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INTRODUCTION TO ELECTROCHEMICAL CELLS

- Electrolysis implies the processes which utilize electrical energy for extraction of metals (Example-Cu, Al, Zn etc) which known as **electro winning** and for purification of metals (Example-Cu, Al, Pb etc) which known as **electro refining**.
- In case of electro winning, the anode is insoluble conductor while in electro refining, it is impure metal itself. The electrolyte in each case is a solution with sufficiently high electrical conductivity and solute concentration. The cathode may be pure metal or a blank of another metal.
- Electrolytic dissociation of ionic media is governed by two laws, which are known as Faraday's laws of electrolysis.

I. Faraday's First Law

II. Faraday's Second Law

Continued…

Faraday's First Law: It states that "The weight of material (W) deposited at an electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte".

Mathematically can be expressed as

$$W \ \alpha \ Q \Rightarrow W \ \alpha \ (I \times t) \quad [\, Since \ Q = I \times t] \qquad (312)$$

$$\Rightarrow W = Z \times I \times t \qquad (313)$$

[Where , I – Electric Current (in amp), t – Time (in sec.)

W – Weight deposited (in gm.), Z – Electrochemical Equivalent]

N. B.: Electrochemical Equivalent (Z): It is defined as the weight deposited by a current of 1 amp during its passage for duration of 1 sec.

Faraday's Second Law: It states that "The weight of material (W) deposited at an electrode is directly proportional to the equivalent weight (E) of the material".

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Mathematically can be expressed as

$$W \,\alpha\, E \Rightarrow E \,\alpha\, W \Rightarrow E = F \times W \tag{314}$$

$$\Rightarrow F = \frac{E}{W} = \frac{\left(A/_Z\right)}{W} = \frac{A}{(Z \times W)} \tag{315}$$

$$(Since\ E = \frac{Atomic\ wt.(A)}{Valency\ (Z)})$$

[Where, F– Proportionality Constant known as Faraday’s constant $F \approx 96500$ Coulomb/gm. eq.

A – Atomic Mass, W – Weight deposited (in gm.)

Z – Valency, E – Equivalent weight]

Combined 1st and 2nd laws of Faraday, we have

$$W \,\alpha\, Q \times E \Rightarrow (Q \times E) \,\alpha\, W \tag{316}$$

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$$\Rightarrow Q \times E = F \times W \tag{317}$$

Now putting $E = {}^{A}/_{Z}$ and $Q = (I \times t)$ in equation (318), we will get

$$I \times t = \frac{F \times W}{{}^{A}/_{Z}} \tag{318}$$

$$\Rightarrow W = \frac{I \times t \times A}{F \times Z} \tag{319}$$

Some Important Parameters in Electrometallurgy:

1. **Current Efficiency:** It is defined as the ratio of the actual mass of the substance (metal) liberated from an electrolyte by the passage of current to the mass of the substance liberated theoretically according to Faraday’s law.

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Mathematically it is represented as

$$Current\ Efficiency\ (\eta_I) = \frac{Theoretical\ amount\ of\ Electricity\ required}{Actual\ amount\ of\ Electricity\ consumed}$$

$$= \frac{Actual\ amount\ of\ metal\ deposited}{Theoretical\ amount\ of\ metal\ deposited} \qquad (320)$$

2. **Electric Power:** It is defined as the ratio of electric power used per day with actual weight of metal deposited.

Mathematically it is represented as

$$Electric\ Power(in\ watts) = \frac{Electric\ power\ used\ per\ day}{Actual\ weight\ of\ metal\ deposited}$$

$$= \frac{(Voltage\ drop \times Current)}{Actual\ weight\ of\ the\ \ metal\ deposited} \qquad (321)$$

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Thermodynamics of Electrochemical Cells:

- An Electrochemical reaction involves coupling of chemical reaction with the flow of Electric current. Many metals are extracted and refined by electrolytic process (Zn, Al, Mg etc.).
- Electroplating and anodizing are employed for surface protection of metals and alloys from corrosion.
- Electrochemical reactions occur in Corrosion, Hydrometallurgy and slag-metal reactions.
- Electrochemical method used for high temperature measurement tools.
- Batteries are Electrochemical cell.

