MSE-441 Exercise-3 Solutions

1. **High field approximation (HFA): $|\eta| > 0.1$ V**

   Anodic current; $i = i_o \exp\{(1-\alpha)\eta F/RT\}$

   Cathodic current; $i = -i_o \exp\{-\alpha\eta F/RT\}$

2. **Low field approximation (LFA): $|\eta| < 0.01$ V**

   $i = 2i_o \sin(F\eta/2RT) \approx 2i_o(F\eta/2RT) = i_o(F\eta/RT)$

3. **For $\eta \approx 0.01$ V - 0.1V**

   Use the BV-equation.

4. **BV equation can be used as it is under any circumstances.**

<u>Exercise 1:</u>

Calculate the ratio of the rates of the reaction: $Ag^+ + e^- \rightarrow Ag$ at:

a) $\eta = -0.15$V & $\eta = 0.15$ V.
b) $\eta = -0.2$V & $\eta = 0.2$ V.

Assume room temperature at 25°C.

rate = i/(nF)

Therefore, $rate_1/rate_2 = i_1/i_2$

Since it is a cathodic reaction, we compare the cathodic rate for both η.

$i_c = i_o \exp\{-\alpha\eta F/RT\}$

a) $$\frac{i_{c1}}{i_{c2}} = \frac{e^{-0.5(-0.2)\frac{96500}{8.314(298)}}}{e^{-0.5(0.2)\frac{96500}{8.314(298)}}} = \frac{18.56}{0.054} = \mathbf{344}$$

b) $$\frac{i_{c1}}{i_{c2}} = \frac{e^{-0.5(-0.2)\frac{96500}{8.314(298)}}}{e^{-0.5(0.2)\frac{96500}{8.314(298)}}} = \frac{49}{0.02} = \mathbf{2450}$$

A small change in potential from – 0.2 to +2V increases the rate by 2450 times

<u>Exercise 2:</u>

For an overpotential of $\eta = 10$ mV, a current I = 0.62 mA is passed through a 2 cm^2 Pt electrode for a H^+/H_2 half reaction given as: $H^+ + e^- \rightarrow \frac{1}{2}H_2$.

What will be the current density i for (a) $\eta = 100$ mV? (b) $\eta = -100$ mV?

Assume the symmetry factor as 0.5 and a room temperature of 25°C

For η = 10 mV = 0.01V, we have i = I/A = 0.62/2 = 0.31 $mA.cm^{-2}$

The exchange current density i_o is obtained using the BV equation

$i = i_o\,(e^{(1-\alpha)\,\eta F / RT} - e^{-\alpha\,\eta F / RT})$

$0.31 = i_o\,[e^{0.5 \times 0.01 / F / RT} - e^{-0.5 \times 0.01\, F / RT}]$

i_o = 0.79 $mA.cm^{-2}$

a) For η = 100 mV = 0.1 V
   $i = 0.79\,(e^{0.5 \times 0.1 \times 96500 / 8.314 \times 298} - e^{-0.5 \times 0.1 \times 96500 / 8.314 \times 298})$
   i = 5.42 $mA.cm^{-2}$

b) For η = -100 mV = -0.1 V
   $i = 0.79\,(e^{0.5 \times -0.1 \times 96500 / 8.314 \times 298} - e^{-0.5 \times -0.1 \times 96500 / 8.314 \times 298})$
   i = -5.42 $mA.cm^{-2}$

Exercise 3:

The exchange current density of a Pt electrode for the H^+/ H_2 half reaction is i_o = 0.79 $mA.cm^{-2}$ at 25°C.

Calculate the current density across it when the over potential is (a) η = 10 mV (b) η = –200 mV.

a) For η = 10 mV = 0.01 V,
   $i = i_o\,\eta F/RT = 0.79\,\frac{(0.01)\,96500}{8.314\,(298)}$ = **0.308 $mA.cm^{-2}$**
b) η = -200 mV = -0.2 V, negative (net cathodic current)
   $i = i_o\, e^{-\alpha\eta F/RT} = 0.79\, e^{-0.5 \times 0.2 \times 96{,}500/ RT}$ = 38.79 $mA.cm^{-2}$
   $i = i_a - i_c = -\,i_c$ = **-38.79 $mA.cm^{-2}$**

Exercise 4:

Calculate the effective resistance across 1 cm^2 of

a) Pt, H2, H^+ ; i_o = 0.79 $mA.cm^{-2}$
b) Hg, H2, H^+ ; i_o = 0.79 x 10^{-12} $A.cm^{-2}$

What conclusion you can draw from the result?

