CHAPTER 2

PROTON EXCHANGE MEMBRANCE FUEL CELL

Global and local environmental degradation and health danger associated with the emissions of fossil fuel combustion call for alternative fuels and energy sources for sustainable development. Proton exchange membrane fuel cells (PEMFC) is an alternative energy source, have been regards as environmentally friendly power source for transportation, stationary co-generation and portable applications, and compatible with alternative fuels and renewable energy sources.

Fuel cell, which transforms the chemical energy into electricity with high efficiency, high power density, is considered to be a promising power source, especially for transportation application. Fuel cell also proves itself applicable in many others fields, however its performance and efficiency still needed to be improved in order to enhance its performance and reliability. The necessity to learn about the mechanism that causes the performance loss, such as, non-uniform concentration, current density distributions, high ionic resistance due to dry membrane, or high diffusive resistance due to the flooding on the cathode is very important. Accordingly flow field and water/thermal management of fuel cell optimal design are mainly focused.

The flow field and polar plate have been ones of the most important components in PEMFC in which they must perform a number of functions well simultaneously in order to achieve good performance and lifetime. Polar plate supplies the reactant gases through the flow channels to the electrodes and serves the purpose of electronically connecting in cell. These plates also provide structural support for the thin and mechanically weak called membrane electrode assembly (MEAs) and means to facilitate water management within the cell. In the absence of dedicated cooling plates, polar plates also facilitate heat management. Plate topologies and materials facilitate these functions. Topologies can include straight, serpentine or interdigitated flow fields, internal manifold, internal humidification and integrate cooling. Therefore, optimal design must be sought for the plate because the above functions have conflicting requirements on the plate design (i.e. gas diffusion, pressure drop, water management). The flow field design on the polar plate can be conducted both numerical modeling and dedicated experimental technique to ensure by the optimal design of fuel cell system.

The advantage of computational tools in supporting the design process has led to the development of fuel cell models because it has decreased costs and times. In many cases, modeling efforts focus on a specific part or parts of the fuel cell, like the cathode catalyst layer, the cathode electrode, or the membrane electrode assembly. These models are very useful in that they may include a large portion of the relevant fuel cell physics. Models that include all parts of a fuel cell are typically two- or three-dimensional and reflect many of the physical processes occurring within the fuel cell. Comprehensive models rely on the determination of a large number of properties and operating parameters and can be much more computationally intensive, leading to longer solution times.

Many numerical model of PEMFC works have been accomplished during last 15 years. The first two models were published in the early 1990s by Springer et al. (1991) and Bernardi and Verbrugge (1992). These models are one-dimensional and only account for simple diffusive mass transport and electrochemical kinetics. Several two-dimensional models have been presented by Nguyen et al. (1993) and Gurau et al. (1998) and Singh et al. (1999) . Most of these models compute the flow field along a single channel to study the reaction species and current density distributions. Um et al. (2000) considered the two-phase flow model within porous diffusion layer and flow channel to study the flooding of GDL and gas channel, which impedes gas flow and also reduces efficiency. Recently, Mazumder and Cole (2003) and Su et al. (2005) have used three-dimensional models based on computational fluid dynamics approach were presented and computed by commercial software or Beming et al. (2002) and Wang and Lu (2004) and Hu et al. (2004) have presents self-developed numerical model of the SIMPLE algorithm. The three-dimensional models account for the effect of the complex geometry, specifically interdigitated flow field. They allow a parametric study for a realistic flow field, concentration and current distributions. The simulation results are well compared with the experimental data of polarization curve. However, the influence of flow field design upon concentration and current density distributions were less discussed. Mench et al. (2003) proved that the effects of cathode stoichiometry variation and transient flooding on local current density affect the current distribution on serpentine flow field. When voltages are 0.9–0.6V (electrochemical reaction controlled region), the current density in downstream is higher than upstream. On the other hand, when the voltages are 0.4–0.2V, the current density in upstream is higher than downstream. The efforts on fuel cell modeling and experimental measurement technique are valuable for fuel cell developers, which can optimize fuel cell designs and operations.

Although many numerical models of the gas flow field have been presented by many researchers, but most of them focus only on couple parameters. This makes flow field design task very difficult. This research will focus on the gas dynamic within the gas channel using CFD technique. The numerical results will provide understanding the effect of flow field pattern design on performance of the fuel cell. This will lead us to a better design of gas flow field, which improves the gas distribution and water management. This research will investigate the relationship between dimensions of channel, channel length, channel curvature and inlet manifold with pressure drop, velocity distribution and cell performance by using numerical model. The experiments will be set up to confirm the numerical predictions on polarization curve and power curve. The output from this research will enlight researchers on fundamental knowledge in design and operate the fuel cell.

2.1 Technology of Fuel Cell

Fuel cell is an electrochemical cell, which can continuously convert the chemical energy of a cell and an oxidant to electrical energy by a process involving an essentially invariant electrode-electrolyte system. Fuel cells work at high efficiency with emission levels below the most strict standards. Their most important characteristics, namely high efficiency, low emission and noise levels and environment friendly, will be mandatory in the next generation of power plant.

This research focuses on PEMFC because it is one of the most widely interest type. PEMFC works at low-temperature operation, high power density, fast start up, system robustness and low emissions. The knowledge of PEMFC is explained in next paragraph.

2.2 Proton Exchange Membrane Fuel Cell Operation

A single polymer-electrolyte fuel cell is shown schematically in Figure 1. The cell typically consists of bipolar plates (detail in figure 2.4), which are pressed against the membrane-electrode assembly. These plates have a manifold of grooves to distribute the reactant gases to the electrodes. There are also sufficiently electrically conductive to pass the generated current from the cell.

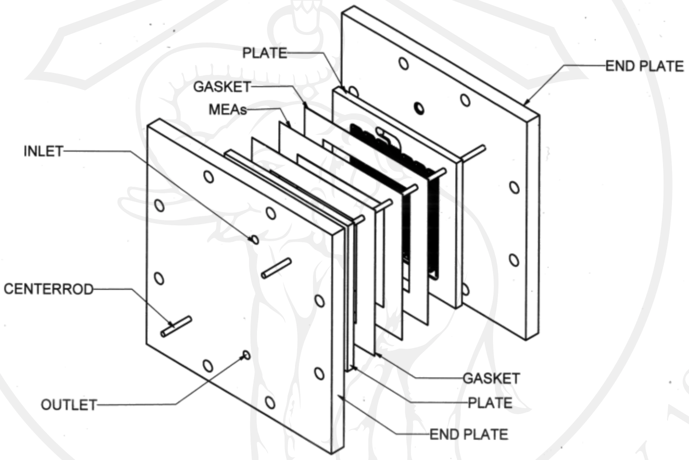


Figure 2.1 Schematic of Proton Exchange Membrane

The membrane-electrode assembly is the heart of the system. On the anode, hydrogen side, hydrogen gas is catalytically disassociated according to the reaction:

$$\text{Anode}: 2H_2 \longrightarrow 4H^+ + 4e^-$$

The hydrogen ions pass through the polymer electrolyte to the cathode, oxygen side, of the cell. There are combined catalytically with oxygen and electrons from the adjacent cell to from water according to the reaction:

$$\text{Cathode}: O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The membrane functions twofold, it acts as the electrolyte which provides ionic communication between the anode and the cathode and it serves as a separator for the two reactant gases. Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces proton conductivity and excess of after can lead to flooding of the electrodes. Both conditions result in poor cell performance.

