

High electrochemical activity of Pt/C cathode modified with NH_4HCO_3 for direct methanol fuel cell

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Received: 30 October 2008 / Revised: 24 February 2009 / Accepted: 6 March 2009 / Published online: 24 March 2009
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Abstract The electrochemical activity of Pt/C cathode for direct methanol fuel cell was improved by introducing NH_4HCO_3 to the catalyst layer as the pore-forming agent during preparation process of catalyst-coated membrane. SEM analysis revealed that NH_4HCO_3 contributed to the formation of additional porosity and the dispersion of the catalyst particles. The modified catalyst layer promoted the electrochemical and mass transport processes. It was suggested that the optimal weight ratio of the catalyst to NH_4HCO_3 was 2:3. As a result, the single cell exhibited a 21% increment in the peak power density at 50 °C, with a highest electrochemical surface area of $446 \text{ cm}^2 \text{ mg}_{\text{Pt}}^{-1}$. However, an extremely high content of NH_4HCO_3 yielded discontinuous pathways for the electron transfer in the catalyst layer.

Keywords Direct methanol fuel cell · Catalyst-coated membrane · Electrochemical surface area · Pore-forming agent

Introduction

The commercialization of direct methanol fuel cells (DMFC) is challenged by minimizing the noble metal loadings under the precondition of the performance requirements [1–5]. Great efforts have been addressed on the novel

fabrication techniques of membrane electrode assembly (MEA), which can increase both the Pt utilization and the cell performance [6–11]. Compared to conventional gas diffusion electrode, catalyst-coated membrane (CCM) is a technique to achieve a better contact between the membrane and the catalyst layer [12–14]. Nevertheless, the degradation of the electro-catalytic activity is still inevitable during the preparation process of the CCM [15]. As far as the cathode is concerned, the agglomeration of catalyst powder in the catalyst ink, the growth of Pt particles at the hot-pressing step, as well as the loss of the electrochemical surface area are all noteworthy issues.

The application of the pore-forming additives is an alternative way to restrict the catalyst agglomeration, which is critical to the performance of the electrode [16, 17]. Previous studies about pore-forming agents mostly focused on the promotion of mass transports due to the higher porosity [6, 18–21]. Tucker et al. [22] added Li_2CO_3 into Pt-Ru black catalyst layer and achieved a 50% increase in power density. Zhao et al. [19] used NH_4HCO_3 , $(\text{NH}_4)_2\text{SO}_4$, and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as the pore-formers to prepare the MEAs, and discovered that NH_4HCO_3 was in favor of the uniform dispersion of the catalysts on the surface of the electrode. Reshetenko et al. [23] reported NH_4HCO_3 was effective for the formation of the mesopores. On the other hand, the introduction of pore-formers changes the distribution of the electrochemical active sites. However, little research concerned about the influence of the textual improvement on the electro-catalytic reactions.

In this work, NH_4HCO_3 was incorporated with the cathode catalyst layer components at different contents. Various electrochemical measurements, including cyclic voltammetry, electrochemical impedance spectroscopy, and steady-state polarization, were employed to investigate the electrochemical performance of the modified cathode and the single cell.

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Experimental

Fabrication of the CCMs

Untreated and wet-proof (25 wt.% PTFE) carbon papers (TGP-H-090, Toray Industries) were used as the anode and cathode backings, respectively. A mixture of 95 wt.% carbon black (Vulcan XC-72, E-TEK) and 5 wt.% Nafion ionomer was coated on the anode backing as the anode microporous layer (MPL). The cathode MPL supported on the cathode backing was comprised of 75 wt.% carbon black and 25 wt.% PTFE. Nafion[®] 117 membranes were pretreated in 3 wt.% H₂O₂ solution and ultra-pure water, and then converted to Na⁺ form membranes to strengthen their tolerance against high temperature. The commercial 30 wt.% Pt-Ru/C (20 wt.% Pt and 10 wt.% Ru) (HiSpec 5000, Johnson Matthey Plc.) and the home-made 40 wt.% Pt/C based on impregnation–reduction method [24, 25] were used as the anode and cathode catalysts, respectively. The catalyst loadings were 3.0 mg cm⁻² Pt-Ru on the anode and 2.0 mg cm⁻² Pt on the cathode, and the active area of each electrode was 5 cm². The catalyst inks were prepared by the method reported in our previous publication [26, 27]. The compositions of the cathodes were varied in the weight ratio of the catalyst powders to NH₄HCO₃, as shown in Table 1. According to the decal method [28], the catalyst inks were sprayed on the Teflon films. Subsequently, the decals were positioned on each side of the membrane and the catalyst layers were transferred onto the membrane by hot-pressing at 185 °C and 15 MPa for 90 s. After re-protonated in 0.5 mol L⁻¹ H₂SO₄ solution, the CCMs were combined with the anode and cathode diffusion layers by hot-pressing at 135 °C and 8 MPa for 90 s.

