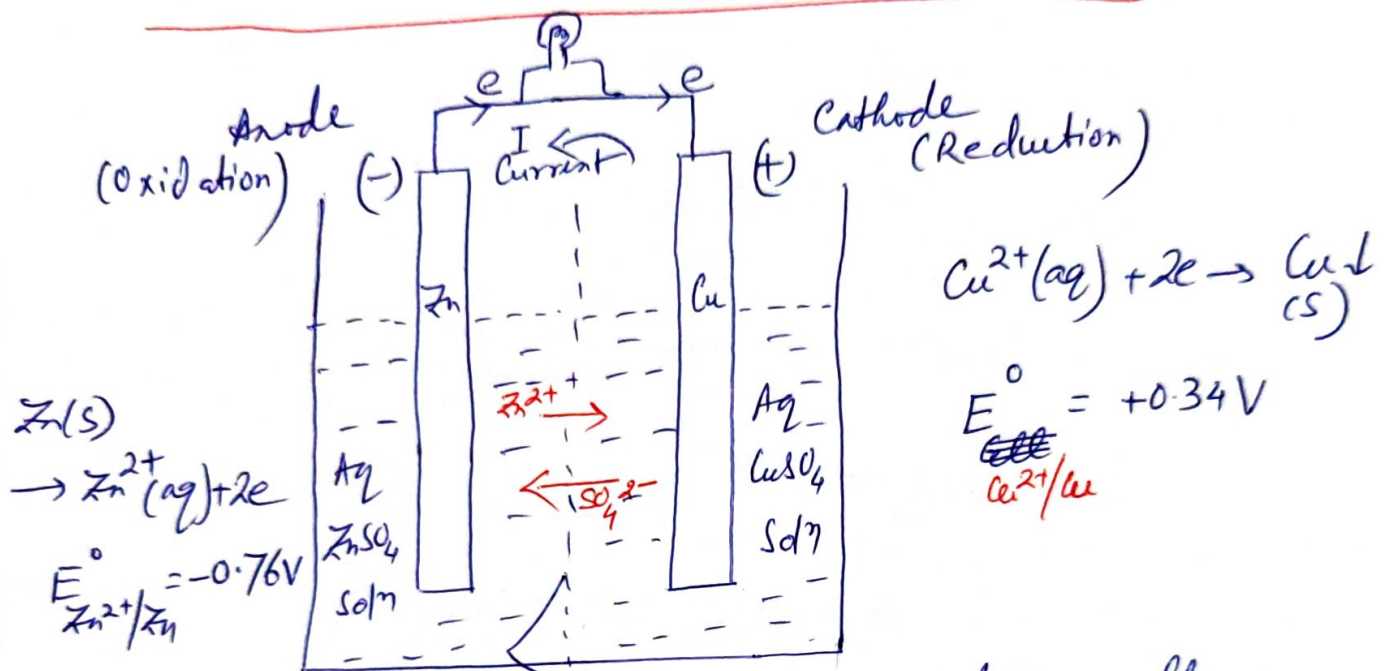


Electrochemistry

Electrochemical Cell, Electrochemical potential, Different parameters affecting the half-cell potential, Potentiometric Titration:



Daniell Cell

[Galvanic Cell]

[Otherwise, solutions may be electrically connected through a salt-bridge]

\Rightarrow Chemical energy is converted spontaneously into Electrical energy.

$$\Delta G_{T,P} \rightarrow (-) ; \quad \boxed{-\Delta G_{T,P} = +nFE_{\text{cell}}}$$

$\Rightarrow nFE_{\text{cell}} \Rightarrow$ Electrical energy produced.

Overall cell Redn: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
 for the passage of $2F$ of electricity per mole of Cu^{2+} reacted.

Standard potential of the cell:

$$E_{\text{cell}}^0 = (E_{\text{red}}^0)_{\text{RHS}} - (E_{\text{red}}^0)_{\text{LHS}}$$

$$= [0.34 - (-0.76)] \text{ V} = \underline{1.1 \text{ V}}$$

Standard potential \Rightarrow when the concentrations of the active species (i.e. Zn^{2+} ion & Cu^{2+} ion) are unity (i.e. 1 M)

% concⁿ of active species deviates from unity?

Nernst Eqⁿ.