For η < 0.01 V and using $I = i_o \frac{\eta F}{RT}$, the overpotential is obtained as $\eta\; = I\frac{\eta F}{RT}$.

With V = IR, then area specific resistance $ASR\; = \frac{RT}{i_o F}$ and the resistance is R = ASR x A

a) $ASR = \frac{8.314\,(298)}{(0.790 * 10^{-3})\,96{,}495} = \mathbf{32.5\;\Omega.\,cm^2}$
   Less resistance, the electrode can be less polarizable (non-polarizable)
b) $ASR = \frac{8.314\,(298)}{(0.790 * 10^{-12})\,96{,}495} = \mathbf{3.25 * 10^{10}\;\Omega.\,cm^2}$
   Greater resistance, the electrode can be more polarizable

Exercise 5:

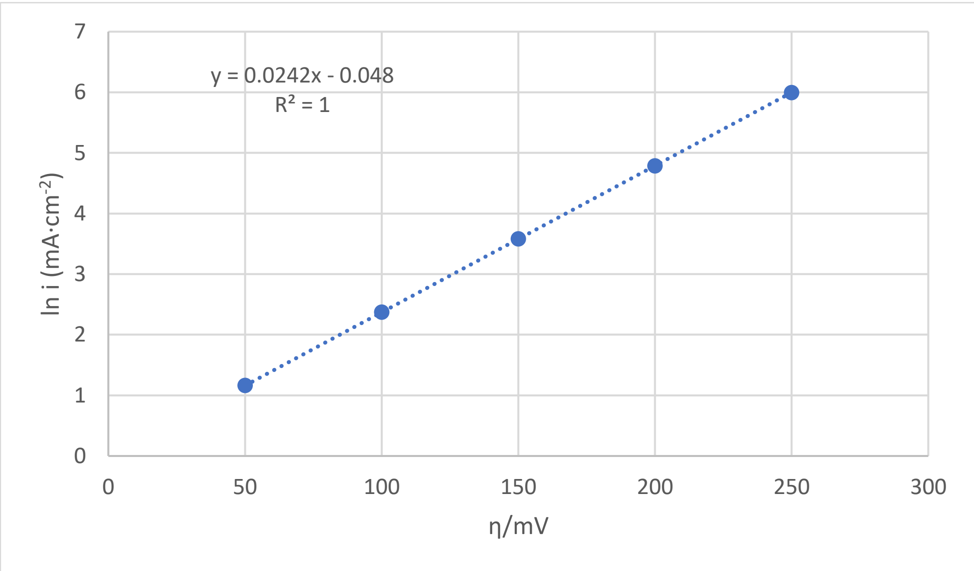
In an experiment involving Pt, H_2, H^+ electrode, the following data were obtained at 298 K. Determine α_{anodic} and i_0

η/mV	50	100	150	200	250
i / mA·cm^{-2}	3.19	10.69	35.88	120.00	402.00

Answer:

Do the Tafel plot:

η/mV	50	100	150	200	250
ln(i) / mA·cm^{-2}	1.16064768	2.369496	3.58018	4.787492	5.996452



The reaction is anodic (η>0, and i>0), use B-V equation for anode:

$$i = i_0 \times \exp\left(\frac{z\alpha_{anodic}F\eta}{RT}\right)$$

$$\ln(i) = \ln(i_0) + \frac{z\alpha_{anodic}F\eta}{RT}$$

$$slope = 0.0242 = \frac{z\alpha_{anodic}F}{RT} = \frac{2 \times \alpha_{anodic} \times 96485\ A \cdot \frac{s}{mol} \times 0.001\ \frac{V}{mV}}{8.314\ \frac{J}{mol \cdot K} \times 298\ K}$$

