1. Introduction

1.1 Background and Motivation

In 1838, W. R. Grove [1] developed a "wet-cell battery" called "Grove Cell". It used a platinum electrode immersed in nitric acid and a zinc electrode in zinc sulfate to generate about 12 amps of current at about 1.8 volts. In 1960s, fuel cell studies were actively performed, because NASA used fuel cells as the electrical power in space shuttles. Today, there are many types of fuel cells, defined according to different electrolytes, such as AFC (Alkaline Fuel Cell), PAFC (Phosphoric Acid Fuel Cell), MCFC (Molten Carbonate Fuel Cell), SOFC (Solid Oxide Fuel Cell), and PEMFC (Proton Exchange Membrane Fuel cell).

A fuel cell generates electricity by chemical reactions. Each fuel cell has a positive and a negative electrode respectively called the anode and cathode. The reactions that produce electricity take place at the electrodes. It also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which enhances the reactions at the electrodes.

Compared with traditional power sources, fuel cells have higher power and energy density, higher efficiency, relatively lower or even no pollution emission, lower working temperature and noise level, and more rapid response to changes in the power demand.

Direct methanol fuel cell (DMFC) using PEM as electrolyte is one kind of Proton Exchange Membrane Fuel Cell (PEMFC). But the direct methanol fuel cells appear more promising than hydrogen-fueled polymer electrolyte fuel cells for portable devices. Because methanol is directly oxidized at the surface of catalytic electrodes to generate electricity, DMFC has a high energy density and is much easier to store and carry without auxiliary devices for intermediate fuel processing and fuel reforming steps. Furthermore, byproducts of DMFC are ecologically harmless CO_2 and water. These are the reasons why the DMFC system has been considered as a potential substitution to traditional batteries for powering various micro-systems or portable devices. Fig. 1.1 illustrates a schematic DMFC system.

However, development of the DMFC faces many challenges. The gas byproduct (CO_2 gas bubbles) generated at the anode is one of such problems, not only in large scale but also in microscale. Because if the CO_2 bubbles accumulate on the catalyst layer the chemical reactions will be barricaded to cause efficiency degrade of the fuel cell. The CO_2 separator is needed to solve this problem. Generally speaking, the working principle of CO_2 separator is dividing carbon dioxide and unconsumed methanol by their different physical (such as density, boiling point, buoyancy…etc.) or chemical characteristics. In miniaturizing DMFC, the CO_2 bubbles problem becomes more serious. Because in microscale, the surface tension is so strong that bubbles are trapped easily, and the Renolds number is too low to wash CO_2 bubbles away. New technology for solving CO_2 bubbles problem in micro direct fuel cell (µDMFC) for portable device should be developed. This problem is one of the major barriers to be solved for the performance improvement of µDMFC.

