Effect of hydrophilic SiO₂ additive in cathode catalyst layers on proton exchange membrane fuel cells

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Abstract
Hydrophilic nanosized SiO₂ and sulfonated SiO₂ particles were added to the cathode catalyst layer (CL) to improve the water wettability and the performance of a proton exchange membrane fuel cell (PEMFC) at low humidity. It was found that both nanosized SiO₂ and sulfonated SiO₂ additive improved the hydrophilicity of the cathode CL by the contact angle measurement. Contrary to nanosized SiO₂, sulfonated SiO₂ improved the conductivity of the cathode CL. Increased wettability of the cathode CL from SiO₂ maintained fuel cell at hydration conditions. This phenomenon had a profound influence on electrode performance at low humidity. Since the sulfonic groups in sulfonated SiO₂ improved the proton conductivity of the cathode CL, the cell with sulfonated SiO₂ showed better performance.

1. Introduction

It is well known that proper amount of water in the membrane-electrode assembly (MEA) is necessary for the proton conduction in the membrane and the catalyst layer (CL) for proton exchange membrane (PEM) fuel cells. Thus, the inlet flows are usually humidified. On the other hand, high humidity of inlet flows may lead to flooding of the pores in the CL [1,2].

To reduce the energy consumption of the humidifier, researchers are trying to operate PEMFCs at low humidity. Kannan et al. [3] designed multilayer nano-porous gas diffusion layers (GDL) for PEM fuel cells operation at low humidity. Self-humidifying membranes were prepared by dispersing catalyst particles [4,5] and the hydrophilic material, such as SiO₂ and TiO₂ [6,7] into Nafion resin to prepare organic/inorganic composite membranes. Jung et al. [8] added nanosized SiO₂ particles to the CL to improve the hydrophilicity. The silica sol (prepared from hydrolysis of TEOS solution) and catalyst inks were mixed and sprayed on a membrane [9]. However, the performance of these cells degraded at fully humidification and the improvement at low humidity was not obvious.

In this work, SiO₂ particles were added to the cathode CL to improve the wettability and performance of the MEAs at low humidity. To avoid the negative effect of the dielectric characteristic of SiO₂, nanosized SiO₂ particles and 1.3 propane sultone were mixed to prepare sulfonated SiO₂ [10,11]. The characters of the cathode CL and the performance of the MEAs with various contents of nanosized SiO₂ or sulfonated SiO₂ were evaluated.

2. Experimental

2.1. Preparation of MEAs

2.1.1. Standard MEAs
Forty weight percent of Pt/C (Johnson Matthey Inc.), 5 wt.% Nafion solution (DuPont) and isopropyl alcohol were mixed to form the catalyst inks for electrodes. The catalyst ink was firstly sprayed onto a PTFE membrane, and then was transferred onto a Nafion® membrane. The platinum loading for the anode and the cathode were both 0.4 mg cm⁻². The fabricated catalyst coated membrane (CCM) was pressed with wet-proofed Toray carbon paper to form a MEA. The effective area of the MEA was 4 cm².

2.1.2. SiO₂-doped MEAs
SiO₂ (20 nm, Zhejiang China) was added to the catalyst inks for the cathode CL, and the catalyst inks of anode were the same as that of the standard MEAs. The SiO₂-doped MEAs were prepared by the same method as that described for standard MEAs.

2.1.3. Sulfonated SiO₂-doped MEAs
The sulfonated SiO₂ was prepared with 1.3 propane sultone (1,3-PS) according to the method reported by Munakata et al. [10,11]. Then sulfonated SiO₂ was mixed with the standard catalyst inks for the cathode CL. The anode catalyst inks and the method of
sulfonated SiO2-doped MEAs preparation was the same as that described for SiO2-doped MEAs.

2.2. Contact angle measurement of the cathode CL

The hydrophilicity of the cathode CL used in this work was tested with the KRÖSS DSA100 Drop Shape Analysis System. The contact angle was fitted with a tangent to the three-phase interface where the liquid surface touched the solid surface with the tangent method of Sessile Drop Fitting. An image was taken to analyze the contact angle of the drop water at room temperature.

2.3. Conductivity

The samples made by Nafion@212 and the cathode CL with different content of nanosized SiO2 or sulfonated SiO2 were soaked in deionized water at room temperature for 12 h. The conductivity of the samples was measured by the electrochemical impedance spectroscopy using a PARSTAT 2273A (Princeton, USA) electrochemical system.

2.4. Cell performance

The cell temperature was kept at 60 °C and the reactant gas flow was controlled as 30 ml min⁻¹/100 ml min⁻¹ for H₂/O₂ at atmospheric pressure. The polarization curve was recorded by a KFM 2030 impedance meter (Kikusui, Japan).

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After the initial performance test, the cells were purged with air of RH 20% at room temperature until the out gas RH was 50% [12]. Then, the cells were stabilized at 0.25 A cm⁻² for 0.5 h at RH 100% for the inlet gases. After that, the inlet gases of both the anode and the cathode were changed into dry gas (RH 20%) at room temperature, and the cells were operated at 0.20 A cm⁻² for 3 h.

