Construction of a high-performance air-breathing cathode using platinum catalyst supported by carbon black and carbon nanotubes

Zi'ang Xiong, Shijun Liao¹, Sanying Hou, Haobin Zou, Dai Dang, Xinlong Tian, Haoxiong
Nan, Ting Shu, Li Du

¹Corresponding author. Tel./Fax: +86 20 8711 3586. E-mail address: chsjliao@scut.edu.cn.

Abstract

It is well recognized that pore structure and the hydrophilicity/ hydrophobicity balance are key factors for the cathodes of air-breathing proton exchange membrane fuel cells (AB-PEMFCs). In this work, we attempted to adjust the pore structure and hydrophilicity of an air-breathing cathode by using two types of catalysts, Pt/C and Pt/CNT, to prepare the catalyst layer for the air-breathing cathode instead of using a single catalyst. An MEA with the dual-catalyst cathode exhibited significantly improved single-cell performance, which was affected by the ratio of Pt/C to Pt/CNT. Our optimized MEA, which had a ratio of 54:46 in the cathode catalyst layer, achieved a current density of up to 290 mA cm^{-2} at 0.6 V, which was 14 % higher than that of a MEA without Pt/CNT. The Pt/CNT in the catalyst layer played the key role in the overall performance of the AB-PEMFC. We propose that the CNT improved charge transfer and enabled better electrical conductivity than carbon black. In addition, the tubular structure of Pt/CNT made the catalyst layer more porous and permeable to gas. Furthermore, the addition of Pt/CNT may have changed the cathode's hydrophilicity/hydrophobicity balance, giving the cathode better water balance and consequently yielding better performance.

Keywords: CNTs, low electrical resistance, proton transfer path, porosity, water management

1. Introduction

Air-breathing proton exchange membrane fuel cells (AB-PEMFCs) offer several advantages, including small volume, low operating temperature, high power density, high energy conversion efficiency, and zero emissions, making them ideal power sources for portable electronics or electric vehicles^[1-2]. However, a key obstacle to

making AB-PEMFC technology commercially available is cathode performance in an ambient atmosphere. The thickness and porosity of cathode catalyst layers (CLs) are important macroscopic parameters. The structure of a CL is influenced by both fabrication method and materials (e.g., the species and their ratio). Generally, the catalytic properties of the electrocatalysts are affected by the specific area, stacking density, electrical conductivity and electrochemical oxidation resistance of carbon supports, which are various with their shapes and structures^[3]. Different carbon materials have been used as catalyst carriers, such as carbon black^[4-5], carbon nanotube (CNT)^[6-7], carbon nanofiber^[8-10], Graphene sheet^[11-13] and so on. Vulcan XC72 carbon black has been most widely used to support metal nanoparticles because of its high surface area and low electrical resistance. However, both corrosion and the structural density of carbon black-based carriers cause the resulting electrocatalysts to suffer from low Pt utilization, poor durability, and low mass transport capability^[14].

The carbon nanotube (CNT) has a distinctive structure and unique properties, such as electrochemical oxidation resistance, good electrical conductivity, and high surface area^[15]. Previous research has shown that CNT-supported Pt catalysts can increase the performance of PEMFCs^[16-18]. The exchange current density on a metal/CNT electrode is much higher than on a metal/graphite or glassy carbon electrode^[19].

Catalyst activity is highly dependent not only on particle size but also on the dispersion of Pt on the carriers. Generally, the electrical conductivity of carbon supports significantly affects the catalytic activity; the higher the carbon's graphitization degree, the better the electrical conductivity^[20-21]. However, the 3D character of a CNT catalyst layer is not suitable for gas conditions, since only the Pt nanoparticles that are very close to the membrane (i.e., within 10 μm) are the active

components at the anode (and the cathode) of H₂/O₂ fuel cells ^[22].