Let, a general electrochemical cell:



$$\Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore, -nFE = -nFE^0 + RT \ln \left[\frac{\prod [\text{Prod}]^x}{\prod [\text{Reactant}]^y} \right]$$

$$\therefore, E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \left\{ \frac{\prod [\text{Prod}]^x}{\prod [\text{Reactant}]^y} \right\}$$

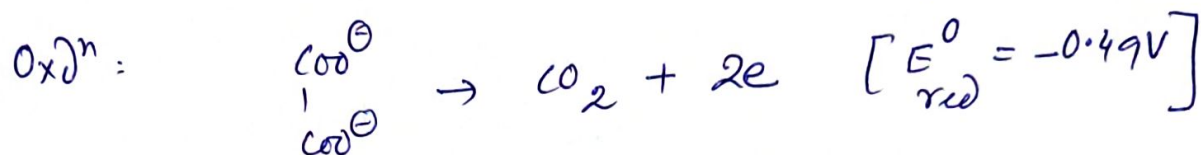
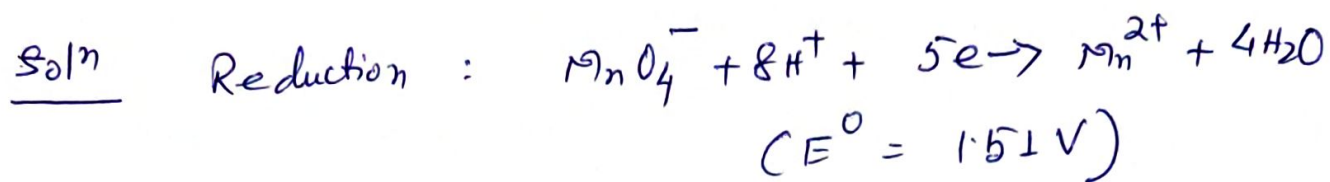
At 25°C ,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \left\{ \frac{\prod [\text{Prod}]^x}{\prod [\text{Reactant}]^y} \right\}$$

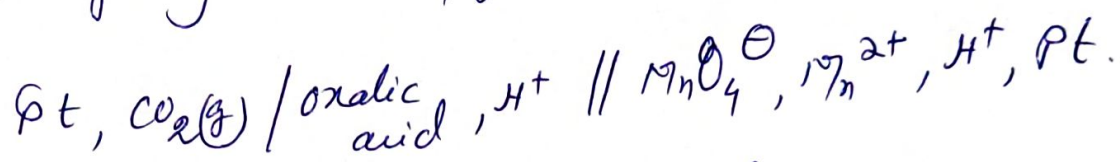
$n \Rightarrow$ No. of electron transferred in the cathodic/anodic rxn.

(3)

Will permanganate ions in acidic medium oxidize oxalic acid?



The cell giving these half cell reactions:



With: $E_{cell}^0 = E_{MnO_4^-/Mn^{2+}}^0 - E_{CO_2/COO^-}^0$
 $= 1.51 - (-0.49V)$
 $= 2.00V$

As E_{cell}^0 is (+); Hence, $\Delta G_{T,P}^0$ is (-) \Rightarrow
 spontaneous redn.

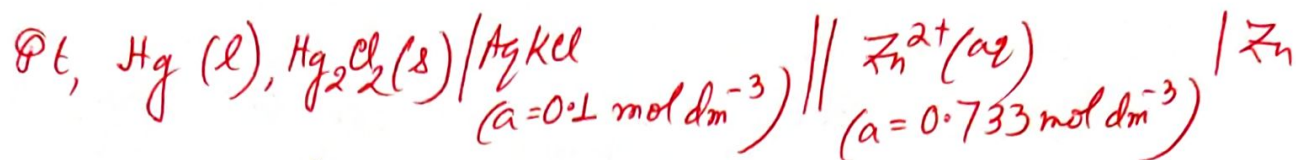
[JW] i) Will dichromate ions in acidic medium oxidize Fe^{2+} to Fe^{3+} ?

ii) Will Fe^{3+} ions be reduced to Fe^{2+} by S_n^{2+} ion?

iii) Would you use silver spoon to stir a solⁿ. of $Cu(NO_3)_2$?

