Homework 4 - Solutions

a) The activation energy can be calculated from equation (eq. 4.64 in O'Hayre)

$$\sigma \mathrm{T} = \mathrm{A_{SOFC}} \cdot \mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}}, \tag{1}$$

where $\sigma = \frac{\mathrm{L}}{\mathrm{ASR}}$ is the material conductivity, T is temperature, $\mathrm{A_{SOFC}}$ is a constant including different exponential factors, $-\Delta\mathrm{G_{act}}$ is the activation energy and R is the molar gas constant. The constant $\mathrm{A_{SOFC}}$ is the same independent of the cell temperature and therefore we can solve for it in the equation and put two expressions for $\mathrm{A_{SOFC}}$ in different temperatures equal to each other:

$$\mathrm{A_{SOFC}} = \frac{\sigma \mathrm{T}}{\mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}}} \tag{2}$$

$$\mathrm{A_{SOFC,T1}} = \mathrm{A_{SOFC,T2}} \tag{3}$$

$$\frac{\sigma_1 \mathrm{T}_1}{\mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}_1}} = \frac{\sigma_2 \mathrm{T}_2}{\mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}_2}} \tag{4}$$

$$\frac{\mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}_1}}{\mathrm{e}^{-\Delta \mathrm{G_{act}}/\mathrm{RT}_2}} = \frac{\sigma_1 \mathrm{T}_1}{\sigma_2 \mathrm{T}_2} \tag{5}$$

$$\mathrm{e}^{\frac{-\Delta \mathrm{G_{act}}}{\mathrm{RT}_1} \frac{+\Delta \mathrm{G_{act}}}{\mathrm{RT}_2}} = \frac{\sigma_1 \mathrm{T}_1}{\sigma_2 \mathrm{T}_2} \tag{6}$$

$$\frac{-\Delta \mathrm{G_{act}} \mathrm{T}_2 + \Delta \mathrm{G_{act}} \mathrm{T}_1}{\mathrm{RT}_1 \mathrm{T}_2} = \ln(\frac{\sigma_1 \mathrm{T}_1}{\sigma_2 \mathrm{T}_2}) \tag{7}$$

$$\Delta \mathrm{G_{act}} = \frac{\mathrm{RT}_1 \mathrm{T}_2 \ln(\frac{\sigma_1 \mathrm{T}_1}{\sigma_2 \mathrm{T}_2})}{\mathrm{T}_1 - \mathrm{T}_2} = \frac{\mathrm{RT}_1 \mathrm{T}_2 \ln(\frac{\mathrm{T}_1 \mathrm{ASR}_2}{\mathrm{T}_2 \mathrm{ASR}_1})}{\mathrm{T}_1 - \mathrm{T}_2} \tag{8}$$

$$-\Delta \mathrm{G_{act}} = \frac{8.314 \mathrm{m^2 kgs^{-2} K^{-1} mol^{-1}} \cdot 1000\mathrm{K} \cdot 1200\mathrm{K} \cdot \ln(\frac{1000\mathrm{K} \cdot 0.05 \Omega \mathrm{cm^2}}{1200\mathrm{K} \cdot 0.2 \Omega \mathrm{cm^2}})}{1000\mathrm{K} - 1200\mathrm{K}} \approx 78249 \mathrm{J/mol} = 78 \mathrm{kJ/mol}. \tag{9}$$

Activation energy for conduction in this electrolyte material is therefore 78 kJ/mol.

b) The limiting current density can be calculated from equation (eq. 5.10 in O'Hayre)

$$\mathrm{j_L} = \mathrm{nFD}^{eff} \frac{\mathrm{C_R^0}}{\delta}, \tag{10}$$

where n is the number of electrons participating in the reaction (in our case we use value n=4 because the oxygen reaction is the rate determining reaction because of its slowness), F is the Faraday constant, $\mathrm{D^{eff}}$ is the effective reactant diffusivity, $\mathrm{C_R^0}$ is the bulk reactant concentration and δ is the diffusion layer thickness.

The effective reactant diffusivity can be calculated with the help of porosity (eq. 5.3 in O'Hayre)

$$D^{eff}_{O2,N2} = \epsilon^{1.5} D_{O2,N2} = 0.4^{1.5}(0.2cm^2/s) = 0.0506cm^2/s \tag{11}$$

(Oxygen-nitrogen binary diffusion constant was gained from O'Hayre, page 182) and the bulk reactant concentration with the help of the ideal gas law from

$$C^0_R = \frac{n^0_R}{V} = \frac{P^0_R}{RT} = \frac{0.21 \cdot (101300Pa/atm)}{8.314J/molK \cdot 293K} \approx 8.733mol/m^3 = 8.73 \cdot 10^{-6} mol/cm^3. \tag{12}$$

Inserting the values we get a limiting current density of

$$j_L = 4 \cdot 96485C/mol \cdot 0.0506cm^2/s \cdot 8.73 \cdot 10^{-6} \frac{mol/cm^3}{0.05cm} \approx 3.4A/cm^2 \tag{13}$$