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

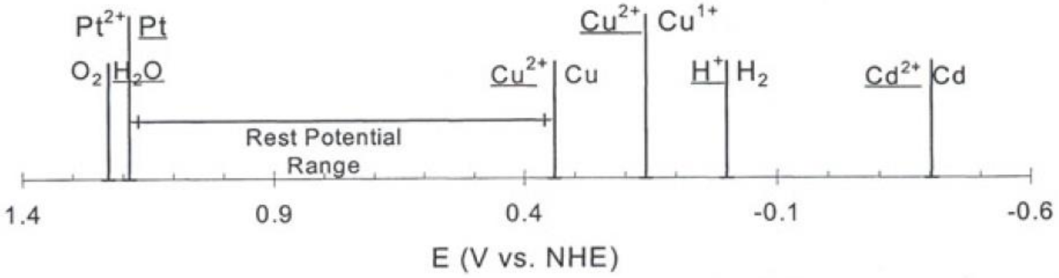
(1) Do problems 1.1, 1.5, 1.6, and 1.10 in Bard and Faulkner (B&F).

<u>Answers</u>: 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.

E^0 vs. NHE (V)	Reaction
1.229	$O_2 + 4H^+ + 4e \rightleftharpoons H_2O$
1.188	$Pt^{2+} + 2e \rightleftharpoons Pt$
0.340	$Cu^{2+} + 2e \rightleftharpoons Cu$
0.159	$Cu^{2+} + e \rightleftharpoons Cu^+$
0.000	$2H^+ + 2e \rightleftharpoons H_2$
-0.4025	$Cd^{2+} + 2e \rightleftharpoons Cd$

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 $\log \frac{[O]}{[R]} = -n\left(E - E^0\right)/0.059$.



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_2O) 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 equilibrium potential by the Nernst equation cannot be made.

Current will flow when the potential is moved negatively from the rest potential 0.340 V (or 0.340+ (−0.2412) = 0.099 V vs. SCE) so that Cu^{2+} is reduced at the electrode surface first.

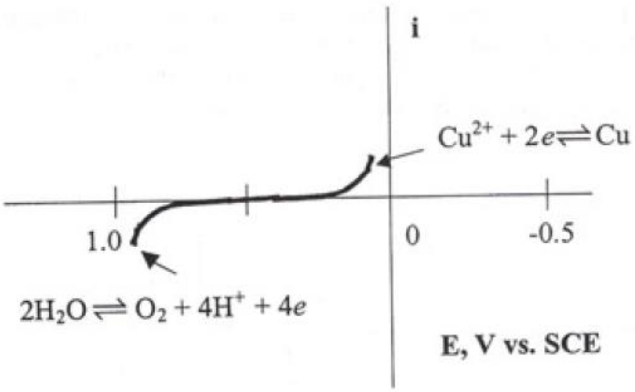
$Cu^{2+} + 2e \rightleftharpoons Cu$ (first reduction, ≈ 0.1 V vs. SCE)

A positive movement from the rest potential first causes significant current flow when platinum and water are oxidized.

$Pt \rightleftharpoons Pt^{2+} + 2e$ (first oxidations, ≈ 1.0 V vs. SCE)

