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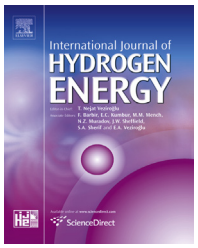

A novel multi-porous and hydrophilic anode diffusion layer for DMFC

Yituo Wang [a,b], Le Zheng [a,b], Guimei Han [c], Lixin Lu [a,b], Meng Wang [a,b], Jianling Li [a,b], Xindong Wang [a,b,*]

[a] State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, 30 College Road, Beijing 100083, China

[b] Department of Physical Chemistry, University of Science and Technology Beijing, 30 College Road, Beijing 100083, China

[c] Chinese Research Academy of Environmental Sciences, 30 Beiyuan Road, Beijing 100012, China

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ABSTRACT

The effect of hydrophilic treatment within the anode diffusion layer for direct methanol fuel cell (DMFC) has been investigated. By nitrated treatment, the surface structure and wettability of diffusion layer can be tuned. The anode micro-porous surface of carbon paper with hydrophilic adhesive after nitrated treatment presents more multi-hole structures with about 30 μm large pores and about 5 μm small pores, which were significantly larger than commercial carbon cloth and carbon paper without nitrated treatment. FTIR and EDS show that the surface of micro-porous layer has more oxygenic groups and the contact angles test also indicates that it becomes more hydrophilic after nitrated treatment. It is indicated that the anode charge transfer resistance and internal resistance dramatically decrease after nitrated treatment on the EIS test. The performance of assembled cell is also evaluated of which the power density of cell using novel diffusion layer (260 mW/cm^2) is significantly higher than cell using commercial diffusion layer. The results indicate that this novel multi-porous and hydrophilic anode diffusion layer is suitable to DMFC.

Introduction

Direct methanol fuel cell (DMFC), an active research topic of proton exchange membrane fuel cell, with characteristics of small size, light weight, low working temperature, high energy density and convenient fuel storage etc., is expected to have the best commercialization prospect for small mobile type fuel cell. However, two main fetters prevent DMFC from commercial production, including low catalytic activity of anode catalyst for methanol oxidation reaction and high methanol permeability of proton exchange membrane which will cause the cathode catalyst poisoned and "mixed-

* *Corresponding author*. Department of Physical Chemistry, University of Science and Technology Beijing, 30 College Road, Beijing 100083, China.
E-mail address: 493321145@qq.com (X. Wang).
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potential". Therefore, one key objective of the current DMFC research is to optimize anode methanol oxidation reaction.

For improving anode reaction, the concentration of reactants is very important. Relatively low methanol concentration may limit the anodic methanol oxidation reaction, while methanol permeation will restrict the cathode electrochemical reaction when anode methanol concentration is too high. Therefore, a moderate methanol concentration should be applied [1]. In the meanwhile, in order to optimize the anode methanol ingoing and carbon dioxide outgoing transmission, modified diffusion layer is adopted. Diffusion layer contains micro-porous layer and support layer. Carbon paper or carbon cloth constitutes the whole structure of support layer, and the hydrophobic or hydrophilic treatment to support layer is needed; micro-porous layer locates between support layer and catalyst layer, and is made with carbon black and hydrophobic or hydrophilic adhesives which are blended and coated on the surface of carbon paper or carbon cloth. The diffusion process of anode diffusion layer mainly includes both methanol's ingoing and carbon dioxide's outgoing. Hence, the electrode transmission channel for the two processes must be well-built. Based on this consideration, current researches aim to optimize mass diffusion and enhance the electronic conductivity of diffusion layer and the main method is to modify the wettability of diffusion layer [2,3].