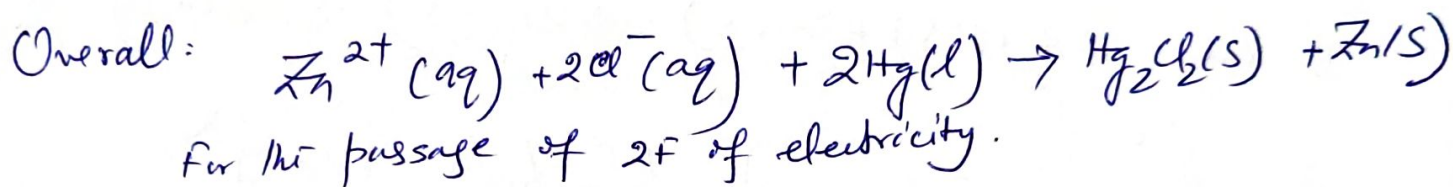
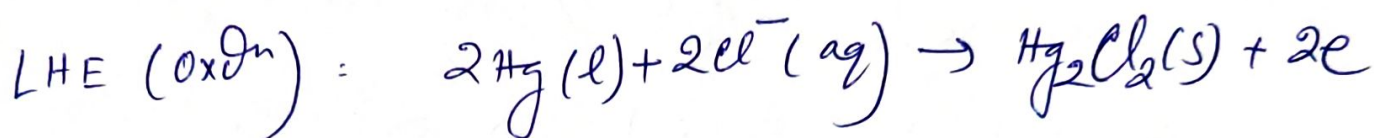
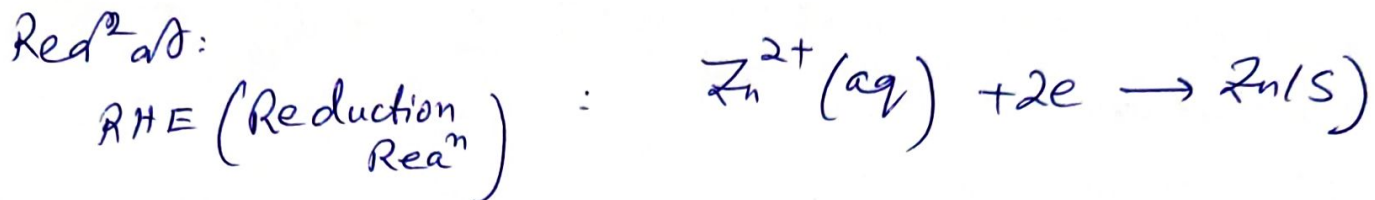
Determine the cell redⁿ and E_{cell}

(4)



Calomel electrode

Redⁿ at:



Hence:

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{2F} \ln \left\{ \frac{1}{[\text{Cl}^-]^2 [\text{Zn}^{2+}]} \right\}$$

$$E^{\circ} = \left(E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} \right) - E^{\circ}_{\text{Hg}_2\text{Cl}_2/\text{Hg}/\text{Cl}^-}$$

$$= (-0.76 - 0.337) = -1.1 \text{ V}$$

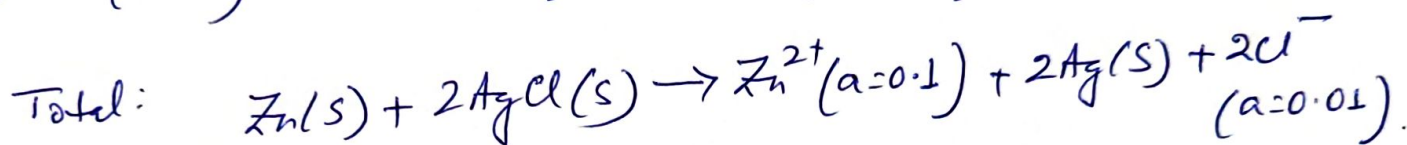
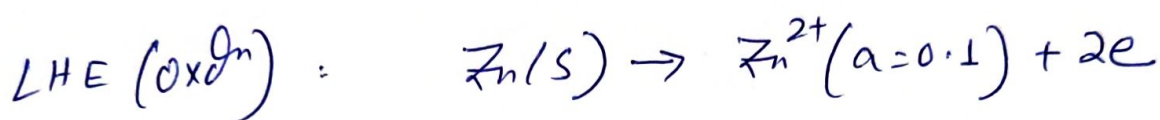
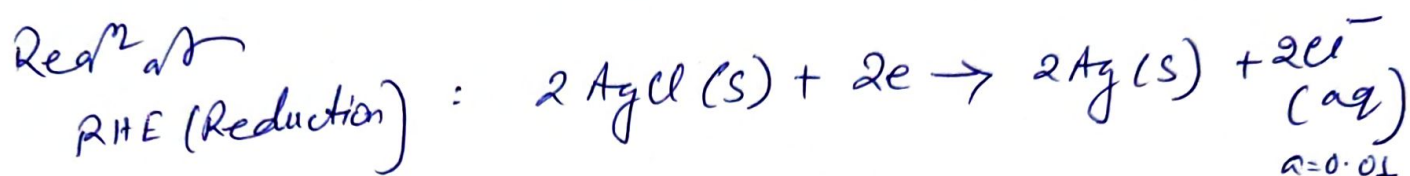
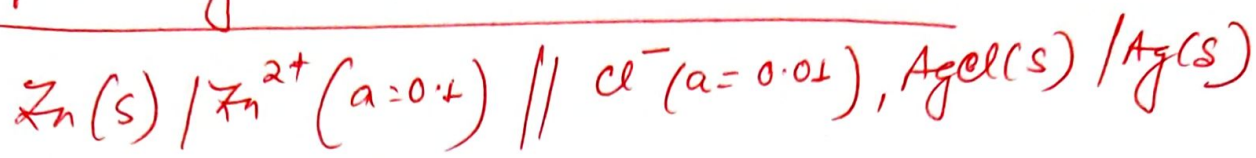
$$\therefore E = -1.1 + \frac{0.059}{2} \log \left\{ [\text{Cl}^-]^2 [\text{Zn}^{2+}] \right\}$$

$$= -1.1 + \frac{0.059}{2} \log \left\{ (0.1)^2 \times (0.733) \right\}$$

$$= -1.163 \text{ V.}$$

As E_{cell} is \ominus ; then $\text{Ag} \rightarrow (+)$: NOT spontaneous.
If we reverse the polarity of the cell \Rightarrow spontaneous cell redⁿ.

