CHAPTER 1
INTRODUCTION

1.1. Background

There are several different types of fuel cell technologies, such as Alkaline Fuel Cells (AFC), Molten Carbonate Fuel Cells (MCFC), Phosphoric Acid Fuel Cells (PAFC), Solid Oxide Fuel Cells (SOFC), Proton Exchange Membrane Fuel Cells (PEMFC), and Direct Methanol Fuel Cells (DMFC). Each of these offers specific advantages with respect to the applications in which they are implemented. (See Table 1-1)

Fuels cells do not store electricity but produce it directly from fuel. They simply need to be fed with fuel and oxygen to work. They can be divided into low-temperature and high-temperature types. Low temperature technologies, including PAFC, PEMFC, and DMFC, target transportation, portable power, and lower-capacity distributed power applications. High temperature technologies, including MCFC and SOFC, focus on larger stationary power applications, niche stationary and distributed power, and certain mobile applications. A combination of technology developments and market forces will determine which of these technologies are successful.

There are two main choices of fuels for portable power: hydrogen and methanol. Because these electrochemical devices convert fuels such as hydrogen and methanol directly into electrical energy without combustion, they create virtually no pollution.

DMFC technology has been generally recognized as a promising energy source for portable electronic devices. The performance of conventional rechargeable batteries of these power devices is still unsatisfactory but miniaturized fuel cell has shown many advantages over rechargeable batteries. It possesses a number of advantages such as a liquid fuel, quick refueling, and low cost of fuel. The compact cell is designed to make it suitable for various potential applications including stationary and portable applications.

1.2. Application of Direct Methanol Fuel Cell

The benefits of fuel cell systems include increased power and energy densities, higher efficiency, silent operation, and modularity design. Among various types of fuel cells, the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC) are applicable for the portable electronics due to their low operation temperatures.

PEMFC is the most promising fuel cell and shows excellent performance when fed with hydrogen. However, production, storage and use of hydrogen are still a key limitation.

Methanol releases six protons and electrons per molecule during its oxidation. Its high energy density makes methanol a suitable fuel for fuel cells. DMFC works at low temperature and is fed with a dilute aqueous solution of methanol in water. Since methanol is fed with large amount of water to the anode it also avoids complex humidification and thermal management problems associated to PEMFC. Because of

these qualities, DMFC is ideally electronic applications typically powered by electrochemical battery systems.

1.3. Issues of Direct Methanol Fuel Cell

Although the DMFC has the above advantages, the development of DMFC still faces bottlenecks, such as cathode flooding, catalyst performances, methanol crossover reduction, and carbon dioxide bubble removal, etc.

1.3.1. Methanol Crossover

In a DMFC, the fuel diffuses through membrane due to concentration gradient between anode and cathode. Methanol that crosses over reacts with oxygen at the cathode. Methanol brought directly from the anode to the cathode along with electrons results in an internal short circuiting and consequently a loss of current. Besides, the cathode catalyst, which is pure platinum, is fouled by methanol oxidations.

Crossover can be limited by using a low methanol concentration in the anode. A compromise should be found for the concentration. It should be small enough to reduce crossover as much as possible but also supply the anode catalytic layer with enough methanol to produce an acceptable current density. Heinzel et al. [2] reviewed several methods to reduce crossover and makes a summary for the general influence of different operating parameters on the crossover.

1.3.2. Carbon Dioxide Bubble

Most of the carbon dioxide (CO_2) formed during methanol oxidation is in the gas phase and has to be removed via the feed channel. CO_2 is formed in the anode catalytic layer and diffuses to the top of the gas diffusion layer. Yang et al. [3] have clearly investigated this phenomenon. After they reach a certain size, these bubbles are released into the methanol solution. The high concentration of bubbles makes them coalesce and form slugs. This results in a reduction of the methanol diffusion area. Consequently, the supply of methanol may not be sufficient to maintain a desired current density.

