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Comparative studies of anode gas diffusion layers for direct methanol fuel cells

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Abstract: Comparative studies of four common-used anode gas diffusion layers (A-GDLs), namely carbon cloth, carbon paper, carbon paper based on XC-72 (in short XC-72) and GDL made of carbon nanotubes (CNT) for direct methanol fuel cells (DMFCs) were carried out and discussed. The results of scanning electron microscope (SEM), mercury intrusion porosimeter (MIP) and electrochemical test show that CNT has large pore size distribution in pore size of 1 000-3 000 nm and the largest total porosity compared with those of the other three. Carbon paper and XC-72 show disadvantageous influences on cell performances at high current density, because carbon paper has many large pores which are unsuited for water transport, while XC-72 has many small pores which are unsuited for gas transport. Though cell with carbon cloth has the highest methanol diffusion coefficient, it shows a little lower performance than that with CNT due to its thickness. Anode polarization (AP) results also display that the cell with CNT has the least methanol mass transfer resistance. As a result, the cell with CNT shows the best performance with the highest limiting current density and peak power density of 460 mA · cm^{-2} and 110 mW · cm^{-2}, respectively.

Key words: direct methanol fuel cells (DMFCs); gas diffusion layer (GDL); porosity; mass transfer; methanol diffusion coefficient

0 Introduction

Direct methanol fuel cells (DMFCs) are promising candidates in portable power sources for their high energy density, relatively low operating temperatures and lower emissions[1-3]. As an important component, anode gas diffusion layer (A-GDL) ensures reactants/products effectively transport into/out of the electrodes. Methanol must be transported through the gas diffusion layer to the anode catalyst layer, where it is consumed. Carbon dioxide is produced on the catalyst surface, which must continuously be removed to avoid blockage of the reaction sites. There have been many researches into the material and structure of GDLs. Oedegaard, *et al.*[4] studied the effect of the diffusion layer, such as carbon cloth, carbon paper and metal wire cloth on the performance and mass transfer in a direct methanol fuel cell. They found that metal wire cloth is superior to carbon paper and carbon cloth for low temperature DMFC.

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Escribano, *et al*.[5] compared different types of carbon fibers-based supports and suggested optimizing the materials' properties to enhance the cell performance. In addition, different kinds of carbon powders used in the micro porous layer have been studied, and acetylene-black is found to be superior to others[6-7].

In this paper, comparative studies of four common-used A-GDLs for DMFCs, namely carbon cloth, carbon paper, carbon paper based on XC-72 (in short XC-72) and GDL made of carbon nanotubes (CNT) will be reported. According to the characterization results of scanning electron microscope (SEM), mercury intrusion porosimeter (MIP), gas permeability, water permeable pressure and single cell performance, a detailed understanding of the effect of A-GDL on DMFC performance can be obtained, which might be helpful to the future structural design of A-GDL.

1 Experiments

1.1 Description of A-GDLs

Detailed parameters of A-GDLs are shown in Tab. 1. Carbon paper is the commercial Toray-060H carbon paper which is water-proof with 10% PTFE; Carbon cloth is the commercial ELAT carbon cloth without detailed parameters (offered by MTI); XC-72 is the above carbon paper covered by a MPL made of 10% PTFE and 2 mg · cm^{-2} XC-72 carbon powder; CNT is a homemade GDL made of CNT (supplied by Tsinghua University), polyacrylonitrile-based carbon fibre (PCF) and PTFE, which is described in Lit. [8].

Tab. 1 Parameters of A-GDLs

Type	Substrate PTFE/%	MPL PTFE/%	MPL carbon powder loading/(mg · cm^{-2})	Thickness/μm
Carbon paper	10	0	0	210
Carbon cloth	—	—	—	360
XC-72	10	10	2	224
CNT	10	0	0	120

The cathode GDLs are all made of Toray-060H carbon paper (with 10% PTFE), covered by a MPL made of 60% PTFE and 2 mg · cm^{-2} XC-72 carbon powder.

1.2 Preparation of CCM and single cell

The catalyst coated membrane (CCM) was prepared using a common decal method[9]. The 5.25 mg · cm^{-2} Pt-Ru black (Johnson Matthey Company, Hispec 6000) and the 2 mg · cm^{-2} Pt 60% Pt/C (Johnson Matthey Company, Hispec 9100) were loaded on the anode and cathode, respectively.

