Fuel Cell Fundamentals
Solutions

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Solution companion to *Fuel Cell Fundamentals*, third edition.
Suggested grading schemes are given after the problem numbers.

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

4. To use the circulating ion $(OH)^-$, you may construct the full-cell reaction $\frac{1}{2}O_2 + H_2 + H_2O \rightarrow 2H_2O$ from the half-cell reactions $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$ as the oxidizing, or anode reaction, and $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ as the cathode (reducing) reaction.

Problem 1.5 (10 points) From Figure 1.7, $H_2(l)$ has a higher volumetric energy density but lower gravimetric energy density than $H_2(g)$ at 7500 PSI. On a big bus, the gravimetric energy density is probably a greater concern, so choose $H_2(g)$. 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.(η_{conc})
2. Electrochemical reaction–voltage loss from the sluggishness of the electrochemical reaction (η_{act})
3. Ionic conduction–resistance to ion flow in the electrolyte (η_{ohmic})
4. Product removal–in a PEM, water flooding blocks active reaction sites (η_{conc})

Problem 1.7 (20 points) First, we multiply the whole reaction by 2 because you cannot formally describe a bond in $\frac{1}{2}O_2$. We will later divide by 2 at the end to find the energy of the reaction given. For the reaction $2H_2 + O_2 \rightarrow 2H_2O$, we form 2 O-H bonds in H_2O, so
$E_{2*H_2O} = -2*2*E_{\text{O-H}} = -4*460$ kJ/mol
$E_{O_2} = +494\,\text{kJ/mol}$
$E_{2H_2} = +2*432$ kJ/mol
The energy released by the reaction is

$$\frac{1}{2}(E_{2*H_2O} + E_{O_2} + E_{2H_2}) = \frac{1}{2}(-4*460 + 494 + 2*432) = \boxed{-241\text{ kJ/mol}}$$

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 kW $* \frac{1\text{ L}}{1\text{ kW}} = 30$ L and the weight is 30 kW $* \frac{1\text{ kg}}{500\text{ W}} = 60$ 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 W = 1 J/s. Taking into account the 40% efficiency, you need to hold an excess quantity of fuel, 540 MJ/0.40 = 1350 MJ. The hydrogen is compressed to supply 4 MJ/L and 8 MJ/kg, so the fuel tank must be 1350 MJ $* \frac{1\text{ L}}{4\text{ MJ}} = 337.5$ L and 1350 MJ $* \frac{1\text{ kg}}{8\text{ MJ}} = 168.75$ kg.

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

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

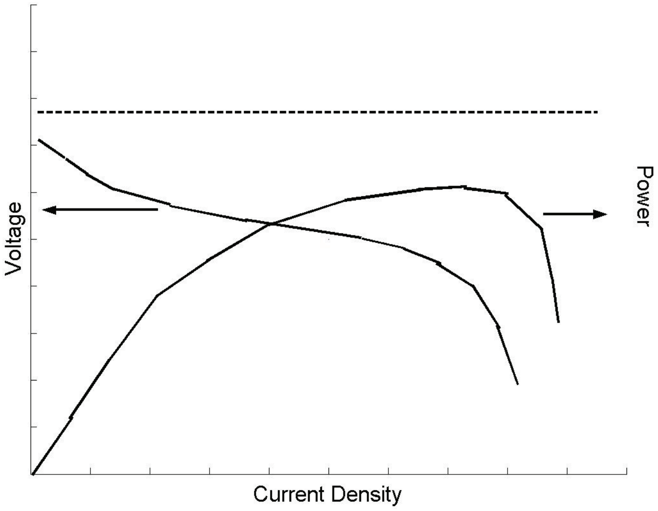

Figure 1: Sketch of Voltage and Power as a function of current density for the fuel cell described in problem 1.9.

Problem 1.10 (20 points) Since the container can hold 900 L of H_2 in the form of MH (i.e., LiH), we have a lot of H_2 stored in a relatively small volume. Let's convert 900 L to moles. H_2 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_2 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: $\frac{Energy}{Volume}$

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

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

$\boxed{\text{Answer D}}$

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 ΔG 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 ΔG.

Problem 2.5 (6 points) The Nernst equation

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

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 ϕ_P and on the reactants side see the potential ϕ_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:

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

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 $\Sigma \mu_i^o dn_i = \Delta G^o$ 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 ΔH of reaction (the output is the useful heat energy of hydrogen), divided by the energy input ΔG. 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 ΔH negative and ΔS positive. The trick is to use a solid or liquid reactant to make ΔS 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,

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

$$\Delta H = H_{CO} - \frac{1}{2}H_{O_2} - H_C = -110.5 - 0.5 * 0 - 0 \text{ (in kJ/mol)}$$
$$= -110.5 \text{ kJ/mol}$$

then
$\epsilon = 1 - T\frac{\Delta S}{\Delta H} = 1 - (\textit{negative number}) > 1$

Problem 2.8 (not graded) The full-cell reaction for a DMFC is given by 2.32, the half cell reactions are $CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^-$ and $\frac{3}{2}O_2 + 6e^- + 6H^+ \rightarrow 3H_2O$, so there are six electrons transferred per methanol molecule.

