10.626 Electrochemical Energy Systems
Spring 2014 MIT, M. Z. Bazant

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

1. **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.

2. **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.

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

   (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.

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

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

$$\text{anode:} \quad H_2 \rightarrow 2H^+ + 2e^- \quad E^\Theta = 0$$

$$\text{cathode:} \quad Br_2 + 2e^- \rightarrow 2Br^- \quad E^\Theta = 1.087V$$

The electrolyte is 1M HBr(aq) with 1M Br_2(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?

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

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

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

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

$$\mathrm{Br_2 + Br^- \to Br_3^-} \quad K_3 = 16.7$$

$$\mathrm{2Br_2 + Br^- \to Br_5^-} \quad K_5 = 37.7$$

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,

$$\mathrm{Br_3^- + Br_2 \to Br_5^-} \quad K = ?$$

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

$$\mathrm{3Br_2} + 2e^- \to \mathrm{2Br_3^-} \quad E_3^{\ominus} = ?$$

$$\mathrm{5Br_2} + 2e^- \to \mathrm{2Br_5^-} \quad E_5^{\ominus} = ?$$

(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?

(d) If instead the total concentration of bromine (in all forms: Br_2, Br_3^-, Br_5^-) is fixed at 1M in equilibrium with a reservoir of 1M HBr, what is the open circuit voltage of the hydrogen-bromine battery?

(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 and reach equilibrium (finite tanks, no reservoir), what is the open circuit voltage?

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