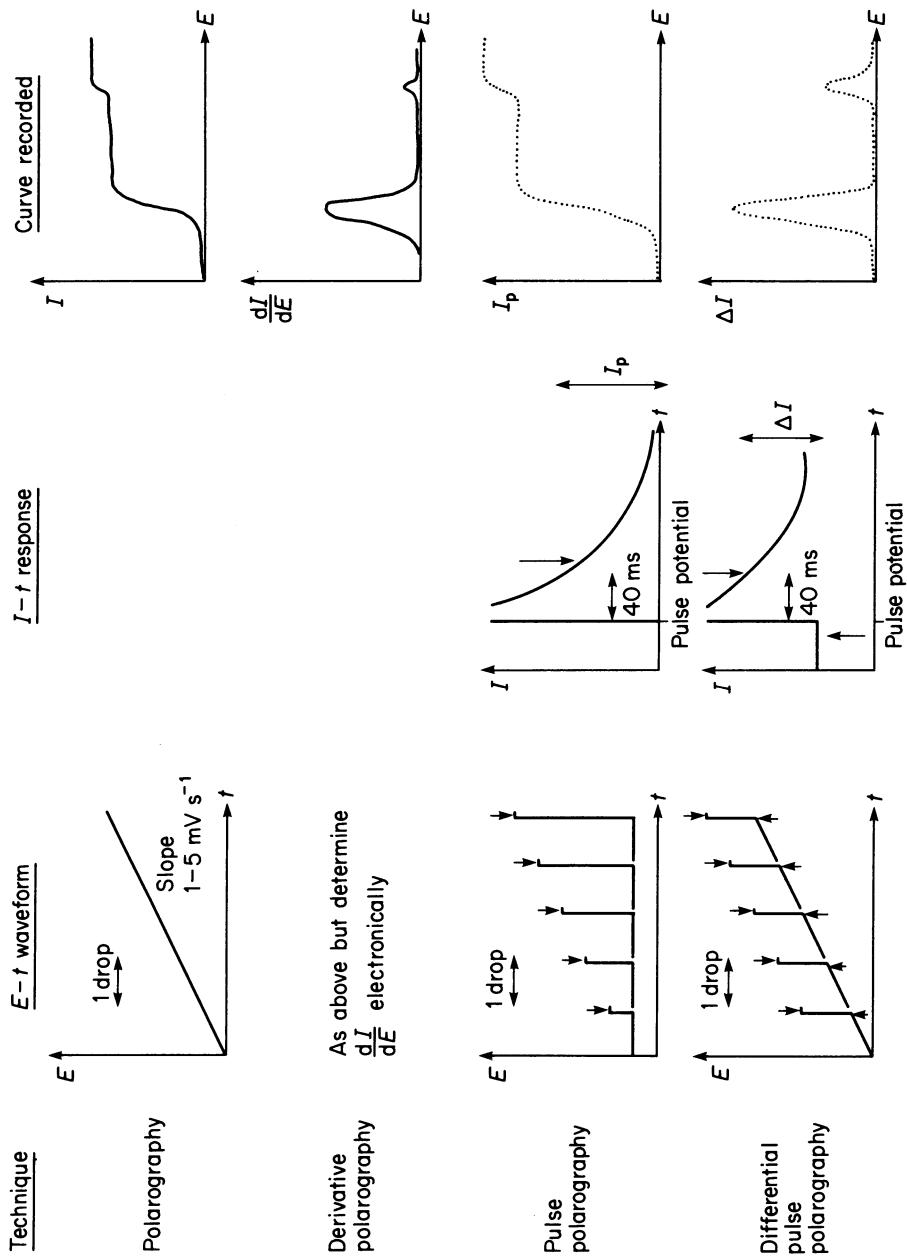


Figure 11.13 Modern polarographic techniques: ↑ or ↓ indicate times when current is measured.

Table 11.3 Comparison of modern polarographic methods.

Method	Measurables		Selectivity Minimum $\Delta E_{1/2}$ (mV)	Sensitivity Minimum detection limit (M)	Wave order important?
	Qualitative analysis	Quantitative analysis			
Polarography	$E_{1/2}$	$I_L$	200	$5 \times 10^{-6}$	Yes
Derivative polarography	$E_{\max}$	$(dI/dE)_{\max}$	50–100	$5 \times 10^{-6}$	No
Pulse polarography	$E_{1/2}$	$I_L^P$	200	$10^{-8}$	Yes
Differential pulse polarography	$E_{\max}$	$\Delta I_{\max}^P$	50	$10^{-9}$	No

In anodic stripping voltammetry, additional sensitivity is obtained by pre-concentrating the metal ion or ions to be determined in the mercury electrode in the form of an amalgam and the determination is carried out by measuring the current for the reoxidation of the amalgam. Hence the experiment has three parts.

