

**Frequently asked questions Fuel Cell Technology**  
**by K Prof. S Basu , Chemical Department, IIT Delhi, New Delhi.**

**Fundamentals of Fuel Cell Technology**

**Module 2: Fuel Cell Thermodynamics**

---

1. Comment on spontaneity of reaction, when

- (i)  $\Delta h$  is -ve and  $\Delta s$  is -ve
- (ii)  $\Delta h$  is -ve and  $\Delta s$  is +ve
- (iii)  $\Delta h$  is +ve and  $\Delta s$  is -ve
- (iv)  $\Delta h$  is +ve and  $\Delta s$  is +ve

**4 points**

2. Predict the sign of  $\Delta s$  for the following reactions with reason

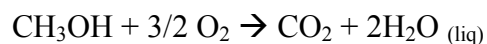
- a)  $A(g) + O_2 \longrightarrow X(l)$
- b)  $B(l) + O_2 \longrightarrow 2Y(l) + 4Z(g)$

Both reactions are exothermic and spontaneous.

**2 points**

3. A direct methanol fuel cell uses methanol as fuel. Calculate

- (i)  $\Delta h^\circ_{\text{rxn}}$ ,  $\Delta s^\circ_{\text{rxn}}$ ,  $\Delta g^\circ_{\text{rxn}}$
- (ii) Standard reversible voltage

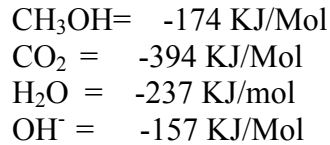


| Chemical Species                  | $\Delta h^\circ_f$ (kJ/mol) | $s^\circ$ (J/mol.K) |
|-----------------------------------|-----------------------------|---------------------|
| CH <sub>3</sub> OH                | -200.95                     | 239.83              |
| O <sub>2</sub>                    | 0                           | 205.14              |
| CO <sub>2</sub>                   | -393.51                     | 213.8               |
| H <sub>2</sub> O <sub>(liq)</sub> | -285.83                     | 69.95               |

**6 points**

4.

- (i) Write half-cell reaction for direct methanol fuel cell for both acid and alkali medium  
 (ii) Calculate half-cell potential and compare anode, cathode and total thermodynamic potential for both medium.  $\Delta G_f$  values



From thermodynamic point of view, tell which reaction is more favorable and why?

2+4 = 6 points

5. Calculate the change of reversible voltage at STP for  $\text{H}_2\text{-O}_2$  fuel cell if air is used instead of pure  $\text{O}_2$ .

$$E^0 = 1.229V, p_{\text{H}_2} = 3\text{atm}, p_{\text{air}} = 5\text{atm}$$

4 points

6. You are operating a SOFC at  $800^\circ\text{C}$  with  $\text{H}_2$  as the fuel. If the anode pressure is held constant at 1.5 atm and the  $\text{O}_2$  pressure in the cathode is held constant at 1.5 atm, find the open circuit voltage at 80% fuel utilization. The OCV at operating temperature and standard pressure (1 atm) could be determined by calculating  $\Delta G^\circ$ . For convenience,  $E^\circ$  is 0.98.

4 points

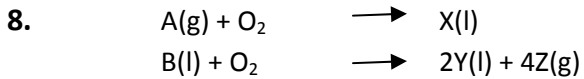
7. The operating temperature of a PEMFC typically ranges from  $30^\circ\text{C}$  to  $100^\circ\text{C}$ . Assuming an ideal gas:  
 Calculate the maximum voltage,  $E$ , of the fuel cell operating at standard pressure and  $30^\circ\text{C}$ .

| Species              | State  | $\Delta H_{f,298}^0 / \text{J mol}^{-1}$ | $\Delta G_{f,298}^0 / \text{J mol}^{-1}$ |
|----------------------|--------|--|--|
| $\text{H}_2$         | Gas    | 0  | 0  |
| $\text{O}_2$         | Gas    | 0  | 0  |
| $\text{H}_2\text{O}$ | Liquid | -285830                                  | -237129                                  |

For  $C_p/R$  values

| Species              | State  | A     | $10^3 \text{ B}$ | $10^6 \text{ C}$ | $10^{-5} \text{ D}$ |
|----------------------|--------|-------|------------------|------------------|---------------------|
| $\text{H}_2$         | Gas    | 3.249 | 0.422            | 0                | 0.083               |
| $\text{O}_2$         | Gas    | 3.639 | 0.506            | 0                | -0.227              |
| $\text{H}_2\text{O}$ | Liquid | 8.712 | 1.25             | -0.18            |                     |

10 points



Both reactions are exothermic and spontaneous.

