

## Materials for Devices: Problem Set 3

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

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

where  $n$  is the concentration of diffusing ions,  $q$  their charge,  $D$  is the diffusion coefficient, and  $\sigma$  is the conductivity.

- (i) Sketch a one-dimensional energy landscape for ionic diffusion, labelling the energy barrier  $E_B$ .
- (ii) Sketch the same one-dimensional energy landscape, but now in the presence of an external constant electric field such that there is a voltage difference  $\Delta V$  between ionic sites.
- (iii) Show that, in the presence of an external constant electric field, the net probability  $p$  of a jump from one site to the other is proportional to:

$$p \propto e^{-\frac{E_B}{k_B T}} \left( 1 - e^{-\frac{q\Delta V}{k_B T}} \right)$$

- (iv) Consider the limit of a small applied electric field, such that  $q\Delta V \ll k_B T$ . Show that, in this limit, the net probability  $p$  of a jump from one site to the other can be approximated as:

$$p \propto e^{-\frac{E_B}{k_B T}} \left( \frac{q\Delta V}{k_B T} \right).$$

- (v) Therefore, show that:

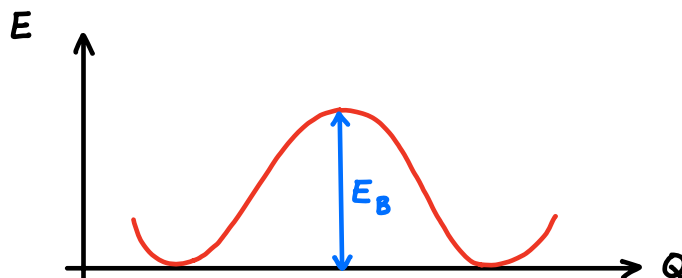
$$\frac{\partial n}{\partial x} = -\frac{nq}{k_B T} \frac{\partial V}{\partial x}.$$

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

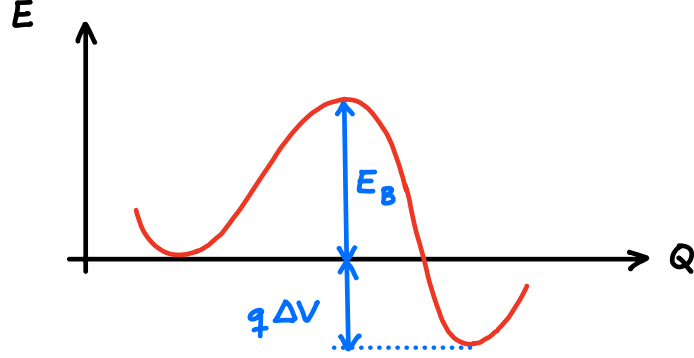
$$\frac{\sigma}{D} = \frac{nq^2}{k_B T}.$$

*Solution*

- (i) The requested schematic is given by:



(ii) The requested schematic is given by:



(iii) Let  $p_{L \rightarrow R}$  be the probability of an ionic jump from the left site to the right site. This probability is proportional to:

$$p_{L \rightarrow R} \propto e^{-E_B/k_B T}.$$

Similarly, let  $p_{R \rightarrow L}$  be the probability of an ionic jump from the right site to the left site. This probability is proportional to:

$$p_{R \rightarrow L} \propto e^{-(E_B + q\Delta V)/k_B T}.$$

Therefore, the net probability of a jump from one site to the other is:

$$\begin{aligned} p = p_{L \rightarrow R} - p_{R \rightarrow L} &\propto e^{-E_B/k_B T} - e^{-(E_B + q\Delta V)/k_B T} \\ &\propto e^{-E_B/k_B T} \left( 1 - e^{-q\Delta V/k_B T} \right). \end{aligned}$$

(iv) In the limit  $q\Delta V \ll k_B T$ , we can expand the exponential in the bracket to first order to obtain:

$$\begin{aligned} p &\propto e^{-E_B/k_B T} \left( 1 - \left( 1 - \frac{q\Delta V}{k_B T} \right) \right) \\ &\propto e^{-E_B/k_B T} \left( \frac{q\Delta V}{k_B T} \right). \end{aligned}$$