- (a) In the first, a potential is applied to a mercury electrode such that one or all of the metal ions in solution are reduced to their amalgam at a mass-transfer-controlled rate. Clearly the sensitivity of the analysis can be increased by extending the period of formation of the amalgam, minimizing the volume of the mercury electrode and carrying out the deposition under conditions of forced convection. For the latter reasons, it is now common to use as the working electrode a rotating carbon disc plated with a thin film of mercury. The traditional working electrode is a stationary mercury drop.
- (b) After the period of deposition, the electrode is allowed to stand on open circuit for a short period so that the concentration of metal(s) in the mercury becomes uniform throughout the film electrode.
- (c) Finally the concentration of metal(s) in the amalgam is determined by programming the electrode potential to values where the metal(s) are reoxidized to their ions in solution. In practice the optimum presentation is obtained using the potential/time profile of differential pulse polarography.

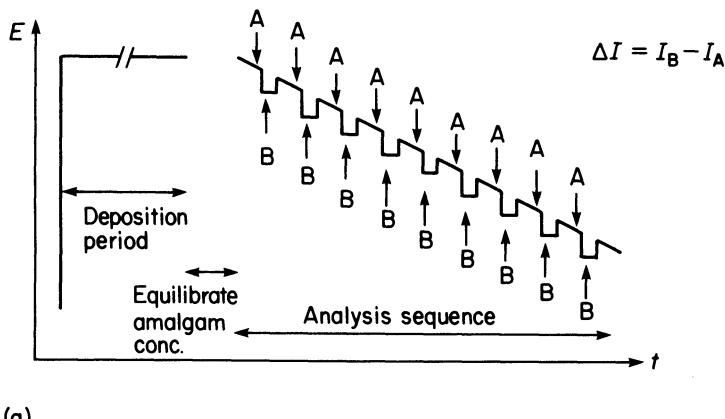
The potential/time profile for anodic stripping voltammetry and a typical experimental curve for the determination of a mixture of heavy metal ions is shown in Fig. 11.14. The method is clearly limited to the determination of metals which form simple amalgams (inter-metallic compounds must also be avoided). This limitation, however, introduces some desirable selectivity and most organic compounds will not interfere with the determination of the metals. Using acceptable deposition times, analysis of very low concentrations is possible. Certainly for heavy metal ions, the sensitivity of anodic stripping analyses compares well with that of atomic absorption spectroscopy even with non-flame atomization (see Table 11.4). Moreover, these data do not represent the ultimate detection limit since the plating time can be extended.

Hence anodic stripping voltammetry is the method of choice for the analysis of very low concentrations of heavy metal ions in water and effluents. Pulse and differential pulse polarography also have their advocates for particular analyses but they do not have the same general acceptance.

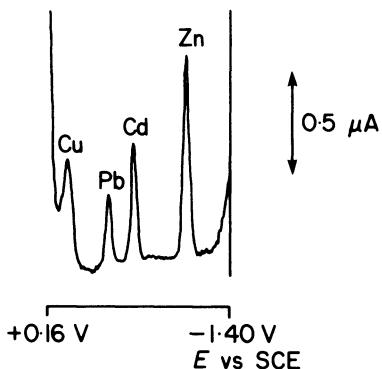
### 11.6.2 Ion-selective electrodes

Glass electrodes sensitive to proton concentration were first introduced in 1909 and have long been the generally accepted way of determining pH. Similar electrodes which respond selectively to other ions are a much more recent development dating back only to the mid-1960s; even so, ion-selective electrodes now have many applications in water and environmental analysis, for example the determination of pH,  $\text{F}^-$ ,  $\text{CN}^-$ ,  $\text{NH}_3$  and total hardness ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ).

The cell for the determination of the concentration of an ion,  $\text{M}^{z+}$ , with an



(a)



(b)

Figure 11.14 (a) The  $E-t$  sequence for anodic stripping analysis. (b) Anodic stripping voltammogram of a solution of  $\text{KCl}$  (1 M) containing  $1.5 \times 10^{-7} \text{ M } \text{Zn}^{2+}$ ,  $8.8 \times 10^{-8} \text{ M } \text{Cd}^{2+}$ ,  $4.8 \times 10^{-8} \text{ M } \text{Pb}^{2+}$  and  $1.55 \times 10^{-7} \text{ M } \text{Cu}^{2+}$ ,  $\text{Hg}$  drop electrode. Plating for 120 s at  $-1.4 \text{ V}$ . Results supplied by J. D. Burton and A. M. Ortega, Department of Oceanography, University of Southampton.

ion-selective electrode is shown schematically in Fig. 11.15, although in many cases the ion-selective electrode and the external reference electrode are mounted in a single probe. The measurement of the potential between the two reference electrodes allows the determination of the membrane potential caused by the difference in concentration of the ion  $M^{z+}$  between the analyte and the internal reference solution. For application in analysis the membrane potential  $E_M$  should be given by

$$E_M = \frac{2.3RT}{zF} \log \left( \frac{C}{C_S} \right) \quad (11.5)$$

Table 11.4 Comparison of lowest detection limits by anodic stripping voltammetry and atomic absorption spectroscopy.