(i) For any of two fuel cells using A and B as fuel, respectively; can the thermodynamic efficiency be greater than 100%?

(ii) Why practical efficiency of a fuel cell is less than 100%? Write an expression for real efficiency of a fuel cell

9. Contd. from Q4 of Tut 2. We found out the Gibbs free energy & maximum voltage for the given reaction. (The operating temperature of a PEMFC typically ranges from 30°C to 100°C. Assuming an ideal gas: Calculate the maximum voltage, E, of the fuel cell operating at standard pressure and 30°C.)

Now calculate the maximum efficiency limit of a PEMFC operating at standard pressure and 30°C.

10. A direct methanol PEMFC operated at a voltage of 0.5 V generates 600 mA current, if 1 M methanol is supplied at a flow rate of 100  $\mu$ Lm. Calculate real efficiency at STP.

$$\Delta h = -720 \text{ KJ/mol}$$

$$\Delta s = -194 \text{ J/mol K}$$

11. Consider a H<sub>2</sub>-Air 10 cell stack operating steadily in series with 10 cm<sup>2</sup> active surface area per electrode with a current density 100 mA/cm<sup>2</sup>. The nominal voltage is 0.6 V per plate.

(i) calculate molar flow of H<sub>2</sub> & air delivered to anode and cathode, respectively; if fuel utilization efficiency is 50% and cathodic stoichiometry is 2.3

(ii) what is the rate of water generation in g/h

(iii) Can the generation rate of water be greater or lesser than the value calculated?

(iv) What will be stack voltage

12. We know that  $E_T = E^0 + (\Delta S_{rxn}/nF) \cdot (T - T^0)$  Now find out the change in reversible voltage for 100° increase in cell temp for

a) H<sub>2</sub>-O<sub>2</sub> fuel cell with  $\Delta S_{rxn} = -44.43 \text{ J/(mol.K)}$  assuming it to be constant.

b) CH<sub>4</sub> + 3/2O<sub>2</sub> → CO + 2H<sub>2</sub>O with  $\Delta S_{rxn} = 81.59 \text{ J/(mol.K)}$  assuming it to be constant.

What do you infer from these examples?

2+2=4

- 13.** A  $\text{H}_2\text{-O}_2$  fuel cell stack might operate at a voltage of 0.7 V per cell with 90% fuel utilization efficiency.
- Calculate efficiency at STP  
Standard bond formation enthalpies  
H-H: -432 KJ/mol  
O-O: -494 KJ/mol  
H-O: -460 KJ/mol
  - The above stack is used for powering a vehicle which draws 10 KW of power at 60 km/h. Calculate the minimum volume required for the fuel cell system (fuel cell stack + fuel tank) so that a driver can go at least 300 km before refueling.  
Stack Power density: 1 KW/L, Fuel tank energy density (compressed  $\text{H}_2$ ): 9 MJ/L  
**4+6=10**

- 14.** A company is developing a new car powered by a fuel cell system that runs on  $\text{H}_2$ . You have been asked to consider generating the  $\text{H}_2$  by electrolysis with a fuel cell. The  $\text{H}_2$  tank to be used is 10 liters in volume and a fill-up requires a pressure of 34 atm.
- Calculate the current required to operate at a voltage of 1.8V.
  - Calculate the rate of hydrogen production per membrane area and the total membrane area required to fill the tank in 2 minutes.
- Consider the following specifications of the system. 60% conversion of  $\text{H}_2\text{O}$   $E_0 = 1.172$  V The cathode pressure is maintained at 1 atm. The anode pressure is maintained at 1 atm Membrane thickness = 100  $\mu\text{m}$  Membrane conductivity ( $\sigma$ ) = 0.1 S/cm ( $S = 1/\Omega$ ) Electrolysis T = 373 K (assume water is in the gas phase) .  $\text{H}_2$  storage tank T = 298 K  
**4+4=8**

## Solutions-2

1.

$$\Delta g = \Delta h - T\Delta s$$

The reaction will be spontaneous, if  $\Delta g$  is -ve.

