

*Problem 3-1*

$$MW = 0.32924 \text{ [kg/mol]}$$

$$T = 298.15 \text{ [K]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$m = 0.00001 \text{ [kg]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

$$c_K = 3 \cdot \frac{m}{MW \cdot V}$$

$$c_{ferri} = c_{ferro}$$

$$c_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

$$U = 0.26 \text{ [V]} \text{ because potential is at std potential, the concentration of ferri and ferro are the same}$$

## SOLUTION

**Unit Settings: SI C kPa kJ mass deg**

$$c_{ferri} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$c_K = 0.9112 \text{ [mol/m}^3\text{]}$$

$$m = 0.00001 \text{ [kg]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$U = 0.26 \text{ [V]}$$

$$c_{ferro} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$MW = 0.3292 \text{ [kg/mol]}$$

$$T = 298.2 \text{ [K]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

No unit problems were detected.

**Problem 3-1b&c**

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298 \text{ [K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$MW = 0.32924 \text{ [kg/mol]}$$

$$m = 0.00001 \text{ [kg]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

$$C_K = 3 \cdot \frac{m}{MW \cdot V}$$

$$C_{ferri} = C_{ferro}$$

$$C_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

$$I = C_K + C_{ferri} + C_{ferro}$$

$$\lambda = \sqrt{\varepsilon \cdot \varepsilon_r \cdot R \cdot \frac{T}{F \cdot F \cdot I}}$$

$$\varepsilon = 8.854 \times 10^{-12} \text{ [m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^4 \cdot \text{A}^2\text{]}$$

$$\varepsilon_r = 78$$

**Part c**

*increase the ionic strength, neglect ferri and ferro cyanide concentrations*

$$c = 100 \text{ [mol/m}^3\text{]}$$

$$I_n = 2 \cdot c$$

$$\lambda_n = \sqrt{\varepsilon \cdot \varepsilon_r \cdot R \cdot \frac{T}{F \cdot F \cdot I_n}}$$

**SOLUTION****Unit Settings: SI C kPa kJ mass deg**

$$c = 100 \text{ [mol/m}^3\text{]}$$

$$C_{ferri} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$C_{ferro} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$C_K = 0.9112 \text{ [mol/m}^3\text{]}$$

$$\varepsilon = 8.854\text{E-}12 \text{ [m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^4 \cdot \text{A}^2\text{]}$$

$$\varepsilon_r = 78$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$I = 1.215 \text{ [mol/m}^3\text{]}$$

$$I_n = 200 \text{ [mol/m}^3\text{]}$$

$$\lambda = 1.230\text{E-}08 \text{ [m]} \quad (\text{b}) \quad \text{see figure 3.2 for sketch of potential}$$

$$\lambda_n = 9.586\text{E-}10 \text{ [m]} \quad (\text{c})$$

$$m = 0.00001 \text{ [kg]}$$

$$\text{MW} = 0.3292 \text{ [kg/mol]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298 \text{ [K]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

No unit problems were detected.

Repeat Illustration 3-2(a) for the situation where the potential (0.10V) is relative to a Ag/AgCl reference electrode. The equilibrium potential for the saturated Ag/AgCl electrode is 0.197 V. Please comment on any differences that you observe between the two solutions.

From Illustration 3-2,  $3966 \text{ A m}^{-2}$

The equilibrium potentials are as follows

$$\begin{array}{lll} U_{SCE}^{\theta} = 0.2576 \text{ V} & \text{saturated} & U_{SCE} = 0.242 \text{ V} \\ U_{Ag/AgCl}^{\theta} = 0.222 \text{ V} & \text{saturated} & U_{Ag/AgCl} = 0.197 \text{ V} \end{array}$$

For the ferri-ferro cyanide reaction,  $U=0.3674 \text{ V}$ , see illustration 3-2.

The overpotential is therefore

$$\eta_s = 0.1 + 0.197 - 0.3674 = -0.074 \text{ V}$$

Using the Butler-Volmer equation

$$i = i_o \left[ \exp\left(\frac{(1-\beta)F\eta_s}{RT}\right) - \exp\left(-\frac{\beta F\eta_s}{RT}\right) \right]. \quad (3-16)$$

$$i = i_o \left[ \exp\left(\frac{F\eta_s}{2RT}\right) - \exp\left(-\frac{F\eta_s}{RT}\right) \right].$$

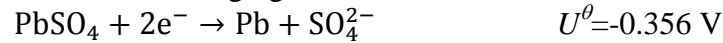
solving for the current density

using an area of  $0.75 \text{ cm}^2$

$\begin{array}{l} i = -14,602 \text{ A m}^{-2} \\ I = -1.095 \text{ A} \end{array}$
---

Because the potential of the AgCl reference electrode is smaller than that of the SCE, the absolute value for the overpotential at 0.1 V is higher, resulting in a larger cathodic current.

Hydrogen gassing can be a serious problem for lead-acid batteries. Consider two reactions on the negative electrode: the desired reaction for charging



and an undesired side reaction



- a) The exchange-current densities for the two reactions are  $i_{o,\text{PbSO}_4} = 100 \text{ Am}^{-2}$ , and  $i_{o,\text{H}_2} = 6.6 \times 10^{-10} \text{ Am}^{-2}$ , where the exchange current density for the hydrogen reaction is on pure lead. Calculate the current density for each reaction if the electrode is held at a potential of  $-0.44 \text{ V}$  relative to a hydrogen reference electrode. The temperature is  $25^\circ\text{C}$ , and the transfer coefficients are  $0.5$ .
- b) With Sb impurity in the lead, the exchange current density of the hydrogen reaction increases to  $3.7 \times 10^{-4} \text{ A m}^{-2}$ . Repeat the calculation of part (a) in the presence of antimony. Assuming that all impurities cannot be eliminated, what implications do these results have for the operation of the battery?

$$\text{a) } \eta_s^{\text{Pb}} = -0.44 - (-0.356) = -0.084 \text{ V}$$

$$\eta_s^{\text{H}_2} = -0.44 - (0.0) = -0.44 \text{ V}$$

Using the Butler-Volmer equation

$$i = i_o \left[ \exp\left(\frac{\alpha_a F \eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_s}{RT}\right) \right], \quad (3-17)$$

Solving for the current density

$$i_{\text{Pb}} = -493 \text{ A m}^{-2}$$

$$i_{\text{H}_2} = -3.5 \times 10^{-6} \text{ A m}^{-2}$$

- b) Use the provided exchange current density for the case of hydrogen evolution in the presence of impurities,

$$i_{\text{H}_2} = -1.9 \text{ A m}^{-2}$$

There is a large increase in current density. The increase is not so large as to affect the energy efficiency—less than one percent of the current is going to hydrogen formation. On the other hand, this generated hydrogen must be managed; that is vented or recombined with oxygen to prevent a build-up of hydrogen in the cell.

Data for the exchange current density for oxygen evolution on a lead oxide surface are provided as a function of temperature. Develop an expression for  $i_o$  as a function of temperature. What is the activation energy? If the transfer coefficient is a constant at 0.5 and the overpotential is 0.7 V, at what temperature will the current density for oxygen reduction be  $5 \text{ A m}^{-2}$ ?