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❑ Electrochemical cells are broadly classified into two categories

a. Galvanic Cells: In this case, stored chemical energy is converted into electrical energy.
b. Electrolytic Cells: In this case, stored electrical energy is used to do chemical work.

Thermodynamic studies/predictions/measurements can be done properly only for Galvanic cells. These are can be made to operate reversibly.

Daniel Cell:

Most common example of Galvanic cell is Daniel cell.

Overall Reaction: $Zn(S) + CuSO_4(aq) = Cu(S) + ZnSO_4(aq)$

Overall reaction (Ionic form): $Zn(S) + Cu^{+2}(aq) = Cu(S) + Zn^{+2}(aq)$

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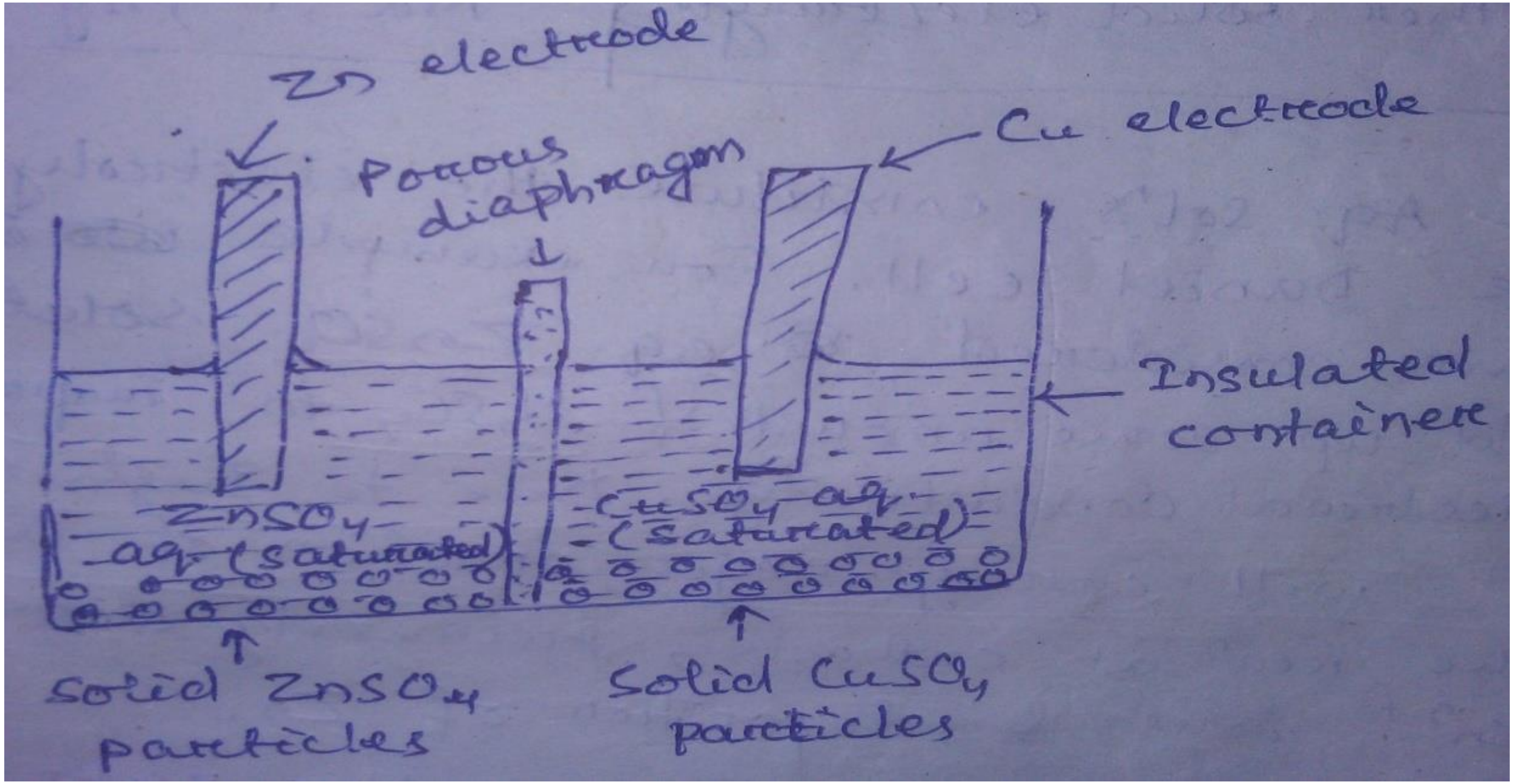
Reaction Consists of