- (i) If  $T|\Delta s| < \Delta h$ , then  $\Delta g$  is -ve and the reaction is spontaneous. It is only possible at low temperature. So, spontaneity of reaction depends mainly on temperature of reaction.
- (ii) The reaction is spontaneous always.
- (iii) The reaction is never spontaneous.
- (iv) If  $T|\Delta s| > \Delta h$ , then  $\Delta g$  is -ve and the reaction is spontaneous. It is only possible at high temperature. So, spontaneity of reaction depends mainly on temperature of reaction.

2.

For reaction (a), there is decrease in volume, as 2 mole gas ( $O_2$  is always in gas phase) is producing 1 mole liquid. Decrease of volume indicates increase of regularity or decrease of randomness of a system, so  $\Delta s$  is -ve.

On the other hand, for reaction (b), there is increase in volume, as 1 mole gas ( $O_2$  is always in gas phase) is producing 4 mole gases. Increase of volume indicates decrease of regularity or increase of randomness of a system, so  $\Delta s$  is +ve.

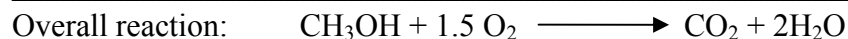
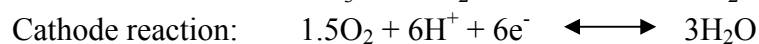
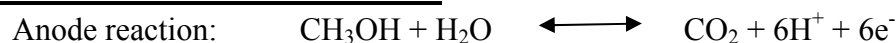
3.

$$\begin{aligned} \text{(i)} \quad \Delta h^\circ_{\text{rxn}} &= -393.51 - 285.83 \times 2 - 3/2 \times 0 + 200.95 = -764.22 \text{ kJ/mol} \\ \Delta s^\circ_{\text{rxn}} &= 213.8 + 69.95 \times 2 - 3/2 \times 205.14 - 239.83 = -193.84 \text{ J/mol.K} \\ \Delta g^\circ_{\text{rxn}} &= \Delta h^\circ_{\text{rxn}} - T \Delta s^\circ_{\text{rxn}} \\ &= -764.22 + (193.84/1000) \times 298 \\ &= -706.45 \text{ kJ/mol} \end{aligned}$$

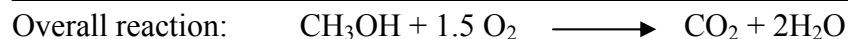
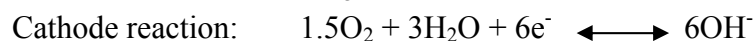
$$\begin{aligned} \text{(ii)} \quad \Delta g^\circ_{\text{rxn}} &= nFE \\ E &= -706.45 \times 1000 / (6 \times 96500) \\ &= 1.22 \text{ V (ans)} \end{aligned}$$

4.

(i) **Half cell reactions in acid medium:**



**Half cell reactions in alkali medium:**



(Note that change in rxn mechanism with different electrolytes)

(ii) **Half cell potential in acid medium**

$$\begin{aligned} \text{Anode Potential: } & -\Delta G_{\text{reaction}}/nF \\ & = - [(-394) - (-237) - (-174)] \times 10^3 / (6 \times 96485) = -0.03 \text{ V} \end{aligned}$$

$$\begin{aligned} \text{Cathode potential: } & -\Delta G_{\text{reaction}}/nF \\ & = - [3(-237)] \times 10^3 / (6 \times 96485) = 1.23 \text{ V} \\ \text{Thermodynamic potential} & = (1.23 - 0.03) \text{ V} = 1.2 \text{ V} \end{aligned}$$

**Half cell potential in alkali medium**

$$\begin{aligned} \text{Anode potential: } & -\Delta G_{\text{reaction}}/nF \\ & = - [(-394) + 5(-237) - (-174) - 6(-157)] \times 10^3 / (6 \times 96485) = 0.8 \text{ V} \end{aligned}$$

$$\begin{aligned} \text{Cathode potential: } & -\Delta G_{\text{reaction}}/nF \\ & = - [6(-157) - 3(-237)] \times 10^3 / (6 \times 96485) = 0.4 \end{aligned}$$

$$\text{Thermodynamic potential} = (0.8 + 0.4) \text{ V} = 1.2 \text{ V}$$

From thermodynamic point of view, anode reaction in alkali medium is more favorable than that of acid medium as  $\Delta G_{\text{reaction}}$  is +ve in case of acid medium ( $\Delta G_{\text{reaction}} = 17.4 \text{ KJ/mol}$ ). So the half cell anode reaction in anode medium is not spontaneous, but it is -ve (-711 KJ/mol) in alkali medium.

