Fall 2022 Solid State Ionics

Homework 1

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Problem 1: Defect chemistry of acceptor-doped $SrTiO_3$

$SrTiO_3$ is a prototypical perovskite oxide which often serves as a good model system to understand the defect chemistry of functional oxides.

1. Even "pure" $SrTiO_3$ is doped with some amount of acceptor dopant due to inevitable impurity contaminations during processing. Assume that a single crystal $SrTiO_3$ is doped with 800 ppm of Mn (with oxidation state of Mn^{2+}), write down the Kröger-Vink notations for a Mn acceptor dopant (occupying the site of Ti^{4+}), an oxygen vacancy, an electron, and an electron hole.
2. Write down the electro-neutrality condition considering Mn acceptor dopants, oxygen vacancies, electrons and electron holes.
3. Try to sketch the Brouwer diagram for acceptor-doped $SrTiO_3$ by considering two regimes below:
   i) "Intrinsic" Regime: acceptors and oxygen vacancies are majority defects;
   ii) "Oxygen-poor" Regime: oxygen vacancies and electrons are majority defects.

   Draw the Brouwer diagram to show the relationship of log **[def]** ~ log $\boldsymbol{p}$**O₂**, and mark the slopes for each defect in the Brouwer diagram. (**Note:** the concentration of the Mn acceptor dopants is a constant).
4. Below is the logσ ~ log $\boldsymbol{p}\mathbf{O_2}$ plot of such a $SrTiO_3$ single crystal (taken from Ohly *et al.*, *J. Am. Ceram. Soc.*, **89**(9) 2845–2852 (2006)). Try to calculate the bandgap (E_g) of $SrTiO_3$. **Hint:** consider the meaning of the minimum in the logσ ~ log $\boldsymbol{p}\mathbf{O_2}$ plot.

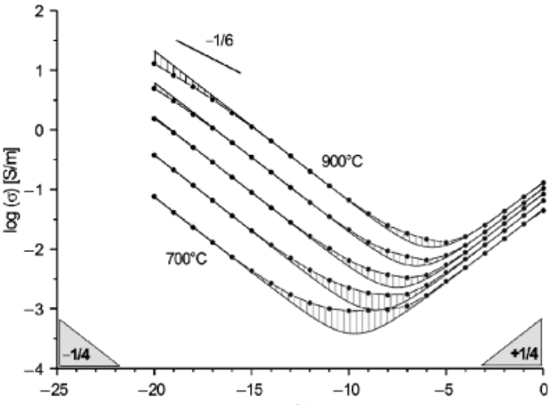

Figure 1 log$\boldsymbol{\sigma}$ ~ log $\boldsymbol{p}\mathbf{O_2}$ plot of acceptor-doped $SrTiO_3$ single crystal (Ohly *et al.*, *J. Am. Ceram. Soc.*, **89**(9) 2845–2852 (2006)).

5. Why is there a difference between the solid lines and the actual data points in Figure 1 (*i.e.*, the shaded area)? Try to calculate the migration enthalpy of oxygen vacancies by using the data in Figure 1.

Problem 2: "p-n junction" in yittria-stablized zirconia (YSZ)

Yittria-stablized zirconia $Y_xZr_{1-x}O_{2-\delta}$ (YSZ) is the most commonly used electrolyte for solid oxide fuel cells. Doping Y^{3+} into ZrO_2 stabilizes the cubic phase and also introduce oxygen vacancies for oxygen ion conduction.

1. As shown in **Figure 2**, the ionic conductivity of 8YSZ ($(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$) is almost a constant throughout the entire pO_2 range, while the hole and electron conductivities strongly changes with pO_2. Try to write the electroneutrality condition for YSZ (consider Y dopants, oxygen vacancies, electrons, and holes) and then specify the Brouwer condition. Write down the equation for the total electronic conductivity (σ_e+σ_h) as a function of pO_2.