Anodic Reaction: $Zn(S) = Zn^{+2}(aq) + 2\overline{e}(Oxidation)$

Cathodic Reaction: $Cu^{+2}(aq) + 2\overline{e} = Cu(S)(Reduction)$



Schematic of Daniel Cell

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Electrolytes: Electrolytes are ionic liquids or solids and classified as follows

Classification of Electrolytes		
Sl. No.	Electrolytes	Examples of current carrying Ions
1	Aqueous Solutions	Na^+, H^+, Cl^- etc
2	Molten Salts	$Na^+, K^+, Cd^+, Cl^-, F^-$etc
3	Molten Slags	Ca^{+2}, Mn^{2+} etc
4	Solid Oxide Electrolytes	O^{2-}
5	Other Solid Electrolytes	Na^+, Ag^+, F^-, Li^+ etc

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- ❑ Aqueous solutions constitute the electrolytes in the Daniel cell. For example if we have considered aq. $ZnSO_4$ solution, then add up some amount of H_2SO_4 to improve its electrical conductivity. Due to high mobility H^+, it will carry major fraction of current. The reaction at cathode, primarily discharge of Zn^{2+} ions and deposition of Zn.
- ❑ Similarly by taking molten salts at high temperature may consists of NaCl, KCl and $CdCl_2$. But only Cd^{2+} will participate in electrochemical reaction.
- ❑ Generally, for aqueous solutions as electrolyte, the electrochemical cell operated at room temperature.
- ❑ For molten salts, it is about (400-900) ^{0}C.
- ❑ For molten slag case, it is about (1000-1500) ^{0}C.

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Solid Electrolyte:

- In case of solid electrolytes, the operated temperature generally very high and it depends upon the nature of electrolytes.
- Out of many, Zirconia (ZrO_2) is well known solid electrolyte. It is a high temperature ceramic material.
- Zirconia is stable at high temperature but it undergoes some phase transformation during heating and cooling. Due to which there thermal stresses developed and that may be cause failure in service.
- To remove these chances, there are various oxides such as CaO, MgO and Y_2O_3 added and as a result melting point of ZrO_2 get increased to approximately 2400 ^{0}C.