(a)The methanol consumption is therefore

$$mol\ MeOH/s = i * (mol\ MeOH)/C = i/(6 * N_a * q) = i/6F$$

and the output mass flux, assuming the input flux is x mol/s, is $v_{MeOH,out} = x - i/6F$. The oxygen consumption is $\frac{3}{2}$ as large as the methanol consumption, and air is approximately 21% oxygen. Assuming the air input is y mol/s, the air output is $v_{air,out} = y - 0.21 * i/4F$. The water output is twice the methanol output. Assuming no water flows into the cell, the water output is $v_{H_2O,out} = i/3F$. The (molar) carbon dioxide output is equal to the methanol consumption, so the output is $v_{CO_2,out} = i/6F$.

(b) The stoichiometric factor is the excess reactant delivered over that required for operation at current i. $\lambda_{MeOH} = 6Fx/i$ and $\lambda_{air} = 0.21y*4F/i$.

Problem 2.9 (15 points) Assuming constant specific heats,
$\Delta H(T) = \Delta H^o + c_p(T - T^o)$ and $\Delta S(T) = \Delta S^o + c_p \ln(T/T^o)$.

Find the temperature that satisfies:

$$\Delta G(T) = 0 = \Delta H(T) - T\Delta S(T) = \sum [\Delta H_i^o + c_{p_i}(T - T^o) - T(S_i^o + c_{p_i} \ln(T/T^o))]$$

taking out the ΔH^o and ΔS^o,

$$0 = \Delta H_{rxn}^o - T\Delta S_{rxn}^o + \sum [c_{p_i}(T - T^o - T\ln(T/T^o))]$$

or

$$0 = \Delta H_{rxn}^o - T\Delta S_{rxn}^o + (T - T^o - T\ln(T/T^o)) \sum c_{p_i}$$

Substituting numbers,

$$0 = -41.13 \text{ kJ/mol} - \text{T}(-42.00 \text{ J/mol·K}) + (T - T^o - T\ln(T/T^o))(3.2 \text{ J/mol·K})$$

A numerical solution (MATLAB or Excel or your graphing calculator work fine) gives $\boxed{T \approx 1020 \text{ K} \approx 747°\text{C}}$. The error of neglecting the dependence of ΔS and ΔH on temperature led to an answer that was off by about 40 degrees in this case. A more sophisticated solution would include the variance of c_p with temperature, requiring an iterative solution or an expansion for c_p in terms of T.

Problem 2.10 (a) **(10 points)** Remember that the effect of temperature enters into the first term of the Nernst equation. From the Nernst equation, if the reactants and products are ideal,

$$E = E_T - \frac{RT}{nF} \ln \left[\frac{(P/P_o)^{\nu_P} \prod_P x_i^{\nu_i}}{(P/P_o)^{\nu_R} \prod_R x_i^{\nu_i}} \right] = E_T - \frac{RT}{nF} \ln \left[(P/P_o)^{\nu_P - \nu_R} \frac{\prod_P x_i^{\nu_i}}{\prod_R x_i^{\nu_i}} \right]$$

In a reaction, the change in number of moles $\Delta n_G = \nu_P - \nu_R$. The temperature dependent term is

$$E_T = E^o + \frac{\Delta S}{nF}(T - T_o)$$

For the voltages to be equal

$$E(T_1, P_1) = E(T_2, P_2)$$

$$\begin{aligned} E^o + \frac{\Delta S}{nF}(T_1 - T_o) - \frac{RT_1}{nF} \ln \left[(P_1/P_o)^{\Delta n_G} \frac{\prod_P x_i^{\nu_i}}{\prod_R x_i^{\nu_i}} \right] &= \\ E^o + \frac{\Delta S}{nF}(T_2 - T_o) + \frac{RT_2}{nF} \ln \left[(P_2/P_o)^{\Delta n_G} \frac{\prod_P x_i^{\nu_i}}{\prod_R x_i^{\nu_i}} \right] & \end{aligned}$$

Canceling constant terms that appear on both sides of the equation and solving for T_2,

$$T_1 \frac{\frac{\Delta S}{nF} - \frac{R}{nF} \ln \left[(P_1/P_o)^{\Delta n_G} \frac{\prod_P x_i^{\nu_i}}{\prod_R x_i^{\nu_i}} \right]}{\frac{\Delta S}{nF} - \frac{R}{nF} \ln \left[(P_2/P_o)^{\Delta n_G} \frac{\prod_P x_i^{\nu_i}}{\prod_R x_i^{\nu_i}} \right]} = T_2$$

