CL-611 Mid Sem Solution [Spring 2024-25]

Q1> (1) Galvanic Cell → Derives energy through spontaneous redox rxn
- → Battery in Discharge mode, fuel cell
- → Spontaneous rxn
- → ~~Chemical Energy~~ Electrical Energy as Output

Electrolytic Cell →
- → Requires external source to drive non-spontaneous rxn
- → Battery in Charging Mode, Electrolysis
- → Electrical Energy as Input

(2) Faraday's Law → relation b/w amount of current flowing through external circuit and amount of material consumed/produced in half cell rxn.

eg: $Cu^{+2} + 2e^- \longrightarrow Cu$

$$m = \frac{M.W. \times Q}{n \times F}$$

mass of species

no. of e^-

(3)

$$i \left[\frac{A}{m^2}\right] = -K \frac{d\phi}{dx}$$

$$\frac{d\phi}{dx} = -\frac{i}{K}$$

$$\int_{\phi_1}^{\phi_2} d\phi = -\frac{i}{K}\int_{x_1}^{x_2} dx$$

$$\Delta\phi = -i\frac{\Delta x}{K} = -\underbrace{i \times A}_{I} \times \frac{\Delta x}{K A}$$

$$\Delta\phi = -I \times R$$

where $\boxed{R = \frac{\Delta x}{K_c A}}$

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$$\left.\frac{\partial U}{\partial T}\right|_P = ?$$

we know,

$$\cancel{\Delta G = -nFU}$$

$$dG = V\,dP - S\,dT$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$-nF\left(\frac{\partial U}{\partial T}\right) = -\Delta S$$

$$nF\left(\frac{\partial U}{\partial T}\right)_P = \Delta S$$

Assuming ΔS does not change ~~so~~ over temp^r range of Interest

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_P = \frac{\Delta S}{nF}}$$

ΔS = Entropy change (J/k)
n = no. of electrons
F = faraday Constant (C/mol)

5 $$U = U^\circ_{cell} - \frac{RT}{nF}\ln K$$

where $K = \prod (a_i)^{s_i}$

for a rx^n at equilibrium, $\underline{U = 0}$ $\{\because \Delta G = 0\}$

$$\ln K = \frac{nF}{RT} U^\circ_{cell}$$

$$\boxed{K = \exp\left(\frac{nF}{RT} U^\circ_{cell}\right)}$$

(6) $2H^+ + 2e^- \longrightarrow H_2$

$$E_{H^+/H_2} = E^0 - \frac{RT}{nF} \ln\left[\frac{a_{Red}}{a_{Ox}}\right]$$

$$= 0 - \cancel{0.314}\frac{RT}{2F} \ln\left[\frac{P_{H_2}}{[H^+]^2}\right]$$

$$= 0 + \frac{RT}{2F} \times 2.303 \log_{10}\left[\frac{1}{[H^+]^2}\right] - \frac{RT}{2F} \ln P_{H_2}$$

$$\boxed{E_{H^+/H_2} = -\frac{RT}{2F} \ln(P_{H_2}) - 2.303\frac{RT}{F} \times pH}$$

$$\boxed{E_{H^+/H_2} = -29.5\,[mV] \log_{10} P_{H_2} - 59\,[mV]\, pH}$$ at 25°C

(7) Liquid Junction Potential

when mobility of $\oplus$ ion and $\ominus$ ion is different in soln

$$\boxed{E_{junction} = (\phi_l - \phi_R) = (t_+ - t_-) \times \frac{RT}{nF} \ln\left(\frac{a_{Right}}{a_{Left}}\right)}$$

(8)

$$i_o = k_o e^{-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \sqrt{C_O}\sqrt{C_R}$$

when C_o increased by a decade

i_o increased by $\sqrt{10} = 3.16$ times

when T increased from 25°C to 35°C

i_o increased by $\exp\left(-\frac{40000}{8.314}\left(\frac{1}{308} - \frac{1}{298}\right)\right)$

$= 1.689$ times

(9) Tafel slope, $b = 60\ mV$

$$\eta = a + b \log i$$

(a) when η_s increased from 0 mV to 60 mV

when $\eta_s < \frac{b}{3}$, linear regime valid

$\eta_s > \frac{b}{2}$, Tafel regime valid

$\eta_s < 20\ mV \rightarrow$ linear

$\eta_s > 30\ mV \longrightarrow$ Tafel

So full Butler volmer should be used.

