CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

In the past, many power sources were generated from natural resources such as oil, coal and natural gas. But now, due to the consciousness of environmental protection and the crisis of depletion for natural resources, scientists and engineers make efforts in finding other inexpensive, environment-friendly and reliable power sources.

"Fuel Cell" is one of the new feasible power sources that meet these requirements. The history of fuel cells can be traced back to the nineteenth century. The following events marked the milestones of the development of fuel cells.

- In 1839, William Grove first discovered the principle of the fuel cell.
- In 1889, Ludwig Mond and Carl Langer first used the term "fuel cell".
- In 1959, Francis Bacon developed a 5KW alkaline fuel cell.
- In 1950s, General Electric invented proton exchange membrane fuel cells.
- In 1960s, NASA used fuel cells to power on-board during the Apollo space missions. This was the first "commercial" use of fuel cell.
- In 1980s, the US Navy applied fuel cells on submarines.

Basically, fuel cells can be classified into six main categories according to the nature of the electrolyte: 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 type requires particular fuels and materials and is suitable for different applications. The typical features of different fuel cells are listed in Table 1-1 [1].

Among them, DMFC is the most suitable for portable applications because of its low operation temperature and non-corrosive electrolyte. In addition, a DMFC does not have many of the fuel storage problems as for PEMFC since liquid methanol has a higher energy density than gaseous hydrogen. Unlike a battery, a DMFC does not require recharging and never runs down as long as fuel is supplied. Basically, a DMFC consists of two electrodes (porous anode and cathode) sandwiched around an electrolyte. Methanol is fed into the anode and oxygen into the cathode. The electrolyte serves as the bridge for the proton exchange. Activated by a catalyst, methanol molecules are decomposed into hydrogen protons and carbon dioxide with electrons generated. The protons pass through the electrolyte from the anode to the cathode and combine with oxygen to form water molecules, while the electrons pass through the external circuit to produce electrical power. Carbon dioxide released from the anode forms bubbles in the anode channels which are to be expelled in order not to block the channels. Fig. 1-1 [2] illustrates the electrochemical reactions of a DMFC.

Although the DMFC has several advantages, such high energy density, continuous power, environmentally safe, recyclable fuel cartridge, and no

capacity degradation with reuse and recharging, the development of DMFC still faces bottlenecks, such as cathode flooding, catalyst performance, methanol crossover reduction, and carbon dioxide bubble removal, etc. It can be seen that the development of fuel cells involves technology from many disciplines. The following sections will discuss on the cathode flooding and water recycling problems, which are the focus of this study.

1.2 Review on the Cathode Flow Field and Flooding

The flow field structure in fuel cells has to meet several requirements such as homogeneous fluid distribution, good current transport, product water removal, high conductivity, and chemical inertness. Each factor considerably influences the performance of fuel cells. However, we focus our discussion on the effects of flow field structure in PEMFC and DMFC for both macro and micro scales.

1.2.1 Macro Fuel Cells

Based on a simulation model considering heat management, water management and other transport parameters, in 1993 Nguyen and White [3] showed that when a PEMFC operates under high current (1A/cm^2), the potential loss caused by the membrane contributes a large proportion to the total loss of fuel cell stacks. In order to reduce this loss, reactants at the anode must be humidified. As for the cathode, if air, instead of pure oxygen, is used, humidification is also needed.

Afterwards, to improve the flooding problem at the cathode side

within the fuel cell, Nguyen [4] proposed a new design in 1996, named interdigitated flow field. It was designed to drain out the product liquid water and hence promote the reaction at the catalyst layer as a result of more effective diffusion of the oxidizer. In 1999, Kazim et al. [5] compared the performance of different flow fields shown in Fig. 1-2 using theoretical simulation. Their results suggested that the current density of the interdigitated flow field was about three times as much as that of parallel flow field, and with the maximum power density of interdigitated flow field being twice as much as that of the conventional one.

