



Short communication

Hierarchy carbon paper for the gas diffusion layer of proton exchange membrane fuel cells

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ABSTRACT

This communication described the fabrication of a hierarchy carbon paper, and its application to the gas diffusion layer (GDL) of proton exchange membrane (PEM) fuel cells. The carbon paper was fabricated by growing carbon nanotubes (CNTs) on carbon fibers via covalently assembling metal nanocatalysts. Surface morphology observation revealed a highly uniform distribution of hydrophobic materials within the carbon paper. The contact angle to water of this carbon paper was not only very large but also particularly even. Polarization measurements verified that the hierarchy carbon paper facilitated the self-humidifying of PEM fuel cells, which could be mainly attributed to its higher hydrophobic property as diagnosed by electrochemical impedance spectroscopy (EIS).

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1. Introduction

Proton exchange membrane (PEM) fuel cells are very promising alternative energy conversion devices for portable and stationary applications due to the advantages of high efficiency and low emission. To achieve high performance of PEM fuel cells, the reactant gases are usually humidified through an external humidifying system before entering into the fuel cells, because the proton conductivity of the PEM, usually Nafion®, depends highly on the water content of the membrane. However, the external humidifying system increases weight, volume and complexity to the system. Therefore, operation of PEM fuel cells without external humidifying system is highly desirable [1,2]. Theoretical calculation has revealed that PEM fuel cells might be operated without external humidification by delicately self-humidifying the membrane with water produced from the cathode [3,4].

To self-humidify the membrane, many studies were focused on the fabrication of self-humidifying membranes by incorporating well dispersed nano-sized Pt or hydrophilic oxide particles in the membranes [5–8]. Although some positive results were obtained, this method increased the thickness or decreased the proton-transfer channels of the membranes. Actually, gas diffusion layer (GDL), which usually consists of a carbon paper or carbon cloth sublayer and a PTFE/carbon black sublayer, is also a crucial component in PEM fuel cells [9–13]. It has been found that, by

optimizing the composition and structure, the PTFE/carbon black sublayer could increase the water content of the membrane, and thus the performance of PEM fuel cells [14,15]. However, to the best of our knowledge, the carbon paper or cloth sublayer still receives not much attention for self-humidifying the membrane of PEM fuel cells. The effect of the carbon paper or cloth sublayer on self-humidifying the membrane depends highly on its hydrophobic property. Hydrophobic property of the conventional carbon paper or cloth sublayer is not desirable, because the carbon paper or cloth is often wetproofed by impregnating in suspension of hydrophobic materials (e.g., FEP [15] or PTFE [16]) and then sintering at 300–350 °C [17,18]. This wetproofing procedure leads to a problem that the hydrophobic materials may migrate and agglomerate via capillary force during the drying and sintering process. The migration of hydrophobic materials not only reduces hydrophobicity of the carbon paper or cloth sublayer but also increases the mass transport resistance by blocking the pores. In the present paper, mainly in order to depress the migration of hydrophobic materials during the wetproofing process, a novel hierarchy carbon paper with carbon nanotubes (CNTs) uniformly grown on carbon fibers is presented for GDL of PEM fuel cells. By the conventional wetproofing procedure, this remarkable carbon paper showed excellent hydrophobic property and significantly facilitated self-humidifying the membrane of PEM fuel cells.

2. Experimental

The hierarchy carbon paper was fabricated by a gas phase thermal decomposition method. At first, carbon paper (TGP-H-

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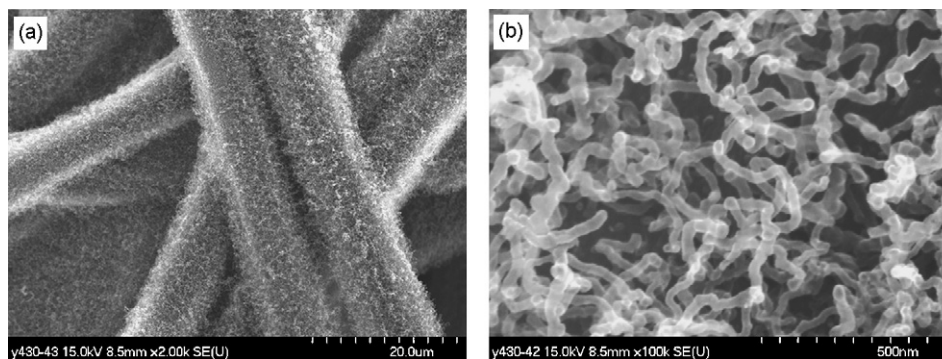


Fig. 1. (a) SEM image of the hierarchy carbon paper with CNTs grown on carbon fibers by covalently assembling nanocatalysts, (b) close-up of the grown CNTs on a carbon fiber.