$T, ^\circ\text{C}$	$i_o, \text{A m}^{-2}$
15	$6.9 \times 10^{-7}$
25	$1.7 \times 10^{-6}$
35	$7.6 \times 10^{-6}$
45	$1.35 \times 10^{-5}$

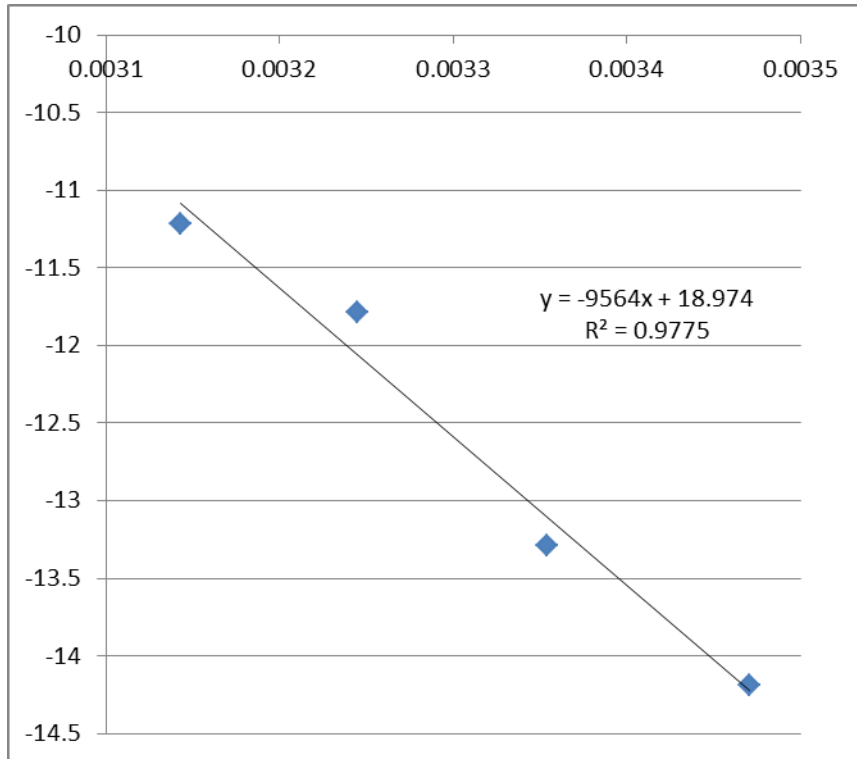
Assume a form for the dependence on temperature

$$i_o(T) = A \exp\left\{\frac{-E_a}{RT}\right\}. \quad (3-18)$$

or

$$\ln i_o = \ln A - \frac{E_a}{RT}.$$

The tabulated data are plotted as shown the figure: the logarithm of exchange current density versus reciprocal of temperature, and the data fitted with a line.



$$\ln i_o(T) = \frac{-9564}{T} + 18.974$$

$$\frac{E_a}{R} = 9564 \text{ K}$$

$$E_a = R(9564 \text{ K}) = 79.5 \text{ kJ mol}^{-1}$$

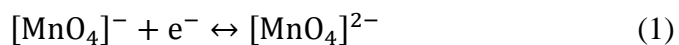
$$\alpha_a=0.5 \quad \eta_s=0.7 \text{ V}$$

$$i = i_o(T) \exp\left\{\frac{\alpha_a}{RT} \eta_s\right\} = 5 \text{ A m}^{-2}$$

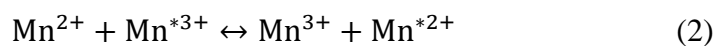
Solve for T,

$$T = 317 \text{ K} = 44 \text{ }^\circ\text{C}$$

The following reaction is an outer-sphere reaction that occurs in KOH.



Would you expect the reaction to have a larger or small reorganizational energy compared to an isotope exchange reaction for manganese? What does this imply about the reaction rate?



Just as in the iron (II)/iron (III) example from the text, it is expected that the reorganizational energy would be smaller for the larger permanganate ions. We would expect that the rate for this first reaction to be faster than the isotope exchange reaction.

Reactions with Mn(II) are challenging experimentally because of disproportionation,



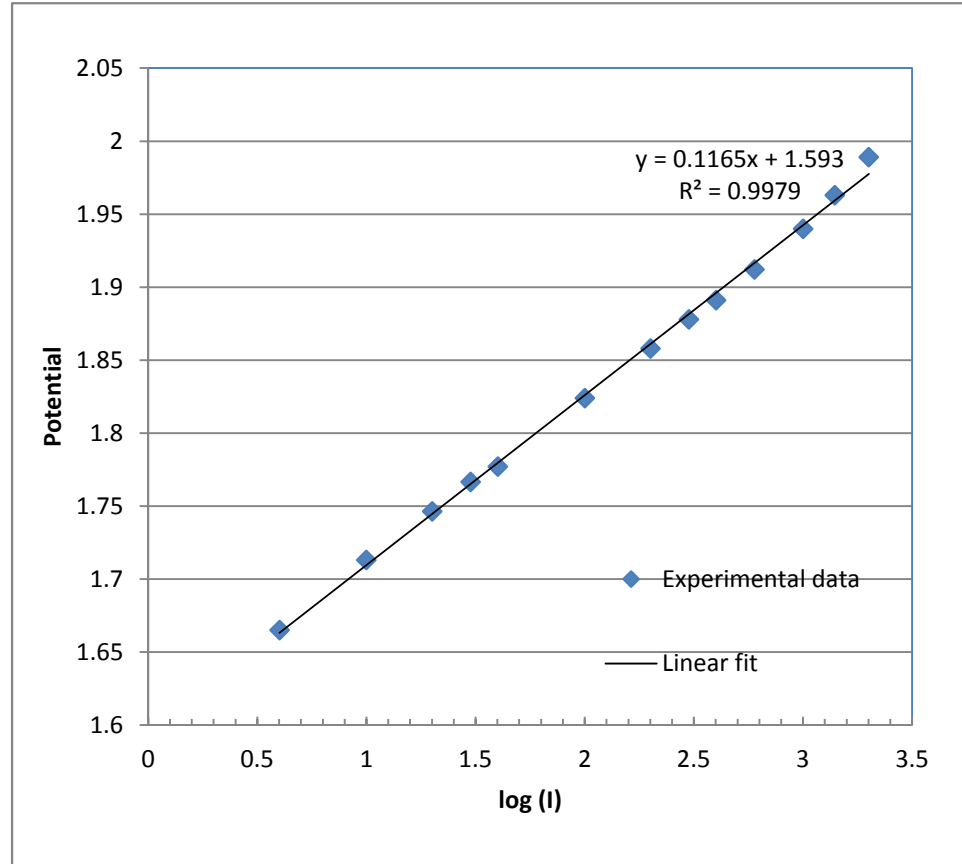
Nonetheless, the rate constant for the first reaction is orders of magnitude larger than for the isotope exchange. A. G. Sykes, *Advances in Inorganic Chemistry and Radiochemistry*, **10**, 153-245 (1968).



Problem 3-6

I, Am-2	log (I)	Potential, V
4	0.60206	1.665
10	1	1.713
20	1.30103	1.7465
30	1.477121	1.7665
40	1.60206	1.777
100	2	1.824
200	2.30103	1.858
300	2.477121	1.878
400	2.60206	1.891
600	2.778151	1.912
1000	3	1.94
1400	3.146128	1.963
2000	3.30103	1.989

From fit: Tafel slope is 0.12 V/decade  
 To get the exchange current density one would need  
 to know how the potential is referenced



The evolution of oxygen is an important process in the lead-acid battery. Assume that the positive electrode of the flooded lead-acid battery is at its standard potential (entry 2 in Appendix A), calculate the overpotential for the oxygen evolution reaction. It is reported that the Tafel slope for this reaction is 120 mV/decade at 15 °C. What is the transfer coefficient,  $\alpha_a$ ? If the exchange current density is  $6.9 \times 10^{-7} \text{ A} \cdot \text{m}^{-2}$ , what is the current density for oxygen evolution? You may neglect the small change in equilibrium potential with temperature.

