Exercise 4 solutions

1. O'Hayre (2016) Review Question 4.4

Problem

Why are the electron conductivities of metals so much larger than the ion conductivities of electrolytes?

Solution

In case of electrolyte, the current is associated with the transport of relatively large and massive ions, rather than by nearly weightless electrons. Electrons move largely unimpeded through the metal.

2. O'Hayre (2016) Review Question 4.5

Problem

List at least four important requirements for a candidate fuel cell electrolyte. Which requirement is often the hardest to fulfill?

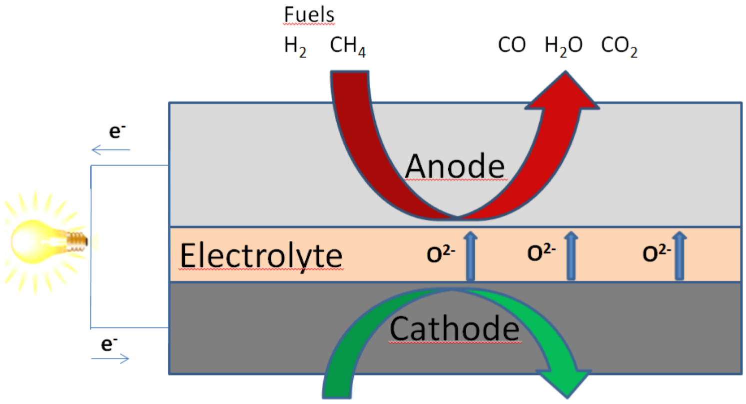
Solution

1) negligible electronic conduction
2) high ionic conductivity (H^+ in case of PEMFC and O^{2-} in case of SOFC)
   a. high ion mobility (i.e. "fast" transport)
   b. high mobile ion concentration
3) thermodynamic stability over a wide range of temperature and oxygen/hydrogen partial pressure
4) thermal expansion coefficient suitable and compatible with that of electrodes and other cell materials
5) chemically stable and suitable mechanical properties

3. O'Hayre (2016) Calculation 4.8

Problem

Given that fuel cell voltages are typically around 1 V or less, what would be the absolute minimum possible functional electrolyte thickness for a Solid Oxide Fuel Cell (SOFC) if the dielectric breakdown strength of the electrolyte is 10^8 V/m?



Solution

$$Thickness_{min} = \frac{Fuel\ cell\ voltage}{dielectric\ breakdown\ strength} = \frac{1\ (V)}{1\times10^{8}(V/m)} = 1 \times 10^{-8}\ \text{m} = 10\ \text{nm}$$

4. O'Hayre (2016) Calculation 4.9

Problem

Fuel cell electrolyte scales with thickness (in general as L/σ). Several practical factors can limit the useful range of electrolyte thickness. Fuel crossover can cause an undesirable parasitic loss which can eventually become so large that further thickness decrease is counterproductive. In other words, at a given current density, an optimal electrolyte thickness may exist, and reducing the electrolyte thickness below this optimal value will actually increase the total fuel cell losses. We would like to model this phenomenon. Assume that the leak current j_{leak} across an electrolyte gives rise to an additional fuel cell loss of the following form: $\eta_{\text{leak}} = A \ln j_{\text{leak}}$. Furthermore, assume that j_{leak} varies inversely with electrolyte thickness L as $j_{\text{leak}} = B/L$. For a given current density j determine the optimal electrolyte thickness that minimizes $\eta_{\text{ohmic}} + \eta_{\text{leak}}$.

Solution

$$\eta_{ohmic} = j\ (R_{elec} + R_{ionic}) = j\ \left(R_{elec} + \frac{L}{\sigma}\right)$$

$$\eta_{leak} = A\ lnj_{leak} = A\ ln\frac{B}{L}$$

$$\eta_{total} = \eta_{ohmic} + \eta_{leak} = j\ \left(R_{elec} + \frac{L}{\sigma}\right) + A\ ln\frac{B}{L}$$

$$\frac{d\eta_{total}}{dL} = 0 + \frac{j}{\sigma} - \frac{A}{L} = 0$$

$$L = \frac{A\ \sigma}{j}$$

The optimal thickness is:

- **proportional to the factor *A***, i.e. the higher the voltage loss from a given leakage current is, the thicker an electrolyte we need to keep the leakage low;
- **proportional to the electrolyte conductivity**, i.e. the more conductive the electrolyte is, the thicker an electrolyte we can afford to have without causing too much voltage loss;
- **inversely proportional to the current density**, i.e. the higher the current density we want to operate is, the thinner the electrolyte layer should be.

The optimum thickness is a combination of these three factors.

5. O’Hayre (2016) Calculation 4.10

Problem

A 5 cm^2 fuel cell has $R_{\text{elec}} = 0.01\ \Omega$ and $\sigma_{\text{electrolyte}} = 0.10\ \Omega^{-1}\ \text{cm}^{-1}$. If the electrolyte is 100 µm thick, predict the ohmic voltage losses for this fuel cell at $j = 500$ mA/cm^2.

