Exercise 3 solutions

1. O'Hayre (2016) Review Question 3.1

Problem

This problem is composed of three parts:
a) For the reaction:
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$$
the standard potential is +1.23 V. Under standard-state conditions, if the electrode potential is reduced to 1.0 V, will this bias the reaction in the forward or reverse direction?
b) For the reaction
$$H_2 \leftrightarrow 2H^+ + 2e^-$$
the standard potential is 0.0 V. Under standard-state conditions, if the electrode potential is increased to 0.1 V, will this bias the reaction in the forward or reverse direction?
c) Considering your answers to parts a) and b), in a H_2-O_2 fuel cell, if we increase the overall rate of the fuel cell reaction
$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$
which is made up of the previous half reactions, what happens to the potential difference (voltage output) for the reaction?

Solution

a) If the electrode is at a more negative potential than the standard potential of the electrode (as in this case), there are extra electrons in it, compared to the equilibrium condition at the standard potential. Because the electrons are on the reactant side in the reaction, the reaction is biased to the forward direction. (Increasing reactant concentrations biases a reaction to forward direction). The reduced electrode potential 1.0 V, and the corresponding amount of extra electrons, is maintained by electrons arriving from the external circuit, which forms a steady state current flowing in the cell corresponding to the forward reaction.

b) If the electrode is more positive than the standard potential (as in this case), it is missing some electrons compared to the equilibrium situation. Because in this case the electrons are on the products side of the reaction, the reaction will again be biased to forward direction. (Decreasing the product concentrations biases a reaction to forward direction.)

c) Both in a) and b) the reaction was biased to the forward reaction, which corresponds to the forward direction of the total reaction. We can therefore directly look at what happened to the electrode potentials in a) and b). At standard-state conditions the cell voltage was $V_{cell} = V_{cathode} - V_{anode} = 1.23 \text{ V} - 0.0 \text{ V} = 1.23 \text{ V}$, whereas in the biased conditions it is $V_{cell} = V_{cathode} - V_{anode} = 1.0 \text{ V} - 0.1 \text{ V} = 0.9 \text{ V}$. In other words, the cell voltage decreased. In general, the cell voltage decreases when we allow the fuel cell reaction to occur continuously to its spontaneous direction, by connecting the anode and cathode via an external electrical circuit. The voltage decrease comes from the overpotentials (voltage losses) associated running the charge transfer (activation), charge transport and mass transport processed, and appear as an internal voltage loss of the cell.
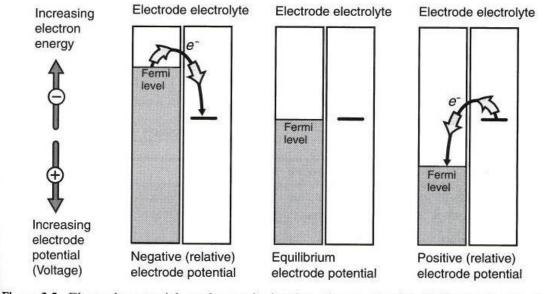
Figure 3.2. Electrode potential can be manipulated to trigger reduction (left) or oxidation (right). The thermodynamic equilibrium electrode potential (middle) corresponds to the situation where the oxidation and reduction processes are balanced.

2. O'Hayre (2016) Calculation 3.11

<u>Problem</u>

Consider two electrochemical reactions. Reaction A results in the transfer of 2 mol of electrons per mole of reactant and generates a current of 5 A on an electrode 2 cm² in area. Reaction B results in the transfer of 3 mol of electrons per mole of reactant and generates a current of 15 A on an electrode 5 cm² in area. What are the net reaction rates for reactions A and B (in moles of reactant per square centimeter per second)? Which reaction has the higher net reaction rate?

<u>Solution</u>

Reaction A	**Reaction B**
$n = 2$	$n = 3$
$i = 5$ A	$i = 15$ A
$A = 2$ cm²	$A = 5$ cm²

From eq. 3.11 on O'Hayre (2016):

$$J = \frac{1}{A}\frac{dN}{dt} = \frac{i}{nFA} = \frac{j}{nF}$$

where $j = i/A$ is current density, and $J = j/nF$ is the reaction rate per unit area.