The tailored anode and cathode GDLs (2 cm × 2 cm) were placed onto the corresponding sides of the CCMs and sandwiched between two punctual stainless steel flow field plates with an effective area of 4 cm^2 for electrochemical tests.

1.3 Characterization methods

The surface morphologies of GDLs were examined by SEM (JSM 6360LV) and the porosities of GDLs were examined by MIP (Quantachrome Corp.).

The gas permeability and water permeable pressure of GDLs were obtained by homemade apparatus as shown in Lit. [10].

Performances of DMFCs were obtained by using a Fuel Cell Test System (Arbin Instrument Corp. USA). The anode polarization curves and methanol crossover current densities were measured by EG&G PAR 273A potentiostat /galvanostat at 60 ℃. With the cell resistance, the IR-corrected anode polarization curves could be calculated[11]. Depending on the IR-corrected anode polarization results, the macroscopic methanol transport coefficient could be calculated according to Eq. (1)[4]:

$$D_{\mathrm{MeOH}} = \frac{i_{\lim} \cdot l}{nFc_i} \tag{1}$$

In which D_{MeOH} is the diffusion coefficient of methanol in GDL ($m^2 \cdot s^{-1}$), $i_{\lim}$ is the limiting current density of anode polarization ($A \cdot m^{-2}$), l is the thickness of GDL (m), n is the

stoichiometric number of electrons involved in an electrode reaction, F is the Faraday's constant (96 485 C · mol^{-1}), c_i is the methanol concentration supplied to the anode (mol · L^{-1}).

The anode differential pressures between the inlet and outlet were recorded by a homemade manometer, when the cell was operating at 100 mA · cm^{-2}.

2　Results and discussion

2.1　Structural characterization

The surface morphologies of the four A-GDLs are observed, and the images are shown in Fig. 1. It can be seen from Fig. 1 that carbon paper consists of long carbon fibers with pore size of 10-20 μm. XC-72 is made of carbon powder and PTFE mixture, which has a plat and compact surface without carbon fibers appearing. There are large cracks with 2-3 μm widths appearing on the surface of XC-72. Commercial carbon cloth shows a coarse and porous surface but without apparent cracks. CNT has fluffy appearance with abundant porosity.

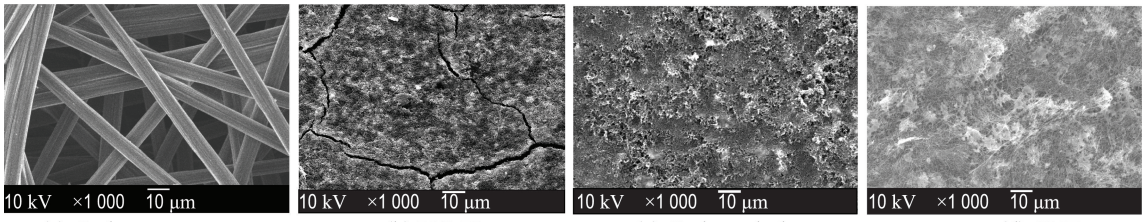


Fig. 1　The surface SEM images of carbon paper, XC-72, carbon cloth and CNT

The pore size distributions in the four A-GDLs measured by MIP are shown in Fig. 2. Here the pores could be divided into two scales. Porosity between 30-300 nm is noted as small pores, while porosity between 300-5 000 nm is noted as large pores. The results show that carbon paper has few pores in the test range, which also prove that the pore sizes of carbon paper are almost larger than 5 μm, as shown in Fig. 1 (a). The pores in XC-72 are mainly small pores, while carbon cloth has both large and small pores in a certain ratio. CNT has abundant micro-nano pores and the largest total porosity.

