A new hydrophobic thin film catalyst layer for PEMFC

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ARTICLE INFO

Article history:
Received 25 March 2009
Received in revised form 15 December 2009
Accepted 15 January 2010

Keywords:
Fuel cell
Proton exchange membrane (PEM)
Thin film catalyst layer
PTFE
Decal method

ABSTRACT

A new hydrophobic thin film catalyst layer (CL) was prepared by the decal method in this work. Polytetrafluoroethylene (PTFE) was introduced to the catalyst ink with 1 wt.% Nafion® ionomer as the hyperdispersant. Aluminum foil was adopted as the transferring medium which enabled the sintering process of PTFE. Then an appropriate amount of Nafion® ionomer was sprayed onto the CL for proton conduction. At last, the CL was transferred onto a Nafion® membrane and the catalyst-coated membrane (CCM) was formed. Contact angle measurement and mercury intrusion porosimetry test were conducted to characterize the hydrophobicity and porosity of the thin film CL. The results showed that PTFE addition favored the CL hydrophobicity and porosity. The optimal PTFE content was also deduced by comparing the fuel cell performance under different PTFE contents. Electrochemical analysis revealed that PTFE addition decreased the electrochemical active area (ECA) but enhanced the diffusion process in the CL.

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1. Introduction

Proton exchange membrane (PEM) fuel cells have attracted much attention due to the merits of high power density, high energy conversion efficiency and friendly environmental adaptability. As the core component of PEM fuel cells, the membrane electrode assembly (MEA) directly impacts on the cell performance. During the past years, much effort has been paid on improving the MEA preparation [1,2]. M. S. Wilson proposed a decal fabrication method of the thin film catalyst layer, in which the CL was directly supported on the membrane [1]. In this method, PTFE is eliminated and the dispersion of ionomer throughout the CL is improved. The typical thickness of the thin film CL is 5–10 μm [2,9]. However, a hydrophobic path does not form in this kind of CL, which increases the risk of water flooding. Thereafter, much attention has been paid on improving the fabrication process of the thin film CL. Park [10] reported a modified decal method in 2008, the catalyst transfer ratio during the decal process was promoted. Effects of Nafion® content, catalyst loading and membrane thickness on the performance of the thin film CL were investigated by Passos [11]. Except for the decal method, the thin film CL can also be fabricated by a direct spraying method. Catalyst ink is directly sprayed onto the membrane to form the catalyst-coated membrane (CCM). However, the Nafion® membrane swells severely when it encounters organic solvents in this method. To avoid the swelling phenomenon and make sure the CL is homogenous, Sun et al. proposed an improvement method [9]. According to their report, the Nafion® membrane was soaked in ethylene-glycol (EG) and a small amount of EG was added into the catalyst ink during the fabrication process. Furthermore, some research relevant to the depositing process of Pt and the enhancement of the interfacial properties was carried out [12,13]. No matter if direct spraying method or decal method is adopted, the gas diffusion path in the thin film CL is necessary for the cell performance. Some pore forming methods were also reported aiming at decreasing the gas diffusion resistance of the thin film CL [14–16]. The constructed pores were easy to be compressed. Besides the gas diffusion resistance, water management in the thin film CL is also

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doi:10.1016/j.ssi.2010.01.022
important. A hydrophilic CL can have a negative effect on the water removal rate during cell operation [20]. To improve the gas penetration and water management, the fabrication process of MEAs still can be improved.

In this work, a decal fabrication process for the hydrophobic thin film CL was proposed. By adopting 1 wt.% Nafion® ionomer as the hyperdispersant, PTFE was mixed homogeneously in the catalyst ink. Five relative low PTFE contents were investigated. The physical characteristics of the prepared catalyst-coated membrane (CCM) were measured. The electrochemical active area (ECA) and the fuel cell performance were also studied.

2. Experimental

2.1. Preparation of the CCMs

Nafion® ionomer was introduced into a 10 wt.% PTFE solution in an ultrasonic environment to form a PTFE-Nafion® solution, in which the Nafion® content was 1 wt.%. A mixture composed of Pt/C catalyst (50 wt.% Pt from Johnson Matthey Inc.), distilled water and isopropyl alcohol was agitated with ultrasonic for 30 min. Then a certain PTFE-Nafion® solution was added, and another 30 min ultrasound treatment was carried out. Finally, the catalyst ink was formed.

