

Electrometallurgy

- **Electrowinning** refers to a process that produces a metal by the electrolysis of an aqueous solution or a fused salt.
- **Electrorefining** is a refining process based on electrolytic phenomena.
- **Electrodeposition** refers to the technique of depositing one metal on another at the cathode.

Faraday's laws of Electrolysis:-

(i) The quantity of material deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

(ii) The quantity of material deposited at an electrode is proportional to the equivalent weight of the same.

$$m \propto It$$

$$m = \frac{W It}{nF}$$

$m = \text{mass of the substance discharged}$

$W = \text{atomic mass}$

$I = \text{current (A)}, t = \text{time (s)}$

$F = \text{Faraday constant (96500)}$

$\frac{W}{n} = Z = \text{chemical or electrochemical equivalent}$

$$m = Z It / F$$

$$\text{Current efficiency} = \frac{\text{Actual amount of metal deposited}}{\text{Amount of the same metal expected to be deposited according to Faraday's law}} \times 100$$

Ques Determine the current efficiency of a chromium plating cell in which a current of 10 A flowing for 60 min deposits 0.9 g. of chromium from chromic acid electrolyte (Cr_2O_3) comprising Cr^{6+} ions. The relative atomic mass of Cr is 52.

$$m = \frac{52 \times 10 \times (90 \times 60)}{6 \times 96500} = 4.85 \text{ g}$$

$$\text{Current efficiency} = \frac{0.9}{4.85} \times 100 = 18.6\%$$

Voltage Requirements :-

The energy consumed per unit time during electrolysis = $V \times I$

I = current, V = voltage across the cell

Since the current is directly related to metal output, the energy consumption can be minimized through

- (i) Maximizing the current efficiency
- (ii) Minimizing the voltage requirement consistent with other requirements.

The total voltage requirement for an electrolytic cell can be given as

$$V_A = V_D + V_R + V_O + V_E$$

V_A = Voltage applied across the cell

V_D = Decomposition voltage (thermodynamic voltage requirement for overall cell reaction)

V_R = Ohmic voltage drop due to resistance of the electrolyte

V_O = Sum of the over-potentials for cathode and anode (η_c and η_a)

V_E = Voltage drop due to electronic resistance in the circuit (i.e. electrode, contact points, busbars etc.)

Except V_D all other factors in the right hand side depend on the current density (i) [i.e. current per unit area of electrode surface]. The higher the value of i the values of V_R , V_O and V_E will be higher.

$$\text{Energy efficiency (\%)} = \text{current efficiency (\%)} \times \frac{\text{theoretical cell voltage}}{\text{Applied voltage}}$$

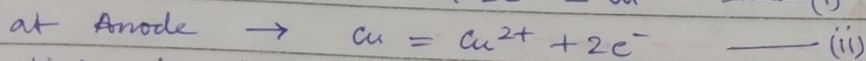
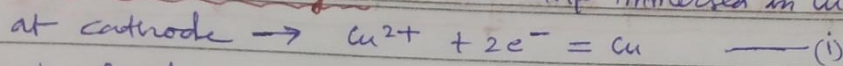
unit: kW h kg^{-1}

for Cu refining
At "

0.2 kW h kg^{-1}

20 kW h kg^{-1}

Decomposition Voltage: — Cu strip immersed in CuSO₄ solⁿ.



Combining (i) and (ii) $\text{Cu (at cathode)} = \text{Cu (at anode)}$

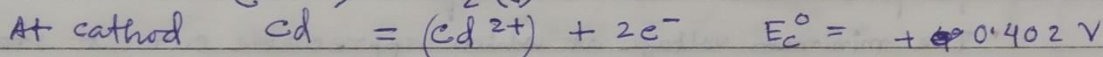
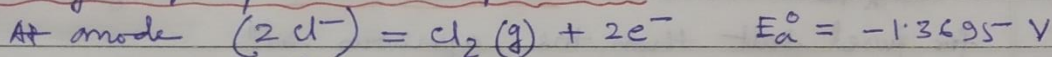
If the activity of Cu is assumed same in either electrode, then the free energy change for the reaction is zero and so it is the theoretical voltage requirement.