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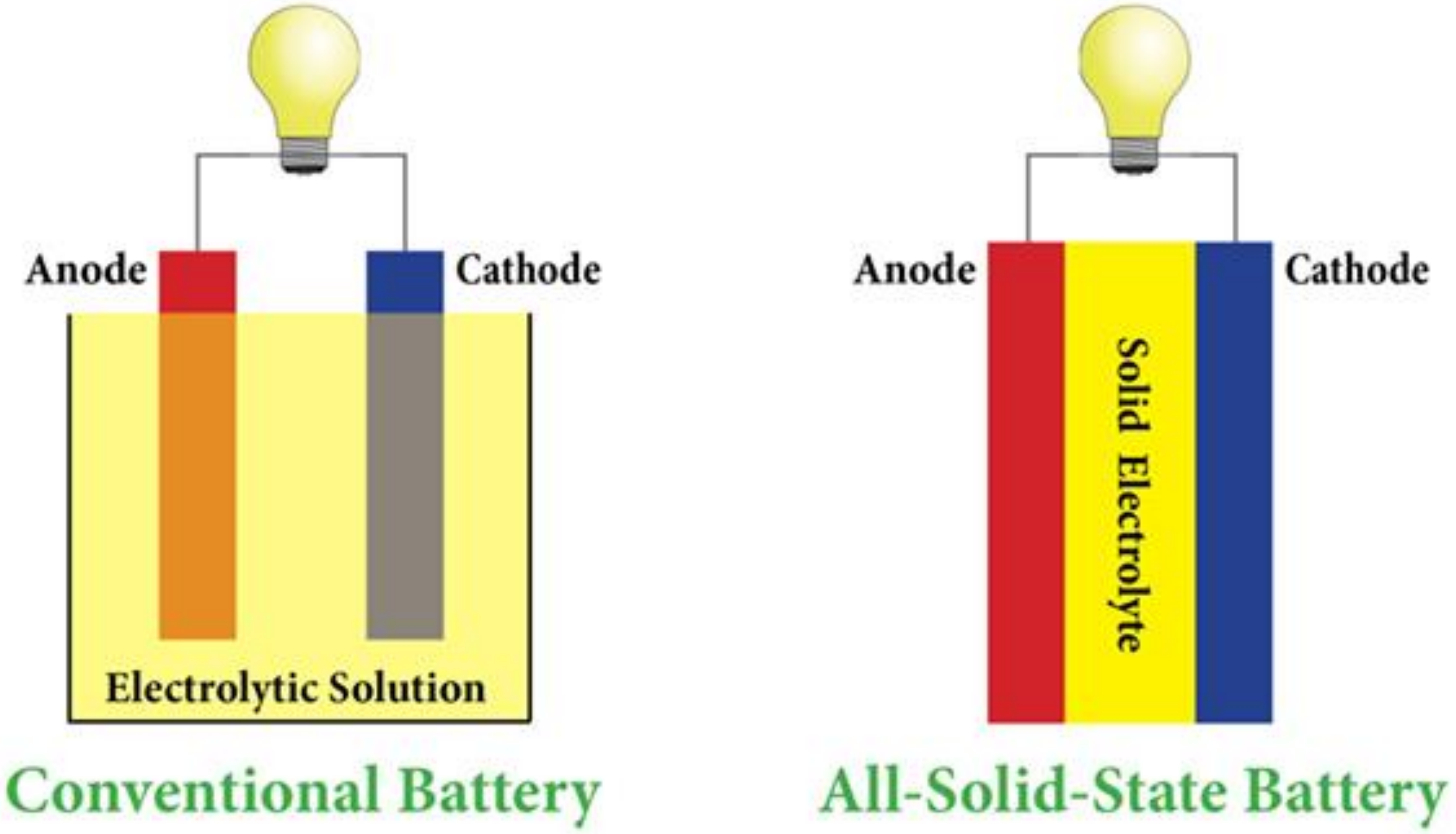

Schematic of solid-state electrolyte used battery and compared with conventional battery

Ref: https://chargedevs.com/newswire/japanese-researchers-use-superionic-conductors-as-electrolytes-for-solid-state-batteries/

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- ☐ Let us consider the example of ZrO_2-CaO solid solution.
- ☐ In pure ZrO_2, Zr^{4+} ions occupy cationic sites and O^{2-} ions occupy anionic sites. So after the addition of CaO to ZrO_2, some of Ca^{2+} replace the Zr^{2+} from the cationic sites and allows the movement of O^{2-} ions.
- ☐ Since Ca^{2+} and Zr^{4+} are almost immobile around above $(700\text{-}800)^0$C. Thus the cell operated at high temperature.
- ☐ Besides ZrO_2-CaO solid electrolytes, other important solid electrolytes are ZrO_2-Y_2O_3, ThO_2-Y_2O_3, CaF_2 doped with YF_3 etc.

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THERMODYNAMIC OF REVERSIBLE GALVANIC CELLS:

Some electrical cell can be made to behave either as a Galvanic cell or as an electrolytic cell.

Example: Daniel Cell.

- If external DC source connected to the cell having imposed voltage (V_{ext}), that opposes that of the Daniel Cell voltage (V_{cell}). Then depending on magnitude of V_{ext} and V_{cell}, we have two conditions

Condition-1: $V_{ext} < V_{cell} \Rightarrow Cell\ behaves\ as\ Galvanic\ cell$

Cell reaction: $Zn(S) + CuSO_4(aq) = ZnSO_4(aq) + Cu(S)$

Condition-2: $V_{ext} > V_{cell} \Rightarrow Cell\ behaves\ as\ elecrolytic\ cell$

Cell reaction: $Cu(S) + ZnSO_4(aq) = CuSO_4(aq) + Zn(S)$

Continued…

- ❑ In an electrolytic cell, chemical reaction occurs only if current allowed to flow through the cell. But if no current flow i. e. circuit becomes open then at that time voltage is known as emf or electromotive force of the Galvanic cell.