Write overall cell redⁿ, calculate cell potential and E_{eq}^m const of the overall cell redⁿ for the following electrochemical cell:



for the passage of $2F$ of electricity per mole of Zn^{2+} .

$$E_{cell}^{\circ} = \left(E_{\text{Cl}^{-}/\text{AgCl}, \text{Ag}}^{\circ} \right) - \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} \right) = 0.222 - (-0.76) = 0.982 \text{ V.}$$

From Nernst E_{eq}^m ; at 25°C

$$E_{cell} = E_{cell}^{\circ} - \frac{0.059}{2} \log [\text{Zn}^{2+}] [\text{Cl}^{-}]^2$$

$$= 0.982 - \frac{0.059}{2} \log (0.1) (0.01)^2$$

$$= 1.132 \text{ V.}$$

$$\Delta G = \Delta G^{\circ} + RT \ln \left\{ \frac{[P]}{[R]} \right\} \quad ; \text{At } E_{eq}^m: \Delta G_{T,P}^{\circ} = 0.$$

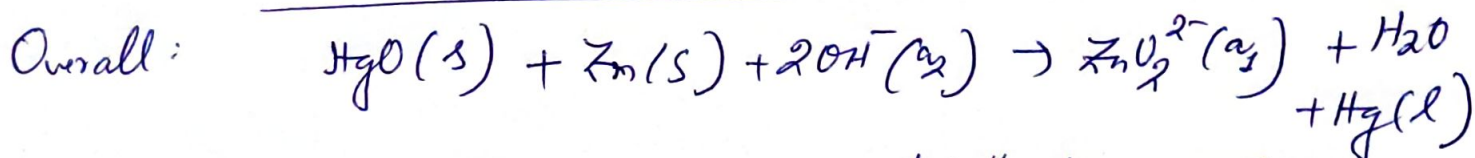
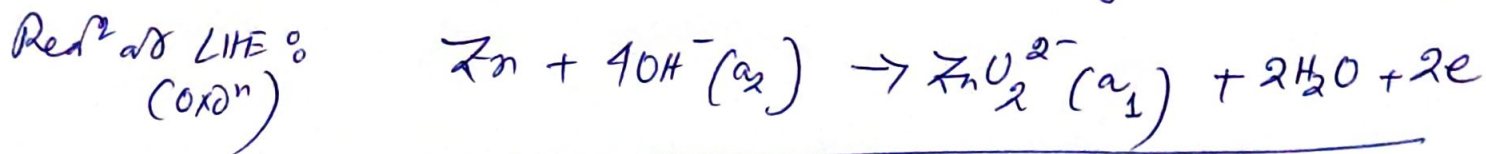
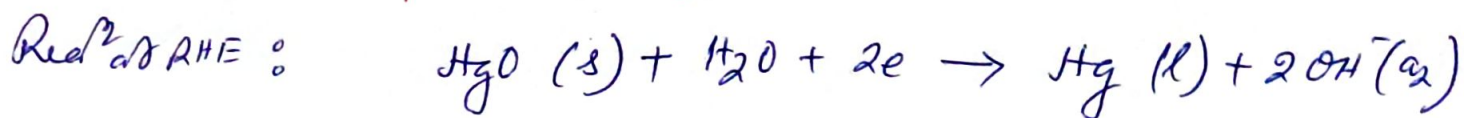
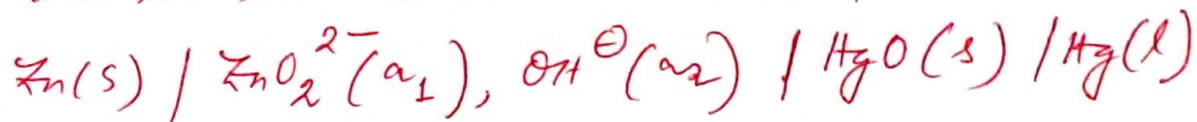
$$\left\{ \frac{[P]}{[R]} \right\}_{E_{eq}^m} = K_{eq}$$

$$\therefore \text{At } E_{eq}^m: \Delta G^{\circ} = -RT \ln K_{eq}$$

$$\therefore, E^{\circ} = + \frac{RT}{nF} \ln K_{eq} = \frac{0.059}{n} \log K_{eq} \quad (\text{at } 25^{\circ}\text{C})$$

