**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.

   ![Impedance Spectrum](http://ocw.mit.edu/help/faq-fair-use/)


   (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.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \quad E^\Theta = -0.76V \\
\text{Zn} + 4\text{OH}^- & \rightarrow \text{Zn(OH)}_2^- + 2e^- \quad E^\Theta = -1.36V \\
\text{Zn}^{2+} + 4\text{OH}^- & \rightarrow \text{Zn(OH)}_4^{2-}
\end{align*}
\]
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 $\varepsilon$, maximum voltage $V_{\text{max}}$ (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 $\lambda$, 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 changes remain unchanged.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\varepsilon / (\varepsilon_0)$</th>
<th>$V_{\text{max}}$ (V)</th>
<th>$D$ ($10^{-6}$ cm$^2$/s)</th>
<th>$\lambda$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aqueous</td>
<td>80</td>
<td>1.2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>organic</td>
<td>60</td>
<td>2.4</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

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

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

(c) What is the charging time ratio, $\tau_{\text{aq}}/\tau_{\text{org}}$?

(d) What is the power density ratio (capacity per charging time), $P_{\text{aq}}/P_{\text{org}}$?
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 \( \epsilon_p \) with a \( z : z \) binary electrolyte of concentration \( c_0 \), permittivity \( \varepsilon \) 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 \( \sigma \) of the pores to the Debye screening length \( \lambda_D \).

(d) Relate \( D_e / D \) to \( R_p / \lambda_D \). 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 $\mu_{ads}^\Theta = -E_a$ 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 $\Theta_{eq}$.

(b) Assume Butler-Volmer kinetics for the charge-transfer step with symmetry factor $\alpha$, 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 $E_{a}^{\text{max}}$ corresponding to the maximum exchange current (electrocatalytic activity). Explain why the current is lower for $E_a \neq E_{a}^{\text{max}}$. 

---

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

Consider a dilute $z : z$ binary electrolyte of bulk concentration $c_0$, permittivity $\varepsilon$, 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, $\lambda_D$.

(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 $\lambda_D$ is the length scale for charge screening.

(d) Show that $\tau = \varepsilon/\sigma$ is the time scale for charge relaxation, where $\sigma$ 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 \( \omega \) 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 \( \rho^*_c(x) \), up to a constant prefactor.

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

(c) Derive the impedance

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