

CHAPTER 2

FUNDAMENTALS

2.1 Structure of DMFC

As mentioned in Chapter 1, a fuel cell is simply like a sandwich structure. Each component is described as follows.

2.1.1 Bipolar Plate

In a fuel cell stack, individual fuel cells are assembled in series. The bipolar plate is the electronically conductive plate positioned next to the anode end of one cell and the cathode end of another cell. In general, each surface of the bipolar plate contains grooved channels with inlet and outlet as flow path of the fuel and oxidant, respectively. The flow field design is described in Chapter 1.

2.1.2 Gas Diffusion Layer (GDL)

The gas diffusion layer (GDL) is usually made of carbon paper or cloth with a porous structure treated with hydrophobic agent. It has to meet several requirements such as electronic conductivity, heat conductivity, fluid permeability, wettability, and mechanical stability. Recently, Liu et al. [25] adopted sintered stainless steel felt as GDL. Their results showed that this kind of GDL yielded a higher power density than a carbon paper for a DMFC. The advantage mainly came from the anode because its high electronic conductivity and hydrophilicity. But their DMFC system seriously degraded once water flooding occurred at the cathode.

2.1.3 Proton Exchange Membrane (PEM)

The “core” of a fuel cell comprises a solid perfluorsulphonic acid polymer, usually Nafion from *DuPont*®. It functions as a path for protons. The protons are transferred by migration and convection with water. The membrane, therefore, not only need to be maintained hydrous but free from flooding.

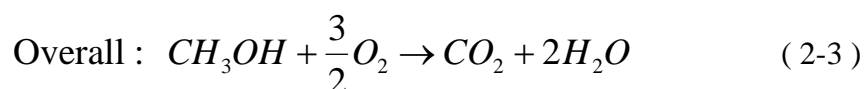
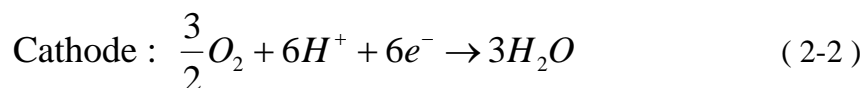
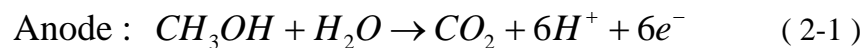
2.1.4 Active Layer

The active layer contains catalysts with porous structure and is positioned between PEM and GDL. For a DMFC, this layer is usually a carbon-supported Platinum-Ruthenium (Pt-Ru) compound metal in the anode and carbon-supported Pt in the cathode. The function of Ru metal is to prevent anode from being poisoned by carbon monoxide (CO), and that of Pt is to activate the electrochemical reactions.

2.2 Principle of DMFC

2.2.1 Working Principle

A fuel cell is not limited by the Carnot efficiency because it is a device that directly converts chemical energy into electric energy. The basic reactions for a DMFC are:



The change of Gibbs free energy can be shown as

$$\Delta G = \sum G_{\text{reactant}} - \sum G_{\text{product}} \quad (2-4)$$

Considering Gibbs Energy at the standard state ($T = 298.15\text{K}$, $P = 1\text{atm}$), we can calculate the reversible potential for a DMFC:

$$\begin{aligned} \Delta G^0 &= -167.91 \text{Kcal/mol} = -703005.588 \text{J/mol} \\ \therefore \Delta G^0 &= -n \times F \times E_{25^\circ\text{C}}^0 \\ \text{Thus} & \\ E_{25^\circ\text{C}}^0 &= \frac{-\Delta G^0}{n \times F} = \frac{703005.588}{6 \times 96487} = 1.21 \text{V} \end{aligned} \quad (2-5)$$

where ΔG^0 is the change of the Gibbs free energy,

$E_{25^\circ\text{C}}^0$ is the cell's reversible potential,

n is the number of electrons released from the oxidation per mole of fuel, and

F is the Farady's constant ($F = 96487 \text{ C/mol}$).