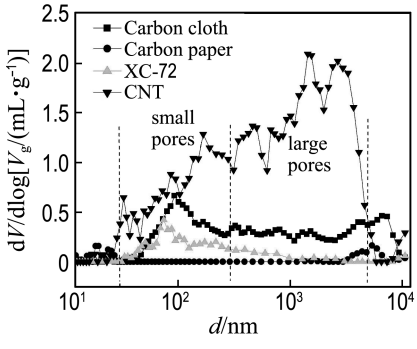


Fig. 2　Porosity measurements of A-GDLs

During DMFC practical operating, gas/liquid convection occurs in the anode and a GDL with bifunctional mass transfer channels is needed. Most researchers thought that large pores are mainly used as gas channels and small pores as liquid channels[4]. Carbon paper with only large pores may be suitable for gas transport, but disadvantageous for liquid transport. XC-72 has only small pores through which both methanol and CO_2 need to be transported and then a competition arises. As mentioned above, carbon cloth and CNT show the most clear gas/liquid mass transfer channels, in which small pores are used for methanol transfer and large pores for CO_2 ejecting. The porosity of GDL is very important for the performance of DMFC as it significantly affects the reactants/products transport in the electrodes. Thus, the micro-nano complex structure of CNT maybe produces so-called multi-scale effect offering proper gas/liquid

transfer channels and improving the single cell performance.

Total porosity r of A-GDLs is tested and shown in Fig. 3. XC-72, carbon cloth and carbon paper have the similar total pores (about 70%), while CNT has the highest value (up to 93%), which is consistent with the results of Fig. 2. Abundant pores may be helpful to offering respective gas/liquid transfer channels and improving the mass transfer ability for cells' longtime stability.

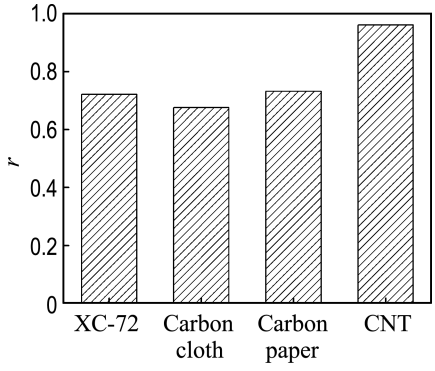


Fig. 3 Total porosity of A-GDLs

2.2 Mass transfer analysis

Appropriate gas permeability could ensure CO_2 flow out of anode continuously and improve the cell performance. The gas permeabilities of A-GDLs in the through-plane direction are tested and shown in Fig. 4. It could be seen that the gas flow rates of four A-GDLs all increase with the increasing of pressure difference. The gas permeability coefficient of carbon paper is higher than those of the other three. CNT with many pores in pore size range of 0.3-5.0 μm has a gas permeability coefficient of 4.16×10^{-12} m^2 closely next to that of carbon paper. So carbon paper and CNT have the predominance of CO_2 ejecting. Carbon cloth with large thickness and XC-72 with compact microstructure might block gas transmitting in the GDL, so their gas permeability coefficients are lower, which could depress the cell performances.

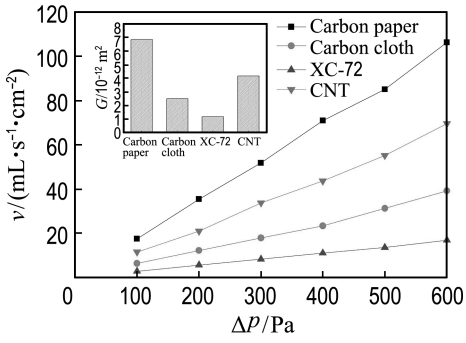


Fig. 4 Gas permeability of A-GDLs

Fig. 5 demonstrates the results of water permeable pressure. It denotes the pressure the water needs to flow through the pore with the smallest resistance, namely the liquid transfer ability. In four A-GDLs, XC-72 has the most compact structure, so it has the highest water permeable pressure (about 13 kPa) and liquid transfer resistance. Carbon cloth and carbon paper follow decreasing. CNT shows the lowest water permeable pressure of only 0.5 kPa, which may be attributed to its abundant small pores facilitating the liquid transport.

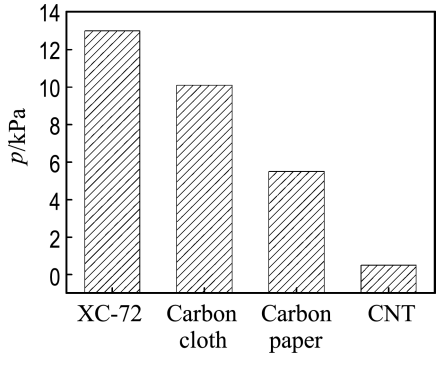
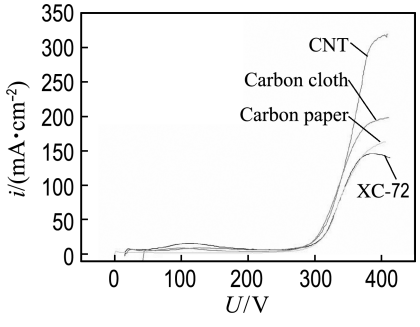