In 2001, Kulikovsky [6] performed a quasi-3D numerical simulation for three parallel meander-like flow fields. In their flow field at the cathode side a different pressure is provided, i.e., the inlet pressure in middle channel is lower than the other two channels. The results showed that the reduction of pressure in middle channel at the cathode side lead to a significant water vapor flux to this channel without degradation of cell performance, and the middle channel can serve as the liquid water collector. But their conclusions still cannot make a distinct explanation about the influence of this design on fuel cell performance.

In 2003, Tüber et al. [7] developed a computer algorithm to provide multiple ramified fluid network called the fractal flow field, as shown in Fig. 1-3. The main idea of this newly designed fractal flow field was to achieve a uniform fluid distribution and simultaneously minimize the auxiliary energy demand. Comparing the fractal flow field with the parallel and the serpentine flow fields for a DMFC (active area = 25 cm^2), it was shown that the serpentine flow field still had the most stable and

highest power output. This study indicated that there was no flooding problem at the cathode in the investigated fuel cells and the major disadvantages of parallel and fractal channels was due to anode channel blockage by carbon dioxide bubbles. But contradictorily, from another earlier work [8], based on a correlation found between cathode outlet temperature and output current, the liquid water in the cathode side has a greater influence on cell performance than the carbon dioxide bubbles in the anode side.

In general, the flow field can be classified into the following four types: parallel, interdigitated, serpentine, and multi-parallel serpentine flow fields, as shown in Fig. 1-4. Recently, the development of flow field design for macro fuel cells appear to merge toward to the interdigitated and the multi-parallel serpentine (meander-like) types, due to their better water removal and high power output. But these flow fields consume more auxiliary energy for their higher pressure drops than the parallel type. For micro fuel cells, however, the demand of auxiliary energy should be minimized.

1.2.2 Small and Micro Fuel Cells

In the past few years, the demand for portable electronic equipments activated the studies of micro fuel cells. In 2002, Maynard and Meyers [11] proposed two designs: a bipolar design using Si wafer for anode/cathode and a monolithic design incorporating anode/cathode onto a single Si wafer. Fig. 1-5 illustrates the top view of the bipolar plate design (a) and the monolithic design (b). Their experimental results suggested that many system-level issues must be considered in order to

achieve high performance. These issues included thermal management, air movement, fuel delivery, humidification control, water management, power load management, and system integration.

For the studies for micro PEMFC and DMFC, the MEMS technology and Si-based substrate have been widely used. For example, Kelley et al. [12], Yu et al. [13], Shah et al. [14], Cha et al. [15], and Lua et al. [16] all fabricated flow field structures using Si wafers. Other materials have also been used. For example, Müller et al. [17] and Zhang [18] used precision micromachining to pattern on stainless and brass. Shah et al. [14] used the micro-molding method to fabricate flow fields with Polydimethylsiloxane (PDMS). Hsieh et al. [19] used excimer laser micromachining to pattern on PMMA, followed by thin gold layer deposition. Cha [15] used the negative photo-resistance SU-8 as the structure layer and deposited a thin gold layer on the structure surface. Fig. 1-6 illustrates various archetypes of micro fuel cells.

In 2003, Cha et al. [15] theoretically and experimentally studied the transport phenomena associated with the gas flow through parallel micro-channels within PEMFCs. The theoretical model was generated and solved with computational fluid dynamics package (CFD-RC) and the channel widths varied from 5μm to 500μm. The experimental channel widths were 20μm and 100μm. Their results showed higher performance for smaller channels. Besides, the net pressure drop was relatively small for micro fuel cells compared to larger fuel cells, benefited by the short absolute length. Afterwards, Cha et al. [20] continued with numerical analysis for three types of flow patterns (interdigitated, serpentine and spiral interdigitated). The investigation ranged from micro (<100μm) to

macro (>500μm) scale. Their results reached to several conclusions. The serpentine channel might be unfavorable to micro-scale (<100μm) due to excessive pressure drop and flooding. The interdigitated channel exhibited excellent performance but as the scale decreased, flooding and pressure drop losses became more significant to degrade the performance. The spiral interdigitated channel showed similar features as the interdigitated channel under smaller channel dimension. Therefore, they concluded that for most flow patterns, the optimal scale occur at an intermediate channel dimension.

