Problem Set 2

Due: Wednesday 10/1/25 at the start of class

Feel free to use any resource to work these problems, including books, websites, and your classmates. However, your problem set submission must be your own work.

Problem 1. Solid-Oxide Fuel Cells

Solid oxide fuel cells (SOFC) involve a solid ceramic electrolyte. Advantages of SOFCs include fuel flexibility, use of cheaper catalysts, high power densities, and high quality waste heat for cogeneration. Physically, a SOFC conducts O^{2-} anions through a solid electrolyte, replacing the proton and hydroxide conductors we discussed in class. In order to be conductive for O^{2-} ions, these cells must be operated at high temperatures.

a) Draw a solid oxide fuel cell given a feed of hydrogen and oxygen. Label the reactants and products, write out the half reactions, draw the path of the electrons in an external circuit, and indicate the direction of movement of the O^{2-} ion in the solid electrolyte.
b) Repeat the above for feeds of methane and oxygen to the anode and cathode, respectively (remember that the cell is operating at very high temperatures; what is the electrochemically active feed?).

Use your result from (a) for the rest of the problem.

c) Using values for the thermodynamics of each species found in NIST, write out an expression for the open circuit potential of the cell as a function of temperature. Please state all assumptions clearly.
d) In practice, there is significant ionic resistance in the electrolyte, particularly at lower temperatures. Given the following expression for electrolyte conductivity, write out a complete expression for the cell voltage as a function of temperature, accounting for ionic resistive losses due to O^{2-} conduction, but ignoring all other loss mechanisms.

$$\sigma(S/cm) = A \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

For Y$_2$O$_3$-doped ZrO$_2$ (8% Y$_2$O$_3$), $A = 0.14 S/cm$ and $E = 75 kJ/mol$ at 1000°C (Arachi et al. *Solid State Ionics.* 121 (1999)). While conditions vary depending on the material and the exact desired optimization, for our purposes assume the solid electrolyte is 150 microns thick. Assume the current is 500 mA/cm^2.

e) Plot of cell voltage as a function of temperature. What temperature does the maximum potential occur at and what is that potential? How does this optimal temperature change for: (i) 1 A/cm2, (ii) $A = 0.014 S/cm$, (iii) $A = 1.4 S/cm$
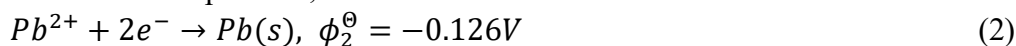
Problem 2. Corrosion Currents

Under some conditions, corrosion can refer 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

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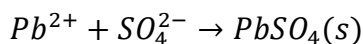
can occur at both electrodes. At the anode, the half reaction

$$Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-, \ \phi_1^\Theta = -0.356V \tag{1}$$
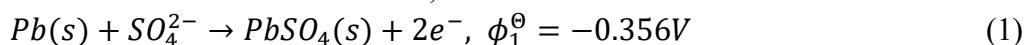
couples to lead electrodeposition,

$$Pb^{2+} + 2e^- \rightarrow Pb(s), \ \phi_2^\Theta = -0.126V \tag{2}$$

and at the cathode, the half reaction

$$PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O, \ \phi_3^\Theta = 1.685V \tag{3}$$

couples to lead oxide electrodeposition,

$$Pb^{2+} + 2H_2O \rightarrow PbO_2(s) + 4H^+ + 2e^-, \ \phi_4^\Theta = 1.455V \tag{4}$$
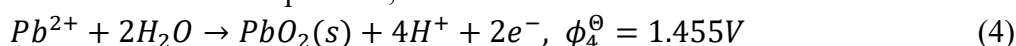
With these coupled reactions, there is no net passage of charge at each electrode despite the fact that charge transfer reactions are occurring at the electrode surface.

a) For each reaction ($i = 1,2,3,4$), relate the equilibrium electrode potential ϕ_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. ($p[ion] = -\log_{10}[ion]$)

b) Assume that the anode potential is $\phi_a = \frac{\phi_1 + \phi_2}{2}$ and the cathode potential is $\phi_c = \frac{\phi_3 + \phi_4}{2}$ (we will derive in the kinetics section!) What is the open circuit potential as a function of pH, $p[SO_4^{2-}]$, and $p[Pb^{2+}]$.

c) If the sulfuric acid concentration reaches $[H_2SO_4] = 3M$ and it fully dissociates at room temperature after the corrosion reactions equilibrate at both electrode, what is the lead ion concentration, $[Pb^{2+}]$?