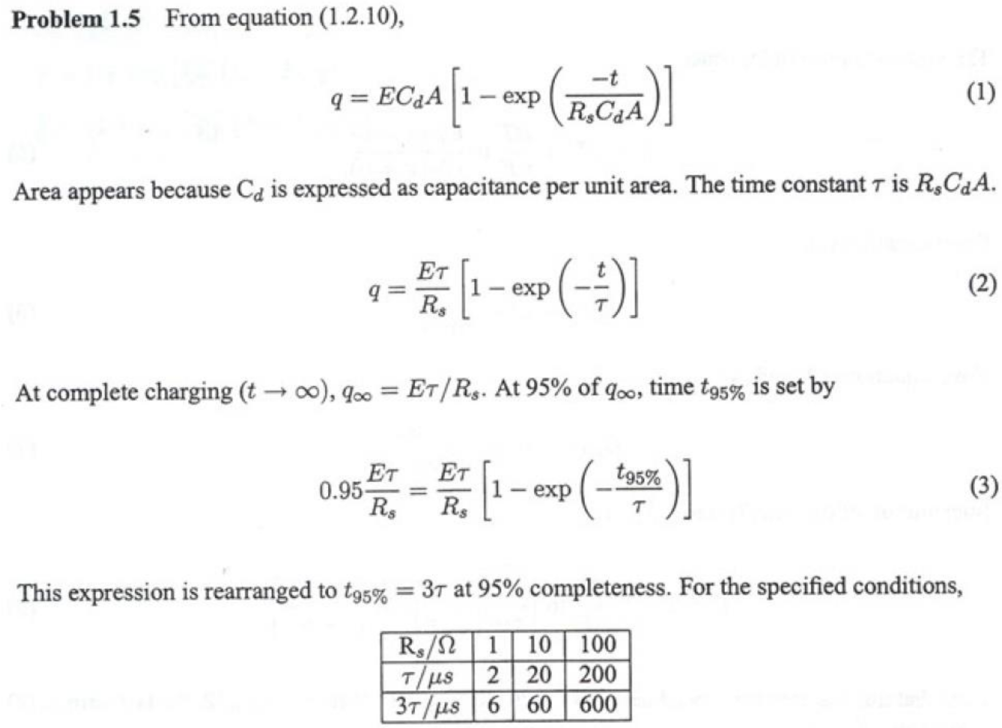
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e$

Actually, Pt would form a thin oxide film, then it would stabilize, and only the oxygen evolution reaction would occur. The current-potential curve would look like the following.



(b) $E^0(Sn^{4+/2+})$ = 0.15 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 $[Sn^{2+}]/[Sn^{4+}]$ and both are at 0.01 M, $E_{oc} = E^0(Sn^{4+/2+})$ = 0.15 V vs. SHE. **When the potential is moved in the <u>negative</u> direction, immediately, $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ at –0.09 V vs. SCE (because = 0.15 V + (–0.2412 V)). When the potential is moved in the <u>positive</u> direction, immediately, $Sn^{2+} - 2e^- \rightarrow Sn^{4+}$ also at –0.09 V vs. SCE (because = 0.15 V + (–0.2412 V)).**

(c) Like in part (a), both halves of a redox couple are not present and thus E_{oc} is ill-defined. $E^0(\underline{Zn^{2+/0}}) = -0.7626$, $E^0(\underline{Cd^{2+}}/Cd(Hg)) = -0.3515$, $E^0(\underline{H^+}/H_2) = 0$, $E^0(Hg_2Cl_2/\underline{Hg,Cl^-}) = +0.26816$, $E^0(Hg_2^{2+}/\underline{Hg}) = +0.7960$, $E^0(O_2/\underline{H_2O}) = +1.229$, $E^0(Cl_2/\underline{Cl^-}) = +1.3583$, $E^0(H_2O_2/\underline{H_2O}) = +1.763$, 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_{oc} range. **When the potential is moved in the <u>negative</u> direction, $2H^+ + 2e^- \rightarrow H_2$ at –0.2412 V vs. SCE (because = 0 V + (–0.2412 V)). When the potential is moved in the <u>positive</u> direction, $2Hg + 2Cl^- - 2e^- \rightarrow Hg_2Cl_2$ at +0.02696 V vs. SCE (because = 0.26816 V + (–0.2412 V)).**



Problem 1.5 From equation (1.2.10),

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

Area appears because C_d is expressed as capacitance per unit area. The time constant τ is R_sC_dA.

$$q = \frac{E\tau}{R_s}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \qquad (2)$$

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

$$0.95\frac{E\tau}{R_s} = \frac{E\tau}{R_s}\left[1 - \exp\left(-\frac{t_{95\%}}{\tau}\right)\right] \qquad (3)$$