The thermodynamic voltage requirement for cell reaction (V_D) is related to overall free energy change (ΔG) $\Delta G = -Z F V_D$ — (1)

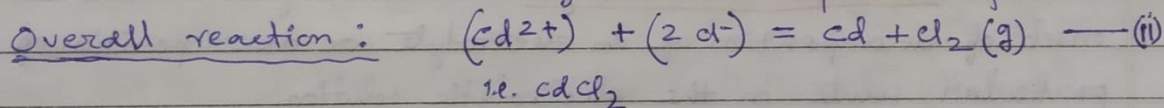
If the product and reactants are at their standard state, then

$$\Delta G = \Delta G^\circ \text{ and } V_D = V_D^\circ$$

Electrolysis of aqueous solⁿ of CdCl₂:



E° values are standard single electrode potential for the reaction.



$$V_D^\circ = (-1.3695 - 0.402) = 1.7715 \text{ V}$$

$$\Delta G = \Delta G^\circ + RT \ln K$$

From (ii) $\Delta G = \Delta G^\circ + RT \ln \left\{ \frac{[\text{Cd}] \cdot P_{\text{Cl}_2}}{(a_{\text{Cd}^{2+}}) \cdot (a_{\text{Cl}^-})^2} \right\}$

From (i) and (ii) & $Z=2$

$$V_D = V_D^\circ - \frac{RT}{2F} \ln \left\{ \frac{a_{\text{Cd}} \cdot P_{\text{Cl}_2}}{(a_{\text{Cd}^{2+}}) \cdot (a_{\text{Cl}^-})^2} \right\}$$

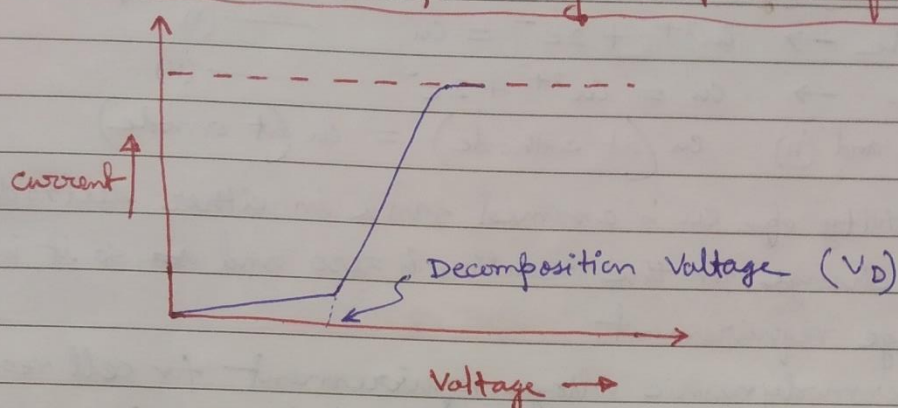
If the metal deposited is pure and chlorine gas evolves at 1 atm. pressure

then $a_{\text{Cd}} = P_{\text{Cl}_2} = 1$

$$V_D = V_D^\circ + \frac{RT}{2F} \ln (a_{\text{Cd}^{2+}}) \cdot (a_{\text{Cl}^-})^2$$

V_D = thermodynamic decomposition voltage under non-ideal condⁿ.

Current voltage relationship during decomposition of an electrolyte :-



- Voltage across the electrode increases from an initial zero.
- Very small current flows through the cell until the voltage reaches a critical value, beyond which current increases rapidly.
- This current ~~this~~ is known as residual current. It is generally larger for fused salt than the aqueous solⁿ.
- The minimum voltage at which appreciable current starts flowing is called decomposition voltage. This voltage indicates the onset of decomposition of an electrolyte or decomposition of a particular solute in the electrolytic solution.
- Beyond the decomposition voltage, the current increases sharply with increase in the applied voltage & ~~then current~~ levels off to a constant value known as limiting current. The maximum current that can be drawn per unit area of an electrode is known as limiting current density (i_d) for that electrode.

Electrode potential

- Difficult to measure in absolute term, as only potential difference can be measured experimentally.
- Potential of the electrode determined against a standard hydrogen electrode (Pt electrode, coated with black Pt, dipped in hydrogen gas at 1 atmosphere)

in contact of HCl solution of 1.2 mole/lit) at 25°C, whose potential is arbitrarily 0.0 Volt.

- The value of potential thus obtained is called standard electrode potential.
- When elements are arranged in order of their standard electrode potential give rise to *emf* series.