Reaction A	**Reaction B**
j = 5 A / 2 cm² = 2.5 A/ cm²	j = 15 A / 5 cm² = 3 A/ cm²
J = 2.5 A/ cm² / (2 x 96485 C/mol)	J = 3 A/ cm² / (3 x 96485 C/mol)
= 12.96 µmol cm^{-2} s^{-1}	= 10.36 µmol cm^{-2} s^{-1}
= **13 µmol cm^{-2} s^{-1}**	= **10 µmol cm^{-2} s^{-1}**

Reaction A has higher net reaction rate per unit are, although it has lower current density. This is because only two moles of electrons per mole of reactant is required to transfer compared to reaction B, where three electrons are transferred.

The following questions deal with the effect of temperature, reactant concentration and activation barrier height on the exchange current density.

3. **O'Hayre (2016) Calculation 3.13**

<u>Problem</u>

Everything else being equal, write a general expression showing how the exchange current density for a reaction changes as a function of temperature [e.g., write an expression for j_0 (T) at an arbitrary temperature T as a function of j_0 (T_0) at a reference temperature T_0]. If a reaction has $j_0 = 10^{-8} A/cm^2$ at 300 K and $j_0 = 10^{-4} A/cm^2$ at 600 K, what is $\Delta G^{\ddagger}$ for the reaction? Assume that the preexponent portion of j_0 is temperature independent.

Show from the general expression of j_0, does j_0 increase or decrease with temperature.?

<u>Solution</u>

③ From O'Hayre (2016) eq. 3.36 (or 3.25, or 3.27),
the exchange current density is:

$$j_0 = nFc_R^* f_1 e^{-\Delta G^{\ddagger}/(RT)} \quad (1)$$

at temperature T : $\quad j_0(T) = nFc_R^* e^{-\frac{\Delta G^{\ddagger}}{RT}} \quad (2a)$

at temperature T_0 : $\quad j_0(T_0) = nFc_R^* e^{-\frac{\Delta G^{\ddagger}}{RT_0}} \quad (2b)$

Dividing $(2a)/(2b)$ we get

$$\frac{j_0(T)}{j_0(T_0)} = e^{-\frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} = e^{\frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)} \quad (3)$$

$$\ln\left(\frac{j_0(T)}{j_0(T_0)}\right) = \frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right) \quad (4)$$

$$\Delta G^{\ddagger} = R\ln\left(\frac{j_0(T)}{j_0(T_0)}\right)\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)^{-1} \quad (5)$$

$$= 8.314\frac{J}{mol\cdot K}\cdot\ln\left(\frac{10^{-8} A/cm^2}{10^{-4} A/cm^2}\right)\left(\frac{1}{600K}-\frac{1}{300K}\right)^{-1}$$

$$= 8.314\frac{J}{mol\cdot K}\cdot\ln(10^{-4})\cdot(-600\ K)$$

$$= 45.944 \ \frac{kJ}{mol}$$

$$= 46 \ \frac{kJ}{mol}$$

In eq. (3) we have $\Delta G^{\ddagger} > 0$ (activation barrier), and so, if $T > T_0$, $\left(\frac{1}{T_0}-\frac{1}{T}\right) > 0$, which means that $j_0(T) > j_0(T_0)$, in other words, increasing temperature increases the exchange current density, i.e. "improves kinetics".

4. O'Hayre (2016) Calculation 3.14

Problem

(a) Everything else being equal, write a general expression showing how the exchange current density varies as a function of reactant concentration.

(b) Use this result and your answer from problem 3.13 to answer the following question: For a reaction with $\Delta G^{\ddagger} = 20$ kJ/mol, what temperature change (starting from 300 K) has the same effect on j_0 as increasing the reactant concentration by one order of magnitude? Assume that the preexponent portion of j_0 is temperature independent.

Solution

④

a) From eq. (1) on problem 3, we see that j_0 is linearly proportional to C_R^*. Therefore in the same way as in problem 3 we get:

$$\frac{j_0(C_R^4)}{j_0(C_R^{*0})} = \frac{C_R^*}{C_R^{*0}} \quad \Leftrightarrow \quad j_0(C_R^+) = j_0(C_R^{+0}) \cdot \frac{C_R^*}{C_R^{*0}} \quad (6)$$

b) We require that

$$\frac{j_0(T)}{j_0(T_0)} = \frac{j(C_R^4)}{j_0(C_R^{*0})} \overset{(6)}{=} \frac{C_R^*}{C_R^{*0}} = 10$$

From eq (4) therefore

$$\ln(10) = \frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$T = \left(\frac{1}{T_0} - \frac{R\ln(10)}{\Delta G^{\ddagger}}\right)^{-1}$$

$$= \left(\frac{1}{300k} - \frac{8.314 \frac{J}{mol \cdot k} \cdot \ln(10)}{20\,000 \;\; \text{J / mol}}\right)^{-1}$$

$$= 421\,K$$

5. O'Hayre (2016) Calculation 3.15

Problem

All else being equal, at a given activation overvoltage, which effect produces a greater increase in the net current density for a reaction: doubling the temperature (in degrees Kelvin) or halving the activation barrier? Defend your answer with an equation. Assume that the preexponent portion of j_0 is temperature independent.