(v) The number density of ions decreases by the fraction undergoing a net jump:

$$\Delta n = -n_0 e^{-E_B/k_B T} \left( \frac{q\Delta V}{k_B T} \right),$$

where  $n_0$  is the total number density of ions. If this jump is associated with displacement  $\Delta x$ , we can write:

$$\frac{\Delta n}{\Delta x} = -n_0 e^{-E_B/k_B T} \frac{q}{k_B T} \frac{\Delta V}{\Delta x}.$$

In the limit  $\Delta x \rightarrow 0$ , and using the Boltzmann distribution for the number of diffusing ions  $n = n_0 e^{-E_B/k_B T}$ , we obtain:

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

(vi) Frick's first law in the steady state  $j_x = 0$  reads:

$$\sigma \frac{\partial V}{\partial x} = -qD \frac{\partial n}{\partial x}.$$

Using the result from part (v) to re-write  $\frac{\partial n}{\partial x}$ , we obtain:

$$\sigma \frac{\partial V}{\partial x} = -qD \left( -\frac{nq}{k_B T} \frac{\partial V}{\partial x} \right).$$

Re-arranging, we end up with the Nernst-Einstein equation:

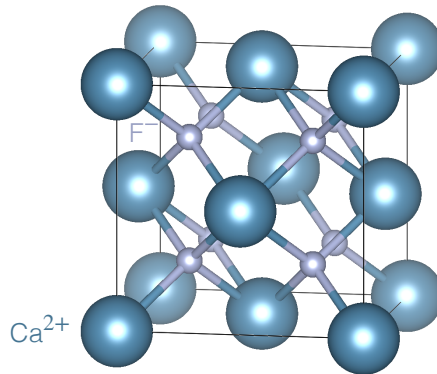
$$\frac{\sigma}{D} = \frac{nq^2}{k_B T}.$$

The Nernst-Einstein equation relates the conductivity and the diffusivity in the steady state.

10. (i) Sketch a unit cell of  $\text{CaF}_2$  and describe the coordination of calcium by fluorine and of fluorine by calcium.
- (ii) In  $\delta\text{-Bi}_2\text{O}_3$ , the bismuth sublattice is the same as that of calcium in  $\text{CaF}_2$ , but the stoichiometry means that there are vacant anion sites, randomly distributed. Sketch a possible unit cell of  $\delta\text{-Bi}_2\text{O}_3$ .
- (iii) Explain why  $\delta\text{-Bi}_2\text{O}_3$  is a fast ionic conductor whilst stoichiometric  $\text{CaF}_2$  is not. How many oxygen vacancies are there, on average, per unit cell?
- (iv) Consider yttria-stabilised zirconia  $\text{Zr}_{1-x}\text{Y}_x\text{O}_{[2-(x/2)]}$ , which is made of  $\text{ZrO}_2$  doped with  $\text{Y}_2\text{O}_3$ . Calculate the composition of yttria-stabilised zirconia which would give one quarter of the average oxygen vacancy content of  $\delta\text{-Bi}_2\text{O}_3$ .

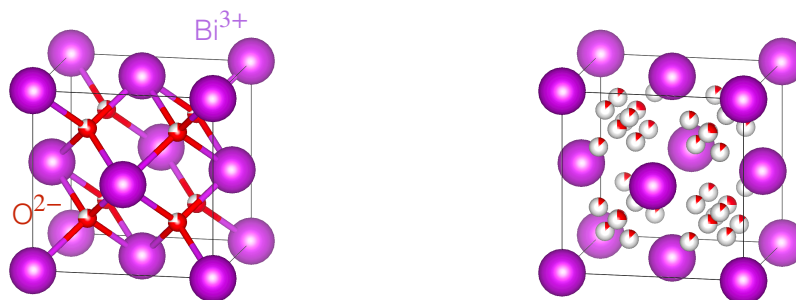
*Solution*

- (i) Fluorite  $\text{CaF}_2$  gives its name to the fluorite structure in which the calcium atoms occupy a face-centred cubic (fcc) sublattice, and the fluorine atoms occupy all tetrahedral interstices. The fluorite structure is depicted in the Figure below:



Each calcium atom is at the centre of a cube whose vertices are eight fluorine atoms. Each fluorine atom is at the centre of a tetrahedron whose vertices are four calcium atoms.