2.3 Fuel Cell Performance

The performance of a fuel cell can be presented by a graph of its current-voltage characteristics. This graph, called a current-voltage (i-V) curve, shows the voltage output of the fuel cell for a given current output. An example of a typical i-V curve for a PEMFC is shown in Figure 2. The current has been normalized by the area of the fuel cell, giving a current density (A/cm^2). Because a larger fuel cell can produce more electricity than a smaller fuel cell, i-V curves are normalized by fuel cell area to make results comparable.

An ideal fuel cell would supply any amount of current while maintaining a constant voltage determined by thermodynamics. In practice, the actual voltage output of a real fuel cell is less than the ideal thermodynamically predicted voltage. Furthermore, the more current that is drawn from a real fuel cell, the lower the voltage output of the cell, limiting the total power that can be delivered. The power (P) delivered by a fuel cell is given by the product of current and voltage.

$$P = iV \tag{2.1}$$

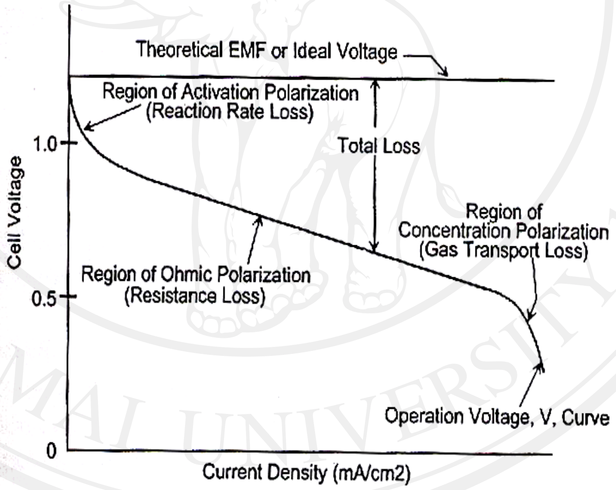


Figure 2.2 Schematic of fuel cell polarization curve (Kordesch, 1996)

A fuel cell power density curve, which gives the power density delivered by a fuel cell as a function of the current density, can be constructed from the information in a fuel cell i-V curve. The power density curve is produced by multiplying the voltage at each point on the i-V curve by the corresponding current density. Figure 3 shows the combination of fuel cell i-V and power density curves. Fuel cell voltage is given on the left-hand y-axis while power density is given on the right-hand y-axis.

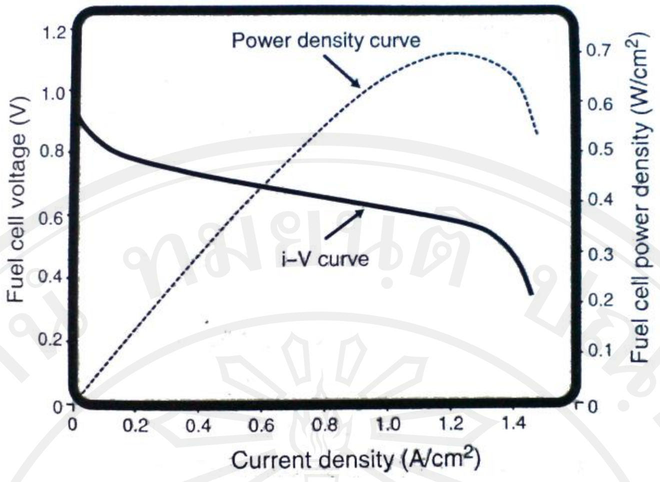


Figure 2.3 Combined fuel cell polarization and power density curve (Frano Barbir, 2005)

The current supplied by a fuel cell is directly proportional to the amount of fuel consumed. Therefore, as fuel cell voltage decreases (see in figure 2), the electric power produced per unit of fuel also decreases. In this way, fuel cell voltage can be seen as a measure of fuel cell efficiency. In other words, the fuel cell voltage axis can be considered as an “efficiency axis.” Maintaining high fuel cell voltage, even under high current loads, is therefore critical to the successful implementation of the technology.

In practice, it is difficult to maintain a high fuel cell voltage under high current. The output voltage of a fuel cell is less than thermodynamically predicted voltage due to irreversible losses. The more current that is drawn from the cell, the greater these losses. There are three major types of fuel cell losses, which give a fuel cell I-V curve its characteristic shape. Each of these losses are associated with one of the basic fuel cell steps discussed in the previous section:

1. activation losses (losses due to electrochemical reaction),
2. ohmic losses (losses due to ionic and electronic conduction),
3. concentration losses (losses due to mass transport).

The voltage output for a fuel cell can thus be written by starting with thermodynamically predicted voltage output of the fuel cell and then subtracting the voltage drops due to the various losses:

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \tag{2.2}$$

where

V = real output voltage of fuel cell,
E_{thermo} = thermodynamically predicted fuel cell voltage output,
η_{act} = activation losses due to reaction kinetics,
η_{ohmic} = ohmic losses from ionic and electronic conduction,
η_{conc} = concentration losses due to mass transport.

Each major loss contributes to the characteristic shape of the fuel cell i-V curve, as shown in Figure 2. The activation losses mostly affect the initial part of the curve; the ohmic losses are most apparent in the middle section of the curve, and the concentration losses are most significant in the tail of the i-V curve. The result of the chemical reactions inside a fuel cell is the reversible single electrode potential, E_{thermo}, given by the Nernst equation.

$$E_{thermo} = E^{0}_{thermo} - \left[\left(\frac{RT}{nF} \right) ln \left(\frac{\rho_{H_2O}}{\rho_{H_2} \times \sqrt{\rho_{O_2}}} \right) \right] \tag{2.3}$$

where

E^{0}_{thermo} = the standard electrode potential,
R = the gas constant (8.3144 J/mol K),
T = the temperature in Kelvin scale,
n = the number of electrons per reacting ion or molecule,
F = Faraday's constant (96,500 C/mol),
ρ_{H_2O} = the partial pressure of water,
ρ_{H_2} = the partial pressure of hydrogen,
ρ_{O_2} = the partial pressure of oxygen.

The activation loss due to reaction kinetics at the electrodes of a PEMFC is equation (2.4). This equation is more commonly known as Tafel equation.

$$\eta_{act} = -\left(\frac{RT}{\alpha nF} \right) ln(i_o) + \left(\frac{RT}{\alpha nF} \right) ln(i) \tag{2.4}$$

where

α = the activity coefficient,
i_o = the exchange current density for the reaction with constant value,
i = the applied current density.

Since fuel cell are generally compared on a per-unit-area basis using current density instead of current, it is necessary to use area-normalized fuel cell resistances when discussing ohmic losses. Area-normalized resistance, also known as area-specific resistance (*ASR*).By using *ASR*, ohmic losses can be calculated from current density as.

$$\eta_{\mathrm{ohmoc}} = \mathrm{i}\left(\mathrm{ASR}_{\mathrm{ohmic}}\right) \tag{2.5}$$

where

ASR_{ohmic} = the *ASR* of the fuel cell.