The catalyst ink was sprayed onto a smooth aluminum foil, which was sintered at 240 °C for 30 min and 340 °C for 30 min under a nitrogen atmosphere. This high temperature process destroyed the surfactant and made the PTFE hydrophobic. It was reported that the sulphonate functionality on the Nafion® polymer would be lost in the temperature range of 275–380 °C [21]. In this experiment, the 1 wt.% Nafion® from the PTFE-Nafion® solution decomposed due to the 30 min treatment at 340 °C.

A 5 wt.% Nafion® solution from DuPont was diluted in isopropyl alcohol, which was sprayed onto the catalyst layer. During this process, Nafion® penetrated the catalyst layer to form the proton transfer network. After all the residual solvent was evaporated, the catalyst layer was hot-pressed onto a Nafion® 212 (N212) membrane on both sides. Then the CCM was prepared. The Pt loading of the prepared CCM was 0.4 mg cm\(^{-2}\) on each side.

Fig. 1 shows the whole fabrication process of the CCM. A patent referring to this fabrication method has been registered in the Chinese State Patent Office [22]. Thin film hydrophobic CLs with 0 wt.%, 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.% PTFE were fabricated. In these CLs, the mass ratios of PTFE/carbon were 0, 0.025, 0.088, 0.15 and 0.21, respectively. The mass ratios of Nafion® to carbon were always 0.8.

2.2. Physical characterization of the CCMs

The cross-section morphology of the CCM was investigated with the Super Depth Surface Profile Measurement Microscope VK-8550 from KEYENCE. The image was obtained by zooming in for 1000 times. The contact angle of the CCM surface was measured by the KRÜSS DSA100 Drop Shape Analysis System. 3 μL distilled water was dropped onto the surface of the CCM at room temperature. Ten seconds after the water drop was placed on the surface, the contact angle image was taken. The contact angle was analyzed with the tangent method of Sesville Drop Fitting.

The porosity of the CCMs was measured by the mercury intrusion method with a Poremaster GT60 (Quantachrome). The pressure was from 1.38 × 10\(^5\) to 4.13 × 10\(^7\) Pa (0.2–0.6 × 10\(^4\) psi) and the mercury contact angle was 140°.

2.3. Single cell performance and electrochemical tests

Toray carbon paper (TGP-H-060) was chosen as the diffusion layer for anode/cathode. Two graphite polar plates machined with parallel flow channels acted as the current collectors and gas flow channels. With two organic glasses as the end plates, a single cell was assembled. The effective area of the single cell was 4 cm\(^2\). Cycling water was introduced between the graphite polar plates and the end plates to control the cell temperature.

The fuel cell performance was tested at H\(_2\)/O\(_2\) and H\(_2\)/Air conditions. When testing the H\(_2\)/O\(_2\) performance, pure hydrogen was used as the fuel and oxygen as the oxidant at atmospheric pressure. The flow rates were set at 40 ml min\(^{-1}\) and 100 ml min\(^{-1}\) for H\(_2\) and O\(_2\), respectively. The cell temperature was kept at 60 °C and the humidification temperatures were set at 65 °C/60 °C for H\(_2\)/O\(_2\). When testing the H\(_2\)/Air performance, the flow rates were set at 40 ml min\(^{-1}\) and 600 ml min\(^{-1}\) for H\(_2\) and air, respectively. The high gas flow rate removed more water out. As a result, the cell temperature was set at 65 °C and the humidification temperature was set at 70 °C/70 °C for H\(_2\)/Air. The utilization of O\(_2\)/Air at 0.5 A cm\(^{-2}\) was 6.7%/5.5%, and that at 1 A cm\(^{-2}\) was 13.9%/11.1% for O\(_2\)/Air.

The fuel cell was firstly activated until the steady state. Then the polarization curve of the cell was measured with a KFM 2030 Impedance Meter (Kikusui, Japan) using the Fuelcell-Load & Impedance Meter software (Kikusui, Japan). The i–V curve was obtained by measuring the voltage in intervals of 0.05 A cm\(^{-2}\) between 0 and 1 A cm\(^{-2}\). At each current step the equilibration time was 8 s. Along with each cell voltage, the corresponding ohmic resistance was also recorded. To ensure the measurement reproducibility, this testing process was repeated 3 times. The obtained three curves were almost consistent and the third curve was used. Then the EIS at two current densities were measured.