1.3.3. Flooding

Water production at the cathode side of a DMFC comes from three major mechanisms:

(i) electrochemically produced water

(ii) electro-osmotic drag

(iii) methanol crossover

When the water vapor pressure exceeds the saturation level (Fig. 1-1), condensation starts to form a tree-like liquid water percolation in the porous GDL. Liquid water further accumulates at the cathode surface. Water production at the cathode via methanol oxidation is according to:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \qquad (1\text{-}1)$$

Excessive water at the cathode can cause flooding i.e., liquid water accumulation at the cathode surface that prevents oxygen access to the

reaction sites and leads to reduced cell performance. Flooding is most likely near the cathode exit under high current density, high humidification, low temperature, and low flow rate conditions. Consequently, the used flow field has to discharge the liquid water properly. To prevent flooding, cathode airflow must be adequate to remove water at the rate that it arrives at the cathode surface. Therefore, typical cathode stoichiometries are significantly greater than that needed to supply adequate oxidant to the reaction site.

1.4. Literature Survey

Although external humidification is not needed in DMFC due to the liquid anode solution, prevention of cathode flooding is critical to ensure adequate performance. Flooding is of more concern for DMFC than PEMFC. In the following, we focus on the flow field structure for reduction flooding.

Zhukovsky [5] proposed the multi-parallel serpentine structure (Fig. 1-2). They simulated and experimented with 2, 3, 4, 5, 7 and 10 parallel-serpentine channels on a square plate to identify the best geometry of the maximum cell current. It demonstrates about 25% higher cell current for 3-channel configuration against 10-channel configuration in the high current regime with the same air flux. They also showed that the liquid water was moved by shear gas flow.

Nguyen [6] proposed the interdigitated cathode flow field to improve the flooding problem. Sugiura [7] showed that the performance of serpentine channel is higher than for parallel channels. It is because, for parallel channels, a channel is blocked by the product water, the

floodwater hardly moves in this location. They installed the water absorption layer (WAL) in the cathode channels composed of stainless steel (Fig. 1-3), with a porosity of 60%. The WAL can reduce flooding and raise the performance. However, the performance of serpentine channel is higher than the WAL type.

Maharudrayya [8] studied the pressure drop and the relative flow distribution in the Z-type and U-type parallel channel shown in Fig. 1-4. The experiment data shows that it is necessary to have very large header, a buffer zone in front of the channels, dimensions compared with channel dimensions. Therefore, the flow distribution is nearly uniform. Afterward, the U-type gives better performance than the Z-type at high flow rates. One should have a larger header-to-channel ratio to attain uniform or near-uniform flow distribution. A large header for a small fuel cell is not possible, and one has to design the header and the channel dimensions carefully.

Barreras [9] used planar laser induced fluorescence (PLIF) to visualize the flow pattern (Fig. 1-5) and numerically simulated to measure the velocity field in the plate channels. The experiment and model showed that the flow along the central channels is slow because the methanol is injected from the lateral entrance. The bipolar plate tested did not satisfy the requirements of homogeneous distribution of the flow. They showed that this effect could be alleviated by modifying the channel entrance to achieve the optimal distribution of the reactant gases inside the fuel cell.

Li et al. [10] summarized the flow fields as follows: 1) pin-type flow field, 2) series-parallel flow field, 3) serpentine flow field, 4) integrated

flow field, 5) interdigitated flow field, and 6) flow field designs made from metal sheets as shown in Fig. 1-6. More forms of flow field which are being developed. However, the main goal is to supply effective air and avoid flooding.

For the studies for micro PEMFC and DMFC, the MEMS technology and Si-based substrate have been widely used [11-15]. Hermann et al. [16, 17] experimentally studied and reviewed various types of materials, including non-porous graphite, coated metallic sheets, and polymer composites, etc. The benefits and drawbacks of each type of BP material are summarized in Table 1-2. Stainless steel (SS) is suitable for bipolar plate (BP) due to their relatively high strength, high chemical stability, low gas permeability, wide range of alloy choice, and applicability to mass production and low cost [18]. However, non-coated SS has the problem of a surface-insulating layer. A thin coating of a chemically stable and electrically conducting film is required before it can be used as bipolar plates.

Chen [19] designed a multi-sectional cathode flow field for small DMFC using MEMS technologies. The flow field can be divided into three sections: (I) parallel channels for air flow and water collection, (Π) buffer channels, and (Ш) water recycling channels and reservoir (Fig. 1-7). The dimensions of parallel channels are 500μm*500μm to generate capillary force. Beside, the air flow generates convective shear force. The above forces drive the product water into the buffer zone. The water recycling channels has significant capillary force with smaller dimensions and collects water finally.