However, focusing on wettability of diffusion layer to anode methanol transfer process, the different researchers gain different conclusions. Kyungmun Kang [4] thought if diffusion layer contained hydrophobic skeleton (PTFE), the methanol permeation would be restrained, so the cell's performance rose. A current density of 250 mA/cm^2 was obtained at 0.4 V. At the same time, Yuan [5] get the same result that hydrophobic skeleton was better for anode layer. The maximum power density of ca. 32.2 mW/cm^2 at a temperature of ca. 25 °C and under air-breathing mode is achieved with pure CNTs as anode MPL material. On the contrary, Kim [6] insisted that diffusion layer with hydrophilic porous structure was better and used silicon as electrode precursor of micro-porous layer and PVDF as binding skeleton. He thought this kind of micro-porous layer could improve the methanol's diffusion. Another reason why the performance was improved was that adsorb of carbon dioxide at diffusion layer was inhibited. The novel MEA with composite membrane showed power density of 48 mW/cm^2 at 0.3 V. It is worth noting that hydrogen-air fuel cell's cathode and anode was gas supply, which required to use hydrophobic material improve the transfer of hydrogen and air, so the current commercial diffusion layer generally conducted hydrophobic treatment. However, the direct methanol fuel cell's anode fuel is liquid, and therefore the hydrophilic treatment to diffusion layer is better for anode methanol transmission. The difference between hydrophobic and hydrophilic treatment can be seen in Fig. 1. If the diffusion layer is hydrophobic, carbon dioxide bubble will be easy to fill the porous structure and form transfer path, and thus this kind of carbon dioxide's filling will influence methanol's diffusion path. However, if the diffusion layer is hydrophilic, carbon dioxide bubble will not be easy to fill the porous structure, and methanol's diffusion path will be more unimpeded.

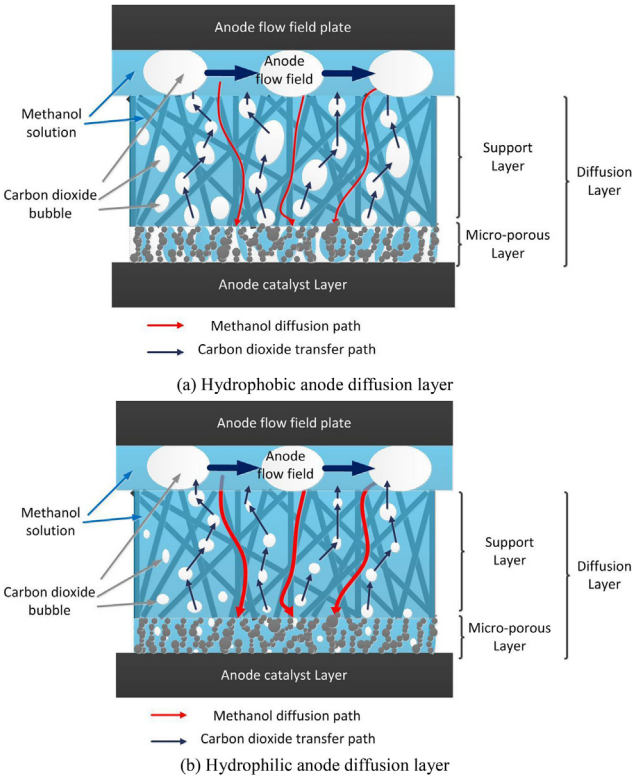

Fig. 1 – Hydrophobic and hydrophilic anode diffusion layers.

Carbon black is lamellar graphite structure, of which the Π electron cloud leads to a hydrophobic surface [7], but if carbon black is oxidized by oxide, it will generate a number of oxygen-containing functional groups on the surface [8], such as –COOH, =O, –OH and etc., and become hydrophilic. These kinds of hydrophilic functional group may enhance methanol's ingoing. Moreno-Castllaa [9] used HF HCl and HNO_3 treat activated carbon and found that the decomposition temperature of carboxylic anhydride was higher than carboxyl groups, and liquid-phase oxidation wound make activated carbon has more carboxyl groups than gas-phase oxidation. Wang [10] had studied the HF HCl and HNO_3 treatment to Ni–C, and the result showed that the catalyst particles size was related with the thermostability of oxygenic groups. Zhu [11] studied the surface functional group of activated carbon after HF HCl and HNO_3 treatment with TPD-MS method, and found that there were two kinds of functional group, which were CO_2-yield functional group and CO_2-yield functional group, and the dispersity of supported catalyst Cu_2O was consistent with the content of CO_2-yield functional group.

Our previous research revealed that the heating spray method [12] and pore former [13] would improve the mass transfer in catalyst layer. However, this paper aimed at the modification to diffusion layer, which will influence the transfer process of methanol and carbon dioxide at anode. In this paper, nitrated treatment was used to improve the surface of carbon, and this method made it gain richer oxygen-containing groups and become more hydrophilic, so anode methanol oxidation was optimized.