The Tafel slope is

$$\ln 10 \frac{RT}{\alpha_a F} = 0.12 \text{ V}$$

$$\alpha_a = \frac{\ln 10 RT}{0.12 F} = 0.48$$

$$\eta_s = 1.685 - 1.229 = 0.456 \text{ V}$$

$$i = i_o e^{\frac{\alpha_a F}{RT} \eta_s}$$

$$i_o = 6.9 \times 10^{-7} \text{ A m}^{-2}$$

$$i = 4.4 \text{ mA m}^{-2}$$

i

The tabulated data are for the dissolution of zinc in a concentrated alkaline solution. These data are measured using a Hg/HgO reference electrode. Under the conditions of the experiment, the equilibrium potential for the zinc electrode is -1.345 V relative to the HgO electrode.

Potential, V	$i$ , A m <sup>-2</sup>
-1.335	58
-1.325	150
-1.315	300
-1.305	600
-1.295	1100
-1.285	1970
-1.275	3560
-1.265	6300
-1.255	11,500
-1.245	20,000
-1.235	36,800
-1.225	66,000

- Please determine the exchange current density and Tafel slope that best represent these data.
- For the same electrolyte, the potential of a SCE electrode is 0.2 V more positive than the Hg/HgO reference. If the potential of the zinc is held at -1.43 V relative to the SCE electrode, what is the current density for the oxidation of zinc?

a)

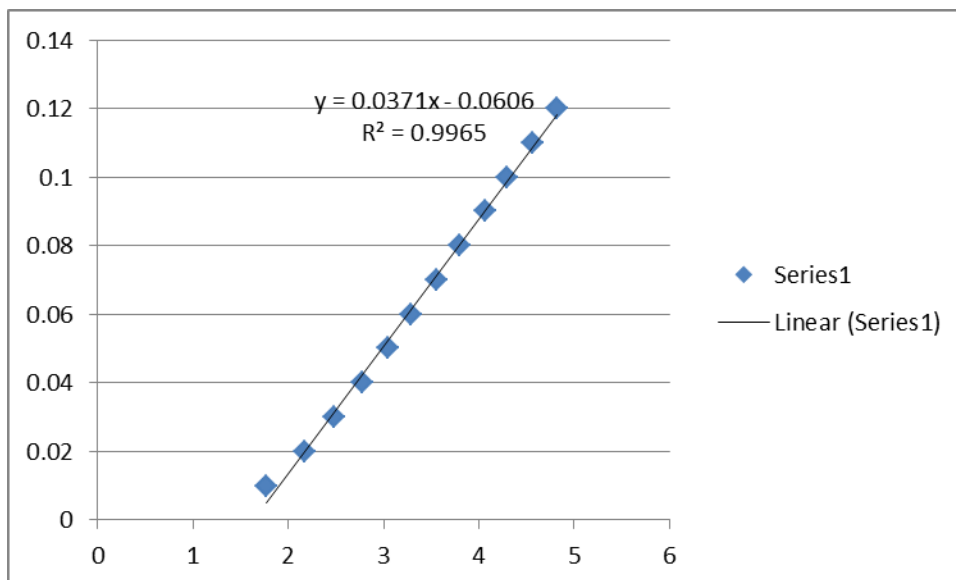
$$\eta_s = V - U$$

The data provide  $V$ , subtract ( $U=-1.345$ ) to get the overpotential. Then create a Tafel plot, fit line through data

$$\eta_s = 0.037 \log i - 0.0606$$

The Tafel slope is

37 mV per decade



Find current density where the overpotential is zero,

$$\eta_s = 0.037 \log i - 0.0606 = 0$$

$$\log i_o = \frac{0.0606}{0.037}$$

$$i_o = 43.4 \text{ A m}^{-2}$$

b)  $V = -1.43 \text{ V}$  (relative to SCE)

$$V_{HgO} = V_{SCE} - 0.2$$

$$\eta_s = -1.43 + 0.2 + 1.345 = 0.115 \text{ V}$$

$$i = 55.7 \text{ kA m}^{-2}$$

Derive Equation 3-28. For a reaction at 80 °C, and with  $(\alpha_a + \alpha_c) = 2$ , at what value for the overpotential will the error with the Tafel equation be less than 1 percent?

$$\text{error} = \frac{\text{Tafel} - BV}{BV} = \frac{T}{BV} - 1 = E$$

$$1 + E = \frac{T}{BV}$$

$$1 + E = \frac{i_o e^{\frac{\alpha_a F}{RT} \eta_s}}{i_o \left\{ e^{\frac{\alpha_a F}{RT} \eta_s} - e^{\frac{-\alpha_c F}{RT} \eta_s} \right\}}$$

$$\frac{1}{1 + E} = 1 - e^{\frac{-(\alpha_c + \alpha_a)F}{RT} \eta_s}$$

$$\frac{E}{1 + E} = e^{\frac{-(\alpha_c + \alpha_a)F}{RT} \eta_s}$$

$$|\eta_s| = \frac{RT}{F} \frac{1}{(\alpha_c + \alpha_a)} \ln \frac{E}{1 + E}$$

$E = 0.01$ ,  $T = 298$  K

$$|\eta_s| = \frac{B}{298} \frac{T}{(\alpha_c + \alpha_a)} = \frac{RT}{F} \frac{1}{(\alpha_c + \alpha_a)} \ln \frac{E}{1 + E}$$

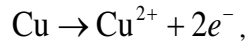
$$B = \frac{298R}{F} \frac{1}{(\alpha_c + \alpha_a)} \ln \frac{E}{1 + E} = 0.119 \text{ V}$$

b) at 80 °C,  $\alpha_c + \alpha_a = 2$

$$|\eta_s| = \frac{RT}{F} \frac{1}{(\alpha_c + \alpha_a)} \ln \frac{E}{1 + E} = 0.070 \text{ V}$$