Solution

⑤ Effect of $\Delta G^{\ddagger}$ as derived for T in eq (3):

$$\frac{j(\Delta G^{\ddagger})}{j(\Delta G^{\ddagger 0})} = e^{\left(\frac{\Delta G^{\ddagger 0} - \Delta G^{\ddagger}}{RT}\right)} \qquad (7)$$

Temperature-dependence of Butler-Volmer equation, looking only on the forward reaction term:

$$j(T) = j_0(T) \frac{C_R^{\ddagger}}{C_R^{*0}} e^{\alpha n F \eta / (RT)} \qquad \text{(using (1))}$$

$$j(T) = n F C_R^{*0} f_1 e^{-\Delta G^{\ddagger}/RT} \cdot \frac{C_R^{\ddagger}}{C_R^{*0}} e^{\alpha n F \eta / RT}$$

$$j(T) = n F f_1 C_R^{\ddagger} e^{\frac{\alpha n F \eta - \Delta G^{\ddagger}}{RT}} \qquad (8)$$

$$\Rightarrow \quad \frac{j(2T_0)}{j(T_0)} = e^{\frac{\alpha n F \eta - \Delta G^{\ddagger}}{R}\left(\frac{1}{2T_0} - \frac{1}{T_0}\right)} = e^{\frac{\Delta G^{\ddagger} - \alpha n F \eta}{R T_0}} \qquad (9)$$

$$(7) \Rightarrow \quad \frac{j(\frac{1}{2}\Delta G^{\ddagger})}{j(\Delta G^{\ddagger})}\Big|_{a+T^0} = e^{\frac{\Delta G^{\ddagger 0} - \frac{1}{2}\Delta G^{\ddagger}}{R T_0}} = e^{\frac{\Delta G^{\ddagger}}{2 R T_0}} \qquad (10)$$

$(9) > (10)$ if:

$$\frac{\Delta G^{\ddagger} - \alpha n F \eta}{R T_0} > \frac{\Delta G^{\ddagger}}{2 R T_0} \quad (\Leftrightarrow) \quad \frac{\Delta G^{\ddagger}}{2} > \alpha n F \eta \quad (\Leftrightarrow) \quad \eta < \frac{\Delta G^{\ddagger}}{2 \alpha n F} \qquad (11)$$

Ans: Doubling T has bigger effect if the activation over potential is small (eq.(11)), and opposite is true if η is large.

The following questions consider the selection of catalyst material and design of the catalyst-electrode structure.

6. O'Hayre (2016) Review Question 3.7

<u>Problem</u>

List the major requirement for an effective fuel cell

   a) catalyst material,
   b) catalyst particle, and
   c) catalyst-electrode structure.

<u>Solution</u>

The overall catalytic performance of the fuel cell electrode, characterized by the exchange current density per electrode area j_0 (A/cm^2), depends not only on the catalyst material used, for example platinum, but how the material is employed in the catalyst-electrode structure. The catalyst material is typically used as small particles dispersed in a porous electrode structure, and therefore it is natural to divide the discussion of the desired properties between the ***catalyst material***, the ***catalyst particles*** made of that material, and the ***catalyst-electrode structure*** that is hosting the catalyst particles (See Figures 1 - 3).
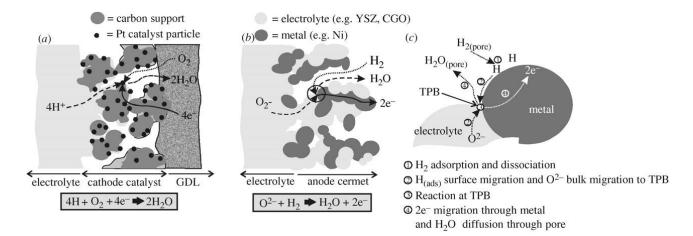
Figure 1. Schematic structure and operation of **a**) PEMFC cathode and **b**) SOFC anode. **c**) Closer look at the operation of the triple-phase boundary (TBP) at the SOFC anode catalyst particle. Source: Brandon, N. P., and D. J. Brett. "Engineering porous materials for fuel cell applications." Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 364.1838 (2006): 147-159.
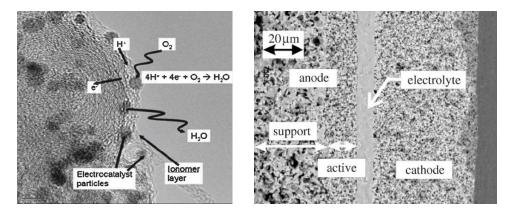