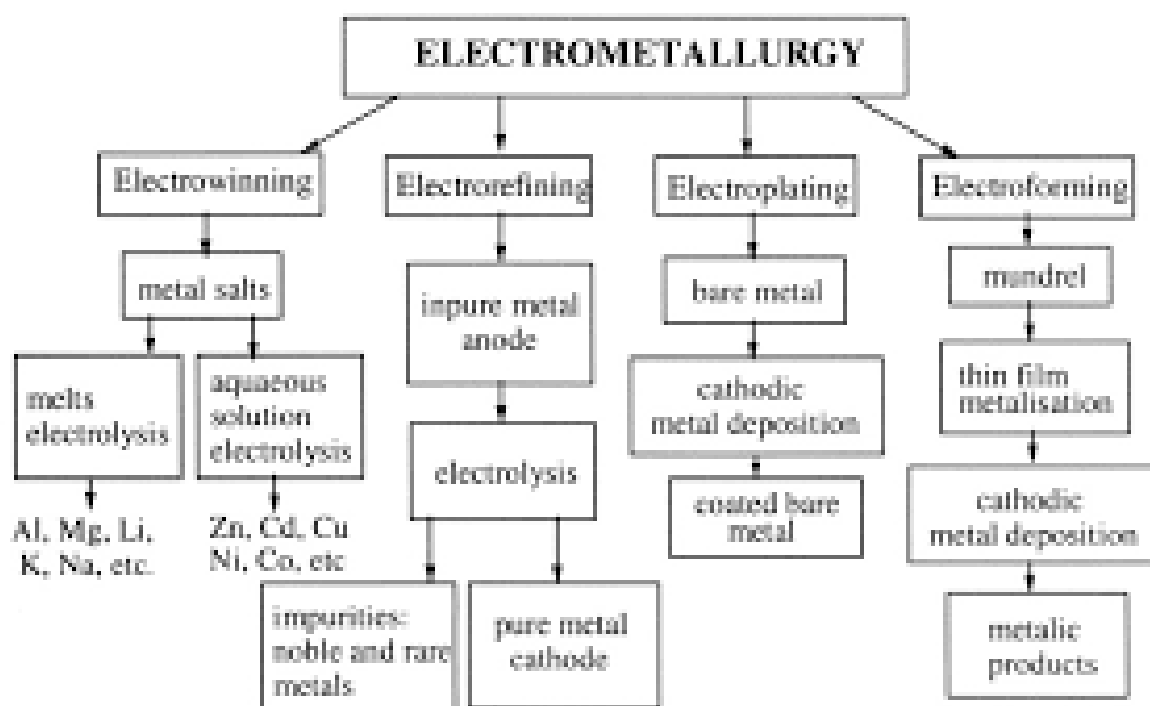


Fig. Classification of electrometallurgical process

ELECTROLYSIS OF FUSED SALTS

Molten salts have some distinct advantages over aqueous salt solution.

- (1) The conditions are favourable for attaining a more complete heterogeneous equilibrium because all the reactions are accelerated.
- (2) The metal produced, if molten, may be easily removed.
- (3) Overvoltages on molten metals are often small enough to allow high current densities and, therefore, greater throughput.
- (4) Further, at high temperatures, diffusion rates are high and therefore, during electrorefining processes, impurities can be transferred from the anode to the cathode so as to purify the metal.

Disadvantages

- (1) The efficiency is lowered due to the increased possibility of side reactions taking place in high temperature.
- (2) In most molten salt electrolytic processes, the anode material is graphite, which leads to formation of CO and CO₂, unless inert gases are used.
- (3) In most fused salt electrolytic processes, several side reactions may take place apart from the desired decomposition reaction.
- (4) Consequently, the current efficiency is far below the optimum value of 100 per cent due to apparent deviation from Faraday's laws.

The factors lead to a lower current efficiency. How these can be avoided.

- (1) Mechanical losses (handling losses) of the substances formed at the electrodes.

These losses can be minimized by using improved operational techniques.

- (2) The evaporation of the metal from the cathode. This may take place during the electrolytic liberation of sodium from fused sodium chloride because the operating temperature would be close to the boiling point of the metal.

The problem can be solved by dissolving the sodium chloride in a suitable medium to form a low melting mixture, thus lowering the operating temperature.

- (3) Chemical side reactions.

The unwanted side reactions can be controlled by choosing the proper electrolyte and using a lower operating temperature.

- (4) The formation of lower valency compounds at the cathode. For example, in the electrolysis of SnCl₄, in the initial stages, tin reacts with the electrolyte to form SnCl₂, and the cathode current efficiency is zero. In most instances, the melt is soon saturated with the lower valency compounds, and after a while, the metal starts depositing on the cathode.

- (5) The formation of higher valency compounds at the anode. This reduces to zero the anode current efficiency in the initial stages of electrolysis. For example, during the electrolysis of SnCl₄ in the initial stages, the chlorine liberated at the anode reacts to produce SnCl₄. However, after some time, the melt becomes saturated with SnCl₄, and further reaction would cease.

(6) The dissolution of the metal in the fused salt.

This drawback can be eliminated to a great extent by dissolving the metal salt in a more stable salt to form a relatively dilute solution.

