Fall 2022 Solid State Ionics

Homework 2

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Problem 1: "Job-sharing" mass transport

In a recent paper by Chen et al. (Nature **536**, 159–164 (2016)), the authors developed the concept of "job-sharing mass transport" and demonstrate ultrafast mass transport (even faster than NaCl in liquid water) at the interfaces between a pure ionic conductor and a pure electronic conductor (see Figure 1).

1. In a mixed ionic and electronic conductor (MIEC), assume that the charge neutral species of mass transport is Ag. Write down the expression of chemical diffusivity D_{Ag}^{δ} based on the electronic/ionic conductivity ($\sigma_{e^-}/\sigma_{Ag^+}$) and the concentration of electronic/ionic species (c_{e^-}/c_{Ag^+}, assume the dilute limit).
2. In the expression you reached in 1, please specify which part is related to the chemical resistance R^{δ} and which part is related to the chemical capacitance C^{δ}?

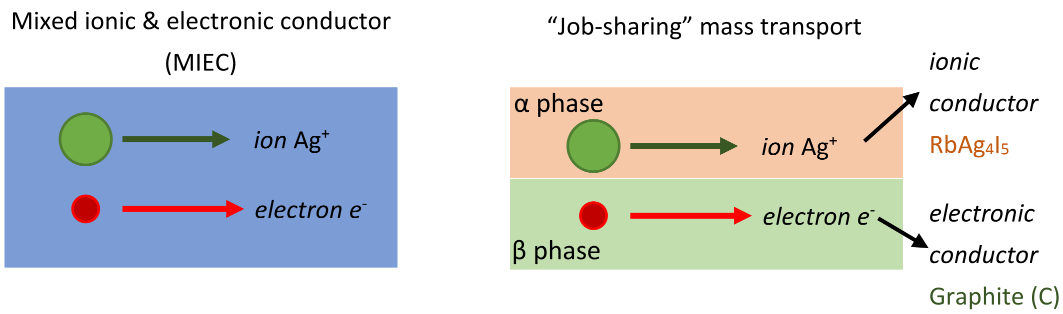

Figure 1 Chemical diffusion in MIEC and job-sharing composites.

3. Now let's consider the "job-sharing" case as shown in Figure 1 (Right). Assume the α phase is a pure ionic conductor $RbAg_4I_5$ with very high ionic conductivity $\sigma_{Ag^+}^{\alpha}$ but very low electronic conductivity $\sigma_{e^-}^{\alpha}$. On the other hand, the β phase graphite is a pure electronic conductor with very high $\sigma_{e^-}^{\beta}$ but very low $\sigma_{Ag^+}^{\beta}$, we will reach the expression of chemical diffusivity in this "job-sharing" composites with the steps below:
   a) Write down the expression of ionic flux in α phase $J_{Ag^+}^{\alpha}$ and electronic flux in β phase $J_{e^-}^{\beta}$ based on the conductivities and the gradient of electrochemical potential of ionic

($\tilde{\mu}^{\alpha}_{Ag^+}$) and electronic species ($\tilde{\mu}^{\beta}_{e^-}$).

b) Follow the process of deriving the chemical diffusivity shown in the lectures, try to reach the expression of the flux of charge neutral species Ag, by recognizing: $J_{Ag} = J^{\alpha}_{Ag^+} = J^{\beta}_{e^-}$. Notice in this case, the electrostatic potentials for α phase and β phase are no longer the same (*i.e.*, $\phi^{\alpha} \neq \phi^{\beta}$). You can leave the $\phi^{\beta} - \phi^{\alpha}$ term unchanged in this step.

c) If we just focus on the contribution of conductivity (ignore the effect of other terms for a minute). Let's plug in some numbers: for $RbAg_4I_5$, $\sigma^{\alpha}_{Ag^+} = 0.27\ S/cm$, $\sigma^{\alpha}_{e^-} = 3 \times 10^{-9}\ S/cm$, while for graphite, $\sigma^{\beta}_{e^-} = 1250\ S/cm$. If we compare the chemical diffusivity of $RbAg_4I_5$/graphite composite with that of pure $RbAg_4I_5$, how much enhancement do we expect from the conductivity term?

d) Now let's look at the concentration (capacitance) term. For $RbAg_4I_5$, $c^{\alpha}_{Ag^+} \approx 10^{22} cm^{-3}$, while for graphite, $c^{\beta}_{e^-} \approx 10^{19}\ cm^{-3}$. Which concentration term will be dominate? Ionic or electronic?

e) Finally let's calculate the $\phi^{\beta} - \phi^{\alpha}$ term. Consider the simplified case in Figure 2. The length separating the two charged layers at the interfaces of α and β phase is s, which is on the same order magnitude of lattice spacing (~1 nm). Try to derive the expression of the $\phi^{\beta} - \phi^{\alpha}$ term based on this simplification. Assume the relative permittivity ε_r= 5. Compare this term to the concentration terms in d), is the electrostatic term important or can it be safety ignored?

