

## Chapter 1 Solutions

**Problem 1.1 (10 points)** Possible answers include:

FC advantages over other power conversion devices:

1. *Potentially* higher efficiency.
2. Solid state components have no moving parts, giving higher reliability and lower maintenance costs.
3. Silent operation.
4. Low emissions.
5. Fuel cells refuel rather than recharge, which could be faster.

Disadvantages:

1. Cost.
2. Low power density.
3. Problems of hydrogen storage, production, and transport.
4. Lower energy density for non-hydrogen fuels.
5. Temperature problems: PEMs can't start in the cold, high temperatures of SOFCs create materials, thermal cycling, and sealing problems.
6. Water management issues in PEMs.

Applications:

1. Portable applications (such as laptops, cell phones, etc.) where their fast refueling, silent operation, and independent scaling of fuel reservoir and power make fuel cells an attractive option.
2. Transportation applications where their low emissions and high efficiency make fuel cells an attractive option.
3. Power generation applications where their silent operation, low emissions, and high efficiency make fuel cells amenable to siting in cities for distributed generation (DG) applications, reducing the cost of power distribution and possibly making process heat available for combined heating and power applications.

**Problem 1.2 (5 points)** Fuel cells have lower power density than engines or batteries, but can have large fuel reservoirs, so they are much better suited to the high capacity/long runtime applications.

**Problem 1.3 (10 points)** You can easily tell which reactions are reduction and which are oxidation by finding which side of the reaction the electrons appear on.

1.  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$  Electrons are liberated, so this is an **Oxidation** reaction.
2.  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  **Reduction**
3.  $\text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{e}^-$  **Oxidation**
4.  $\text{CH}_4 + 4\text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-$  **Oxidation**
5.  $\text{O}^{2-} + \text{CO} \rightarrow \text{CO}_2 + 2\text{e}^-$  **Oxidation**
6.  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$  **Reduction**
7.  $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$  **Oxidation**

**Problem 1.4 (15 points)** You can write full-cell reactions and then split them into the half-cell reactions. You don't need to be an expert chemist to do this, just use the half-cell reactions given and make sure your equations balance with species number (e.g., that O is conserved) and charge (e.g., electrons are conserved).

1.  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$  is a full-cell reaction common in SOFCs; the half-cell reactions would be  $\text{O}^{2-} + \text{CO} \rightarrow \text{CO}_2 + 2\text{e}^-$ , which is an oxidation, or anode, reaction, and  $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ , which is a reduction, or cathode reaction.
2.  $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$  is a full-cell reaction in SOFCs or PEMs, depending on the circulating ion ( $\text{O}^{2-}$  or  $\text{H}^+$ , respectively). The half-cell reactions would be:  $\frac{1}{2}\text{O}_2 + 2\text{e}^- + 2\text{O}^+ \rightarrow \text{H}_2\text{O}$  at the cathode of a PEM and  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$  at the anode of a PEM; or  $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$  at the cathode of an SOFC and  $\text{O}^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O}$  at the anode of an SOFC.
3. Another full-cell reaction in an SOFC could be  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  with the half-cell reactions  $8\text{e}^- + 2\text{O}_2 \rightarrow 4\text{O}^{2-}$  as the reducing, or cathode reaction, and  $\text{CH}_4 + 4\text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-$  as the oxidizing, or anode reaction.

4. To use the circulating ion  $(\text{OH})^-$ , you may construct the full-cell reaction  $\frac{1}{2}\text{O}_2 + \text{H}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}$  from the half-cell reactions  $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2e^-$  as the oxidizing, or anode reaction, and  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2(\text{OH})^-$  as the cathode (reducing) reaction.

**Problem 1.5 (10 points)** From Figure 1.7,  $\text{H}_2(l)$  has a higher volumetric energy density but lower gravimetric energy density than  $\text{H}_2(g)$  at 7500 PSI. On a big bus, the gravimetric energy density is probably a greater concern, so choose  $\text{H}_2(g)$ . Other considerations that could affect the choice include safety, the amount of hydrogen lost to boil-off, and the cost of liquefaction versus compression.

