ME 446.671 Fuel Cell Science and Technology

Final Exam Solution

2007 Jul 7 14:30~16:30

1. (15 pts) A hydrogen fuel cell vehicle uses a 100kW motor for good acceleration. The fuel cell vehicle uses a power conditioning unit that changes dc input from the fuel cell to ac power for the motor. The efficiency of the unit is 80%.

The I/V characteristic of a unit fuel cell is measured to be

$$V(\text{V}) = 1.0 - 500 \ \text{X} \ 10^{-6} \ I(\text{A})$$

The maximum internal heat dissipation capability of the unit cell is 300 W. Assuming product water exits in vapor form only, find the input voltage of the fuel cell to the power conditioning unit if the smallest possible number of unit cells are used. (you may use 241.8 kJ/mole as hydrogen/oxygen reaction enthalpy.)

Ans) $V_{enthalpy}$ = G/nF = 241800/(2*96500) = 1.25V

$V_{Loss} = V_{enthalpy} - V = 1.25 - (1.0 - 500 \ \text{X} \ 10^{-6} \ I) = 0.25 + 500 \ 10^{-6} \ I$

$P_{Heat} = V_{Loss} \ \text{X} \ I = (0.25 + 500 \ 10^{-6} \ I) \ I = P_{Heat,Max} = 300 \ W$

Thus I = 561A

$V_L = 1.0 - 500 \ \text{X} \ 10^{-6} \ I = 1.0 - 500 \ \text{X} \ 10^{-6} \ 561 = 0.72V$

P_{Max} (per cell) = V_L I = 0.72 X 561 = 403W

Since the stack needs to produce 100kW / 0.8 = 125 kW

No. of cell = 125kW / 403W = 309 cells

Voltage of fuel cell stack = 0,72 X 309 = 222 V

2. (10 pts) We fabricated a special PEMFC with normal the anode but with the special cathode composed of two *platinum particles*. The anode side has the normal structure, say, Pt/C catalyst and carbon cloth electrode of 2 cm² area. But, the cathode Pt particle is only 50 um X 50 um size each. A special experimental setup has been developed to measure the performance of the fuel cell with normal anode and the very small Pt particle cathode (see the 1st figure). Pure hydrogen is provided to the anode with parallel flow channel. At the cathode, a microprobe is in contact with one Pt particle that is exposed to the ambient air. Using this setup, we can measure the fuel cell

performance of each Pt particles on the cathode.