SEM analysis

The morphologies of the normal cathode catalyst layer and that treated by NH₄HCO₃ were observed by a Sirion 200 Scanning Electron Microscope (SEM) (FEI Electron Optics, Netherlands) at a magnification of 4×10⁴.

Table 1 Relationship between cathode composition and electrochemical surface area

Cathodes	Weight ratio of catalyst to NH ₄ HCO ₃	ESA/cm ² mg _{Pt} ⁻¹
Reference	–	379
1	2:1	408
2	1:1	431
3	2:3	446
4	1:2	425

Electrochemical measurements

A commercial single cell (Electrochem, USA) was employed to investigate the electrochemical performances of the CCMs at 50 °C. The *I-V* and power density curves of the CCMs were measured by a Fuel Cell Test System (Arbin Instruments, USA). A 2 mol L⁻¹ methanol solution was pumped to the anode at a flow rate of 2 mL min⁻¹. Meanwhile, humidified oxygen at ambient pressure was fed to the cathode at a flow rate of 200 mL min⁻¹.

Electrochemical impedance spectroscopy of the CCMs was tested by a CHI 604B Electrochemical Analyzer (Shanghai Chen-Hua Instruments, China) when the cells operated at a current density of 200 mA cm⁻². The AC amplitude of the sinusoidal voltage signal was 0.005 V and the frequency was ranged from 10⁵ Hz to 10⁻² Hz.

Cyclic voltammetry (CV) technique was performed to calculate the electrochemical surface areas (ESA) of the cathodes. During the test, the anode was delivered with humidified hydrogen at a flow rate of 200 mL min⁻¹ and functioned as a dynamic hydrogen electrode (DHE). Simultaneously, the cathode was under the circumstance of ultra-pure nitrogen at a flow rate of 200 mL min⁻¹. The CV sweep was stepped at a scan rate of 0.01 V s⁻¹ in a potential range of between 0.05 V and 1.2 V vs. the DHE. The ESA of the cathode was determined by calculating the charge for the hydrogen desorption peak.

Results and discussions

Morphological characteristics

The surface micrographs of the cathode catalyst layers are shown in Fig. 1. The normal catalyst layer in Fig. 1a displays a dense and flat morphology, which is unfavorable to the diffusion of the oxygen into the triple-phase boundary. In addition, the Pt particles inside the agglomerates cannot take part in the reactions. By contrast, the catalyst particles are well-dispersed and the formation of larger agglomerates is suppressed [29], as shown in Fig. 1b. More mesopores in favor of the oxygen transport emerge in the catalyst layer after the pore-former decompose.

Electrochemical performance

Cyclic voltammograms of Pt/C cathodes in Fig. 2 reveal the change of the electrochemical surface area. The peaks at 0–0.4 V corresponded to the hydrogen desorption process. The ESAs of the cathodes are calculated by means of Eq. 1 [30]. Here, *Q*_H symbolizes the coulombic charge for hydrogen desorption (mC cm⁻²), [Pt] represents the Pt loading on the electrode (mg cm⁻²) and 0.21 (mC cm⁻²) is