Simplifying for the H_2/O_2 fuel cell with liquid water as product and for pure components ($x_{H_2} = x_{O_2} = 1$) and dropping the P_o, which is understood to be 1 *atm* the expression simplifies to

$$T_1 \frac{\Delta S + 1.5R \ln P_1}{\Delta S + 1.5R \ln P_2} = T_2$$

(b) **(5 points)** At STP, using the data from Appendix B,

$$\begin{aligned} \Delta S_{rxn} &= S_{H_2O(l)} - S_{H_2} - 0.5 S_{O_2} = 69.95 - 130.86 - 0.5 * 228.3 \\ &= -175.06 \text{ J/mol} \cdot \text{K} \end{aligned}$$

If $P_2 = P_1/10$ then from the above expression,

$$T_2 = T_1 \frac{\Delta S + 1.5R\ln P_1}{\Delta S + 1.5R\ln(P_1/10)} = 298\frac{-175.06 + 1.5 * 8.314 * \ln 1}{-175.06 + 1.5 * 8.314 * \ln(1/10)}$$

Then $\boxed{T_2 = 256\text{ K}}$. Note that at this temperature of −17°C, there will be no $H_2O_{(g)}$ (so we shouldn't use the ΔS for water vapor), but there will also not be liquid water—the product will be ice! A full solution would use the ΔS for liquid water down to 0°C and then the ΔS for ice below that.

To interpret the result, since ΔS is negative, the Nernst voltage decreases with an increase in temperature. The decrease in pressure decreases the Nernst voltage, so we must compensate by raising the Nernst voltage by decreasing temperature; therefore, $T_2 < T_1$.

Problem 2.11 (15 points) Two ways of attacking this problem yield the same result. First, you could imagine a box with water, air, and hydrogen, and the reaction $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O_{(l)}$ is in equilibrium. To find how much hydrogen is consumed by oxygen, find the equilibrium quantity of hydrogen when oxygen is present. That is to say, find at what P_{H_2} does $\Delta G_{rxn} = 0$. From the Van't Hoff isotherm

$$\Delta G = \Delta G^o + RT\ln\frac{\Pi a_{prod}^{\nu_i}}{\Pi a_{react}^{\nu_i}}$$

assuming air at the cathode ($x_{O_2} = 0.21$):

$$\Delta G = \Delta G^o + RT\ln\frac{a_{H_2O}^1}{a_{H_2}^1 a_{O_2}^{0.5}} = \Delta G^o + RT\ln\frac{1}{(P/P_o)^{1.5} x_{H_2} x_{O_2}^{0.5}} = \Delta G^o - RT\ln(1)^{1.5}(x_{H_2})(0.21)^{0.5}$$

Solving for x_{H_2},

$$\frac{\Delta G^o}{RT} = \ln\left[(0.21)^{0.5}x_{H_2}\right]$$

$$x_{H_2} = \frac{1}{0.21^{0.5}}\exp\left[\frac{\Delta G^o}{RT}\right] = (2.18)\exp\left[\frac{(-237\text{ kJ/mol})}{(8.314\text{ J/mol}\cdot\text{K})(298\text{ K})}\right] = 5.41{\cdot}10^{-42}$$

so $\boxed{P_{H_2} = 5.41 \cdot 10^{-42}\ atm.}$

Note that the partial pressure is very low, because it is very energetically favorable for hydrogen to react with oxygen to form water.

The alternate way to solve the problem is to solve a concentration cell where a voltage develops (1.23 V because it is a hydrogen/air system) but

$E^o = 0$ because the concentration cell reaction is $H_2 + O_2 \rightarrow H_2 + O_2$. In this formulation, you solve the Nernst equation where the reactants have activity 1 because they are pure:

$$1.23 = 0 - \frac{RT}{nF} \ln \frac{P_{H_2}/P_o (0.21)^{0.5}}{1}$$

This gives the same equation:

$$x_{H_2}(0.21)^{0.5} = \exp\left[-\frac{1.23 * nF}{RT}\right]$$

Problem 2.12 (5 points) The efficiencies of each part multiply to give the total efficiency of the cell: $\epsilon = \epsilon_{thermo}\epsilon_{Voltage}\epsilon_{fuel}$. For pure H_2/O_2 at STP, $\epsilon_{thermo} = 0.83$. We are given V, so $\epsilon_{Voltage} = \frac{V}{E} = \frac{0.75}{1.23}$. We are given λ, so $\epsilon_{fuel} = \frac{1}{\lambda} = \frac{1}{1.1}$. Therefore,

$$\epsilon = 0.83 * \frac{0.75}{1.23}\frac{1}{1.1}$$

$$\boxed{\epsilon = 46\%}$$

Problem 2.13 (not graded) (a) The output flux of MeOH is $v_{MeOH,out} = v_{MeOH,in} - i/nF = 0.003 - 1000/(6 * 96485) = 0.001$ mol/s. The output flux of air is $v_{air,out} = 0.03 - 0.21 * 1000/(4 * 96485) = 0.029$ mol/s. $v_{H_2O,out} = 1000/(3 * 96485) = 0.03$ mol/s and $v_{CO_2,out} = 1000/(6 * 96485) = 0.02$ mol/s.