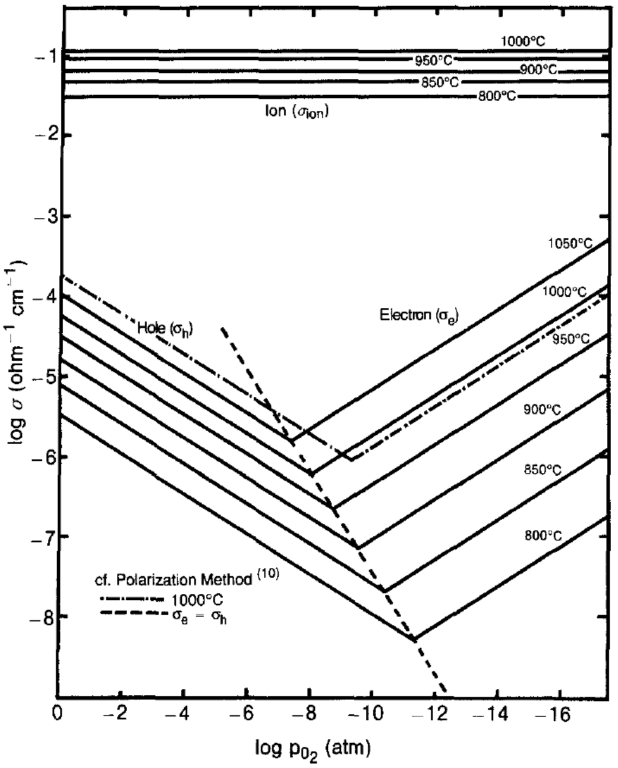

Figure 2 Electronic and ionic conductivity of 8YSZ (Park *et al.*, *J. Electrochem. Soc.*, **136**(10) 2867 (1989)).

2. Consider a model solid oxide fuel cell under open circuit conditions with different pO_2 at cathode and anode, denoted as pO_2(c) and pO_2(a) (see **Figure 3**). Try to write down the open-circuit equilibrium condition regarding the electrochemical potential of oxide ion O^{2-}. Write down the expression of chemical potentials of oxygen gas phase for the cathode and anode.
3. If we consider the local equilibrium condition as shown below:

$$\frac{1}{2}O_2 + 2e^- \leftrightharpoons O^{2-}$$

If the equilibrium is reached, write down the relationship between the chemical potential of oxygen gas, the electrochemical potential of electrons and the electrochemical potential of oxide ions.

4. Express the charge flux of electrons and holes (*i.e.*, electronic current density) by using the total electronic conductivity and the gradient of electrochemical potential of electrons. (**Hint 1**: you can replace the electron conductivity σ_e with σ_e+σ_h by recognizing z_e= -z_h and $\tilde{\mu}_{e'} = -\tilde{\mu}_{h^{\cdot}}$) We know that the electronic current density should be the same along the x-axis of the

electrolyte (in other words, the *divergence* of j_e should be zero). If we set temperature to 800°C, $pO_2(c)$ to 1 atm, $pO_2(a)$ to 10^{-16} atm, try to **sketch** (not solve for) the electrochemical potential of electrons, oxide ions and chemical potential of oxygen gas from one end of the electrolyte ($x = 0$) to another end ($x = L$). See Figure 3. (**Hint 2:** notice that there is a minimum in the total electro conductivity of YSZ as a function of pO_2)

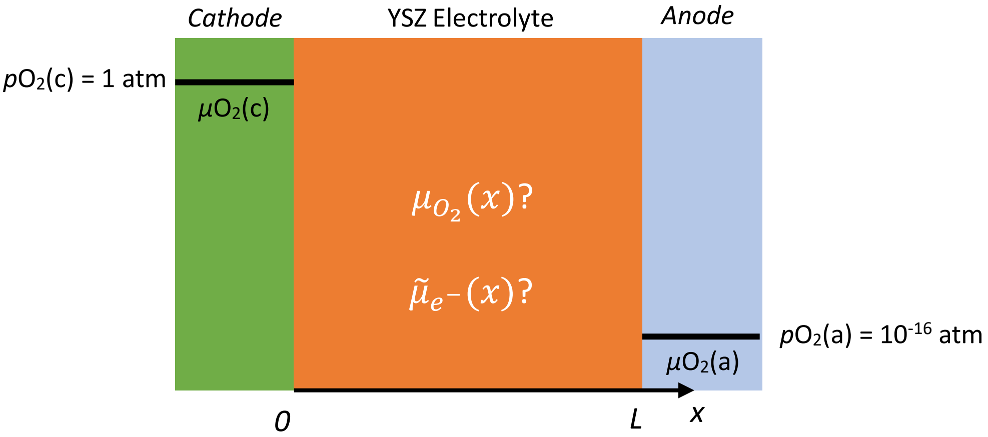

Figure 3 Schematic of a model solid oxide fuel cell with YSZ as the electrolyte.

5. In the sketch you draw, identify the majority **electronic** charge carrier in each part of the electrolyte. Try to discuss the factors that determines the fraction of the length of the "p-type" and "n-type" region in the electrolyte.
6. **(Bonus point)** Try to solve for the profiles of the electrochemical potential of electrons and the chemical potential of oxygen **numerically**.