In the experiments, Chen has observed homogeneous reactant

distribution and effective water transport along the parallel channels (Fig. 1-8). All the channels are not clogged by the condensed water even at a low air flow rate (10ml/min). The Si-based flow field was coated with gold to increase electric conductivity. The current density is 308 mA at 0.016V. The maximum current and power output are about 4.6 and 5.6 times better than the non-coated condition.

An advantage of the serpentine flow path is that any obstruction in the path, such as a water slug, will not block all active area downstream of the obstruction. In an obstructed serpentine channel, the reactant gas is forced to bypass the channel by flowing under the current collecting rib, through the porous backing layer, into the adjacent channels. Therefore, the net effect of the obstruction will be an increased pressure drop, without loss of active area. But in micro-DMFC, excessive pressure drop is not desired.

In a parallel flow flied an obstruction in one channel results in flow redistribution among the remaining channels and a dead zone downstream of the blockage. This dead zone will become deprived of reactants, and hence be inactive. Therefore, parallel operates with low pressure drop to such an extent that the whole system only consume small amount of energy. Therefore, parallel channels with capillarity assisted with capillary force to remove water; can be suitable for micro-DMFC.

1.5. Operation range for experimental parameters

1.5.1 Contact Pressure

W. Lee et al. [22] studied the effect of fuel cell pressures. The bolts

were employed to clamp the fuel cell with different torque. Because commercially available gas diffusion layers each with a different thickness and porosity, its porosity will decrease and the electrical conductivity will increase as the bolt torque increases. Three types of commercially available gas diffusion layers each with a different thickness were studied: TORAY, ELAT, CARBEL Series 100 gas diffusion media combined with TORAY. Among these GDLs, ELAT with 125 in. lb_f/ bolt ($\approx$8.75kg/cm^2) is optimum. A rang of suitable pressure is 100 to 150 in. lb_f/ bolt ($\approx$7 to 10.5 kg/cm^2).

1.5.2 Temperature

J. Ge [23] and N. Nakagawa [24] researched the effects of temperature on the performances of a direct methanol fuel cell. The performances were measured with various temperatures, and the results showed that performances increase as temperature increases. The optimum temperature is about 70℃. When the operating temperature exceeds 70℃, the performances do not increase with temperatures as a result of boiling of the solution. The negative effects of high temperature were followed: (a) small bubbles of the vapor formed in the catalyst layer and diffusion layer may decrease the reactive area, (b) the rate of methanol crossover and water transfer from anode to cathode through the membrane increases with temperature. A range of suitable temperature is room temperature to 70℃.

1.5.3 Methanol Concentration

The effects of methanol concentration were investigated carefully. J.

Ge [23] studied different methanol concentrations with the cell temperature at 70 ◦C. The best concentration is between 1 and 2M. J. Liu [25] also studied different methanol concentrations with room temperature. The limiting current density and the peak power density increase obviously when the methanol concentration was increased from 1 to 2M. Even though the operating temperature is low or high, the optimum methanol concentration is 2M. Unfortunately, the cell performance is not improved, when methanol concentrations exceeds 2M due to methanol crossover.

1.5.4 Methanol and Air Flow Rate

Cowart [26] made an experimental and modeling based investigation into the high stoichiometric flow rates required in direct methanol fuel cells in order to optimize their performance. Over-high flow rate may cause serious fuel crossover and waste too much auxiliary power. Over-low flow rate, on the anode side, the CO_2 bubbles clogging leads to methanol solution can not enter to gas diffusion layer; on the cathode side, excessive liquid water causes flooding. Cowart suggested that high methanol stoichiometries (λ_m>20) were necessary to achieve optimized performance. The air stoichiometries should not too low (suggest λ_{air}>5) so that flooding phenomenon may be improved.

1.6. Objectives

For miniature or micro fuel cells, the required auxiliary energy should be minimized. Hence, it is necessary to select a proper type of

flow field with a small pressure drop. The interdigitated flow field and the serpentine flow field tend to be blocked by the product water without an excessive pressure drop. The Si-based multi-sectional flow field [19] with capillary channels has demonstrated effective water removal. However, silicon plate is more fragile and must be coated with a metal lay for conductivity. In this paper, we employ stainless steel instead of silicon as the bipolar plate material. Finally, this flow field will be integrated into a single-cell micro-DMFC for performance test.