The effect of concentration losses due to mass transport is shown by equation (2.6).

$$\eta_{conc} = \left(\frac{RT}{n\,F}\right) ln\left(\frac{i_L}{i_L - i}\right) \tag{2.6}$$

where

i_L = the limiting current density and i is the applied current density.

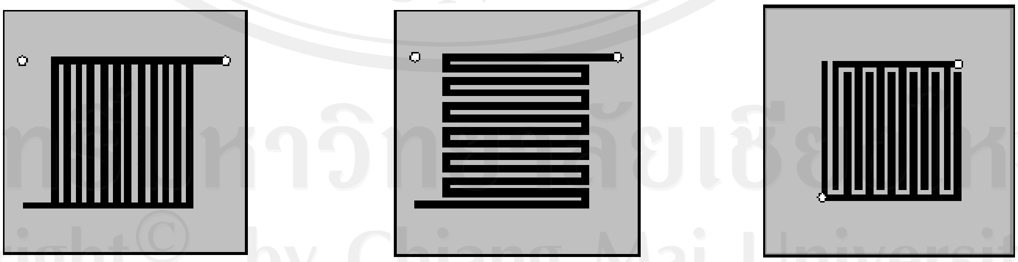
Activation and concentration polarization can occur at both anode and cathode. The cell voltage, V_{cell} , is therefore:

$$V_{cell} = E_{thermo} - (\eta_{act} + \eta_{conc})_a - (\eta_{act} + \eta_{conc})_c - \eta_{ohmic} \tag{2.7}$$

Equation (2.7) is the single cell voltage, which calculated by vary the current density, i .

2.4 Design of Fluid Flow Field Channels on Plates

The flow field of fuel cell should be designed to minimize pressure drop (reducing parasitic pump requirements), while providing adequate and evenly distributed mass transfer through the carbon diffusion layer to the catalyst surface for reaction. Three most popular channel configurations for PEM fuel cells are serpentine, parallel, and interdigitated flow channels are shown in Figure 2.4. Some small-scale fuel cells do not use a flow field to distribute the hydrogen and/or air, but rely on diffusion processes from the environment. Because the hydrogen reaction is not rate limiting, and water blockage in the humidified anode can occur, a serpentine arrangement is typically used for the anode in smaller PEM fuel cells.



a) Parallel b) Serpentine c) Interdigitated

Figure 2.4 Most popular channel configurations (Mennola, 2000)

The serpentine flow path is continuous a single channel from start to finish. An advantage of the serpentine flow path is that it reaches the entire active area of the electrode by eliminating areas of stagnant flow. A disadvantage of serpentine flow is the fact that the reactant is depleted through the length of the channel, so that an adequate amount of the gas must be provided to avoid excessive polarization losses. The pressure drop is high in serpentine channels because flow velocity scales with the square of this type, and the channel length is inversely proportional to this flow field. For high current density operation, very large plates, or when air is used as an oxidant, alternate designs have been proposed based upon the serpentine design.

Several continuous flow channels can be used to limit the pressure drop, and reduce the amount of power used for pressurizing the air through a single serpentine channel. This design allows no stagnant area formation at the cathode surface due to water accumulation. The reactant pressure drop through the channels is less than the serpentine channel, but still high due to the long flow path of each serpentine channel. Although some of the reactant pressure losses can increase the degree of difficulty for hydrogen recirculation, they are helpful in removing the product water in vapor form. The total reactant gas pressure is $P_T = P_{vap} + P_{gas}$, where P_{vap} and P_{gas} are the partial pressures of the partial pressure and reactant gas in the reactant gas stream, respectively. The molar flow rate of the water vapor and reactant can be related as follows:

$$\frac{N_{vap}}{N_{gas}} = \frac{P_{vap}}{P_{gas}} = \frac{P_{vap}}{P_T - P_{vap}} \tag{2.8}$$

The total pressure loss along a flow channel will increase the amount of water vapor that can be carried and taken away by the gas flow if the relative humidity is maintained. This can help remove water in both the anode and cathode flow streams.

The other flow field has good test for PEMFC is interdigitated. The reactant flow for the interdigitated flow field design is parallel to the electrode surface. Often, the flow channels are not continuous from the plate inlet to the plate outlet. The flow channels are dead-ended, which forces the reactant flow, under pressure, to go through the porous reactant layer to reach the flow channels connected to the stack manifold. This design can remove water effectively from the electrode structure, which prevents flooding and enhances performance. The interdigitated flow field pushes gas into the active layer of the electrodes where forced convection avoids flooding and gas diffusion limitations. This design is sometimes noted in the literature as outperforming conventional flow field design, especially on the cathode side of the fuel cell.

2.4.1 Uniform Distribution of Reactants Inside Each Cell

Once the reactant gases enter the individual cell they must be distributed over the entire active area. This is typically accomplished through a flow field, which may be in a form of channels covering the entire area in some pattern or porous structures. The following sections describe the key flow field design variables.

2.4.2 Cross Section of The Flow Field

The flow fields come in different shapes and sizes. The size comes from the power/voltage requirements. The shape is determined by positioning the inlet and outlet manifolds, flow field design, heat management, and manufacturing constraints. The most common shapes of the flow field are square and rectangular, but circular, hexagonal, octagonal, or irregular shapes have been used or at least tried in Figure 2.5.

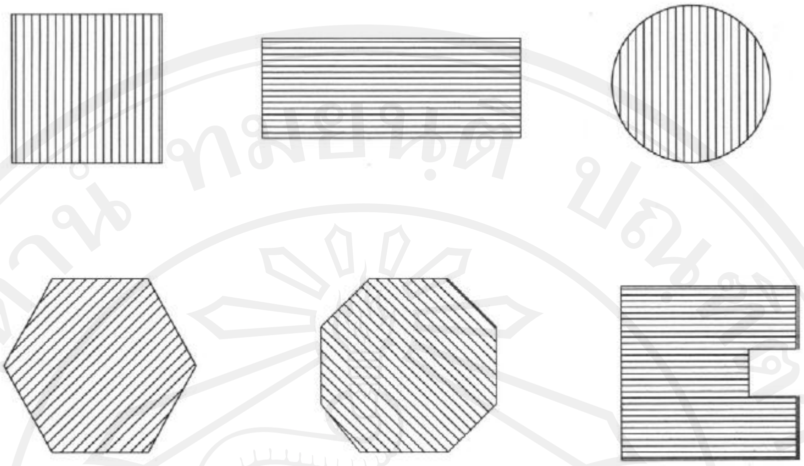


Figure 2.5 Various shapes of the fuel cell active area.

2.4.3 Flow Field Orientation

The orientation of the flow field and positions of inlet and outlet manifolds are important only because of the gravity effect on water that may condense inside the flow field (the effect of gravity on the reactant gases is negligible). Condensation may take place either during operation, depending on the choice of operational conditions, or after shutdown. Numerous combinations are possible, some of which are shown in Figure 2.6. Anode and cathode may be oriented in the same direction, in opposite direction, or in cross-configuration. Anode and cathode positioning may have some effect on fuel cell performance due to varied concentration of reactant gases and water. In some cases, the flow fields are oriented so that the cathode outlet is next to the anode inlet and vice versa, allowing water exchange through the membrane due to water concentration gradient (i.e., the exiting gas has much higher temperature and water content).