If it was in Tafel region only, Then current would have increased 10 times for 60 mV increase in η_s.

But here, current increase will be less than 10 times. for 60 mV increase in η_s.

(b) when η_s increased from 120 mV to 240 mV
Tafel regime is valid here.
Therefore Current will increase by 100 tim

$$\boxed{\frac{i}{i_0} = 10^{\eta/b_a}}$$

(10) Nernst Planck eq^n

$$N_i = \underbrace{-z_i u_i F c_i \nabla\phi}_{\text{migration}} + \underbrace{-D_i \nabla c_i}_{\text{Diffusion}} + \underbrace{c_i v}_{\text{convection}}$$

where

u_i = mobility of ions $\left[\frac{m^2\text{-mol}}{C\text{-}\cancel{\text{Volts}}\text{-sec}}\right]$
z_i = charge on species (equivalent/mol)
F = Faraday constant (C/equivalent)
c_i = concentration $\left(\frac{mol}{m^3}\right)$
$\nabla\phi$ = potential gradient (V/m)
D_i = Diffusivity (m^2/s)
v = fluid velocity (m/s)

(11)

$$i = F \sum z_i N_i$$

$$i = -F^2 \nabla \phi \sum z_i^2 u_i c_i - F \sum z_i D_i \nabla c_i + F v \overset{0}{\cancel{\sum z_i c_i}}$$

(13) Transference No : Fraction of Current carried by an ion at no, concⁿ gradient

(14) Electroneutrality in a solⁿ $\boxed{\sum z_i c_i = 0}$

(12) Kohlrausch's law →

At low concentrations ;

$$\Lambda = \Lambda^{\circ} - K\sqrt{C}$$

equivalent Conductivity

equivalent conductivity at infinite dilution

- Applicable particularly for strong electrolyte.
- For weak electrolyte, where dissociation is not full, it is not fully applicable.

② (a) 0.1 M H_2SO_4 → 0.2 M H^+, 0.1 M SO_4^{-2}

0.1 M $CaCl_2$ → 0.1 M Ca^{+2}, 0.2 M Cl^-

$$\kappa = F^2 \sum z_i^2 u_i c_i$$

$$= F^2 \begin{bmatrix} (1)^2 \times 19 \times 10^{-13} \times 0.2 + (-2)^2 \times 4.3 \times 10^{-13} \times 0.1 \\ + (+2)^2 \times 3.2 \times 10^{-13} \times 0.1 + (-1)^2 \times 4.1 \times 10^{-13} \times 0.2 \end{bmatrix} \times 10^3$$

$$\boxed{\kappa = 7.093 \ S/m}$$

(b) Debye length →

$$\lambda = \sqrt{\frac{\varepsilon RT}{F^2 \sum z_i^2 c_i}} = \sqrt{\frac{6.933 \times 10^{-10} \times 8.314 \times 298}{(96485)^2 \times (200 + 400 + 400 + 200)}}$$

$$= 3.92 \ A^\circ$$

(c) Bonus: Molar Conductivity of 0.1 M $CaCl_2$ in water

$$\Lambda_m = \frac{\kappa}{c}$$

$$= \frac{1000 \times (96485)^2 \times \begin{bmatrix} (+2)^2 \times 3.2 \times 10^{-13} \times 0.1 \\ + (-1)^2 \times 4.1 \times 10^{-13} \times 0.2 \end{bmatrix}}{0.1 \times 1000}$$

$$= 0.0195 \ S \frac{m^2}{mol}$$

(3)

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^- \qquad U = 0$$

$$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^- \qquad U = 1.74$$

Since $V_{desired} = 1.3V$

we need total potential loss of

$1.74 - 1.3 = 0.44V \ (= 440mV)$

which will come from Summation of overpotential loss at Zn side, Overpotential loss at NiOOH side, and the overpotential loss in the Electrolyte. For that we have to change the values of discharge current by trial & error

Remember In Class, we had $i = 1000 \frac{mA}{cm^2}$, and we got ~~final~~ ~~Total voltage loss = 1.~~ final voltage as 1.53V [Total overpotential loss = $1.74 - 1.53 = 0.21V$]

Here, the desired voltage is lesser [1.3V], i.e. Overpotential is more [$1.74 - 1.3 = 0.44V$], Therefore we ~~must~~ should have higher value of discharge current (i).

