

## ***CHAPTER 1:***

### **INTRODUCTION AND OVERVIEW**

1. What is electrochemistry?
2. Modes of Cell Operation
3. Cell Components
4. Fundamental concepts
5. Energy requirements
6. Chemical vs. Electrochemical conversion
7. Unique characteristics of electrochemical processes.  
    Advantages, disadvantages and barriers.
8. Scope of applications,
9. Electrochemical engineering

## **INTRODUCTION AND OVERVIEW**

### **1. What is electrochemistry?**

"All chemical interactions are electrical at the atomic level so that in a sense all chemistry is electrochemistry."

W. J. Moore, "Physical Chemistry," Prentice-Hall, 1962.

Electrochemistry covers a broad range of research and applications including diversified subjects ranging from batteries and electroplating to manufacturing of chlorine, corrosion and electrochemical solar cells. An adequately broad definition will probably state that ***"electrochemistry is the science studying the interaction of charged ionic species under an applied electric field."*** Most often electrochemistry is concerned with chemical processes occurring at the interface of an ionic solution (= electrolyte) and an electronically conducting material (= electrode) with the simultaneous gain or loss of electrons) i.e. oxidation or reduction at an interface).

### **2. Modes of Operation of Electrochemical Cells**

Electrochemical cells can generally take place in one of the two following modes.

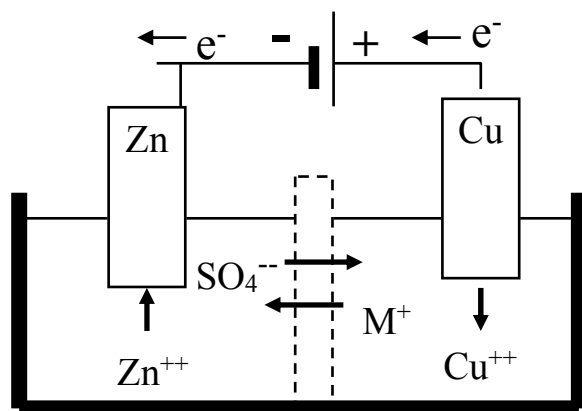
- a. Application of external energy (voltage to drive a chemical reaction (e.g. electrolysis or plating).
- b. Utilization of spontaneous chemical reaction to obtain (electrical) energy.

Because of the reversibility of electrochemical processes, typically, the same cell can be operated in either mode, supplying or removing energy as needed to drive the reaction in the desired mode (direction). If the reactions are such that the reactants 'contain' more energy than the products, the reaction will be spontaneous, releasing electrical energy, such

as in a battery or a fuel cell. In the opposite case, when the reactants ‘contain’ less ‘energy’ than the products, the reaction will not be spontaneous, and in order to drive it, we need to supply external energy (such as in e.g. plating or the charging of a rechargeable battery. The quantitative treatment of this subject will be provided in chapter 4 dealing with thermodynamics. The energy release by spontaneous reactions occurring in electrochemical cells is unique, as it involves the direct conversion of chemical into electrical energy, a process that can proceed at high efficiency in batteries or fuel cells. The direct conversion of solar energy into electrical energy taking place in a liquid junction solar cell can also be considered as longing in this class.

# Electrochemical Cells - Modes of Operation

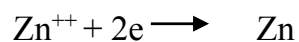
## 1. Electrical Energy $\longrightarrow$ Chemical Products



Electrolysis, Plating  
or Battery Charging

External driving force  
is applied to drive a  
chemical rxn  
*against* its spontaneous  
direction

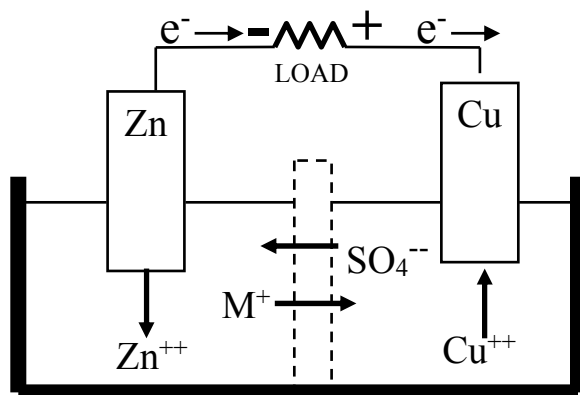
**Cathodic Reduction:**



**Anodic Oxidation:**



## 2. Chemical Reaction $\longrightarrow$ Electrical Energy



Battery or Fuel-Cell

A spontaneous chemical  
reaction is used to produce  
electrical energy

**Anodic Oxidation:**



**Cathodic Reduction:**

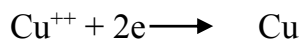


Fig. 1-1: Modes of operations of electrochemical cells.

### 3. The Electrochemical Cell:

Any electrochemical reaction takes place in a cell. The electrochemical cell must consist at least of:

- (i) Minimum of two electrodes
- (ii) Electrolyte
- (iii) An external conductor, or power source.

The reason for having at least two electrodes, is that we cannot generate charge, only circulate it. Furthermore, we cannot accumulate any substantial amount of charge anywhere within the cell (due to electroneutrality, as discussed later), hence any oxidation reaction on one electrode (anode) must be accompanied by a second reduction reaction on another electrode (cathode). In some case, such as in corrosion, we encounter bi-polar electrodes, i.e., a single electrode that has two separate zones on it, one supporting a cathodic reaction, the second, serves as an anode (Fig. 1-3).

The electrolyte is the source sink for products and reactants, and provides ionic conduction. The electrodes provide electronic conduction. The electrode-solution interface is the region where charge passes from electronic medium to ionic medium.