The stack orientation, and so the flow field orientation, may be either vertical or horizontal. In the latter case, either anode or cathode may be facing up in Figure 2.7. Again, this may have some effect on liquid water removal, particularly after shutdown and cooling.

2.4.4 Configuration of Channels

There are many configurations of channels that have been tried in PEM fuel cells, all with the same goal—to ensure uniform reactant gases distribution and water removal capability see in Figure 2.8. Some most common designs will be discussed next.

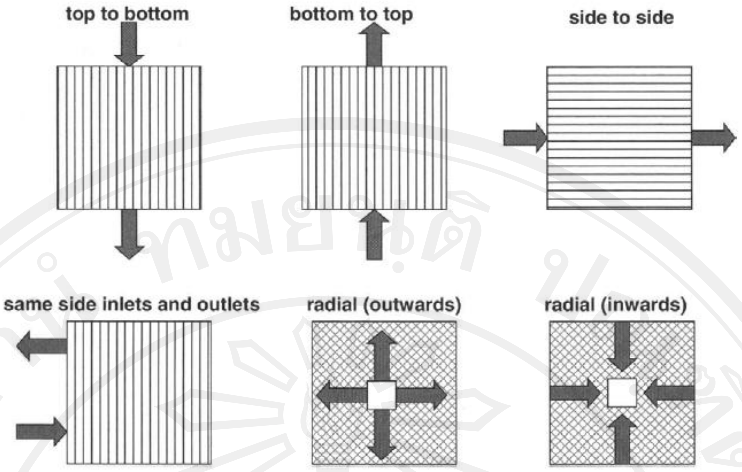


Figure 2.6 Possible flow field orientations.

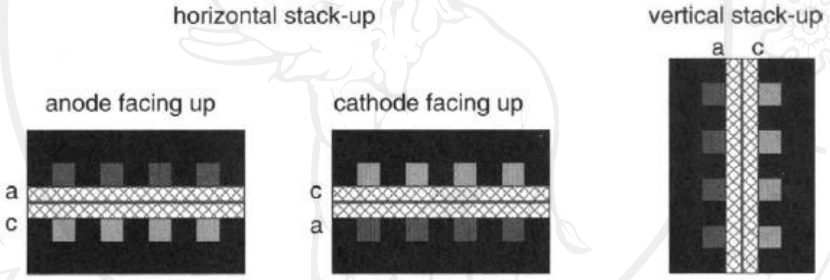


Figure 2.7 Stack and cell orientation options.

- Straight channels with large manifolds-Although this appears to ensure uniform distribution, it actually does not work in PEM fuel cells. Distribution is indeed uniform, but only under ideal conditions. Any water droplet that develops in a channel would effectively block the entire channel, and the velocity would not be sufficient to push the water out (figure 2.8a) .
- Straight channels with small manifolds-This design has the same shortcomings and, in addition, has inherent maldistribution of reactant gases, because the channels immediately below or above the manifold receive most of the flow. The early fuel cells built with such a flow field exhibited low and unstable cell voltages (figure 2.8b).
- Crisscross configuration—This flow field attempts to eliminate the shortcomings of the straight channel flow field by introducing traversal channels allowing the gas to bypass any "trouble" spot, that is, coalescing water droplets. The problems of low velocities and uneven flow distribution due to positioning of the inlet and outlet manifolds are not reduced with this design (figure 2.8c).

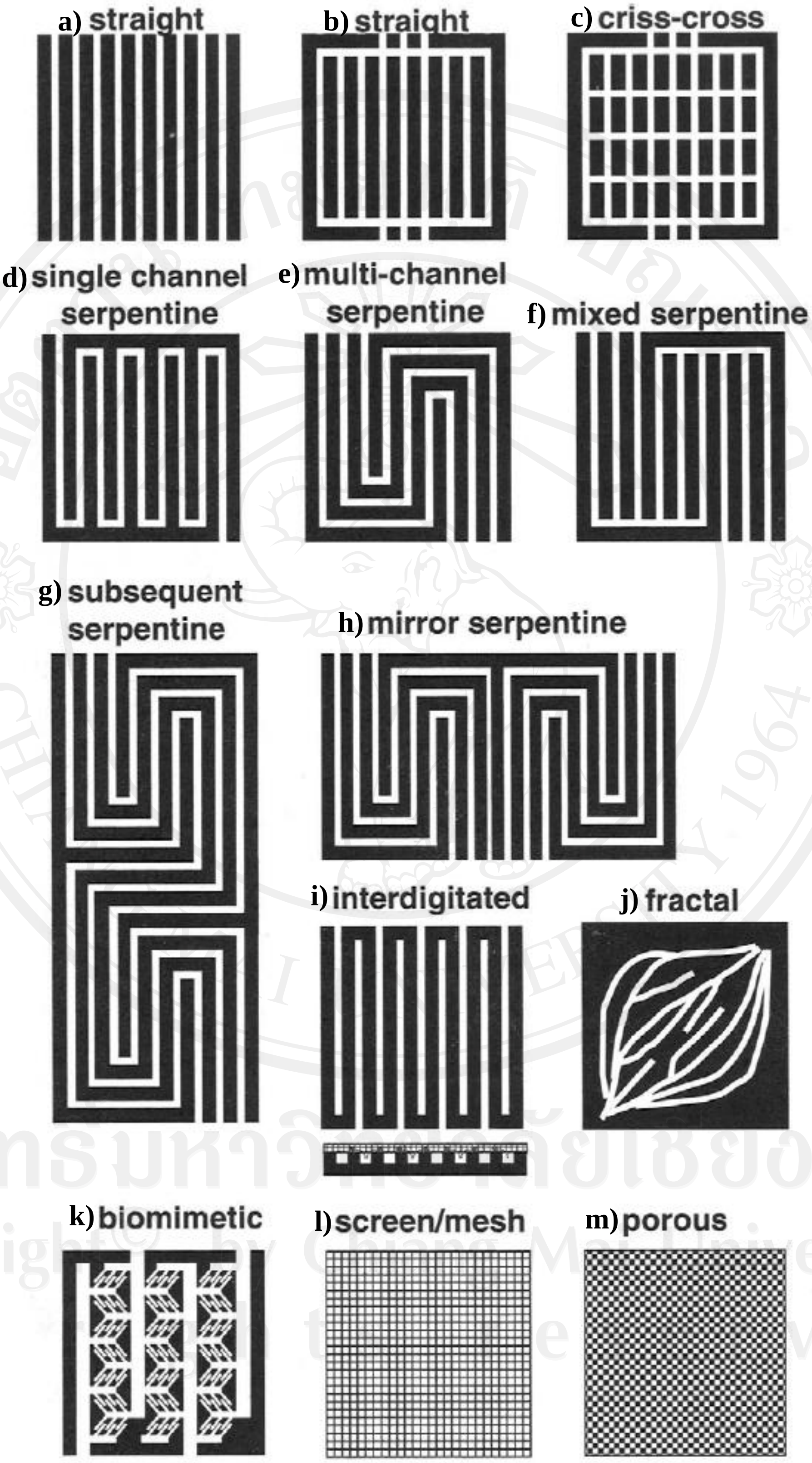


Figure 2.8 Various flow field configurations (Frano Barbir, 2005).

