Fall 2023 Solid State Ionics

Homework 3

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Problem 1: Open-circuit potential of a "hydrogen battery"

Consider an electrochemical cell with electrochemical reactions at the cathode and anode as shown below:

$$\text{Cathode: } xH^+ + xe^- + AO_3 \rightarrow H_xAO_3$$
$$\text{Anode: } x/2\,H_2 \rightarrow xH^+ + xe^-$$

AO_3 denotes a transition metal oxide (*e.g.*, WO_3 or MoO_3) which can accommodate a certain amount of H in the oxide lattice ($0 < x < 1$ in H_xAO_3 and the maximum concentration of H is reached when $x = 1$).

1. If we assume the chemical potential of charge neutral species *H* is 0 at the anode (*i.e.*, $\mu_{H,a} = 0\ eV$), express the open circuit potential of such a hydrogen battery as a function of chemical potential of H at the cathode $\mu_{H,c}$.
2. If we model the cathode oxide H_xAO_3 by using the ***ideal lattice gas model***, ***write down the expression of and plot***
   1) Entropy ***S*** per lattice site;
   2) Gibbs free energy ***G*** per lattice site;
   3) Chemical potential ***μ***;
   4) Open-circuit potential (OCP) ***E*** as a function of concentration ***x***.
3. If we model the cathode oxide H_xAO_3 by using the ***regular solution model***. If the enthalpy per lattice site has the form of $H = h_0x(1-x)$. For the phase separation case, w***rite down the expression and plot***
   1) Entropy ***S*** per lattice site;
   2) Gibbs free energy ***G*** per lattice site;
   3) Chemical potential ***μ*** as a function of concentration ***x***.
   4) In the plots, show the points of the two concentrations for the stable phases x_1 and x_2.
   5) Try to point out in the plots (qualitatively) the range of concentration ***x*** where the phase separation is spontaneous and barrierless (*i.e.*, spinodal decomposition)
4. Following the phase separation case above in question 3, draw the plot of open-circuit potential (OCP) ***E*** vs. concentration ***x***, assuming that the nucleation can occur easily (*i.e.*, phase separation can be triggered outside the spinodal region).
5. Now let's assume that the nucleation is difficult, and the phase separation is only spontaneous within the spinodal decomposition region. Try to draw the OCP ***E*** ~ concentration ***x*** for charging (***x*** changed from 1 to 0) and discharging (***x*** changed from 0 to 1) processes and explain why the charging/discharging curves look different.

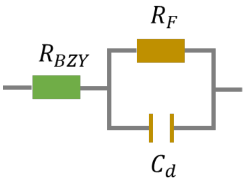
Problem 2: Frumkin effect at Pt/Ba(Zr,Y)O$_3$ interfaces

Consider the electrochemical interfaces of a Pt electrode and a Ba(Zr,Y)O$_3$ (BZY) electrolyte. Hydrogen gas (***H_2***) can be dissociated and adsorbed at the Pt electrode forming adsorbed ***H_{ads}*** and then go through electrochemical reaction to protons and electrons as the Ba(Zr,Y)O$_3$ (BZY) electrolyte is proton-containing. The electrochemical reaction can be written as below:

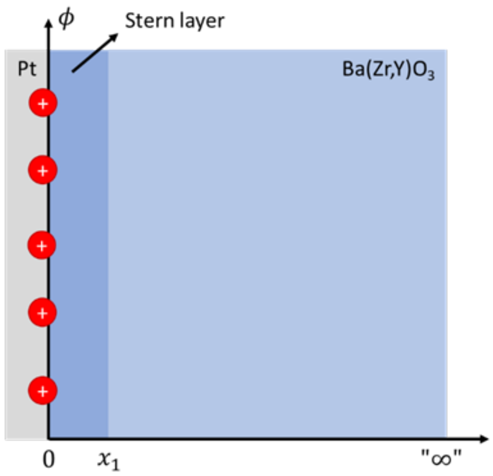
$$\boxed{H^+ + e^- \rightleftharpoons H_{ads}} \quad E^{0\prime} = 0\,V$$