Table 1-1 Different Types of Fuel Cells [1]

	AFC	DMFC	MCFC	PAFC	PEMFC	SOFC
Electrolyte	Potassium hydroxide	Polymer membrane	Immobilised Liquid Molten Carbonate	Immobilised Liquid Phosphoric Acid	Ion Exchange Membrane	Ceramic
Operating Temperature	60-90°C	60-130°C	650°C	200°C	80°C	1,000°C
Efficiency	45-60%	40%	45-60%	35-40%	40-60%	50-65%
Typical Electrical Power	Up to 20 kW	< 10 kW	> 1 MW	> 50 kW	Up to 250 kW	> 200 kW
Possible Applications	Submarines, spacecraft	Portable applications	Power stations	Power stations	Vehicles, small stationary	Power stations

Table 1-2 Characteristics of different types of bipolar plates [16]

Graphite (machined)	Metal	Graphite composites
Benefits		
◆ Stability ◆ Low specific density ◆ Low contact resistance with electrodes ◆ High corrosion resistance	◆ High thermal conductivity ◆ Recyclable ◆ Consistency of product	◆ Lower contact resistance ◆ High corrosion resistance
Drawbacks		
◆ Expensive to machine ◆ Brittle ◆ Thick	◆ Needs coating ◆ Membrane poisoning ◆ Formation of insulating surface oxide	◆ Low bulk electrical conductivity

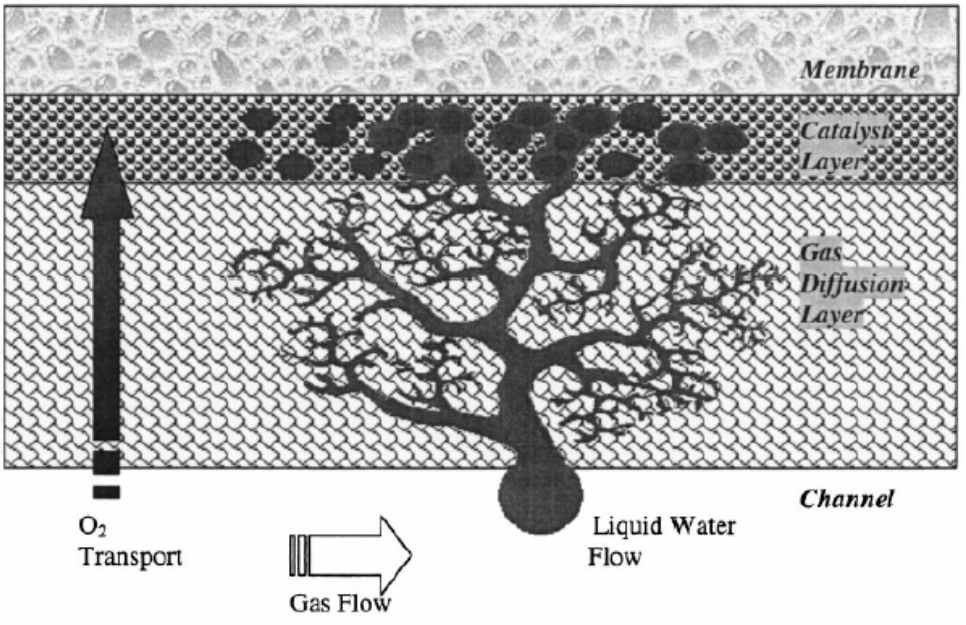


Fig. 1-1 Transport processes in hydrophobic GDL. [4]

