Read Chapter 2, answer the following problems, and indicate with whom you worked: ______________.

(1) Do problems 1.1, 1.5, 1.6, and 1.10 in Bard and Faulkner (B&F).

Answers: See answer key.

**Problem 1.1** (a). In approaching this kind of problem, it is useful to list all the couples in Table C.1 that are relevant to the system.

<table>
<thead>
<tr>
<th>$E^0_{\text{vs. NHE (V)}}$</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.229</td>
<td>$O_2 + 4H^+ + 4e \rightleftharpoons H_2O$</td>
</tr>
<tr>
<td>1.188</td>
<td>$Pt^{2+} + 2e \rightleftharpoons Pt$</td>
</tr>
<tr>
<td>0.340</td>
<td>$Cu^{2+} + 2e \rightleftharpoons Cu$</td>
</tr>
<tr>
<td>0.159</td>
<td>$Cu^{2+} + e \rightleftharpoons Cu^+$</td>
</tr>
<tr>
<td>0.000</td>
<td>$2H^+ + 2e \rightleftharpoons H_2$</td>
</tr>
<tr>
<td>-0.4025</td>
<td>$Cd^{2+} + 2e \rightleftharpoons Cd$</td>
</tr>
</tbody>
</table>

Alternatively, a graphical representation may prove useful. Here, the standard or formal potentials for each redox couple are plotted on a potential axis. The species present in solution are underlined. Note the reduced half of the couple is noted toward more negative potentials. The vertical line indicates the approximate potential range where both halves of the redox couple can exist. For electrode potentials positive of a given line, the oxidized half of the couple is stable at the electrode surface; for electrode potentials negative of the line, the reduced form is stable. Note that for $n = 1$, electrode potentials within 118 mV of $E^0$ require no less than 1% of either the oxidized or reduced halves of the couple as given by $\log \left[ \frac{[O]}{[I]} \right] = -n \left( E - E^0 \right) / 0.059$.

The composition of the system dictates that the rest (zero current) potential be more positive than $E^0_{Cu^{2+}/Cu}$ and more negative than $E^0_{O_2/H_2O}$ or $E^0_{Pt^{2+}/Pt}$, i.e., between about 0.34 V and 1.2 V vs. NHE. Graphically, this is apparent because this is the voltage range over which the oxidized ($Cu^{2+}$) and reduced species (Pt or H$_2$O) present in the solution are most adjacent on the graph. This defines a zone of stability set by the oxidized and reduced species. (Note that the cell would not be at equilibrium if oxidized and reduced species of two or more couples were present such that they were on the outer sides of the lines. For example, if the solution contained Cu and O$_2$, there would be a thermodynamic driving force for these species to react spontaneously to form water and $Cu^{2+}$.) Here, the potential is not well defined in a thermodynamic sense; the electrode is not well poised, because no couple has both oxidized and reduced forms present. Calculation of the
(b) $E^0(\text{Sn}^{4+/2+}) = 0.15 \text{ V vs. SHE}$ and since both halves of this redox couple are present, this dictates the open-circuit potential. Also, because the reaction quotient is simply $[\text{Sn}^{2+}]/[\text{Sn}^{4+}]$ and both are at 0.01 M, $E_{\text{oc}} = E^0(\text{Sn}^{4+/2+}) = 0.15 \text{ V vs. SHE}$. When the potential is moved in the negative direction, immediately, $\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$ at $-0.09 \text{ V vs. SCE}$ (because $= 0.15 \text{ V} + (-0.2412 \text{ V})$). When the potential is moved in the positive direction, immediately, $\text{Sn}^{2+} - 2e^- \rightarrow \text{Sn}^{4+}$ also at $-0.09 \text{ V vs. SCE}$ (because $= 0.15 \text{ V} + (-0.2412 \text{ V})$).

(c) Like in part (a), both halves of a redox couple are not present and thus $E_{\text{oc}}$ is ill-defined. $E^0(\text{Zn}^{2+/0}) = -0.7626$, $E^0(\text{Cd}^{2+/0}/\text{Cd(Hg)}) = -0.3515$, $E^0(\text{H}^+/\text{H}_2) = 0$, $E^0(\text{Hg}_2\text{Cl}_2/\text{HgCl}) = +0.26816$, $E^0(\text{Hg}^{2+/0}) = +0.7960$, $E^0(\text{O}_2/\text{H}_2\text{O}) = +1.229$, $E^0(\text{Cl}_2/\text{Cl}^-) = +1.3583$, $E^0(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = +1.763$, all vs. SHE with the species present underlined. The flip from oxidized to reduced species occurs at $(0, +0.26816)$ V vs. SHE and so this is the $E_{\text{oc}}$ range. When the potential is moved in the negative direction, $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ at $-0.2412 \text{ V vs. SCE}$ (because $= 0 \text{ V} + (-0.2412 \text{ V})$). When the potential is moved in the positive direction, $2\text{Hg} + 2\text{Cl}^- - 2e^- \rightarrow \text{Hg}_2\text{Cl}_2$ at $+0.02696 \text{ V vs. SCE}$ (because $= 0.26816 \text{ V} + (-0.2412 \text{ V})$.}
Problem 1.5: From equation (1.2.10),

\[ q = EC_dA \left[ 1 - \exp \left( \frac{-t}{R_dC_dA} \right) \right] \]  