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

R_s/Ω	1	10	100
$\tau/\mu s$	2	20	200
$3\tau/\mu s$	6	60	600

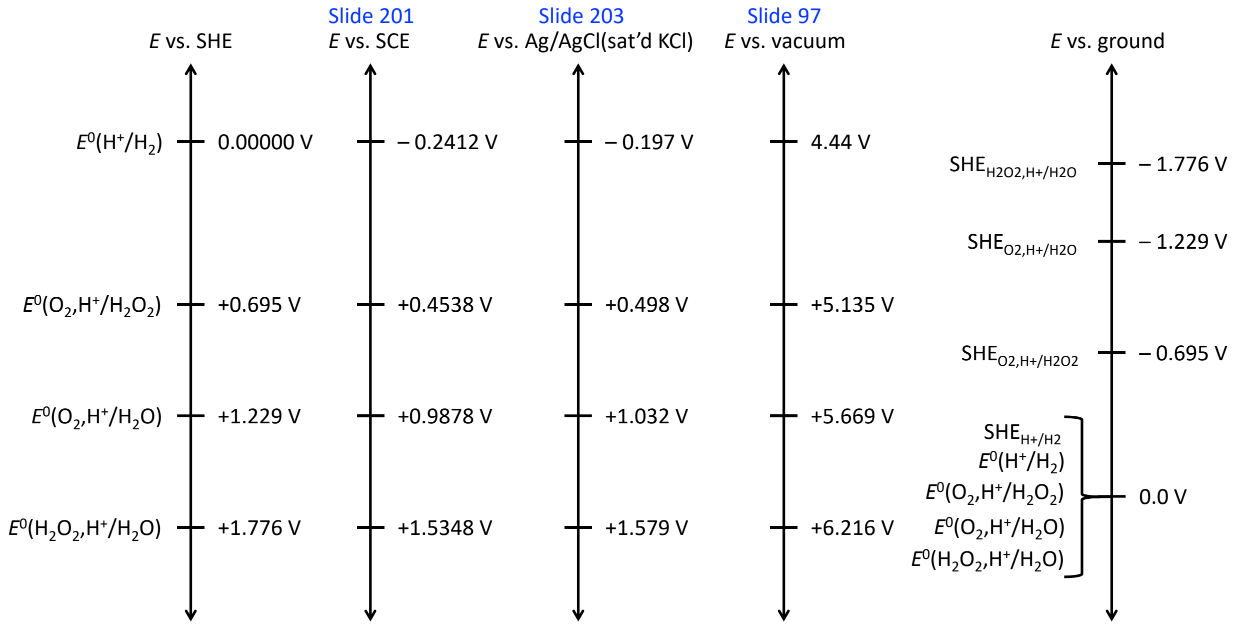
Problem 1.6: $I = C{\cdot}v$ for LSV, and so $C = (20\ \mu F\ cm^{-2})(0.1\ cm^2) = 2\ \mu F = 2\ \mu C\ V^{-1}$, and then just plug in the scan rate: <u>For 0.02 V/s</u>, $I = (2\ \mu C\ V^{-1})(0.02\ V\ s^{-1}) = 0.04\ \mu A$ = **40 nA**; <u>For 1 V/s</u>, $I = (2\ \mu C\ V^{-1})(1\ V\ s^{-1})$ = **2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

Problem 1.10: Charge and potential are related as capacitance. The capacitance of aqueous interfaces is ~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 op(erational) amp(lifier)s each with feedback. With this in mind, answer the following.

a. What is the gain when $R_{f(eedback)}$ = 100 kOhm and R = 100 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.

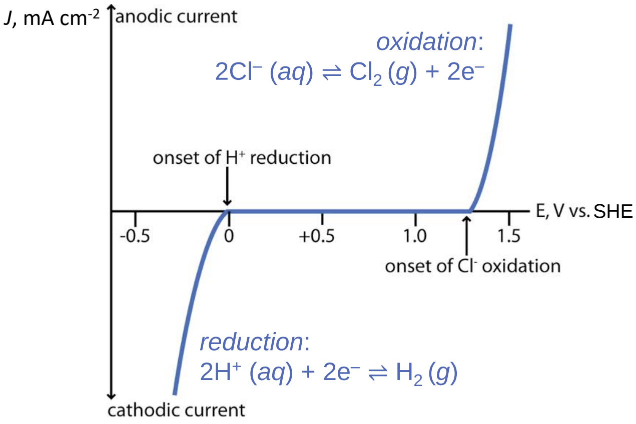
e. Now consider a solution that consists of HCl and H_2 at standard state. If the size and material of the CE is identical to that of the WE, and the RE (SHE) is placed exactly halfway between the WE and CE, draw the response of the WE (versus the RE) and CE (versus the RE) when the potential is swept 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**