- Single-channel serpentine—As described by Watkins et al., this is the most common flow field for small active areas. It ensures that the entire area is covered, although the concentration of reactants decreases along the channel. There is a pressure drop along the channel due to friction on the walls and due to turns. The velocity is typically high enough to push any water condensing in the channel. Attention must be paid to pressure differential between the adjacent channels, which may cause significant bypassing of channel portions (figure 2.8d).
- Multichannel serpentine—A single-channel serpentine configuration would not work for the large flow field areas, because of a large pressure drop. Although a pressure drop is useful in removing the water, excessive pressure drop may generate larger parasitic energy losses. Watkins et al. proposed a flow field that has a multitude of parallel channels meandering through the entire area in a serpentine fashion. Except the lower pressure drop, this flow field has the same features, advantages, and shortcomings of the single channel serpentine. The fact that there are parallel channels means that there is always a possibility that one of the channels may get blocked as discussed previously with straight channels (figure 2.8e).
- Multichannel serpentine with mixing—As suggested by Cavalca et al., this flow field design allows gases to mix at every turn in order to minimize the effect of channel blocking. This does not reduce the chance of channel blockage, but it limits its effect only to a portion of the channel, because the flow field is divided in smaller segments, each with its own connecting channel to both the inlet and the outlet (in figure 2.8).
- Subsequent serially linked serpentine—This flow field also divides the flow field into segments in an attempt to avoid the long straight channels and relatively large pressure differentials between the adjacent sections, thus minimizing the bypassing effect (figure 2.8f).
- Mirror serpentine—This is another design to avoid large pressure differentials in adjacent channels, particularly suited for a larger flow fields with multiple inlets and outlets. These are arranged so that the resulting serpentine patterns in adjacent segments are mirror images of each other, which results in balanced pressures in adjacent channels, again minimizing the bypassing effect (figure 2.8g).
- Interdigitated—First described by Ledjeff, advocated by Nguyen, and successfully employed by Energy Partners in their NG- 2000 stack series, this flow field differs from all of the abovementioned because the channels are discontinued, that is, they do not connect inlet to the outlet manifolds. This way the gas is forced from the inlet channels to the outlet channels through the porous back-diffusion layer. Wilson et al. suggested a variation of interdigitated flow field in which the channels are made by cutting out the strips of the gas diffusion layer. Convection through the porous layer shortens the diffusion path and helps remove any liquid water that otherwise may accumulate in the gas diffusion layer, resulting in better performance, particularly at higher current densities. However, depending on the properties of the gas diffusion layer, this flow field may result in higher pressure drops. Due to the fact that the most of the pressure drop occurs in the porous media, the uniformity of flow distribution between individual channels and between individual cells strongly depends on uniformity of gas diffusion layer thickness and effective porosity (after being squeezed). One of the problems with this flow field is inability to remove

liquid water from the inlet channels. Issacci and Rehg suggested the porous blocks at the end of the inlet channels allowing water to be removed (figure 2.8h).

- BioMimetic—Suggested by Morgan Carbon, this is a further refinement of the interdigitated concept. Larger channels branch tosmaller side channels further branching to really tiny channels interweaving with outlet channels that are arranged in the same fashion—tiny channels leading to larger side channels leading to the large channels. This type of branching occurs in nature (leaves or lungs), hence the name biomimetic (figure 2.8i).
- Fractal—This flow field suggested by the Fraunhoffer Institute is essentially the interdigitated flow field concept, but the channels are not straight and they have branches (figure 2.8j).
- Mesh—Metallic meshes and screens of various sizes are successfully being used in the electrolyzers. The uniformity may greatly be affected by positioning of the inlet manifolds. The researchers at Los Alamos National Lab successfully incorporated metal meshes in fuel cell design. The problems with this design are introduction of another component with tight tolerances, corrosion, and interfacial contact resistance (figure 2.8k).
- Porous media flow field-This is similar to mesh flow field; the difference is in pore sizes and material. The gas distribution layer must be sufficiently thick and have enough pores sufficiently large to permit a substantially free flow of reactant gas both perpendicular to and parallel to the catalyst layer. Although metallic porous materials (foams) are brittle, carbon-based ones may be quite flexible. This type of flow field may only be applicable for smaller fuel cells because of the high pressure drop (figure 2.8m).

2.4.5 Channel Shape, Dimensions and Spacing

Flow channels are typically rectangular in shape, but other shapes such as trapezoidal, triangular, and circular have been demonstrated. The change in channel shape can have an affect upon the water accumulation in the cell, and, therefore, the fuel and oxidant flow rates. For instance, in rounded flow channels, the condensed water forms a film at the bottom of the channel, and in tapered channels, the water forms small droplets (figure 2.9). The shape and size of the water droplets are also determined by the hydrophobicity of the porous media and channel walls. Channel dimensions are usually around 1 mm, but a large range exist for micro- to large scale fuel cells (0.1 mm to 3 mm). Simulations have found that optimal channel dimensions for macro fuel cell stacks (not MEMS fuel cells) are 1.5, 1.5, and 0.5 mm for the channel depth, width, and land width (space between channels), respectively. These dimensions depend upon the total stack design and stack size. The channels' dimensions affect the fuel and oxidant flow rates, pressure drop, heat and water generation, and the power generated in the fuel cell. Wider channels allow greater contact of the fuel to the catalyst layer, have less pressure drop, and allow more efficient water removal. However, if the channels are too wide, there will not be enough support for the MEA layer. If the spacing between flow channels is also wide, this benefits the electrical conductivity of the plate but reduces the area exposed to the reactants, and promotes the accumulation of water.

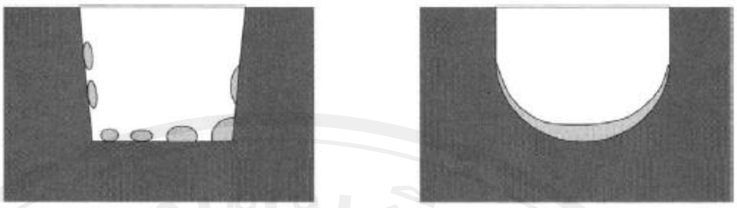
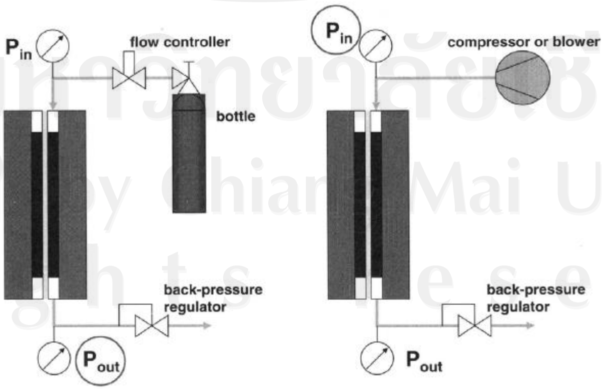


Figure 2.9 The shape of the channel cross-section affects the form of liquid water formation.