Mench et al. [21] proposed a pump-less micro DMFC design which was self-activated by electrochemical reactions. At its cathode side, air flow and circulation were provided by buoyancy forces, as shown in Fig. 1-7. Its principle was based upon natural convection and the fact that the exiting moist air is lighter than the entering dry air. Their calculations showed that under cell operation temperature of 80^{o}C, it was possible to have a stoichiometric ratio about 2 or even higher, depending on the channel length. And these stoichiometries are sufficient to sustain cathode operation. It should be noted that this conclusion was only based on calculations, rather than on experiments. Besides, the cell might suffer from flooding when operating at a temperature lower than 80^{o}C.

Motokawa et al. [22] in 2004 presented a new structure that the anodic and cathodic micro-channels arranged in a silicon plane with extremely small active area (0.018cm^{2}). Besides, the catalyst electrodes were directly fabricated on the bottom and sidewalls of micro-channel, as shown in Fig. 1-8. Therefore, their design offered simplicity in the stepwise integration of fuel cell components. Their result showed lower

voltage output compared with other macro DMFC unit. They attributed this to two reasons: (a) the low contact pressure between Nafion membrane and patterned silicon and therefore increase the ohmic resistance; (b) the non-optimum catalysts.

Yang et al. [23] in 2004 presented a visualization of water transport in a PEMFC. They designed a visualized flow field with gold-plated stainless channels and a cover with polycarbonate (PC) plate and the cross section of channel was 1 *mm* × 1 *mm* and 10 *cm* long. In their study, the inlet conditions were 70^{o}C, 2 atm, and the stoichiometry of fully humidified H_2/air fixed at 2 A/cm^2. They concluded that the occurrence of liquid water required an oversaturated stream and the process of liquid water formation can be summarized as follow (See Fig. 1-9): (1) liquid water ooze from the GDL and nucleate droplets on the surface; (2) droplets coalesce and touch the hydrophilic channel wall; (3) formation of annular liquid film structure and then water gradually migrate along channel to the outlet. They also concluded that the hydrophilic gas channel was the main mechanism of water removal, but if the liquid film became thicker, the gas channel might be blocked.

Akira et al. [24] in 2005 presented a highly water-proof coating of gas flow channel. They suggested that the surface of gas flow channels are perferably hydrophobic to prevent liquid water condenses on the surface. In their study, they used titanium as material and treated it with sand blasting followed by plasma polymerization. After treatment, the contact angle of water can increase about 40 degrees (Fig. 1-10). They concluded that highly water-proof was effective in the condition of lower flow rate.

1.3 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. For micro flow channels with closed ends, such as the interdigitated flow field, or long paths, such as the serpentine flow field, tend to be blocked by the condensed water and lead to an excessive pressure drop. In addition, for micro DMFC, recycling of the condensed water from the cathode back to the anode minimizes the need of water in the fuel solution feeding.

To achieve homogeneous reactant distribution, low pressure drop, and effective water recycling, a novel flow field design comprising a set of multi-sectional micro flow-field will be proposed in this study. The transport behavior of the condensed water in the micro-channels will be investigated. Different surface characteristics will be compared. 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	60-90ºC	60-130ºC	650ºC	200ºC	80ºC	1,000ºC
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

