

Midterm Exam

Instructions. This is a take-home, open-book exam due in **Lecture 22**. Late exams will not be accepted. You may consult any books, handouts, or online material listed on the syllabus, but you must work independently, without consulting any other person.

- Discharge of a Reaction-Limited Battery.** A battery has constant open circuit voltage V_O , constant internal series resistance R_{int} , and variable Faradaic resistance at one electrode, given by the symmetric Butler-Volmer equation

$$I = I_0 \left(e^{-e\eta/2kT} - e^{e\eta/2kT} \right)$$

Derive and sketch the voltage versus current, $V(I)$, for battery discharge at constant current.

***** SOLUTION *****

We begin with

$$V = V_O - \eta_{int} + \eta_c - \eta_a \tag{1}$$

where η_{int} is the loss from the internal resistance and $\eta_{a,c}$ is the activation loss from the Faradaic reactions at the cathode and anode. We know that the loss from internal resistance is given by

$$\eta_{int} = IR_{int}, \tag{2}$$

and the reaction loss, η_{act} , is given.

$$I = I_0 \left(e^{-e\eta_{act}/2kT} - e^{e\eta_{act}/2kT} \right) = -2I_0 \sinh(e\eta_{act}/2kT) \tag{3}$$

$$\eta_{act} = -\frac{2kT}{e} \sinh^{-1} \left(\frac{I}{2I_0} \right). \tag{4}$$

Note that way we have written the current relation is positive when net reduction is occurring. Thus, for current defined as positive during discharge, we are describing the cathode with this relation. We would introduce a sign change to describe the current at the anode where net oxidation is occurring. For simplicity, we assume the relation applies to the cathode and assume no losses at the anode. Thus,

$$V = V_O - IR_{int} - \frac{2kT}{e} \sinh^{-1} \left(\frac{I}{2I_0} \right), \tag{5}$$

which is sketched in Figure 1.

- Voltage Hysteresis in a Li-ion Battery.** The homogeneous free energy per site of a Li-ion battery cathode at filling fraction x is given by the regular solution model. The enthalpy of mixing is positive $h_0 > 0$, and the temperature is below the critical temperature for phase separation. Neglect the interfacial tension between phases and finite size effects. *Assume that nucleation is not possible.* The anode and electrolyte remain at constant chemical potentials, and the open circuit voltage is V^0 at half filling of the cathode.

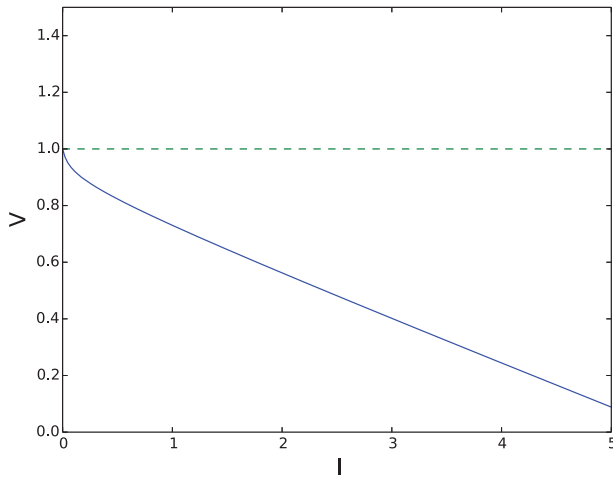


Figure 1: Sketch of I-V curve for P1. The dotted green line represents the open circuit voltage.

- (a) Write down and plot the open circuit voltage versus *mean* filling fraction x , for both homogeneous and phase-separated states.

***** SOLUTION *****

Keeping the anode and electrolyte at constant chemical potential, the battery voltage is given by the chemical potential of the reduced state in the cathode, μ ,

$$V = V_O - \frac{\mu}{e}. \quad (6)$$

We begin with the regular solution model as a function of the local concentration, non-dimensionalized to the max concentration, c

$$\mu_h(c) = kT \log\left(\frac{c}{1-c}\right) + \Omega_a(1-2c). \quad (7)$$

Thus, for a homogeneously filling cathode, $c = x$, $\mu = \mu_h(x)$, and

$$V = V_O - \frac{\mu_h(x)}{e} \text{ (homogeneously filling)}. \quad (8)$$

This is plotted in Figure 2a.

