Defect Diffusion and Conduction in Ceramics

1. What are the parameters governing diffusion? Can all of these parameters be expressed in terms of chemical potential gradient?

2. Draw a schematic plot of diffusivity vs temperature showing intrinsic and extrinsic regions for CaO doped ZrO_2. Clearly explain both regions.

3. Write the Schottky defect reaction for TiO_2 and then calculate the equilibrium oxygen vacancy concentration in TiO_2 at 1400°C given that enthalpy of defect formation is 5.2 eV. You can neglect the entropy of defect formation. Calculate the ionic and electrical conductivities at the same temperature using the data.

   - Assume that the Bandgap of TiO_2 is 3.2 eV. Assume that the electron and hole mobilities are equal (0.1 $cm^2.V^{-1}s^{-1}$) and m_e=0.33 m_o and m_h=0.77m_o. $(N_c.N_v)^{1/2}$=1.75*10^{21}.$T^{3/2}$ m^{-3}
   - Diffusivity of oxygen vacancies is given as 2.2*10^{-7} (m^2/s).exp(-200 kJ/RT)
   - Density of TiO_2 is 4 g/cc, Molecular weight is 80 g/mol.

4. Now imagine a sensor made of TiO_2 whose inside is maintained at atmospheric pressure (1 atm) and is inserted into molten steel at 1400°C to determine its oxygen content. If the voltage generated in 0.5 V, calculate the partial pressure of oxygen in the melt. Use the data of the the problem (3). Given that F = 96500 C/Mole.

5. Take the case of $Ca_{0.14}Zr_{0.86}O_{1.86}$ and assume that doping leads to creation of oxygen vacancies. The bandgap of ZrO_2 is ~5.2 eV. At high Temperatures, the diffusion coefficient is measured as $D_{V_O} = 1\times10^3 exp[-0.84$ eV$/kT]$ cm^2/s . At 1823 K, electron concentration, n_e, using band model, is estimated to be 1.32×10^{13} cm^{-3} and electron mobility, μ_e, is 24 cm^2/V.s. Calculate the ionic conductivity and electronic conductivities in this compound at 1873 K. Analyze the results and think how can we make ZrO_2 as perfect ionic conductor at this temperature.

6. NiO has a rocksalt structure and has a bandgap of 4.2 eV. The energy for Schottky defect formation is estimated to be 6 eV. In non-stoichiometric form, Ni ions have a tendency to be oxidized to Ni^{+3} state and as result NiO tends to be slightly cation deficient.

   a. Now considering a pure and stoichiometric form of NiO, what type of conductivity in NiO would you expect at 1200K. Show the procedure.

   b. How will the cation deficiency be accommodated in the non-stoichiometric state? Write the defect reactions and reaction constants and mention why a particular oxidation mechanism is favoured.

   c. What will the nature of electronic conductivity in the non-stoichiometic material? Explain.

   d. Determine the pO_2 dependence of electronic conductivity (just the expression).

7. A sample of potassium ferrite with chemical formula $K^+_{1.25}Fe^{2+}_{0.25}Fe^{3+}_{10.75}O^{2-}_{17}$ is a mixed ionic/electronic conductor with the β-Alumina structure. It contains 4.07×10^{27} potassium ions per m^3 located in (001) planes. For this material, the total electrical conductivity at 573 K is 1.53×10^{-2} S/m and the diffusion coefficient at 573K for K^+ ions is 1.89×10^{-14} m^2/s. Calculate the transport number for K^+ ions at 573K. If the energy of migration of K^+ ions is 23 kJ/mol, what will be the ionic conductivity of the sample at 298 K?