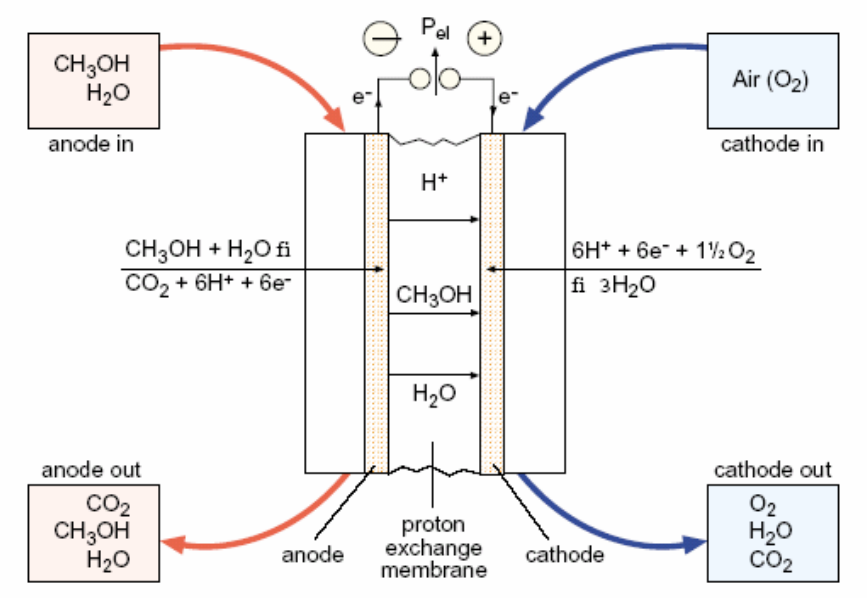


Fig. 1-1 Principle of DMFC [2]

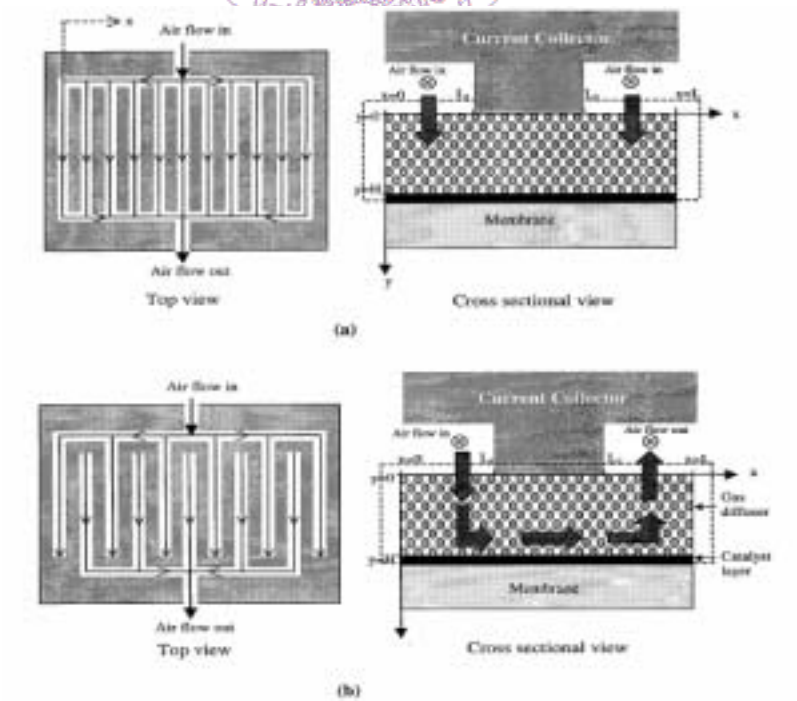


Fig. 1-2 Schematic diagram of gas flow direction with (a) parallel and (b) interdigitated flow fields [3]