- (ii) There are multiple models for  $\delta\text{-Bi}_2\text{O}_3$  in the literature, and two of these are sketched in the Figure below:



In both models there is an average of six oxygens and two vacancies per unit cell. In the left model, oxygens occupy ideal tetrahedral interstice sites of the fcc structure. For the right model, the oxygen sites are displaced from the ideal tetrahedral interstice sites of the fcc structure.

- (iii) Ionic motion in ionic conductors is typically mediated by vacancies.  $\delta\text{-Bi}_2\text{O}_3$  is a fast ionic conductor because there are native vacancies in the tetrahedral interstices in the fcc bismuth sublattice. Specifically, for the eight tetrahedral interstice sites in the conventional fcc unit cell, there are only six oxygens and therefore two vacancies. By contrast, all tetrahedral interstices are occupied in  $\text{CaF}_2$ , preventing ionic motion.

- (iv) The unit cell of  $\delta\text{-Bi}_2\text{O}_3$  has two oxygen vacancies, and one quarter of this would be half an oxygen vacancy per unit cell. In yttria-stabilised zirconia, for every two  $\text{Zr}^{4+}$  ions replaced by two  $\text{Y}^{3+}$  ions, and oxygen  $\text{O}^{2-}$  vacancy is created. This means that there is half an oxygen vacancy for every  $\text{Y}^{3+}$  ion, so we need one  $\text{Y}^{3+}$  ion per unit cell. As each unit cell has four yttrium-zirconium sites, this means we need a composition with  $x = 0.25$ , ending up with  $\text{Zr}_{0.75}\text{Y}_{0.25}\text{O}_{1.875}$ .

11. Yttria stabilised zirconia with a cation ratio of 8:92 (Y:Zr) is produced by mixing appropriate quantities of yttria ( $\text{Y}_2\text{O}_3$ ) with zirconia ( $\text{ZrO}_2$ ). What is the molar oxygen composition,  $x$ , in the resulting material,  $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_x$ ?

*Solution*

In yttria-stabilised zirconia, for every two  $\text{Zr}^{4+}$  ions replaced by two  $\text{Y}^{3+}$  ions, and oxygen  $\text{O}^{2-}$  vacancy is created. This means that for every  $\text{Y}^{3+}$  ion, half an oxygen vacancy is created, and we end up with  $\text{Zr}_{1-y}\text{Y}_y\text{O}_{[2-(y/2)]}$ . For  $y = 0.08$ , we obtain an oxygen concentration of:

$$x = 2 - \frac{y}{2} = 2 - \frac{0.08}{2} = 1.96$$

Overall, we have  $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{1.96}$

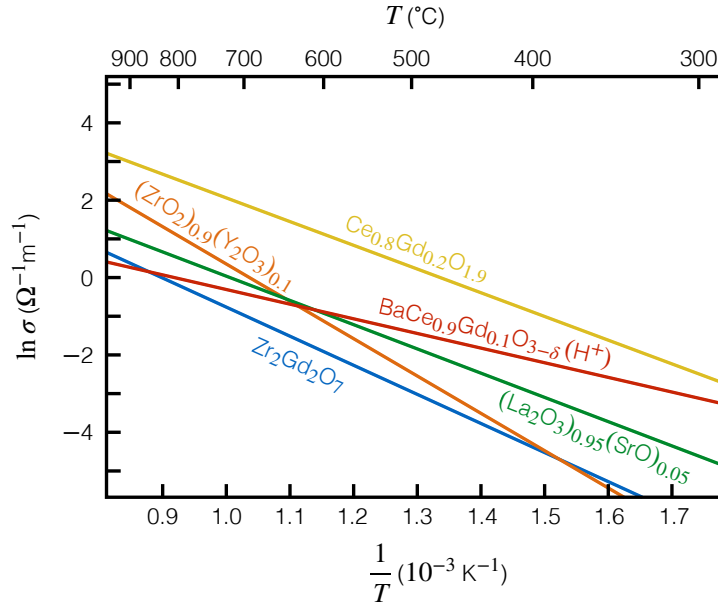
12. The diffusivity of an ionic conductor is given by the Arrhenius equation  $D = D_0 e^{-E_B/k_B T}$ , where  $E_B$  is the energy barrier,  $D_0$  is the pre-exponential factor, and  $T$  is the temperature.