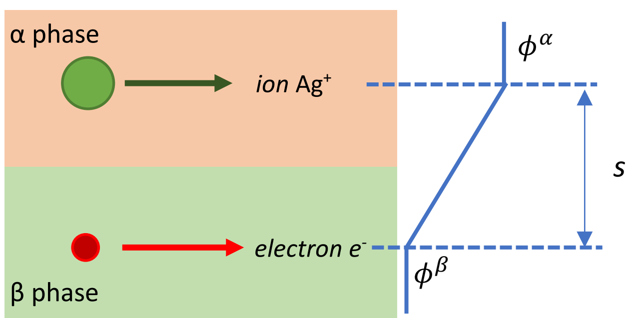

Figure 2 Interfacial electrostatic potential difference in job-sharing composites.

Problem 2: The exact solution of the potential profile in Gouy-Chapman case

In Lecture 7, we derive the potential profile in the Gouy-Chapman case with the assumption of a low ϕ_0 so that we can linearize the equation. In this problem, we are going to relax this assumption and find the exact solution of the potential profile of the Gouy-Chapman case.

1. The same as we have discussed in Lecture 7, consider two mobile defects with opposite charge ze and -ze, a bulk concentration of c_∞ and a positive core charge Q_{core}. Express **1)** the concentrations of these two mobile defects ($c_+(x)$ and $c_-(x)$) **2)** charge density $\rho(x)$ **3)** Poisson's equation as a function of position x and electrostatic potential ϕ.

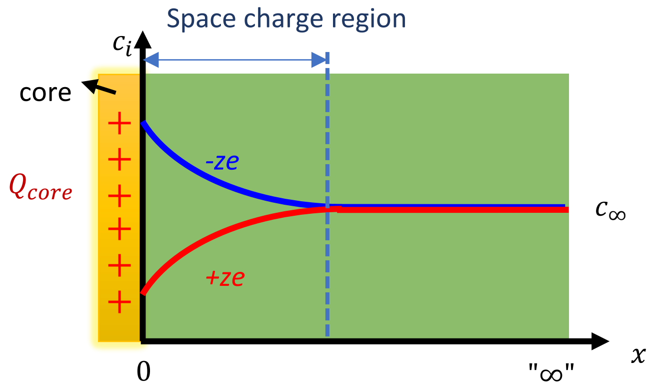

Figure 3 Space charge layer: Gouy-Chapman case

2. Solve the Poisson's equation analytically by taking the steps below:

   a) Notice $\frac{d^2\phi}{dx^2} = \frac{1}{2}\frac{d}{d\phi}(\frac{d\phi}{dx})^2$, try to find the solution for $(\frac{d\phi}{dx})^2$

   b) Consider the position far away from the space charge core, we should have: $\phi = 0$ and $\frac{d\phi}{dx} = 0$. Find the solution for $\frac{d\phi}{dx}$ based on this boundary condition. Think carefully which square root you should choose.

   c) Try to solve the integral and find the solution for $\phi(x)$. You can simplify the solution by denoting the potential at $x = 0$ as ϕ_0 and defining the Debye length (also write down the expression for the Debye length). **Hint**: you might find this integral useful: $\int \frac{1}{\sinh(x)} = \ln\left(\tanh\left(\frac{x}{2}\right)\right) + C$.

3. Use your favorite scientific graphing software/code (*e.g.*, Originlab, Python Matplotlib, Matlab) to plot the following cases:

   a) z = 1, c_∞ = 1 mM, ε_r= 5, plot normalized electrostatic potential profile $\phi(x)/\phi_0$ for **1)** ϕ_0 = 10 mV, **2)** ϕ_0 = 100 mV, **3)** ϕ_0 = 1000 mV in the same plot.

   b) z = 1, ε_r= 5, ϕ_0 = 100 mV, plot normalized electrostatic potential profile $\phi(x)/\phi_0$ with x/λ_D as *x*-axis for **1)** c_∞ = 10^{20} cm^{-3}, **2)** c_∞ = 10^{21} cm^{-3}, 3) c_∞ = 10^{22} cm^{-3}