The reaction on the anode and cathode of a DMFC are respectively

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

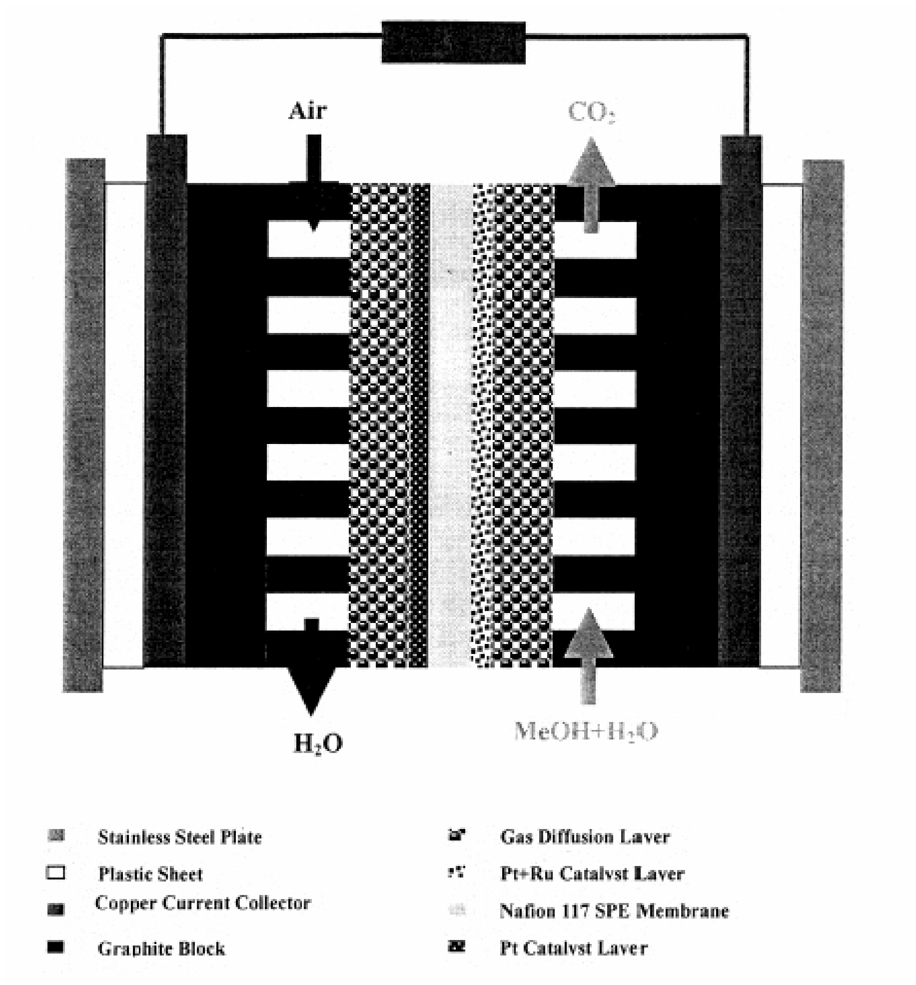

Fig. 1.1 DMFC system schematic [2]

1.2 Literature Survey on Bubble Separators

The principle of the DMFC has been known since 1922. Until now many separators for DMFC to exhaust CO_2 gas have been developed. However, most of the designs in papers, patents, or even in commercial products are used for macro-DMFC. For example, heat exchanger [3], gas scrubber [4], or filter element [5], etc. have been used to deal with the CO_2 bubble problem.

For microscale bubble separation, Tsai and Lin [6] developed a filter to separate gas bubbles based on the fact that the surface energy of a gas bubble increases when it is forced into a narrower channel. Fig. 1.2 shows the experimental result. The fine liquid microchannels have a higher threshold pressure than the gas bubble channels such that gas bubbles pass through the latter ones without entering the former. Although this was not aimed for μDMFC, but for micro-mixer separator, it provides a concept for separating liquid and gas in microstructures.

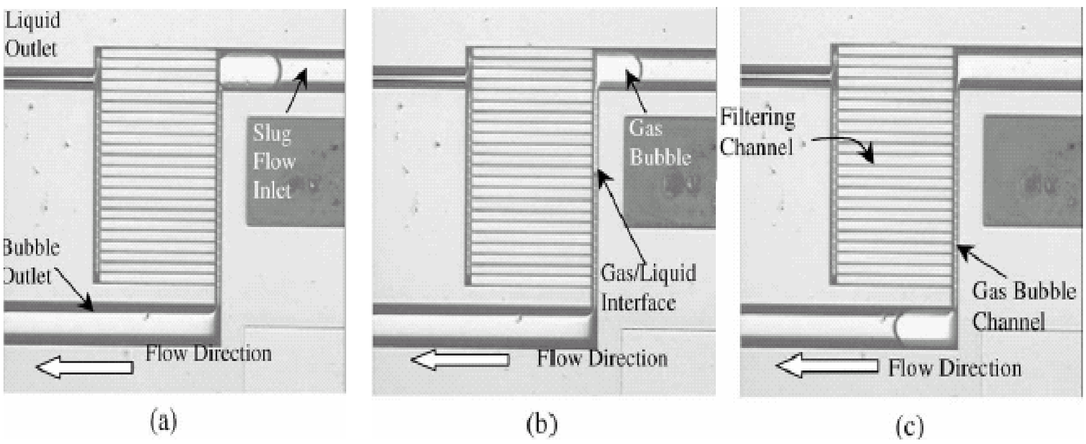

Fig. 1.2 Sequential pictures of the gas bubble filter in operation actuated by the nozzle-diffuser bubble pump: (a) gas bubble reaching the filter; (b) bubble filtered into the gas bubble channel; (c) bubble separation from liquid outlet [6].