3. Results and discussion

3.1. Contact angle of the cathode CL

The contact angle images of the cathode CL with nanosized SiO₂ or sulfonated SiO₂ are given in Fig. 1. The samples S0, S10, S10h stand for with no SiO₂, 10 wt.% nanosized SiO₂ and 10 wt.% sulfonated SiO₂ (based on the whole cathode CL) in each cathode CL. Both nanosized SiO₂ and sulfonated SiO₂ additive can improve the wettability of the cathode CL. However, the contact angle of the cathode CL with sulfonated SiO₂ is larger than that with the same content of nanosized SiO₂ because 1,3-PS affects the surface and the holes’ structure of the SiO₂ decreases the content of the –OH for the treatment. Therefore, the hydrophobic chain molecule decreases the water absorption ability.

3.2. Conductivity of the cathode CL

Fig. 2 presents the proton conductivities of the samples with different nanosized SiO₂ and sulfonated SiO₂ content at fully hydrated states. The proton conductivity of the sample without SiO₂ is 9.3 mS cm⁻¹. As nanosized SiO₂ in the cathode CL increases, the proton conductivity decreases due to the dielectric characteristic of SiO₂ in Fig. 2a. The conductivities of the samples with sulfonated SiO₂ are shown in Fig. 2b. When sulfonated SiO₂ content is 10 wt.%, the proton conductivity is 12.6 mS cm⁻¹, which is 3.3 mS cm⁻¹ higher than that contains no SiO₂. As the concentration of sulfonated SiO₂ increases, the proton conductivity increases due to the additional sulfonic groups in the sulfonated SiO₂.

3.3. Cell performance

The polarization curves of the cells with nanosized SiO₂ operated at fully humidity are shown in Fig. 3a. In the low current density region, the performance is not affected by the addition of SiO₂.
obviously. While in the high current density region, the added SiO$_2$ in the cathode CL causes a voltage drop due to the cathode CL flooding [8]. The voltages of the cells with nanosized SiO$_2$ in the cathode CL at 0.2 A cm$^{-2}$ at 20% relative humidity are shown in Fig. 3b. The voltage of the cell without SiO$_2$ keeps unstable within the initial 40 min, then the voltage becomes 0.58 V when the cell runs for 3 h. The cell does not produce enough liquid water immediately but after the water vapor concentration in the gas reaches the saturation value in the low humidity cases and the catalyst layer could not keep enough water to retain MEA hydration, therefore the cell suffers from membrane dry out in the initial 40 min and the cell performance does not present stable [13,14]. Hydrophilic SiO$_2$ in the cathode CL at the low humidity improves the cell performance. The voltage of the cell with 2 wt.% nanosized SiO$_2$ is also unstable within the initial 30 min, and it is almost as the same as the voltage of the cell without SiO$_2$ at static-state. But the performance of the cells with 5 and 10 wt.% nanosized SiO$_2$ is more stable, and the voltages are 0.65 and 0.64 V, respectively. SiO$_2$ particles in the cathode CL could keep the MEA fully hydrated and play an important role in improving the voltages of the cells at low humidity. Due to back-diffusion driven at a lager cathode water concentration resulting from ORR, the anode water concentration increases, and the membrane could be hydrated [13,14]. Therefore, the performance of the cells with proper content of SiO$_2$ is improved.

To improve the cell performance at fully humidity, nanosized SiO$_2$ is substituted with sulfonated SiO$_2$. Fig. 4a shows the polarization curves of the MEAs with sulfonated SiO$_2$ in the cathode CL. When 2 and 5 wt.% sulfonated SiO$_2$ are added, the cells performance are improved, but the performance of the cell with 10 wt.% sulfonated SiO$_2$ degraded. So an optimal sulfonated SiO$_2$ content exists, which is about 5 wt.% The improvement of the performance could be attributed to the conductivity promotion caused by sulfonated SiO$_2$. The cells voltages at 0.20 A cm$^{-2}$ at 20% relative humidity are given in Fig. 4b. The cells with various amounts of sulfonated SiO$_2$ show higher and more stable performance than that without SiO$_2$. As the sulfonated SiO$_2$ content increases, the voltage of the cell also increases, the one of S5 h arrives the maximum 0.70 V. However, too much sulfonated SiO$_2$ (S10 h) additive does not improve the cell performance further.

4. Conclusions

By varying the contents of nanosized SiO$_2$ and sulfonated SiO$_2$ in the cathode CL, the effect of SiO$_2$ addition on the cathode CL contact angle, cathode CL conductivity and cell performance were investigated. As the content of nanosized SiO$_2$ or sulfonated SiO$_2$ increased, the cathode CLs became more hydrophilic. With the increase of the added nonconductive nanosized SiO$_2$, the conductivities of the cathode CLs decreased, but sulfonated SiO$_2$ additive improved the conductivity of the cathode CL.
For the cells with nanosized SiO$_2$ additive in the cathode CLs, the performances decreased at fully humidity. However, the results of stable operation with RH 20% reactant gas showed that SiO$_2$ additive in the cathode CL would favor the cell performance. The performances of cells with sulfonated SiO$_2$ increased at fully humidity. Addition of 5 wt.% sulfonated SiO$_2$ to the cathode CL showed the best performance at both fully humidity and low humidity conditions.

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References