Fig. 5 Water permeable pressures of A-GDLs

2.3 The performances of single cells

Fig. 6 presents the IR-corrected anode polarization curves of the cells constructed with different A-GDLs. When the anode is fed with 0.5 mol/L methanol at 60 ℃, it can be seen that the anode potentials are almost identical at low current densities ($<$ 100 mA · cm^{-2}) and the difference is mainly shown at high current densities. XC-72 with the poorest gas permeability has a serious methanol transfer

resistance and shows a limiting current density at early 150 mA • cm^{-2}. Carbon paper with many large pores has a disordered gas/liquid transfer process and a low limiting current density. Carbon cloth has better porosity than that of the former two, which could harmonize the gas/liquid transfer issue in the high current density region. And the limiting current density appears at 200 mA • cm^{-2}. CNT with suitable porosity shows the highest limiting current density of 323 mA • cm^{-2}. The anode limiting current density presents the current density when methanol arriving at the triple-phase interface is completely oxidized. When the current density increases, CO_2 produced by methanol oxidation also increases and the obvious gas/liquid convection occurs. At this time, the mass transfer circumstance in anode would influence the cell performance significantly. The perfect anode polarization performance of the cell with CNT could increase the whole cell performance especially at high current density.



Anode operation conditions: 0.5 mol/L methanol at 1 mL • min^{-1}. Cathode operation conditions: ambient pressure H_2 at 40 mL • min^{-1}

Fig. 6　IR-corrected anode polarization curves of the cells constructed with different A-GDLs at 60 ℃

Depending upon the IR-corrected anode polarization results, the methanol diffusion coefficients are calculated and shown in Fig. 7. Carbon cloth shows the best methanol diffusion ability. But due to its large thickness, carbon cloth has longer methanol transfer channels than other A-GDLs, which means a bigger mass transfer resistance. Next is CNT with appropriate methanol transfer channels and minor mass transfer resistance. Carbon paper with many large pores and XC-72 with many small pores may be unsuitable for methanol/CO_2 transfer and show lower methanol diffusion coefficients.

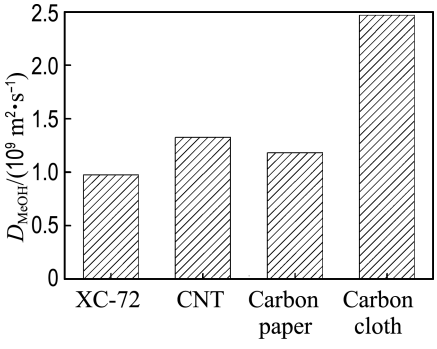
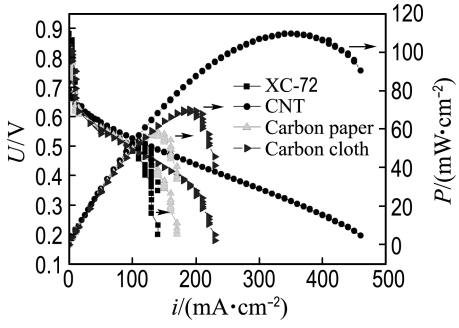


Fig. 7　Methanol diffusion coefficients of A-GDLs

A-GDLs have the functions of mass transfer and redistributing the fuel of methanol. The microstructures of A-GDLs control the methanol concentrations arriving at the catalyst triple-phase interfaces. A low methanol concentration would cause an earlier mass transfer polarization and a lower corresponding single cell performance. While a high methanol concentration would cause a serious methanol crossover problem and decrease the cell performance and the fuel efficiency. With the converse ejection of CO_2 during the cell operation, the anode has a much serious requirement for the A-GDLs. The performances of DMFCs with different A-GDLs are shown in Fig. 8. It can be seen that different A-GDLs have obvious influences on cell performances, especially in the latter high current density region which is mainly controlled by mass transfer polarization. The cell with XC-72 shows the lowest performance and the highest power density is only 52.4 mW • cm^{-2}. Carbon paper with many large pores is also disadvantageous