In this work, we designed MEAs by mixing Pt/CNT and Pt/C together in the cathode CL, hoping to enhance the utilization and electrochemical performance of Pt nanoparticles, since CNTs can bridge adjacent carbon black particles and inhibit the aggregation of carbon spheres. Pt/C filled the spaces within the framework constructed by Pt/CNT. The electron transfer rate depended on the distance between electron donor and electron acceptor, and the interaction within Pt/CNT or between Pt/C and Pt/CNT enhanced the electrical conductivity. In addition, high porosity led to a high mass transport rate, caused by the CNTs overlapping with one another. The micromorphology of the cathode CLs was characterized by scanning electron microscopy (SEM). Contact angle and electrochemical impedance spectroscopy (EIS) were used to evaluate each CL's performance in a single AB-PEMFC.

2. Experimental

2.1. Preparation of the Pt/CNT

The Pt/CNT catalysts were prepared using an organic colloid method reported previously by our group ^[23]. The Pt content of the prepared catalysts was ca. 40 wt%. The typical procedure included the following steps. First, sodium citrate was dissolved in ethylene glycol, then the mixture was ultrasonically dispersed for 30 min to entirely dissolve the citrate. Next, hexachloroplatinic acid was thoroughly mixed with the resulting solution. Then the CNTs were added into the mixture, which was then stirred, after which KOH/ethylene glycol solution was added drop-wise to make the pH less than 10. Second, the mixture was transferred into an autoclave with a Teflon liner and left to react at 170°C for 480 min; after this, the pH was adjusted to below four by adding 10 % HNO₃. Last, the reactant was filtered and washed, then

dried in a vacuum drying oven overnight at 60° C. Ethylene glycol was used as the solvent as well as the reducing agent, sodium citrate was used as a complexing agent and stabilizer, and multiwalled CNTs were used as the carriers.

2.2. Preparation of the MEAs

Nafion 211 membranes (DuPont, USA) were treated at 80° C in a 5 wt% H₂O₂ aqueous solution for 0.5 h, then treated in 0.5 M H₂SO₄ solution at 80° C for 0.5 h, and subsequently in distilled water at 80° C for another 0.5 h. We then mixed a commercial Johnson Matthey Hispec 4100 Pt/C catalyst (40 wt%) (denoted as JM Pt/C) with Nafion dispersion (5 % Nafion ionomer solution, DuPont, USA) and isopropanol (IPA) using sonication for 0.5 h to fabricate the anode CLs. The Pt loading at the anode was 0.2 mg cm⁻², and the dry Nafion content in the anode CLs was adjusted to 25 wt%. Cathode inks were prepared by mixing JM Pt/C, homemade Pt/CNT, Nafion dispersion, Teflon (60 % PTFE dispersion, Aldrich, USA), and IPA. The weight percentages of Pt/CNT in terms of the total amount of JM Pt/C and Pt/CNT were 0, 31, 46, 62, and 100, respectively. Teflon (60 % PTFE dispersion) was added to the catalyst ink to replace part of the Nafion and thereby make the cathode CLs hydrophobic. The PTFE content with respect to the entire cathode CL was 10 wt%, the dry Nafion content in the anode CLs was adjusted to 15 wt%, the Pt loading at the cathode was 0.3 mg cm⁻², and the active electrode area was 26 cm². The inks were sprayed on both sides of a Nafion 211 membrane to form the CLs. We have labeled MEAs with a Pt/CNT content in the cathode of 0, 31, 46, 62, and 100 wt% MEA-CNT0, MEA-CNT31, MEA-CNT46, MEA-CNT62, and MEA-CNT100, respectively.

