Materials for Devices: Problem Set 3

9. From Fick's first law, we have that under an applied voltage V, the current density obeys:

$$j_x = -qD\frac{\partial n}{\partial x} - \sigma\frac{\partial V}{\partial x}, \tag{1}$$

where n is the concentration of particles, q their charge, D is the diffusion coefficient, and σ is the conductivity.

   (i) Assume that the concentration n of diffusing particles in the presence of a potential V is given by the Boltzmann distribution $n = n_0 e^{-qV/k_B T}$. Show that:

$$\frac{\partial n}{\partial x} = -\frac{nq}{k_B T}\frac{\partial V}{\partial x}. \tag{2}$$

   (ii) Hence, prove the validity of the Nernst-Einstein equation:

$$\frac{\sigma}{D} = \frac{nq^2}{k_B T}. \tag{3}$$

10. (i) Sketch a unit cell of CaF_2 and describe the coordination of calcium by fluorine and of fluorine by calcium.

   (ii) In δ-Bi_2O_3, the bismuth sublattice is the same as that of calcium in CaF_2, but the stoichiometry means that there are vacant anion sites, randomly distributed. Sketch a possible unit cell of δ-Bi_2O_3.

   (iii) Explain why δ-Bi_2O_3 is a fast ionic conductor whilst stoichiometric CaF_2 is not. How many oxygen vacancies are there, on average, per unit cell?

   (iv) Consider yttria-stabilised zirconia, Y_2O_3 doped with ZrO_2, $Zr_{1-x}Y_xO_{[2-(x/2)]}$. Calculate the composition of yttria-stabilised zirconia which would give one quarter of the average oxygen vacancy content of δ-Bi_2O_3.

11. Yttria stablilised zirconia with a cation ratio of 8:92 (Y:Zr) is produced by mixing appropriate quantities of yttria (Y_2O_3) with zirconia (ZrO_2). What is the molar oxygen composition, x, in the resulting material, $Y_{0.08}Zr_{0.92}O_x$?

12. The diffusivity of an ionic conductor is given by the Arrhenius equation $D = D_0 e^{-E_B/k_B T}$, where E_B is the energy barrier, D_0 is the pre-exponential factor, and T is the temperature. The concentration of diffusing ions is given by the Boltzmann distribution $n = n_0 e^{-qV/k_B T}$.

   (i) Consider the limit of a small applied electric field, such that $qV \ll k_B T$. Show that in this limit, $n \simeq n_0$.

   (ii) Using this approximation in the Nernst-Einstein equation, show that:

$$\ln\sigma \simeq \ln\sigma_0 - \frac{E_B}{k_B T}, \tag{4}$$

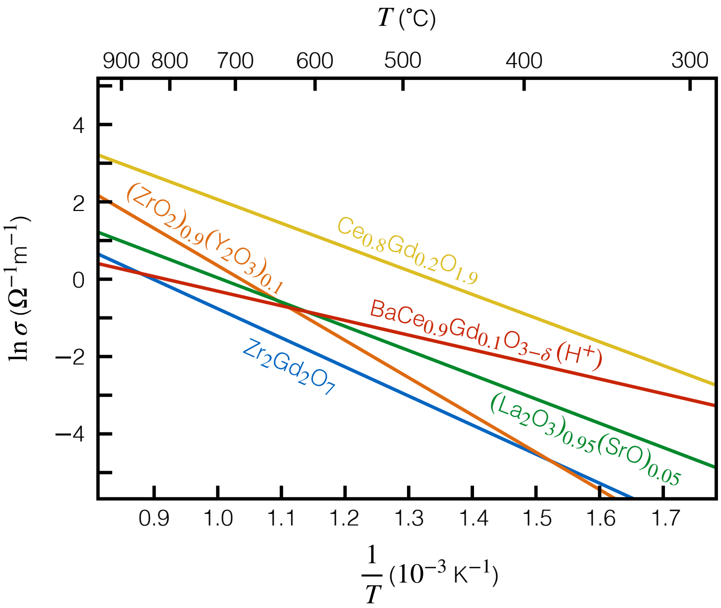
   where $\sigma_0 = \frac{D_0 n_0 q^2}{k_B T}$.

(iii) By comparing $\frac{1}{T}$ and $\ln\left(\frac{1}{T}\right)$, argue that $\ln\sigma_0 \simeq$ constant. Therefore, explain how a plot of $\ln\sigma$ against $\frac{1}{T}$, called an Arrhenius plot, can be used to understand the behaviour of ionic conductors.

(iv) Consider the Arrhenius plot shown in the Figure below. Estimate the activation energy for ion transport in yttria-stabilised zirconia.

(v) In $Zr_{0.8}Y_{0.2}O_{1.9}$, how many oxygen vacancies are there per unit cell? If the lattice parameter of cubic yttria-stabilised zirconia is 0.54 nm, calculate the number of vacancies per unit volume.

(vi) The Nernst-Einstein equation indicates that the ratio $\frac{\sigma}{D}$ for a given material varies only with temperature. Calculate $\frac{\sigma}{D}$ for $Zr_{0.8}Y_{0.2}O_{1.9}$ at 800 °C.



13. The α phase of silver iodide (AgI) has a iodine atoms arranged in a body centred cubic lattice with $a = 5.0855$ Å for the conventional cubic cell. It is an ionic conductor with Ag^+ cations being the mobile species, and the diffusivity at 150 °C is $4.5 \times 10^{-11}\,m^2s^{-1}$. A potential difference is applied across a sample of AgI, using Ag for both electrodes, and current is allowed to flow. The half cell reactions are:

$$\text{cathode (reduction):} \quad Ag^+ + e^- \longrightarrow Ag \quad (5)$$
$$\text{anode (oxidation):} \quad Ag \longrightarrow Ag^+ + e^- \quad (6)$$

Consider:

(i) What is the number of charge carriers per unit volume in AgI?

(ii) What is the conductivity of AgI at 150 °C?

(iii) What is the mass of silver deposited at the cathode if a current of 5 mA flows through the circuit for 5 minutes?