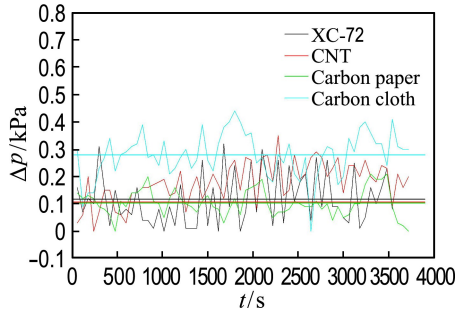
for methanol transfer at high current density, and the highest power density is 58.7 mW · cm^{-2}. The cell with carbon cloth shows better performances than those of XC-72 and carbon paper for its high methanol transfer ability. At 60 ℃, the cell constructed with CNT shows a limiting current density of 460 mA · cm^{-2}, which is higher than 230 mA · cm^{-2} of carbon cloth, 169 mA · cm^{-2} of carbon paper and 140 mA · cm^{-2} of XC-72. It is shown that the mass transfer abilities of CNT is much better than those of the other three and the performance of single cell is not only related to the cathode mass transfer ability, but also affected by the anode structures. The cell with CNT has proper gas/liquid transfer channels through which there would be enough methanol diffusion into the reaction sites even at the high current density and the performance could be improved.



Anode operation conditions: 0.5 mol/L methanol at 1 mL · min^{-1}. Cathode operation conditions: ambient pressure pure air at 80 mL · min^{-1}

Fig. 8 Performances of single cells with different A-GDLs at 60 ℃

Fig. 9 presents the anode differential pressures between the inlet and outlet at constant current density of 100 mA · cm^{-2}. Carbon cloth has the largest differential pressure of about 0.28 kPa. The other three have the similar differential pressures of about 0.1 kPa. A certain differential pressure could intensify the mass transfer and help methanol/CO_2 diffuse into/out of the anode. Then, the cell performance and stability could also be improved. However, a larger differential pressure maybe presents a larger mass transfer resistance and a proper differential pressure is needed to maintain the cell operating stably. Combined with the results of Fig. 8, CNT with an anode differential pressure of 0.1 kPa is suitable for mass transfer and shows better performances than those of the other three.



Anode operation conditions: 0.5 mol · L^{-1} methanol at 1 mL · min^{-1}. Cathode operation conditions: ambient pressure pure air at 80 mL · min^{-1}

Fig. 9 Anode differential pressure between the inlet and outlet at constant current density of 100 mA · cm^{-2} at 60 ℃

3 Conclusion

Different microstructure-designs of A-GDLs were compared and characterized by SEM, MIP and single cell performance. Carbon paper and XC-72 show disadvantageous influences on cell performances, because carbon paper has many large pores which are unsuited for water transfer, while XC-72 has many small pores which are unsuited for gas transfer. The cell with CNT has the least methanol mass transfer resistance for its proper porosity. Though carbon cloth has the highest methanol diffusion coefficient, the cell with carbon cloth shows a lower performance than that with CNT due to its thickness. As a result, the CNT is suitable for DMFC anode for its optimal porosity and mass transfer ability. The cell with CNT shows the highest limiting current density and peak power density of 460 mA · cm^{-2} and 110 mW · cm^{-2},

respectively.

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直接甲醇燃料电池阳极扩散层比较研究

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摘要： 采用扫描电子显微镜(SEM)、汞注入孔隙计(MIP)和电化学方法考察了 4 种常用的阳极扩散层——碳布、碳纸、XC-72 碳粉修饰的碳纸(以下简称 XC-72)、碳纳米管扩散层——对直接甲醇燃料电池性能的影响. 结果表明：碳纳米管扩散层在 1 000～3 000 nm 具有丰富的孔径分布和最大孔隙率；碳纸和 XC-72 扩散层组装的单电池在大电流密度下分别由于孔径大不利于输水和孔径小不利于输气而使得电池性能较差；碳布扩散层组装的单电池虽然具有最大的甲醇扩散系数，但是由于其厚度问题使得性能稍差于碳纳米管扩散层电池. 阳极极化结果也表明碳纳米管扩散层电池具有最小的甲醇传质阻力. 因此碳纳米管扩散层组装的单电池具有最优性能，最大电流密度为 460 mA·cm^{-2}，最大功率密度为 110 mW·cm^{-2}.

关键词： 直接甲醇燃料电池(DMFCs)；气体扩散层(GDL)；孔隙率；传质；甲醇扩散系数

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