Metal ion	Lowest detection limit ( $10^{-9}$ g cm $^{-3}$ )		
	Anodic stripping voltammetry*	Atomic absorption spectroscopy	
		Flame	Non-flame
Bi $^{3+}$	0.01	46	3
Cd $^{2+}$	0.005	0.7	0.01
Cu $^{2+}$	0.005	2.0	0.3
Ga $^{3+}$	0.4	38	—
In $^{3+}$	0.1	38	—
Pb $^{2+}$	0.01	15	0.5
Sn $^{4+}$	2.0	30	0.1
Tl $^+$	0.01	13	1
Zn $^{2+}$	0.04	1	0.008

\* Mercury film electrode. Plating for 120 s with rotation at 3600 r.p.m. Analysis by differential pulse polarographic waveform.

where  $C$  and  $C_S$  are the concentration of  $M^{z+}$  in the analyte and the internal reference solution respectively. The cell potential will be given by

$$E_{\text{CELL}} = E_M + \Delta E_{\text{REF}} \quad (11.6)$$

where  $\Delta E_{\text{REF}} = 0$  if identical reference electrodes are used. Since  $C_S$  is a constant, the equation for the cell potential can be simplified to

$$E_{\text{CELL}} = \text{constant} + \frac{2.3RT}{zF} \log C \quad (11.7)$$

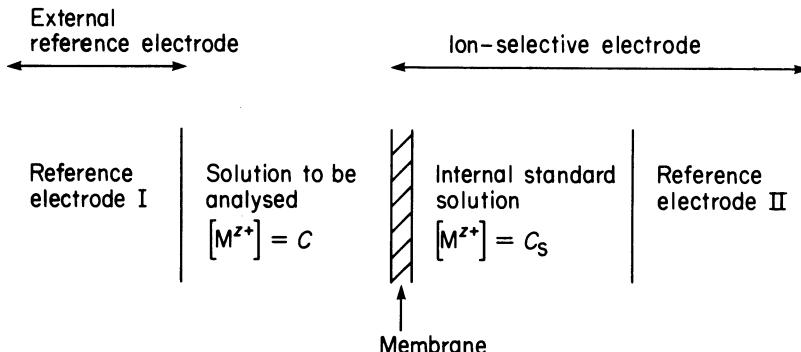


Figure 11.15 Scheme of cell for analysis of  $M^{z+}$  in solution with an ion-selective electrode.

so that concentration can be determined from a plot of  $E_{\text{CELL}}$  versus  $\log C$ , a plot which should be linear with a slope of  $60/z \text{ mV}$ .

The success of an analysis with an ion-selective electrode is almost totally dependent on the properties of the membrane. The response of the membrane to changes in the concentration of  $M^{z+}$  should be given by equation (11.5), but on the other hand, it should be completely independent of the concentration of other species in the solution. Moreover a stable potential should be reached rapidly. The design of membranes is largely empirical because, although it is thought that there is a contribution from both Donnan equilibria at the two membrane/solution interfaces and a diffusion potential within the membrane, the origin of the membrane potential is not fully understood. Certainly the factors which introduce selectivity for a single ion and speed of response are unclear. In practice the selectivity is discussed in terms of selectivity constants  $K_i$ , where

$$E_{\text{CELL}} = \text{constant} + \frac{2.3RT}{zF} \log \left( C + \sum_i K_i C_i^{z/z_i} \right) \quad (11.8)$$

where  $C_i$  is the concentration of the ion  $M_i^{z_i+}$  and clearly  $K_i$  should be as small as possible. Some typical selectivity coefficients, in fact for a calcium electrode based on a liquid ion exchange material  $(\text{RO})_2\text{PO}_2^-$ , R =  $\text{C}_8$  to  $\text{C}_{16}$  alkyl chains, in dioctylphenylphosphonate, are shown in Table 11.5.

Table 11.5 Selectivity coefficients for interferences to a  $\text{Ca}^{2+}$  ion electrode based on  $(\text{RO})_2\text{PO}_2^-$  in  $(\text{C}_8\text{H}_{17}\text{O})_2\text{PO}(\text{OC}_6\text{H}_5)$  where R =  $\text{C}_8$  to  $\text{C}_{17}$  alkyl chains.

Interfering ion	$K_i$
$\text{Mg}^{2+}$	$3 \times 10^{-2}$
$\text{Ba}^{2+}$	$2 \times 10^{-2}$
$\text{Zn}^{2+}$	$7 \times 10^{-2}$
$\text{K}^+$	$1 \times 10^{-4}$
$\text{Na}^+$	$1.5 \times 10^{-4}$

Several quite different types of membrane have been used in the construction of ion-selective electrodes. Namely:

(i) *Glasses*. The selectivity of such membranes depends on the composition of the glass. Generally they are based on  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$  mixtures; those rich in  $\text{SiO}_2$  but low in  $\text{Al}_2\text{O}_3$  are selective to protons while those with a high content of  $\text{Al}_2\text{O}_3$  respond more strongly to alkali-metal ions. Unfortunately selectivity between