(b) $\lambda_{MeOH} = nFv/i = 6 * 96485 * 0.003/1000 = 1.7$ and $\lambda_{air} = 0.21 * 0.03 * 96485 * 4/1000 = 2.4$.

(c) The methanol usage rate is $i/nF = 1000/(6 * 96485) = 0.0017$ mol/s so the power usage is 719.19 kJ/mol * 0.0017 mol/s = 1.24 kW. To find the heat production, we need to know the efficiency. The electrical power generated is $P_e = i * V = 1000 * 0.3 = 300\,\mathrm{W}$, and the rest of the energy in the fuel is converted to heat. Therefore, the heat production rate is $1.24\,\mathrm{kW} - 300\,\mathrm{W} = \boxed{P_h = 942\,\mathrm{W}}$.

Problem 2.14 (5 points)

$$\text{Area} = \frac{\text{Total power}}{\text{Power per area}} \Rightarrow 2000 \text{ W} * \frac{1}{1.5\frac{\text{W}}{\text{cm}^2}} = 1333.3 \text{ cm}^2$$

$$\boxed{\text{Answer b}}$$

Problem 2.15 (10 points)

$$i = \frac{dQ}{dt} \Rightarrow i = nF\frac{dN}{dt} \Rightarrow \frac{dN}{dt} = \frac{i}{nF} \Rightarrow N = \frac{i}{nF}(t_f - t_i)$$

Using current density and area from 2.14, we can solve for current and use that to find the number of moles of fuel.
$N = \frac{4000\ A}{(2\frac{\text{mol e}^-}{\text{mol H}_2})(96400\ \frac{\text{C}}{\text{mol e}^-})} * \frac{60\ \text{sec}}{\text{min}} * \frac{60\ \text{min}}{\text{hr}} * \frac{24\ \text{hr}}{\text{day}}$=1792.53 mol H_2 in 24 hrs
We know that the reaction is: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ which means that we have a 1:1 H_2 to H_2O molar ratio. So we have 1792.52 moles of H_2O. To connect to L, we need atomic mass and density.

$$\frac{1792.53\ \text{mol H}_2\text{O}}{1} * \frac{18\ \text{g}}{\text{mol H}_2\text{O}} * \frac{1\ \text{cm}^3}{\text{g}} = 32265.6\ \text{cm}^3\ \textit{or}\ 32.3\ \text{L}$$

$$\boxed{\text{Answer c}}$$

Problem 2.16 (5 points) Le Chatelier's principle tells us that the reaction will favor the forward direction, increasing the thermodynamic voltage.

$$\boxed{\text{Answer b}}$$

Problem 2.17 (10 points)

(a)

Electrode	Reaction 1	Reaction 2
Cathode	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$	$2(O_2 + 4e^-) \rightarrow 2(2O^{2-})$
Anode	$CO + O^{2-} \rightarrow CO_2 + 2e^-$	$CH_4 + 4O^{2-} \rightarrow 8e^- + 2H_2O + CO_2$
Full Reaction	$\frac{1}{2}O_2 + CO \rightarrow CO_2$	$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$

(b)

Electrode	Reaction 1	Reaction 2
Cathode	$8e^- + 2H_2O + 2CO_2 \rightarrow 4O^{2-} + CH_4$	$CO_2 + 2e^- \rightarrow CO + O^{2-}$
Anode	$4O^{2-} \rightarrow 8e^- + 2O_2$	$O^{2-} \rightarrow 2e^- + \frac{1}{2}O_2$
Full Reaction	$2H_2O + CO_2 \rightarrow 2O_2 + CH_4$	$CO_2 \rightarrow CO + \frac{1}{2}O_2$

Problem 2.18

(a) **(5 points)**

$$A = \frac{P}{j * V} \Rightarrow \frac{3000\ \text{W}}{(1\frac{A}{\text{cm}^2} * \frac{100^2\ \text{cm}^2}{\text{m}^2})(0.6\,\text{V})} = 0.5\,\text{m}^2$$

(b) **(10 points)** The heat generated is the difference between the power put in and the generated electrical power.

$$P_{heat} = P_{in} - P_{elec}$$

$$P_{in} = \frac{\lambda \mid \Delta H \mid i}{nF} = \frac{(1)(802,000\frac{J}{\text{mol CH}_4})(5000A)}{(8\frac{\text{mol } e^-}{\text{mol CH}_4})(96485\frac{C}{\text{mol } e^-})}$$

$$P_{elec} = i * V = 5000A * 0.6V = 3000W$$

$$P_{heat} = P_{in} - P_{elec} = 5.2 \text{ kW} - 3.0 \text{ kW} = \boxed{2.2\,\text{kW}}$$