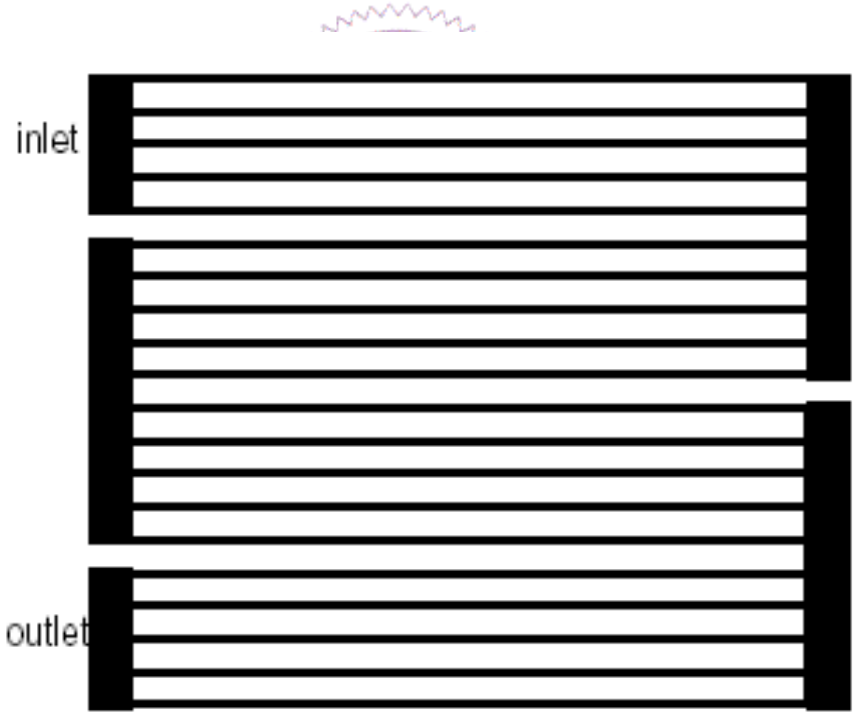


Fig. 1-2 Schematic illustration of serpentine configuration of n parallel gas channels in a PEFC. [5]

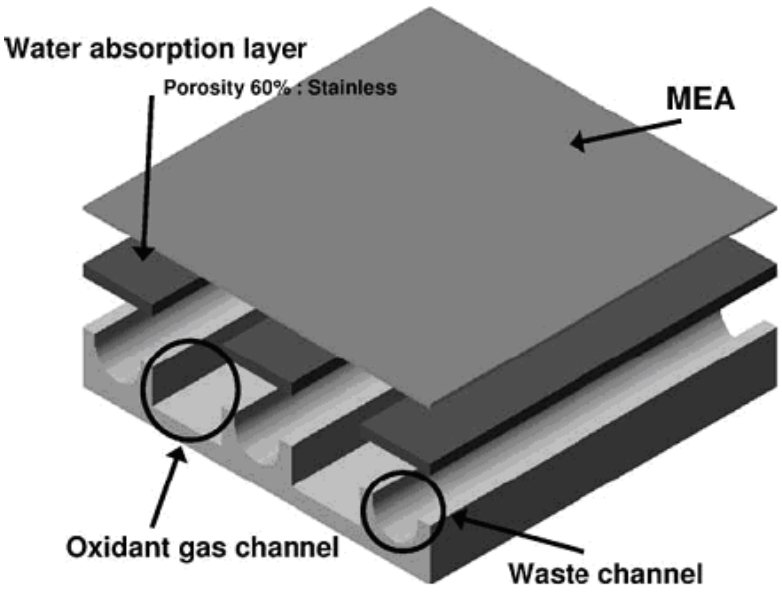


Fig. 1-3 shows a schematic diagram of the cathode separator with the water absorption layer and the waste channel. [7]