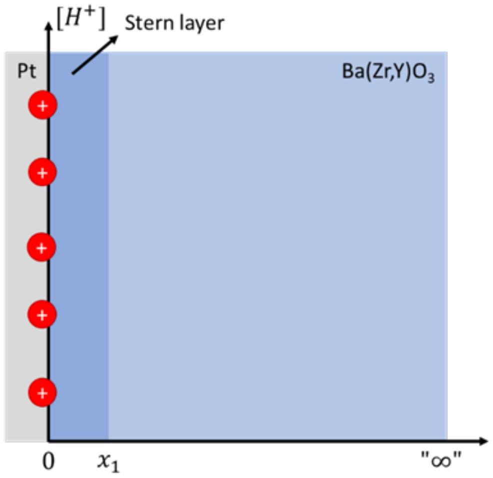
The forward reaction is cathodic (hydrogen evolution), and the backward reaction is anode (hydrogen oxidation).

1. Assume that the diffusion in the BZY electrolyte is fast and there is no space charge layer at the Pt/BZY interface, write down the Bulter-Volmer equation for
   1) cathodic (hydrogen evolution) current density ***j_c***;
   2) anodic (hydrogen oxidation) current density ***j_a***;
   3) the total current density ***j*** as a function of applied potential ***E*** (notice that the formal potential ***$E^{0\prime}$*** is 0 V), the bulk concentration of protons in BZY $[H^+]_{x=\infty}$ and the surface coverage of ***H_{ads}*** $\theta_{H_{ads}}$ ($\theta_{H_{ads}}$ can be treated as the concentration of ***H_{ads}***). Assume that the symmetry coefficient α = 1/2.
2. 1) Write down the Nernst equation for the electrochemical reaction $H^+ + e^- \rightleftharpoons H_{ads}$.
   2) If the overpotential ***η*** is defined as ***η*** = ***E*** - ***E_{eq}***, rewrite the Bulter-Volmer equation of the current density ***j*** using ***η*** rather than ***E***.
   3) Derive the expression of exchange current density ***j_0***
3. If the overpotential ***η*** is ***small***, then ***j*** – ***η*** curve can be ***linearized***.
   1) Derive the charge transfer (Faradaic) resistance ***R_F*** = ***η/j*** under this limit.
   2) For the Pt/BZY electrochemical cell, the impedance of the system can be modeled using the equivalent circuit below:



   In the circuit, ***R_{BZY}*** is the Ohmic resistance of the electrolyte, ***R_F*** is the Faradaic resistance and ***C_d*** denotes the double layer capacitance. Derive the complex impedance (***Z(ω)***) and draw a Nyquist plot (***Z'(ω)*** ~ ***-Z''(ω)***) and mark the intercepts with the real axis in the plot.
4. Assume that a positively charged space charge core exists at the Pt/BZY interface. Consider the case that both a stern layer (linearly varying electrostatic potential) and a diffuse layer (Gouy-Chapman case) coexist. In the figures below, try to sketch
   1) electrostatic potential distribution;
   2) H$^+$ concentration distribution (***only in the diffuse layer***). Assume that H$^+$ is the only mobile positive charged defect.





5. Consider the case that the ***cathodic*** current density is much higher than the anodic current ($j \approx j_c$). If the space charge exists as shown in question 3, and the electrochemical reaction occurs at $x = x_1$, try to rewrite the expression of j as a function of $[H^+]_{x=\infty}$ and the electrostatic potential at $x = x_1$ (ϕ_1). Assume that the symmetry coefficient $\alpha = 1/2$. ***Note:*** you can either use E or η in the Bulter-Volmer equation, but remember that $E^{0'}$ or E_{eq} is changed since $[H^+]_{x=\infty} \neq [H^+]_{x=x_1}$.
6. Derive the expression of the Tafel slope (the slope of $\ln j \sim \eta$) with the Frumkin effect as shown in question 4. Show and explain why the Tafel slope is not a constant anymore.