After the cell shut down, high-purity nitrogen was fed to the cathode with a flow rate of 50 ml min\(^{-1}\). The cyclic voltammetry (CV) measurement was carried out using BI-STAT 2 channel Potentiostat.
(USA, Princeton). The scan rate was 50 mV s$^{-1}$ and the voltage range was 0–0.8 V referring to the hydrogen electrode.

3. Results and discussions

3.1. Physical characteristics of the CCMs

According to Mao’s results [23], the Nafton® ionomer can act as a hyperdispersant for the PTFE water dispersion when preparing the gas diffusion layer. In this work, the Nafton® hyperdispersant is introduced into the PTFE dispersion for the CL fabrication. Since the investigated PTFE contents are relatively low (0 wt.%–5 wt.%) and the Nafton® hyperdispersant is adopted, the aggregation phenomenon of PTFE is improved. The cross-section morphology of the CCM is shown in Fig. 2. The picture clearly shows the three layers of the CCM. The central layer is the N212 membrane, neighboring to which are the catalyst layers. The thicknesses of the hot-pressed membrane and the catalyst layer are about 50 μm and 10 μm, respectively. As shown in the image, the transfer process does not affect the membrane thickness severely.

The contact angles of the CCM surface are measured to analyze the hydrophobicity of the CLs with different PTFE contents. The images of the contact angle measurements are shown in Fig. 3, and the results are listed in Table 1. Here, the five CCMs with 0 wt.%, 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.% PTFE are named CCM0, CCM1, CCM3, CCM5 and CCM7, respectively. Their corresponding contact angles are 126.7°, 139.9°, 146.1°, 146.1° and 158.9°. Obviously, the addition of PTFE improves the hydrophobicity of the CL surface. However, there is no effective method for measuring the internal hydrophobicity of the inhomogeneous material by now. The optimal PTFE content should be further confirmed with the cell performance measurements in the following section.

To improve the porosity of the CL and enhance the mass-transport properties during the oxygen reduction reaction, PTFE is added into the CL. To investigate the effect of the PTFE content on the CL pore size, mercury intrusion porosimetry is carried out. During the measurement, larger pores are firstly intruded with mercury. As the pressure increases, mercury gradually enters the smaller pores. Different pressures correspond to different pore sizes. So the pore size

![Fig. 2. Micrograph of the CCM cross-section, ×1000.](image1)

![Fig. 3. Images of the contact angle measurement.](image2)
distribution is obtained basing on the relationship between pore size and intruded mercury amount. Fig. 4 shows the integrated pore size distribution of the four CCMs with PTFE and the detailed results are listed in Table 1. In this work the range of pore size is between 0.0036 μm and 0.1 μm. Since the pore size of the membrane is small enough to be neglected [24,25], the calculated pore volume accounts for the catalyst layer. The pore size of the CCM with 0 wt.% PTFE has been tested before, which is referred to in Table 1 [20]. Here, the mean pore diameter represents the average pore size of the whole CL, which is obtained by dividing the four times specific pore volume with the specific surface area. The medium pore diameter stands for the pore size when the mercury intrusion percentage is 50%. As the PTFE content increases from 0 wt.% to 7 wt.% the mean pore size increases by 5.94 nm and the medium pore size increases by 16.54 nm. Obviously, more PTFE results in larger mean pore size. It has been reported by both Watanabe [26] and Uchida [17] that there exists a pore size boundary in the CL. In this experiment, there are also two distinctive pore distributions with the boundary at about 0.01 μm. As for CCM1, the percentage of the pores smaller than 0.01 μm is 51.8%, and those of CCM3, CCM5, and CCM7 are 53.2%, 41.7% and 37.5%, respectively. Simultaneously, the percentages of the pores between 0.01 μm and 0.1 μm are 48.2% for CCM1, 46.8% for CCM3, 58.3% for CCM5 and 62.5% for CCM7. As a result, the addition of PTFE increases the percentage of larger pores which may act as the main gas transport channels [26].