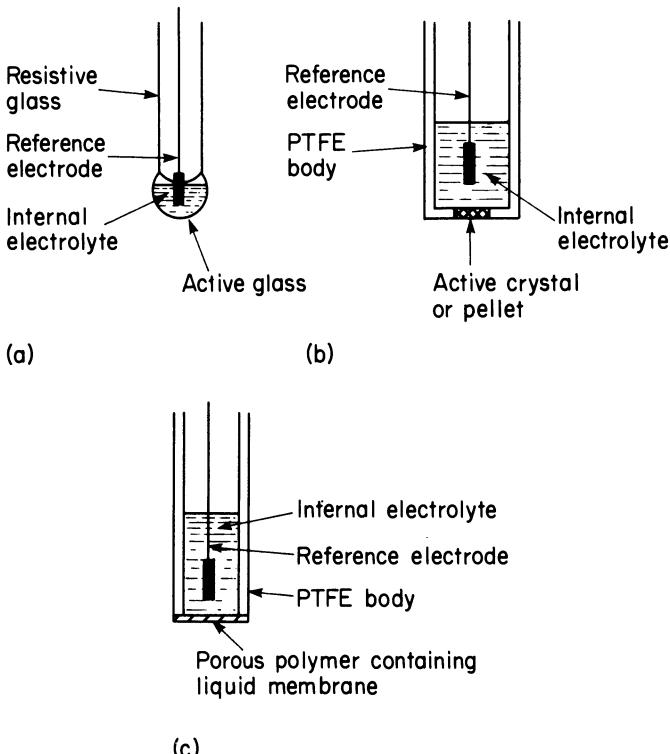
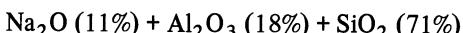


Figure 11.16 *Common constructions of ion-selective electrodes: (a) glass electrode; (b) crystal or pellet membrane electrode; (c) liquid membrane electrode.*

alkali-metal ions is not good with glass membranes. Two typical compositions are



responds to  $\text{H}^+$  – no interferences below pH 13



low pH,  $\text{H}^+$  predominates; intermediate pH,  $\text{Na}^+ > \text{Li}^+ > \text{K}^+$

The thin membrane of the active glass is sealed to an electrode body of non-responsive, high-resistance glass. The electrode is completed by filling with a buffered chloride solution which connects the inner membrane surface to a  $\text{Ag}/\text{AgCl}$  reference electrode.

(ii) *Solid-state membranes.* The most successful of these ion-selective electrodes is that for fluoride ion. It is based on a lanthanum fluoride crystal (doped with  $\text{EuF}_2$  to increase its conductivity) and is stable and reproducible with no interferences provided the solution is approximately neutral (excess free  $\text{OH}^-$  and the formation of HF must be avoided). The electrode is usually manufactured with a Teflon body and the  $\text{LaF}_3$  crystal is held in position with epoxy resin. The filling solution contains  $\text{NaF} + \text{NaCl}$  and the internal reference electrode is again  $\text{Ag}/\text{AgCl}$ .

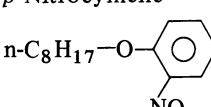
In a related type of electrode the membrane is a pressed disc of  $\text{Ag}_2\text{S} + \text{AgX}$  where  $\text{X}^-$  may be  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  or  $\text{SCN}^-$  and the electrode responds to  $\text{X}^-$ . With such a membrane, it is a very low concentration of  $\text{Ag}^+$  ions on both sides of the disc which determines the membrane potential and the selectivity is a function of the solubility product; any anion which forms a silver salt with a solubility product lower than the ion being determined will be a serious interference. Hence the electrode responds strongly to  $\text{Ag}^+$  and  $\text{S}^{2-}$  and for the determination of other ions their presence is catastrophic. Similarly  $\text{I}^-$  and  $\text{Br}^-$  is a serious interference to the  $\text{Cl}^-$  electrode and  $\text{I}^-$  to the  $\text{Br}^-$  electrode. A  $\text{M}^{2+}$  electrode ( $\text{M} = \text{Cu}, \text{Pb}, \text{Cd}$ ) may be prepared by making a pellet from a mixture of  $\text{Ag}_2\text{S}$  and  $\text{MS}$ . In these electrodes, the  $\text{M}^{2+}$  ion activity controls the  $\text{S}^{2-}$  activity and thereby the  $\text{Ag}^+$  activity and hence the electrode response. The pellet is again positioned in an inert electrode body with epoxy resin.

(iii) *Heterogeneous membranes.* The active component is deposited into the pores of an inert support such as silicone rubber instead of being pressed into a pellet. Otherwise the systems used are similar to those discussed in the pellet electrodes.

(iv) *Liquid membranes.* In these electrodes, the active material is a large organic molecule capable of interacting specifically with an anion or cation. Typical of these materials are the phosphate diesters,  $(\text{RO})_2\text{PO}_2^-$ , used for calcium ion electrodes, metal complexes used for anion electrodes and the neutral macrocyclic crown ethers which are suitable for alkali-metal electrodes. The active organic molecule is adsorbed onto an inert porous support or dissolved in an organic solvent, and indeed their selectivity can be affected by the choice of medium. Some typical electrodes are shown in Table 11.6.

While such electrodes can have acceptable selectivity they are not as robust as some of the other membrane electrodes and they can only be used in certain conditions where the solubility of the active organic molecule is very low. Their response times can also be undesirably long.

Table 11.6 Ion-selective electrodes based on liquid membranes.

