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

Problem Set 4 – Kinetics and Transport

1. **Quantum tunneling in electron transfer.** In classical Marcus theory, electron transfer occurs at an activation barrier ε_b, where the reduced and oxidized state (with electron) have the same energy. In classical mechanics, a particle can only cross a barrier if it has higher energy than the barrier energy, but in quantum mechanics there is always a probability (even at zero temperature) that an electron can "tunnel" through the barrier at a lower energy $\varepsilon < \varepsilon_b$. For a flat barrier of spatial width d between free domains, the tunneling probability is

$$p_t = \exp\left(-2d\frac{\sqrt{2m_e(\varepsilon_b - \varepsilon)}}{\hbar}\right) \tag{1}$$

where $\hbar = h/2\pi$, $h =$ Planck's constant, and $m_e =$ electron mass[1] .

   (a) For a given tunneling distance d what is the effective lowering of the barrier $\Delta\varepsilon = \varepsilon_b - \varepsilon$ where $p_t = 0.5$.

   (b) Estimate $\Delta\varepsilon$ and compare with the reorganization energy λ for the case of electron transfer into $LiFePO_4$ from a metallic carbon coating[2]. Is tunneling important an outer sphere reaction like this?

   (c) Explain why tunneling is more important for inner sphere reactions.

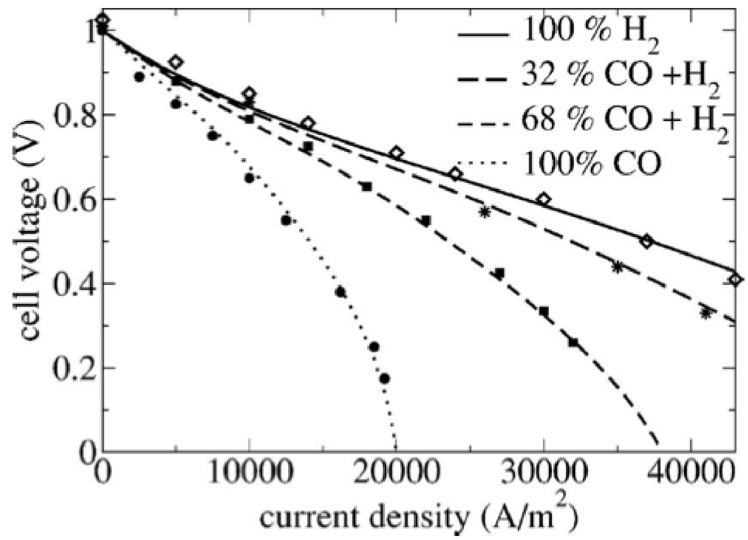

Figure 1: The data above are for H_2/CO fuel mixtures in the same cell with $L =$ 1mm and $c = 7 \times 10^{18}$ cm^{-3}. For each question below, explain your reasoning and make a rough estimate (without a calculator). [Pisani & Murgia, J. Electrochem. Soc. (2007)].

2. **SOFC Performance.** A solid oxide fuel cell is fed carbon monoxide gas as the fuel at the anode, where electrochemical oxidation to carbon dioxide occurs:

$$\mathrm{CO} + \mathrm{O}^{2-} \rightarrow \mathrm{CO}_2 + 2e^-$$

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[1] See lecture 20, 2009.

[2] See P. Bai and M. Z. Bazant, *Nature Communications* (2014).

(a) Relate I_{lim} to the CO diffusivity D in the porous anode, the inlet CO concentration c, and the anode thickness L.

(b) Estimate D from the data.

(c) Estimate the solid electrolyte Ohmic resistance R_{el} (in $\Omega\cdot\text{cm}^2$).

(d) Estimate the maximum power density P_{max} for 100% CO fuel.

3. **DMFC fuel crossover.** In the direct methanol fuel cell (DMFC), the anode is fed with a methanol-water fuel and produces carbon dioxide, which escapes into the solution. The reaction produces protons, which cross a proton exchange membrane (PEM) to the cathode, where reduction occurs with oxygen gas (from air exposure) to produce water. The half-cell reactions are

$$\begin{aligned}\text{anode:} \quad & CH_3OH + H_2O \to 6H^+ + 6e^- + CO_2 \\ \text{cathode:} \quad & \frac{3}{2}O_2 + 6H^+ + 6e^- \to 3H_2O \\ \text{net reaction (combustion):} \quad & CH_3OH + \frac{3}{2}O_2 \to 2H_2O + CO_2\end{aligned}$$

Consider steady-state 1D diffusion of methanol with diffusivity D_a in the porous anode of thickness l_a, and also in the membrane of thickness l_m and diffusivity $D_m \ll D_a$, where c_M is continuous across the anode/membrane interface. The latter corresponds to "fuel crossover" which is a problem in DMFC, since combustion will rapidly consume any methanol that makes it to the cathode, where we set $c_M = 0$. Let $\bar{c}_M$ be the (constant) methanol concentration, just outside the porous anode.

(a) Derive the cell voltage, $V(I, c_M)$, neglecting concentration polarization at the anode, $c_M = \bar{c}_M$, and any polarization at the cathode. Assume Butler-Volmer kinetics with $\alpha = 1/2$ and $n = 6$ electrons transferred. Rescale the anode exchange current to be K_0 under standard conditions.

(b) What is the limiting current I_{lim}? Assume the anode has an active area A. Qualitatively, how will fuel crossover influence the current-voltage relation?

(c) Relate c_M at the anode/membrane interface to the applied current I. Show that the dimensionless group, $\gamma = D_m l_a / D_a l_m$, controls the importance of fuel crossover. Derive the cell voltage $V(I, \bar{c}_M, \gamma)$.

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