*24-643 // 27-700*
Energy Storage Materials & Systems

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1: RK polynomials (6 points)

As we discussed in HW 2, Li-rich cathodes are a family of cathodes that can store more than one Li per transition metal. Here, let's instead consider two voltage curves for the following disordered rock salt anode, $Li_3V_2O_5$[1] which undergoes the following reaction:

$$Li_{3+x}V_2O_5 \rightleftharpoons xLi^+ + xe^- + Li_3V_2O_5 \qquad (1)$$
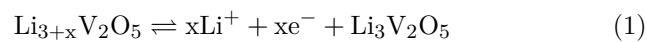
The voltage curve as a function of state of charge is given for both discharge (`discharge.csv`) and charge (`charge.csv`), which contains a list of state-of-charge, x and the voltage at that state of charge, $U(x)$. We will develop a R-K thermodynamic model for both modes of operation and compare them.

(a) Plot the voltage as a function of the state-of-charge for both discharge and charge. Is there any voltage hysteresis present? (1 point)

(b) Perform an appropriate transformation, x_1 of state-of-charge, x such that the R-K model can be applied (use $x_{max} = 2.0$). (0.5 point)

(c) Using the transformed variable, x_1, perform an R-K polynomial fit of the data, including the mixing entropy to degree $n = 6$. Plot the experimental voltage data and the R-K fit voltage curves (both discharge and charge) as a function of the state-of-charge. Discuss the R-K polynomial fits and do these voltage curves obey second-law of thermodynamics? (1.5 points)

(d) Using the transformed variable, x_1, perform an R-K polynomial fit of the data, including the mixing entropy to degree $n = 16$. Plot the experimental voltage data and the R-K fit voltage curves (both discharge and charge) as a function of the state-of-charge. Discuss the R-K polynomial fits and do these voltage curves obey second-law of thermodynamics? (1.5 points)

(e) Compare the $n = 6$ vs $n = 16$ cases and discuss the differences. (0.5 point)

(f) Using our R-K fits for both charge and discharge, what is the average voltage gap from $x_1 = 0.25$ to $x_1 = 0.45$? (1 point)

2: Phase Separation in Lithium Metal Anodes (10 points)

In this problem, we will analyze the initial thermodynamics and dynamics of lithium in an anode-free battery. In an anode-free lithium metal battery, lithium metal is directly plated on the current collector surface, typically copper, as shown in the figures. In this problem, we will analyze the initial nucleation and growth of deposited lithium.

We will assume that the sites available on the current collector (copper) surface can be occupied by lithium. The interaction (molar) enthalpy for adsorbing lithium on the surface of copper is given by,

$$h = \Omega x(1 - x) \tag{2}$$

where x is the fraction of sites on the on the copper surface occupied by lithium atoms. You may assume the standard chemical potentials for the empty surface, to be $\mu^0_{empty} = 0$ eV and fully covered surface, $\mu^0_{full} = 0.1$ eV. Use: $\Omega = 0.1$ eV, $T = 300$ K.

(i) Write down the electrochemical reaction associated with lithium metal anode battery. Identify the two 'phases' for this system. (1 point)

(ii) Derive an expression for the mixing (molar) entropy, s associated with the described system. (1 point)

(iii) Write down an expression for the molar gibbs free energy, g, and using that derive the chemical potential, μ for the system. (1 point)

(iv) Is there a region of instability? If yes, find out the values of filling fractions 'x_1' and 'x_2' between which the phase separation would occur. Determine the miscibility gap $(x_2 - x_1)$ and the coexistence chemical potential μ_{coex}.

