Fall 2022 Solid State Ionics

Homework 3

Instructor: Qiyang Lu
TA: Kaichuang Yang
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Problem 1: The Nernst term in the Butler-Volmer Equation

Consider the electrochemical reaction below:

$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R, \quad E^{0'} = 0\ V$$

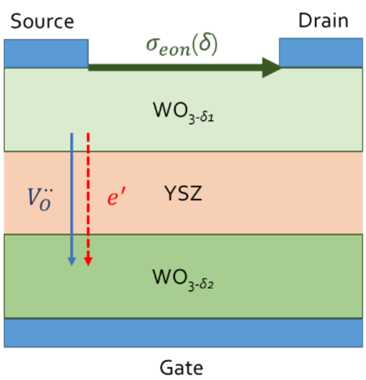
1. Express the current density j ($j = I/A$, I: current, A: electrode area) as a function of bulk concentration of O and R (c_O and c_R, unit: mol/L, assume that diffusion is fast), reaction rate constant k^0 (unit: cm/s) and the potential E with $E^{0'}$ as the reference ($\Delta E = E - E^{0'}$).
2. Write down the Nernst equation correlating equilibrium potential E_{eq} with concentrations c_O and c_R. Then rewrite the Bulter-Volmer (B-V) equation using overpotential $\eta = E - E_{eq}$. Define the exchange current density j_0 using the B-V equation rewritten.
3. If the temperature is fixed at 300 K and the symmetry coefficient α is fixed to 0.5, draw the $j \sim \eta$ curves with the numbers below using your favorite scientific graphing software/code (*e.g.*, Originlab, Python Matplotlib, Matlab) with the range of potential E = -0.3 V ~ 0.3 V:

a) If $c_O = c_R =$ 0.1 mol/L, in a single plot, draw the $j \sim \eta$ curves with 1) k^0=10^{-4} cm/s; 2) k^0=10^{-5} cm/s; 3) k^0=10^{-6} cm/s;

b) If c_R = 0.1 mol/L, k^0=10^{-4} cm/s, in a single plot, draw the $j \sim \eta$ curves with 1) $c_O =$ 1 mol/L; 2) $c_O =$ 0.1 mol/L; 3) $c_O =$ 0.01 mol/L;

4. Show that the ratio between anodic and cathodic current density (j_a/j_c) is **independent** on the symmetry coefficient α (so-called *de Donder relation*).

Problem 2: Phase separation in electrochemical ionic synapses



In a recent paper by Kim *et al.* (*Adv. Electron. Mater.* **2022**, 2200958), the authors fabricated an electrochemical ionic synapse with the structure shown as the figure in the left. The device has two symmetric $WO_{3-\delta}$ layers (δ means oxygen non-stoichiometry) with an oxygen ion conducting YSZ electrolyte layer in between. By applying an external voltage across the device, the oxygen ions can be moved from the bottom layer $WO_{3-\delta_2}$ to the top layer $WO_{3-\delta_1}$ (or the reverse). Since the electronic conductivity σ_{eon} of $WO_{3-\delta}$ is dependent on $\boldsymbol{\delta}$, this device can be used as a memory device (synaptic device). However, the YSZ electrolyte has a very low but non-negligible electronic conductivity. This means that after sufficient long time, the *chemical potential of oxygen* will be equilibrated for the two $WO_{3-\delta}$ layers, which can cause the volatility of the device. Kim *et al.* pointed out that the volatility is related to if $WO_{3-\delta}$ will go through phase separation with increasing $\boldsymbol{\delta}$.

1. Let's first consider the case without phase separation, which we will model using ***ideal lattice gas model***. Start with a perfect WO_3 lattice (denote as $\boldsymbol{x = 0}$), then we add oxygen vacancy (charge balanced by electrons) until a maximum non-stoichiometry $\boldsymbol{\delta_{max}}$ is reached (denote as $\boldsymbol{x = 1}$). Write down the quantitative relationship and sketch the entropy, the Gibbs free energy and the chemical potential as a function of $\boldsymbol{x}$ ($\mathbf{x = \delta/\delta_{max}}$).
2. If an external voltage is applied so that $\boldsymbol{\delta_1 << \delta_2}$ and $\boldsymbol{(\delta_1+\delta_2)/\delta_{max}=1}$, the system will slowly be restored to equilibrium so that the chemical potential of the top and bottom $WO_{3-\delta}$ become the same. Show that this means $\boldsymbol{\delta_1 = \delta_2 = \delta_{max}/2}$. (Assume the top and bottom layers are symmetric, and the total amount of oxygen vacancy in the system is fixed.) This means that the top $WO_{3-\delta}$ layer is ***volatile*** (forgetting).
3. We can also calculate the rate that the device is restored to equilibrium by taking the steps below:
    a. The Faradaic current passing through the YSZ electrolyte can be modeled by using the Bulter-Volmer equation. The overpotential is the difference between the chemical potential at $\boldsymbol{\delta_1}$ (or $\boldsymbol{\delta_2}$, again the device is symmetric) and the chemical potential at $\boldsymbol{\delta_{max}/2}$. Write down the expression of current density j as a function of exchange current density j_0, symmetry coefficient α and non-stoichiometry $\boldsymbol{\delta_1}$.
    b. Assume that the chemical diffusion in the $WO_{3-\delta}$ layer is fast, try to calculate the time needed for restoring equilibrium $\boldsymbol{t_{eq}}$. Denote the thickness of each $WO_{3-\delta}$ layer as $\boldsymbol{l}$ and the volume of $WO_{3-\delta}$ unit cell as $\boldsymbol{V}$.
4. Now let's work on the case with phase separation by using the ***regular solution model*** (non-ideal lattice gas model). Suppose that the non-zero enthalpy change is dependent on a positive interaction parameter h_0. Again, write down the quantitative relationship and sketch the entropy, the Gibbs free energy and the chemical potential as a function of $\boldsymbol{x}$ ($\mathbf{x = \delta/\delta_{max}}$).
5. For the phase separation case, explain why in this scenario if an external voltage is applied so that $\boldsymbol{\delta_1 << \delta_2}$ and $\boldsymbol{(\delta_1+\delta_2)/\delta_{max}=1}$, the system can stay with different $\boldsymbol{\delta}$ for the top and bottom $WO_{3-\delta}$ layer. This means that now the top $WO_{3-\delta}$ layer is ***non-volatile*** (not forgetting).