2.5 Fuel Cell Operation Conditions

2.5.1 Operating Pressure

A fuel cell may be operated at ambient pressure or it may be pressurized. As we have already learned, a fuel cell gains some potential when the pressure is increased, the net gain, when the compression power is taken into account, is at least questionable. The issue of pressurization is also related to the issue of water management, and therefore must be addressed from a system perspective. When a fuel cell is fed the reactant gases from a pressurized tank, its pressure is controlled by a backpressure regulator placed at the outlet in Figure 2.10a. This pressure regulator keeps the desired, preset pressure at the fuel cell outlet. Laboratory set up usually ignore the inlet pressure record. The inlet pressure is always higher because of inevitable pressure drop in tiny channels inside the fuel cell. However, when the reactant gas (for example, air) is fed to a fuel cell by a mechanical device, a blower or a compressor, which is the case in any practical system, it is the inlet pressure that matters in Figure 2.10b. The compressor or the blower must be capable of delivering the required flow rate at desired pressure. The backpressure regulator may still be used to pressurize the cell, or if no backpressure regulator is used, the gas leaves the cell at atmospheric pressure. Note that atmospheric pressure may vary too, depending on weather conditions or elevation (many fuel cell experiments reported by the Los Alamos National Laboratory are actually conducted at substandard pressure, because of elevation).



a) b)

Figure 2.10 Fuel cell operating pressure as a function of reactant gas supply; a) supply from a high-pressure tank, b) supply by a mechanical device, a compressor or blower.

2.5.2 Operating Temperature

The cell temperature is another operating parameter that may be selected and preset. In general, a higher operating temperature results in higher cell potential; however, for each fuel cell design there is an optimal temperature.

The operating temperature of practical fuel cells, similarly to operating pressure, must be selected from the system perspective, taking into account not only the cell performance, but also the system requirements, particularly the size and parasitic power requirements of the heat management subsystem. A fuel cell generates heat as a by-product of the electrochemical reaction. To maintain the desired temperature, heat must be taken away from a fuel cell. Some heat dissipates from the outer surface of the fuel cell and some must be taken away with a cooling system. Medium that takes away the heat may be air, water, or a special coolant. The inner design of the fuel cell must allow the heat transfer to occur. Sometimes, small fuel cells need a heater to reach the operating temperature. This is not very practical, but it is sometimes necessary for testing of fuel cells at a desired temperature.

In other words, the heat generated in the fuel cell, plus the heat brought into the cell with reactant gases, is taken away from the cell by heat dissipation from the cell surface to the surrounding, by the reactant gases leaving the cell, and by the coolant.

The temperature inside a fuel cell may not be uniform; it may vary from inlet to outlet, from inside out, or from cathode to anode. The cell temperature may be approximated by the following temperatures, which are much easier to measure than the cell temperature:

- surface temperature
- temperature of air leaving the cell
- temperature of coolant leaving the cell

Because of finite temperature differences needed for heat transfer inside a fuel cell, none of the above is exactly the cell operating temperature. The surface temperature is clearly lower than the temperature inside a fuel cell in a case when the fuel cell is heating itself, and it is actually higher than the inside temperature if the fuel cell is heated with the heating pads on its surface. Most of the losses in the fuel cell may be associated with the cathode reaction, the temperature of air exiting the fuel cell is a good approximation of the cell operating temperature, although the temperature inside a fuel cell must be at least slightly higher than the air temperature. In case of the cell temperature is maintained by the flow of coolant through the cell, the coolant outlet temperature may be used as the operating temperature. The accuracy of these approximations depends on thermal conductivity of the cell materials and air and coolant flow rates.

2.5.3 Reactants Flow Rates

The reactants flow rate at the inlet of a fuel cell must be equal to or higher than the rate at which those reactants are being consumed in the cell. The rates (mols^{-1}) at which hydrogen and oxygen are consumed and water is generated are determined by Faraday's Law:

$$\dot{N}_{H_2} = \frac{I}{2F} \tag{2.9}$$

$$\dot{N}_{O_2} = \frac{I}{4F} \tag{2.10}$$

$$\dot{N}_{H_2O} = \frac{I}{2F} \tag{2.11}$$

where:
N = consumption rate ($mols^{-1}$)
I = current (A)
F = Faraday's constant ($Cmol^{-1}$)
The mass flow rates of reactants consumption (gs^{-1}) are then:

$$\dot{m}_{H_2} = \frac{I}{2F} M_{H_2} \tag{2.12}$$

$$\dot{m}_{O_2} = \frac{I}{4F} M_{O_2} \tag{2.13}$$

The mass flow rate of water generation (in gs^{-1}) is:

$$\dot{m}_{O_2} = \frac{I}{4F} M_{H_2O} \tag{2.14}$$

Most often, the flow rates of gases are expressed in standard cubic centimeter per minute (sccm). Standard cubic centimeter is a quantity of gas that would occupy 1 cubic centimeter of volume at standard conditions, namely atmospheric pressure, 101.3 kPa, and 15°C. Note that most chemical handbooks and textbooks refer to 25°C as standard or reference temperature, but in technical fluid mechanics standard temperature is 15°C (although some books use 20°C and some use 70°F). To avoid confusion with standard temperatures, in Europe it is common to use normal liter or normal m^3, where the temperature has been normalized to 0°C. For any ideal gas, mols and volumes are directly related by the equation of state:

$$PV = nRT \tag{2.15}$$

Molar volume is:

$$V_m = \frac{V}{N} = \frac{RT}{P} \tag{2.16}$$

At standard conditions, that is, atmospheric pressure and 15°C, molar volume is:

$$V_m = \frac{RT}{P} = \frac{8.314 \times 288.15}{101{,}300} = 0.02365 \qquad m^3mol^{-1} \tag{2.17}$$

$$= 23{,}650 \ \ cm^3mol^{-1}$$

The volumetric flow rates of reactants consumption (in standard cubic centimeter per minute or sccm) are:

$$\dot{V}_{H_2} = 23.65 \times 60 \times \frac{I}{2F} \tag{2.18}$$

$$\dot{V}_{O_2} = 23.65 \times 60 \times \frac{I}{4F} \tag{2.19}$$

Consumption of the reactants, hydrogen and oxygen, and water generation in the fuel cell is summarized in Table 2.1.

Table 2.1 Reactants Consumption and Water Generation (per Amp and per Cell) (Frano Barbir, 2005)

UNIT	Hydrogen Consumption	Oxygen Consumption	Water Generation (liq.)
Mols^{-1}	5.18×10^{-6}	2.59×10^{-6}	5.18×10^{-6}
Gs^{-1}	10.4×10^{-6}	82.9×10^{-6}	93.3×10^{-6}
$Cm^3\ s^{-1}$	0.1225	0.06125	93.3×10^{-6}
slpm	0.00735	0.003675	N/A
Nm^3h^{-1}	0.418×10^{-3}	0.209×10^{-3}	N/A

The reactants may, and in some cases must, be supplied in excess of consumption. For example, this is always necessary on the cathode side where water is produced and must be carried out from the cell with excess flow. The ratio between the actual flow rate of a reactant at the cell inlet and the consumption rate of that reactant is called the stoichiometric ratio, S.

$$S = \frac{\dot{N}_{act}}{\dot{N}_{cons}} = \frac{\dot{m}_{act}}{\dot{m}_{cons}} = \frac{\dot{V}_{act}}{\dot{V}_{cons}} \tag{2.20}$$