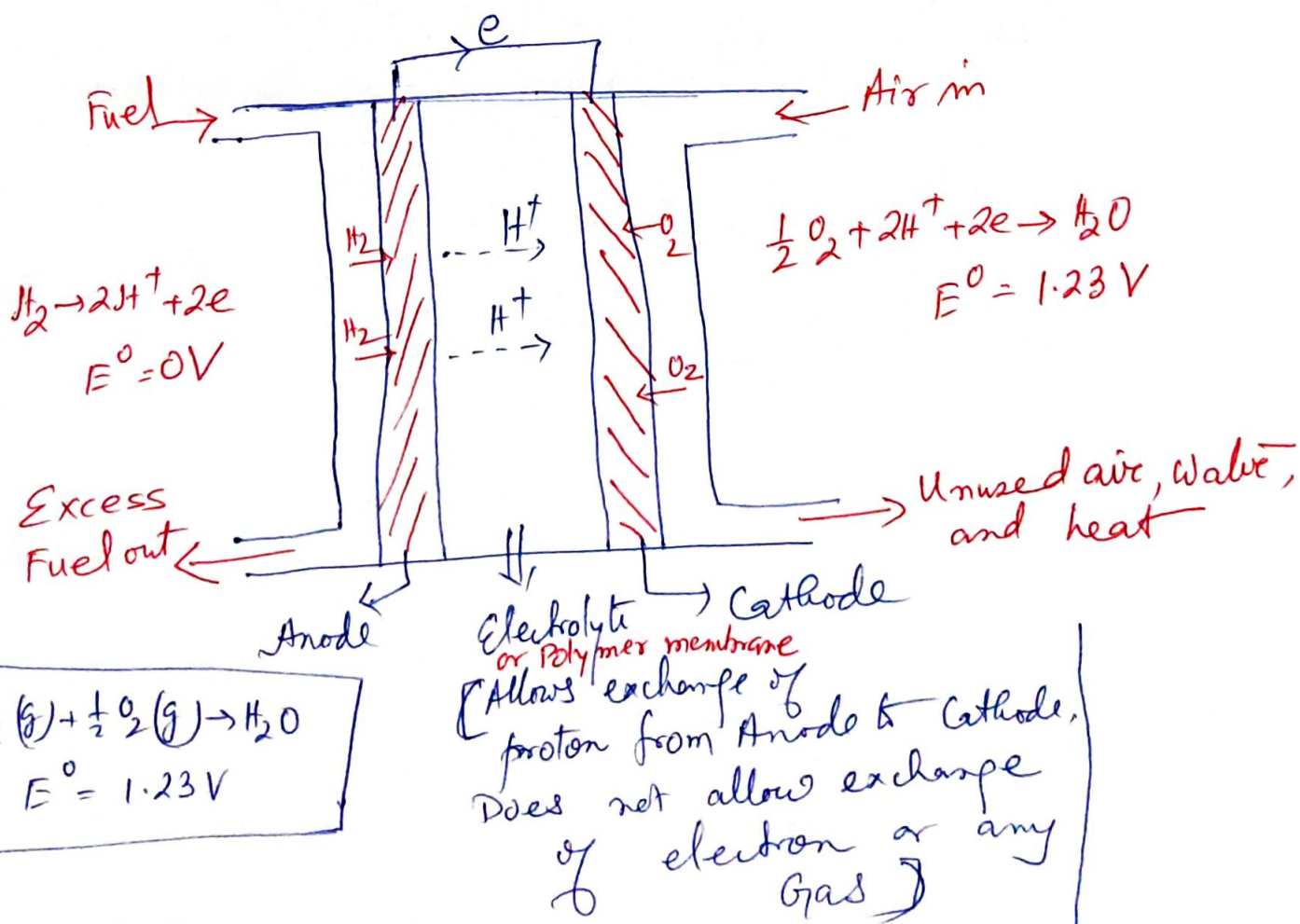
Thus, from E_{cell}° One can calculate K_{eq} .

What will be the overall cell reaction?