- (i) In the limit of a good ionic conductor, the concentration of diffusing ions  $n$  can be approximated as the total equilibrium concentration of ions  $n \approx n_0$ . Using this approximation in the Nernst-Einstein equation, show that:

$$\ln \sigma \simeq \ln \left( \frac{\sigma_0}{T} \right) - \frac{E_B}{k_B T}, \quad (1)$$

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

- (ii) Consider the two terms on the right hand side of Eq. (1). By comparing their change between two characteristic temperatures for ionic conductor operation, for example between 700 K and 1000 K, argue that  $\ln \left( \frac{\sigma_0}{T} \right)$  varies more slowly than  $-\frac{E_B}{k_B T}$ . 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.
- (iii) Consider the Arrhenius plot shown in the Figure below. Estimate the activation energy for ion transport in yttria-stabilised zirconia.
- (iv) In  $\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ , 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.
- (v) The Nernst-Einstein equation indicates that the ratio  $\frac{\sigma}{D}$  for a given material varies only with temperature. Calculate  $\frac{\sigma}{D}$  for  $\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$  at 800 °C.



*Solution*

- (i) Using the approximation  $n \approx n_0$ , we can re-write the Nernst-Einstein equation as:

$$\sigma = \frac{D n q^2}{k_B T} \simeq \frac{D_0 e^{-E_B/k_B T} n_0 q^2}{k_B T}.$$

In the last step, we have used the Arrhenius equation for the diffusivity  $D = D_0 e^{-E_B/k_B T}$ . Re-arranging this last expression, we obtain:

$$\sigma = \frac{D_0 n_0 q^2}{k_B T} e^{-E_B/k_B T}.$$

Taking the logarithm of both sides, we end up with the required expression:

$$\ln \sigma \simeq \ln \left( \frac{\sigma_0}{T} \right) - \frac{E_B}{k_B T},$$

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

- (ii) Let  $T_1 = 700 \text{ K}$  and  $T_2 = 1000 \text{ K}$ . Consider the change in the first term:

$$\begin{aligned} \ln \left( \frac{\sigma_0}{T_2} \right) - \ln \left( \frac{\sigma_0}{T_1} \right) &= \ln \left( \frac{T_1}{T_2} \right) \\ &= \ln \left( \frac{700}{1000} \right) \\ &\simeq -0.4. \end{aligned}$$

The corresponding change in the second term is:

$$\begin{aligned} -\frac{E_B}{k_B T_2} - \left( -\frac{E_B}{k_B T_1} \right) &= \frac{E_B}{k_B} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{E_B}{k_B} \left( \frac{1}{700 \text{ K}} - \frac{1}{1000 \text{ K}} \right) \\ &\simeq (4 \times 10^{-4} \text{ K}^{-1}) \times \frac{E_B}{k_B}. \end{aligned}$$

A typical energy barrier in an ionic conductor is of the order of 1 eV, so that  $\frac{E_B}{k_B} \simeq \frac{1 \text{ eV}}{8.62 \times 10^{-5} \text{ eV K}^{-1}} \simeq 1.2 \times 10^4 \text{ K}$ . This gives a change in the second term as approximately:

$$\begin{aligned} -\frac{E_B}{k_B T_2} - \left( -\frac{E_B}{k_B T_1} \right) &\simeq (4 \times 10^{-4} \text{ K}^{-1}) \times 1.2 \times 10^4 \text{ K} \\ &\simeq 4.8. \end{aligned}$$

Therefore, the variation in the second term is about one order of magnitude larger than the variation in the first term. This suggests that the first term  $\ln \left( \frac{D_0 n_0 q^2}{k_B T} \right)$  can be taken to be constant with respect to the second term  $\frac{E_B}{k_B T}$ . This implies that a plot of the logarithm of the conductivity  $\ln \sigma$  against  $\frac{1}{T}$  will be an approximate straight line with slope  $-\frac{E_B}{k_B}$  and intercept  $\ln \left( \frac{\sigma_0}{T} \right)$ .