Meng, et al.[7] proposed a breathing mechanism modified from biomedical application. The breathing mechanism is shown in Fig. 1.3. Most of the inner surface of the channel is hydrophilic, which incidentally, is necessary for effective fuel flow with minimum flow drag. Only the breathing holes and their immediate vicinity are made hydrophobic, allowing these areas as landing sites for gas bubbles. The inner walls of the breathing holes also need to be hydrophobic to prevent liquid leakage under fluctuations and accidental pressure buildup. Obviously, two essential features are important in the design, one is that gas bubbles should preferentially attach to the breathing spot and the other is that only gas could pass the breathing hole without liquid leakage. Their experimental result is shown in Fig. 1.4. The bubbles in the flow showed a tendency to attach onto hydrophobic spots instead of other hydrophilic areas. The bubbles, produced by sodium bicarbonate solution and weak sulfuric acid, were breathed out through the 50μm diameter holes in about twenty-five seconds.

However, the pressure it could withstand was limited because of the difficulties in the fabrication of microscale breathing holes with uniform hydrophobic coating and mechanically robust structure. Leakage cannot be prevented at all for high-concentration fuels, because the breathing holes are wet much easier by the concentrated fuel with lower surface tension and smaller contact angle.

Recently, Meng, el al. [8] proposed a breather which use hydrophobic membrane (shown in Fig.1.6) instead of hydrophobic micro holes on silicon chip. Shown in Fig.1.5 is their test sample which integrates microchannels, nano-porous hydrophobic membrane, and an on-chip bubble intake mechanism. It was shown that nano-porous membrane achieves successful gas separation from methanol fuel with a concentration as high as 10 M and with pressure tolerance as high as 35 psi without leakage.

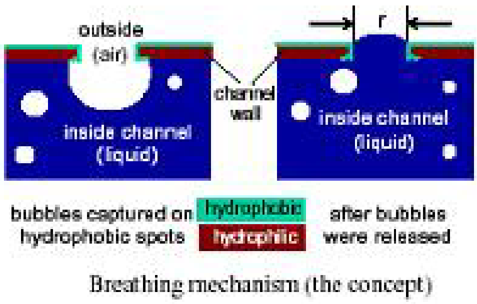

Fig. 1.3 Breathing mechanism [7]