(7) The recombination of the electrolysis products with the original salt.

Recombination can be eliminated by the immediate and complete isolation of the electrolysis products by employing an electrolytic cell with a special design.

(8) Current losses due to the presence of moisture.

This problem is not serious in the case of fluorides because they can be prepared and stored in a dry state without much difficulty.

MOLTEN SALT PROCESSES

Electrowinning is presently being used for extracting a large number of metals from their molten salts. The most outstanding example is the electrolysis of alumina that has been dissolved in a cryolite bath.

Metal	System	Cell voltage (V)	Temperature (°C)	Current efficiency (%)	Current density (A/cm ²)	Other data
Al	Al ₂ O ₃ in NaAlF ₃ , CaF ₂ , and NaF	4.5–5	960–1000	85	0.5–1.2	Carbon anode (consumable), 0.5 kg/kg Al; energy efficiency, 35%; cell body, steel ceramic
Mg	MgCl ₂ in NaCl-KCl	6.5–7.5	700–750	75–90		Cell body, steel ceramic; carbon anode (theoretically inert); maximum consumption, 100 kg/ton metal; energy required, 18.5 kWh/kg Mg
Ti	TiCl ₄ in Li-Na-K-Cl eutectic	6–8	500	90	0.5	Graphite anode; metal screen cathode
Be	BeCl ₂ in KCl-NaCl	6–9	900		1.0	Graphite anode; stainless steel cathode

4.27 ELECTROLYSIS OF LOW-TEMPERATURE NONAQUEOUS SYSTEMS

In this section, *nonaqueous systems* refer to organic solutions in which metals can be deposited and dissolved at the anode. We now list the general advantages of such systems:

(1) In some instances, the organic medium is better suited than other media for plating purposes. For example, aluminium and zinc can be coated by deposition from organic solutions to give more coherent coatings than those usually achieved in aqueous solutions.

(2) Reactive metals cannot be plated in aqueous media, therefore, nonaqueous media must be used. For example, uranium, which requires plating for corrosion resistance, can be plated with zinc by employing an organic medium.

(3) Reactive metals may be produced electrolytically at low temperatures using solutions of various salts in organic media.

ELECTROPLATING

Electroplating is a process in which an object, usually metallic, is coated with one or more relatively thin but adherent layers of some other metal or alloy. This process is used to impart better surface characteristics and protection against corrosion.

Since the aim of electroplating is to produce only a thin coating layer, the characteristics of the surface to be coated must be taken into account. For example, in chromium plating, if the underlying metal has already been polished, then, the chrome will retain this polish if a thin layer is deposited.

The potential (E_d) required for the electrodeposition of a metal is given by a modified form of the Nernst equation as

$$E_d = E_0 + \frac{RT}{ZF} \ln a + P$$

Where E_0 is the decomposition potential, a is the activity of the depositing cation on the cathode film, and P a rate factor expressed as the additional potential that must be provided to maintain a uniform rate of deposition. It is possible to achieve codeposition of two metals by adjusting values of a and P .

Table 4.8 Electroplating Baths (after Mann and Barns, 1970) (cont.)

Metal	Electrolyte	Remarks
Cadmium	$\text{Cd}(\text{CN})_2$ in water or Cd in CdCN with relatively large amounts of addition agents such as glue, casein, and molasses	
Chromium	CrO_3 plus small amount of sulphate in dilute acid	Coating is good for resistance to oxidation; it allows mirror-like finish, but does not prevent corrosion of iron because it is porous
Copper	Acid sulphate, alkaline cyanide, fluoborate, and pyrophosphate solutions	Good as base for ornamental other finishes by additional plating with other metals
Gold	Cyanide with $\text{KAu}(\text{CN})_2$ in water (Gold deposits of 14 carat shades are produced from solutions with copper salts; green gold by addition of AgCN ; red gold by addition of CuCN or $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$; white gold by addition of double nickel cyanide)	Codeposition of alloys of various compositions allow coloured coatings
Lead	Fluosilicate, fluoborate, and perchlorate	
Nickel (cobalt)	NiSO_4 , NiCl_2 , H_3BO_3 , CoSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and some formaldehyde in hot acidic medium	Lustrous deposits of Ni-C alloys
Silver	Cyanide solutions containing $\text{KAg}(\text{CN})_2$ or $\text{NaAg}(\text{CN})_2$	
Tin	Sodium stannate along with an oxidizing agent such as H_2O_2 or sodium perborate to maintain tin in the stannous form and sodium acetate as a buffer	
Copper-zinc alloys	Solutions containing cyanide salts of copper and zinc	
Lead-tin alloys	Fluoborate solutions	