In addition, the net energy released from a fuel cell can be defined as the enthalpy difference between the reactants and the products. Thus

$$\Delta H = \sum H_{\text{reactant}} - \sum H_{\text{product}} \quad (2-6)$$

The intrinsic efficiency (η) is given by the maximum effective work of the enthalpy difference per unit mole of fuel under constant temperature and pressure. Hence,

$$\begin{aligned} \Delta G &= -167.91 \text{Kcal/mol}, \\ \Delta H &= -173.67 \text{Kcal/mol}, \\ \eta &= \frac{\Delta G}{\Delta H} = 96.7\%. \end{aligned} \quad (2-7)$$

From the relation of thermodynamics, we know that

$$\Delta H = \Delta G - T\Delta S = -nFE - Q \quad (2-8)$$

where T is temperature, and ΔS is the change of entropy

The theoretical conversion efficiency of a DMFC is 96.7%, and at least 3.3% of energy converts into heat.

2.2.2 Polarization Curve

The performance of a fuel cell is usually shown on a diagram of polarization curve, which is the cell voltage versus the cell current density. From Eq. (2-5), we can get the theoretical reversible potential. But the actual output voltage is much lower than the theoretical value. These losses in voltage can be attributed to many factors and generally result from three major irreversibilities, as illustrated in Fig. 2-1 [\[26\]](#).

Region I : Activation Overpotential

From the plot, it can be seen that the polarization curve approaches the open circuit potential, which is lower than the reversible cell potential, as the current approaches zero. This rapid drop is caused from the crossover of methanol.

Additionally, the chemical reaction mechanism usually involves many sequential steps, some of which may need higher activation energies. It means that a proportion of the voltage generated is lost in driving the chemical reactions. This is so called activation overpotential. For a fuel cell, it is associated with the catalysts in contact with the electrodes accessible by reacting gases or fuels.

Region II : Ohmic Overpotential

The voltage drop for this region appears nearly straight and is

essentially proportional to the current density. This results from the electronic and ionic resistances in the materials or the contact resistance between materials.

Region III : Concentration Overpotential

For a fuel cell, with the increasing of current density the reactant gases or fuels may be depleted at the reactant interface as their transport to the reaction sites fails to keep up with the reaction rate. This leads to concentration differences adjacent to the anode and the cathode. The transfer process will eventually become mass-transfer limited.

2.2.3 Evaluation of Water Production

Theoretically, the water production at the cathode side of a DMFC comes from three major mechanisms: (i) electrochemically produced water, (ii) electro osmotic drag, as a result of proton drifting through the membrane, and (iii) cross-over of the methanol solution. In this study we mainly concern about the flooding issue at the cathode side of a DMFC. The following evaluation will provide an approximate estimation of the water production at the cathode side.

Assume that a DMFC operates at $i \text{ mA/cm}^2$.

I. Electrochemically produced water:

$$i \text{ mA/cm}^2 = 0.001i \text{ (C / sec cm}^2\text{)} = (6.242 \times 10^{15})i \text{ (e / sec cm}^2\text{)}$$

From Eq. (2-2), we can see that three water molecules are produced with six electrons passing through the external circuit of the cell, i.e. $e^- : H_2O = 2 : 1$. Hence, the product rate of H_2O is

$$P_{H_2O,E} = (3.121 \times 10^{15})i \text{ (e / sec cm}^2\text{)} = (3.4 \times 10^{-4})i \text{ (g / hr cm}^2\text{)}$$

II. Electro osmotic drag:

According to Ren and Gottesfeld [27], each proton migrating from the anode to the cathode can drag 2 to 3 water molecules. Make a higher estimation, then

$$P_{H_2O,P} = (3.4 \times 10^{-4})i \text{ (g / hr cm}^2\text{)} \times 3 = 2.04 \times 10^{-3}i \text{ (g / hr cm}^2\text{)}$$

III. Cross-over of methanol solution:

For a DMFC, some methanol may diffuse from the anode through the electrode to the cathode, and it will react directly with the oxygen, producing no current. This is known as “fuel cross-over”. Therefore, assuming 30% cross-over in Nafion, we have

$$\begin{aligned} P_{H_2O,C} &= (1.13 \times 10^{-4})i \text{ (g / hr cm}^2\text{)} \times 30\% \times 2 \\ &= 6.8 \times 10^{-5}i \text{ (g / hr cm}^2\text{)} \end{aligned}$$

Following experiments will follow these calculated values.