### Problem 3-10

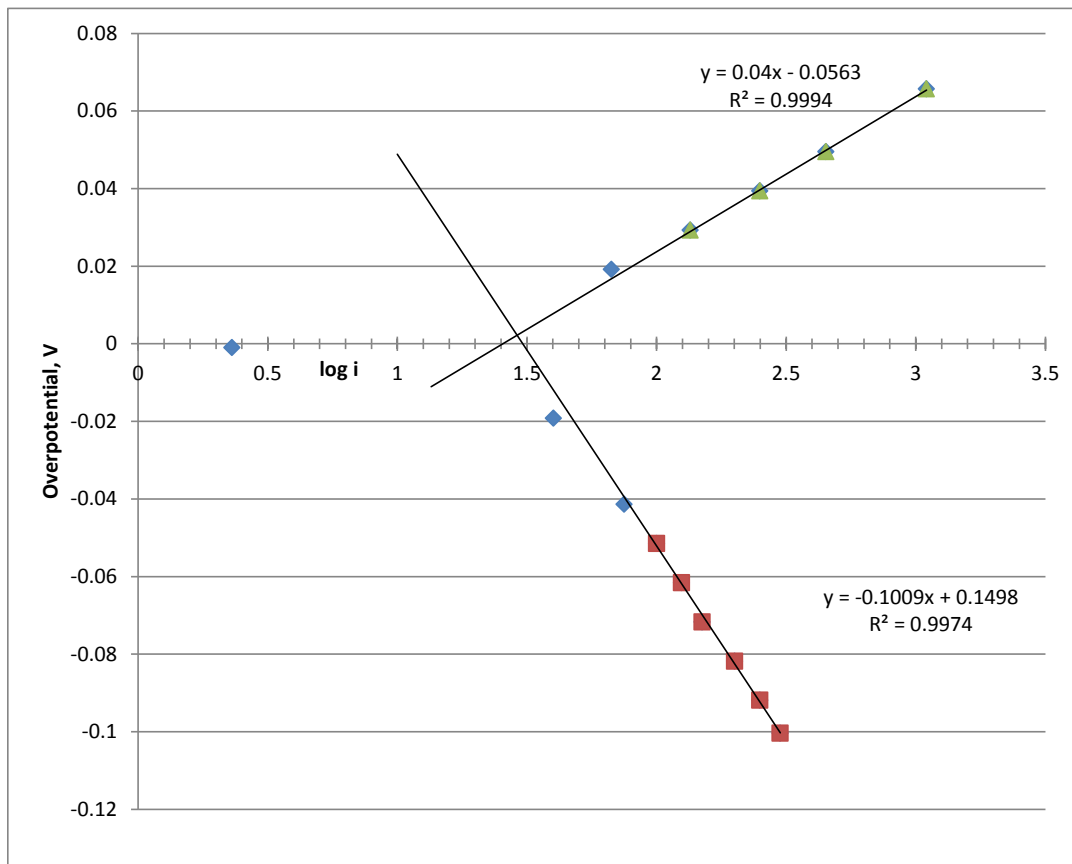
In order to model the deposition of copper, the following data have been collected for 1 M CuSO<sub>4</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>. The temperature is 25 °C, and a copper plated reference electrode was used. From these data determine the parameters for the Butler-Volmer kinetic expression. The reaction is



$$U^{\theta} = 0.337 \text{ V}$$

I, A/m <sup>2</sup>	η <sub>s</sub> , V	I, A/m <sup>2</sup>	η <sub>s</sub> , V
-300	-0.1004	-40	-0.0192
-250	-0.0919	-2.3	-0.00101
-200	-0.0818	67	0.0192
-150	-0.0717	135	0.0293
-125	-0.0616	250	0.0394
-100	-0.0515	450	0.0495
-75	-0.0414	1100	0.0657

Option 1. Plot high and low overpotential on Tafel plot

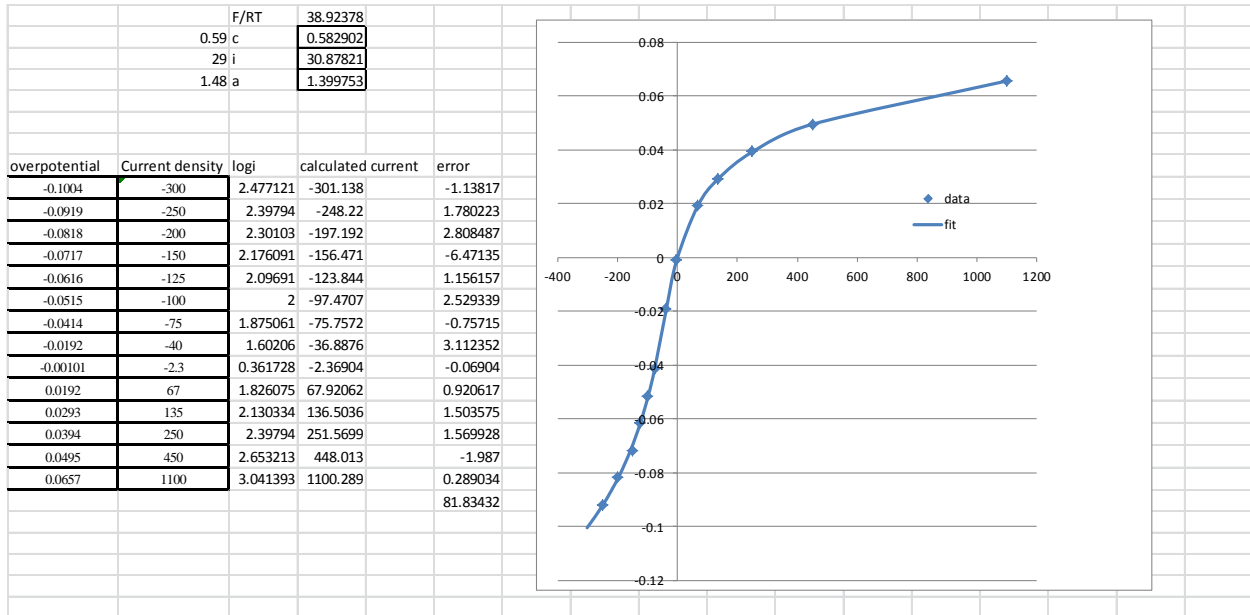


Point where the lines cross,  $i_o = 10^{1.45} = 28 \text{ A/m}^2$

Slopes of line are  $2.303RT/(F\alpha)$

### Problem 3-10

Option 2. One can fit the entire range with the full Butler Volmer equation.



	Option 1	Option 2
$\alpha_c$	0.59	0.58
$\alpha_a$	1.48	1.40
$i_0$	28	30.9 A/m <sup>2</sup>

In section 3.7, equation 3-33 was developed using Tafel kinetics, illustrating the effect of mass transfer on the current density. Derive the equivalent expression for linear kinetics. Explain the difference in shape of graphs for  $i$  vs.  $\eta_s$  between linear and Tafel kinetics.

For linear kinetics

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

at steady state

$$nFk_c(c_b - c_s) = i_o(\alpha_c + \alpha_a) \frac{F}{RT} \eta_s$$

$$nFk_c(c_b - c_s) = i_{o,ref} \frac{c_s}{c_b} (\alpha_c + \alpha_a) \frac{F}{RT} \eta_s = i$$

$$(c_b - c_s) = \frac{i}{nFk_c} \quad c_s = \frac{i}{i_{o,ref}} c_b \frac{RT}{(\alpha_c + \alpha_a) \eta_s F}$$

$$c_b \left\{ 1 - \frac{i}{i_{o,ref}} \frac{RT}{(\alpha_c + \alpha_a) \eta_s F} \right\} = \frac{i}{nFk_c}$$

$$i \left\{ \frac{1}{nFk_c c_b} + \frac{RT}{i_{o,ref} (\alpha_c + \alpha_a) \eta_s F} \right\} = 1$$

$$i = \frac{1}{\frac{1}{nFk_c c_b} + \frac{RT}{i_{o,ref} (\alpha_c + \alpha_a) F \eta_s / RT}}$$

$$i_{lim} = nFk_c c_b$$

$$\frac{i}{i_{lim}} = \frac{1}{1 + \frac{i_{lim}}{i_o(\alpha_c + \alpha_a) F \eta_s / RT}}$$



Metal is deposited via a two-electron reaction with current voltage data as shown at the right. The equilibrium potential is  $-0.5$  V vs. the same reference electrode used to measure the data. The bulk concentration is  $100 \text{ mol/m}^3$ . You may assume that the exchange current density is linearly dependent on the concentration of the reactant (*i.e.*, you may use Eq. 3-33). Assume  $25^\circ\text{C}$ .