5.

For,  $\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$

The Nernst equation is,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{H}_2\text{O}}}{a_{\text{H}_2} a_{\text{O}_2}^{0.5}}$$

Activity of the following species can be replaced by their partial pressure &  $a_{\text{H}_2\text{O}} = 1$

$$E = E^0 - \frac{RT}{nF} \ln \frac{1}{p_{\text{H}_2} p_{\text{O}_2}^{0.5}}$$

The amount of reduction in reversible voltage will be

$$E = 1.229 - \frac{(8.314)(298.15)}{(2)(96400)} \ln \frac{1}{(3)(5 * 0.21)^{0.5}}$$

$E = 1.224 \text{ V}$  ans.

6.

- 1<sup>st</sup> to calculate partial pressures of gases at the anode ( $\text{H}_2$  &  $\text{H}_2\text{O}$ ) we need to consider fuel utilization as well as total pressure.

For 80% fuel utilization

$$P_{\text{H}_2} = 1.5(1-0.8) = 0.3 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 1.5(0.8) = 1.2 \text{ atm}$$

- Now, we need to calculate partial pressure of gases at cathode ( $\text{O}_2$ )  
As  $\text{O}_2$  is consumed and no product gas is generated at cathode, the pressure can be assumed constant  $\rightarrow P_{\text{O}_2} = 1.5 \text{ atm}$
- Using Nernst eqn

$$E = E^0 - \frac{RT}{nF} \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{0.5}}$$

$$= 0.98 - (8.314 * 1073/2 * 96485) \ln(1.2/0.3 * 1.5^{1/2})$$

$$= 0.925 \text{ V}$$

7.

$$\Delta G_{f,298}^0 = \Delta H_{f,298}^0 - T^* \Delta S_{f,298}^0$$

$$\begin{aligned} \Rightarrow \Delta S_{fH_2,298}^0 &= 0 \\ \Rightarrow \Delta S_{fO_2,298}^0 &= 0 \\ \Rightarrow \Delta S_{fH_2O,298}^0 &= -163.43 \text{ J/mol.K} \end{aligned}$$

The enthalpy of formation should be calculated at 30 C.

$$\begin{aligned} \Delta H_{fH_2O,303}^0 &= \Delta H_{fH_2O,298}^0 + R \int_{298}^{303} C_p dT \\ &= \Delta H_{fH_2O,298}^0 + R \int_{298}^{303} (A + BT + CT^2 + DT^{-2}) dT \\ &= \Delta H_{fH_2O,298}^0 + R \left[ AT + \frac{B}{2} T^2 + \frac{C}{3} T^3 - \frac{D}{T} \right]_{298}^{303} \\ &= -285453 \text{ J/mol} \end{aligned}$$

Similarly

$$\Delta H_{fH_2,303}^0 = 144 \text{ J/mol}$$

$$\Delta H_{fO_2,303}^0 = 147 \text{ J/mol}$$

Similarly entropy needs to be calculated at 30 C.

$$\begin{aligned} \Delta S_{fH_2O,303}^0 &= \Delta S_{fH_2O,298}^0 + R \int_{298}^{303} \frac{C_p}{T} dT \\ &= \Delta S_{fH_2O,298}^0 + R \int_{298}^{303} \left( \frac{A}{T} + B + CT + DT^{-3} \right) dT \\ &= \Delta S_{fH_2O,298}^0 + R \left[ A(\ln(T)) + BT + \frac{C}{2} T^2 - \frac{D}{2} T^{-2} \right]_{298}^{303} \\ &= -162.18 \text{ J/mol.K} \end{aligned}$$