090, Toray) was ultrasonically cleaned in ethanol solution for 30 min. Then, Ni-Co nanocatalysts for CNT growth on carbon fibers were loaded onto the carbon paper. Specifically, the carbon paper was covalently modified with 4-aminobenzoic acid in anhydrous ethanol solutions containing 3 mM 4-aminobenzoic acid and 0.1 M LiClO₄ by electrochemically scanning between 0 and 0.9 V (vs Ag/Ag⁺) at a scan rate of 100 mV s⁻¹ for 200 cycles. After sufficient rinsing, the 4-aminobenzoic acid modified carbon paper was placed in 0.3 M Co(NO₃)₂ + 0.3 M Ni(NO₃)₂ solution for 20 h, resulting in exchange of Co²⁺ and Ni²⁺ in solution with H⁺ in 4-aminobenzoic acid. The Co²⁺ and Ni²⁺ were then reduced to metal particles by heating the carbon paper in a tube furnace at 500 °C in the presence of hydrogen for 5 min. Finally, CNTs were grown on carbon fibers by the carbon paper at 800 °C for 5 min with a gas mixture of 90% Ar, 5% H₂, and 5% ethylene fed into the tube furnace.

The membrane electrode assembly (MEA) for evaluating the hierarchy carbon paper was fabricated as follows. At first, carbon paper was wetproofed by soaking in a 20% PTFE suspension for 3 min and then drip-dried at room temperature. This process was repeated several times until 20% PTFE content was obtained. An ink of PTFE and carbon black mixture containing 25% PTFE was applied to the wetproofed carbon paper and dried at room temperature. The GDL was then obtained by drying the carbon paper at 110 °C, 280 °C and sintering at 350 °C for 30 min, respectively. After that, an ink of 40% of Pt/C electrocatalyst (Johnson Matthey) and 5% Nafion solution (Du Pont) was sprayed onto the cathode and anode GDLs that used the hierarchy and conventional carbon papers, respectively. The platinum loadings for the anode and cathode were 0.1 and 0.2 mg cm⁻². Finally, the MEA was formed by hot-pressing the electrodes and a Nafion 112 (Du Pont) membrane at 135 °C and 5 MPa for 3 min. For comparison, the MEA for the conventional carbon paper was also fabricated by the same procedure as described above.

The morphology of the hierarchy and conventional carbon papers was recorded by a field-emission scanning electron microscope (FESEM, HITACHI S-4100). The hydrophobicity of the hierarchy and conventional carbon papers was characterized by its contact angle to water determined by a contact angle goniometer (Solon Tech. Inc. SL200A).

The electrochemical performances of the MEA were measured at 65 °C under an atmospheric pressure by using the single cell fixture composed of a MEA and a pair of graphite bipolar plates with serpentine flow channels of 1 mm width and 1 mm depth (Electrochemistry Corp.). Hydrogen without humidification was fed to the anode as the fuel at a flow rate of 100 mL min⁻¹, and air humidified at 75 °C was supplied to the cathode as the oxidant at a flow rate of 200 mL min⁻¹. Before measurement, the single cell was activated according to the procedure in Ref. [19]. Polarization behavior of the single cell was recorded by a Fuel Cell Testing System (Arbin Instru-

ment Corp.). Electrochemical impedance spectroscopy (EIS) was measured using an electrochemical analysis instrument (model CHI 604b) in a frequency range from 100 kHz to 0.1 Hz with AC voltage amplitude of 5 mV.

3. Results and discussion

Fig. 1a presents an SEM image of the hierarchy carbon paper. Clearly, a large amount of CNTs grown from the covalently assembled Co-Ni particles uniformly covered the carbon fibers and no any visible fraction of bare fibers was observed. It was difficult to accurately estimate the length of these CNTs because they were quite tortuous, but some tubes were at least 1 μm long. A close-up of the CNTs (Fig. 1b) showed that the obtained CNTs were curly with uniform diameters of about 30–40 nm. According to Dodelet and co-workers [20], under our experimental condition, the growth of CNTs followed mainly a tip-growth mechanism and the dimension of the catalyst particles controlled the CNTs' diameters, which indicated that the Co-Ni particles be evenly deposited on the surface of carbon fibers in our case. This might be ascribed to the method of our depositing the Ni-Co nanoparticles on carbon fibers. In our experiments, the Ni-Co particles were deposited on carbon fibers through forming a 4-aminobenzoic acid monolayer, followed by an ion exchange and reduction process. The monolayer was stable because 4-aminobenzoic acid was covalently grafted on carbon paper fibers by electrochemically inducing amine cation radicals and subsequently forming a strong carbon–nitrogen linkage. In addition, the monolayer was much even because the carbon paper was highly conductive and easily wetted by ethanol solution, which led to the even electrochemical oxidation of 4-aminobenzoic acid on the surface of all carbon fibers. This method, therefore, resulted in much more uniform Ni-Co particle distribution on carbon fibers than that in Ref. [20], where a physically attached silicate gel was used for anchoring the Ni²⁺ and Co²⁺ and no uniform contact between the gel and carbon fibers was guaranteed.