- Is mass transfer important? If so, please determine a value for the mass-transfer coefficient.
- Assuming Tafel kinetics, find the values of  $\alpha_c$  and  $i_o$ . Comment on the applicability of this assumption. Can the normal Tafel fitting procedure be used for this part? Why or why not?
- If the mass-transfer coefficient were reduced by a factor of 2 (cut in half), please predict the current that would correspond to an applied potential of  $-0.9$  V.

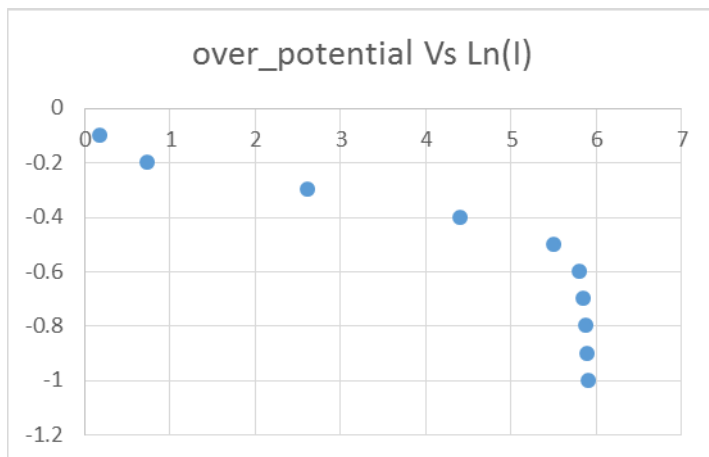
Additional Hints: You need to consider carefully which points you use in fitting the kinetic parameters. Also, it is a good idea to normalize the error when fitting the current.

a) Inspection of the data clearly shows the current plateauing at about  $360 \text{ A m}^{-2}$ . This feature is an indication of mass-transfer limitations.

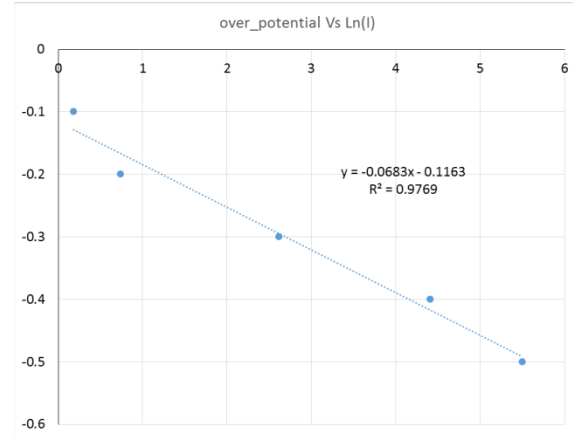
$$i_{lim} = nFk_c c_b$$

$$k_c = \frac{i_{lim}}{nF c_b} = \frac{360}{(2)(96485)(100)} = 1.87 \times 10^{-5} \text{ m s}^{-1}$$

b) The kinetic parameters can be obtained from a Tafel plot,



We clearly see from the Semi log Tafel plot of all of the data that the line we get is not straight, thus the Tafel slope cannot be used since the points are out of Tafel region. However we may smartly choose the first few data points in the kinetic region and use those to fit to a line to get the Tafel slope, as in graph. Then this slope can be used to find the BV parameters and by doing so we get the following values



$$\eta_s = -0.1163 - 0.068 \ln i$$

$$0.0683 = \frac{RT}{\alpha_c F} \quad \alpha_c = 0.378$$

$$\text{at } i=1, \eta_s = -0.1163$$

$$i_o = e^{\frac{-\alpha_c F}{RT} \eta_s}$$

$$i_o = 0.077 \text{ A m}^{-2}$$

c)

$$V_{app} = -0.9 \text{ V} \quad \eta_s = -0.4 \text{ V}$$

$$i_{lim} = \frac{360}{2} = 180 \text{ A m}^{-2}$$

$$\frac{1}{i} = \frac{1}{i_{lim}} + \frac{1}{i_o e^{\frac{-\alpha_c F}{RT} \eta_s}}$$

Solve for the current density

$$i = -24 \text{ A m}^{-2}$$

**Chapter 3 problem 13, create polarization curve for hydrogen oxygen fuel cell**

$$I = 10000 \text{ [A/m}^2\text{]} \text{ set current density}$$

for polarization curve, comment out line above and use table

$$U_c = 1.229 \text{ [V]}$$

**ANODE POLARIZATION**

linear kinetics

$$i_{oa} = 14000 \text{ [A/m}^2\text{]}$$

$$I = i_{oa} \cdot 2 \cdot \frac{F}{R \cdot T} \cdot -\phi_{2a}$$

$$\eta_a = -\phi_{2a}$$

**OHMIC POLARIZATION**

$$L = 0.00004 \text{ [m]}$$

$$\kappa = 10 \text{ [1/\Omega-m]}$$

$$R_{ohm} = \frac{L}{\kappa}$$

$$\eta_{ohm} = I \cdot R_{ohm}$$

$$\phi_{2c} = \phi_{2a} - \eta_{ohm}$$

**CATHODE POLARIZATION**

$$i_{oc} = 9.0 \times 10^{-7} \text{ [A/m}^2\text{]}$$

$$I = i_{oc} \cdot \exp \left[ -a_c \cdot \frac{F}{R \cdot T} \cdot (\phi_{1c} - \phi_{2c} - U_c) \right]$$

$$a_c = 1$$

$$F = 96485 \text{ [Coulomb/mol]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298 \text{ [K]}$$