(v) Changing the current collector from copper to a lithium alloy, changes the strength of the interaction, $\Omega = 0.05$ eV. For this case, is there a region of instability? If yes, find out the values of filling fractions 'x_1' and 'x_2' between which the phase separation would occur. Determine the miscibility gap $(x_2 - x_1)$ and the coexistence chemical potential μ_{coex}. (3 points total for the two sub-parts)

(vi) Now, let us consider the non-equilibrium case for copper current collector ($\Omega = 0.1$ eV), treated with Butler-Volmer kinetics with symmetric transfer coefficient and standard states. Derive an expression for the non-equilibrium chemical potential (total including the equilibrium portion) as a function of the fraction 'x'. You
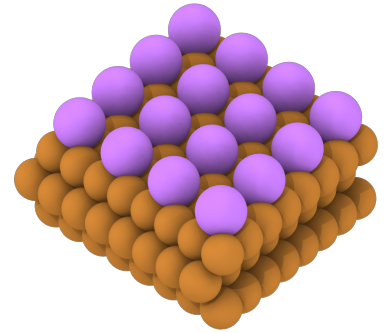

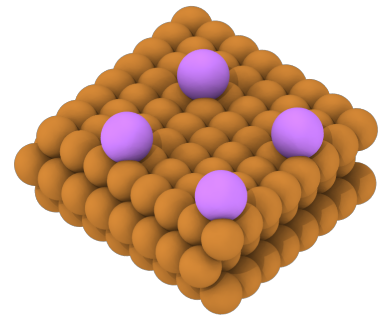Figure 1: A lithiated Cu111 surface at 1/4ML coverage.

Figure 2: A lithiated Cu111 surface at 1/16ML coverage.

may assume, similar to the LFP example, that the exchange current density is proportional to the "free" sites available on the copper surface. The intrinsic current density, $j_0^o = 1$ mA/cm^2. Plot the non-equilibrium chemical potential (total including the equilibrium portion) as a function of fraction 'x' for $j = 0.5, 5, 10$ mA/cm^2. (1.5 point)

(vii) Combining the equilibrium and non-equilibrium case, do any of the cases undergo phase separation? if yes, determine the miscibility gap and co-existence chemical potential (using either Maxwell construction or common tangent) for the same. If not, how does this happen? (2.5 points)

(viii) **Bonus:** Discuss what implications this has for a fast-charging anode-free battery. (1 point)

3: Marcus and Marcus-Hush Chidsey Kinetics (9 points)

In 2020 Boyle et al. [2], performed transient voltammetry on ultra microelectrodes, a method by which they were able to measure the current and overpotential relationship for the charge transfer reaction during lithium electrodeposition and stripping. This provides crucial information about quantities like exchange current density of electrodeposition and stripping which are important for understanding working mechanisms of Li-metal anode based batteries and other devices where lithium electrodes are used.

[2] David T Boyle, Xian Kong, Allen Pei, Paul E Rudnicki, Feifei Shi, William Huang, Zhenan Bao, Jian Qin, and Yi Cui. Transient voltammetry with ultramicroelectrodes reveals the electron transfer kinetics of lithium metal anodes. *ACS Energy Lett.*, 5(3):701–709, 2020

You are provided with the current-overpotential data for two electrolytes (electrolyte A and electrolyte B), using our understanding of various kinetic theories, we will analyze this data to draw inferences about kinetics of Li-metal electrodes.

(i) Write down the reversible electrochemical reaction for lithium electrodeposition and stripping processes and identify the oxidized and reduced species. (1 point)

(ii) Using the Butler-Volmer theory, estimate the exchange current density for the electrodeposition and stripping reaction in the two electrolytes. (2 points)
Note: Feel free to truncate the data such that only the linear response region of the current-overpotential data is used for fitting the BV expression.

(iii) Comment about the fit obtained using Butler-Volmer theory between the full dataset and truncated dataset for linear region alone. (1 point)

Marcus theory introduces the concept of solvent reorganization energy which can be incorporated within the the Butler-Volmer formalism using a potential dependent α as follows (λ in eV):

$$\alpha = \frac{1}{2} + \frac{\eta}{4\lambda} \tag{3}$$

(v) What are the reorganization energies estimated using the Marcus-Hush theory for each of the electrolytes? Please provide a table of reorganization energies and current densities. (4 points)

(vi) Comment about the fit obtained using the Marcus-Hush theory compared to the Butler-Volmer theory. Under what conditions can the Marcus-Hush theory be usable for this dataset? (1 point)

(vii) **Bonus:** Are there other theories that could be more appropriate for this dataset? If yes, which theory and discuss why it is applicable? (1 point)