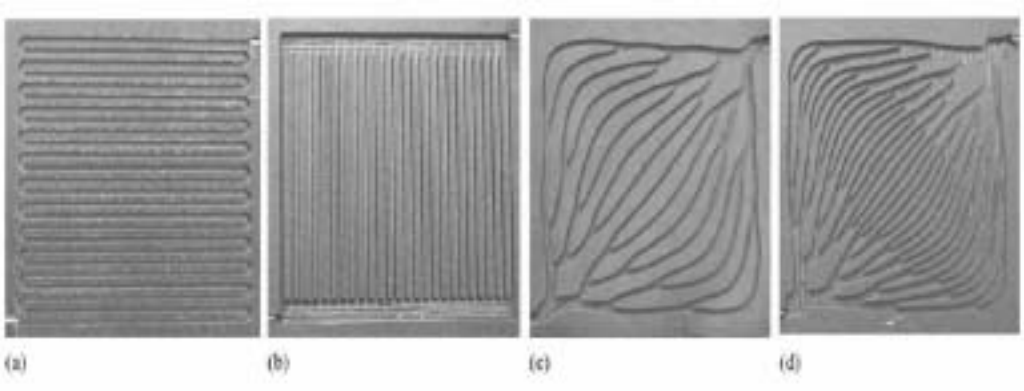
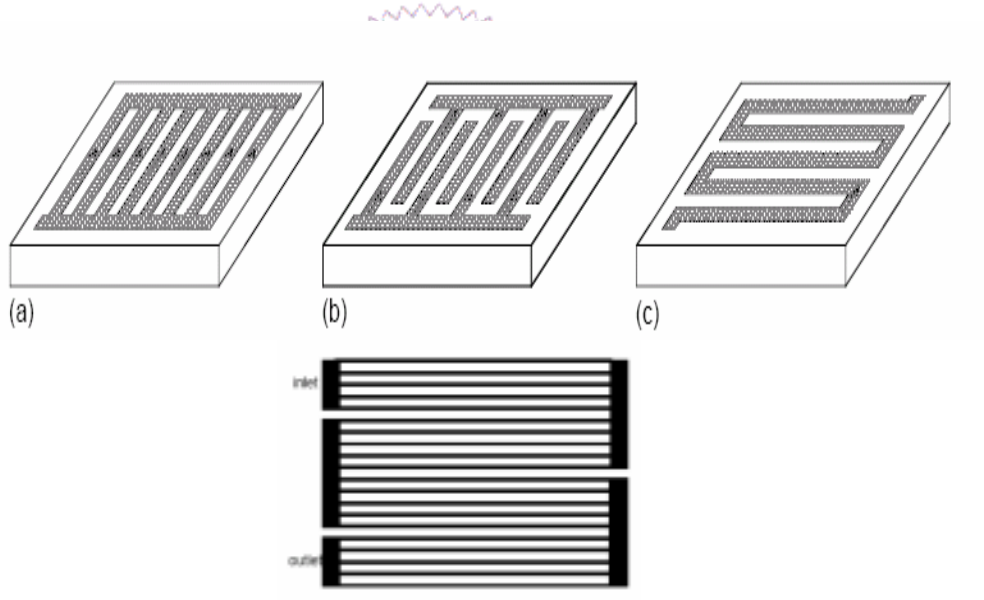


Fig. 1-3 Various flow fields for DMFC [7]



(d)

Fig. 1-4 Different types of flow fields: (a) parallel ; (b) interdigitated ; (c) serpentine ; (d) multi-parallel serpentine [9-10]

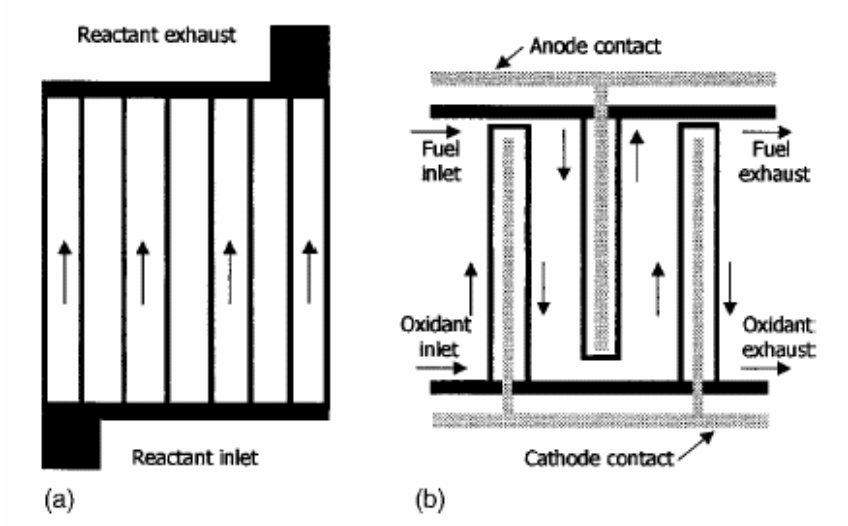


Fig. 1-5 Top view of (a) bipolar plate design and (b) monolithic design [11]