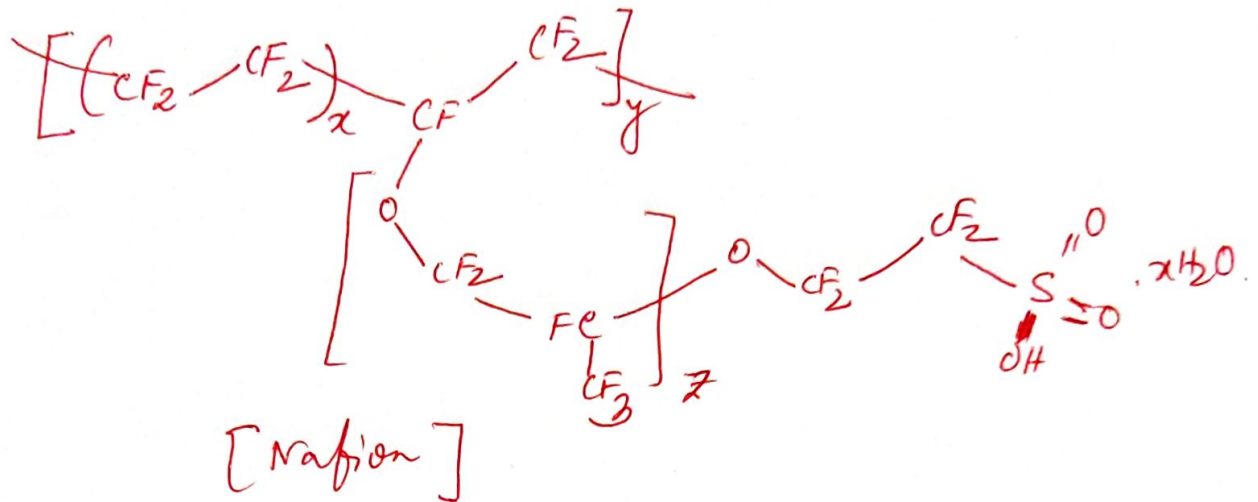


for the passage of 2F of electricity per 2mole of OH^- reacted.

H_2 - O_2 Fuel Cell Proton-exchange membrane fuel cell (PEMFC): Also known as Polymer electrolyte Membrane (PEM) Fuel cell:

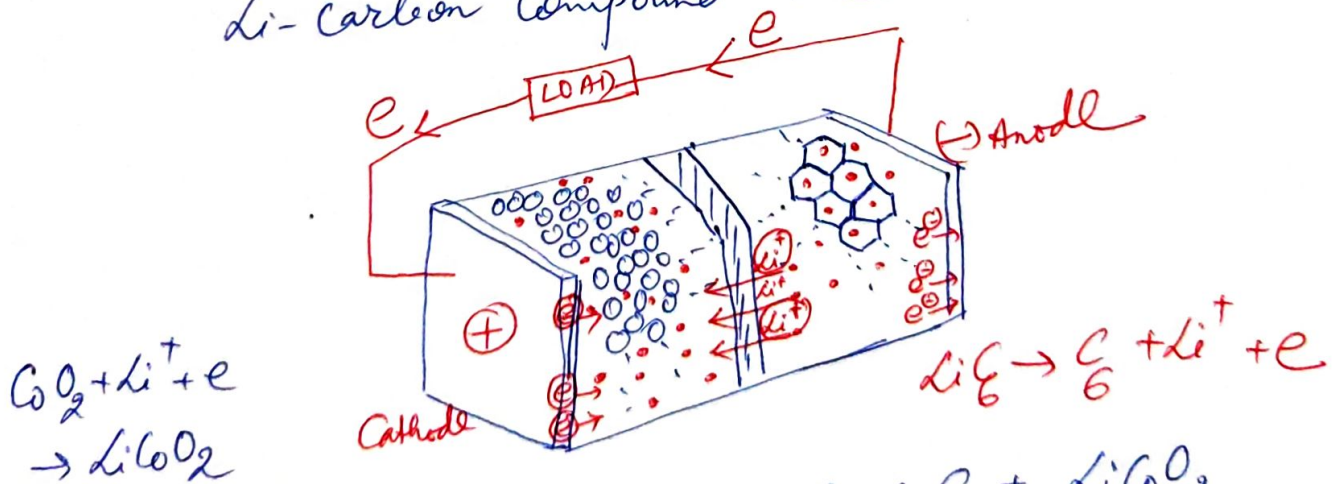


Electrode: Carbon support (electrical conductor)
 Pt nanoparticles (reaction sites)
 Nafion ionomer (paths for proton conduction)
 Teflon binder (increases hydrophobicity)



Li-Carbon Battery:

