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

Final Exam

Instructions. This is a three-hour "closed book" exam. You are allowed to have *five double-sided pages of personal notes* during the exam, but otherwise, you may not consult any notes, books, other people, or internet resources during the exam. Please write your name or initials on every page. Point totals out of 100 are given for each problem.

1. **Fuel Cell Impedance.** (10 POINTS)

   The figure shows Nyquist plots of the impedance spectrum of a PEM fuel cell.

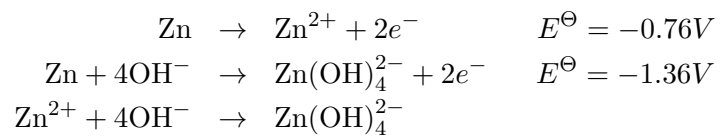   [X. Yuan et al., Int. J. Hydrogen Energy (2007)]
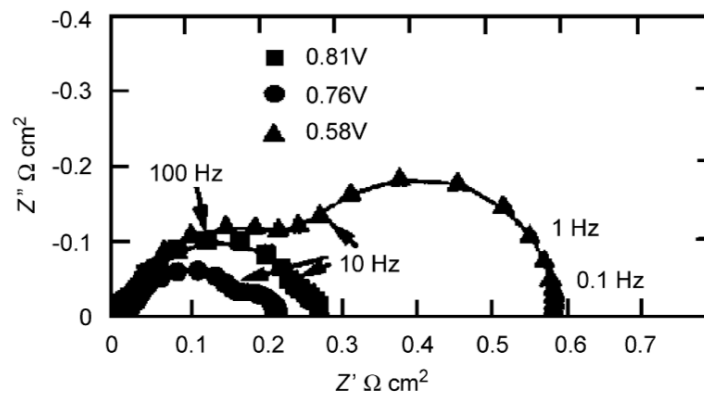
   (a) What is the likely rate-limiting process at the lowest voltage?

   (b) Why might the intermediate voltage have the lowest high-frequency resistance?

2. **Aqueous Zinc Electrochemistry.** (15 POINTS)

Plot the equilibrium lines for following reactions on a Pourbaix diagram and indicate which form of zinc is stable in each region.

$$
\begin{aligned}
\text{Zn} &\rightarrow \text{Zn}^{2+} + 2e^- & E^{\ominus} &= -0.76V \\
\text{Zn} + 4\text{OH}^- &\rightarrow \text{Zn(OH)}_4^{2-} + 2e^- & E^{\ominus} &= -1.36V \\
\text{Zn}^{2+} + 4\text{OH}^- &\rightarrow \text{Zn(OH)}_4^{2-}
\end{aligned}
$$

3. **Electrolyte Selection for an Electrochemical Capacitor.** (15 POINTS)

Two electrolytes are being considered for use in an electrochemical double-layer capacitor. The table shows the relative permittivity ε, maximum voltage V_{max} (before solvent decomposition), and typical diffusivity D. In each case, the salt concentration (1M) is large enough that the double layer has a constant effective thickness λ, set by the solvation radius (Stern layer). Calculate how the energy storage performance of the capacitor changes by switching from the organic to the aqueous electrolyte, assuming all other system properties remain unchanged.

solvent	ε (ε_0)	V_{max} (V)	D (10^{-6} cm^2/s)	λ (Å)
aqueous	80	1.2	4	2
organic	60	2.4	1	3

(a) What is the total capacitance ratio, C_{aq}/C_{org}?

(b) What is the capacity ratio (energy stored at max voltage), E_{aq}/E_{org}?

(c) What is the charging time ratio, τ_{aq}/τ_{org}?

(d) What is the power density ratio (capacity per charging time), P_{aq}/P_{org}?

4. **Effective Charge Diffusivity of a Porous Supercapacitor.** (15 POINTS)

The porous electrode of an electric double-layer supercapacitor has area density a_p (pore area / total volume) and porosity ϵ_p with a $z : z$ binary electrolyte of concentration c_0, permittivity ε and equal effective diffusivities, D (accounting for tortuosity). The electrolyte is dilute in this case, so the compact part of the double layer can be neglected and the diffuse part described by Debye-Huckel theory. Electron transport is fast compared to (Ohmic) ion transport and double layer charging, so the pore potential and double-layer charge density each satisfy a linear diffusion equation with effective diffusivity D_e.

(a) Assuming identical cylindrical pores, what is the pore radius R_p?

(b) What is the double-layer capacitance per volume of the porous electrode?

(c) Relate the bulk ionic conductivity σ of the pores to the Debye screening length λ_D.

(d) Relate D_e/D to R_p/λ_D. Which is typically larger, D_e or D?

5. **Sabatier Principle for Electrocatalysis.** (15 POINTS)

A Faradaic reaction consists of three steps: 1. fast gas adsorption on a catalytic surface, 2. fast surface diffusion, and 3. rate-limiting charge transfer. The adsorbed gas molecules (and vacancies) form an ideal solution over the surface sites. Let $\mu_{ads}^{\ominus} = -E_a$ be the reference chemical potential at half coverage, $\Theta = 1/2$, where E_a is the adsorption energy of an adatom relative to the gas under standard conditions. Let p be the gas pressure in atm.

(a) Calculate the equilibrium coverage Θ_{eq}.

(b) Assume Butler-Volmer kinetics for the charge-transfer step with symmetry factor α, and relate the exchange current I_0 to E_a and p.

(c) Sketch the "volcano plot" of I_0 vs E_a and find the adsorption energy E_a^{max} corresponding to the maximum exchange current (electrocatalytic activity). Explain why the current is lower for $E_a \neq E_a^{max}$.

6. **Charge Relaxation in Dilute Electrolytes.** (15 POINTS)

Consider a dilute $z : z$ binary electrolyte of bulk concentration c_0, permittivity ε, and equal effective diffusivities, D in a 1D geometry. Assume Debye-Huckel approximation of small voltages to linearize the Poisson-Nernst-Planck equations.

(a) Show that the current density $J(x,t)$ is related to the potential $\phi(x,t)$ and charge density $\rho_e(x,t)$ via

$$J = -D\left(\frac{\partial \rho_e}{\partial x} + \frac{\varepsilon}{\lambda_D^2}\frac{\partial \phi}{\partial x}\right)$$

and use this formula to define the Debye length, λ_D.

(b) Derive the charge transport equation:

$$\frac{\partial \rho_e}{\partial t} = D\left(\frac{\partial^2 \rho_e}{\partial x^2} - \frac{\rho_e}{\lambda_D^2}\right)$$

(c) Show that λ_D is the length scale for charge screening.

(d) Show that $\tau = \varepsilon/\sigma$ is the time scale for charge relaxation, where σ is the conductivity of the bulk electrolyte.

7. **Electrolyte Transport Impedance.** (15 POINTS)

Consider the response of the dilute electrolyte from the previous problem to a small alternating current of frequency ω applied at an electrode at $x = 0$ relative to a counter electrode at $x = \infty$ (more accurately, $x \gg \lambda_D$).

(a) Derive the complex amplitude of the charge density $\rho_e^*(x)$, up to a constant prefactor.

(b) Derive the complex amplitude of the potential $\phi^*(x)$, up to a constant prefactor.

(c) Derive the impedance

$$Z(\omega) = \frac{\phi^*(x = 0)}{J^*(x = 0)}$$

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