Similarly

$$\Delta S_{fH_2,303}^0 = 0.48 \text{ J/mol.K}$$

$$\Delta S_{fO_2,303}^0 = 0.49 \text{ J/mol.K}$$



Now,

$$\begin{aligned}\Delta H_{\text{rxn},303}^0 &= \Delta H_{\text{f H}_2\text{O},303}^0 - \Delta H_{\text{f H}_2,303}^0 - \frac{1}{2} \Delta H_{\text{f O}_2,303}^0 \\ &= -285671 \text{ J/mol}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn},303}^0 &= \Delta S_{\text{f H}_2\text{O},303}^0 - \Delta S_{\text{f H}_2,303}^0 - \frac{1}{2} \Delta S_{\text{f O}_2,303}^0 \\ &= -162.91 \text{ J/mol.K}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{rxn},303}^0 &= \Delta H_{\text{rxn},303}^0 - T^* \Delta S_{\text{rxn},303}^0 \\ &= -236309 \text{ J/mol}\end{aligned}$$

$$\begin{aligned}\text{Maximum voltage, } E &= -\Delta G_{\text{rxn},303}^0 / nF \\ &= 1.22 \text{ V}\end{aligned}$$

8.

- (i) As both the reaction is exothermic and spontaneous, both  $\Delta h$  and  $\Delta g$  are  $-ve$ . Thermodynamic efficiency =  $100\% \times \Delta g / \Delta h$ . If  $\Delta g$  is more  $-ve$  than  $\Delta h$ , then thermodynamic efficiency will be greater than  $100\%$ . It is possible when  $\Delta s$  is  $+ve$ , as  $\Delta g = \Delta h - T\Delta s$

So, thermodynamic efficiency will be greater than  $100\%$  for fuel cell using B as fuel. Thermodynamic efficiency cannot be greater than  $100\%$  for fuel cell using A as fuel.

- (ii) Because  $\epsilon_{\text{real}} = \epsilon_{\text{thermo}} * \epsilon_{\text{voltage}} * \epsilon_{\text{fuel}}$   
 $= (\Delta g / \Delta h) * (V/E) * ((i/nF)/v_{\text{fuel}})$

So, thermodynamic efficiency may be  $\geq 100\%$  but other efficiencies will pull it down below  $100$ . An example is covered in Q4

9.

$$\begin{aligned}\text{Max efficiency, } \eta_{\text{max}} &= (\Delta G_{\text{rxn}, 303\text{K}} / \Delta H_{\text{rxn}, 303\text{K}}) * 100 \\ &= (-236309 / -285830) * 100 \\ &= 82.7\%\end{aligned}$$

10.

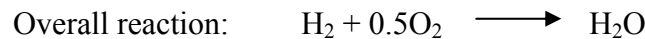
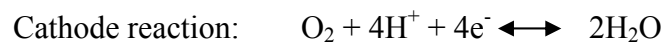
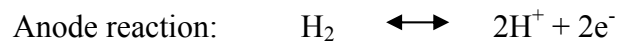
$$100 \mu\text{lm} = 0.1 \text{ cc} / 60 \text{ s} = 1.67 \times 10^{-3} \text{ cc/s}$$

1 M methanol means 1 mol methanol in 1000 cc.

$$1.67 \times 10^{-3} \text{ cc/s fuel means } 1.67 \times 10^{-6} \text{ mol/s}$$

$$\begin{aligned} \text{Real efficiency } \epsilon_{\text{real}} &= 100\% \times (\epsilon_{\text{thermo}}) \times (\epsilon_{\text{voltage}}) \times (\epsilon_{\text{fuel}}) \\ &= 100\% \times (\Delta g / \Delta h) \times (V/E) \times (I / (v_{\text{fuel}} \times nF)) \\ &= 100\% \times (\Delta g / -720 \times 10^3) \times (0.5nF / (-\Delta g)) \times (0.6 / (1.67 \times 10^{-6} \times nF)) \\ &= 25\% \text{ (real efficiency)} \end{aligned}$$

11.



It can be noticed that, number of electrons exchanged are 2 and 4 respectively for 1 mol of hydrogen and oxygen.

