Fall 2023 Solid State Ionics

Homework 1

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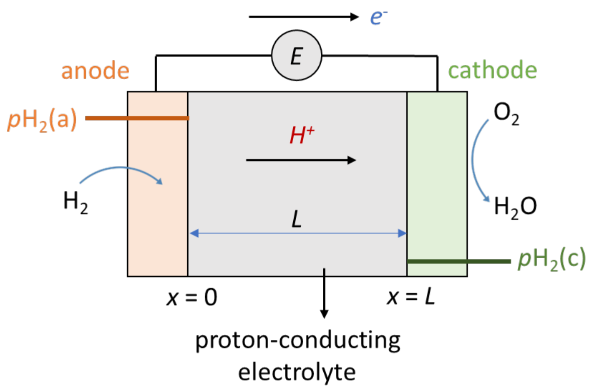
Problem 1: Ionic defects in halide perovskites

Halide perovskites with chemical formula of ABX_3 (A = inorganic ions, *e.g.* Cs^+ or organic ions, *e.g.* Methylammonium (MA^+); B = Pb or Sn, *etc.*, X = I or Br) have attracted widespread attention due to the excellent optoelectronic properties, and have been widely used in solar cells, light-emitting diodes (LEDs) and photodetectors. Recently, researchers have found that the halide perovskite can accommodate a non-negligible concentration of ionic defects, which have important effects on the physical properties and device performance.

1. For a halide perovskite $MAPbI_3$ (A-site cation = MA^+, B-site cation = Pb^{2+}, X-site anion = I^-), write down the Kröger-Vink notations for:
   a) MA^+ vacancies;
   b) I^- vacancies;
   c) Electrons and holes;
   d) O impurities occupying the I^- site (assume O takes the form of O^{2-})
2. Write down the condition of charge neutrality by considering the following four defects: MA^+ vacancies + I^- vacancies (Schottky pairs), electrons and holes.
3. Try to sketch the Brouwer diagram (log [*def*] ~ log pI_2) for $MAPbI_3$ with MA^+ & I^- vacancies (Schottky pairs) as the main *ionic* defects by taking the steps below:
   a) Write down the formula of defect chemical reactions and the expression of chemical equilibrium conditions (chemical equilibrium constants and concentrations) for i) formation of Schottky pairs (with chemical equilibrium constant as K_s); ii) formation of electron-hole pairs (with chemical equilibrium constant as K_{el}); iii) Iodine exchange reaction, *i.e.*, formation of I^- vacancies and charge-balancing electronic defects by taking out an I^- ion at a regular site (with chemical equilibrium constant as K_I).
   b) For the intrinsic region (Schottky pairs dominate), write down the Brouwer condition and solve for concentrations of all four defects.
   c) For the I-rich region (MA^+ vacancies & holes dominate), write down the Brouwer condition and solve for the expressions for concentrations of all four defects.
   d) For the I-poor region (I^- vacancies & electrons dominate), write down the Brouwer condition and solve for the expressions for concentrations of all four defects.
   e) Sketch the Brouwer diagram for all three regions above. Assume that $K_{el} << K_s$. Mark the important slopes in each region.
4. Solve for the pI_2 for the ***stoichiometric*** point.
5. Studies have shown that the MA^+ ions are mostly immobile, which means that the ionic conductivity of $MAPbI_3$ is mostly contributed by I^- vacancies. Write down the expressions for ionic, electronic and the total conductivity of $MAPbI_3$. Plot the ionic and electronic conductivity as a function of pI_2.

Problem 2: Chemical potential profiles in a proton-conducting oxide

In recent years, proton-conducting oxides have attracted a lot of attention due to the high H^+ conductivity even at relatively low temperatures (<500°C). Therefore, using proton-conducting oxides to replace the conventional O^{2-} conducting electrolyte can potentially enable fuel cells with much lower operation temperatures.



The working principle of such a fuel cell can be shown as the figure above. The proton-conducting electrolyte is sandwiched between an anode and a cathode. Consider the open-circuit condition with $pH_2(a)$ and $pH_2(c)$ as the (effective) hydrogen partial pressure at the anodic and cathodic side, respectively.

1. Write down the chemical reactions (involving gas molecules, ions and electrons) and chemical equilibrium conditions at the anode/electrolyte interface and the cathode/electrolyte interface.
2. What is the equilibrium condition for H^+ at open-circuit condition?
3. Combine 1&2, express the cell voltage as a function by using i) $pH_2(a)$ and $pH_2(c)$; ii) $pH_2(a)$ and $pH_2O(c)/pO_2(c)$.
4. In reality, the proton-conducting electrolyte has a very small but non-negligible electronic conductivity. Write down the expression of the ***flux*** of protons and electrons as a function of the gradient of appropriate thermodynamic potentials and the protonic/electronic conductivity $\sigma_{ion}/\sigma_{eon}$.
5. We also want to know the profile of chemical potentials (μH_2) inside the electrolyte. Again assume the equilibrium condition at the open circuit condition, and that σ_{eon} is a constant (independent of pH_2), try to calculate and sketch the profile of μH_2 in the electrolyte (from $x = 0$ to $x = L$). You will accomplish this by taking the steps below:
    i. For each point x in the electrolyte, write down the relationship between the chemical potential of H_2 and the electrochemical potential of H^+ and e^-;
    ii. We know that the flux of electrons must be the same everywhere in the electrolyte. Try to write down the expression of the flux of electrons using the chemical potential of H_2; (***Hint:*** in 1-dimension, this means that the derivative of the flux should be 0)
    iii. Based on what you found in the above two steps, sketch the profiles of chemical potential of H_2 and the electrochemical potential of H^+ and e^- ($0 < x < L$).