HEAT AND MASS TRANSFER AND TWO PHASE FLOW IN HYDROGEN PROTON EXCHANGE MEMBRANE FUEL CELLS AND DIRECT METHANOL FUEL CELLS

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ABSTRACT

Fuel cells are related to a number of scientific and engineering disciplines, which include electrochemistry, catalysis, membrane science and engineering, heat and mass transfer, thermodynamics and so on. Several thermophysical phenomena such as heat transfer, multicomponent transport and two phase flow play significant roles in hydrogen proton exchange membrane fuel cells and direct methanol fuel cells based on solid polymer electrolyte membrane. Some coupled thermophysical issues are bottleneck in process of scale-up of direct methanol fuel cells and hydrogen proton exchange membrane fuel cells. In present paper, experimental results of visualization of condensed water in fuel cell cathode microchannels are presented. The equivalent diameter of the rectangular channel is 0.8mm. Water droplets from the order of 0.08mm to 0.8mm were observed from several different locations in the channels. Several important problems, such as generation and change characteristics of water droplet and gas bubble, two phase flow under chemical reaction conditions, mass transfer enhancement of oxygen in the cathode porous media layer, heat transfer enhancement and high efficiency cooling system of proton exchange membrane fuel cells stack, etc., are discussed.

Keywords: Direct methanol fuel cells; Proton exchange membrane fuel cells; Heat and mass transfer; Two phase flow; Microchannels.

INTRODUCTION

A fuel cell is a device that can continuously convert the chemical energy of the fuel and the oxidant directly into electrical energy by electrochemical reaction.

The research of fuel cells began with a report of a British lawyer and scientist, William Robert Grove, in 1839. That fuel cell was called "gas battery" by Grove at that time. In 1889, chemists Ludwig Mond and Charles Langer first adopted the term "fuel cell" when they attempted to build the first practical device of fuel cell using industrial coal gas and air. Development of fuel cells was slow in their initial decades, but fuel cells had gained extensive attention since 1950s. In 1955, chemist Willard Thomas Groubb of U.S General Electric Company applied sulphonated polystyrene ion exchange membrane as electrolyte of fuel cells. Another chemist of General Electric Company, Leonard Niedrach, invented a method of depositing platinum on to this membrane in 1958. Those fuel cells using solid polymer membrane as electrolyte and using platinum as catalyst were called "Grubb-Niedrach Fuel Cell" at that time. This was considered the beginning of PEMFC. First applied low temperature polymer electrolyte membrane fuel cells were developed by General Electric Company in the 1960's for NASA's Gemini space program. At that time, the PEMFC acted as auxiliary power, and by-product of fuel cell reaction is drinkable pure water for astronauts.

The proton exchange membrane fuel cell (PEMFC) was called firstly the ion exchange membrane fuel cell (IEMFC). It was ever called the solid polymer electrolyte fuel cell (SPEFC), polymer electrolyte fuel cell (PEFC), solid polymer fuel cell (SPFC) and polymer electrolyte membrane fuel cell (PEMFC), etc. The proton exchange membrane fuel cell is the name used popularly at present. Whatever name is used, this kind of fuel cells uses solid electrolyte membranes as its electrolyte. The membrane is not only an electronic insulator, but also excellent conductors of hydrogen ion (proton). At present, PEMFCs still use oxygen as oxidant and use hydrogen or methanol as fuels in general. According to different fuels used, PEMFC can be classified as three types: hydrogen proton exchange membrane fuel cells (H_2 PEMFCs), methanol reforming fuel cells (MRFCs), direct methanol fuel cells (DMFCs). Earlier DMFC did not belong to PEMFC because alkaline or acidic

liquid were used as electrolyte in the DMFC. The performance of the DMFC using such electrolyte is quite poor because the activity of electro-catalyzed oxidation of methanol is very low. Since 1990s, DMFC has gradually become a new member of PEMFC as solid polymer electrolyte membrane was adopted.

Hydrogen PEMFCs and DMFCs generate electricity with high efficiency and low emission (pollution). In recent years, the development and commercialization of hydrogen PEMFCs and DMFCs for primary or auxiliary power for stationary, mobile, portable, and urban transportation systems have received increasing attention (Kordesch and Simader, 1996; Dresselhaus et al., 2001). There are many thermophysical issues in the research and development field of H_2 PEMFC and DMFC (Djilali et al., 2002; Guo et al., 2001, 2002).