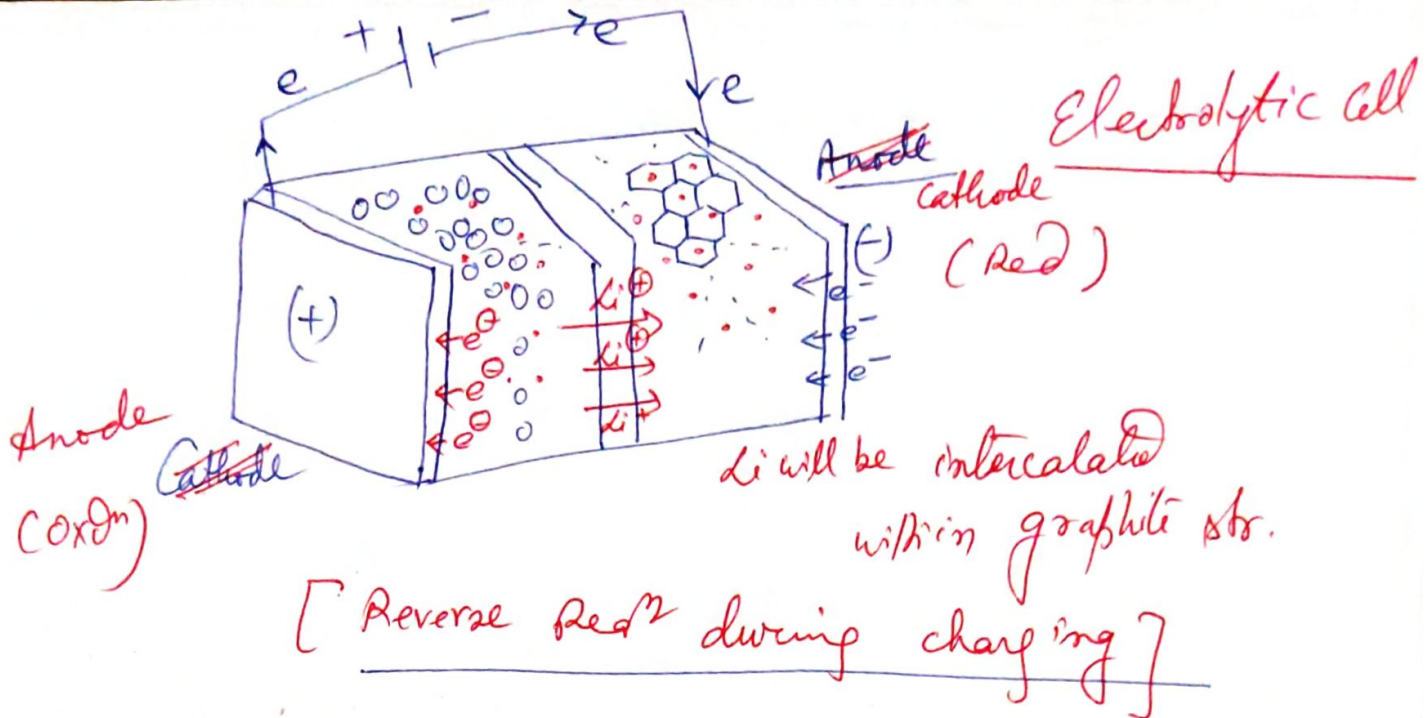
Li-Cobalt oxide (LiCoO_2) used in the cathode.
 Li-carbon compound used in the anode.



Overall: $\text{LiC}_6 + \text{CoO}_2 \rightleftharpoons \text{C}_6 + \text{LiCoO}_2$
 Cell voltage $\sim 3.6 \text{ V}$.

Li \Rightarrow Most electropositive element.
 It loses e^- very easily \Rightarrow ex.
 produce a lot of energy
 Li-ion battery \Rightarrow has highest charge-density

Li remains intercalated within graphite structure.
 Li^+ produced will migrate from anode to cathode through separator.



[HW] i) Overall cell reaction is given as:

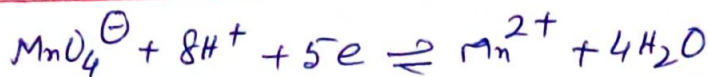


Construct the cell.

From standard electrode potential values predict if this cell red² will proceed to the forward or backward direction.

Factors affecting Redox Potential:

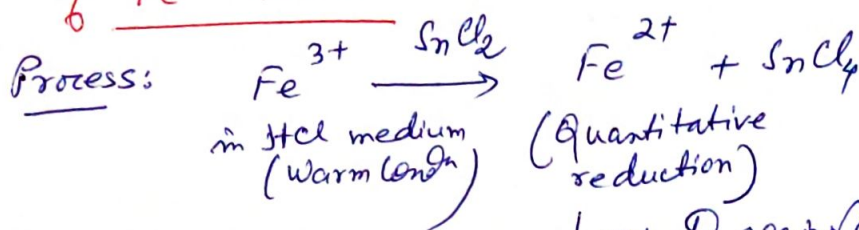
i) Effect of pH: [If any redox red² involves H⁺ or OH⁻]



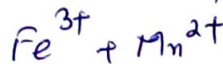
$$E = E^0 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-] [\text{H}^+]^8}{[\text{Mn}^{2+}]} \text{ at } 298\text{K}$$

$$\therefore E = E^0 - 0.093 \text{ pH} + \frac{0.059}{5} \log \left\{ \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \right\}$$

Application of above eqⁿ during estimation of Fe²⁺ ion:



↓ Titrated against
 KMnO₄ in acidic medium



From E⁰ values, MnO₄⁻ will oxidise both Fe²⁺ and Cl⁻ ions present in solⁿ.