2.3 Driving Force in Cathode-Side Micro-channels

2.3.1 Capillary Driving Force

According to Bond number, the ratio of the gravitational force to the surface tension, defined as

$$Bo = \frac{\Delta\rho g d^2}{\sigma}$$

where $\Delta\rho$ the density between gas and liquid, σ the surface tension

g the gravitational acceleration, d the droplet diameter

The gravitational force is less by one order than surface tension for water droplet with diameter less than 1 mm at room temperature. Hence, the surface tension becomes more significant than gravitational force

while size becomes smaller and following section will discuss the capillarity that caused from surface tension.

For a rectangular channel, as shown in Fig. 2-2, the capillary force can be calculated as follows.

First, the total energy of the capillary channel is expressed as

$$E_s = xw\gamma_{s_1l} + xh\gamma_{s_2l} + xh\gamma_{s_3l} + xw\gamma_{s_4l} + (L-x)w\gamma_{s_1a} + (L-x)h\gamma_{s_2a} + (L-x)h\gamma_{s_3a} + (L-x)w\gamma_{s_4a} \quad (2-9)$$

where γ is the surface energy per unit area.

Considering a droplet on a solid surface as shown in Fig. 2-3, the relation between the surface energy and the contact angle can be described by the Young's equation.

$$\gamma_{sa} = \gamma_{sl} + \gamma_{la} \cos \theta \quad (2-10)$$

where θ is the contact angle between the solid and the liquid.

Eq. (2-9) can therefore be written in terms of contact angle.

$$E_s = -(xw\gamma_{la} \cos \theta_1 + xh\gamma_{la} \cos \theta_2 + xh\gamma_{la} \cos \theta_3 + xw\gamma_{la} \cos \theta_4) + Lw\gamma_{s_1a} + Lh\gamma_{s_2a} + Lh\gamma_{s_3a} + Lw\gamma_{s_4a} \quad (2-11)$$

Taking derivative of Eq. (2-11) with respect to x , we can obtain the equivalent force F applied on the capillary fluid column along the x direction.

$$F_{capi} = \Delta P_{la} \cdot w \cdot h = -\frac{dE_s}{dx} = w\gamma_{la} \cos \theta_1 + h\gamma_{la} \cos \theta_2 + h\gamma_{la} \cos \theta_3 + w\gamma_{la} \cos \theta_4 \quad (2-12)$$

Finally, the pressure drop across the liquid-air interface can be written as

$$\Delta P_{la} = \frac{\gamma_{la}}{h} (\cos \theta_1 + \cos \theta_4) + \frac{\gamma_{la}}{w} (\cos \theta_2 + \cos \theta_3) \quad (2-13)$$

From the above equation, we know that the capillary force is a function of contact angle and channel dimension. When the value of Eq. (2-13) is positive, the channel is hydrophilic and has an attractive force on the liquid. And the capillary attraction increases with decreasing channel dimensions. On the contrary, a negative value means that the channel is hydrophobic and exerts rejecting force on the liquid.

2.3.2 Convective Driving Force

Depending on the output current ($I(mA)$) and the oxidant stoichiometry (λ) for a DMFC, the air flow rate in the cathode side can be evaluated from the equation used by Larminie and Dicks [28],

$$\text{Charge} = 4F \times \text{amount of } O_2$$

$$O_2 \text{ usage} = I\lambda / 4000F \text{ (moles sec}^{-1}\text{)}$$

Similarly, for anode side

$$MeOH \text{ usage} = I\lambda / 6000F \text{ (moles sec}^{-1}\text{)}$$

Take some transformations to “Air usage” and “ $L \text{ sec}^{-1}$ ”:

$$\begin{aligned} \text{Air usage} &= I\lambda M_{air} / 840F_{air} \text{ (m}^3 \text{ sec}^{-1}\text{)} \\ &= 3.056 \times 10^{-7} \times I\lambda \text{ (L sec}^{-1}\text{)} \end{aligned}$$

From the above discussion, the net driving force in the cathode-side micro-channels can be roughly evaluated with the capillary force and the convective driving forces as:

$$F_{net} = F_{cap} + F_{conv}$$

The main objective of this study is to investigate the water transport phenomena under various flow rates and the effects of the capillary force and the convective driving forces on the water removal process.