Problem 3. Electrochemical Pressurization

In addition to driving otherwise unspontaneous reactions, such as water splitting, at room temperature, electrochemistry can also be used to promote difficult physical processes. An example of one such process is pressurization of gases, which can be done electrochemically with no moving parts.

a) One of the most developed examples of this technology is electrochemical pressurization of hydrogen. The cell consists of two gas diffusion electrodes in contact with a proton conducting membrane. Write down the reactions occurring at the cathode and anode of the cell.

b) Derive the open circuit potential of the cell in analytic form using the fact that

$$\mu_i = \mu_i^0 + RT ln\left(\frac{P_i}{P_0}\right),$$

Where P_i is the partial pressure of component i. This is valid if we assume that the gases are ideal. The hydrogen partial pressures at the anode and cathode must appear in your final expression. Note that P_0 is the reference potential, 1 bar.

c) Typical electrochemical pressurizers can achieve hydrogen pressures of 5000 psia. Compute the minimum voltage that needs to be applied to the cell, assuming the hydrogen is fed at 15 psia, to drive the process. What is the electrical minimum work required to pressurize 1 mole of hydrogen? How does this compare to the work required by a conventional compressor (given by the formula below)?

$$W_{compress} = nRT ln \left(\frac{P_f}{P_0}\right)$$

d) At one point, NASA was looking into creating an electrochemical oxygen compressor, which uses a wet proton conducting membrane as a separator. Because there has been interest in creating fuel and oxidizers off-Earth in recent years, this technology may need to be resurrected. Draw a schematic of the cell, denoting half reactions at the anode and cathode, the species that need to be fed to each electrode and motion of species through the membrane.

Problem 4. Vanadium Flow Battery

Flow batteries store chemical energy and generate electricity by a redox reaction between vanadium ions dissolved in the electrolytes. For example, the vanadium flow battery is a type of rechargeable flow battery that employs vanadium ions in different oxidation states. The redox reactions of the vanadium flow battery during charge and discharge are described in the following figure.
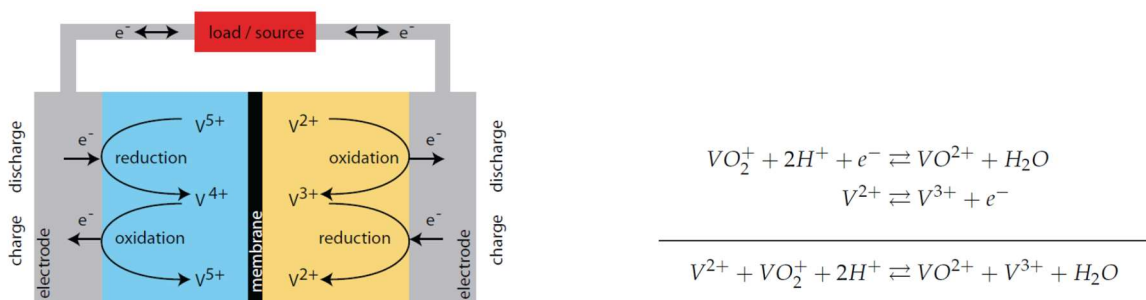

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$
$$V^{2+} \rightleftharpoons V^{3+} + e^-$$

$$\overline{V^{2+} + VO_2^+ + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O}$$

Figure 1. The scheme and reactions of the vanadium flow battery. [Blanc et al., Paths to Sustainable Energy]

(a) Given the thermodynamic data at 298.15 K in the table below, calculate the open circuit potential U at standard state conditions.

Formula	State	ΔG_f (kJ/mol)
V^{2+}	aq	-218
V^{3+}	aq	-251.3
VO^{2+}	aq	-446.4
VO_2^+	aq	-587.0
H_2O	liq	-237.2
H^+	aq	0

(b) Assuming all activity coefficients γ_i are equal to one, the concentrations of V^{2+}, V^{3+}, VO^{2+}, and VO_2^+ are 0.1, 0.1, 1, and 1 M, respectively, and the pH of the electrolyte is 1, calculate the actual open circuit potential of the vanadium flow battery.

(c) You just joined a lab studying a vanadium battery. For your initial study, you are looking at a system with no flow, with the species at the concentrations described in part b within a 1 L volume. Plot the concentrations of all reactant species at a function of time if you discharge the battery (see diagram above) with a current of 1 A for 1 hour. Assume the electrolyte compartments are evenly mixed.

(d) Plot the equilibrium potential of the device as a function of time during the discharge process.