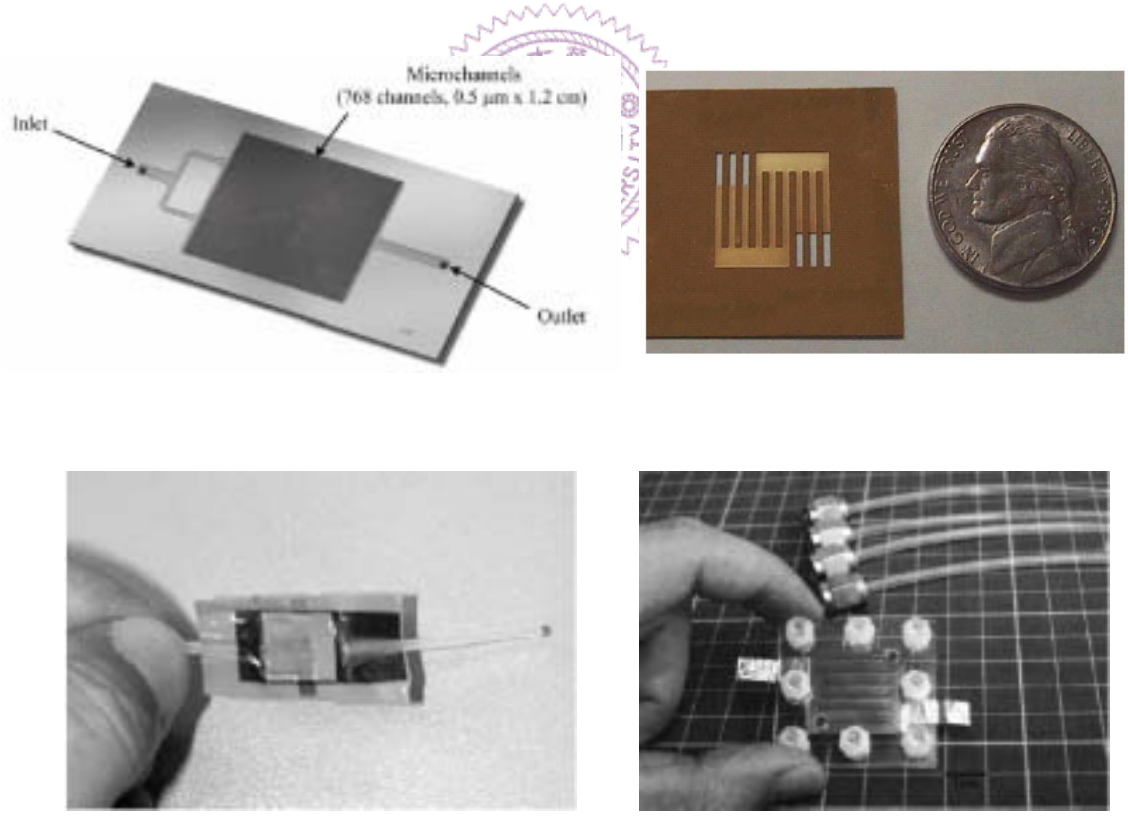


Fig. 1-6 Different archetypes of micro fuel cells [14、16、17、19]