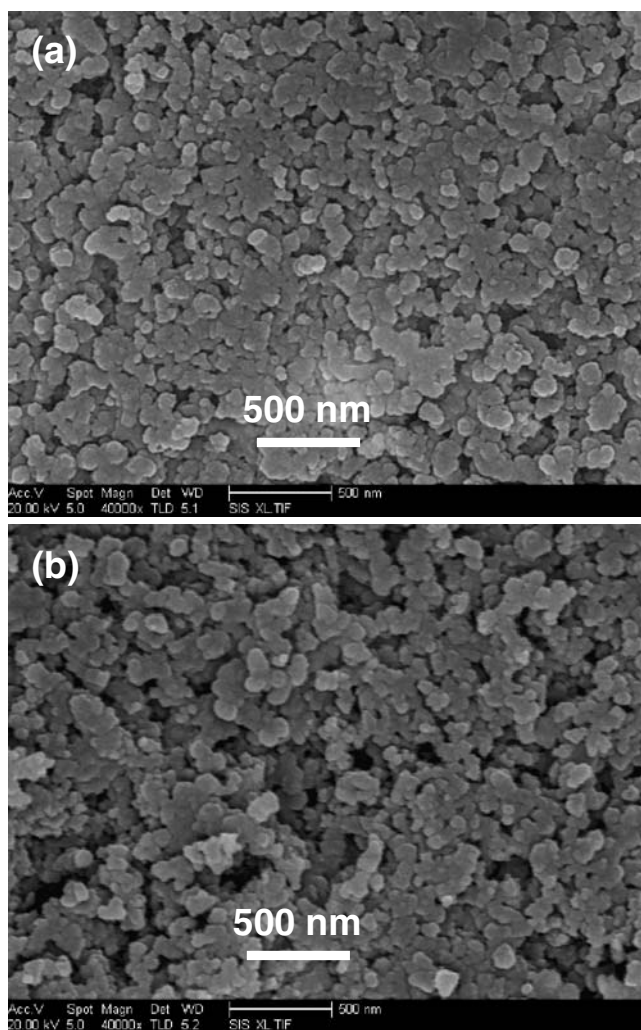


Fig. 1 Surface micrographs of cathode catalyst layers. **a** Normal, **b** adding NH_4HCO_3

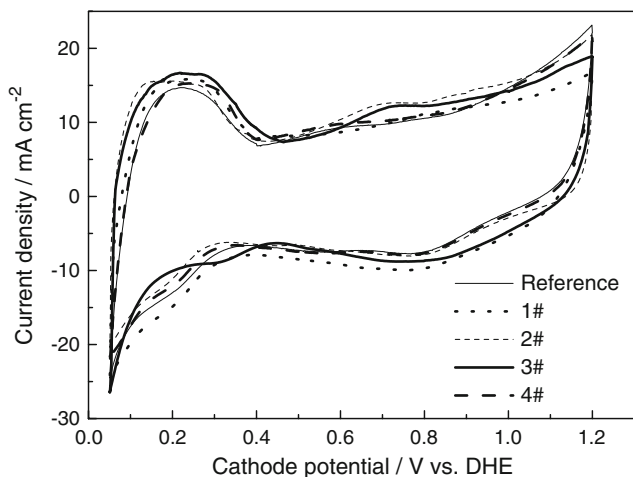


Fig. 2 Cyclic voltammograms of Pt/C cathodes in a range of 0.05–1.2 V at a scan rate of 0.01 V s^{-1}

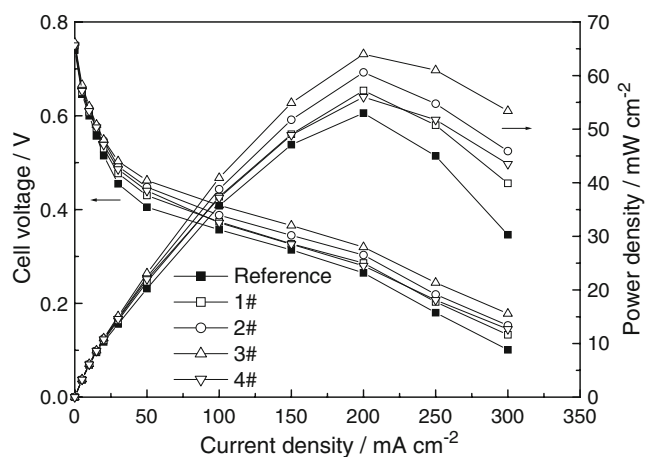


Fig. 3 Comparison of power density curves of single cell using different CCMs at 50°C