2nd figure shows the how two Pt particles looks like. Two particles have identical sizes of 50 um X 50 um. One particle has a pattern of single flat square shape. But, the other has internal patterns of 25 squares which gives 5 times more perimeter than the first particle. At OCV, we measure the EIS of the two particle fuel cells respectively. The result is also shown in the 2nd figure. Interestingly, even though two particles have same area, the impedance measurement exhibits quite different result. Explain the reason of impedance difference quantitatively.
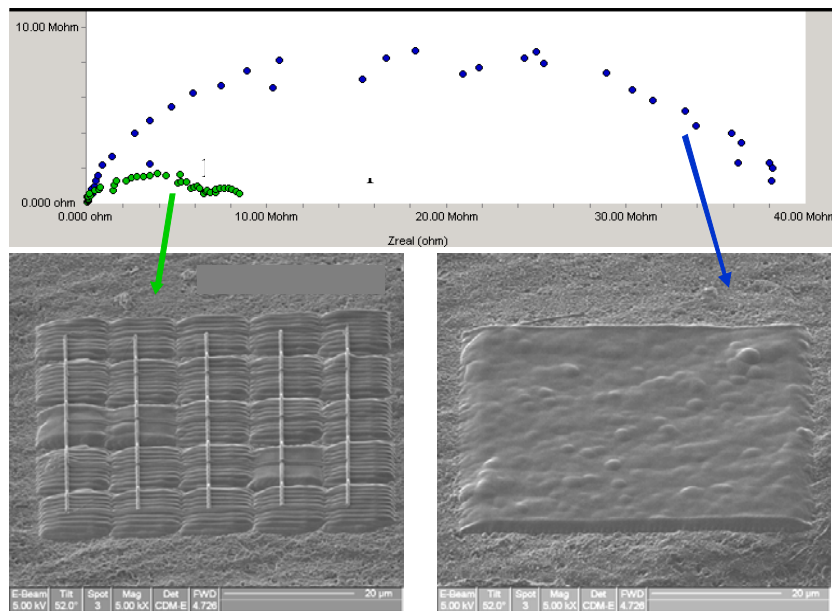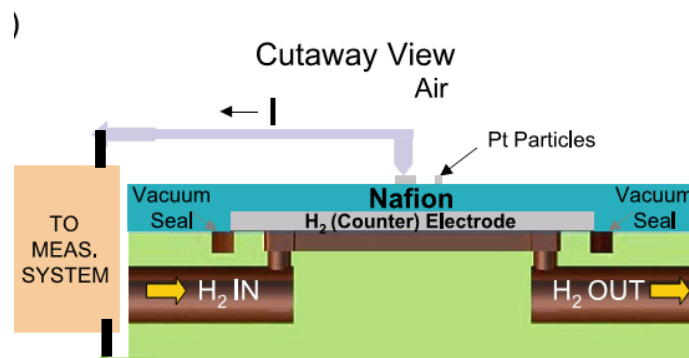
Ans) Among three major internal losses in fuel cells, only activation loss is prominent near OCV region. Ohmic loss and concentration loss is negligible as we learned in class at very low current density. From the impedance plot, the high frequency end goes to 0

ohm in real axis. This indicates that the cell has 0 ohmic resistance as we assumed. Since no concentration loss is observable, the size of half circle in the impedance should indicate the magnitude of activation resistance. More precisely, the cathodic resistance account for the impedance as the experiment setup has a large and normal anode vs small and poor cathode. This is clearer when you compare the impedance of two cathode catalyst particles whose TPB show 5 times difference. The impedance plot exhibits about 5 times difference due to the 5 times difference of TPB length. Thus, the impedance difference results from the TPB length difference of each particle.

3. (10 pts) We continue our experiments from previous problem. Now, we use circular Pt particles of different diameter (see the figure). We measure the Faradaic (or charge transport) resistance of each particles. From the measurement result, 1um diameter particle has 10 MOhm Faradaic resistance.
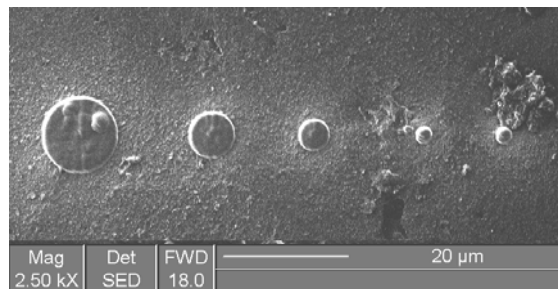

a) Assuming we have an ideal fuel cell, find the Faradaic resistance for 10 um diameter particle

Ans) Since TPB accounts for the Faradaic resistacne, 10 um diameter particle has 1 MOhm.

b) Establish the relationship between Faradaic resistance and particle size. In other word, sketch a curve in the plot with log of Faradaic resistances as y axis and log of the particle diameter as x axis. What is the slope of the curve?