In this paper, we discussed several thermophysical phenomena and their roles in development of hydrogen proton exchange membrane fuel cells and direct methanol fuel cells based on solid polymer electrolyte membrane. We also presented our experimental results related visualization of condensed water and two phase flow in fuel cell cathode microchannels.

GENERATION AND CHANGE CHARACTERISTICS OF WATER DROPLETS AND GAS BUBBLES

In H_2 PEMFCs and DMFCs, liquid droplet emergence and gas bubble generation seem to be similar to the condensation and boiling in traditional thermophysics. But the mechanism is quite different; those phenomena are the result of chemical reactions.

At the anode of a H_2 PEMFC, hydrogen is consumed; electrons are released to the anode and transported via external circuit. The producing hydrogen ions (protons) are transported to the cathode side through a polymer electrolyte membrane. Oxygen in the air combines with electrons and protons to produce water at the cathode.

$$\text{Anode reaction: } H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

$$\text{Cathode reaction: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2)$$

$$\text{Overall reaction: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (3)$$

The DMFC can use vapor or liquid methanol as fuel and undergo electrochemical reactions as follows:

$$\text{Anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (4)$$

$$\text{Cathode: } \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (5)$$

$$\text{Overall: } CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2 \quad (6)$$

In our experiment, appearance, growth and drop out of water droplets in a vertical cathode channels of a H_2 PEMFC with $5cm^2$ active area were observed under reaction condition. The equivalent diameter of the rectangular channel is 0.8mm. Water droplets from the order of 0.08mm to 0.8mm were observed from different locations in the channel (see Fig. 1). Our membrane electrode assembly (MEA) was based on Nafion 112 membrane and carbon papers. Both anode and cathode catalyst are platinum with loading of $0.4mg/cm^2$. Cell temperature was kept constant of 55℃. The experimental results indicated that liquid water easily form at relative low temperature, high inlet relative humidity, low flow rate and high current density. Water droplets formation was not observed when flow rate of dry oxygen was above 30ml/min.

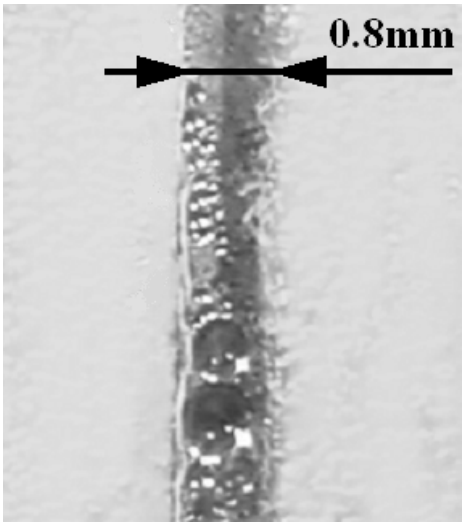


Fig. 1 Water droplets in cathode microchannel of a PEMFC

Characteristics of water droplets appearance and growth in the cathode of H_2 PEMFCs and gas bubbles generating, growing and escaping in the anode of liquid feed DMFCs affect the multiphase flow in channels of fuel cell. Gas bubbles behavior influence mass transfer resistance in the anode of DMFC. Behavior of water droplets also relate to cathode flooding. Investigations on these essential problems not only will be of benefit to optimization of fuel cell design, but also broaden the research field of thermophysics.

MULTIPHASE FLOW UNDER CHEMICAL REACTION CONDITIONS

Multiphase flow in channels of the fuel cell takes place under chemical reaction conditions, moreover, the electrochemical reaction and multiphase flow interact each other.

In the liquid feed DMFC anode, there is the aqueous methanol solution (reactant) and the carbon dioxide bubble (product of chemical reaction of fuel cell). Carbon dioxide dissolvability in liquid water-methanol mixtures is fairly low. The presence of a lot of carbon dioxide bubbles reduces the flow area and penetration of reactants to catalyst layer. Scott and his colleagues (1999) observed the two phase flow in channels of a DMFC with either carbon paper or carbon cloth membrane electrode assembly (MEA), they found that comparing with the case of carbon cloth was used, large carbon dioxide slugs were formed relative easily when the carbon paper MEA was adopted. Those large gas slugs blocked the channels and led a rapid deterioration of the cell electrical performance. Argyropoulos et al. (1999) indicated that a high inlet flow rate is beneficial and effective for removing carbon dioxide bubbles and slugs from interior of the fuel cell. Carbon dioxides bubbles accumulate along the side-walls of the channels (Sundmacher and Scott, 1999). The gas bubbles were not only generated on the backing layer surface, which revealed between the flow bed channels, but also emerged under the ribs (Schultz et al., 2001).