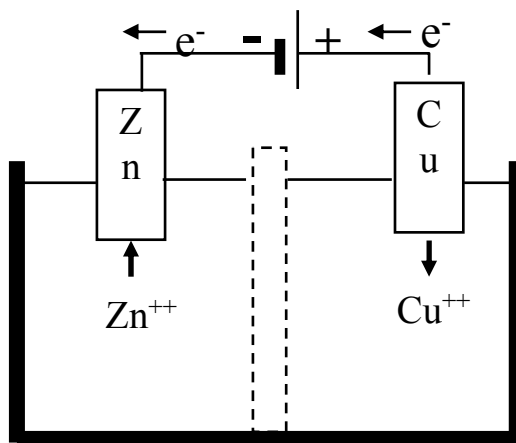
Electrochemical reactions always take place at the interface between the electrode which is an electronic conductor (electrons move within the conduction band) , and the electrolyte - in *which* current is carried only through ions. Since all electrochemical reactions involve oxidation or reduction, electrons must be transported across this interface, to or from the ions. The important difference in the mechanism of charge transport through any electrochemical system must be emphasized: Ionic charge carriers in the electrolyte (both positive and negative ions move in opposite directions *and* both contributing to the current), and only electrons, (i.e., negative charge carriers) in the electrode and wires. (We should recognize that liquid mercury in which electronic conduction takes place is an electrode, whereas solid  $\alpha$ -alumina in which current is carried by movement of ions is considered an electrolyte).

### 4. The Electrochemical Interface:

Right at the electrode and extending into the solution is a narrow region of molecular dimension scale (10 - 100 Å) called the electrical double layer. This layer which consists of

charged ions absorbed or attracted to the electrode, acts like a capacitor and is unique by virtue of the fact that the electroneutrality condition which must persist in the bulk of the electrolyte, and inside the electrode, does not hold inside this double layer. Although the double layer and the phenomena associated with it are of extreme importance to many electrochemical processes, because of its thinness it usually can be neglected in macroscopic studies of current and voltage balances.

## THE ELECTROCHEMICAL CELL



### MAJOR COMPONENTS:

1. Electrolyte (ions)
2. Cathode(s)
3. Anode(s)
4. Electron Pathway (Power Supply or Load)
5. Separator

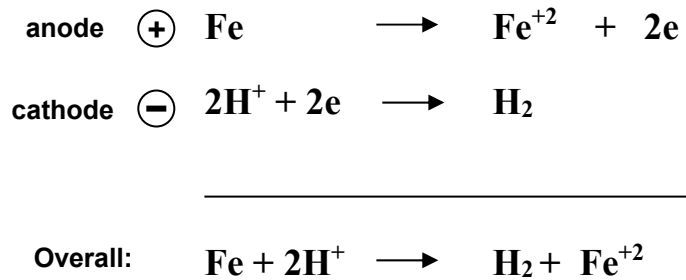
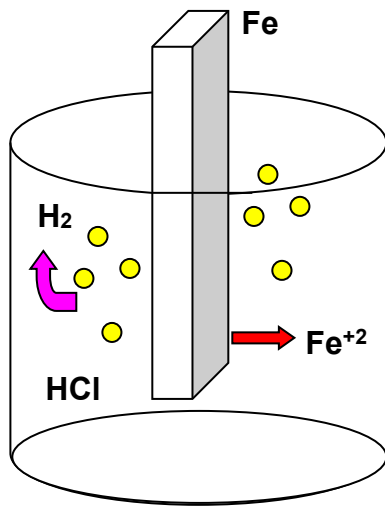
- **Conservation of Charge** - Charge may only be circulated around, not generated
- **Electroneutrality:**  $\sum Z_i C_i = 0$
- **Electrode/Electrolyte Interface** - The Double Layer (serves as a capacitor)
- **Energy requirements at the electrode:** 10 - 100 KCal  $\sim$  4 eV  
0 - 4 Volts

**Water decomposition:** 1.23 V

**Organics ( CHO )** 1 V

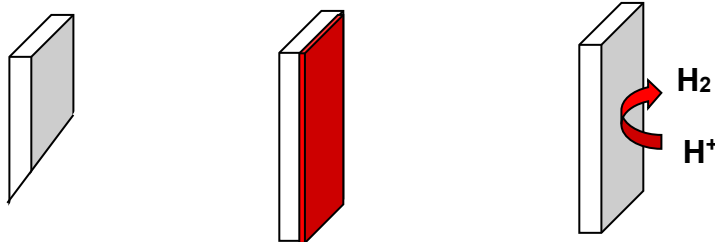
**Li :** - 4 V

**Electrochemical process at an open-circuit cell (single electrode)**  
**A bi-polar or corroding electrode**



### Electrode Types

- **Active** – plating or dissolving
- **Passivated** – covered with a resistive layer, typically anodic film, often highly polarized
- **Inert (or dimensionally stable)** – typically gas evolving electrode
- **Single or multiple simultaneous reactions**