(i) Molal flow rate of  $\text{H}_2$  required =  $(iA/nF) / \text{fuel efficiency} = 0.1 \times 10 / (0.5 \times 2 \times 96485) = 1.036 \times 10^{-5} \text{ mol/s}$

Molal flow rate of air required =  $(iA/nF) \times \text{cathodic stoichiometry} / \text{mole fraction of O}_2 \text{ in Air mixture} = 0.1 \times 10 \times 2.3 / (0.21 \times 4 \times 96485) = 2.838 \times 10^{-5} \text{ mol/s}$

(ii) Mol of water generated =  $(iA/nF) \times 18 \times 3600 \text{ g/h} = (0.1 \times 10 / 2 \times 96485) \times 18 \times 3600 = 0.336 \text{ g/h}$

(iii) The value of water produced cannot be greater for a given current, since this would violate conservation of mass. However, it can be lesser than the predicted value if some parallel or side electro-chemical reaction is taking place that consumes some of the charge passed.

(iv) As the cells in the stack are in series, Stack voltage =  $0.6 \times 10 = 6 \text{ V}$

12.

a)  $E_T = E^0 + (\Delta S_{\text{rxn}} / nF) * (T - T^0) = E^0 + (-44.43 / 2 * 96400) * (100) = E^0 - 0.023 \text{ V}$

b)  $E_T = E^0 + (\Delta S_{\text{rxn}} / nF) * (T - T^0) = E^0 + (81.59 / 6 * 96400) * (100) = E^0 + 0.014 \text{ V}$

Reactions with +ve  $\Delta S_{\text{rxn}}$  will experience increase in reversible voltage whereas the opposite will happen with reactions which have -ve  $\Delta S_{\text{rxn}}$ .

### 13.

a)  $\Delta h_{rxn} = [2 \times (-460 \text{ KJ/mol}) - (-432 \text{ KJ/mol}) - 0.5 \times (-494 \text{ KJ/mol})] = -241 \text{ KJ/mol}$  At STP, Real efficiency  $\epsilon_{real} = 100\% \times (\epsilon_{thermo}) \times (\epsilon_{voltage}) \times (\epsilon_{fuel})$   
 $= 100\% \times (\Delta g / \Delta h) \times (V/E) \times (\text{fuel efficiency})$   
 $= 100\% \times (\Delta g / -241 \times 10^3) \times (0.7 \text{ nF} / -\Delta g) \times (0.9) = 100\% \times (0.7 \times 2 \times 96485 \times 0.9 / 1 / 241 \times 10^3)$   
 $= 50\%$

b) Stack gives electrical power. So 10 KW/ 1KW/L = 10 L stack is required.  
For 300 km drive without recharging means, 300/60 h = 5 h uninterrupted drives.  
The energy drawn by vehicle in 5 h =  $10 \times 10^3 \times 5 \times 3600 = 180 \times 10^6 \text{ J} = 180 \text{ MJ}$   
As Fuel tank supply is hydrogen energy, 50% of the energy stored in hydrogen will be converted to electrical energy as the fuel cell efficiency is 50%.  
Considering fuel tank energy density (compressed H<sub>2</sub>): 9 MJ/L,  
Tank volume required for storing hydrogen is  $180 / (9 \times 0.5) = 40 \text{ L}$  fuel tank is required.  
So, total volume of fuel cell system (fuel cell stack + fuel tank) = (10 + 40) L = 50 L

### 14.

60% conversion

$$P_{H_2O} = 1 \text{ atm} (1 - 0.6) = 0.4 \text{ atm}, P_{O_2} = 1 \text{ atm} \times \text{conversion} \times \frac{1}{2} = 1 \times 0.6 \times 0.5 = 0.3 \text{ atm}$$

But, there is a constant anode pressure of 1 atm, therefore

$$\text{Normalized } P_{H_2O} = 0.4 / (0.4 + 0.3) = 0.57 \text{ atm}$$

$$\text{Normalized } P_{O_2} = 0.3 / (0.4 + 0.3) = 0.43 \text{ atm}$$

$$\Rightarrow E_{ocv} = 1.172 - (8.314 \times 373 / (2 \times 96500)) \times \ln (0.57 / (1 \times 0.43^{0.5})) = 1.174 \text{ V}$$

$$\Rightarrow RA = l / \sigma = 0.01 \text{ cm} / (0.1 \text{ S/cm}) = 0.1 \Omega \cdot \text{cm}^2$$

$$E_{op} = E_{ocv} - i \cdot RA$$

$$1.8 = 1.174 - i \cdot 0.1 \rightarrow i = -6.26 \text{ A} \cdot \text{cm}^{-2}$$