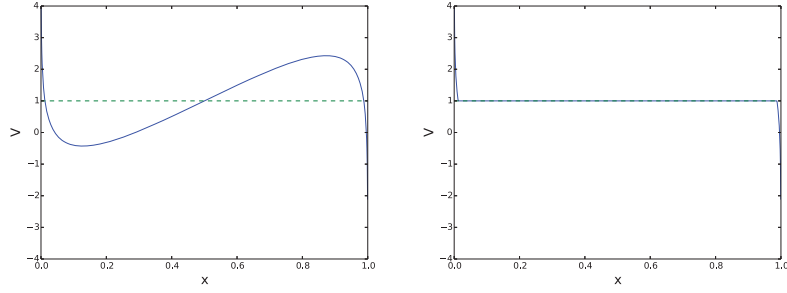
In the phase separating state, we accept two different responses. First, at true equilibrium, whenever the system is between the two free energy minima, it should be in the free energy minimum – the phase separated state. The two free energy minima occur at the “binodal”, which we will refer to as $x_{b,\pm}$ for the upper and lower spinodal points. Because of the symmetry in our free energy model, we can solve for these points by setting $\mu_h(c) = 0$ and picking the solutions near 0 and 1 (i.e. $c \neq 0.5$), which can be solved numerically.

$$V = \begin{cases} V_O & x \in [x_{b,-}, x_{b,+}] \\ \mu_h(x) & \text{else} \end{cases}. \quad (9)$$

This is plotted in Figure 2b.

A second acceptable response follows: If a (very small) finite current is assumed without nucleation, phase separation will occur at the spinodal, which occurs when $g''(c) = 0$ or $\mu'_h(c) = 0$.

$$\mu'_h(c) = kT \left(\frac{1}{c} + \frac{1}{1-c} \right) - 2\Omega_a. \quad (10)$$



(a) Homogeneous cathode voltage. (b) Equilibrium phase separating cathode voltage.

Figure 2: Voltage of homogeneous and phase separating cathodes.

Thus, denoting the lower and upper spinodal homogeneous compositions as x_{s-} and x_{s+} , they are given by

$$x_{s,\pm} = 0.5 \left(1 \pm \sqrt{1 - 2/\tilde{\Omega}_a} \right) \quad (11)$$

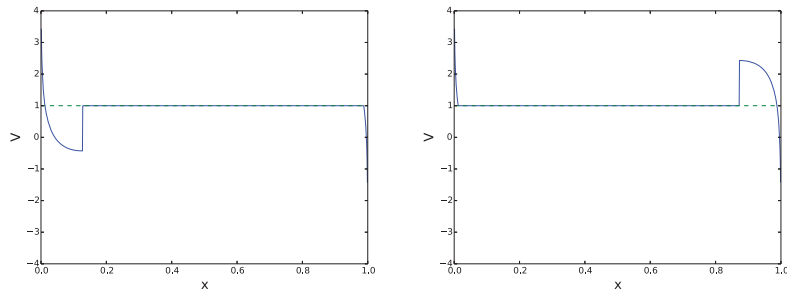
where $\tilde{\Omega}_a = \Omega_a/kT$. After phase separation, because our model for the free energy is symmetric around $c = 0.5$, the chemical potential will be 0 until the filling fraction reaches the other free energy minimum and returns to a homogeneous state. Again because the symmetry in our model for the free energy, we can solve for this point by setting $\mu_h(c) = 0$, which can be solved numerically. We will denote these two limits $x_{b,\pm}$. Thus, with spinodal phase separation, there will be different voltages when filling (discharging) or emptying (charging) the cathode. For filling,

$$V = \begin{cases} V_O & x \in [x_{s,-}, x_{b,+}] \\ \mu_h(x) & \text{else} \end{cases} \quad (12)$$

And for emptying,

$$V = \begin{cases} V_O & x \in [x_{b,-}, x_{s,+}] \\ \mu_h(x) & \text{else} \end{cases} \quad (13)$$

These are plotted in Figures 3a and 3b.



(a) Phase separating cathode voltage upon filling (discharge). (b) Phase separating cathode voltage upon emptying (charge).

Figure 3: Voltage of phase separating cathodes assuming very slow (dis)charge currents.

- (b) On this plot, also sketch a closed curve to represent slow cyclic voltammetry, where the voltage is swept very slowly back and forth between large and small values. Explain why there is hysteresis, i.e. different curves for discharging and charging.