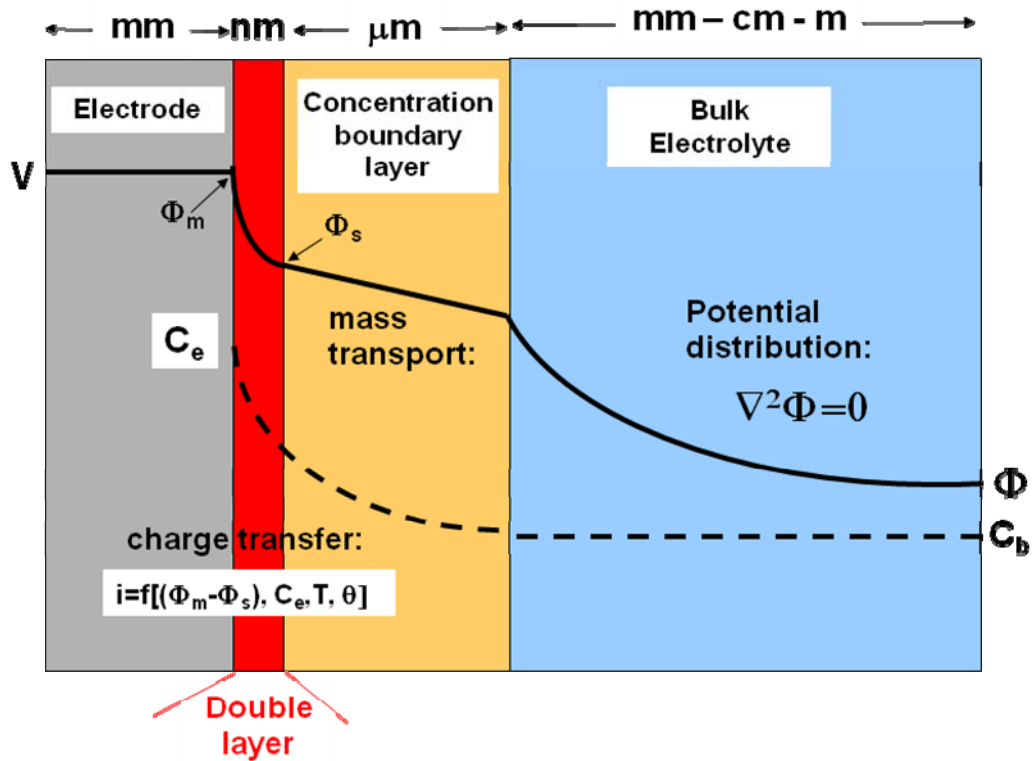


### Separator Types

- **Porous diaphragm** (non-selective, slows diffusion)
- **Ion-selective membrane** (permeable to only single ion or groups of ions)
  - **Ion exchange** (Nafion, PBI)
    - **Cationic**
    - **Anionic**
  - **Ceramic** (beta-alumina, Ceria stabilized zirconia)