$$\eta_c = \phi_{1c} - \phi_{2c} - U_c$$

**SOLUTION**

**Unit Settings: SI C kPa kJ mass deg**

$$a_c = 1$$

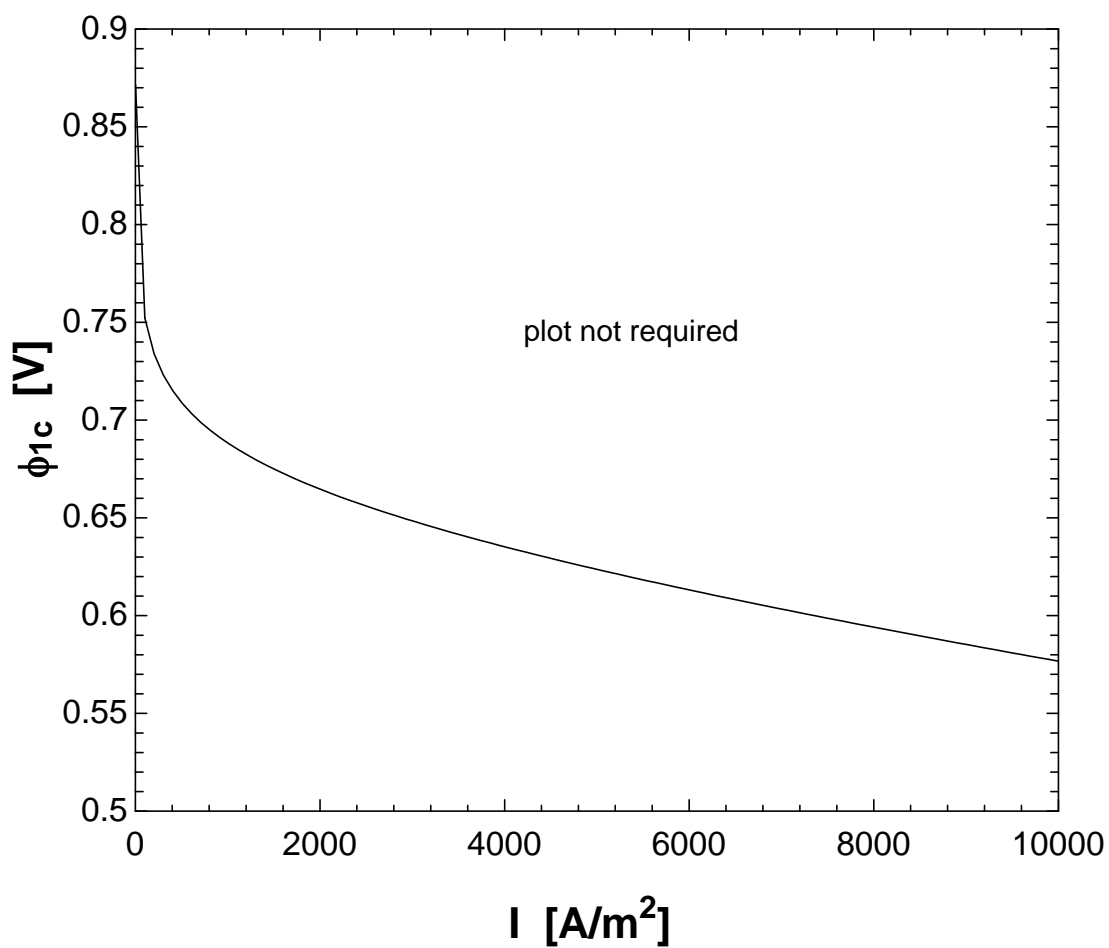
$$\eta_c = -0.594 \text{ [V]}$$

$$\eta_a = 0.009171 \text{ [V]}$$

$$\eta_{ohm} = 0.04 \text{ [V]}$$

$F = 96485$  [Coulomb/mol] $I = 10000$  [A/m<sup>2</sup>] $i_{oa} = 14000$  [A/m<sup>2</sup>] $i_{oc} = 9.000E-07$  [A/m<sup>2</sup>] $\kappa = 10$  [1/ $\Omega$ -m] $L = 0.00004$  [m] $\phi_{1c} = 0.5859$  [V] $\phi_{2a} = -0.009171$  [V] $\phi_{2c} = -0.04917$  [V] $R = 8.314$  [J/mol-K] $R_{ohm} = 0.000004$  [ $\Omega$ -m<sup>2</sup>] $T = 298$  [K] $U_c = 1.229$  [V]

No unit problems were detected.



**PROBLEM 3-14***Full cell Zn/Ni battery**part B and C*

$$I = -821 \text{ [A/m}^2\text{];}$$

*current density of cell*

$$\phi_{2m} = 2.0 \text{ [V]}$$

$$\phi_{m1} = 0 \text{ [V]} \text{ potential of zinc metal arbitrarily set to zero}$$

*Butler Volmer Kinetics for Zn reaction*

$$I = Rf1 \cdot i_{10} \cdot [\exp(\eta_{a1} \cdot frt \cdot aa1) - \exp(-\eta_{c1} \cdot frt \cdot ac1)]$$

$$Rf1 = 2 \text{ roughness factor for Zn electrode}$$

$$i_{10} = 60 \text{ [A/m}^2\text{]} \text{ exchange current density for Zn}$$

$$\eta_{a1} = \phi_{m1} - \phi_{21} - U1$$

$$U1 = 0 \text{ [V]}$$

$$F = 96485 \text{ [Coulomb/mol]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298 \text{ [K]}$$

$$frt = \frac{F}{R \cdot T}$$

$$aa1 = 1.5$$

$$ac1 = 0.5$$

*Ohm's law for separator*

$$L = 0.002 \text{ [m]} \text{ thickness of separator}$$

$$\kappa = 60 \text{ [1/\Omega-m]} \text{ conductivity of electrolyte}$$

$$\phi_{22} = \phi_{21} - L \cdot \frac{I}{\kappa}$$

*Butler-Volmer equation for Ni Reaction**reduction, therefore current is negative*

$$-I = Rf2 \cdot i_{20} \cdot [\exp(\eta_{a2} \cdot frt \cdot aa2) - \exp(-\eta_{c2} \cdot frt \cdot ac2)]$$