The surface morphology of the hierarchy and conventional carbon papers wetproofed by PTFE was compared in order to find out the effect of growing CNTs on improving the PTFE distribution on the surface of carbon fibers. Fig. 2 shows the SEM images for the hierarchy and conventional carbon papers wetproofed by 20% PTFE. Apparently, after PTFE wetproofing, no visible CNTs were observed on fibers of the hierarchy carbon paper, indicating that PTFE was evenly covered on the surface of all carbon fibers, due to the anchoring effect of grown CNTs on PTFE during wetproofing procedure. In contrast, for conventional carbon paper, there were still many bare carbon fibers uncovered by any PTFE, which meant that PTFE was not uniformly distributed in the conventional carbon paper, and therefore, a more number of pores formed by intersecting carbon fibers would be blocked by PTFE because the same amount of

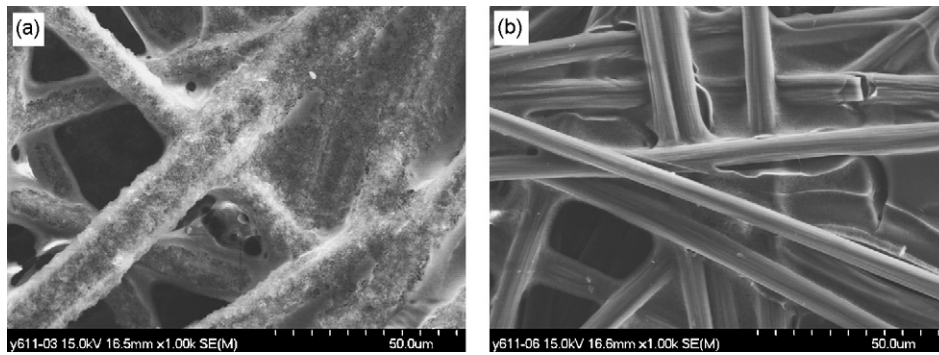


Fig. 2. SEM images of the carbon papers wetproofed with 20% PTFE: (a) hierarchy carbon paper, (b) conventional carbon paper.

PTFE was applied to the two carbon papers. From this morphology analysis, it was believed that the hierarchy carbon paper would be appreciably beneficial to hydrophobicity and gas transport of the GDL.

Fig. 3 presents the contact angles to water of the wetproofed hierarchy and conventional carbon papers. Apparently, the contact angle value for the hierarchy carbon paper was higher than that for the conventional carbon paper. Moreover, the variation of the contact angle at different positions of the hierarchy carbon paper was significantly lower than that of the conventional carbon paper, indicating that the hierarchy carbon paper had much more uniform distribution of hydrophobicity. As has been demonstrated by Lim and Wang [15], contact angle of the wetproofed carbon paper depends not only on the PTFE content, but also on the uniformity of the PTFE distribution. Therefore, although the two carbon papers had almost the same PTFE content, the hierarchy carbon paper had higher and more uniform hydrophobicity than the conventional carbon paper, due to its even PTFE distribution as observed in Fig. 2.

Fig. 4 presents the single cell performance of the MEA with the hierarchy and conventional carbon papers at 65 °C under dry H₂ and air atmosphere. In this operating condition, the membrane must be self-humidified by the water from the cathode. The MEA with the cathode GDL from the hierarchy carbon paper showed a current density of 750 mA cm⁻² at 0.5 V, whereas the MEA with the cathode GDL from the conventional carbon paper recorded a current density of 600 mA cm⁻² at 0.5 V, i.e., only about 75% compared to the case of the hierarchy carbon paper. As to the power density, a maximum power density of 377 mW cm⁻² was obtained for the case of the hierarchy carbon paper, representing 0.25 times increase from the case of the conventional carbon paper. These results showed that the hierarchy carbon paper was significantly useful to enhancing

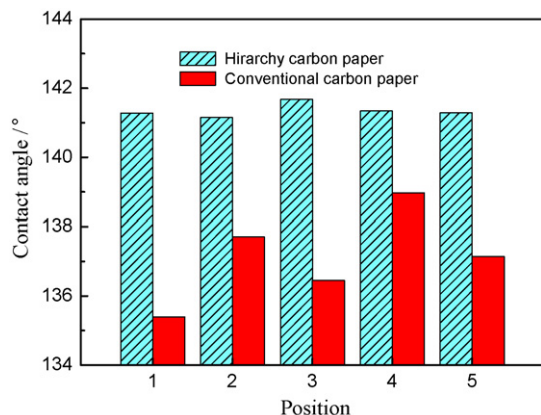


Fig. 3. Water contact angles at different positions of the carbon papers.