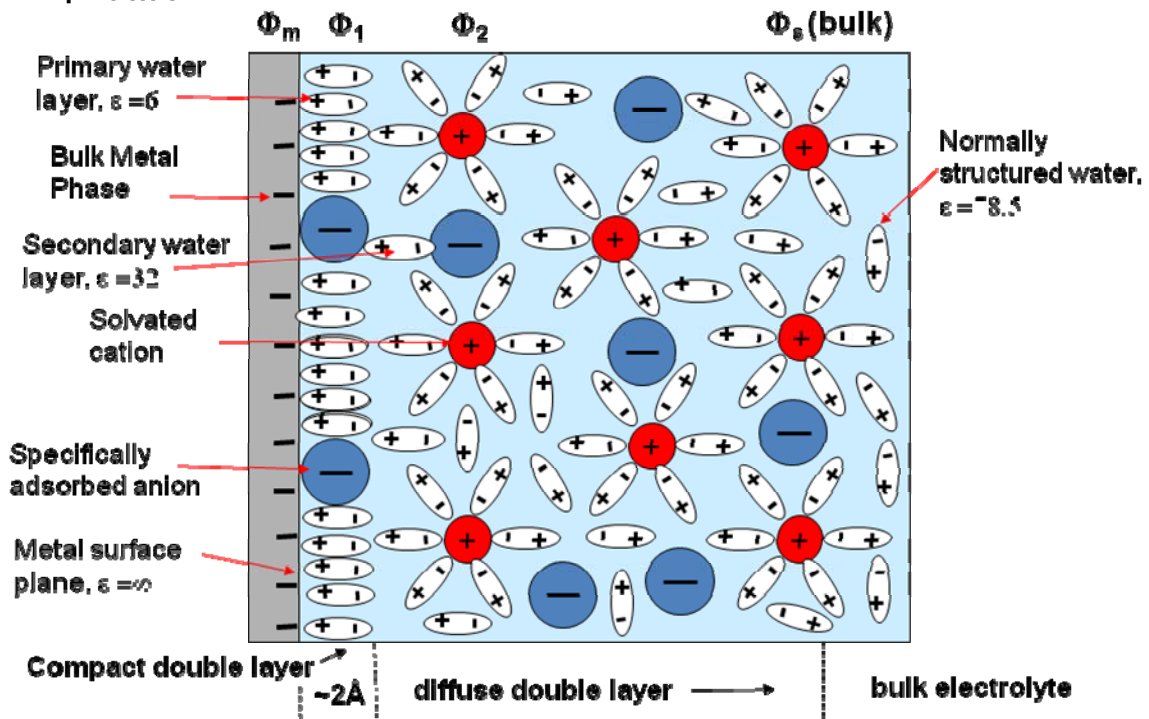
Fig. 1-3: Electrode and Separator types

## Characteristics Scales of the Electrochemical Cell



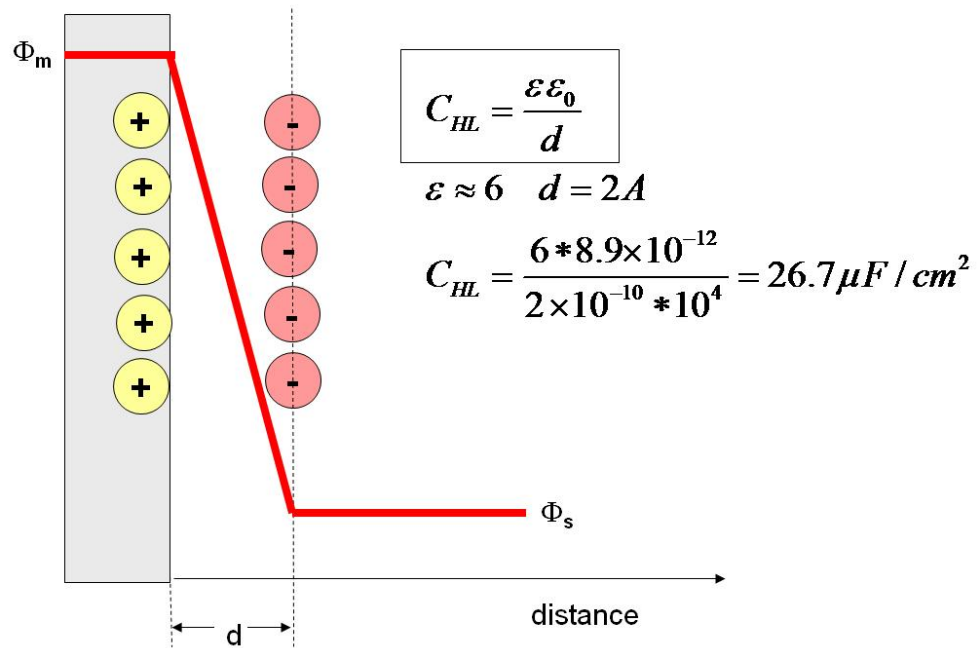
## The Double-Layer Structure

The electrode-electrolyte interface exhibits impedance characteristics similar to an electrical capacitor...

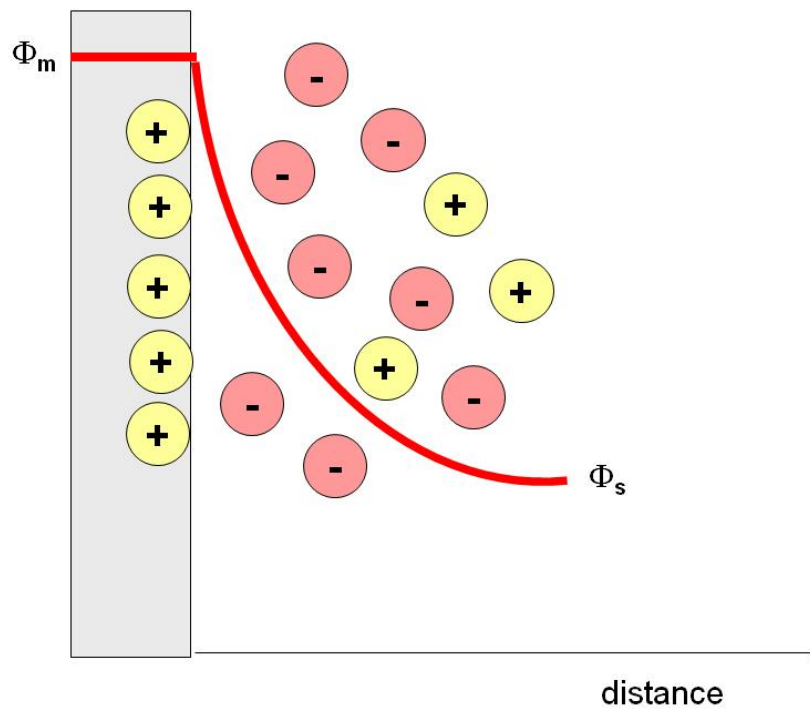




## The Helmholtz Compact Double-Layer Model



## The Gouy-Chapman Double-Layer Model



## 5. Role of the electrode:

Any electrochemical cell consists of at least two electrodes, a cathode and an anode, immersed inside an electrolyte. The role of the electrode is:

1. Source or sink for electrons
2. Site for chemical reactions
3. Source of reactants, sink for products

Illustrations:

1. redox couple:  $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$  (oxidation)
2. metal electrodeposition:  $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{metal lattice})$
3. electrochemical generation of  $\text{H}_2$ :  
 $2\text{H}_2\text{O} + 2\text{e}^- + 2\text{ sites (metal)} \rightarrow 2\text{H} - \text{sites (metal)} + 2\text{OH}^-$   
 $2\text{H} - \text{sites (metal)} \rightarrow \text{H}_2 + 2\text{ sites (metal)}$
4. battery oxide reaction (mercury cell)  
 $\text{HgO (solid)} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg (liquid)} + 2\text{OH}^- (\text{solution})$

Electrodes can be divided into different kinds:

- Catalytic electrodes (Platinum black, DSA)
- Consumable electrodes (Chlor-alkali, aluminum)
- Dimensionally Stable Electrodes (DSA)

## 6. Function of the electrolyte phase:

1. Source of reactants, sink for products
2. Provide ionic conduction path between the electrodes.

## 7. Comparison of electrochemical processes to chemical processes in general:

Electrochemical reactions are directly driven by applying (or removing) external energy through the voltage applied to the electrodes, causing current to flow. This implies that unlike a regular chemical reaction which can proceed only spontaneously, in the direction

of an overall lower Gibbs free energy, an electrochemical reaction can normally be driven in any desired direction. Furthermore, since one can control the amount and rate of this external energy application, the rate of electrochemical reactions can be precisely monitored and controlled and their endpoint accurately determined. This makes electrochemical reactions extremely useful as far as their utilization is concerned. They can be used reversibly for energy storage and generation, or production of chemicals under extremely well controlled conditions.