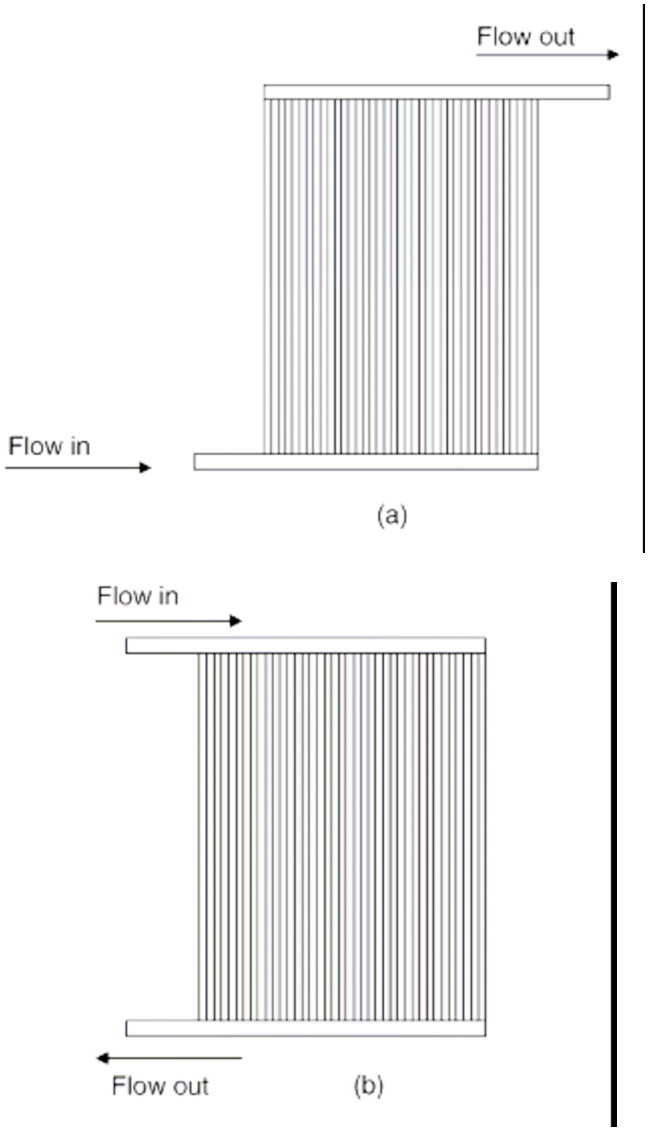


Fig. 1-4 (a) Z-type and (b) U-type parallel-channel flow configurations. [8]

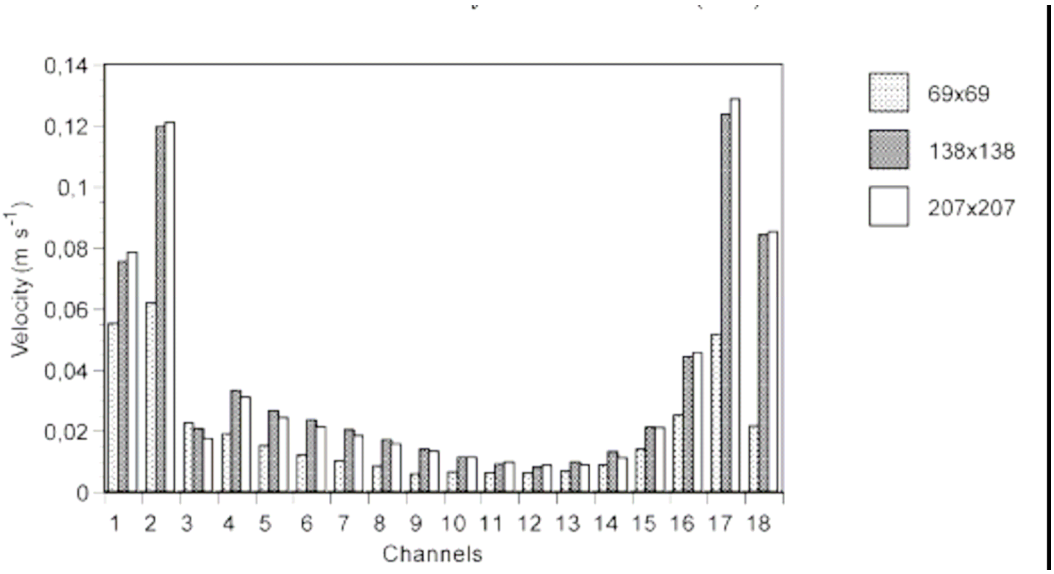


Fig. 1-5 (a) Calculation of velocity values of the flow [11]