Active materials	Solvent	Ion electrode
$\text{tris}\text{-}(1,10\text{-Phenanthroline})\text{Fe}^{2+}(\text{ClO}_4^-)_2$	$p\text{-Nitrocymene}$	$\text{ClO}_4^-$
$(\text{C}_{12}\text{H}_{25})_3\text{C}_{16}\text{H}_{33}\text{N}^+\text{NO}_3^-$	$n\text{-C}_8\text{H}_{17}\text{---O---}$ 	$\text{NO}_3^-$
Valinomycin	Hydrocarbon	$\text{K}^+$
$(\text{C}_{10}\text{H}_{21}\text{O})_2\text{PO}_2^-$	$(\text{C}_8\text{H}_{17}\text{O})_2\text{PO}(\text{OC}_6\text{H}_5)$	$\text{Ca}^{2+}$
	$\text{C}_{10}\text{H}_{21}\text{OH}$	$\text{Ca}^{2+} + \text{Mg}^{2+}$

A wide variety of ion-selective electrodes are now available (see Table 11.7) and the only instrumentation required is a high-impedance voltmeter to monitor the potential difference between the measuring electrode and the external reference electrode. The voltmeter must, however, be capable of accurate measurement since an error of 0.1 mV in the measurement of potential introduces an inaccuracy of almost 1% in the ion analysis (a 1 mV error in potential leads to a concentration error of 4% and 8% for singly and doubly charged ions respectively).

Table 11.7 Typical specifications for some commercial ion-selective electrodes.

Ion electrode	Membrane	Concentration range (M)	Major interferences
H <sup>+</sup>	Glass	10 <sup>-14</sup> –1	None
K <sup>+</sup>	Valinomycin	10 <sup>-6</sup> –1	Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>
Na <sup>+</sup>	Glass	10 <sup>-6</sup> –sat.	Ag <sup>+</sup> , H <sup>+</sup> , Li <sup>+</sup>
F <sup>-</sup>	LaF <sub>3</sub>	10 <sup>-6</sup> –sat.	OH <sup>-</sup> , H <sup>+</sup>
Cl <sup>-</sup>	Ag <sub>2</sub> S/AgCl	10 <sup>-5</sup> –1	Br <sup>-</sup> , I <sup>-</sup> , CN <sup>-</sup> , S <sup>2-</sup>
Br <sup>-</sup>	Ag <sub>2</sub> S/AgBr	10 <sup>-6</sup> –1	I <sup>-</sup> , CN <sup>-</sup> , S <sup>2-</sup>
I <sup>-</sup>	Ag <sub>2</sub> S/AgI	10 <sup>-7</sup> –1	CN <sup>-</sup> , S <sup>2-</sup>
CN <sup>-</sup>	Ag <sub>2</sub> S/AgI	10 <sup>-6</sup> –10 <sup>-2</sup>	I <sup>-</sup> , S <sup>2-</sup>
S <sup>2-</sup>	Ag <sub>2</sub> S	10 <sup>-7</sup> –sat.	Hg <sup>2+</sup>
Ag <sup>+</sup>	Ag <sub>2</sub> S	10 <sup>-7</sup> –1	Hg <sup>2+</sup>
Cd <sup>2+</sup>	CdS/Ag <sub>2</sub> S	10 <sup>-7</sup> –1	Ag <sup>+</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup>
Pb <sup>2+</sup>	PbS/Ag <sub>2</sub> S	10 <sup>-7</sup> –1	Ag <sup>+</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup>
Cu <sup>2+</sup>	CuS/Ag <sub>2</sub> S	10 <sup>-8</sup> –sat.	Ag <sup>+</sup> , Hg <sup>2+</sup> , S <sup>2-</sup>
Ca <sup>2+</sup>	(RO) <sub>2</sub> PO <sub>2</sub> <sup>-</sup> /(RO) <sub>3</sub> PO	10 <sup>-5</sup> –10 <sup>-1</sup>	Zn <sup>2+</sup> , Fe <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup>
Ca <sup>2+</sup> + Mg <sup>2+</sup> (hardness)	(RO) <sub>2</sub> PO <sub>2</sub> <sup>-</sup> /ROH	10 <sup>-7</sup> –1	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup>
NO <sub>3</sub> <sup>-</sup>	R <sub>4</sub> N <sup>+</sup> /ether	10 <sup>-5</sup> –1	ClO <sub>4</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , I <sup>-</sup> , Br <sup>-</sup>

Moreover ion-selective electrodes can be manufactured in very robust probes and, provided they are protected from fouling and physical attrition, they can often be used for continuous and on-line analyses as well as laboratory determinations. Their application is expected to increase substantially in the coming years.

### 11.6.3 Portable and on-line devices

The criteria used to judge an analytical device for fieldwork and on-line monitoring are often quite different from those for a procedure to be employed in a laboratory with full facilities. Clearly, such devices should be small, light, robust and auxiliary equipment such as gas supplies should be avoided; both the active components and the control electronics must be capable of miniaturization and should not require frequent adjustment or calibration. On the other hand, the device need only have

the selectivity, sensitivity and speed of response essential to the particular analysis. Thus, for example, the method need only discriminate against potential interferences to be found in the particular medium. Electrochemical cells and their control circuits are much more able to meet these requirements than the other common analytical techniques, e.g. chromatography and spectroscopy, and their output is well suited to continuous monitoring or as an input to a control loop or an automatic warning.