$$Rf2 = 100 \text{ roughness factor for Ni electrode}$$

$$i_{2o} = 0.61 \text{ [A/m}^2\text{]} \text{ exchange current density for Ni}$$

$$\text{eta2} = \phi_{2m} - \phi_{22} - U2$$

$$U2 = 1.74 \text{ [V]}$$

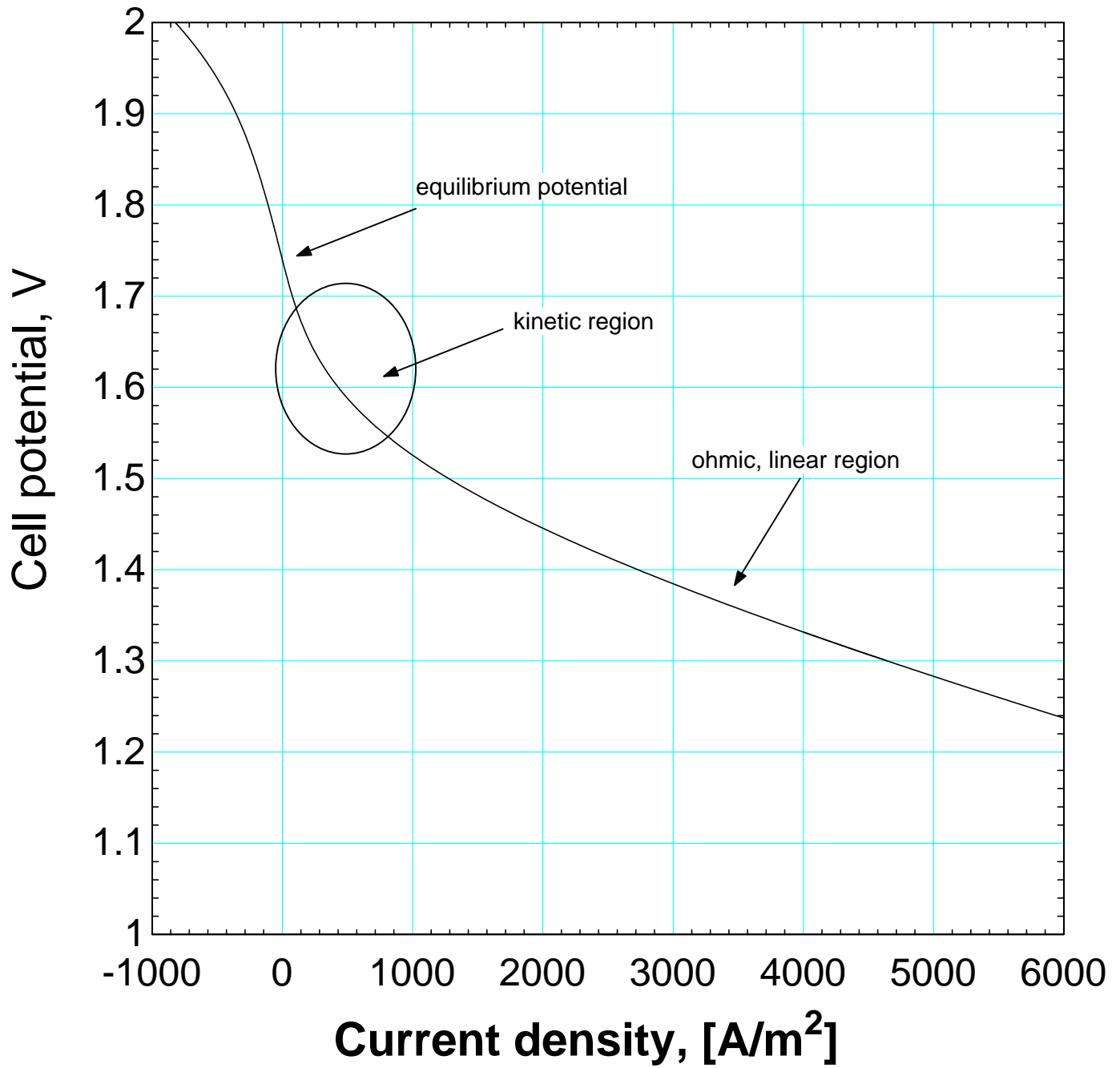
$$\text{aa2} = 0.5$$

$$\text{ac2} = 0.5$$

$$p1 = \phi_{21} - \phi_{22}$$

$$p2 = p1 + \text{eta1}$$

$$p3 = p2 - \text{eta2}$$

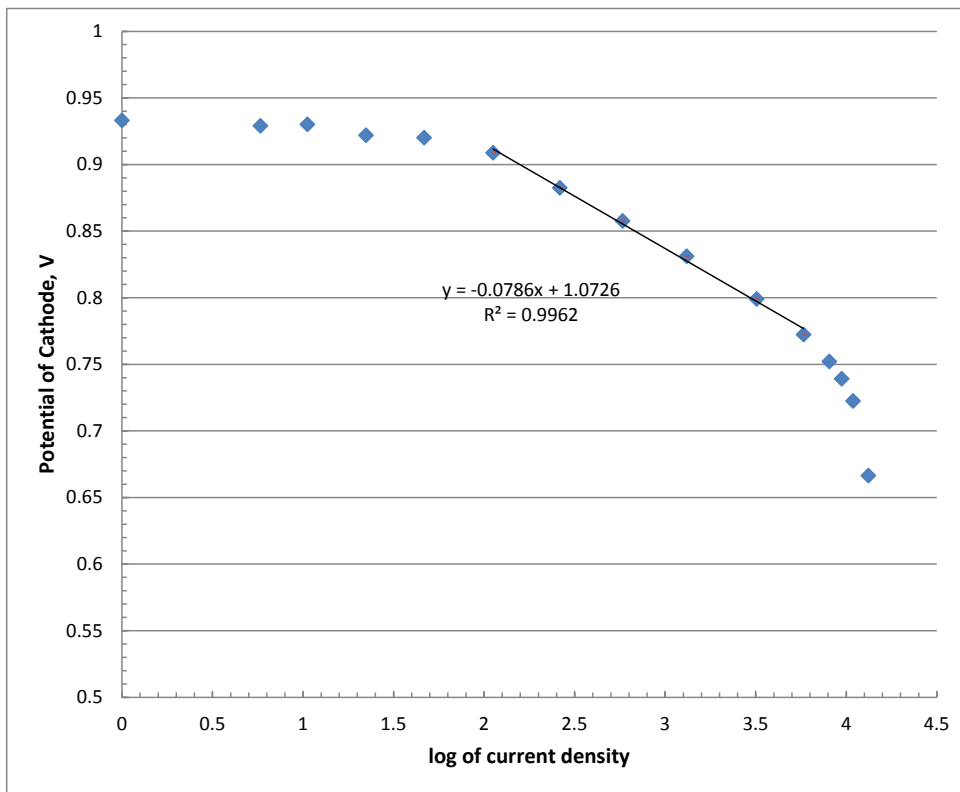


### Problem 3-15

1. The following data are provided for the oxygen reduction reaction in acid media at 80 °C. The potential of the cathode,  $\phi_1$ , is measured with respect to a hydrogen reference electrode, which in this case also serves as the counter electrode. Additionally, any ohmic resistance has been removed from the potentials tabulated.
  - a. Plot these data on a semi-log plot (potential vs.  $\log i$ ). You may assume that the kinetics for the hydrogen reaction is fast, and thus the anode polarization is small. What is the Tafel slope (mV/decade) in the mid-current range?
  - b. Even though ohmic polarizations have been removed, at both low and high currents, the slope is not linear on the semi-log plot. Suggest reasons why this may be the case.

$I, \text{A/m}^2$	$\phi_1, \text{V}$	$I, \text{A/m}^2$	$\phi_1, \text{V}$	$I, \text{A/m}^2$	$\phi_1, \text{V}$
1	0.933	112.1	0.9087	5815	0.7722
5.83	0.929	262.3	0.8825	8081	0.7521
10.58	0.93	582.2	0.8576	9442	0.7391
22.26	0.922	1317	0.831	10905	0.7223
46.64	0.92	3201	0.799	13247	0.6664

#### Solution



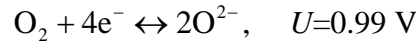
The Tafel slope is 79 mV/decade



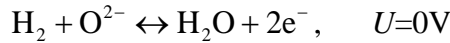
### Problem 3-15

b. At high current densities, mass transfer effects may be present. As the concentration of oxygen at the electrode decreases, the overpotential increases and the cell potential decreases. The separator of the fuel cell is not perfect, a small amount of hydrogen from the anode can dissolve and diffuse across the membrane. This hydrogen reacts with oxygen at the cathode, resulting in a small amount of oxygen reduction even in the absence of external current flow. Furthermore, because the ORR is so sluggish, there is a large overpotential even for a small amount of hydrogen crossover.

One common fuel-cell type is the solid oxide fuel cell, which uses a solid oxygen conductor in place of an aqueous solution for the electrolyte. The two reactions are



and at the positive electrode



I, A m <sup>-2</sup>	V <sub>cell</sub> , V
-6981	1.5006
-4871	1.3554
-2946	1.2074
-967	1.0549
930	0.9047
2799	0.7545
4753	0.6020
6836	0.4518
9328	0.3000

Data for the polarization of a solid oxide fuel cell/electrolyzer are provided in the table. These potentials are the measured cell potentials, although the anodic overpotential is small and can be neglected. The temperature of operation is 973 K. The ohmic resistance of the cell is 0.067 Ω·cm<sup>2</sup>. After removing ohmic polarization, how well can the reaction rate for oxygen be represented by a Butler-Volmer kinetic expression? Comment of the values obtained