(c) **(10 points)** Rate of water production:

$$\nu_{H_2O} = \frac{\lambda i}{nF} = \frac{(1)(5000A)}{(4\ \frac{\text{mol } e^-}{\text{mol H}_2\text{O}})(96485\ \frac{C}{\text{mol } e^-})} = 0.013\ \frac{\text{mol H}_2\text{O}}{\text{s}}$$

Convert to moles per day:

$$0.013\ \frac{\text{mol H}_2\text{O}}{s} * \frac{60 \text{ s}}{1 \text{ min}} * \frac{60 \text{ min}}{1 \text{ hr}} * \frac{24 \text{ hr}}{1 \text{ day}} = 1119.17\ \frac{\text{mol H}_2\text{O}}{\text{day}}$$

Use molecular weight to convert to volume:

$$V_{H_2O} = 1119.17\frac{\text{mol H}_2 O}{\text{day}} * \frac{18 \text{ g}}{1 \text{ mol H}_2\text{O}} * \frac{1 \text{ cm}^3}{1 \text{ g}} * \frac{1 \text{ mL}}{1 \text{ cm}^3} * \frac{1 \text{ L}}{1000 \text{ mL}}$$

$$\boxed{V_{H_2O} = 20.145\,\text{L}}$$

(d) **(2 points)** $\boxed{\text{No.}}$

$20.145\ \frac{\text{L}}{\text{day}} \ll 750\frac{\text{L}}{\text{day}}$ average consumption.

Chapter 3 Solutions

Problem 3.1 (a) **(5 points)** Reducing the potential raises the energy of electrons in the electrode. To reduce their energy, electrons leave the electrode, so the reaction proceeds faster in the forward direction.
(b) **(5 points)** Increasing the potential lowers the energy of electrons in the electrode, so the reaction is biased in the forward direction.
(c) **(5 points)** We want to increase both reaction rates in the forward direction. At the anode ($H_2 \rightleftharpoons H^+ + 2e^-$) you want to draw electrons to the electrode, so increase the potential. At the cathode ($2H^+ + 2e^- + \frac{1}{2}O_2 \rightleftharpoons H_2O$) you want electrons to leave the electrode, so reduce this potential. The overall voltage output falls from both effects.

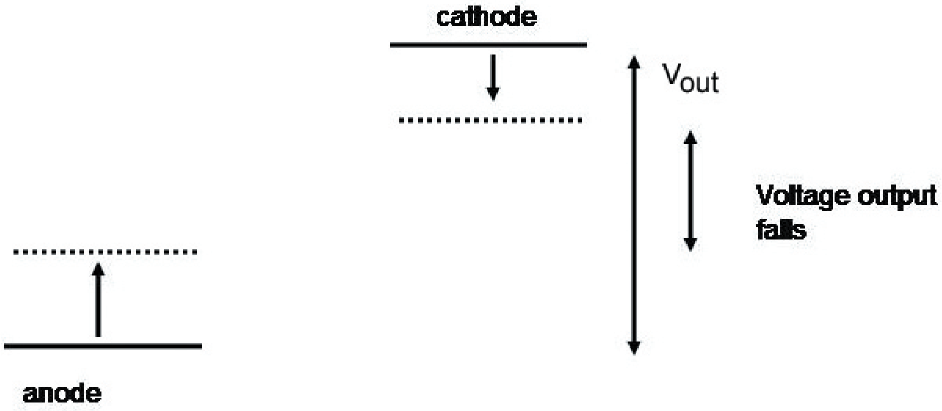

Figure 2: Schematic of activation voltage losses for problem 3.1.

Problem 3.2 (5 points) Yes, it is possible to have a negative Galvani potential at one electrode. It means that one half-cell reaction requires energy input, and the other results in energy output. So long as the total potential adds up to the measured full-cell potential, it is impossible to know what each half-cell potential is!

Problem 3.3 (10 points) Alpha is the charge transfer coefficient. It describes whether the "center of the reaction," or peak of the reaction activation barrier, falls nearer to one side of the reaction or the other. In this figure, note that alpha does not change the final electrochemical energy change, only the height of the peak in electrochemical energy.

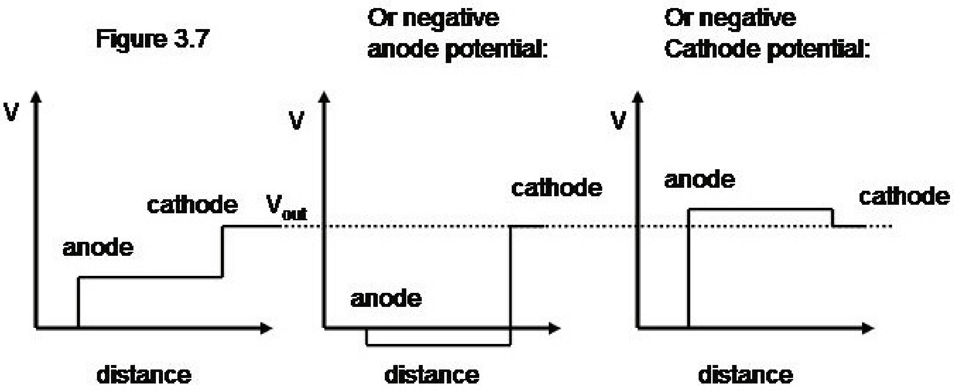

Figure 3: Schematic of different Galvani potentials, problem 3.2.