2.3. Physical Characterization of the MEAs

We observed the thickness of the cathode CLs using a scanning electron

microscope (S-3700N, Japan). The samples for cross-sectional SEM were fabricated by breaking up the MEAs in liquid nitrogen to acquire smooth cathode cross-sections. We also measured the static contact angle using a contact angle meter (OCA 40 Micro, DataPhysics, Germany) with a droplet volume of 5 μL . EIS measurements were carried out at a cell voltage of 0.8 V with an amplitude of 5 mV and in the frequency range of 10 kHz to 100 mHz. The pore size distribution in the CL was measured by cutting into pieces membranes that on one side were covered with cathode CLs and on the other side had nothing, then using a Tristar 3020 (Micromeritics, USA).

2.4. Single-cell Evaluation of the MEAs

The MEAs were tested with our designed air-breathing testing cell on an FCT Fuel Cell Testing System (Arbin, USA), in an air-conditioned room at a temperature of 26°C . The cell temperature was not controlled because the cathode was open to the atmosphere. The flow rate of dry hydrogen was tuned according to the discharge current, and the cathode obtain oxygen directly by exposure to the atmosphere.

3. Results and Discussion

Generally, water management is one of the biggest challenges for PEMFCs ^[24]. Cathode flooding causes diminished performance in the high current density region. Fig. 1 shows the **water management ability** of cathode CLs containing different amounts of Pt/CNT. It can be seen that the addition of Pt/CNT enhanced the hydrophobicity of the cathode CL. This is attributable to an enlargement of the cathode CL's accessible specific surface area; the reduced stacking density of the CL led to uniform distribution of Nafion and PTFE within the CL. Well-dispersed binders resulted in superior water management in MEA-CNT46 and consequently better performance.

Figs. 2 and 3 present, respectively, surface and cross-sectional SEM micrographs of cathode CLs containing different amounts of Pt/CNT. The images show that the catalysts were uniformly dispersed and the Pt/C was successfully inserted into the CNT skeleton (see Fig. 2). The composite catalysts exhibited porous and cross-linked architectures, different from those of carbon black and the CNTs. Cathode CLs containing Pt/CNT and Pt/C exhibited more macropores than the CL with only Pt/C, suggesting that the presence of Pt/CNT enlarged the spaces within the CL. The stacking density of Pt/C was significantly reduced by mixing Pt/CNT and Pt/C, consequently enhancing the mass transportation and electrochemical performance of the AB-PEMFC. The Pt/C filled the macropores between the CNTs, helping to reduce the charge-transfer reaction resistance, as we will discuss later. To explore the variation in CL stacking density, we used SEM to measure the thickness of cross-sections of the cathode CLs.

Fig. 3 shows cross-sections of the cathode CLs. We found that the thickness of the CLs increased with the amount of added Pt/CNT; the maximum and minimum thicknesses were 16.54 and 10.83 μm . Our previous study^[25] indicated that the thickness of a cathode CL with an optimized cathode gas diffusion layer has little influence on the physical contact resistance, but the charge transfer resistance increases as the thickness of the cathode CL increases.

To evaluate the structure of the cathode CLs, we characterized their pore size distribution using a nitrogen adsorption method. As shown in Fig. 4, the peak pore diameter of MEA-CNT0 was in the range of 40 to 100 nm; in contrast, after the addition of Pt/CNT, the pore diameter ranged from 110 to 170 nm. Our results indicated that the presence of Pt/CNT and Pt/C made the pore size larger and the pores more widely distributed.

To understand how the Pt/CNT affected cell performance, we used I-V curves and electrochemical characterization to quantify the main sources of voltage loss. Fig. 5 present the performance of single cells containing different amounts of Pt/CNT in the cathode CL. Compared to MEA-CNT0, MEA-CNT100 (with 100 wt% Pt/CNT in the cathode CL) showed inferior performance in the kinetic and ohmic regions, while the other three MEAs with Pt/CNT in the cathode CL exhibited better performance across the whole current density region. This explicitly indicated that the coexistence of appropriate amounts of Pt/CNT and Pt/C in the cathode CL reduced the charge transfer and mass transfer resistance. MEA-CNT46 achieved the best performance: at a working voltage of 0.6 V, the current density was 290 mA cm^{-2} , which was 14 % higher than that of MEA-CNT0 (250 mA cm^{-2}). Evidently, having an appropriate amount of Pt/CNT in the cathode CL played the key role in the overall performance of the AB-PEMFC; too much Pt/CNT decreased the cell performance. We propose that the CNTs improved charge transfer and enhanced electrical conductivity more than carbon black^[26]. In addition, the tubular structure of Pt/CNT made the CL more gas permeable.