Figure 2. **Left:** Transmission electron microscope image of a PEMFC cathode material, showing catalyst particles (typical diameter 5 nm) supported by larger carbon particles and surrounded by a thin ionomer (electrolyte) layer. The presence of the ionomer layer is essential to conduct protons to the catalyst particles where they react with the electrons conducted to the particle through the carbon, and oxygen adsorbed on the available in the gas phases (pores). Source: Martinez-Duarte, R., et al. "Perspectives of micro and nanofabrication of carbon for electrochemical and microfluidic applications." Microfluidics and microfabrication. Springer US, 2010. 181-263. **Right:** Cross-section SEM image of a SOFC, showing porous anode and cathode layers and non-porous electrolyte layer. Brandon, N. P., and D. J. Brett. "Engineering porous materials for fuel cell applications." Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 364.1838 (2006): 147-159.
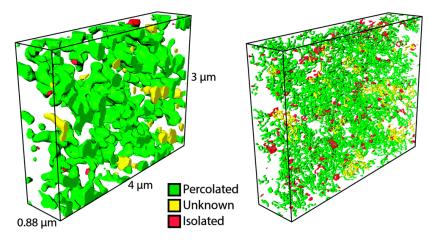

Figure 3. 3D reconstruction of the SOFC anode showing the connectivity of the pore phase (left) and of the TPB (right). The image was obtained with focused ion beam (FIB) milling and scanning electron microscopy (SEM) and 3D-tomographic data analysis and visualization. Only pores and TPB sites continuously connected throughout the whole sample to all three phases, gas inlet, bulk electrolyte and current collectors can contribute to the fuel cell operation.

a) **The major requirements for an effective fuel cell *catalyst material* include:**
1) high catalytic activity towards reduction/oxidation of fuels, i.e. high exchange current density j_0, *per surface area of the catalyst material*
2) high electrical (electron) conductivity
3) high chemical and thermal stability at the fuel cell operating conditions in question
4) chemical compatibility with the electrolyte, e.g. not corroding
5) inertness towards potential contaminations from the fuel, i.e. catalyst "poisons" like CO
6) manageable mismatch in coefficient of thermal expansion with adjacent cell components
7) sufficient mechanical strength (both for fabrication and durability)
8) ease of fabrication into desired micro-structures (e.g. nanoparticles or -wires)
9) low cost; the lower the more catalyst is needed, i.e. the lower the catalytic activity is
10) low toxicity or harmfulness to nature, for the safe of fabrication, use and recycling
11) abundance is the Earth's crust, for scalability to terawatt scale, required for large-scale implementation as a part of the global renewable energy system

b) **The major requirements for an effective fuel cell *catalyst particle* include:**
1) large specific surface area (m^2/g), obtained e.g. by using nanoparticle catalysts, to minimize the quantity of the typically expensive catalyst material (only surface of the particle is catalytically active)
2) sufficiently large to be thermally stable and immobilized
3) all in a) when it comes to the material itself

c) **The major requirements for an effective fuel cell *catalyst-electrode structure* include:**
1) high internal surface area per volume (m^2/m^3), to accommodate large number catalyst particles per unit volume
2) fine dispersion and uniform mixture of catalyst, electrolyte and gas phases, for large (long) triple-phase boundary per unit volume
3) interconnected electrical, electrolyte and gas phases, for continuous transport pathways of electrons to/from the external circuit, ions to/from the bulk electrolyte, and gas to/from the the cell
4) high porosity, for ease of gas transport (porosity = volume fraction of pores = pore volume / electrode volume)
5) low porosity, for low area-specific electrical resistance (compromise with the above!)
6) low tortuosity, for shortest possible transport paths
7) sufficient thickness, for large enough internal surface area per electrode surface area (i.e. roughness factor)
8) sufficiently thin, for low enough area specific resistance (compromise with the above!)
9) sufficient mechanical strength, both for ease of handling and long-term durability
10) ease of fabrication with low-cost and scalable techniques, for example printing