Trial - 1,

Let $i = 2500 \frac{A}{m^2}$

so, Zn side,
$$2500 = 2 \times 60 \times \left[\exp\left(\frac{1.5 \times 10^5 \times \eta_s}{8314 \times 298}\right) - \exp\left(\frac{-0.5 \times 10^5 \times \eta_s}{8314 \times 298}\right)\right]$$

$$\eta_{s_{Zn}} = 0.05044V$$

$$= 50.44mV$$

NiOOH side

$$2500 = -61 \times \{\exp(20.181\,\eta_s) - \exp(-20.181\,\eta_s)\}$$

$$\eta_s = -0.184\ V$$

$$\eta_{s,Ni} = -184\ mV$$

Electrolyte →

$$\Delta V = \overset{A/m^2}{I}\ \overset{(\Omega\, m^2)}{R_{sol^n}}$$

$$= 2500\left(\frac{A}{m^2}\right) \times \frac{2 \times 10^{-3}\ m}{60\ S/m}$$

$$= 83.33\ mV$$

Total potential loss $= [50.44 + 184 + 83.33]$

$$= 317.77\ mV$$

But the desired potential loss is 440 mV.

Therefore – Let $i = 5000\ \frac{A}{m^2}$

then $\eta_{Zn} = 61.7\ mV$

$$\eta_{NiOOH} = -218.34\ mV$$

$$\Delta V_{elyte} = 166.66\ mV$$

Total loss $=$ ~~t 61.~~ $446.7\ mV$

~~desire~~ which is very close to desired value of 440 mV

#3 Let $i = 4800 \frac{A}{m^2}$

$\eta_{Zn} = 61\ mV$

$\eta_{NiOOH} = -216.32\ mV$

$\Delta V_{Elyte} = 160\ mV$

Total loss = 437.32 mV [close to 440 mV]

~~very~~

Let $i = 4900 \frac{A}{m^2}$

$\eta_{Zn} = 61.38\ mV$

$\eta_{NiOOH} = -217.34\ mV$

$\Delta V_{Elyte} = 163.33$

Total loss = 442.05 mV

Answer :- i = b/w 4800 – ~~5000~~ 4900 $\frac{A}{m^2}$

(4)

For Solid Curve

Since the solid curve is symmetric.
therefore, $\alpha_a = \alpha_c = 0.5$

Using Linear approximation for Solid Curve inset in Figure left,

$$i = i_0 \frac{(\alpha_a + \alpha_c) F}{RT} \eta_s$$

taking $i \approx 15$ mV at $\underline{\eta_s = 10\,mV = 0.01V}$ (SI unit)

$$i = \frac{i_0 (0.5 + 0.5) \times 96485}{8.314 \times 298} \times 0.01$$

$$\boxed{i_0 \approx 0.385 \frac{mA}{cm^2}}$$

Similarly, For Dashed Curve using Linear approximation ~~at~~ [inset in figure left]