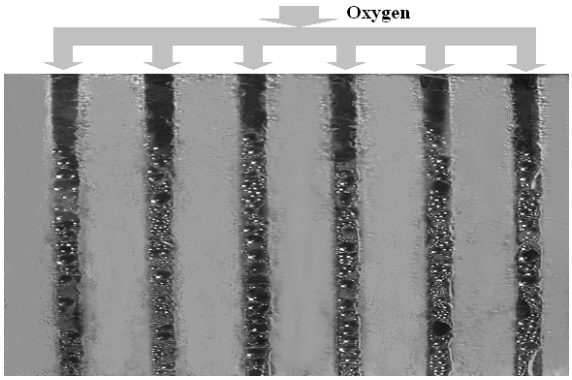
In hydrogen proton exchange membrane fuel cells or direct methanol fuel cells, when the generated water is not removed from cathode at a sufficient flow rate, the accumulation of water will result in rise of partial pressure of water vapor. If this pressure exceeds the saturated vapor pressure, liquid water is formed, cathode flooding may result and the oxygen gas transport is blocked. In the design and operation of H_2 PEMFCs and DMFCs, the research of two-phase flow occurred in microchannels is quite important issue to avoid flooding in the cathode (Wang et al., 2001; He et al., 2000; You et al., 2002).

Our experimental results also showed that the accumulation of liquid water lead to oxygen/water two phase flow in PEMFC cathode channels (see Fig. 2). Large water droplets blocked the channels and induced increase of oxygen transfer resistance

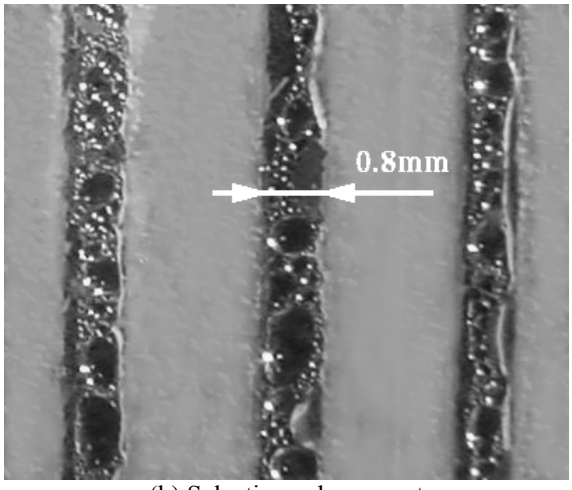
Now, the equivalent diameter of channels in the H_2 PEMFC and DMFC is about 1-2 mm. For improvement of specific energy of fuel cells, this magnitude will decrease to order of 0.1mm (microchannels) in the coming decades. The fuel cell is considered to be one of the most important application areas of microchannels technology. Multiphase flow and heat transfer in microchannels under electrochemical reaction conditions are basic problems for design of next generation fuel cells.

MASS TRANSFER ENHANCEMENT OF OXYGEN IN THE CATHODE POROUS MEDIA LAYER

In a PEMFC or DMFC with conventional (parallel or serpentine) flow bed, the flow through porous media backing layer to reaction layer is governed by diffusion in nature. In real PEMFC and DMFC stack, it is not pure oxygen, but air input into cathode channels. In cathode catalyst layer, concentration of nitrogen and water (product of reaction) increases, while concentration of oxygen decreases due to chemical reaction. The relative high concentration of nitrogen is a barrier, which resists oxygen transport through porous media to cathode catalyst layer.



(a) Visualization of cathode flow



(b) Selective enlargement

Fig. 2 Two phase flow in cathode microchannels of a H_2 / O_2 PEMFC

In order to enhance mass transfer of the reactant, a different flow bed, so called interdigitated flow channels, was proposed. In this particular design, two channels, which are beside each reactant distributor / current collector, have a dead-end. So the reactants are forced to flow through porous media layer. This flow bed design facilitates the removal of inert nitrogen molecules, which accumulate in the porous media layer and produce a diffusion resistance. Many researchers indicated that forced convection could substantially improve mass transport, which brings oxygen to reach cathode reaction sites (Wood, 1998).