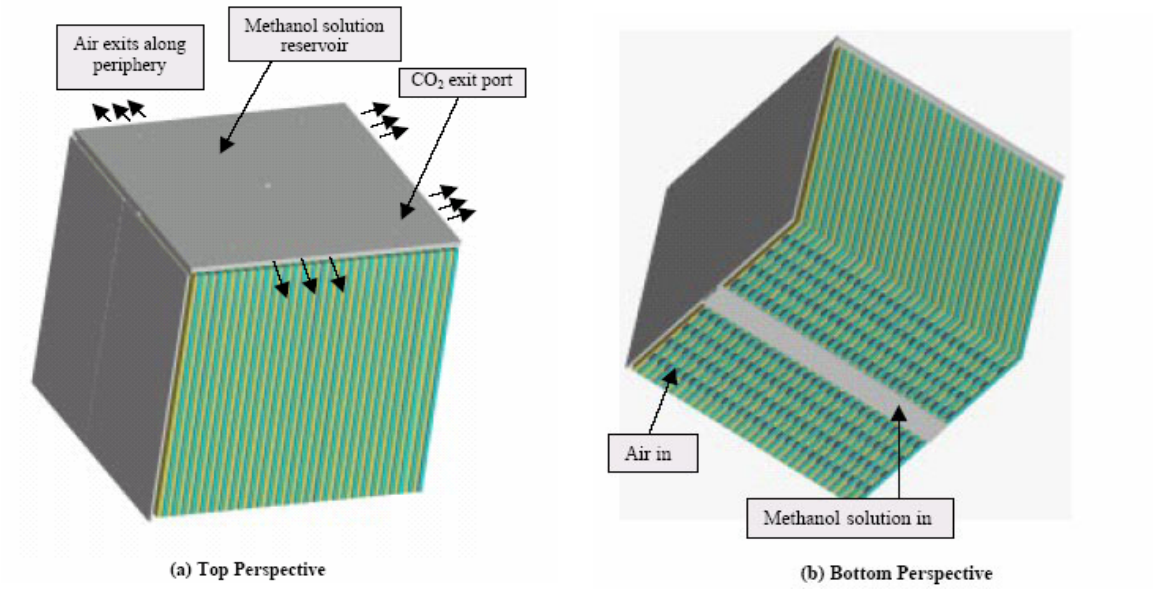


Fig. 1-7 Schematic of a $1cm^3$ pump-less DMFC [21]

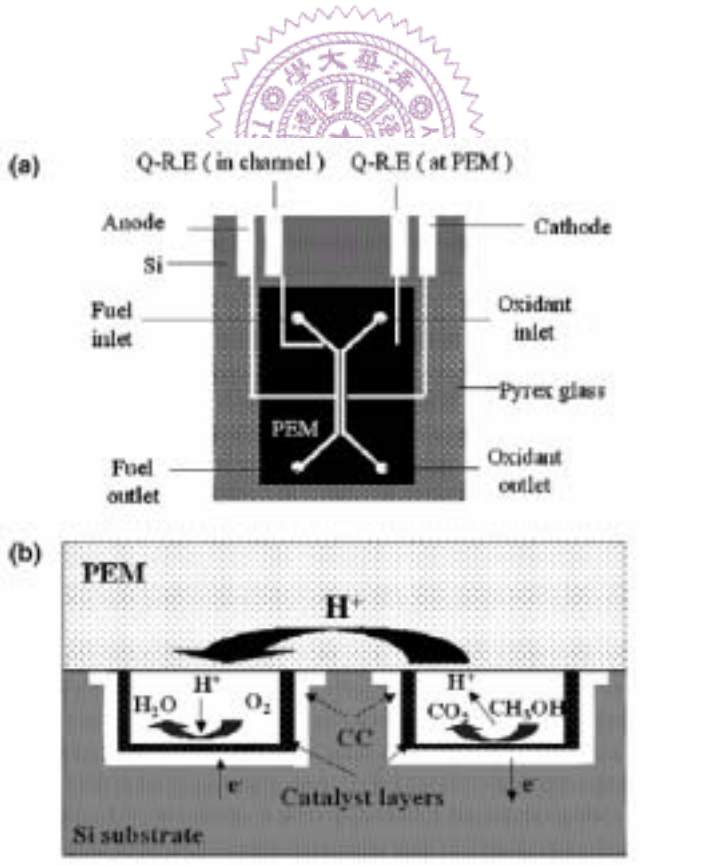


Fig. 1-8 Schematic of novel structure for micro DMFC [22]