Solution

$$\eta_{ohmic} = i\ (R_{elec} + R_{ionic}) = i\ \left(R_{elec} + \frac{L}{\sigma A}\right)$$

$$= \left(500 \times 10^{-3} \frac{A}{cm^2}\right)(5\ cm^2)\left(0.01\ ohm + \frac{0.01\ cm}{0.1\ ohm^{-1}cm^{-1}5cm^2}\right) = 0.075\ V$$

6. O’Hayre (2016) Sections 5.2.3 and 5.2.4

Problem

Derive the following expression for the concentration overpotential, including the concentration effects both on the Nernst voltage (Nernst equation) and the reaction rate (Butler – Volmer equation):

$$\eta_{\text{conc}} = c \ln\left(\frac{j_{\text{L}}}{j_{\text{L}} - j}\right)$$

where c is a constant. Give the expression for c.

Solution

The derivation can be found in O’Hayre (2016) Sections 5.2.3 and 5.2.4. The final result is

$$\eta_{\text{conc}} = \eta_{\text{conc,Nerst}} + \eta_{\text{conc,BV}} = \left(\frac{RT}{nF}\right)\left(1 + \frac{1}{\alpha}\right) \ln \frac{j_L}{j_L - j}$$

where

$$\eta_{\text{conc,Nernst}} = \frac{RT}{nF} \ln \frac{j_L}{j_L - j} \quad ; \quad \eta_{\text{conc, BV}} = \frac{RT}{\alpha nF} \ln \frac{j_L}{j_L - j} \quad ; \quad j_L = nFD^{\text{eff}} \frac{c_R^0}{\delta}$$

The result can be written in short as

$$\eta_{\text{conc}} = c \ln \frac{j_L}{j_L - j}$$

where

$$c = \frac{RT}{nF}\left(1 + \frac{1}{\alpha}\right)$$

7. The shape of the mass transport (concentration) overpotentual – current density curve

Problem

The mass transport overpotential can be modeled with a simplified expression $\eta_{\text{conc}} = c \ln\left(\frac{j_L}{j_L - j}\right)$. Using this expression study the effect of c and j_L on the shape of the iV-curve when the open circuit voltage is 1.2 V (reversible cell voltage), using the following values

a) $c = 0.0388$ V; $j_L = 1.0$ A/cm^2, 1.5 A/cm^2, and 2.0 A/cm^2
b) $j_L = 2.0$ A/cm^2; $c = 0.01, 0.05, 0.1$

Solution

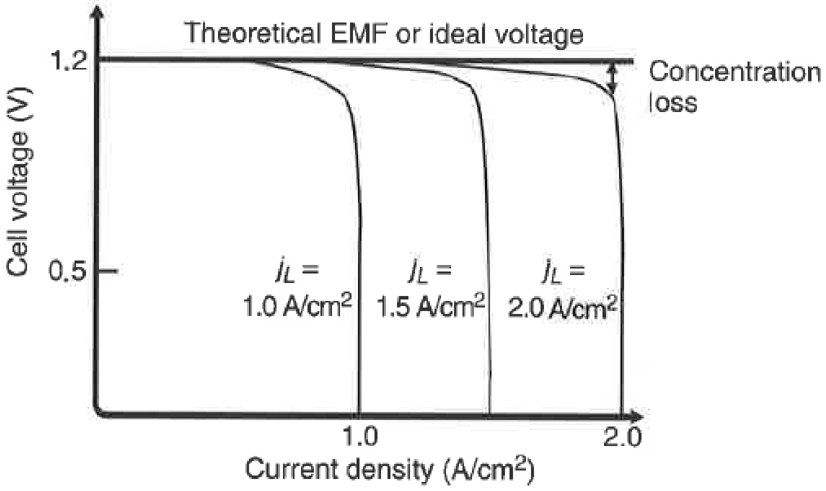


Figure 1. The effect of limiting current density on concentration losses in fuel cell. *C* was fixed at 0.0388 V. (Figure 5.7 in O'Hayre (2016).

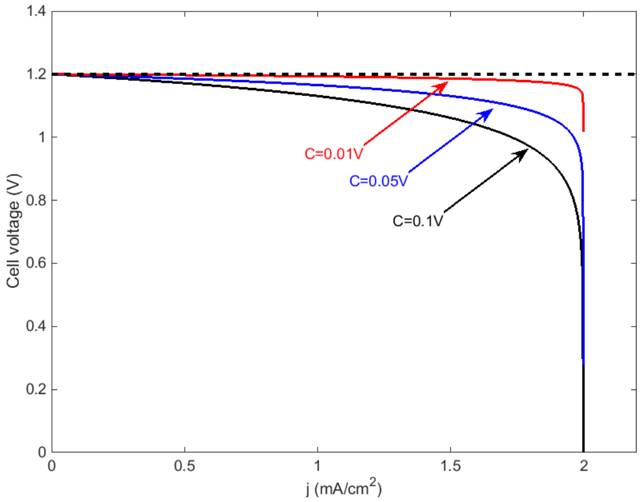


Figure 2. The effect of the prefactor c on the concentration losses with j_L= 2 A/cm^2. The dashed line indicates $E^0 = 1.2$ V.

We can see that c characterizes how abruptly the current limitation due to mass transport set in.