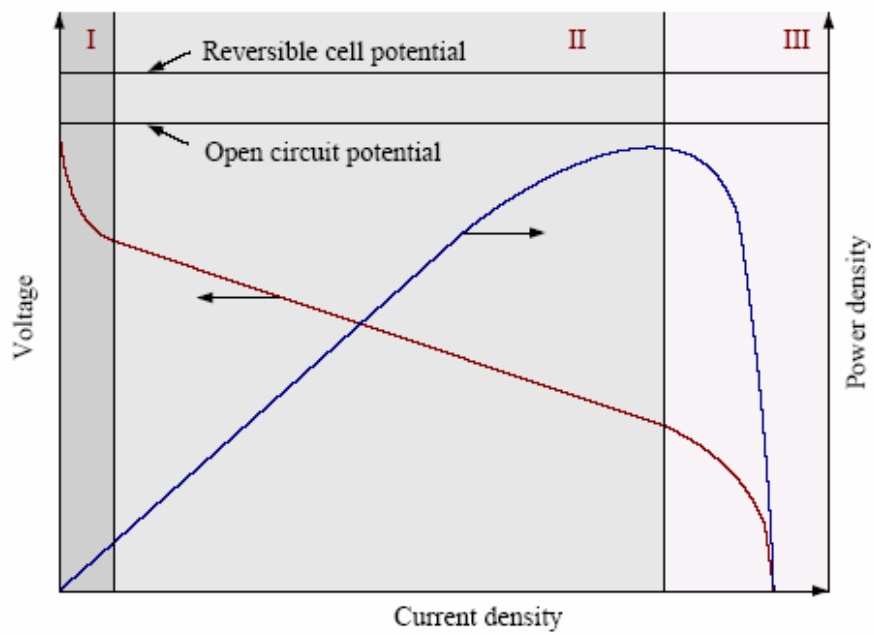


Fig. 2-1 A Schematic of a polarization and power density curves [26]

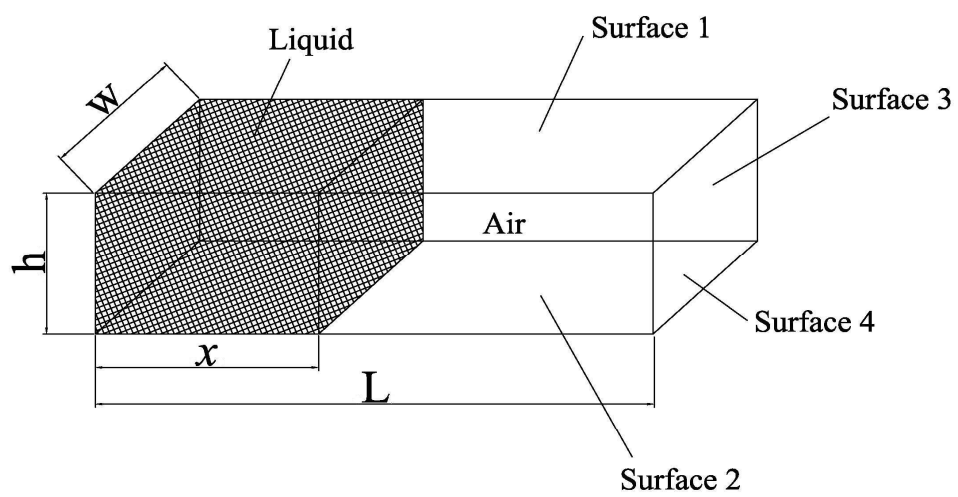


Fig. 2-2 Schematic of a small rectangular channel

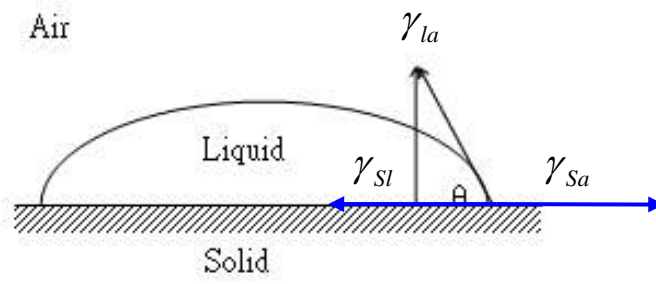


Fig. 2-3 Schematic of the contact angle between solid / liquid / air