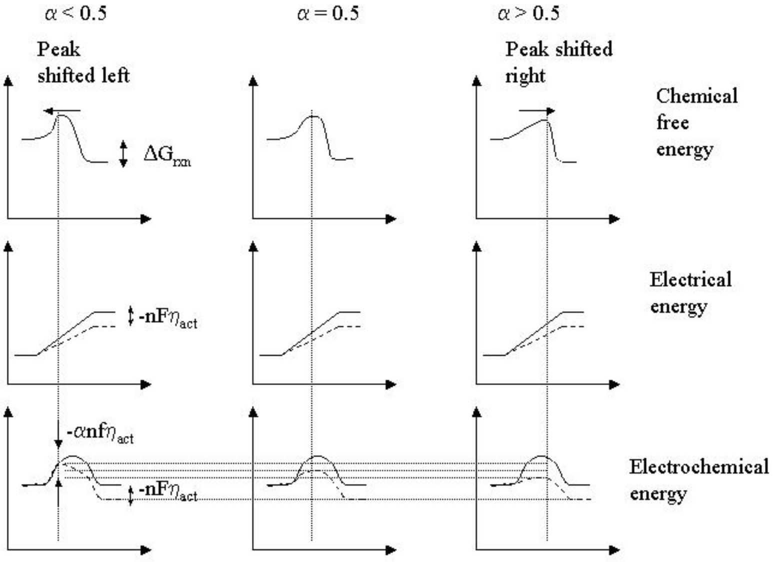

Figure 4: Effect of α on the electrochemical energy pathway for problem 3.3.

Problem 3.4 (5 points) The exchange current density is the current density of the forward and reverse reactions at equilibrium (in an open circuit).

Problem 3.5 (5 points) (a) The Tafel equation reads:

$$\eta_{act} = a + b \log j$$

In the exponential regime, the Butler-Volmer equation simplifies to

$$\eta_{act} = -\frac{RT}{\alpha n F} \ln j_o + \frac{RT}{\alpha n F} \ln j$$

Note: To convert between log and ln, use the conversion $\ln x = 2.3 \log x$. The terms that go as a logarithm with current density are equal:

$$b \log j = \frac{RT}{\alpha n F} \ln j \Rightarrow b/2.3 = \frac{RT}{\alpha n F}$$

$$\boxed{b = 2.3 \tfrac{RT}{\alpha n F}}$$

(b) Identifying the constant terms, we get

$$\boxed{a = -\tfrac{RT}{\alpha n F} \ln j_o}$$

Problem 3.6 (5 points) The full-cell reaction is $CO + \frac{1}{2}CO_2 \rightarrow CO_2$. The half-cell reaction at the anode is $O^{2-} + CO \rightarrow CO_2 + 2e^-$ and at the cathode is $O_2 + 4e^- \rightarrow 2O^{2-}$.

Problem 3.7 (5 points) The main job of a fuel cell catalyst is to be able to form intermediate-strength bonds with reactants and products—that is, to yield a low ΔG_{act}. Also, it should have a long lifetime, which means that it is resistant to poisoning and does not migrate or agglomerate on the membrane. The requirements for an effective fuel cell catalyst-electrode structure are: porosity, a high degree of interconnection between the pores, a high effective catalyst area, high TPB density, high electronic conductivity, and high exchange current density. It also must have a long lifetime, meaning high mechanical strength and resistance to corrosion. Ideally, it would also be cheap and easy to manufacture.

Problem 3.8 (not graded) From equation 3.51, using $n = 1$, $j = 0$ and plugging in reactants and products, we find for the anode:

$$0 = j_0 \left(\left(\frac{C^*_{H_2,i}}{C^{0*}_{H_2,i}}^{0.5} \right) e^{\alpha F \eta / RT} - \left(\frac{C^*_{H^+,i}}{C^{0*}_{H^+,i}} \frac{C^*_{e^-,i}}{C^{0*}_{e^-,i}} \right) e^{-(1-\alpha) F \eta / RT} \right)$$

and for the cathode

$$0 = j_0 \left(\left(\frac{C^*_{O_2,i}}{C^{0*}_{O_2,i}}^{0.25} \frac{C^*_{e^-,i}}{C^{0*}_{e^-,i}} \frac{C^*_{H^+,i}}{C^{0*}_{H^+,i}} \right) e^{\alpha F\eta/RT} - \left(\frac{C^*_{H_2O,i}}{C^{0*}_{H_2O,i}} \right)^{0.5} e^{-(1-\alpha)F\eta/RT} \right)$$