Ans) Since the Faradaic resistance is inversely proportional to the perimeter or diameter of the catalyst particle, we obtain following log-log plot
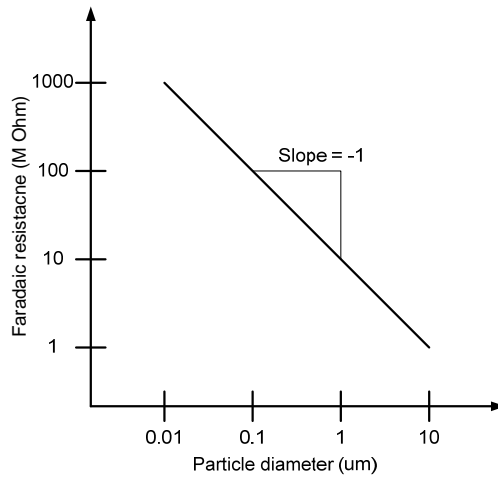
From the curve, we can easily figure out that the slope of the curve is ⁻1

4. (15 pts) It is well known that the oxygen ionic conductivity of YSZ is a strong function of Yittria mole fraction in Zirconia as shown in the figure.
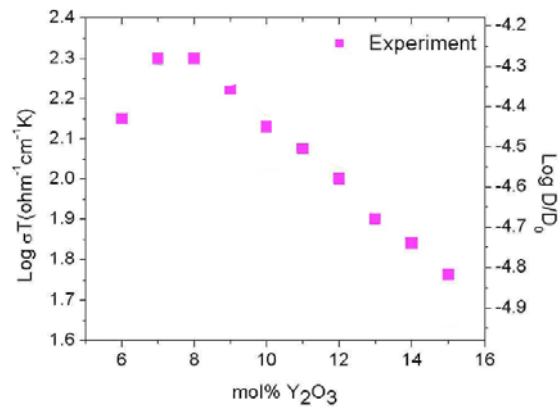
From the class, we learned that ionic conductivity can be expressed as

$$\sigma = \frac{c(z_i F)^2 D}{RT}$$

Explain qualitatively how the Yittria mole fraction affects the variables in the above equation to results in the change of YSZ conductivity as shown in the figure (say, why optimum mole fraction exists.)

Ans) When we increase the Yittria mole fraction, it increase the defect site for oxygen jumping. Thus, we are increasing "c" in the above equation. Thus, we can have higher conductivity as we observe from the graph when Yittria mole fraction is less than 8 %. However, doping of Yittria affect the activation energy of oxygen jumping that affects the diffusivity, D in the following equation.

$$D = D_0 e^{-\frac{\Delta G_{act}}{RT}}$$

Since, oxygen defects by Yittria doping have high activation energy, more doping will cause decrease of diffusivity or conductivity eventually. Thus, the changes of 'c" and "D" in opposite direction decide the optimum mole fraction of Yittria.

5. (15 pts) The following figure shows a typical IV curve from DMFC stack when low concentration methanol and high concentration methanol are provided respectively. Qualitatively explain the difference of polarization curve in terms of typical fuel cell internal losses.
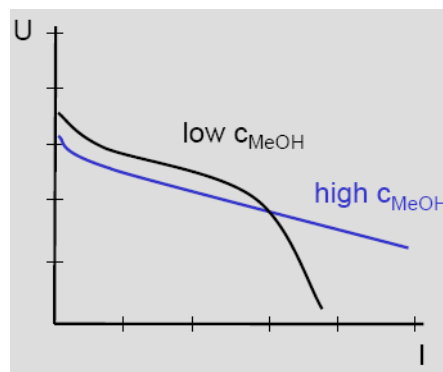

Ans) Low concentration methanol will increase the concentration loss at high current density, which clearly observed from the IV curve. High concentration methanol shows improved limiting current density. Due to methanol crossover in DMFC's, high concentration methanol easily migrates to cathode to burn with oxygen or attack cathode catalyst. This will cause the loss of ideal voltage or increase of cathodic overvoltage. Thus, in overall, high concentration methanol cell exhibits decreased voltage output.