***** SOLUTION *****

A representative CV curve for very slow scan rates involves following the curves in Figures 3a and 3b with some modifications. As the voltage is lowered from some large value, the cathode will be nearly empty, and the voltage will track the left part of Figure 3a. Then, when the spinodal is reached, because we are linearly sweeping the voltage, the filling fraction will rapidly go from the low spinodal limit to the intersection of the homogeneous curve at high filling fraction and the current applied voltage. In reverse (starting at low voltages and high filling fractions), the opposite occurs. The voltage will initially track Figure 3b as the cathode empties, then when the spinodal is reached, the cathode will quickly empty until it reaches the intersection at low filling fractions. This is depicted in Figure 4.

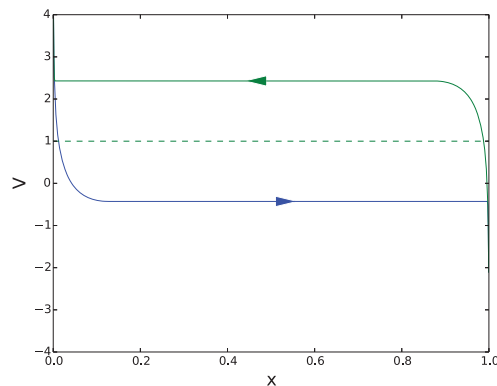


Figure 4: Slow CV scan of a single particle with phase transformations by nucleation.

- (c) Derive a formula for the “voltage gap” between charging and discharging plateaus in the limit of zero current.

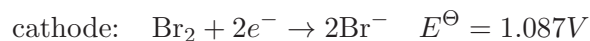
***** SOLUTION *****

The voltage gap is related to the difference in chemical potentials at the lower and upper spinodals. Thus, nondimensionlizing by the thermal voltage/energy

$$\Delta \tilde{V}_{gap} = \tilde{\mu}_h(x_{s,-}) - \tilde{\mu}_h(x_{s,+}) \quad (14)$$

$$= 2 \left(\tilde{\Omega} \sqrt{1 - \frac{2}{\tilde{\Omega}}} - 2 \tanh^{-1} \left(\sqrt{1 - \frac{2}{\tilde{\Omega}}} \right) \right). \quad (15)$$

3. **Hydrogen-Bromine Flow Battery: Water Electrochemistry.** During discharge, the battery converts hydrogen gas (H_2) and liquid bromine (Br_2) to hydrobromic acid (HBr). The half-cell reactions are



The electrolyte is 1M $\text{HBr}(\text{aq})$ with 1M $\text{Br}_2(\text{aq})$ added near the cathode and 1 atm H_2 gas at the anode, at room temperature.

- (a) How does the cell voltage vary with pH?

***** SOLUTION *****

We will denote the reactions as anode = 1, cathode = 2, oxygen evolution = 3. The Nernst equation for each reaction requires (assuming room temperature, taken from class, and given in Volts)

$$E_1 = -0.06 \text{ pH}$$

$$E_2 = 1.087$$

$$E_3 = 1.229 - 0.06 \text{ pH}.$$

Thus, the voltage is $E_c - E_a = E_2 - E_1 = 1.087 + 0.06 \text{ pH}$,

- (b) Make a Pourbaix diagram for the half-cell reactions, as well as the oxygen evolution reaction (i.e. electrolysis, or water splitting).

***** SOLUTION *****

We plot the above equations in Figure 5.

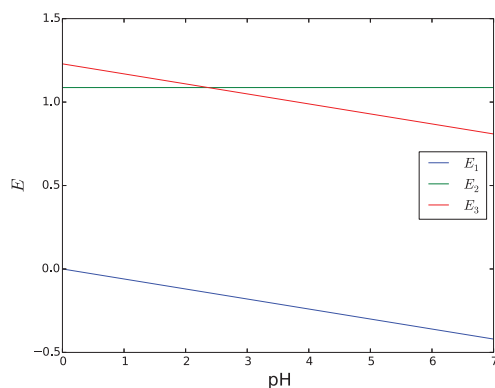


Figure 5: Pourbaix diagram for HBr Flow Battery.

- (c) What is the upper bound for pH to avoid oxygen evolution at the cathode near open circuit conditions?

***** SOLUTION *****

Oxygen evolution will occur whenever an electrode potential lies above the E_3 curve. Near open circuit conditions, this only occurs when $E_2 > E_3$, or $\text{pH} > 2.367$.

