Effect of the Microporous Layer Structure and Hydrophobicity on the Performance of Direct Methanol Fuel Cells

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Abstract. Direct methanol fuel cells (DMFCs) have drawn special attention for their portability and fewer safety concerns because of the use of liquid fuels. The microporous layers (MPLs) play an important role in improving the performance of DMFCs, especially at high current density. In this work, polypyrrole nanowire networks grown on carbon paper by in-situ electrochemical polymerization are used as cathode MPL. The hydrophobicity of the MPL is tuned by changing the amount of polytetrafluoroethylene (PTFE). With the optimized structure and hydrophobicity of the MPL, the peak power density of the DMFC is 102 m W cm\textsuperscript{-2}, which is 24\% higher than that of the DMFC with traditional MPL consisted of carbon black.

Introduction

Direct methanol fuel cells (DMFCs), as one of promising power sources for portable applications, have drawn special attention for their high-energy density and fewer safety concerns because of the use of liquid methanol solution [1, 2]. The membrane electrode assembly (MEA) is the key component of DMFC, which is consisted of gas diffusion layer (GDL), catalyst layer (CL) and membrane. The GDL serves to uniformly distribute reactants over the electrode surface, vent the reaction products and electrically connect the CL and the current collector, which comprises backing layer, typically made of carbon paper and carbon cloth, and microporous layer (MPL) [3, 4]. The MPL creates better electrical and thermal contact between the CL and the backing layer by providing a smoother, more continuous interface and improves water management in the MEA [5]. But the MPL actually adds mass transfer resistance of reactants and products. So the benefit of MPL is debated.

Wang et al. [6, 7] predicted that the water flux from the cathode toward the anode was enhanced with smaller pore size, larger thickness and hydrophobicity and lower porosity of the MPL. Liao et al. [8] believed that the water generated in the cathode CL could be drained by capillary tubes in the MPL. Popov et al. [9] studied the effect of PTFE content in the MPL on water management in PEM fuel cells and they found that the MPL loaded with 40 wt.% PTFE leaded to the best fuel cell performance. Recently, it was found network MPL could improve the mass transfer property and water management of DMFCs [10, 11].

Polypyrrole as an attractive conductive polymer has been extensively employed as nanostructred electrode material [12]. The low cost of polypyrrole, combined with its high conductivity [13], high chemical stability in acid medium [14], good thermal conductivity [15-16], as well as its facile to be constructed in nanowire networks, make it an appealing material for MPL. In this study, a network
cathode MPL through polypyrrole nanowires grown in-situ on the carbon paper through an electrochemical polymerization is reported. And the hydrophobicity of the MPL is tuned by changing the amount of polytetrafluoroethylene (PTFE). The optimized network MPL can improve the performance of DMFC.

Experimental

Preparation Polypyrrole Nanowire Networks on Carbon Paper

The polypyrrole nanowire networks were in-situ electrochemical polymerization on hydrophobic carbon paper using a CHI 760D electrochemical workstation system in a three-electrode cell. The carbon paper (3.5×3.5 cm$^2$) was used as the working electrode. A Pt plate (5×7 cm$^2$) and a saturated calomel electrode (SCE) connected with a saturated potassium chloride (KCl) solution via a salt bridge served as the counter electrode and reference electrode, respectively. The electrolyte comprised PBS (pH=6.86), 0.1 M $p$-toluene sulfonic acid sodium and 0.1 M pyrrole. The potential applied to the working electrode was 0.75 V (vs. SCE) with duration of 30 min. Finally, 1 wt. % PTFE solution was sprayed on the polypyrrole nanowire networks. The amounts of PTFE in MPL were 0, 20, and 40 wt. % and the samples were labeled as PPy-0, PPy-20 and PPy-40, respectively. The samples were heated in a N$_2$ atmosphere at 340 °C for 1 h with increasing rate of 5 °C min$^{-1}$ and used as the cathode MPL.

For comparison, the traditional MPL consisted of carbon black (Vulcan XC-72, Cabot Corp.) was also prepared. The MPL were fabricated by spraying the carbon black slurry (60 wt.% Vulcan XC-72 with 40 wt.% PTFE dispersion in isopropanol) onto carbon paper. The sample was labeled as CB-40. The loading of the carbon black was consistent with the loading of polypyrrole. The method to prepare anode MPL was the same with the cathode MPL consisted of carbon black (CB-40) and the loading of carbon black was 1 mg cm$^{-2}$.