We introduce the shorthand $f = F/RT$ and follow the same procedure as in the text, we get next

$$\ln \left(\frac{C^{*,A}_{H^+,i}}{C^{0*,A}_{H^+,i}} \frac{C^{*,A}_{e^-,i}}{C^{0*,A}_{e^-,i}} \frac{C^{0*,A}_{H_2,i}}{C^{*,A}_{H_2,i}}^{0.5} \right) = f\eta^A$$

and

$$\ln \left(\frac{C^{*,C}_{O_2,i}}{C^{0*,C}_{O_2,i}}^{0.25} \frac{C^{*,C}_{e^-,i}}{C^{0*,C}_{e^-,i}} \frac{C^{*,C}_{H^+,i}}{C^{0*,C}_{H^+,i}} \frac{C^{0*,C}_{H_2O,i}}{C^{*,C}_{H_2O,i}}^{0.5} \right) = -f\eta^C$$

Next we use the definition of activity and subtract the two equations:

$$\ln \left(\frac{a^{*,A}_{H^+} * a^{*,A}_{e^-}}{(a^{*,A}_{H_2})^{0.5}} \right) - \ln \left(\frac{(a^{*,C}_{O_2})^{0.25} * a^{*,C}_{H^+} * a^{*,C}_{e^-}{}^{0.5}}{a^{*,C}_{H_2O}} \right) = f(\eta^A + \eta^C)$$

Using $\eta^A + \eta^C = E^0 - E$, we find

$$E = E^0 - \frac{RT}{F} \left(\ln \frac{(a^{*,C}_{H_2O})^{0.5}}{(a^{*,A}_{H_2})^{0.5}(a^{*,C}_{O_2})^{0.25}} - \ln \frac{a^{*,A}_{H^+}}{a^{*,C}_{H^+}} - \ln \frac{a^{*,A}_{e^-}}{a^{*,C}_{e^-}} \right)$$

We multiply the second term by $\frac{2}{2}$ to find the same formula as 3.63:

$$E = E^0 - \frac{RT}{2F} \left(\ln \frac{a^{*,C}_{H_2O}}{a^{*,A}_{H_2}(a^{*,C}_{O_2})^{0.5}} - \ln \left(\frac{a^{*,A}_{H^+}}{a^{*,C}_{H^+}} \right)^2 - \ln \left(\frac{a^{*,A}_{e^-}}{a^{*,C}_{e^-}} \right)^2 \right)$$

Problem 3.9 (not graded) (Note: the equation should have $1O_2$, not $\frac{1}{2}O_2$) In general, for half cell reactions, equation 3.61 reads

$$\eta^C = \frac{RT}{nF} \ln \left(\frac{\prod (a^{*,C}_P)^{\nu_i}}{\prod (a^{*,C}_R)^{\nu_i}} \right)$$

For the two sequential reactions, intermediates will cancel out, as shown below:

$$\eta^C = \frac{RT}{2F} \ln \left(\frac{a^{*,C}_{H_2O_2}}{(a^{*,C}_{H^+})^2 (a^{*,C}_{e^-})^2 a^{*,C}_{O_2}} \right) \left(\frac{a^{*,C}_{H_2O} a^{*,C}_{O_2}}{a^{*,C}_{H_2O_2}} \right)$$

The rest of the derivation follows the text.

Problem 3.10 (not graded)
(a) At equilibrium,

$$0 = \frac{C_R^{**}}{C_R^{0*}} e^{\alpha n f \eta_A} - \frac{C_P^{**}}{C_P^{0*}} e^{-(1-\alpha) n f \eta_A}$$

$$\ln \frac{C_P^{**}}{C_P^{0*}} - (1-\alpha) n f \eta_A = \ln \frac{C_R^{**}}{C_R^{0*}} + \alpha n f \eta_A$$

$$-n f \eta_A = \ln \left(\frac{C_R^{**}}{C_R^{0*}} * \frac{C_P^{0*}}{C_P^{**}} \right)$$

$$\eta_A = \frac{RT}{nF} \ln \left(\frac{C_R^{0*}}{C_R^{**}} * \frac{C_P^{**}}{C_P^{0*}} \right)$$

(b) The Butler-Volmer equation is

$$j = j_0 \left(\frac{C_R^*}{C_R^{0*}} e^{\alpha n f (\eta' + \eta_A)} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha) n f (\eta' + \eta_A)} \right)$$

Plugging in η_A from above,

$$j = j_0 \left[\frac{C_R^*}{C_R^{0*}} e^{\alpha n f \eta'} * \left(\frac{C_R^{0*}}{C_R^{**}} * \frac{C_P^{**}}{C_P^{0*}} \right)^{\alpha} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha) n f \eta'} * \left(\frac{C_R^{0*}}{C_R^{**}} * \frac{C_P^{**}}{C_P^{0*}} \right)^{-(1-\alpha)} \right]$$

$$j = j_0 e^{\alpha n f \eta'} \left[\frac{C_R^* (C_R^{0*})^{\alpha} (C_P^{**})^{\alpha}}{C_R^{0*} (C_R^{**})^{\alpha} (C_P^{0*})^{\alpha}} - e^{-n f \eta'} \frac{C_P^* (C_R^{0*})^{\alpha-1} (C_P^{**})^{\alpha-1}}{C_P^{0*} (C_R^{**})^{\alpha-1} (C_P^{0*})^{\alpha-1}} \right]$$