- (d) What is the upper bound for cathodic overpotential to avoid oxygen evolution during battery recharging?

***** SOLUTION *****

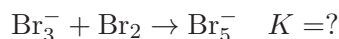
When charging, net oxidation is occurring at the cathode, so the electrode potential there is higher than the equilibrium curves. In order to drive reaction 2 in the oxidation direction, the electrode potential, E_c must be above E_2 . Similarly, for the oxygen to be evolved, the E_c must be above E_3 . Thus we require that $E_2 < E_c < E_3$. Noting that the overpotential for the bromine reaction is $\eta_c = E_c - E_2 < E_3 - E_2 = 0.142 - 0.06 \text{ pH}$. Because we begin with 1M HBr, we can assume that the pH is initially zero, leading to 0.142 V maximum overpotential.

4. **Hydrogen-Bromine Flow Battery: Polybromide complexes.** In hydrobromic acid, bromine can form tribromide and pentabromide ion complexes



where K_3 and K_5 are the equilibrium constants (Molar). Assume room temperature, dilute solution approximations (activity = molar concentration) and hydrogen gas at 1 atm.

- (a) What is the equilibrium constant of the second complexation reaction,



***** SOLUTION *****

When in equilibrium,

$$a_{\text{Br}_3^-}^{\text{eq}} = K_3 a_{\text{Br}_2}^{\text{eq}} a_{\text{Br}^-}^{\text{eq}} \quad (16)$$

$$a_{\text{Br}_5^-}^{\text{eq}} = K_5 (a_{\text{Br}_2}^{\text{eq}})^2 a_{\text{Br}^-}^{\text{eq}}. \quad (17)$$

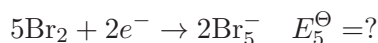
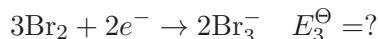
The equilibrium constant of the given reaction is, by definition,

$$K = \frac{a_{\text{Br}_5^-}^{\text{eq}}}{a_{\text{Br}_3^-}^{\text{eq}} a_{\text{Br}_2}^{\text{eq}}} \quad (18)$$

$$= \frac{K_5 (a_{\text{Br}_2}^{\text{eq}})^2 a_{\text{Br}^-}^{\text{eq}}}{K_3 (a_{\text{Br}_2}^{\text{eq}})^2 a_{\text{Br}^-}^{\text{eq}}} \quad (19)$$

$$= \frac{K_5}{K_3} = \frac{37.7}{16.7} \approx 2.26. \quad (20)$$

- (b) What are the standard potentials of bromine reduction to the polybromide complexes?



***** SOLUTION *****

The standard potential is obtained by using the Nernst equation.

$$E_3 = E_3^\ominus + \frac{kT}{2e} \ln \left(\frac{a_{\text{Br}_2}^3 a_e^2}{a_{\text{Br}_3^-}^2} \right) \quad (21)$$

$$= E_3^\ominus + \frac{kT}{2e} \ln \left(\frac{a_{\text{Br}_2}^3 a_e^2}{(K_3 a_{\text{Br}_2} a_{\text{Br}^-})^2} \right) \quad (22)$$

$$= E_3^\ominus - \frac{kT}{e} \ln K_3 + \frac{kT}{2e} \ln \left(\frac{a_{\text{Br}_2} a_e^2}{a_{\text{Br}^-}^2} \right). \quad (23)$$

Now, we note that we can relate the last term to the simple Bromine reduction reaction from P3, which we will now denote as reaction B

$$E_B = E_B^\ominus + \frac{kT}{2e} \ln \left(\frac{a_{\text{Br}_2} a_e^2}{a_{\text{Br}^-}^2} \right). \quad (24)$$

If these reactions are both in equilibrium at the same electrode, there is only one “metal” potential, so $E_3 = E_B = E$, and (in Volts)

$$E = E_3^\ominus - \frac{kT}{e} \ln K_3 + (E - E_B^\ominus) \quad (25)$$

$$E_3^\ominus = \frac{kT}{e} \ln K_3 + E_B^\ominus = 1.087 + 0.026 \ln 16.7 = 1.160. \quad (26)$$

Similarly,

$$E = E_5^\ominus + \frac{kT}{2e} \ln \left(\frac{a_{Br_2}^5 a_e^2}{a_{Br_5^-}^2} \right) = E_5^\ominus - \frac{kT}{e} \ln K_5 + \frac{kT}{2e} \ln \left(\frac{a_{Br_2} a_e^2}{a_{Br^-}^2} \right) \quad (27)$$

$$E_5^\ominus = \frac{kT}{e} \ln K_5 + E_B^\ominus = 1.181. \quad (28)$$

- (c) What are the concentrations of Br_3^- and Br_5^- in equilibrium with a reservoir of 1M HBr + 1M Br_2 ? Can this equilibrium ever be reached?