6. (20 pts) A typical hydrogen-oxygen PEMFC anode and cathode are made of carbon cloth gas diffusion layer (GDL) electrode layer and Pt/C catalyst layer. Carbon cloth GDL provides diffusion path for gases and conductive path for electrons. In Pt/C catalyst layer, mixed porous structure of carbon-supported platinum powder and Nafion fibers provides electronic conduction, ionic conduction, and gas diffusion path for electrochemical reaction on platinum surfaces. In other words, triple phase boundary exists throughout ~10um thickness of the catalyst layer.
Research showed that when PEMFC operates at *medium current density*, oxygen reduction at the cathode uses all available triple phase boundary throughout the 10 um thickness of the catalyst layer. However, hydrogen oxidation at the anode uses only 1

um thick area close to the electrolyte. (see figure) In other words, hydrogen oxidation uses only 10% of available triple phase boundary in the catalyst layer. From this observation answer the following questions. (Note: this may be a fairly difficult question with no clear answer. Write down your logical thought and I'll give scores accordingly)

Reaction area for hydrogen

Reaction area for oxygen
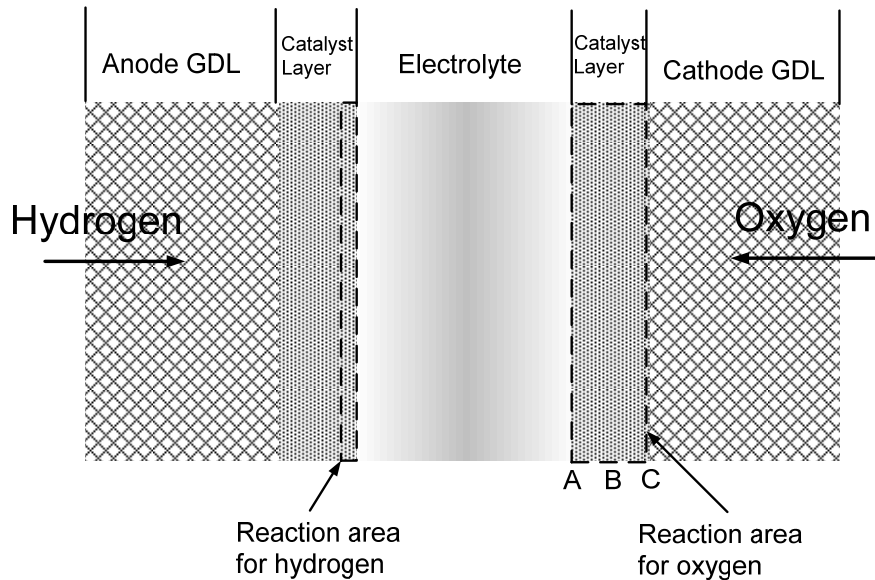
a) Qualitatively explain why hydrogen uses less reaction area.

Ans) Hydrogen oxidation is kinetically faster than oxygen reduction. Accordingly, hydrogen reaction requires smaller amount of catalyst or less reaction site.

b) Why hydrogen reaction zone is formed near electrolyte?

Ans) At the medium current density activation overvoltage and ohmic overvoltage is dominant. In other words, gas transport – source of mass transportation loss – is relatively easy. In this situation, the reaction zone will form near the electrolyte to reduce the ohmic resistance of proton transport in the catalyst layer,

c) At the cathode catalyst layer, which part is most active for oxygen reduction reaction through thickness among A, B and C? Justify your answer.

Ans) Similar to the answer of b), reduction of ohmic resistance is most important at the situation. Thus, the reaction will be most active near the electrolyte (A).

d) Repeat the question c) if the fuel cell operates at very high current density (close to limiting current density).

Ans) In this case, the mass transportation resistance will rise significantly. Thus, the

penetration of gas to the vicinity of electrolyte is not easy. Also, in PEMFC, flooding may occur near the electrolyte where reaction activity is high. Thus, the highly reactive zone may shift from A to B at high current density.

e) If the fuel cell operates at low current density, what change do you expect to observe about the thickness of active reaction area at the anode? Is it going to be thicker or thinner or same?