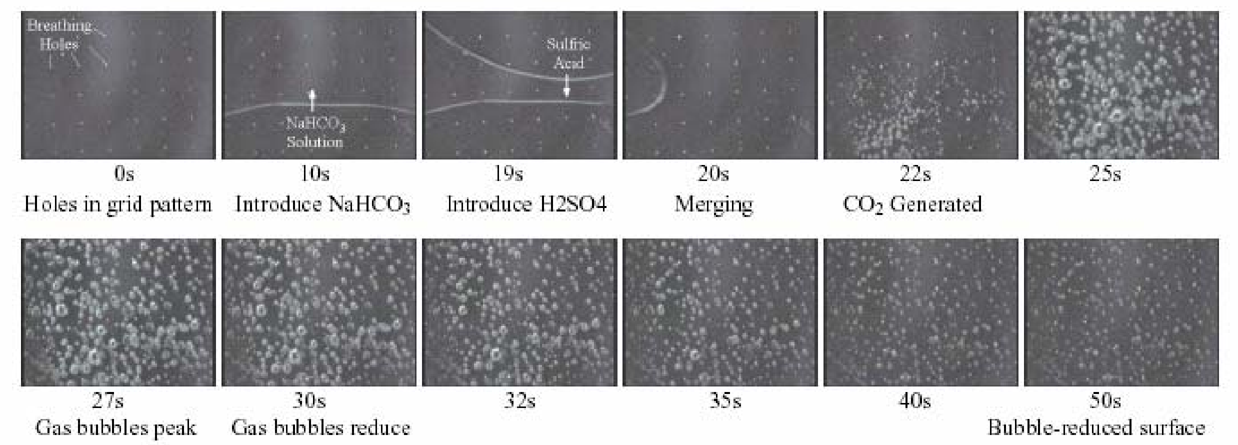

Fig. 1.4 Experiment result of the breathing process [7]

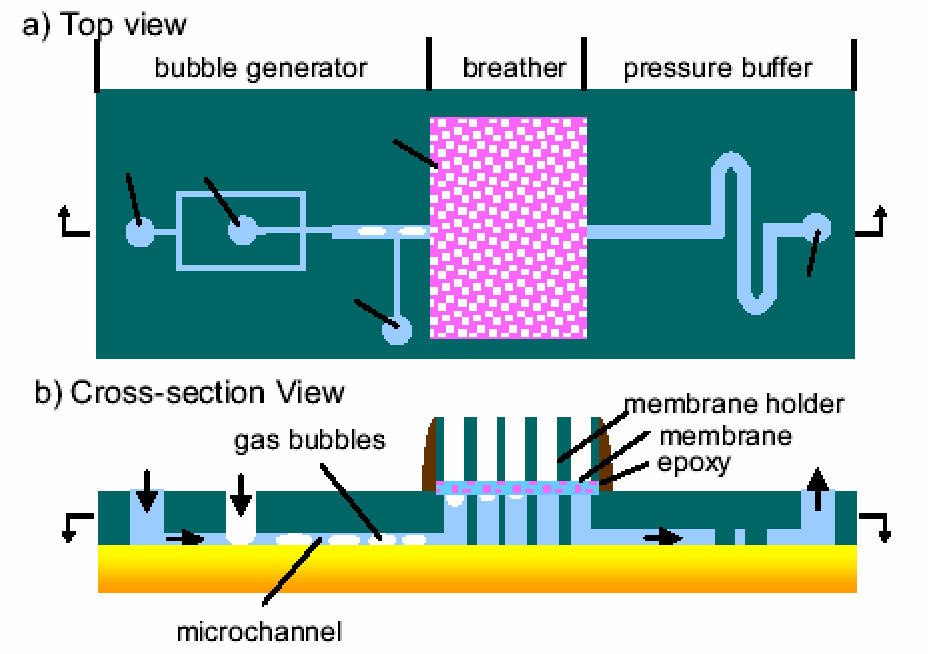

Fig. 1.5 Sandwiched membrane breather [8]

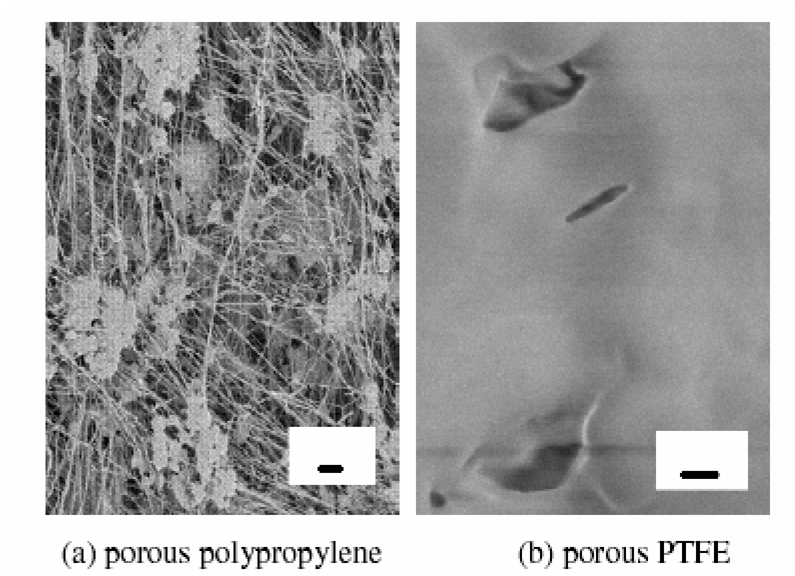

Fig. 1.6 SEM pictures of porous membranes' surfaces [8]