$$\alpha_{anodic} = 0.689$$

$$intercept = -0.048 = \ln(i_0)$$

$$i_0 = 0.953\ mA/cm^2$$

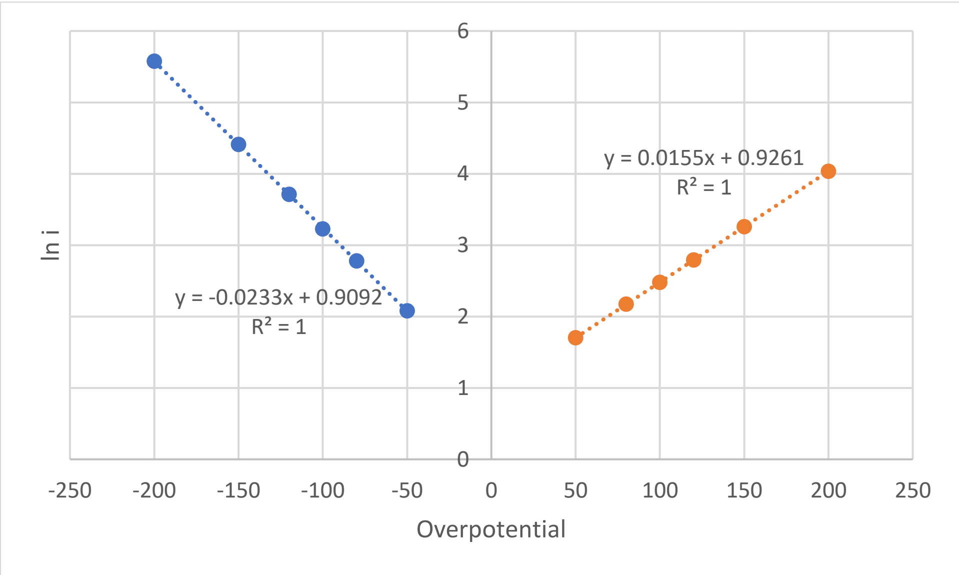
Exercise 6:

For the system Pt /Fe^{3+}, Fe^{2+} at 298K the i were measured as shown below:
Determine α_{anodic}, $\alpha_{cathodic}$ and i_0

η/mV	-50	-80	-100	-120	-150	-200
i / mA·cm^{-2}	-8.01	-16.1	-25.17	-41	-82.4	-264
η/mV	50	80	100	120	150	200
i / mA·cm^{-2}	5.50	8.78	11.91	16.30	26.00	56.60

Answer：

Do the Tafel plot:



For anodic plot (η>0, and i>0):

$$i = i_0 \times \exp\left(\frac{z\alpha_{anodic}F\eta}{RT}\right)$$

$$\ln(i) = \ln(i_0) + \frac{z\alpha_{anodic}F\eta}{RT}$$

$$slope = 0.0155 = \frac{z\alpha_{anodic}F}{RT}$$

$$\alpha_{anodic} = 0.398$$

$$intercept = 0.9261 = \ln(i_0)$$

$$i_0 = 2.52\ mA/cm^2$$

For cathodic plot (η<0, and i<0),

$$|i| = i_0 \times \exp\left(\frac{-z\alpha_{cathodic}F\eta}{RT}\right)$$

$$\ln(|i|) = \ln(i_0) + \frac{-z\alpha_{cathodic}F\eta}{RT}$$

$$slope = -0.0233 = \frac{-z\alpha_{cathodic}F}{RT}$$

$$\alpha_{cathodic} = 0.598$$

$$intercept = 0.9092 = \ln(i_0)$$

$$i_0 = 2.48\ mA/cm^2$$

The value of i_0 estimated from anode and cathode plot should be close.

Not that the sum of $\alpha_{cathodic}$ and α_{anodic} is approximately 1.

$$\alpha_{cathodic} + \alpha_{anodic} = 1$$

Exercise 7:

The exchange current density of Pt /Fe^{3+}, Fe^{2+} is 2.5 mA·cm $^{-2}$. Calculate the current density across the electrode at 25 °C maintained at 1V when [Fe $^{2+}$] = 0.1 M and [Fe $^{+3}$]= 0.2 M
(Standard reduction potential = 0.77l V, $\alpha_{cathodic}$ = 0.58)

Answer:
Reaction is

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

First, the thermodynamic potential of the reaction at operation condition is

$$E = E^o - \frac{RT}{nF}\ln\frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.771 - \frac{8.314 \times 298}{1 \times 96485}\ ln\frac{1}{2} = 0.788\ V$$

To calculate overpotential:

$$E_{applied} = E + \eta$$

$$\eta = 1 - 0.788 = 0.212\ \mathrm{V}$$

The reaction is anodic, use anodic B-V equation:

$$i = i_0 \times \exp\left(\frac{z\alpha_{anodic}F\eta}{RT}\right)$$
$$\alpha_{anodic} = 1 - \alpha_{cathodic}$$

$$i = 2.5 \times \exp\left(\frac{1 \times (1 - 0.58) \times 96485 \times 0.212}{8.314 \times 298}\right) = 80.3\ mA/cm^2$$