Arico et al. (2000) investigated influence of serpentine flow field and interdigitated flow field on the performance of a direct methanol fuel cell. They found that a significantly better performance was achieved in the high current density region with the interdigitated flow field. They observed maximum current density of 2.6 A/cm^2 at short circuit condition.

Um and Wang (2000) researched conventional (parallel) and interdigitated flow fields on PEMFC cathode. By the aid of three-dimensional computational analysis, they found that the oxygen concentration contours are symmetric because both two channels beside the current collector have the same flow direction in the parallel (conventional) flow field. The driving force of oxygen transportation in porous media is diffusion, so the oxygen concentration in backing layer is quite low. In the interdigitated flow field, air flows into the channel, through the porous media backing layer and then exits from another channel. The oxygen mole fraction varies in the flow direction. In cathode backing layer, the area of low concentration zone of oxygen decreases. It is of benefit to improving the performance of fuel cells.

It is believed that optimizing fluid field design can enhance oxygen transportation in cathode porous media layer, and the performance of fuel cells would be certainly improved by this means.

REACTANTS DISTRIBUTION UNIFORMITY

A cell stack consists of hundreds of single cells, and each single cell has tens of flow channels. The phenomena, so called flow maldistribution or misdistribution, can considerably deteriorate the performance of the single cell and cell stacks.

As is well known, when the size of the inlet tube is smaller than the inlet manifold, the fluid tends to go preferentially into the tubes (or channels) that face the inlet tube (Lalot et al., 1999). Improving design of inlet header and tube system benefits creating a uniform flow in all channels of the polar plate (Kee et al., 2002; Ma et al., 2002). However, relatively little literature focuses on this topic in H_2 PEMFCs and DMFCs area.

In liquid feed direct methanol fuel cells, the average concentration of methanol in the anode channel decreases almost linearly along the flow direction. This methanol distribution nonuniformity is result of electrochemical reaction depletion and methanol crossover. In some case, the methanol crossover and lack of methanol supply may occur in a quite long channel at the same time. Both of them deteriorate the performance of direct methanol fuel cells. Redesigning flow field can make a more uniform concentration distribution, and alleviate that negative effect.

HIGH EFFICIENCY COOLING SYSTEM OF THE PEMFC STACK

In PEMFCs, up to 50% of the produced energy dissipate as heat in order to avoid excessive operation temperature and dehydration of the solid polymer membrane (Yi and Nguyen, 1998). Temperature difference between the PEMFC stack and environment is smaller an order of magnitude than that between internal combustion engine and surroundings. Nowadays, the size of external heat exchanger (radiator) of cooling system of the PEMFC stack is so large, even more than that of stack. It is a real challenge in PEMFC commercialization.

Focus on reducing space, weight, support structure and footprint, advanced technology of heat transfer augmentation must be applied to manufacture relatively small size radiator with high performance. Technology of the microchannel heat transfer can be used in liquid flow side of fuel cells radiator to enhance heat transfer. The authors have done some preliminary works in this area (Guo et al., 1998, 1999; Yu and Ma et al., 2001).

In the gas (air) cooling side of the radiator, forced convection cooling is needed. Using fins and increasing effective heat exchange surface area per unit volume, so called area density, can improve heat transfer coefficient of air. Typical surface area density of radiator for internal combustion engine ranges from 900 m^2/m^3 to 1650 m^2/m^3 (Shah, 1997). In PEMFC cooling system, this number can be boosted over 2500 m^2/m^3 by means of adopting compact fins. In the aspect of cooling media, water without phase change is a general choice. But some working fluids with relative low boiling point can be considered to use latent heat and increase cooling capacity.

CONCLUSIONS

Heat and mass transfer and two phase flow coupled with electrochemical reactions are critical important for development and commercialization of hydrogen PEMFCs and DMFCs. Several important problems, such as generation and change characteristics of water droplet and gas bubble, two phase flow under chemical reaction conditions, mass transfer enhancement of oxygen in the cathode porous media layer, heat transfer enhancement and high efficiency cooling system of proton exchange membrane fuel cells stack are discussed in present paper.

Experimental results of visualization of condensed water and two phase flow in fuel cell cathode microchannels are presented. The equivalent diameter of the rectangular channel is 0.8mm. Water droplets from the order of 0.08mm to 0.8mm were observed. Large water droplets blocked the channels and induced increase of oxygen transfer resistance. Further tests are currently underway and will be reported subsequently.

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