Another kind of separator for μDMFC is shown in Fig. 1.7 [9,10], in which two chips are bonded together into a single micro fluidic system. One chip is the gas separation plate and the other is the liquid separation plate. The microchannel used to connect components and the holes on the gas separation plate are fabricated by DRIE (Deep Reaction Ion Etching). Additionally, electrostatic micro pumps and micro valves, and the liquid separation membrane can be made on the liquid separation plate. On the larger holes on the gas separator plate is coated the hydrophobic material, while on the smaller holes coated the hydrophilic material in order to recycle the fuel. The gas passing through the gas holes is collected and exhausted. Besides, the hydrophobic material is coated on the relatively large holes on the gas separation plate. The separator piece will then be connected to the μDMFC system.

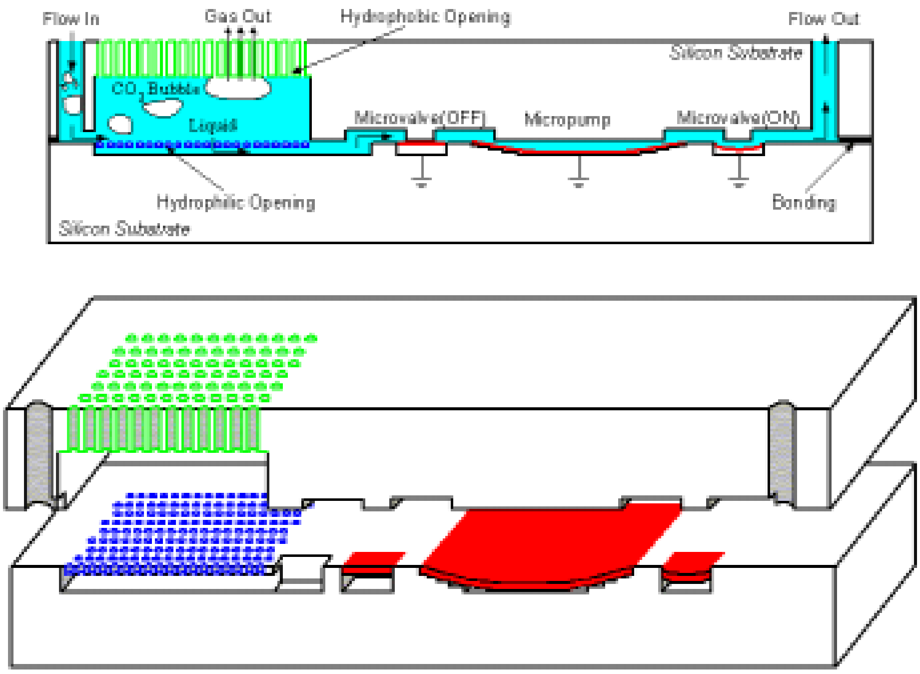

Fig. 1.7 The separator for μDMFC [9,10]

1.3 Objective

The μDMFC is a promising portable micro power source because of its potential for high energy capacity. However, development of μDMFC faces new challenges not associated with its macroscale counterpart. Among them is that the byproduct CO_2 bubbles at the anode side at more difficult to remove due to excessive surface tension. Furthermore, an ideal bubble separator for a portable μDMFC should be able to exhaust bubbles in more than one direction with additional fuel recycle capability. In this paper, we propose a design of micro bubble separator that meets these requirements. The principle for bubble removal is by capillary force, caused by making the surface hydrophobic or hydrophilic at proper parts of the microstructures.