Ans) thinner since hydrogen reaction rate decreases (requires less TPB)

7. (15 pts) Let's assume a ideal thermodynamic device with following configuration.
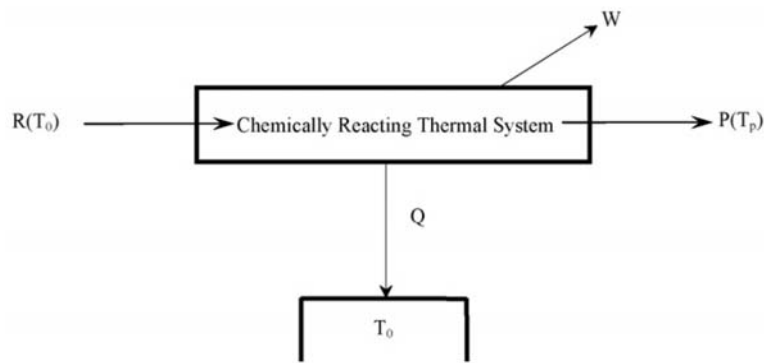
Reactants at ambient temperature T_0 enter the device and products exit at temperature T_p. Through the chemical reaction in the device, it generates some work, W. At the same time the device releases heat, Q to the environment at ambient temperature T_0. (Hints: use thermodynamics laws and following enthalpy and entropy charts of reactant and products)
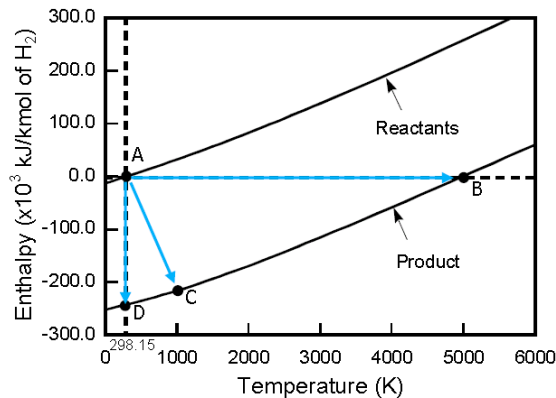
(a) Enthalpy
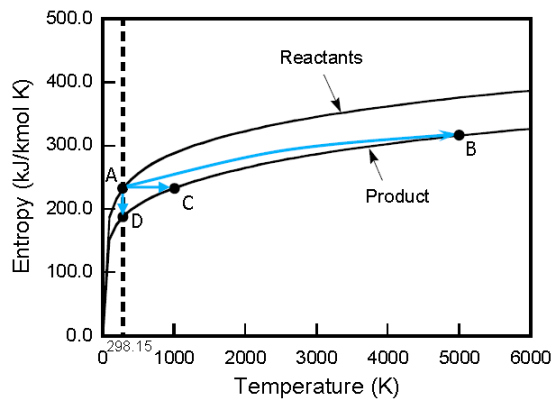
(b) Entropy

a) From the above figure, establish the equation describing the relation between enthalpy of the reactants, $H_R(T_0)$ and products, $H_P(T_P)$.

Ans) $H_R(T_0) = Q + W + H_P(T_P)$

b) From the above figure, establish the equation describing the relation between

entropy of the reactants, $S_R(T_0)$ and products $S_P(T_P)$.

Ans) $S_R(T_0) - Q/T_0 = S_P(T_P)$

c) Using equations from a) and b), show that W is equal to Gibb's energy if the devices is an ideal fuel cell. (Hint: ideal fuel cell operates in isothermal condition)

Ans) Ideal fuel cell operates at isothermal condition ($T_0 = T_P$). Thus we have,

$H_R(T_0) = Q + W + H_P(T_0)$ $\qquad$ – (1)

$S_R(T_0) + Q/T_0 = S_P(T_0)$ $\qquad$ – (2)

Eliminate Q in (1) using (2), we have

$H_R(T_0) = T_0 S_R(T_0) - T_0 S_P(T_0) + W + H_P(T_0)$

$W = H_R(T_0) - H_P(T_0) - T_0 (S_R(T_0) - S_P(T_0))$

$\quad = dH - TdS = dG$