After much rearranging, this gives

$$j = j_0 \frac{(C_R^{0*})^{\alpha-1} (C_P^{**})^{\alpha}}{(C_R^{**})^{\alpha-1} (C_P^{0*})^{\alpha}} e^{\alpha n f \eta'} \left[\frac{C_R^*}{C_R^{**}} - e^{-n f \eta'} \frac{C_P^*}{C_P^{**}} \right]$$

This is the Butler-Volmer equation again with a different j_0 and defined against the new reference concentrations C_R^{**} and C_P^{**}.

Problem 3.11 (5 points) For reaction A, the net reaction rate in $\mathrm{mol/s \cdot cm^2}$ is $\frac{5\ A}{nF \cdot 2\,\mathrm{cm}^2} = \frac{2.5 A/\mathrm{cm}^2}{2F} = 1.30 \cdot 10^{-5}\,\mathrm{mol/s \cdot cm^2}$. For reaction B, the net reaction rate is $\frac{15\ A}{nF \cdot 5\,\mathrm{cm}^2} = \frac{3 A/\mathrm{cm}^2}{3F} = 1.04 \cdot 10^{-5}\,\mathrm{mol/s \cdot cm^2}$. Therefore, reaction A has a higher reaction rate.

Problem 3.12 (a) **(2 points)** $P = IV = (1\ A)(2.5\ V) = 2.5\ W$

(b) **(2 points)** By putting five cells together in series, you get an overall voltage of $5(0.5\ V) = 2.5$ V, the necessary voltage.

(c) **(3 points)** Note that when you stack cells together in series, the current does not change. However, the amount of hydrogen required does increase. One way to think of it is that when you are required to supply 2.5 W of power, you must supply 2.5 J/s of hydrogen, not just the 0.5 J/s per cell. What is going on is that the first fuel cell uses 0.5 J/s of hydrogen to raise the voltage of its cathode up to 0.5 V. When this cathode connected to the anode of the next cell it is raised to a higher voltage, and this cell uses 0.5 J/s of hydrogen to raise its output voltage, and so on. The amount of hydrogen per cell is determined by the current by $\dot{N}_{H_2} = i/nF$. The electric charge needed is $1\text{ A} \cdot 100\text{ hrs.} \cdot \frac{3600\text{ s}}{1\text{ hr}} = 360,000$ C. Converting to moles of hydrogen, $360,000\text{ C}/2\text{F} = 1.866\text{ mol H}_2$. Converting to grams, $1.866\text{ mol} \cdot \frac{2\text{ g}}{1\text{ mol}} = 3.73\text{ g H}_2$ per cell. So the fuel cell stack uses five times that, $\boxed{18.7\text{ g H}_2}$

(d) **(3 points)** From the ideal gas law, $V = nRT/P =$ $(1.866 \times 5\text{ mol})(0.08205\text{ L}\cdot\text{atm/mol}\cdot\text{K})(298\,\text{K})/(500\text{ atm}) = 0.457$ L. $\boxed{V = 457\text{ cm}^3.}$

For storage in a metal hydride, the 5 wt.% hydrogen gives a storage density of $10\text{ g/cm}^3 \cdot 0.05 = 0.5\text{ g/cm}^3$. To store 18.7 grams, you need a volume of $(18.7\text{ g})/(0.5\text{ g/cm}^3) = \boxed{37.3\text{ cm}^3}$. This is a significant improvement over storage at 500 atm!

(e) **(3 points)** From part c above, the electric charge needed = 360,000 C. Converting to moles of methanol, $\frac{360{,}000\text{ C}}{6\text{F}} = 0.6219\text{ mol CH}_3\text{OH}$. Converting to grams: $0.6219\text{ mol} \cdot \frac{32\text{ g}}{1\text{ mol}} = 19.9\text{ g CH}_3\text{OH}$ per cell. The stack requires $\boxed{99.5\text{ g CH}_3\text{OH}}$

Volume of liquid methanol: $99.5\text{ g CH}_3\text{OH} \cdot \frac{1\text{ cm}^3}{0.79\text{ g}} = \boxed{125.9\text{ cm}^3}$

Problem 3.13 (10 points) The exchange current density is given by

$$j_o = nF\frac{C_R^*}{C_R^{o*}}e^{-\frac{\Delta G^\ddagger}{RT}}$$

Grouping the preexponential terms into a constant that is temperature independent,

$$j_o(T) = Ce^{-\frac{\Delta G^\ddagger}{RT}}$$