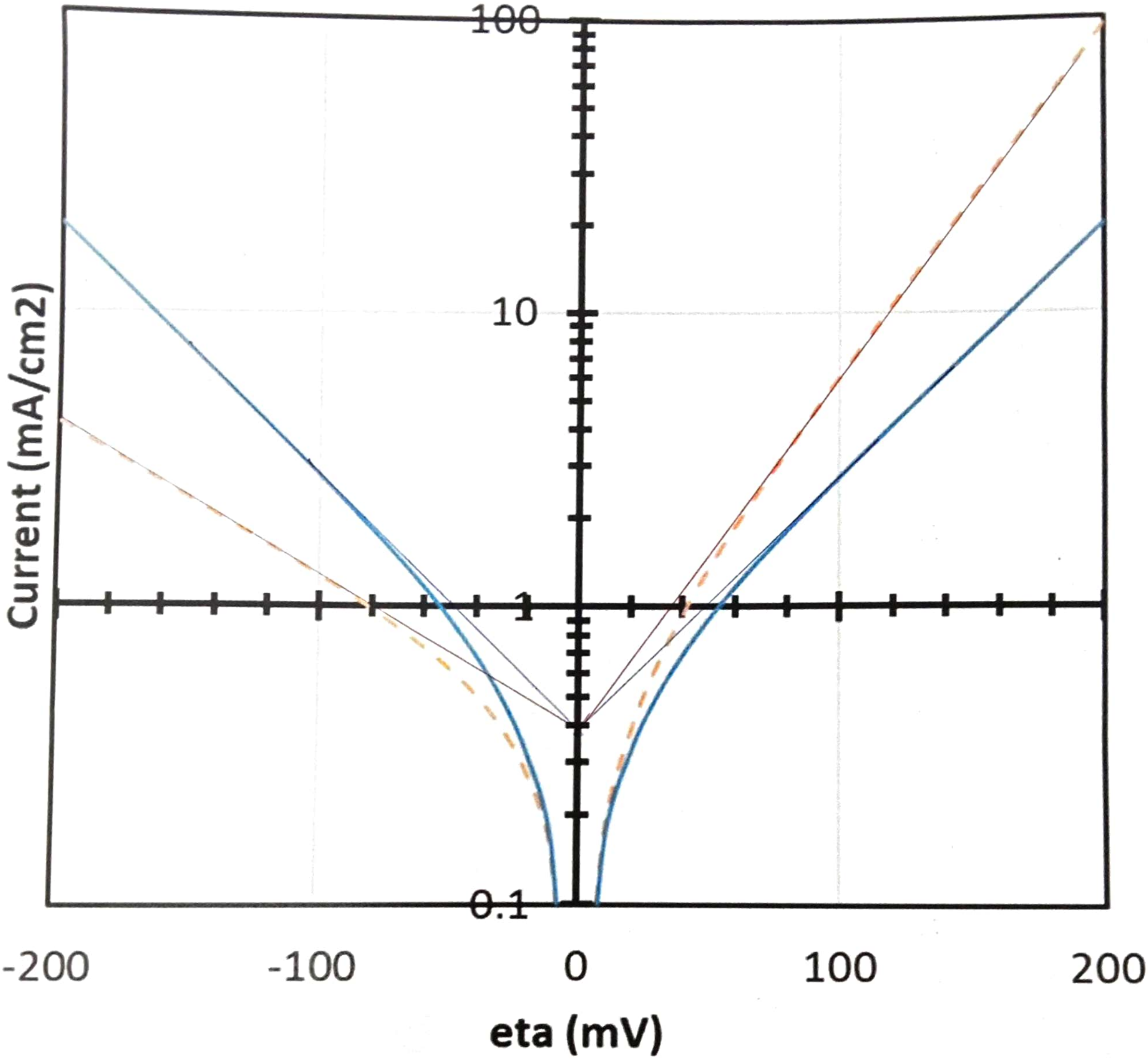
$$i = i_0 \frac{(\alpha_a + \alpha_c) \times 96485}{8.314 \times 298} \times 0.01 [V]$$

since $\underline{\alpha_a + \alpha_c = 1}$

we will get,

$$\boxed{i_0 = 0.385 \frac{mA}{cm^2}}$$

So, value of i_0 will be same for both the curve as curves coincide in linear regime and $\alpha_a + \alpha_c = 1$ in both cases.



100
10
1
0.1
Current (mA/cm2)
-200
-100
0
100
200
eta (mV)

One could also use the right curve attached above ~~below~~ to find i_0 values. Since the linear extrapolation will give i_0 value.

And we get $\boxed{i_0 \approx 0.4 \ \frac{mA}{cm^2}}$ in both cases from the plot. See figure below.

Now: Calculation of Tafel slope and α_a, α_c.

For Solid Curve

$$b_a = b_c = b$$

$$b = \frac{200 - 140}{\log(20) - \log(6)} = 114.749 \ \frac{mV}{decade}$$

For Dashed Curve

Anodic Side: (see the red dashed lines in plot attached)

