Problem Set 3 – Reaction Kinetics
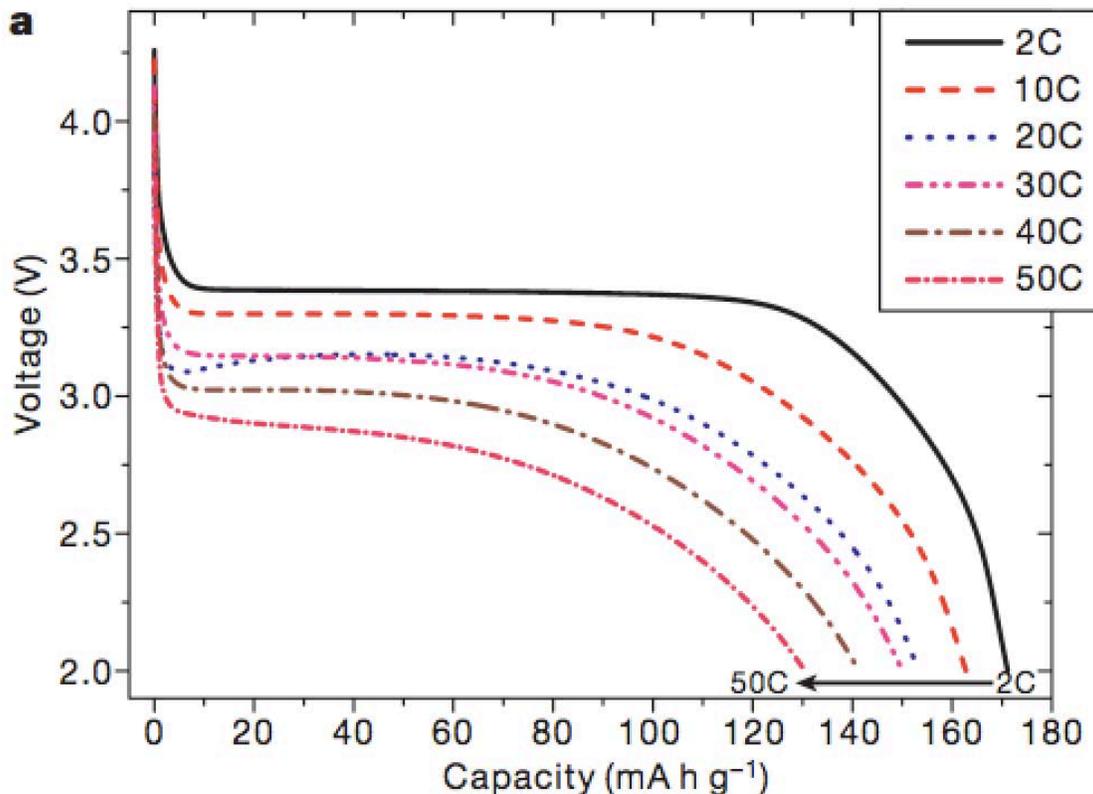
Figure 1: Kang and Ceder, Battery materials for ultrafast charge and discharge, *Nature Materials* (2009)

1. **Rate Limitation in an Ultrafast Li-ion Battery.** The figure shows discharge data for a Li-ion battery, whose cathode consists of nanoparticles of $LiFePO_4$ of mean size 50 nm.

   (a) What is the solid diffusion time for inserted Li^+ in the active particles? The theoretical diffusivity is 10^{-12} m^2/s for the perfect crystal, but defects can reduce this to 10^{-14} m^2/s.

   (b) What is the electrolyte diffusion time across the porous electrode? The electrolyte diffusivity is 10^{-10} m^2/s, and electrode thickness 1μm.

   (c) Explain why the battery is not limited by lithium diffusion. Assume rate limitation by insertion reaction kinetics, and make a Tafel plot of the (natural) logarithm of the applied current versus activation overpotential.

   (d) Is the Tafel plot consistent with Butler-Volmer kinetics? If so, estimate the symmetry factor, α.

   (e) Is the Tafel plot consistent with Marcus kinetics? If so, estimate the reorganization energy, λ.

   (f) How would you explain the "overshoot" of the voltage plateau for the 20C data?