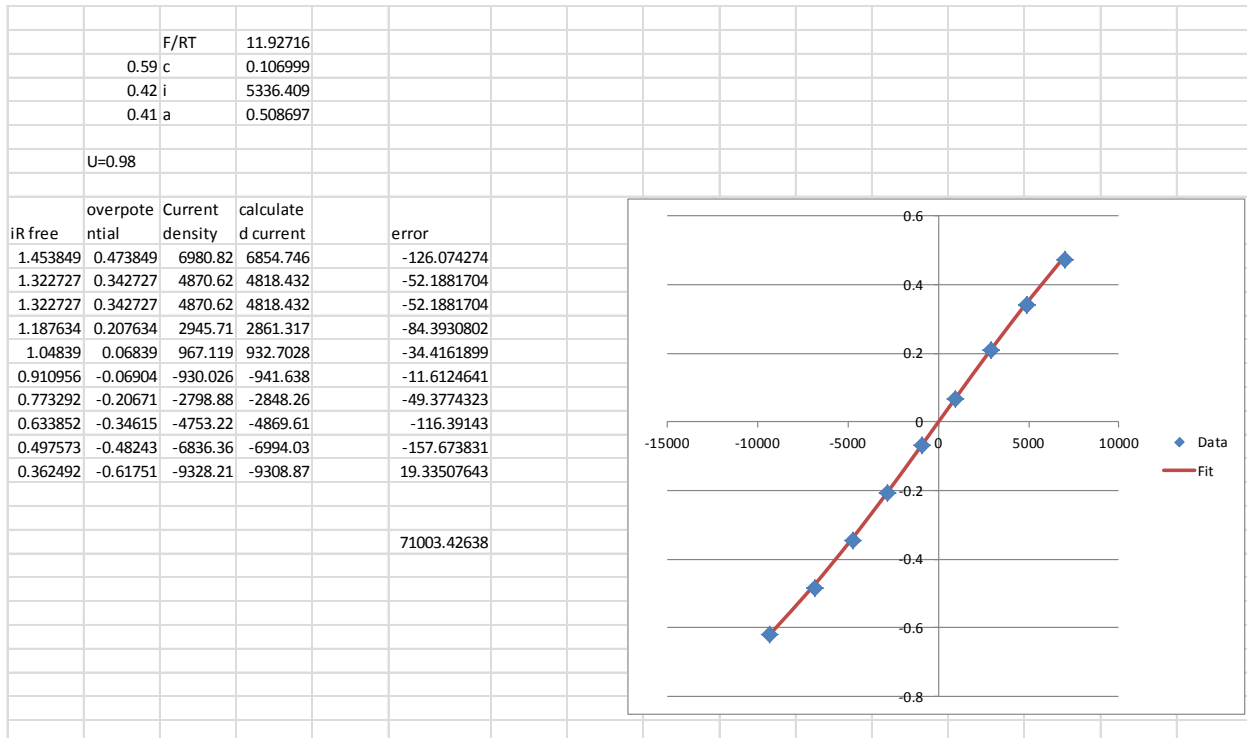
Neglecting the polarization at the anode,

$$V_{\text{cell}} = V_{\text{oc}} - IR_{\Omega} - \eta_{\text{cath}}$$

$$\eta_{\text{cath}} = V_{\text{oc}} - IR_{\Omega} - V_{\text{cell}}$$

use V<sub>oc</sub>=0.98 V

Make the correction for IR, plot the cathode polarization as a function of current density and fit with the Butler-Volmer equation



We obtain the following,

$$\begin{aligned}i_o &= 5336 \text{ A m}^{-2} \\ \alpha_a &= 0.51 \\ \alpha_c &= 0.11\end{aligned}$$

The fit is reasonable, but the reaction is a four electron reaction, and we would expect that  $\alpha_a + \alpha_c = 4$ , which is clearly not the case. Even though the fit is ok, there is no reason to believe that the mechanism is represented by the Butler-Volmer equation.

**PROBLEM 3-17***hydrogen gassing from Lead acid cell*

$$F = 96485 \text{ [Coulomb/mol]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 308.15 \text{ [K]}$$

$$\text{frt} = \frac{F}{R \cdot T}$$

$$te = 2 \text{ temperature effect}$$

*negative electrode of lead acid cell*

$$io_n = te \cdot 100 \text{ [A/m}^2\text{]}$$

$$\phi_1 = -0.44 \text{ V}$$

$$I + I_h = -495.2 \text{ [A/m}^2\text{]} \text{ value calculated in problem 3b}$$

$$U_n = -0.356 \text{ [V]}$$

$$\eta^n = \phi_1 - U_n$$

$$I = io_n \cdot [\exp(0.5 \cdot \eta^n \cdot \text{frt}) - \exp(-0.5 \cdot \eta^n \cdot \text{frt})]$$

*add hydrogen reaction*

$$io_h = 6.6e-10 \text{ [A/m}^2\text{]};$$

*pure Pb*

$$io_h = te \cdot 0.0003715 \text{ [A/m}^2\text{]} \text{ Pb-Sb}$$

$$U_h = 0 \text{ [V]}$$

$$\eta^h = \phi_1 - U_h$$

$$I_h = io_h \cdot [\exp(0.5 \cdot \eta^h \cdot \text{frt}) - \exp(-0.5 \cdot \eta^h \cdot \text{frt})]$$

*calculate current efficiency*

$$\eta^c = \frac{I}{I + I_h}$$

*current efficiency at 298*

$$\eta_c = 0.9961, \phi_1 = -0.44 \text{ V,}$$

SOLUTION

**Unit Settings: SI C kPa kJ mass deg**

$$\eta_c = 0.9965$$

$$\eta_n = -0.05509 \text{ [V]}$$

$$\text{frt} = 37.66 \text{ [1/V]}$$

$$I_h = -1.709 \text{ [A/m}^2\text{]}$$

$$i_{on} = 200 \text{ [A/m}^2\text{]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$te = 2$$

$$U_n = -0.356 \text{ [V]}$$

$$\eta_h = -0.4111 \text{ [V]}$$

$$F = 96485 \text{ [Coulomb/mol]}$$

$$I = -493.5 \text{ [A/m}^2\text{]}$$

$$i_{oh} = 0.000743 \text{ [A/m}^2\text{]}$$

$$\phi_1 = -0.4111 \text{ [V]}$$

$$T = 308.2 \text{ [K]}$$

$$U_h = 0 \text{ [V]}$$

No unit problems were detected.

**Problem 3-18**

$$MW = 0.32924 \text{ [kg/mol]}$$

$$T = 298.15 \text{ [K]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$m = 0.00001 \text{ [kg]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

$$c_K = 3 \cdot \frac{m}{MW \cdot V}$$

$$c_{ferri} = c_{ferro}$$

$$c_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

$$U^{\circ} = 0.26 \text{ [V]} \text{ because potential is at std potential, the concentration of ferri and ferro are the same}$$

$$U = U^{\circ} + a$$

$$a = 0.01 \text{ [V]}$$

$$a = R \cdot \frac{T}{F} \cdot \ln \left[ \frac{c_{n_{ferri}}}{c_{n_{ferro}}} \right]$$

$$c_{n_{ferri}} + c_{n_{ferro}} = 2 \cdot c_{ferri}$$

**SOLUTION****Unit Settings: SI C kPa kJ mass deg**

$$a = 0.01 \text{ [V]}$$

$$c_{n_{ferri}} = 0.1811 \text{ [mol/m}^3\text{]}$$

$$c_{n_{ferro}} = 0.1227 \text{ [mol/m}^3\text{]}$$

$$c_{ferri} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$c_{ferro} = 0.1519 \text{ [mol/m}^3\text{]}$$

$$c_K = 0.9112 \text{ [mol/m}^3\text{]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$m = 0.00001 \text{ [kg]}$$

$$MW = 0.3292 \text{ [kg/mol]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298.2 \text{ [K]}$$

$$U = 0.27 \text{ [V]}$$

$$U^{\circ} = 0.26 \text{ [V]}$$

$$V = 0.0001 \text{ [m}^3\text{]}$$

No unit problems were detected.