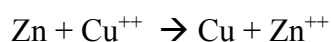
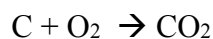
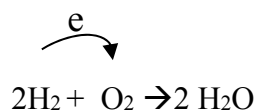
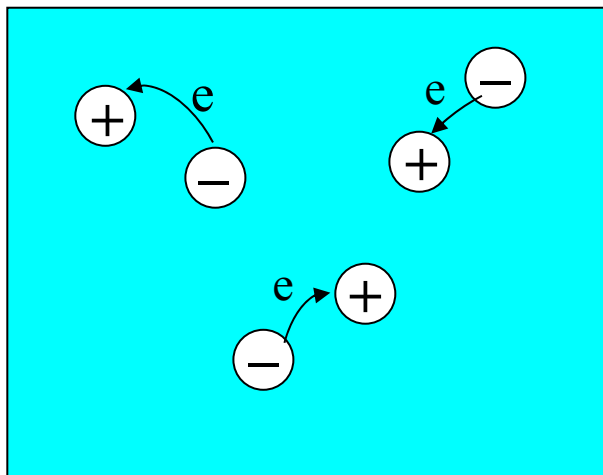
A regular chemical reaction usually involves breaking (or making) a number of different chemical bonds, with the constraint that the overall free energy of the system is decreased.

Electrochemical reactions usually involve ionized species and always involve oxidation and reduction. Unlike regular oxidation-reduction reactions, these however take place at separate locations which can be far removed from one another.

Electrochemical reactions always occur at an electrode-electrolyte interface and therefore always belong to the class of heterogeneous reactions. Chemical processes in general can either be homogenous, i.e., involving one phase only, or heterogeneous. The surface, or electrode area available for the electrochemical reaction is therefore often a critical issue (porous, fluidized bed, or particulate electrodes are examples of addressing this problem).

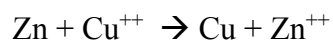
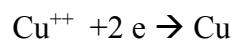
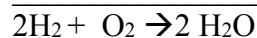
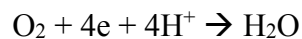
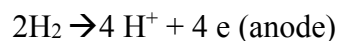
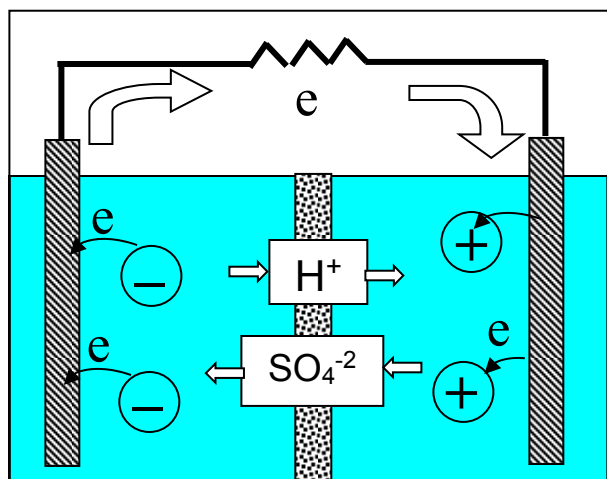
## CHEMICAL VS. ELECTROCHEMICAL CONVERSION

### Chemical Conversion: Direct charge transfer



- Homogenous reaction
- Output: Heat  $[\Delta H]$  (Limited by Carnot efficiency)
- Indirect conversion to electricity

### Electrochemical Conversion: Charge transfer at electrodes



- ✓ Heterogenous reaction (surface dependent)
- ✓ 2 distinctly separate sites (cathode & anode)
- ✓ Separator often required
- ✓ Energy output:  $\Delta G = \Delta H - T\Delta S$
- ✓ Direct conversion to electricity

Fig. 1-4: Chemical vs. electrochemical conversion

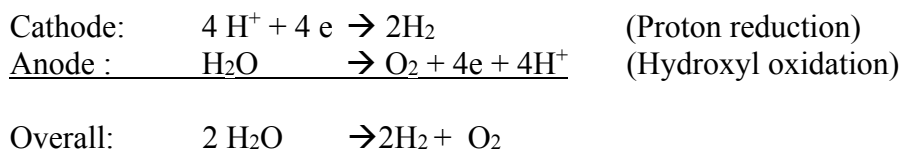
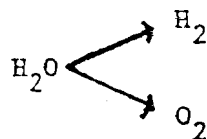
## 7. Energy Requirements at the Electrode:

Since the electrochemical reaction, very much like a regular chemical reaction involves the breaking (or forming) of chemical bonds, we can expect the associated energy to be in the range of 10 - 100 kcal/bond, or up to ~4 eV. This corresponds to a range of 0 - 4 volts. More specifically: splitting water requires 1.23V (implying that a single cell of an aqueous battery can not produce over 1.23 volts); the discharge of Lithium requires ~ 4 volts, and electro-organic reactions involving forming or breaking of CHO type bonds require about 1 volt.

## 8. Unique characteristics of electrochemical processes:

- A. Even the most elementary electrochemical cell must consist of at least **two electrodes** immersed in an **electrolyte**. Any electrochemical reaction is characterized by **two or more products**, each produced at one of the electrodes. An oxidation reaction takes place at the anode, reduction at the cathode.

ILLUSTRATION: Water Electrolysis



- B. **Separator** is often required to separate the two products, prevent or slow down their back mixing and their reacting back to form the reactant thereby reducing the process efficiency. The separator must allow *the* passage of at least some of the ionic species of the solution thereby providing electric continuity. A good separator will provide good separation, will be chemically inert, and will introduce the least amount of ohmic drop into the cell. Separators can be made of fritted glass (pH electrodes), ceramics, plastic

materials (batteries) , asbestos (diaphragm in the chlor-alkali cells) or be ion selective such as the Nafion<sup>R</sup> membrane which is used in the chlor alkali process and in ambient temperature fuel-cells.