To further explore the electrode process kinetics of our MEAs, EIS was used to quantify the voltage loss contributions from the different electrochemical processes. Fig. 6 presents the EIS curves of MEAs with different amounts of Pt/CNT in the cathode CL at a cell voltage of 0.8 V. Through simulation with Ivium software, we determined the corresponding ohmic resistance (R_{Ω}) and charge transfer resistance (R_{ct}). The R_{Ω} of the MEAs dropped as the amount of Pt/CNT in the cathode CL increased, up to 64 wt%. This suggested that adding the appropriate amount of Pt/CNT to the cathode CL improved the MEA's performance, while too much had a negative impact. MEA-CNT46 showed the smallest charge transfer resistance,

implying that it had a more efficient conductive layer than the other MEAs because the CNTs can be bridged across particles. The ohmic resistance of MEA-CNT62 was comparable to that of MEA-CNT46, but the former's charge transfer resistance was larger, which is attributable to the prolonged proton transfer path arising from superfluous Pt/CNT. The lower ohmic resistance of MEA-CNT100 compared with that of MEA-CNT0 may have stemmed from the π electrons of the CNTs interacting with the Pt particles, and the Pt particles deposited on the outer shell of the CNTs interacting strongly with the carriers via π -bonding^[27].

4. Conclusions

Pt/CNT catalysts were successfully synthesized by a sol-gel method and added to cathode CLs to improve cell performance. SEM and pore size distribution results showed that the resulting MEAs had typical porous and cross-linked architectures, and that the synergistic effects between Pt/CNT and Pt/C enhanced the electrochemical activity of Pt particles. The fuel cell performance data indicated that adding an appropriate amount of Pt/CNT to the cathode CL significantly enhanced the ORR activity. MEA-CNT46, containing 46 wt% Pt/CNT in the cathode CL, exhibited the best performance: the current density at 0.6 V was 290 mA cm^{-2} , which was 14 % higher than that of MEA-CNT0 (250 mA cm^{-2}). We suggest that the better performance of the MEAs containing both Pt/CNT and Pt/C may have resulted from several factors: synergistic effects between Pt/CNT and Pt/C, low electrical resistance, a short proton transfer path, porosity, and effective water management.

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A high performance air-breathing cathode for air-breathing PEMFCs is prepared by using the mixture of Pt/C and Pt/CNTs as cathode catalysts. The significantly enhanced performance has been achieved by the PEMFC with the cathode.

Fig. 1. Contact angle on the surface of the cathode CL of: (a) MEA-CNT0; (b) MEA-CNT100; (c) MEA-CNT31; (d) MEA-CNT46; (e) MEA-CNT62.

Fig. 2 SEM micrographs of cathode CLs: (a) MEA-CNT0; (b) MEA-CNT100; (c) MEA-CNT31; (d) MEA-CNT46; (e) MEA-CNT62.

Fig. 3 SEM micrographs of cathode CL cross-sections: (a) MEA-CNT0; (b) MEA-CNT100; (c) MEA-CNT31; (d) MEA-CNT46; (e) MEA-CNT62.

Fig. 4 Pore size distribution in various cathode CLs.

Fig. 5 Polarization curves obtained with different cathode catalyst compositions. Pt loading at the anode: 0.2 mg_{Pt} cm⁻²; Pt loading at the cathode: 0.3 mg_{Pt} cm⁻²; room temperature.

Fig. 6 EIS curves of MEAs with different cathode CL compositions.