- ❑ Reversible Galvanic cell possible if and only

- Use of a voltmeter of very high resistance makes current flow negligible.
- Impose voltage from external source, $V_{ext} \cong V_{cell}$ i. e. emf of the cell and as a result current flow is negligible.

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RELATION BETWEEN CELL EMF (E) AND FREE ENERGY OF CELL REACTION (ΔG)

From a reversible process

$$dG = VdP - SdT - \delta W' \qquad (322)$$

[Where, W' – Work done other than work done against pressure]

At constant P and T,

$$dG = -\delta W' \qquad (323)$$

In case of a reversible Galvanic cell,

$$\delta W' = E\delta q \qquad (324)$$

$$\left(Since\ W = VIt = Eq \Rightarrow \delta W = E\delta q\right)$$

[Where, E – Cell Emf

$\delta q -$ Infinitesimal quantity of electric charge transformed across the cell due to the chemical reaction in the cell.]

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Again from the Faraday’s law of electrolysis,

$$\delta q = ZFdn \tag{325}$$

$$\begin{pmatrix} Since\ Fraday's\ law, we\ know\ that \\ I \times t = \dfrac{F \times W}{{}^{A}/_{Z}} \Rightarrow q = ZF\left(\dfrac{W}{A}\right) = ZFn \\ \Rightarrow \delta q = ZFdn \end{pmatrix}$$

[Where, n – Number of moles]

Putting equation (325) in the equation (324), the equation becomes

$$\delta W' = E \times (ZFdn) = ZFEdn \tag{326}$$

Again putting the equation (326) in equation (323), the equation becomes

$$dG = -\delta W' = -ZFEdn \tag{327}$$

Continued…

So for 1 mol of the above equation (327) becomes

$$dG = -ZFE \Rightarrow \Delta G = -ZFE \tag{328}$$

Similarly, at standard state equation (327) becomes

$$dG^0 = -ZFE^0 \Rightarrow \Delta G^0 = -ZFE^0 \tag{329}$$

Since we know

$$\Delta G = \Delta G^0 + RT \ln J \tag{330}$$

Now using equation (328) and (329) in the equation (330), we will get

$$-ZFE = -ZFE^0 + RT \ln J \tag{331}$$

$$\Rightarrow -E = -E^0 + \frac{RT}{ZF} \ln J \tag{332}$$

$$\Rightarrow E = E^0 - \frac{RT}{ZF} \ln J \tag{333}$$

Continued…

The above equation (333) is known as **Nernst's equation** and it can be written as

$$E = E^0 - \frac{2.303RT}{ZF} \log J \tag{334}$$

Sign Convention for EMF:

$$Zn(S)/ZnSO_4\left(\underbrace{aq}_{Sat}\right)//CuSO_4\left(\underbrace{aq}_{Sat}\right)/Cu(S)$$

- Single vertical lines separate electrode from electrolyte. Double vertical lines represented the porous diaphragm.
- If the reaction proceeds spontaneously from left to right, then the sign of the E will be positive and for reverse case right to left, sign of E is negative.

Assignment – 4(b)

Q.1 – In metallurgical processes, what type of reactions are more preferably happened and why, explain with the help of supportive examples.

Q.2 – How the boundary and phase controlling mechanisms affect the overall rate of reaction?

Q.3 – For mass loss analysis, which type of thermal analysis technique is preferred?

Q.4 – Write the combined expression for 1st and 2nd Faraday’s laws of electrolysis.

Q.5 –Why Zirconia is the more preferred solid electrolyte in contrast to other available solid electrolytes?

Q.6 – Briefly discuss the applications of thermal analysis techniques’ in specific to “metallurgical processes”.

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