- C. The potential applied between the electrodes in an electrochemical cell is directly converted into chemical energy; hence an electrochemical cell is a unique device for **direct energy conversion**, not restricted by the Carnot efficiency which imposes severe limitations on heat engines.
- D. An electrochemical process provides essentially **limitless oxidation and reduction possibilities**. The maximum energy associated with a chemical bond is about. 5 eV corresponding to 5 Volts, which can easily be provided by a simple power supply, rectifier, or a battery. (The assembly of the first batteries led Davy to promptly discover and separate sodium.)
- E. Electrochemical processes are characterized by **high-purity products**. A 99.999 pure product can be typically produced from a contaminated raw material in one stage electrochemical process (copper refining). Electrochemical processes can also be extremely selective.
- F. The reaction rate in electrochemical processes can be **precisely controlled and monitored**. The current is directly proportional to the reaction rate, and the applied voltage is the driving force. This makes the monitoring and control of electrochemical processes, easy, accurate and very reliable. Electrochemical processes are conveniently used as sample reactions for mass transport studies, since the reaction rate can be so easily monitored (the 'limiting current' technique). Electrochemical systems offer the unique advantage in that **local fluxes** can accurately and conveniently be determined by measuring the current. Furthermore, by simply varying the applied potential, i.e., the driving force, the electrochemical reaction rate can be conveniently changed and often reversed.
- G. Electrochemical processes provide good **control over the structure** and appearance of the product. This is used advantageously in a large number of electrochemical surface finishing processes such as applying protective or decorative coatings by electroplating, in anodic polishing or in electrolytic powder formation.
- H. Electrochemical processes are driven by the electric field, a vector quantity providing **directionality** to the electrochemical reaction. This feature is important

when considering the distribution of reaction rates, i.e., the variation of current density along the electrodes and is utilized in processes such as electro-machining.

- I. Detailed understanding of electrochemical systems requires however, additional important information which is often difficult to obtain. This is mainly due to the fact that several charge and mass transport **processes occur simultaneously** even in the simplest systems. Any useful analysis must be capable of separating the effects due to each of these mechanisms. The analysis is further complicated by the fact that the transport processes are inherently coupled and often depend on local system parameters such as concentration or the electric potential which may vary considerably over very short distances near the electrode, and often cannot be locally probed. The potential distribution and its associated dissipative processes must therefore often be determined indirectly. A classical and widely used approach involves driving the electrochemical reaction to regions where only one particular mechanism is dominant. Typical of this approach are the limiting current technique for mass transport studies, the current-interrupter method for ohmic resistance determination, polarographic measurements for double layer studies, or micro-polarization experiments for determination of kinetic parameters.

Two major disadvantages are inherent to this approach. The first stems from the fact that even when one particular mechanism is dominant, other processes are often still operating, hence the accuracy is limited and often the resolution is seriously impaired. The second important disadvantage is associated with the fact that measurements must be performed following this approach while operating under conditions far removed and impractical for industrial or useful systems.

## **UNIQUE CHARACTERISTICS OF ELECTROCHEMICAL PROCESSES**

- Two or more separate reaction sites and products
- $\text{H}_2 \leftarrow \text{H}_2\text{O} \rightarrow \text{O}_2$  (separator)
- Direct conversion between chemicals and electrical energy
- Limitless oxidation and reduction capabilities achievable at moderate (ambient) temperatures and pressures  
(Max. energy of chemical bond  $\sim 5\text{eV} \sim 5\text{V}$ )
- High selectivity, separation factors and product purity  
(Contaminated raw material  $\rightarrow$  99.999% pure material in one stage)
- Rate is precisely controlled
- Control over structure and surface morphology (appearance)  
Applications to surface finishing and fabrication:
  - laying down adherent (thin) metallic layers
  - non abrasive machining of intricate shapes
  - polishing and anodizing
- Control over shape – Directional  
Microfabrication, Electrochemical machining
- Low space-time yield, necessitating large number of parallel units
- Environmentally benign. Oxidation or reducing agents not required
- Reversibility (thermodynamic, not kinetic). Ease in shifting equilibria
- High material and energy efficiency
- Unique applications:
  - batteries and fuel cells
  - surface finishing
  - corrosion protection
  - sensors
  - electro-winning and refining



## 9. Peculiarities and Disadvantages:

- Low specific rates leading to large area and volume requirements.
- Large number of small parallel units (1000-10,000)
- High currents (special equipment, voltage loss in busses)
- Costly maintenance (corrosive environment)
- Energy intensive. Uses costly energy (electricity).
- Interdisciplinary field: requires knowledge from multiple disciplines: Chemistry, Chem. Eng., Mat Science, physics, surface science, electrical engineering.
- Batch processes
- Typically involves unsteady-state processes
- Non uniform distribution of local reaction rates
- Multiple simultaneous reactions.
- Shape change
- Multiple phases
- Practice precedes the science

## 10. Scope of Applications and Industrial Importance:

Electrochemical phenomena form the basis for many essential natural and man-made processes.

- A. The transmission of signals through nerve cells and the transport of ions across cell walls are electrochemical processes, controlled by electrochemical principles. The process of photosynthesis, which provides the source of most of the energy available on earth are biological photo-electrochemical processes which are intricate and sophisticated. The photo-electrochemical liquid junction solar cells are essentially attempts to duplicate such processes on an industrial scale.
- B. Synthesis of many essential chemicals including chlorine, alkali, aluminum, copper and many other elements can only be accomplished by electrolysis. Most of the important metals are produced, or the impure form refined, exclusively by electrolysis.