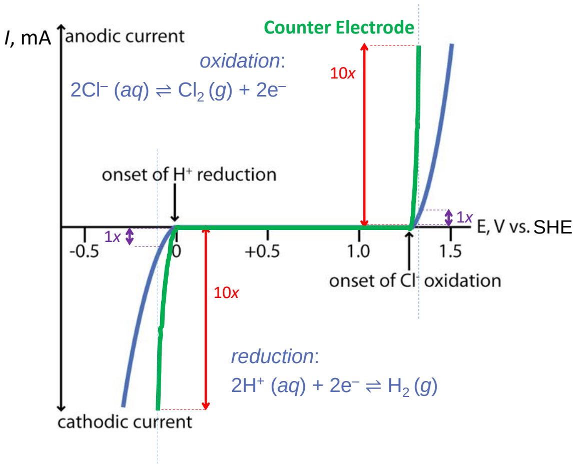
(b) **So that little current is sourced from the RE based on Rule #1 (for op amps with feedback) and thus little redox chemistry occurs in solution to possibly change the potential of the RE.**

(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)



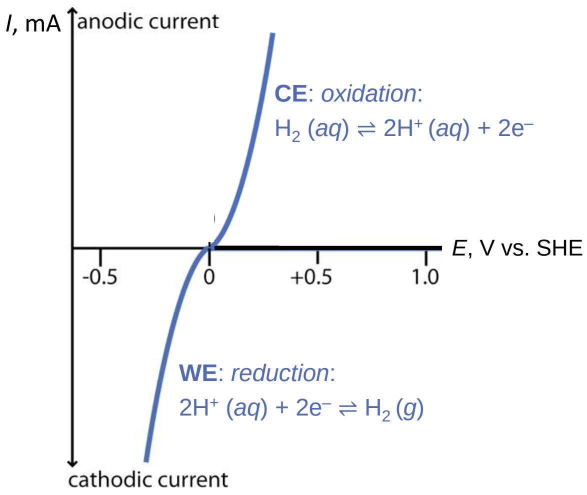
(i) **WE and CE**; (ii) **WE and RE**; (iii) response should be opposite of that of the WE but at a given potential should pass ten times the current; however, the current density should not change and so **the graph of the CE response on a *J*–*E* curve should look identical to that of the WE**. If 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} cm^{-2}) for each high-surface-area electrode. (Average three values per electrode, for four electrodes.)
- c. How did the authors determine the roughness factor (RF) in Figure 3c?

Answers: (a) **So that they would only pass non-Faradaic current**; (i) $E^0(H^+/H_2)$ = -0.2412 V vs. SHE and **protons would be reduced to 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 H_2 evolution

(b) (J / v) has units of (μA cm^{-2}) / (mV s^{-1}) = ((μC s^{-1} cm^{-2}) / (mV s^{-1})), which equals μC mV^{-1} cm^{-2} = mF 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 ~10 μF cm^{-2})

HSE 1: 145 / 500 = 0.29 mF cm^{-2} = 290 μF cm^{-2}
55 / 200 = 0.275 mF cm^{-2} = 275 μF cm^{-2}
30 / 100 = 0.3 mF cm^{-2} = 300 μF cm^{-2}; **average is ~288 μF cm^{-2}**
HSE 2: 290 / 500 = 580 μF cm^{-2}
115 / 200 = 575 μF cm^{-2}
55 / 100 = 550 μF cm^{-2}; **average is ~568 μF cm^{-2}**
HSE 3: 405, 160, 85 μF cm^{-2} results in 810, 800, 850 μF cm^{-2}, with an **average of ~820 μF cm^{-2}**
HSE 4: 495, 200, 100 μF cm^{-2} results in 990, 1000, 1000 μF cm^{-2}, with an **average of ~997 μF 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.**