It will be apparent from the previous section that ion-selective electrodes can be made suitable for analysis in the field and that, in circumstances where the overall composition of the medium is not too variable, they may also be used directly to monitor metal ion and/or anions in plant streams, effluents, water supplies and even rivers. In such applications of ion-selective electrodes, however, it is necessary to avoid electrical pick-up and ground loops by correct placement and shielding of the electrodes. There are also many other situations where the capabilities of electrochemistry and the characteristics of an analysis can be matched to allow the manufacture of on-line or portable devices. The actual measurement may be the potential of an ion-selective electrode, the mass-transport-controlled current at an electrode held at constant potential or even conductivity. This latter measurement, for example, remains the optimum way of estimating the total salt concentration in solution.

The manufacturers of ion-selective electrodes market a number of gas sensing electrodes which function by interposing a gas-permeable membrane between the test solution and the sensing element (see Fig. 11.17). The gas diffuses through the organic polymer membrane (e.g. PTFE, polyethylene, silicone rubber) into a thin film of electrolyte between the membrane and the ion-selective electrode. The electrolyte and the ion-selective electrode are chosen to introduce selectivity between gases and the film of electrolyte is as thin as possible so that it equilibrates rapidly following a change in the composition of the test solution. The probes are complete cells including a reference electrode. Some typical gas sensing electrodes are described in Table 11.8.

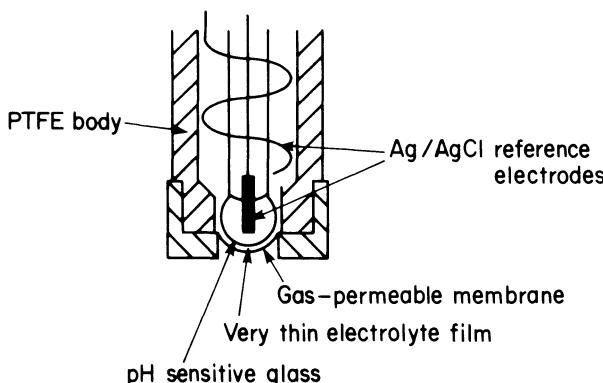


Figure 11.17 The construction of a gas sensing ion-selective electrode. The example shown has a pH sensing electrode.

Table 11.8 Construction and performance of gas sensing ion-selective electrodes.

Gas	Ion-selective electrode	Electrolyte	Membrane	Concentration range (M)	Serious interferences
H <sub>2</sub> S	S <sup>2-</sup>	Citrate buffer pH 5	Polypropylene	10 <sup>-6</sup> -10 <sup>-2</sup>	None
NH <sub>3</sub>	pH	0.1 M NH <sub>4</sub> Cl	PTFE	10 <sup>-1</sup> -1	Volatile amines
CO <sub>2</sub>	pH	0.01 M NaHCO <sub>3</sub> + 0.1 M NaCl	PTFE	10 <sup>-2</sup> -10 <sup>-4</sup>	Volatile weak acids
NO <sub>2</sub>	pH	0.1 M NaNO <sub>2</sub> + 0.1 M NaCl	PTFE or polypropylene	10 <sup>-6</sup> -10 <sup>-2</sup>	Volatile weak acids
SO <sub>2</sub>	pH	0.1 M K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> + 0.1 M NaCl	PTFE or silicone rubber	10 <sup>-6</sup> -10 <sup>-2</sup>	Volatile weak acids
HCN	Ag <sup>+</sup>	10 <sup>-2</sup> M KAg(CN) <sub>2</sub>	Polypropylene	10 <sup>-7</sup> -10 <sup>-1</sup>	Sulphide

Monitors for oxygen are also available. They are again based on the diffusion of the gas through a permeable membrane but in this case the parameter measured is the limiting current for the cathodic reduction of the oxygen. Devices for measuring oxygen in blood levels via the oxygen diffusing through the skin and atmospheric oxygen are also commercially available. This latter measurement is particularly favourable since the oxygen range normally of interest is 15–21% and there are no other gases which are reducible and present in significant concentration. Figure 11.18 illustrates the principles of design of two such oxygen meters, and a portable unit is shown in Fig. 11.19. In the first, a PTFE membrane is stretched across a head containing a gold disc working electrode surrounded by a silver ring which acts as the counter and reference electrode since the electrolyte is a chloride solution. In the second the metal for the working electrode is deposited by sputtering techniques directly onto the PTFE membrane; this minimizes the response time of the detector which can then be less than 1 s. The metal used is silver since this was found to give the best formed reduction wave for oxygen. Similar cells are available for monitoring chlorine in atmospheres and in solution. Typically the cells with the control electronics are the size of a small torch and they may have meter or digital readouts or audible alarms.