- C. Batteries and fuel cells - portable energy generation and storage devices for direct conversion of chemical to electrical energy, which are essential to our technology are electrochemical devices.
- D. The surface finishing plating and shaping of metals is an electrochemical process carried throughout the world on a large scale. This includes electroplating, -forming, -machining, -polishing and -anodizing.
- E. Purification of waste water and trace removal of chemicals, sewage treatment and water desalination can be accomplished electrochemically.

The above examples were all of controlled processes. All except for "C" involved non-spontaneous reactions where we must supply external energy. item "C " covers batteries and fuel cells where a controlled spontaneous chemical reaction supplies energy.

Corrosion reactions are a different class of electrochemical processes which cause humanity staggering losses in resources, money and lives. These are essentially uncontrolled-spontaneous reactions which are electrochemical in nature. The study of electrochemistry provides us the means of understanding these phenomena and often of preventing it.

### **Scope of Applications:**

- Electroreduction of metals from molten salts:
  - Al, Mg, (Ti), Na, Li, K
- Electrowinning and refining of metals:
  - Cu, Zn, Pb, Ni, Cr, Cd, Sn, Mn, Ag, Au, Pt, Pd
- Industrial electrolysis: (the chlor-alkali industry, chlorates, water electrolysis).
  - $\text{Cl}_2$ , NaOH, Chlorates,  $\text{H}_2$ ,  $\text{O}_2$
- Surface Finishing
  - Plating, Electroforming, Electrotyping
  - Electropolishing, Electrochemical Machining, deburring, Anodizing
- Energy conversion:
  - batteries (primary, secondary)
  - fuel cells,

- ‘hydrogen economy’
  - solar cells.
- Electroorganic synthesis:
  - Nylon
  - Pharmaceuticals
- Electrolytic capacitors
- Corrosion and its prevention
- Electrochemical sensors, electro-analytical techniques: pH, Ion Specific, p02
- Electrochemical Separations
  - Electrophoresis, Electrodialysis, Electrosmosis, Membranes, Waste Disposal
- Biological Implications
  - Transport across cells, Nerve conduction, Brain processes, Photosynthesis

Electrochemical processes consume over 110 billion kwhr annually - about 6% of the electrical energy produced in the U.S. (1974 data).

aluminum	70%
chlor alkali	20%
electro-winning and refining	10%

Total estimated value of electrochemical products: 0.6% of total U.S. manufacturing

Annual cost of corrosion to U.S.:

- a. 1969 estimate of H. Uhlig<sup>2</sup>: \$5.5 billion per year
- b, 1966 estimate of Liechtenstein: \$10 billion per year
- c. 1977 estimate of Battelle<sup>25</sup>: \$70 billion per year

Period 1 2 3 4 5 6 7

Group\*\* 1 2 13 14 15 16 17 18

1A 2A 3A 4A 5A 6A 7A 8A

1 H 1.008 He 4.003

2 Li 6.941 Be 9.012 B 10.81 C 12.01 N 14.01 O 16.00 F 19.00 Ne 20.18

3 Na 22.99 Mg 24.31 Al 26.98 Si 28.09 P 30.97 S 32.07 Cl 35.45 Ar 39.95

4 K 39.10 Ca 40.08 Sc 44.96 Ti 47.88 V 50.94 Cr 52.00 Mn 54.94 Fe 55.85 Co 58.47 Ni 58.69 Cu 63.55 Zn 65.39 Ga 69.72 Ge 72.59 As 74.92 Se 78.96 Br 79.90 Kr 83.80

5 Rb 85.47 Sr 87.62 Y 88.91 Zr 91.22 Nb 92.91 Mo 95.94 Tc (98) Ru 101.1 Rh 102.9 Pd 106.4 Ag 107.9 Cd 112.4 In 114.8 Sn 118.7 Sb 121.8 Te 127.6 I 126.9 Xe 131.3

6 Cs 132.9 Ba 137.3 La\* 138.9 Hf 178.5 Ta 180.9 W 183.9 Re 186.2 Os 190.2 Ir 190.2 Pt 195.1 Au 197.0 Hg 200.5 Tl 204.4 Pb 207.2 Bi 209.0 Po (210) At (210) Rn (222)