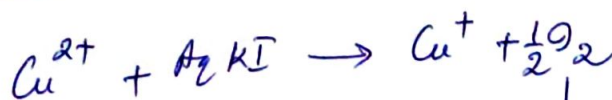
To eliminate the oxⁿ of Cl⁻ by MnO₄⁻, during the titration, Zimmermann-Reinhardt's reagent (ZR reagent) is ~~used~~ added: (MnSO₄, H₂SO₄, H₃PO₄ in aq solⁿ)

Then, [Mn²⁺] increases. As a result, effective

E_{MnO₄⁻/Mn²⁺} decreases and becomes less than 1.36V.

Then, under this situation, KMnO₄ can oxidise only Fe²⁺ present and not the Cl⁻ ion present.

ii) Effect of precipitation: Consider estimation of Cu²⁺ iodometrically.



↓ Titrated against
 standardised Na₂S₂O₃.

$$\begin{array}{l} E^0 = 0.15\text{V} \\ E^0_{\text{Cu}^{2+}/\text{Cu}^+} \\ E^0 = 0.54\text{V} \\ E^0_{\text{I}_2/\text{I}^-} \end{array}$$

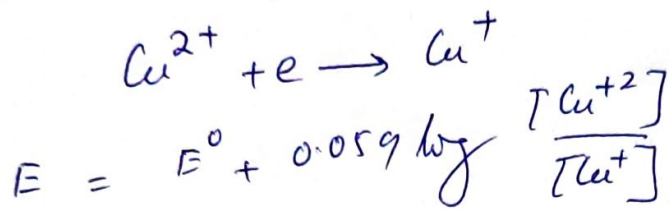
$$\begin{array}{l} E^0 = 1.52\text{V} \\ E^0_{\text{MnO}_4^-/\text{Mn}^{2+}} \\ E^0 = 1.36\text{V} \\ E^0_{\frac{1}{2}\text{Cl}_2/\text{Cl}^-} \\ E^0 = 0.34\text{V} \\ E^0_{\text{Cu}^{2+}/\text{Cu}} \\ E^0 = 0.15\text{V} \\ E^0_{\text{Cu}^{2+}/\text{Cu}^+} \\ E^0 = 0.77\text{V} \\ E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} \\ E^0 = -0.76\text{V} \\ E^0_{\text{Zn}^{2+}/\text{Zn}} \end{array}$$

As $E_{\text{O}_2/\text{O}^-}^0 > E_{\text{Cu}^{2+}/\text{Cu}^+}^0$; thus,

It is expected that O^- can not reduce Cu^{2+} .
But, it is actually happening.

$\text{Cu}^{2+} + \text{O}^- \rightarrow [\text{Cu}^+]$ \Rightarrow reacts with excess O^- present in the system and Cu_2O is precipitated out.

Net effect of this precipitation:



As Cu^+ is coming out of the system, its concn. is decreasing to a very low value.

As a result, effective $E_{\text{Cu}^{2+}/\text{Cu}^+}$ is increasing and eventually exceeds $E_{\text{O}_2/\text{O}^-}^0$ value.
Thus, Cu^{2+} is being reduced to Cu^+ and O_2 is liberated from O^- .

3) Effect of complex formation:

Electrodeposition of Brass \Rightarrow Requires simultaneous deposition of Cu and Zn.

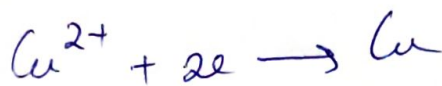
$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}; \quad E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$$

Expected: Cu will be deposited first and Zn will be precipitated on the already deposited Cu. i.e. we will not get brass, rather will get Zn coated Cu.

Soln: Use AgNO_3/KCN bath during electrodeposition:
Excess CN^- will react with both Zn^{2+} and Cu^{2+} to form $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{2-}$ complexes.
 \downarrow Labile \downarrow Stable.
i.e. weak complex

Thus, $\text{Zn}(\text{CN})_4^{2-}$ will again decompose to give Zn^{2+} ion.
 But, as $\text{Cu}(\text{CN})_4^{2-}$ is a stable complex, then,
 concⁿ of free Cu^{2+} is decreasing in the mixture.

Net effect:



$$E = E^0 + \frac{0.059}{2} \log [\text{Cu}^{2+}]$$

As $[\text{Cu}^{2+}]$ is decreasing, effective $E_{\text{Cu}^{2+}/\text{Cu}}$ is decreasing
 to such an extent, that eventually a condition
 will arrive when:

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\text{eff}} \approx E_{\text{Zn}^{2+}/\text{Zn}}^{\text{eff}} \quad \Bigg| \quad E_{\text{Cu}(\text{CN})_4^{2-}/\text{Cu}} \approx E_{\text{Zn}(\text{CN})_4^{2-}/\text{Zn}}$$

Under this condⁿ, Cu and Zn will be
 deposited simultaneously at the cathode and
 we get electrodeposited brass.