Area appears because \( C_d \) is expressed as capacitance per unit area. The time constant \( \tau \) is \( R_dC_dA \).

\[ q = \frac{E\tau}{R_s} \left[ 1 - \exp \left( \frac{-t}{\tau} \right) \right] \]

At complete charging (\( t \to \infty \)), \( q_{\infty} = E\tau / R_s \). At 95% of \( q_{\infty} \), time \( t_{95\%} \) is set by

\[ 0.95 \frac{E\tau}{R_s} = \frac{E\tau}{R_s} \left[ 1 - \exp \left( \frac{-t_{95\%}}{\tau} \right) \right] \]

This expression is rearranged to \( t_{95\%} = 3\tau \) at 95% completeness. For the specified conditions,

<table>
<thead>
<tr>
<th>( R_s / \Omega )</th>
<th>1</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau / \mu s )</td>
<td>2</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>( 3\tau / \mu s )</td>
<td>6</td>
<td>60</td>
<td>600</td>
</tr>
</tbody>
</table>

Problem 1.6: \( I = C \cdot v \) for LSV, and so \( C = (20 \ \mu F \ cm^{-2})(0.1 \ cm^2) = 2 \ \mu F = 2 \ \mu C \ V^{-1} \), and then just plug in the scan rate: For \( 0.02 \ V/s \), \( I = (2 \ \mu C \ V^{-1})(0.02 \ V \ s^{-1}) = 0.04 \ \mu A = 40 \ nA \); For \( 1 \ V/s \), \( I = (2 \ \mu C \ V^{-1})(1 \ V \ s^{-1}) = 2 \ \mu A \); For \( 20 \ V/s \), \( I = (2 \ \mu C \ V^{-1})(20 \ V \ s^{-1}) = 400 \ \mu A \)

Problem 1.10: Charge and potential are related as capacitance. The capacitance of aqueous interfaces is \( \sim 10 \ \mu F \ cm^{-2} \) irrespective of salt concentration and so for a \( 1 \ cm^2 \) electrode, \( C = 10 \ \mu F = 10 \ \mu C \ V^{-1} \). Multiply this by the desired potential change (\( 1 \ mV = 0.001 \ V \)) to get \( 10 \ nC \).

**Changing the concentration of electrolyte should not affect the double layer capacitor’s capacitance but will increase the Debye screening length.**

(2) Using the CRC Standard Reduction Potentials table, and the lecture notes for the reference electrode potentials vs. SHE, plot on a vertical line (with negative toward the top) the standard reduction potentials for \( H^+ \), \( H_2O_2 \), and \( O_2 \) (both of them) in acidic conditions versus the following references:

a. SHE  
b. SCE  
c. Ag/AgCl (KCl saturated)  
d. absolute (vacuum) scale  
e. “ground scale;” assume these were measured using a classical three-electrode potentiostat; include the potential for SHE for each of the four half reactions (i.e. reduction of \( H^+ \), \( H_2O_2 \), and \( O_2 \)).
Answers:

(3) Integral to the function of a classical three-electrode potentiostat are three different types of operational amplifiers each with feedback. With this in mind, answer the following.

a. What is the gain when $R_{\text{feedback}} = 100 \text{ kOhm}$ and $R = 100 \text{ Ohm}$?
   i. Then, explain where the power comes from that results in this gain in potential.

b. The voltage follower at the RE has a gain of 1. Why, then, do we use it?

c. How, and where, is the current that flows between the WE and CE measured?

d. Like in the lecture notes, draw a three-electrode $J$–$E$ curve and label the predominant redox processes that occur for an aqueous solution of deaerated HCl at standard state.
   i. Between which two electrodes does the majority of the current flow?
   ii. Between which two electrodes is the potential, $E$, measured?
   iii. On this plot, draw the response from a counter electrode made from the same material as the WE but whose geometric surface area is 10 times larger.
   iv. Explain the rationale for choosing the location, size, and material of the CE.

e. Now consider a solution that consists of HCl and H$_2$ at standard state. If the size and material of the CE is identical to that of the WE, and the RE (SHE) is placed exactly halfway between the WE and CE, draw the response of the WE (versus the RE) and CE (versus the RE) when the potential is swept in the negative direction starting at the open-circuit condition.
   i. Would a Pt wire have made for a good quasireference electrode in place of the RE (SHE)? Why or why not?