the charge required for the adsorption of H_2 monolayer on the smooth Pt surface. As shown in Table 1, the CCM-3# characterizes the highest ESA of $446 \text{ cm}^2 \text{ mg}_{\text{Pt}}^{-1}$ with the weight ratio of 2:3. Nafion ionomers embed into the catalyst particles more easily owing to the increase in the porosity, which is beneficial to the extension of the triple-phase boundary. Therefore, the improvement of the cathode texture results in the increase of the Pt utilization. A noteworthy phenomenon is that the ESA decreases with even more NH_4HCO_3 content. This is mainly because an extremely high porosity yields discontinuous pathways for the electron transfer in the catalyst layer.

$$\text{ESA} = \frac{Q_{\text{H}}}{[\text{Pt}] \times 0.21} \quad (1)$$

The I - V and power density curves of the CCMs at 50°C are illustrated in Fig. 3. It is indicated that the introduction of NH_4HCO_3 results in the increase in cell output. For the

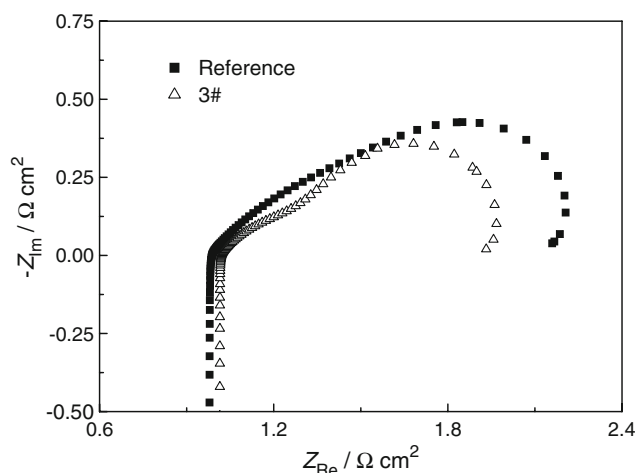


Fig. 4 Nyquist diagrams of the reference CCM and CCM-3# at a current density of 200 mA cm^{-2} and 50°C

modified CCMs, the overpotentials are reduced at low current density region due to the increase in Pt utilization. Moreover, the additional mass transport passages help to the decrease in the concentration polarization at high current density region. The optimal weight ratio of the catalyst to NH_4HCO_3 is found to be 2:3, and a 21% increment of the peak power density (from 53 mW cm^{-2} to 64 mW cm^{-2}) is obtained. However, the cell performance degrades with a further increase in the NH_4HCO_3 content.

Nyquist diagrams of the CCM-3# with the highest performance and the reference are presented in Fig. 4. According to the I - V curves in Fig. 3, the electrode kinetics is controlled by the oxygen transport process at a current density of 200 mA cm^{-2} . The diagrams are similarly shaped by two capacitive semi-circles. It is difficult to model this complicated cell system, which involves charge and mass transfers, as well as crossover behaviors, with a suitable equivalent circuit. Nevertheless, the loops at high-frequency regions are associated with the electro-catalytic activity of the electrodes and the loops at low frequency are attributive to the mass transport processes [31, 32]. Although CCM-3# displays a little higher ohmic resistance (intercept at high-frequency region) than that the normal CCM, the significant decreases in the electrochemical and mass transport resistances due to the modification of cathode catalyst layer contribute to the promotion of the cell performance.

Conclusions

The electrochemical performance of the DMFC cathode was improved after the modification of the catalyst layer by NH_4HCO_3 . It was indicated by SEM analysis that the pore-forming agent not only promoted the oxygen diffusion into the catalyst layer, but also prevented the agglomeration of the catalyst particles. The optimal weight ratio of the catalyst to NH_4HCO_3 was found to be 2:3. In that case, the single cell displayed a 21% increment in the maximum power density. The higher electrochemical surface area and the lower cathode reaction resistance both benefited from the textual improvement of the catalyst layer.

Acknowledgements The authors are grateful to the financial supports from Natural Science Foundation of China (No. 50872027) and Coslight International Group.

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