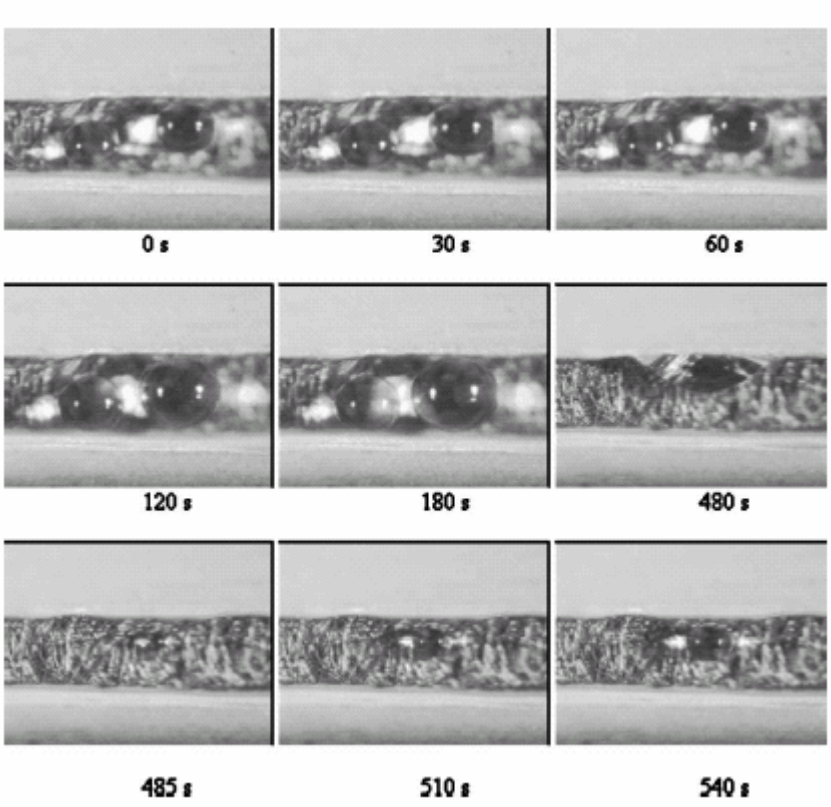


Fig. 1-9 Schematic of the dynamic process of water droplets in a cathode-side gas channel for a PEMFC [23]

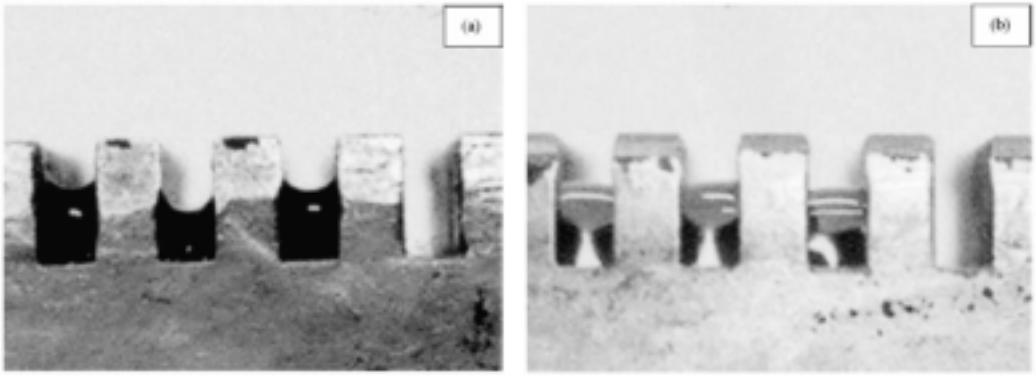


Fig. 1-10 Schematic of water droplets in gas flow channels of PEMFC [24] (a) before treatment; (b)after hydrophobic treatment