**Problem 1.6 (5 points)**

1. Reactant transport—at high current density, there is a depletion effect. Reactants cannot reach active sites quickly enough. The voltage loss results from a lower concentration of reactants. ( $\eta_{conc}$ )
2. Electrochemical reaction—voltage loss from the sluggishness of the electrochemical reaction ( $\eta_{act}$ )
3. Ionic conduction—resistance to ion flow in the electrolyte ( $\eta_{ohmic}$ )
4. Product removal—in a PEM, water flooding blocks active reaction sites ( $\eta_{conc}$ )

**Problem 1.7 (20 points)** First, we multiply the whole reaction by 2 because you cannot formally describe a bond in  $\frac{1}{2}\text{O}_2$ . We will later divide by 2 at the end to find the energy of the reaction given. For the reaction  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ , we form 2 O-H bonds in  $\text{H}_2\text{O}$ , so

$$E_{2*\text{H}_2\text{O}} = -2 * 2 * E_{\text{O-H}} = -4 * 460 \text{ kJ/mol}$$

$$E_{\text{O}_2} = +494 \text{ kJ/mol}$$

$$E_{2\text{H}_2} = +2 * 432 \text{ kJ/mol}$$

The energy released by the reaction is

$$\frac{1}{2}(E_{2*\text{H}_2\text{O}} + E_{\text{O}_2} + E_{2\text{H}_2}) = \frac{1}{2}(-4 * 460 + 494 + 2 * 432) = \boxed{-241 \text{ kJ/mol}}$$

The energy is negative because an energy *input* to the system is required to break bonds.

**Problem 1.8 (20 points)** You can see the benefits of the independent scaling of the fuel reservoir and the fuel cell stack. For this problem, you may compute the volume of the stack and the reservoir independently.

For the stack, you need to supply 30 kW with a fuel cell that supplies power at 1 kW/L and 500 W/kg. Therefore, the volume needed is  $30 \text{ kW} * \frac{1 \text{ L}}{1 \text{ kW}} = 30 \text{ L}$  and the weight is  $30 \text{ kW} * \frac{1 \text{ kg}}{500 \text{ W}} = 60 \text{ kg}$ .

For the fuel tank, you need to hold a quantity of fuel equal to

$$30 \text{ kJ/s} * \frac{1 \text{ hr}}{60 \text{ miles}} * \frac{3600 \text{ s}}{1 \text{ hr}} * 300 \text{ miles} = 540 \text{ MJ}$$

Note that  $1 \text{ W} = 1 \text{ J/s}$ . Taking into account the 40% efficiency, you need to hold an excess quantity of fuel,  $540 \text{ MJ}/0.40 = 1350 \text{ MJ}$ . The hydrogen is compressed to supply 4 MJ/L and 8 MJ/kg, so the fuel tank must be  $1350 \text{ MJ} * \frac{1 \text{ L}}{4 \text{ MJ}} = 337.5 \text{ L}$  and  $1350 \text{ MJ} * \frac{1 \text{ kg}}{8 \text{ MJ}} = 168.75 \text{ kg}$ .

The entire system must occupy a volume  $V_{system} = V_{tank} + V_{cell} = 337.5 \text{ L} + 30 \text{ L} = 367.5 \text{ L}$  and weighs  $W_{system} = W_{tank} + W_{cell} = 168.75 \text{ kg} + 60 \text{ kg} = 228.75 \text{ kg}$