Hydrogen may be supplied at the exact rate at which it is being consumed, in so-called dead-end mode (figure 2.11a). If hydrogen is available at elevated pressure, such as in a high-pressure storage tank, the dead-end mode does not require any controls, that is, hydrogen is being supplied as it is being consumed. In a dead-end mode S = 1. If hydrogen loss due to crossover permeation or internal currents is taken into account then the hydrogen flow rate at the fuel cell inlet is slightly higher than the consumption rate corresponding to the electrical current being generated:

$$S = \frac{\dot{N}_{cons} + \dot{N}_{loss}}{\dot{N}_{cons}} > 1 \qquad (2.21)$$

Fuel utilization is reverse of stoichiometric ratio (η_{fu}):

$$\eta_{fu} = \frac{1}{S} \qquad (2.22)$$

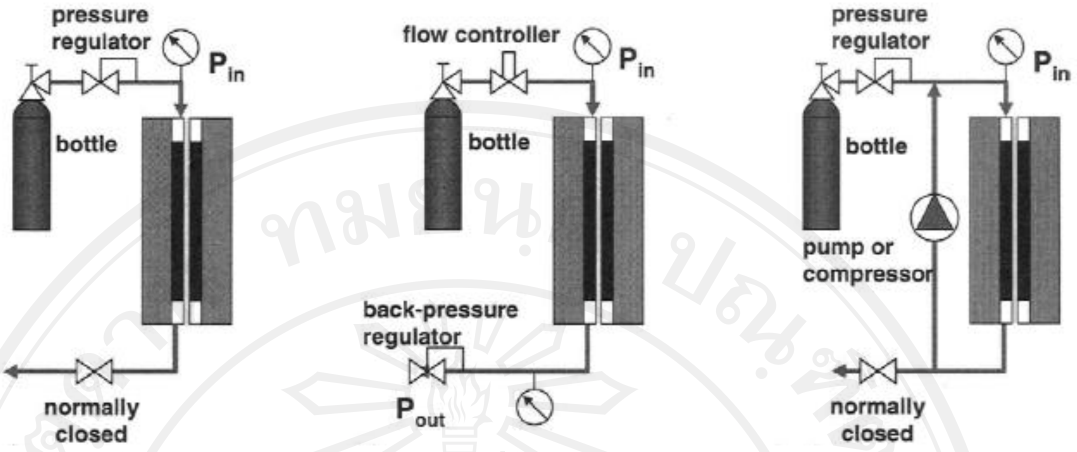
Even in a dead-end mode, hydrogen has to be periodically purged, because of accumulation of inerts or water. The frequency and duration of purges depends on purity of hydrogen, rate of nitrogen permeation through membrane, and water net transport through the membrane. In calculating the fuel cell efficiency, the loss of hydrogen due to purging must be taken into account through fuel utilization.

$$\eta_{fu} = \frac{\dot{N}_{cons}}{\dot{N}_{cons} + \dot{N}_{loss} + \dot{N}_{prg}\tau_{prg} f_{prg}} \qquad (2.23)$$

where:

N_{loss} = rate of hydrogen loss (mols^{-1})
N_{prg} = rate of hydrogen purge (mols^{-1})
T_{prg} = duration of hydrogen purge (s)
f_{prg} = frequency of purges (s^{-1})

Instead of purging, hydrogen may be supplied in excess (S > 1) in so-called flow-through mode in figure 2.11b. In that case fuel utilization is given by equation 2.22. Air is almost always supplied in a flow-through mode, with stoichiometry about S = 2 or higher. In case of pure reactants (hydrogen and/or oxygen), a recirculation mode may be utilized in figure 2.11c. In this case the unused gas is returned to the inlet by a pump or a compressor, or sometimes a passive device such as an ejector (based on a Venturi tube) may be employed. Note that in case of recirculation, a cell may operate at stoichiometric ratio much higher than 1, but because unused reactant (hydrogen or oxygen) is not wasted but returned for consumption back to the cell inlet, fuel or oxidant utilization on a system level is high (close to 1). Fuel utilization in various modes of operation is summarized below.



a) b) c)

Figure 2.11 Modes of reactant supply: a) dead-end mode, b) flow-through mode and c) recirculation mode.

In dead-end and recirculation mode:

$$\eta_{fu} = \frac{\dot{N}_{cons}}{\dot{N}_{cons} + \dot{N}_{loss}} \tag{2.24}$$

flow-through mode:

$$\eta_{fu} = \frac{\dot{N}_{cons}}{\dot{N}_{act}} \tag{2.25}$$

In general, higher flow rates result in better fuel cell performance. Although pure hydrogen may be supplied in a dead-end mode (S = 1) or with a stoichiometry slightly higher than 1 (1.1 to 1.2), hydrogen in a mixture of gases (such as that coming out of a fuel processor) must be supplied with higher stoichiometrics (1.1 to 1.5). The exact flow rate is actually a design variable. If the flow rate is too high the efficiency will be low (because hydrogen would be wasted), and if the flow rate is too low the fuel cell performance may suffer. Similarly, for pure oxygen flow rate, the required stoichiometry is between 1.2 and 1.5, but when air is used, typical stoichiometry is 2 or higher. Although higher air flow rates result in better fuel cell performance. Air is supplied to the cell by means of a blower or a compressor (depending on operating pressure) whose power consumption is directly proportional to the flow rate. Therefore, at higher air flow rates the fuel cell may perform better, but power consumption of a blower or particularly of a compressor may significantly affect the system efficiency. There are at least two reasons why fuel cell performance improves with excess air flow rate, namely:

1. Higher flow rate helps remove product water from the cell.
2. Higher flow rates keep oxygen concentration high.

Because oxygen is being consumed in the cell, its concentration at the cell outlet depends on the flow rate. If air is supplied at exact stoichiometric ratio (S = 1), all the oxygen in the supplied air will be consumed in the fuel cell, that is, oxygen concentration in air exhaust will be zero. The higher the flow rate, the higher the oxygen concentration at the outlet and throughout the cell is going to be, as shown in figure 2.12.

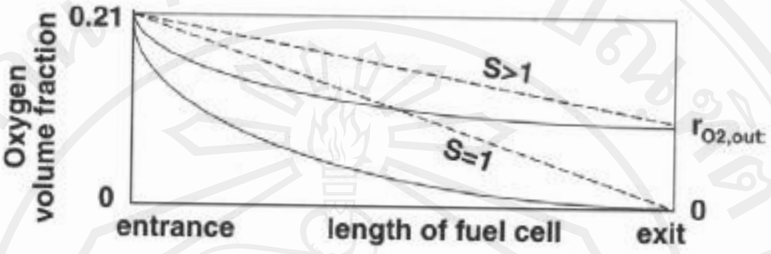


Figure 2.12 Oxygen volume or molar fraction through a fuel cell (dashed lines represent an ideal case where the rate of oxygen consumption is constant, and solid lines are more realistic, because the consumption rate is a function of oxygen concentration).