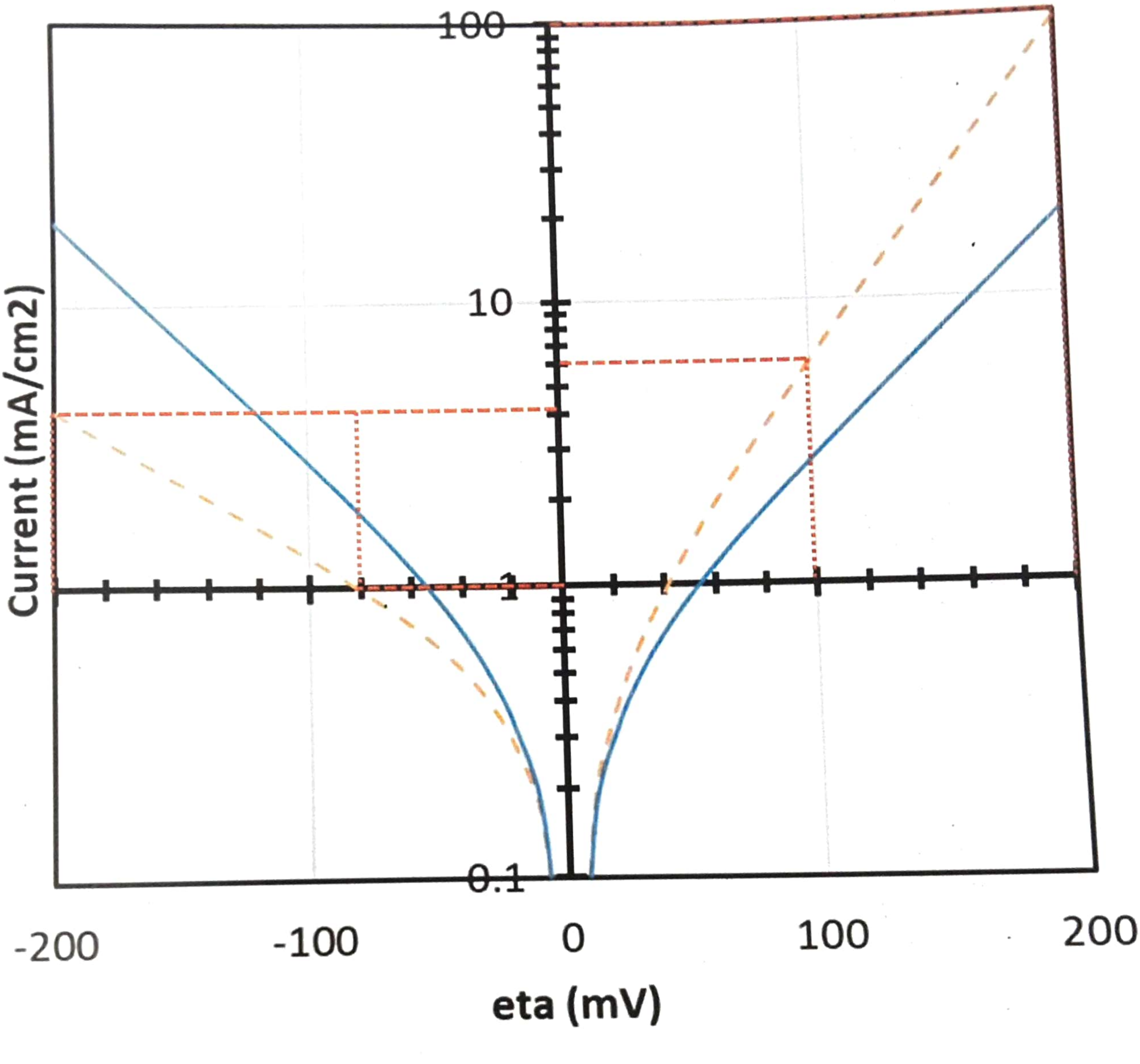
$$b_a = \frac{200 - 100}{\log(100) - \log(6)} = 81.84 \ \frac{mV}{decade}$$

Since

$$b_a = \frac{2.303\,RT}{\alpha_a F} = \frac{59\ [mV]}{\alpha_a}$$

[@ 25°C]

$$\therefore \alpha_a = \frac{59\ [mV]}{81.84\ [\frac{mV}{decade}]} = 0.7209$$



100
10
1
0.1
Current (mA/cm2)
-200
-100
0
100
200
eta (mV)

one could find $\alpha_c = 1 - 0.7209$

$\simeq 0.2791$ {without calculating from slope}

and

$$b_c = \frac{59\,[mV]}{\alpha_c} = \frac{59}{0.2791} \simeq 211.408\ \frac{mV}{decade}$$

Alternatively: from the value (in red ~~dashed~~ dashed line)

$$b_c = \frac{-200 - (-80)}{\log 4 - \log(1)} \simeq 200\ \frac{mV}{decade}$$

&

$$\alpha_c = \frac{59\,[mV]}{200\left(\frac{mV}{decade}\right)} \simeq 0.295$$

$\left\{ \because b_c = \frac{2.303\,RT}{\alpha_c F} \right\}$