**Problem 1.9 (5 points)**  $P = VI$ . See the figure.

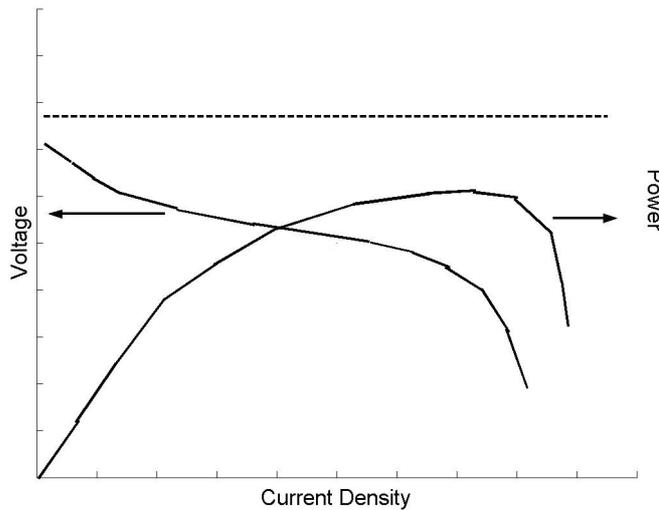


Figure 1: Sketch of Voltage and Power as a function of current density for the fuel cell described in problem 1.9.

**Problem 1.10 (20 points)** Since the container can hold 900 L of H<sub>2</sub> in the form of MH (i.e., LiH), we have a lot of H<sub>2</sub> stored in a relatively small volume. Let's convert 900 L to moles. H<sub>2</sub> density is 0.089  $\frac{g}{L}$ .

$$900 \text{ L} * \frac{0.089 \text{ g H}_2}{\text{L}} * \frac{1 \text{ mol H}_2}{2 \text{ g}} = 40.05 \text{ mol H}_2$$

We know that if H<sub>2</sub> reacts to form water, a total energy of 244  $\frac{\text{kJ}}{\text{mol}}$  can be released. (Not all will be used by our fuel cell.)

$$40.05 \text{ mol} * \frac{244 \text{ kJ}}{\text{mol}} = 9777.2 \text{ kJ in 900 L H}_2$$

Next we convert kJ to Wh:  $[W] = \frac{J}{s} \Rightarrow [Wh] = [\frac{J}{s} * h]$  or  $[Wh] = 3.6 [kJ]$

$$9777.2 \text{ kJ} * \frac{1 \text{ Wh}}{3.6 \text{ kJ}} = 2715.89 \text{ Wh}$$

For volumetric energy density:  $\frac{\text{Energy}}{\text{Volume}}$

$$V_{\text{container}} = \pi(r)^2(L) \Rightarrow \pi \left(\frac{9}{2}\right)^2 (42.5) = 2703.73 \text{ cm}^3 \text{ or } 2.7 \text{ L}$$

$$\text{Energy Density} = \frac{2715.89 \text{ kWh}}{2.7 \text{ L}} \approx 1 \frac{\text{kWh}}{\text{L}} \text{ or } \approx 0.92 \frac{\text{kWh}}{\text{L}}$$

Answer D

## Chapter 2 Solutions

**Problem 2.1 (6 points)** When a gas undergoes a volume constriction, possible configurations of the gas are removed. Entropy is a measure of disorder—that is, the number of possible configurations a system can assume—so the entropy of a gas in a smaller volume is lower (given that the temperature of the gas remains constant—entropy is also a function of temperature). Therefore, the entropy change is negative.

**Problem 2.2 (6 points)**  $G = H - TS$ , so for an isothermal reaction ( $\Delta T = 0$ ),  $\Delta G = \Delta H - T\Delta S$ .

(a) if  $\Delta H < 0$  and  $\Delta S > 0$ , then  $\Delta G < 0$  and the reaction is spontaneous.

(b) in this case, you cannot determine the sign of  $\Delta G$  unless you are given the temperature and the size of the changes in entropy and enthalpy.

(c)  $\Delta H > 0$  and  $\Delta S < 0$ , so in this case,  $\Delta G > 0$  and the reaction is non-spontaneous.

(d) again, you cannot make a determination from the information given.

**Problem 2.3 (6 points)** The reaction rate is determined by the activation barrier, and not by the overall energy change of the reaction. You cannot determine which reaction proceeds faster.

**Problem 2.4 (6 points)** While the current scales with the amount of reactants, the voltage does not. The thermodynamic potential comes from the energy drop going from products to reactants, which does not scale with reactant amount. Since  $E = -\Delta G/nF$ , you can think of the scaling in  $n$  cancelling the scaling in  $\Delta G$ .