In recent years there has been some success in modifying such membrane polarographic cells for monitoring toxic gases from car exhausts and industrial discharges, e.g. SO<sub>2</sub>, NO<sub>2</sub>, NO and CO. These analyses are, however, much more challenging because (a) the concentration range of interest is 1–100 p.p.m., much lower than for oxygen, (b) the electrode reactions are subject to poisoning and vary in rate with the state of the electrode surface, and (c) there is an interference problem because all the gases mentioned may be oxidized. In general, sufficient sensitivity and selectivity can be obtained even if it is necessary to introduce gas

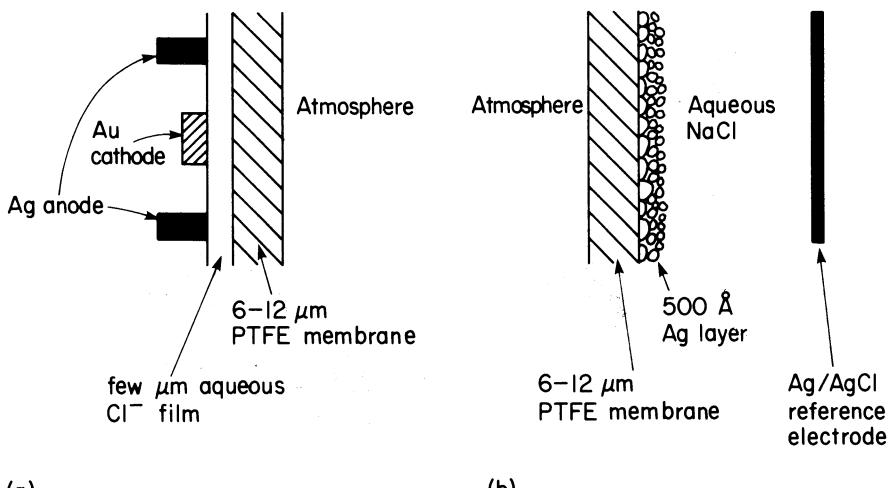


Figure 11.18 Design principles of two atmospheric oxygen meters.

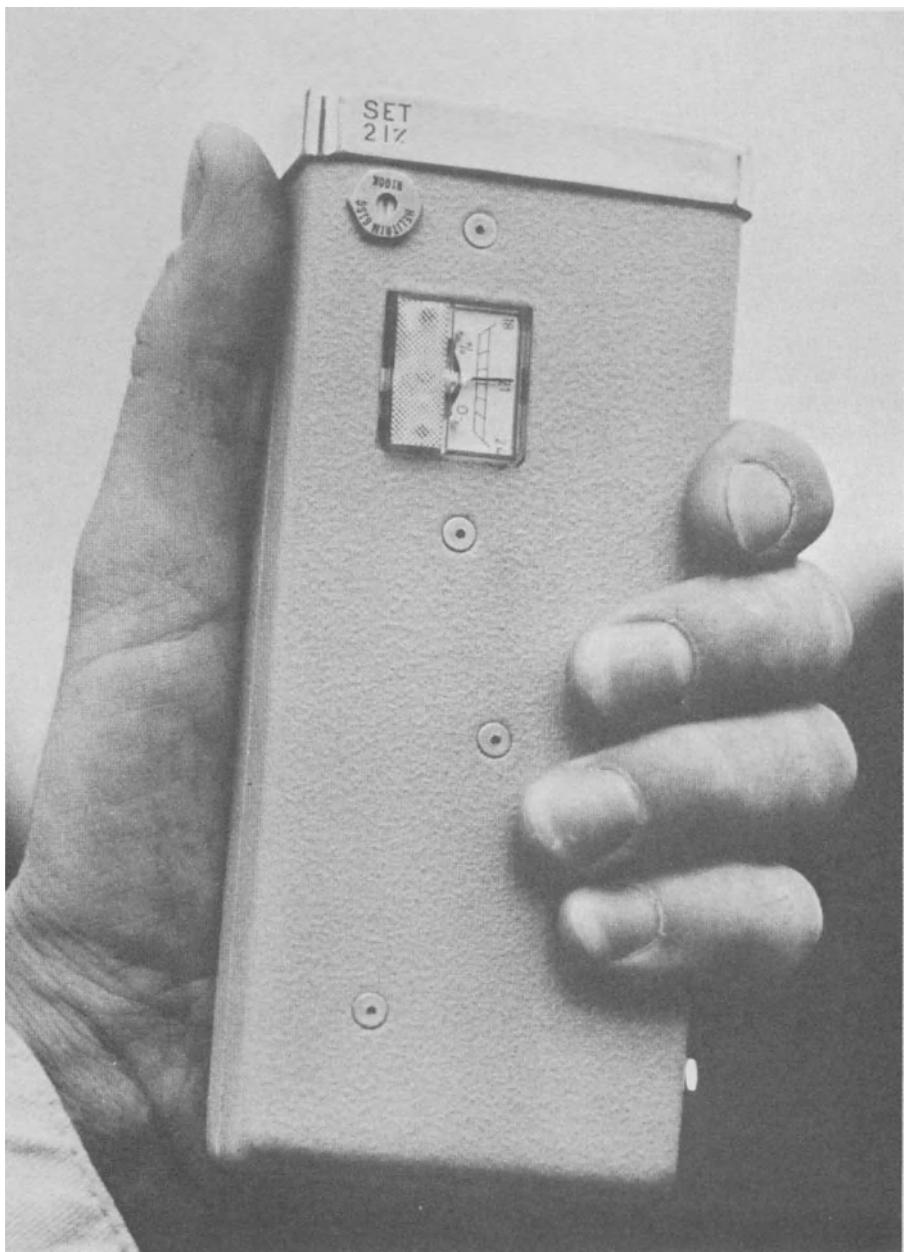


Figure 11.19 Portable oxygen meter. Photograph supplied by Draeger Manufacturing Ltd.

filters into the gas feed to the cell, but it remains necessary to calibrate the meters regularly, even daily, and this is inconvenient.

