

Homework 3, solution

Problem

A PEM fuel cell operates at 60 °C and ambient pressure. Exchange current density on cathode side, $j_{0,c}$, is 0.005 mAcm⁻². Assume charge transfer coefficient on cathode side, α_c , to be 0.5 and that there is an excess amount of gases available (no concentration limitation).

- a) Calculate the activation voltage losses at 0.01 Acm⁻², 0.1 Acm⁻² and 1 Acm⁻².
- b) If the resistive losses at 1 Acm⁻² are one third of the activation losses, calculate the area specific cell resistance, R .
- c) Assume there are no other losses besides the activation and ohmic losses and that E_{theor} is 1.2 V. Calculate cell voltage at 0.01 Acm⁻², 0.1 Acm⁻² and 1 Acm⁻².

Hints:

O'Hayre (2016) sections:

- a) Section 3.7
- b) Sections 4.2 and 4.3
- c) Section 1.7

Anode side reaction is much faster than cathode side reaction in PEMFC. This means that anode activation losses are often neglected.

Solution

- a) Activation losses at the cathode can be calculated using the Butler-Volmer equation, which in the absence of concentration limitations of reactants and products, can be written as

$$j = j_{0,c} \left(\exp\left(\frac{\alpha_c n F \eta_{\text{act},c}}{RT}\right) - \exp\left(\frac{-(1-\alpha_c) n F \eta_{\text{act},c}}{RT}\right) \right) \quad (1)$$

The activation voltage loss, $\eta_{\text{act},c}$, can be solved in different ways, depending on the value of α_c and whether or not an approximate solution is accurate enough. In general, if $\alpha_c \neq \frac{1}{2}$ eq. (1) cannot be solved analytically, but a numerical solution is needed. This can be done for example in Excel, using its Solver tool, by finding value of $\eta_{\text{act},c}$ that sets the difference between the left and right hand side of eq. (1) zero, given all the other variables are known

$$j_{0,c} \left(\exp\left(\frac{\alpha_c n F \eta_{\text{act},c}}{RT}\right) - \exp\left(\frac{-(1-\alpha_c) n F \eta_{\text{act},c}}{RT}\right) \right) - j = 0 \quad (\text{solve numerically}) \quad (2)$$

On the other hand, if $\alpha_c = \frac{1}{2}$, as is the case in this problem, eq. (1) becomes

$$j = j_{0,c} \left(\exp\left(\frac{n F \eta_{\text{act},c}}{2RT}\right) - \exp\left(\frac{-n F \eta_{\text{act},c}}{2RT}\right) \right) \quad (3)$$

$$j = j_{0,c}(\exp(x) - \exp(-x)) \quad ; \quad x = \frac{nF\eta_{act,c}}{2RT} \quad (4)$$

$$j = j_{0,c} \cdot 2 \cdot \sinh(x) \quad (5)$$

This we can solve for x and then $\eta_{act,c}$ analytically using the inverse hyperbolic sine function asinh(x)

$$x = \operatorname{asinh}\left(\frac{j}{2j_{0,c}}\right) \quad (6)$$

$$\eta_{act,c} = \frac{2RT}{nF} \operatorname{asinh}\left(\frac{j}{2j_{0,c}}\right) \quad (7)$$

Here $n = 2$, so our final result is

$$\eta_{act,c} = \frac{RT}{F} \operatorname{asinh}\left(\frac{j}{2j_{0,c}}\right) \quad (8)$$

For $j = 0.01 \text{ A/cm}^2$ we get

$$\eta_{act,c} = \frac{8.314 \frac{\text{J}}{\text{mol K}} \cdot 338.15 \text{ K}}{96485 \frac{\text{C}}{\text{mol}}} \operatorname{asinh}\left(\frac{0.01 \frac{\text{A}}{\text{cm}^2}}{2 \cdot 0.005 \frac{\text{mA}}{\text{cm}^2}}\right) \quad (8)$$

$$\eta_{act,c} \approx 29.14 \text{ mV} \cdot \operatorname{asinh}(10^3) \approx 29.14 \text{ mV} \cdot 7.60 \approx 221 \text{ mV}$$

Repeating the calculation for the other current densities and collecting the results:

$$j = 0.01 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{act,c} \approx 0.221 \text{ V} \quad (9)$$

$$j = 0.1 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{act,c} \approx 0.289 \text{ V}$$

$$j = 1 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{act,c} \approx 0.356 \text{ V}$$

On the other hand, because the current densities we are interested in are more than three orders of magnitude higher than the exchange current density, and therefore give high overpotentials, the B-V equation (1) could be approximate by leaving the smaller (2^{nd}) exponential term out, to allow easy analytical solution

$$j \approx j_{0,c} \exp\left(\frac{\alpha_c n F \eta_{act,c}}{RT}\right) \quad (10)$$

$$\eta_{act,c} \approx \frac{RT}{\alpha_c n F} \ln\left(\frac{j}{j_{0,c}}\right) = \frac{RT}{F} \ln\left(\frac{j}{j_{0,c}}\right) \quad (11)$$

For $j = 0.01 \text{ A/cm}^2$ we get

$$\eta_{act,c} \approx \frac{8.314 \frac{\text{J}}{\text{mol K}} \cdot 338.15 \text{ K}}{96485 \frac{\text{C}}{\text{mol}}} \ln\left(\frac{0.01 \frac{\text{A}}{\text{cm}^2}}{0.005 \frac{\text{mA}}{\text{cm}^2}}\right)$$

$$\eta_{act,c} \approx 29.14 \text{ mV} \cdot \ln(2 \cdot 10^3) \approx 29.14 \text{ mV} \cdot 7.60 \approx 221 \text{ mV}$$

The result is the same as obtained with the exact solution (8). The error is less than 10^{-8} and even less for the higher current densities. So, both equation (8) and (11) are equally right for this purpose.

b) Ohmic losses at $j = 1 \frac{\text{A}}{\text{cm}^2}$ were one third of the activation losses. Therefore

$$\frac{\eta_{act}}{3} = \eta_{Ohmic} = R_A j \rightarrow R_A = \frac{\eta_{act}}{3j} = \frac{0.356 \text{ V}}{3 \cdot 1 \frac{\text{A}}{\text{cm}^2}} \approx 0.12 \Omega \text{cm}^2$$

c) At the used current densities we get

$$j = 0.01 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{Ohmic} \approx 0.0012 \text{ V}$$

$$j = 0.1 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{Ohmic} \approx 0.012 \text{ V}$$

$$j = 1 \frac{\text{A}}{\text{cm}^2} \rightarrow \eta_{Ohmic} \approx 0.12 \text{ V}$$

If there are no other losses, cell voltage is given by

$$E = E_{theor} - \eta_{act} - \eta_{Ohmic}$$

Using the previous results and $E_{theor} = 1.2 \text{ V}$ we get

$$j = 0.01 \frac{\text{A}}{\text{cm}^2} \rightarrow E \approx 0.98 \text{ V}$$

$$j = 0.1 \frac{\text{A}}{\text{cm}^2} \rightarrow E \approx 0.90 \text{ V}$$

$$j = 1 \frac{\text{A}}{\text{cm}^2} \rightarrow E \approx 0.73 \text{ V}$$

As can be seen, activation losses are much larger than ohmic losses at low current densities.