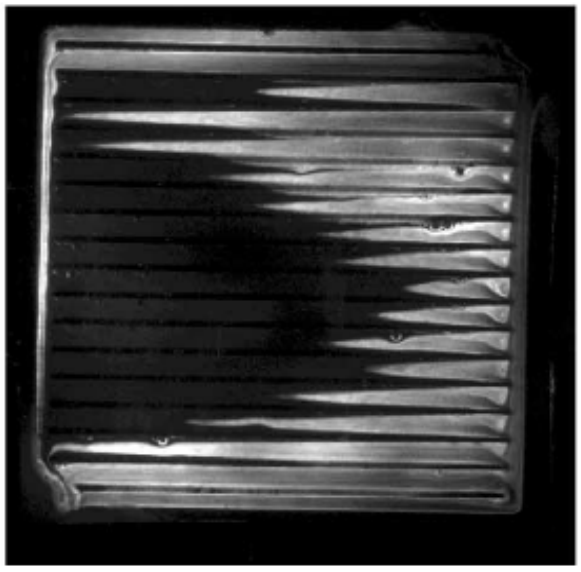
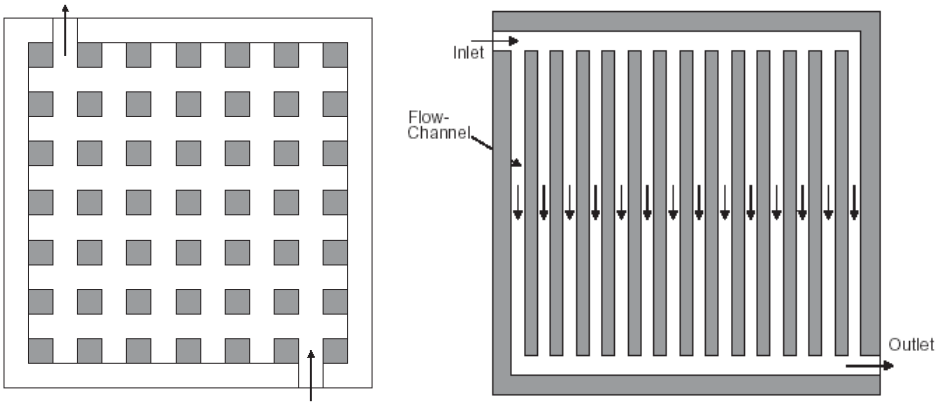
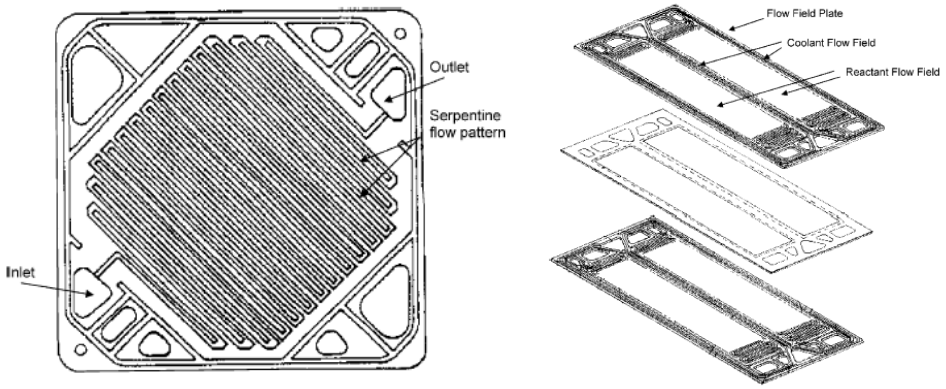


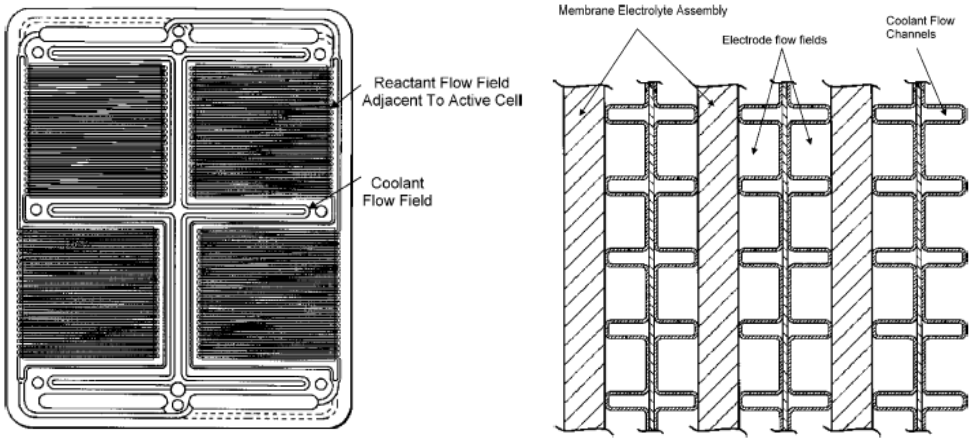
Fig. 1-5 (b) Visualization images [9]