**Problem 2.5 (6 points)** The Nernst equation

$$E = E_T - \frac{RT}{nF} \ln \frac{\prod a_{prod}^{\nu_i}}{\prod a_{react}^{\nu_i}}$$

shows that increasing the activity of the reactants decreases the argument of the ln, which raises the reversible cell voltage ( $E$ ) because the ln term is negative. This, in essence, is Le'Chatlier's principle.

**Problem 2.6 (Not graded)** When the reaction is in equilibrium, the electrochemical potential of the system is everywhere zero. The electrochemical potential of electrons is simply the electrical potential. Electrons on the products side see the electrical potential  $\phi_P$  and on the reactants side see the potential  $\phi_R$ . Note that different species do not experience different

electrical potentials. Then, if  $\Delta\phi$  is the difference in electrical potential from one side to the other,

$$0 = \sum \tilde{\mu}_i dn_i = \sum \mu_i^o dn_i + \sum RT \ln a_i dn_i + nF \Delta\phi$$

First, note that:

$$\sum RT \ln a_i dn_i = RT(\ln a_M^m + \ln a_M^n - \ln a_A^1 - \ln a_B^b) = RT \ln \frac{a_M^m a_M^n}{a_A a_B} = RT \ln \frac{\prod a_{prod}^{\nu_i}}{\prod a_{react}^{\nu_i}}$$

Rearranging (2) and inserting the above result, you get

$$\Delta\phi = -\frac{\sum \mu_i^o dn_i}{nF} - \frac{RT}{nF} \ln \frac{\prod a_{prod}^{\nu_i}}{\prod a_{react}^{\nu_i}}$$

From the thermodynamic definition of chemical potential,  $\mu_i \equiv \frac{\partial G}{\partial n_i}$  so that  $\sum \mu_i^o dn_i = \Delta G^o$  where the  $^o$  in this case denotes reference concentration. We relate this term to  $E$  by  $-\frac{\Delta G^o}{nF} = E^o$ , but note that the  $^o$  refers only to reference concentration. The  $E^o$  term may still depend on temperature, so we rename the quantity  $E_T$ . Identifying  $E$  as the electrical potential across the cell  $\Delta\phi$ , we arrive at the Nernst equation (1).

**Problem 2.7 (15 points)** Yes, you can have a thermodynamic efficiency greater than 1. We chose the metric of fuel cell efficiency to be  $\Delta G/\Delta H$ , but it is in some sense an arbitrary choice.

To break the intuitive barrier against efficiencies greater than unity, consider the efficiency of an electrolyzer, a device that makes hydrogen and oxygen gas from water using electricity (this is the reverse of a fuel cell, and may be used to generate hydrogen for some fuel cell applications). An electrolyzer has an efficiency defined to be the  $\Delta H$  of reaction (the output is the useful heat energy of hydrogen), divided by the energy input  $\Delta G$ . Therefore, the efficiency of the electrolyzer is the inverse of fuel cell efficiency—so the fuel cell at STP with an efficiency of 0.83, if ran in reverse as an electrolyzer, would have an efficiency of  $1/0.83$ , which is greater than 1.

For a fuel cell, consider the following example:  $\epsilon \equiv \Delta G/\Delta H$ . For an isothermal reaction,  $\Delta G = \Delta H - T\Delta S$ , so  $\epsilon = 1 - T\frac{\Delta S}{\Delta H}$ . To get an efficiency greater than 1, we can have  $\Delta H$  negative and  $\Delta S$  positive. The trick is to use a solid or liquid reactant to make  $\Delta S$  positive because solids and liquids have very low entropy compared to gases. For the fuel cell reaction  $C_{(s)} + \frac{1}{2}O_2 \rightarrow CO$  at 298 K and 1 bar,

$$\begin{aligned} \Delta S &= S_{CO} - \frac{1}{2}S_{O_2} - S_C = 197.7 - 0.5 * 205.1 - 5.7 \text{ (in J/mol} \cdot \text{K)} \\ &= 89.45 \text{ J/mol} \cdot \text{K} \end{aligned}$$