If oxygen volume or molar fraction at the fuel cell inlet is r_{O_2},in, then the oxygen volume or molar fraction at the outlet is:

$$r_{O_2,out} = \frac{S-1}{\left(\frac{S}{r_{O_2,in}} - 1\right)} \tag{2.26}$$

2.5.4 Reactants Humidity

Because the membrane requires water to maintain protonic conductivity, both reactant gases typically must be humidified before entering the cell. In some cases have to be saturated, but in some cases excess humidity is needed on the anode side and less-than saturated conditions may be sufficient on the cathode side. Humidity ratio is a ratio between the amount of water vapor in a gas stream and the amount of dry gas. Humidity mass ratio (grams of water vapor/grams of dry gas) is:

$$x = \frac{G_v}{G_a} \tag{2.27}$$

Humidity molar ratio (mols of water vapor/mols of dry gas) is:

$$\chi = \frac{N_v}{N_a} \tag{2.28}$$

The relationship between mass and molar humidity ratios is:

$$x = \frac{M_w}{M_a}\chi \tag{2.29}$$

Molar ratio of gases is the same as a ratio of partial pressures:

$$\chi = \frac{P_v}{P_a} = \frac{P_v}{P - P_v} \tag{2.30}$$

where P is the total pressure and P_v and P_a are the partial pressures of vapor and gas, respectively.

Relative humidity is a ratio between the water vapor partial pressure, P_v, and saturation pressure, P_{vs}, which is the maximum amount of water vapor that can be present in gas for given conditions:

$$\varphi = \frac{P_v}{P_{vs}} \tag{2.30}$$

Saturation pressure is a function of temperature only. The values of saturation pressure may be found in thermodynamic tables. ASHRAE Fundamentals provides an equation that allows us to calculate the saturation pressure (Pascal) for any given temperature between 0°C and 100°C:

$$P_{vs} = e^{aT^{-1}+b+cT+dT^2+eT^3+f\ln(T)} \tag{2.31}$$

where a, b, c, d, e, and f are the coefficients by Frano Barbir, 2005:

$a = -5800.2206$
$b = 1.3914993$
$c = -0.048640239$
$d = 0.41764768 \times 10^{-4}$
$e = -0.14452093 \times 10^{-7}$
$f = 6.5459673$

The humidity ratios may be expressed in terms of relative humidity, saturation pressure, and total pressure, by combining the Equations (2.28), (2.29), and (2.30):

$$x = \frac{M_w}{M_a}\frac{\varphi P_{vs}}{P - \varphi P_{vs}} \tag{2.32}$$

and

$$\chi = \frac{\varphi P_{vs}}{P - \varphi P_{vs}} \tag{2.33}$$

Figure 2.13 shows the water vapor content in gas at different temperatures and pressures. As it follows from Equation 2.33, at lower pressure a gas can contain more water vapor, and as it follows from Equations 2.31 and 2.33, water content in gas increases exponentially with temperature. At 80% and ambient pressure, water content in air is close to 50%. Water vapor content by volume is:

$$r_{H2O,v} = \frac{\chi}{\chi+1} = \frac{\varphi P_{vs}}{P} \qquad (2.34)$$

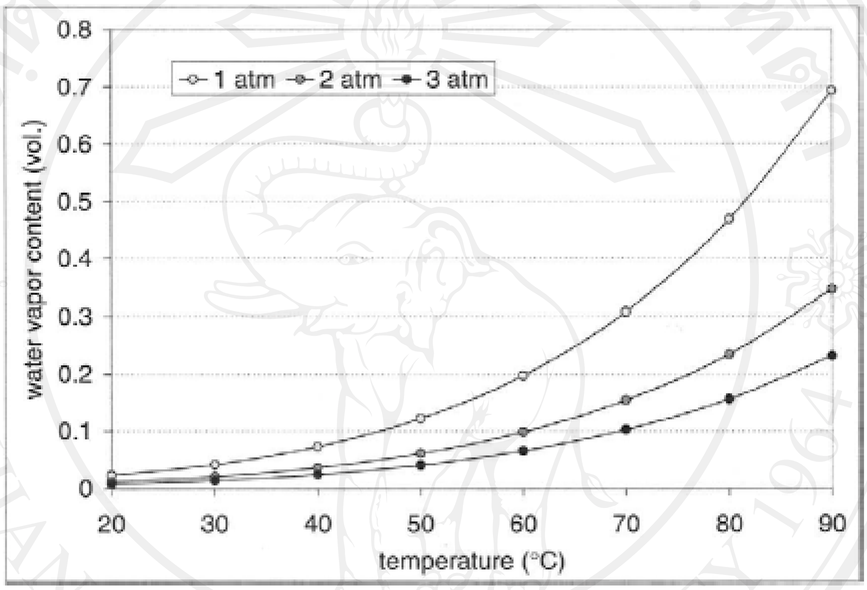


Figure 2.13 Water vapor content in a gas at different pressures and temperatures (Frano Barbir, 2005).

2.6 Water Management

Water is produced not as steam, but as liquid in a PEMFC. A critical requirement of these cells is maintaining a high water content in the electrolyte to ensure high ionic conductivity. The ionic conductivity of the electrolyte is higher when the membrane is fully saturated, and this offers a low resistance to current flow and increases overall efficiency. The water content in the cell is determined by the balance of water or its transport during the reactive mode of operation. Contributing factors to the water transport are the water drag through the cell, back diffusion from the cathode, and the diffusion of any water in the fuel stream through the anode. The water transport is a function of the cell current and the characteristics of the membrane and the electrodes. Water drag refers to the amount of water that is pulled by osmotic action along with the proton. Between 1 and 2.5 molecules are dragged with each proton. As a result, the ion exchanged can be envisioned as a hydrated proton, $H(H2O)_n^{+}$. The water drag increases at high current density, and this makes the water balance a potential concern. During actual operation, however, back diffusion of water from the cathode to the anode through the thin membrane results in a net water transport of nearly zero. A detailed modeling of the reactions and water balance is beyond the scope of this handbook; References and should be reviewed for specific modeling information.

Water management has a significant impact on cell performance, because at high current densities mass transport issues associated with water formation and distribution limit cell output. Without adequate water management, an imbalance will occur between water production and evaporation within the cell. Adverse effects include dilution of reactant gases by water vapor, flooding of the electrodes, and dehydration of the solid polymer membrane. The adherence of the membrane to the electrode also will be adversely affected if dehydration occurs. Intimate contact between the electrodes and the electrolyte membrane is important because there is no free liquid electrolyte to form a conducting bridge. If more water is exhausted than produced, then it is important to humidify the incoming anode gas. If there is too much humidification, however, the electrode floods, which causes problems with diffusing the gas to the electrode. A smaller current, large reactant flow, lower humidity, higher temperature, or lower pressure will result in a water deficit. A higher current, smaller reactant flow, higher humidity, lower temperature, or higher pressure will lead to a water surplus. There have been attempts to control the water in the cell by using external wicking connected to the membrane to either drain or supply water by capillary action. Another alternative is to control the cell water content by humidifying the incoming reactant gases. More reliable forms of water management also are being developed based on continuous flow field design and appropriate operating adjustments. A temperature rise can be used between the inlet and outlet of the flow field to increase the water vapor carrying capacity of the gas streams. At least one manufacturer, Ballard Power Systems of Canada, has demonstrated stack designs and automated systems that manage water balances successfully.

2.7 Summary

This chapter has presented the theory of PEMFC including technology of fuel cell, PEMFC operation, fuel cell performance, design of fluid flow field channel on plates, fuel cell operation condition and water management. Design flow field and its parameters were presented. Parameters and conditions were used to evaluate in modeling and experiment, its showed how to calculate its value to know about limit. We presented a theory of PEMFC and it was behavior in working, its found affect parameters of design flow field for better cell performance. Computational fluid dynamics technique (CFD) which used to as a tool in this simulation was mentioned. CFD is describe in next chapter.