Other oxygen and toxic gas monitors are based on fuel cell technology, the current being measured between a porous fuel cell working electrode and a counter-electrode. The problems and successes of this approach are very similar to those of the membrane cells described above. An interesting variation has been used to manufacture a 'breathalyser' which has been accepted by several national and state police forces. It is based on two Pt catalysed porous fuel cell electrodes (see Fig. 11.20). The cathode is open to the atmosphere so that the reduction of oxygen can occur when a suitable fuel is present at the anode and to activate the cell a fixed volume ( $1\text{ cm}^3$ ) of the suspect's breath is fed to the anode. No potential is applied across the electrodes so that the experiment can be considered as a form of coulometry at the open-circuit potential of the anode in the presence of ethanol and the cathode in the presence of air. In fact, the current is measured as a function of time; the current goes through a peak and this peak current is found to have a satisfactory relationship with alcohol in breath (using the charge for the complete oxidation of the ethanol would be theoretically sounder but would substantially increase the measurement time). Carbon monoxide, hydrogen and acetone found in the breath of some people, e.g. smokers, diabetics, are found not to interfere.

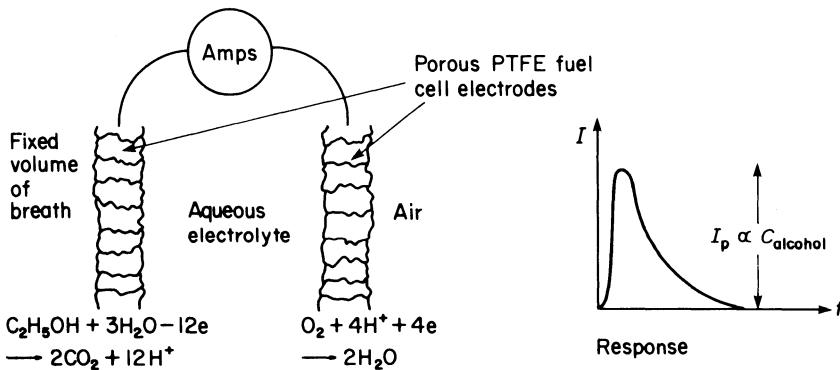


Figure 11.20 Principle of the electrochemical breathalyser.

In specific circumstances where there happen to be no interferences, the simple voltammetric response of an electrode can be a very convenient monitor in process streams and effluents. Such applications, however, have little generality. An application of electrochemical cells of increasing importance, even if outside the immediate scope of this chapter, is as a detector for high-pressure liquid chromatographs. Here, the chromatographic column should have already separated the components of the mixture and the ability to record complete  $I-E$  responses quite rapidly can be used to identify components and to confirm complete separation (does the  $I-E$  curve change through a peak?), while the  $I_L-t$  record may be used for quantitative analysis. Early cell designs attempted to use a dropping

mercury electrode but the additional complications that this electrode introduced have caused its complete displacement by carbon disc electrodes which are usually employed in the wall jet mode, i.e. the solvent from the column is flowed directly onto its surface. Figure 11.21 shows a design of cell. The key features are the very low cell volume, the removable carbon disc working electrode (so that it may periodically be repolished) and the facility to change the solvent (solvents for high-pressure liquid chromatography often have very low dielectric constants) and add base electrolyte after the eluent has left the column and before it enters the cell.

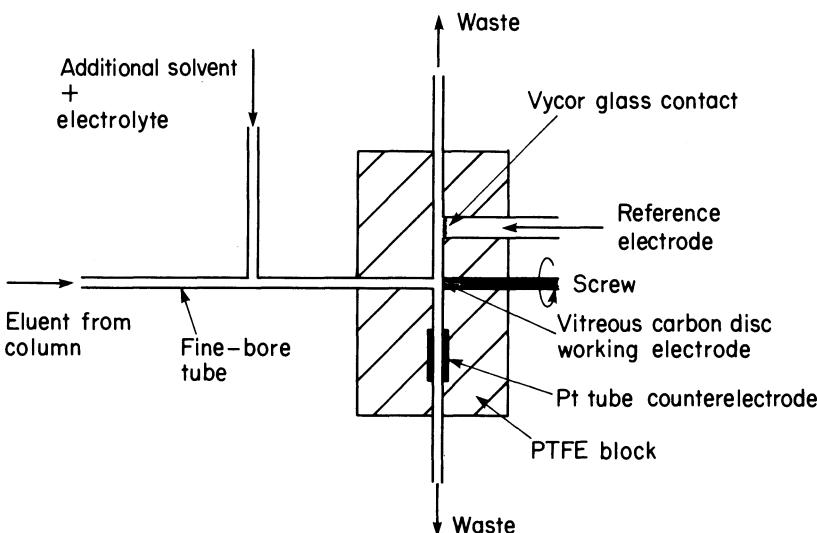


Figure 11.21 *A design of electrochemical cell for a high-pressure liquid chromatography detector.*

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