(a) (b)



(c) (d)



(e) (f)

Fig. 1-6 Schematic illustration of (a)pin-type flow field, (b)series-parallelflow field, (c)serpentine flow field, (d)integrated flow field, (e) interdigitated flow field, and (f) flow field designs made from metal sheets [10]

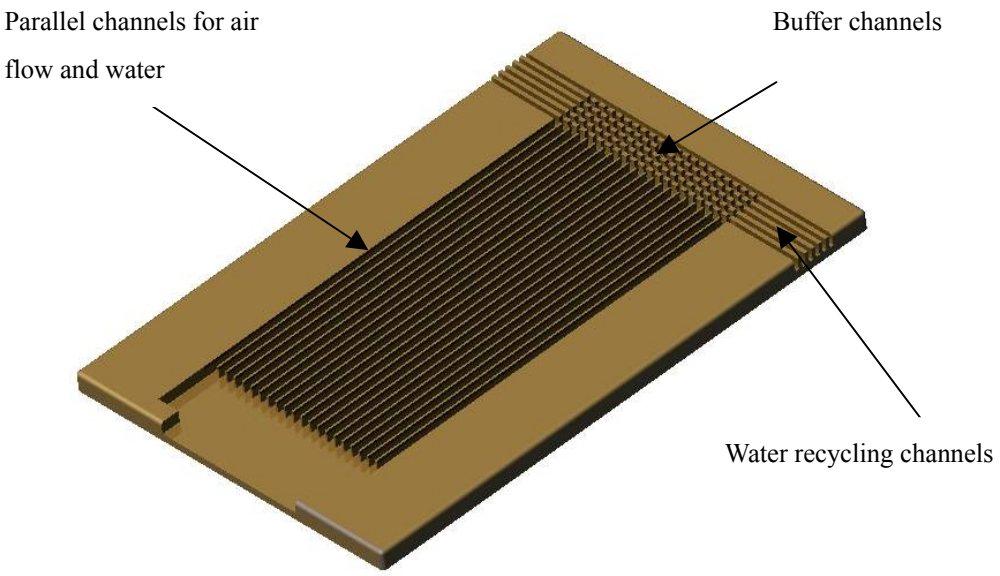


Fig. 1-7 Schematic illustration of multi-sectional cathode flow field [19]

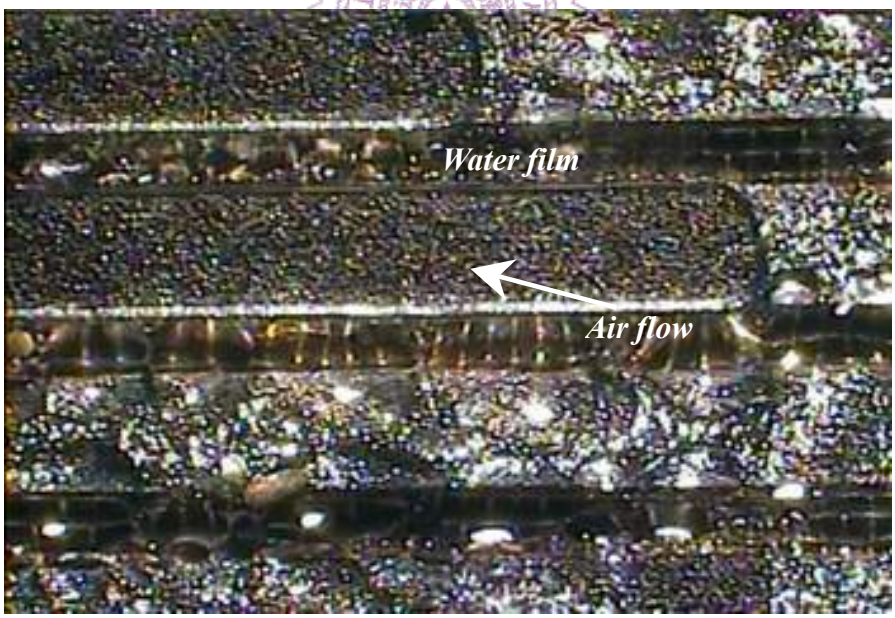


Fig. 1-8 Shape of liquid film for hydrophobic silicon chip [19]