Answers: (a) gain = 100,000/100 = 1000; the power for this gain comes from “the muscles” which are two other inputs into the op amp and are connected to a power supply

(b) So that little current is sourced from the RE based on Rule #1 (for op amps with feedback) and thus little redox chemistry occurs in solution to possibly change the potential of the RE.
(c) Measure the potential drop across the resistor in parallel to the WE op-amp using a high-impedance voltmeter; the current that flows is calculated using Ohm’s law after measuring the potential drop across the resistor.

(d)

(i) WE and CE; (ii) WE and RE; (iii) response should be opposite of that of the WE but at a given potential should pass ten times the current; however, the current density should not change and so the graph of the CE response on a $J$–$E$ curve should look identical to that of the WE. If you made an $I$–$E$ curve instead, I would have looked like the data at the right, in green:

(iv) Location: Far from the WE so that species generated through redox chemistry cannot react at the WE; also, so that the potential drop in solution from the WE to RE ($R_u$) is a small fraction of the total ohmic potential drop ($R_s$); Size: Large so that a large potential need not be applied to it (see part d); Material: One that is catalytic for many reactions and does not corrode/dissolve into solution because those species could then interact with your WE

(e) See next page.

(i) Yes (maybe). You could have replaced the SHE with a Pt wire because the solution had a well-defined potential which is set by $H^+$ and $H_2$ which turned the Pt wire into a non-polarizable RE. However, it will not be perfect because the Pt wire is in solution and thus any changed in the concentration of $H^+$ or $H_2$ due to redox chemistry at the WE and CE will affect the RE potential. (This should be rather small as long as the RE is not really close to either the WE or the CE.)
(4) In Forman, Chen, Chakthranont, and Jaramillo, *Chemistry of Materials*, 2014, 26, 958 (see class website), the electrochemically active surface area of various WEs was indirectly calculated using the data shown in Figure 3. Based on this, answer the following:

a. For Figure 3a, why did the authors choose such a narrow scan window?
   i. At approximately what negative potential would you expect a faradaic reaction to occur? And, what faradaic reaction is likely to occur there?

b. Using the data at the three fastest scan rates in Figure 3b, calculate the average capacitance \( (C_{V^{-1} \text{cm}^{-2}}) \) for each high-surface-area electrode. (Average three values per electrode, for four electrodes.)

b. How did the authors determine the roughness factor (RF) in Figure 3c?

Answers: (a) **So that they would only pass non-Faradaic current**: (i) \( E^\circ(\text{H}^+/\text{H}_2) = -0.2412 \) V vs. SHE and **protons would be reduced to \( \text{H}_2 \) at roughly that potential**.
Because the electrolyte was pH 13.6 NaOH, the resulting shift in \( E \) is \( 0.05916 \) V x 13.6 = 0.804576 V negative. Thus, \( E = -0.2412 \) V – 0.804576 V = **-1.045776 V vs. SCE**
SHE, and \( \text{H}_2 \) evolution

(b) \( (J/\nu) \) has units of \( (\mu\text{A cm}^{-2}) / (\text{mV s}^{-1}) = ((\mu\text{C s}^{-1} \text{cm}^{-2}) / (\text{mV s}^{-1})) \), which equals \( \mu\text{C mV}^{-1} \text{ cm}^{-2} = \mu\text{F cm}^{-2} \) which is capacitance, so just divide the current density by the scan rate (and recall that a perfectly flat and atomically smooth planar electrode will have a capacitance of \( \sim 10 \mu\text{F cm}^{-2} \))

- **HSE 1**: 145 / 500 = 0.29 mF cm\(^{-2}\) = 290 \( \mu\text{F cm}^{-2}\)  
  55 / 200 = 0.275 mF cm\(^{-2}\) = 275 \( \mu\text{F cm}^{-2}\)  
  30 / 100 = 0.3 mF cm\(^{-2}\) = 300 \( \mu\text{F cm}^{-2}\); **average is \( \sim 288 \mu\text{F cm}^{-2} \)**

- **HSE 2**: 290 / 500 = 580 \( \mu\text{F cm}^{-2}\)  
  115 / 200 = 575 \( \mu\text{F cm}^{-2}\)  
  55 / 100 = 550 \( \mu\text{F cm}^{-2}\); **average is \( \sim 568 \mu\text{F cm}^{-2} \)**

- **HSE 3**: 405, 160, 85 \( \mu\text{F cm}^{-2}\) results in 810, 800, 850 \( \mu\text{F cm}^{-2}\), with an **average of \( \sim 820 \mu\text{F cm}^{-2} \)**

- **HSE 4**: 495, 200, 100 \( \mu\text{F cm}^{-2}\) results in 990, 1000, 1000 \( \mu\text{F cm}^{-2}\), with an **average of \( \sim 997 \mu\text{F cm}^{-2} \)**
(c) They divided the capacitance of each high-surface-area electrode by the capacitance of a model, nominally perfectly atomically smooth, planar electrode. However, by AFM they determined that their model electrode (Planar ITO) was not perfectly smooth and assigned it a roughly factor of 1.1 which they then used to correct all of the roughness factors.