7 Fr (223) Ra (226) Ac~ (227) Rf (267) Db (268) Sg (283) Bh (282) Hs (285) Mt (288) --- 0 --- 0 --- 0 --- 0 --- 0 --- 0

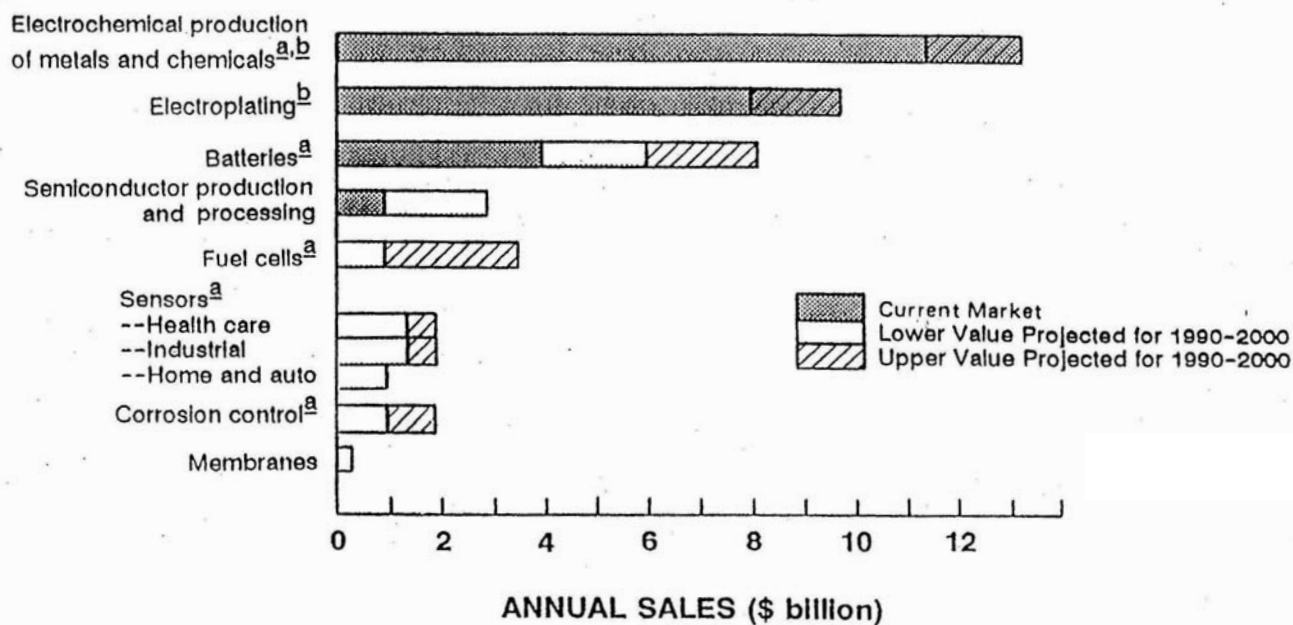
Plated from aqueous media

Lanthanide Series\*

56 Ce 140.1 59 Pr 140.9 60 Nd 144.2 (147) 61 Pm (147) 62 Sm 150.4 63 Eu 152.0 64 Gd 157.3 65 Tb 158.9 66 Dy 162.5 67 Ho 164.9 68 Er 167.3 69 Tm 168.9 70 Yb 173.0 71 Lu 175.0

Actinide Series~

90 Th 232.0 91 Pa (231) 92 U (238) 93 Np (237) 94 Pu (242) 95 Am (243) 96 Cm (247) 97 Bk (247) 98 Cf (249) 99 Es (254) 100 Fm (253) 101 Md (258) 102 No (254) 103 Lr (267)



Summary of electrochemical product and device market value in the United States.  
<sup>b</sup>Projected loss of future markets in international competition.

**TABLE 2: Production of Major Electrochemicals in the United States in**

Product	Domestic Production (thousands of tons per year)	Approximate Price per Ton (\$)	Annual Market (\$ billion)
Aluminum	4,000	1,000	4.0
Caustic	13,000	250	3.3
Chlorine	12,000	200	2.4
Copper (electrolytic)	1,500	1,500	2.2
Magnesium	130	2,500	0.3
Soda ash	8,300	100	0.8
Zinc (electrolytic)	260	1,000	0.3
Total			13.3

\*Publication NMAB 438-1, National Mat. Advisory Board, National Academy Press, 1986

**TABLE 3: Estimated Current Major Domestic electrochemical Markets**

<u>Market Sector</u> <u>billion)</u>	<u>Annual Market (\$</u>
Semiconductor production and processing	1
Metals and chemicals	13
Batteries	4
Electroplating	10
Corrosion control	—
Total	28

## **Electrochemical Engineering and Electrochemical Science**

Electrochemical Engineering is a relatively young discipline within chemical engineering, dedicated to studying the engineering aspects associated with electrochemical processes. It relates to the science of electrochemistry in a similar way that chemical engineering in general relates to chemistry.

Unlike fundamental electrochemistry which concentrates on studying electrode reaction mechanisms, often at equilibrium or close to it -- electrochemical engineering generally addresses itself to the macroscopic aspects of operation and design of entire electrochemical systems. In particular, electrochemical engineers are often interested in problems of current distribution, transport phenomena, and energy dissipation in operating (i.e., "polarized") cells.

Electrochemical processes are technologically and economically highly important. They open essentially unlimited oxidation and reduction possibilities and provide a direct, and often environmentally benign, conversion path between chemical and electrical energy. Many essential chemicals are either produced or refined electrochemically. These include most of the non ferrous metals e.g., aluminum, magnesium, copper, nickel, lead, zinc and non-metals such as chlorine and chlorates. Shaping and modification of surfaces can be uniquely achieved through electrochemical processes such as plating, electroforming, electropolishing, anodizing and electrochemical machining. Other classes of technologically important electrochemical processes include batteries and fuel cells, electrochemical separation processes, electro-chemical sensors for chemical and medical applications and corrosion analysis and its protection.

A major impediment which has limited wider and more effective application of electrochemical processes has been the difficulty in predictive and quantitative design of processes and cells. Typically, electrochemical cells have been designed empirically through costly trial and error procedures rather than on the basis of sound engineering considerations. The major difficulty is associated with the determination of the current distribution which affects the cell performance, its efficiency, product distribution and power consumption.

## The Interdisciplinary Nature of Electrochemistry and Electroplating

Analysis of electrochemical systems is difficult because the local rates are controlled by a number of mechanisms which are coupled in an intricate way. Modelling requires solving coupled equations for the current density, the voltage balance, material and momentum balances. The latter involves also solving the complicated fluid mechanical equations. Precise modeling, accounting accurately for all the parameters involved, is complicated, and has been achieved only for a few simple cell configurations.

Approximate, yet sufficiently accurate models can, however, be constructed by separating, where possible, the various phenomena and incorporating them in terms of analytical or empirical relationships. From these, the current distribution can often be determined, typically through numerical, computer implemented solutions.