- (iii) Yttria-stabilised zirconia corresponds to the orange line. We estimate its slope as:

$$-\frac{E_B}{k_B} \simeq \frac{-4 - 0}{1.48 \times 10^{-3} - 1.08 \times 10^{-3}} = -10^4 \text{ K}.$$

Re-arranging,

$$E_B = 10^4 k_B = 10^4 \times 1.380649 \times 10^{-23} = 1.38 \times 10^{-19} \text{ J} = 0.86 \text{ eV}.$$

This should be compared with the thermal energy associated with room temperature,  $k_B T \simeq 0.03 \text{ eV}$ .

- (iv) In yttria-stabilised zirconia, for every two  $\text{Zr}^{4+}$  ions replaced by two  $\text{Y}^{3+}$  ions, and oxygen  $\text{O}^{2-}$  vacancy is created. This means that for every  $\text{Y}^{3+}$  ion, half an oxygen vacancy is created. The unit cell has four yttrium-zirconium sites, and for  $\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$  we have  $0.2 \times 4 = 0.8$  yttrium per unit cell. This leads to 0.4 oxygen vacancies per unit cell. Finally, this leads to a number of oxygen vacancies per unit volume in SI units give by:

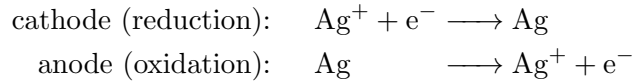
$$\frac{0.4}{(0.54 \times 10^{-9})^3} = 2.54 \times 10^{27} \text{ m}^{-3}.$$



- (v) Oxygen vacancies have an effective charge of  $q = +2e$ , where  $e = 1.602 \times 10^{-19}$  C is the elementary charge. Using the results in the previous parts, we use the Nernst-Einstein equation to obtain the ratio  $\frac{\sigma}{D}$  in SI units as:

$$\frac{\sigma}{D} = \frac{nq^2}{k_B T} = \frac{2.54 \times 10^{27} \times (2 \times 1.602 \times 10^{-19})^2}{1.381 \times 10^{-23} \times 1073.15} = 1.76 \times 10^{10} \text{ Fm}^{-3}.$$

13. The  $\alpha$  phase of silver iodide (AgI) has a iodine atoms arranged in a body centred cubic sublattice with  $a = 5.0855 \text{ \AA}$  for the conventional cubic cell. It is an ionic conductor with  $\text{Ag}^+$  cations being the mobile species, and the diffusivity at  $150 \text{ }^\circ\text{C}$  is  $4.5 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ . 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:



Consider:

- (i) What is the number of charge carriers per unit volume in AgI?
- (ii) What is the conductivity of AgI at  $150 \text{ }^\circ\text{C}$ ?
- (iii) What is the mass of silver deposited at the cathode if a current of 5 mA flows through the circuit for 5 minutes?

*Solution*

- (i) The conventional bcc cubic cell has two atoms, so AgI has two charge carriers (silver atoms) in the conventional cubic cell. The number of charge carriers per unit volume in SI units becomes:

$$\frac{2}{(5.0855 \times 10^{-10})^3} = 1.52 \times 10^{28} \text{ m}^{-3}.$$

- (ii) From the Nernst-Einstein equation, we obtain a conductivity in SI units of:

$$\sigma = \frac{Dnq^2}{k_{\text{B}}T} = \frac{4.5 \times 10^{-11} \times 1.52 \times 10^{28} \times (1.602 \times 10^{-19})^2}{1.381 \times 10^{-23} \times 423.15} = 3.00 \text{ } \Omega^{-1}\text{m}^{-1}.$$

- (iii) The total charge  $Q$  deposited at the cathode for current  $I$  over time  $t$  is given by, in SI units:

$$Q = It = 5 \times 10^{-3} \times 300 = 1.5 \text{ C}.$$

Each silver ion carries a charge  $q = e$ , so the total number  $N_{\text{Ag}^+}$  of silver ions deposited is equal to:

$$N_{\text{Ag}^+} = \frac{Q}{q} = \frac{1.5}{1.602 \times 10^{-19}} = 9.36 \times 10^{18} \text{ atoms}$$

The relative atomic mass of Ag is 107.8682 from [webelements](#), so we obtain a total mass deposited equal to:

$$9.36 \times 10^{18} \times 107.8682 \times 1.661 \times 10^{-27} = 1.68 \times 10^{-6} \text{ kg}.$$

This is equivalent to 1.68 mg of silver.