2. **Electrode protection in lead-acid batteries.** "Corrosion" refers to a spontaneous chemical reaction that results from a neutral combination of Faradaic reactions (redox couple) at the same electrode. Since no electron must pass through the external circuit, corrosion can occur under open circuit conditions. For example, in a lead-acid battery, the corrosion reaction

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$
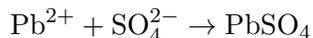
can occur at both electrodes. At the anode, the half-cell reaction

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-, \quad E_1^{\ominus} = -0.356V \tag{1}$$
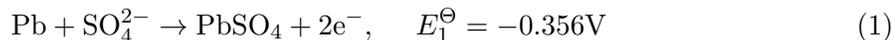
couples to lead electrodeposition,

$$Pb^{2+} + 2e^- \rightarrow Pb, \quad E_2^{\ominus} = -0.126V \tag{2}$$
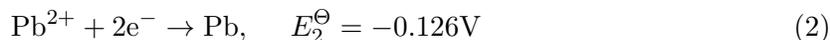
and at the cathode, the half-cell reaction

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_20, \quad E_3^{\ominus} = 1.685V \tag{3}$$
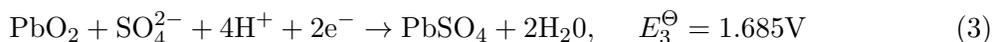
couples to lead oxide electrodeposition,

$$Pb^{2+} + 2H_20 \rightarrow PbO_2 + 4H^+ + 2e^-, \quad E_4^{\ominus} = 1.455V \tag{4}$$

We shall see how these reactions conspire to "protect" both the Pb anode and PbO_2 cathode against dissolution by instead forming a passivating $PbSO_4$ surface film, which is also the product of the net cell reaction.

(a) For each reaction ($i = 1, 2, 3, 4$), relate the equilibrium electrode potential, U_i, vs. the standard hydrogen electrode (SHE) to pH, $p[SO_4^{2-}]$, and $p[Pb^{2+}]$, assuming that the other reactants have unit activities.

(b) Assume that each reaction rate satisfies the Butler-Volmer equation with $\alpha = 1/2$ and the same exchange current I_0. Under open circuit conditions, determine the potentials of the anode and cathode vs SHE, E_a and E_c, respectively, the open circuit voltage, $V_0 = E_c - E_a$, and the corrosion current at each electrode (carried by reactions 2 and 4).

(c) If the sulfuric acid concentration reaches $[H_2SO_4] = 6M$ at room temperature ($k_BT/e = 26mV$) after the corrosion reactions equilibrate at both electrodes, what is the lead ion concentration, $[Pb^{2+}]$?

3. **Oxygen electrocatalysis in solid oxide fuel cells (SOFC).** Assume that the net oxygen reduction reaction (ORR) at the SOFC cathode, $O_{2(g)} \rightarrow 2O_{(s)}^{2-}$, consists of three steps: gas adsorption on the catalyst followed by two charge transfers while inserting oxygen ions into the solid high-temperature ceramic electrolyte.

$$\text{Step 1:} \quad O_{2(g)} \rightarrow 2O_{ads}, \tag{5}$$

$$\text{Step 2:} \quad O_{ads} + e^- \rightarrow O_{(s)}^-, \tag{6}$$

$$\text{Step 3:} \quad O_{(s)}^- + e^- \rightarrow O_{(s)}^{2-}, \tag{7}$$
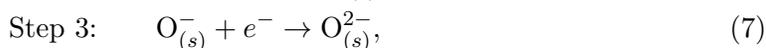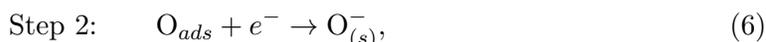
Let p_{O_2} be the partial pressure and $a_{O_2} = Kp_{O_2}$ be the activity of the gas, Θ_O the surface coverage and a_O the activity of the adatoms, and a_{O^-} and $a_{O^{2-}}$ the activities of the ions. Assume steps 1 and 3 are fast, while step 2 is rate limiting and described by modified (concentrated-solution) Butler-Volmer kinetics with $\alpha = 1/2$ and a transition state excluding s sites on the surface.

(a) Relate a_O to Θ_O and p_{O_2} assuming an ideal lattice gas on the surface in equilibrium with the gas (Langmuir adsorption).

(b) Let $\Delta\phi_2^0$ and $\Delta\phi_3^0$ be the standard half-cell potentials of steps 2 and 3, respectively, and derive the Nernst equilibrium voltages, $\Delta\phi_2^{eq}$ and $\Delta\phi_3^{eq}$.

(c) Relate the monovalent ion activity a_{O^-} to p_{O_2}, $a_{O^{2-}}$ and the over potential, η.

(d) Derive a Butler-Volmer equation for the net current, $I(p_{O_2}, a_{O^{2-}}, \eta)$. What is the effective symmetry factor? How does the exchange current scale with p_{O_2} at low and high pressures?

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