***** SOLUTION *****

Using the relations from part (a),

$$a_{Br_3^-}^{eq} = K_3 a_{Br_2}^{eq} a_{Br^-}^{eq} = K_3 = 16.7 M \quad (29)$$

$$a_{Br_5^-} = K_5 (a_{Br_2}^{eq})^2 a_{Br^-}^{eq} = K_5 = 37.7 M, \quad (30)$$

which cannot be achieved because these values exceed the solubility limits.

- (d) If instead the total concentration of bromine (in all forms: Br_2 , Br_3^- , Br_5^-) is fixed at the initial Br_2 concentration of 1M (prior to complexation reactions) and the system equilibrates in contact with a reservoir of 1M HBr, what is the open circuit voltage?

***** SOLUTION *****

First we note that the first two given species each have one equivalent of Br_2 , whereas Br_5^- contains 2 equivalents of Br_2 . Fixing the total concentration of Br_2 and using that to obtain the OCV, we are also in equilibrium

$$c_{Br_2} + c_{Br_3^-} + 2c_{Br_5^-} = 1 \quad (31)$$

$$a_{Br_2} + a_{Br_3^-} + 2a_{Br_5^-} = 1 \quad (32)$$

$$a_{Br_2} (1 + K_3 a_{Br^-} + 2K_5 a_{Br_2} a_{Br^-}) = 1 \quad (33)$$

$$a_{Br_2} (1 + K_3 + 2K_5 a_{Br_2}) = 1 \quad (a_{Br^-} = 1 \text{ from reservoir}) \quad (34)$$

$$2K_5 a_{Br_2}^2 + (1 + K_3) a_{Br_2} - 1 = 0 \quad (35)$$

$$a_{Br_2} = \frac{-(1 + K_3) + \sqrt{(1 + K_3)^2 + 8K_5}}{4K_5} = 0.047. \quad (36)$$

Then, assuming unit activity for electrons, we can use the Nernst equation to determine the OCV,

$$V_O = 1.087 + \frac{kT}{2e} \ln \left(\frac{a_{Br_2} a_e^2}{a_{Br^-}^2} \right) \quad (37)$$

$$= 1.087 + \frac{kT}{2e} \ln (a_{Br_2}) \quad (38)$$

$$= 1.047 V, \quad (39)$$

which demonstrates that “occupying” some of the Br_2 via the complexes, while keeping the Br^- fixed reduces the OCV.

- (e) *Extra credit:* If the total concentrations of all forms of bromine (Br_2 , Br_3^- , Br_5^-) and of bromide (Br^- , Br_3^- , Br_5^-) are each fixed at 1M (for an initial solution of 1M Br_2 + 1M HBr, prior to complexation reactions) and allowed to reach equilibrium in a closed system (no reservoir), what is the open circuit voltage?

***** SOLUTION *****

Here, rather than having $a_{Br^-} = 1$, we have that

$$a_{Br^-} + a_{Br_3^-} + a_{Br_5^-} = 1 \quad (40)$$

$$a_{Br^-} + K_3 a_{Br^-} a_{Br_2} + K_5 a_{Br_2}^2 a_{Br^-} = 1 \quad (41)$$

and from the constraint on bromine,

$$a_{Br_2} + K_3 a_{Br^-} a_{Br_2} + 2K_5 a_{Br_2}^2 a_{Br^-} = 1. \quad (42)$$

These two equations can be solved numerically to obtain

$$a_{Br_2} = 0.12 \quad a_{Br^-} = 0.28. \quad (43)$$

Thus,

$$V_O = 1.087 + 0.013 \ln \left(\frac{0.12}{0.28^2} \right) = 1.093 \text{ V}, \quad (44)$$

which is quite close to the standard potential because both Br_2 and Br^- concentrations were reduced.

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