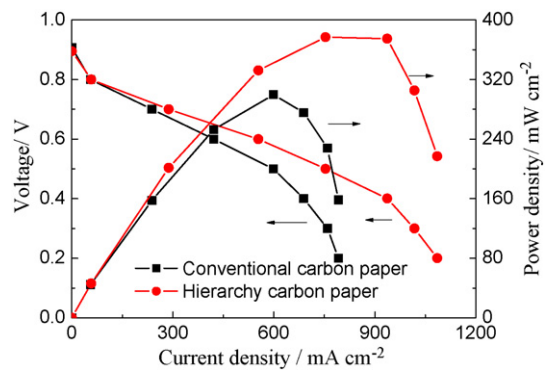


Fig. 4. Single cell voltages and power densities of the MEAs with hierarchy and conventional carbon papers as a function of current density.

the electrochemical performance of the self-humidifying PEM fuel cells.

To give a more detailed diagnosis to the performance difference of the two single cells with the hierarchy and conventional carbon papers, EIS were measured and shown in Fig. 5. Basically, two semicircles were observed on each spectrum, one in the high frequency domain and the other in the low frequency domain. Similar spectra have been widely reported in the literature for PEM fuel cells [21,22]. The intercept on the real axis in the high frequency domain represents the membrane resistance. The first semicircle represents fuel cell reaction kinetics, and the second semicircle represents the mass transfer process with the major contributions coming from the diffusion of reactants within the GDL. It could be observed in Fig. 5 that the resistances of the membrane and the mass transport were significantly lower, whereas the reaction kinetics resistance in the GDL was slightly higher for the hierarchy carbon paper than

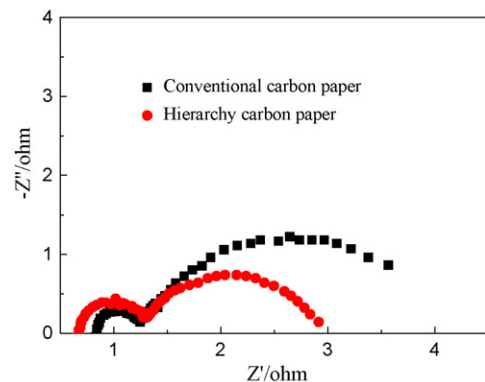


Fig. 5. Electrochemical impedance spectra of the MEAs with hierarchy and conventional carbon papers at a current density of 700 mA cm⁻².

those for the conventional carbon paper. This observation could only be ascribed to the difference of the cathode carbon paper because the other parts of the two MEAs were the same. Compared with the conventional carbon paper, the hierarchy carbon paper with higher hydrophobicity facilitated, on the one hand, the back diffusion of water produced at the cathode to the anode, and on the other hand, water removal from the GDL to the channel. The back diffusion of water humidified the membrane, which resulted in a lower membrane resistance because more water was available for proton electro-osmotic drag. The quick water removal from the GDL lowered the mass transport resistance. The slight larger resistance of the reaction kinetics for the hierarchy carbon paper was probably due to the higher cell voltage as presented in Fig. 4, although an enhanced reaction kinetics had been observed in the well humidified catalyst layers because of the increase of electrochemical Pt surface area [22,23].

4. Conclusions

This paper provides a new method of fabricating a hierarchy carbon paper with CNTs uniformly grown on carbon fibers, and firstly applies this carbon paper to the GDL of PEM fuel cells. Measurements of morphology, contact angle value and electrochemical behavior indicate that this hierarchy carbon paper could improve effect of the wetproofing treatment, which is significant to water management and thus polarization performance of PEM fuel cells. Compared with the conventional carbon paper, the hierarchy carbon paper not only facilitates the stability of wetproofing treatment because of the anchoring effect of the grown CNTs on PTFE, but also favors controlling the PTFE content during the wetproofing treatment by adjusting the length and density of the grown CNTs. In addition, the grown CNTs help reduce the electric contact resistance due to the PTFE deposition at intersecting positions of the

carbon fibers. Therefore, the hierarchy carbon paper is particularly attractive to the self-humidifying PEM fuel cells.

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