DMFC Single Cell Performance Tests

The DMFCs were activated at 0.6 V and 80 °C using a single cell with serpentine flow channels until two polarization curves were coincidental. The performances of DMFCs were evaluated by a fuel cell test system (FCTS, Arbin Co.) with a 0.5 M methanol solution. The flow rates of oxygen and methanol solution is 80 mL min$^{-1}$ and 1 mL min$^{-1}$, respectively.

Results and Discussion

Characterization of the MPL

The typical morphology of MPL fabricated with carbon black is shown in Figure 1a. It can be seen that carbon nanoparticles with an average diameter of 70 nm are randomly accumulated on the surface. Figure 1b shows that the diameters of the polypyrrole nanowires are about 55 nm and the lengths are in the micrometer range. The porosity of the MPL with polypyrrole nanowire networks is larger than that with carbon black, which can be verified by the SEM images in Figure 1.

Figure 1. SEM images of the MPL surface morphology with carbon black (a) and polypyrrole nanowire networks (b).
To research the influence of the heat treatment on the structure of polypyrrole nanowire networks, the TGA curves of PTFE and polypyrrole in N₂ atmosphere are compared in Figure 2. At 340 °C, the weight losses of the PTFE and polypyrrole are about 4.5 wt% and 11.2 wt%, which demonstrate the good thermal stability of the two materials in MPL. 

Figure 2. TGA curves of PTFE and polypyrrole.

Figure 3a-e show the wetting behaviors of different MPLs and CL. The contact angle (CA) of PPy-0 is only 110°, which is more hydrophilic than CL (Figure 3e, CA=119°). Adding PTFE to the polypyrrole nanowire networks can increase the hydrophobicity of the MPLs significantly. The CAs of the PPy-20 and PPy-40 are 148° and 153°, respectively. It is interesting that the CAs of PPy-20 and CB-40 are the same, but the PTFE loadings of the two samples are different. To understand the mechanism of this phenomenon, a schematic illustration of the PTFE chains coating on the polypyrrole nanowires and carbon black based on SEM results is presented in Figure 3f. It is evident that the network MPL needs less PTFE than the tradition MPL to get the same hydrophobicity, which is benefit for improvement electron conductivity and mass transfer in the network MPL.

The mass transport in the MPL is tested by a homemade instrument (Figure 4a) to elucidate the advantage of network MPL. Mass transport behavior is examined by measuring the difference in the pressure of N₂ before and after penetrating through the MPL. As expected, the resistance to mass transport was smaller for the network MPL with larger pores than that for the traditional MPL (Figure 4b, CB-40), and thus the pressure difference is larger in the samples with larger PTFE contents (Figure 4b, PPy-0, PPy-20 and PPy-40).
DMFCs Single Cell Performances

Figure 5 shows the polarization curves and power density curves of DMFCs with different MPLs. Apparently, the DMFC with PPy-20 exhibits the best performance with a peak power density of 102 m W cm\(^{-2}\), which is 24\% higher than that of the DMFC with traditional MPL (CB-40, peak power density of 82 m W cm\(^{-2}\)). For the sample PPy-20, the DMFC performance drops (peak power density of 97 m W cm\(^{-2}\)), while the DMFC with PPy-0 shows the lowest performance (peak power density of 79 m W cm\(^{-2}\)).

Summary

In summary, polypyrrole nanowire networks are in-situ electrochemical polymerization on the carbon paper and used as cathode MPL. The hydrophobicity of the network MPL can be facilely controlled via altering the amount of PTFE. The network MPL needs less PTFE than the tradition MPL to get the same hydrophobicity due to the structural advantages of nanowire, which is benefit for improvement electron conductivity and mass transfer in the network MPL. With the optimized structure and hydrophobicity of the MPL, the peak power density of the DMFC is 102 mW cm\(^{-2}\), which is 24\% higher than that of the DMFC with traditional MPL consisted of carbon black.

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References