### 3.2. Fuel cell performance

The CCMs with different PTFE contents are assembled into fuel cells. Fig. 5 shows the fuel cell performances and the corresponding ohmic resistances (RΩ) under H2/O2 and H2/Air conditions. From the i-V curves, the PTFE content obviously influences the cell performance. Comparing with CCM0, the addition of 1 wt.% 3 wt.% and 5 wt. % PTFE is favorable for the cell performance, among which CCM5 shows the best results. There are several good models for analyzing the polarization curves which can distinguish the kinetic effects, ohmic effects and gas diffusion, such as the model of Kim et al. [27]:

\[
E = E_0 - b \log i - R \Omega - m \exp(\eta t)
\]  

In this model, the exponential term characterizes the mass-transport region of the polarization curve. Besides that Lee et al. [28], Squadrito et al. [29], and L. Pisani et al. [30] have also developed some important models to estimate the polarization curves. Then Santarelli and his partners developed a parameter estimation method for the polarization curve in 2006 [31]. This equation is adopted in this work as follows:

\[
V = -\Delta \bar{g}(T) + \frac{RT}{2F} \ln \frac{P_{H_2}P_{O_2}^{0.5}}{P_{H_2O}^{0.5}} - \frac{RT}{\alpha F} \sin^{-1} \left( \frac{i + l_a}{2l_a} \right) - \frac{RT}{\alpha F} \sin^{-1} \left( \frac{i + l_c}{2l_c} \right) - r(i + l_a) + \frac{RT}{4F} \ln \left( \frac{1 - i + l_a}{l_a} \right) + \frac{RT}{4F} \ln \left( \frac{1 - i + l_c}{l_c} \right)
\]  

where \( \bar{g} \) is the molar Gibbs free energy (J mol\(^{-1}\)), \( \alpha/c/\alpha \) is the anode/cathode transfer coefficient, \( i_{n} \) is the internal current density (A cm\(^{-2}\)), \( l_a/l_c \) is the anode/cathode limiting current density (A cm\(^{-2}\)), \( k_{a/c} \) is the anode/cathode exchange current density (A cm\(^{-2}\)). Since the temperature and other reactant condition are all the same in our experiment, the temperature and reactant gas pressure relevant term can be written into a constant. Since the anode takes a very small effect to the polarization, the anode term is omitted in this paper. The internal current density is also neglected. Then the equation is rewritten as

\[
V = C - \frac{RT}{5F} \sin^{-1} \left( \frac{i}{2l_c} \right) - r(i + l_a) + \frac{RT}{4F} \ln \left( \frac{1 - i}{l_c} \right)
\]  

![Pore size distribution curves of the four hydrophobic CCMs.](image1)

![Steady-state fuel cell polarization curves: (A) H2/O2 performance (B) H2/Air performance.](image2)
3.3. ECA

PTFE can affect the continuity of the electron/proton transfer process in the CL. ECA stands for the active surface area where the catalyst contacts with the proton conductor and the electron conductor. Then ECA of the CL can directly reflect the influence of PTFE addition. Fig. 6 shows the CV scan curves of the CCMs. Obviously, the CLs structure of the CLs. Under the H\textsubscript{2}/O\textsubscript{2} or H\textsubscript{2}/Air condition, the CL with the concentration polarization. Thus, the last column of Table 2 indicates that adding a certain PTFE can improve the concentration polarization of the thin film CL.

3.4. Electrochemical impedance spectra (EIS)

The polarization resistance ($R_p$) is analyzed in Section 3.1 based on the polarization curves. In this section, the $R_p$ in the CL is further discussed using EIS, which is quite an effective diagnostic tool. The cathode acts as the working electrode and the anode acts as the reference and counter electrode. EIS of the cells under the H\textsubscript{2}/O\textsubscript{2} condition were measured at 0.1 A cm\textsuperscript{-2} and 0.5 A cm\textsuperscript{-2}, as shown in Fig. 7.

The Nyquist plots from different references show different patterns. Generally, it contains one or two or three semicircles which indicate different electrode processes [32,33]. The EIS results in this paper are shown in Fig. 8, which clearly show only one semicircle in the experimental frequency range. Quantitative analyses and extraction of reliable system-dependant parameters require the assumption of an electrochemical equivalent circuit (EC). The Randles cell, depicted in Fig. 8, is used to model the system and fit the spectra. The highest frequency intercept with the real axis of this semicircle stands for the $R_\Omega$ (ohmic losses), the charge transfer resistance ($R_{ct}$) and the catalyst layer capacitance ($C_{ct}$). $R_\Omega$ is the exponent value) because the capacitance due to the double layer charging is distributed along the length of the pores in the porous electrode [37]. The ZSimpWin fitting soft is used to fit the data by applying the EC mentioned above, and the $R_{ct}$ results for the cells are listed in Table 3. As it is known, the $R_{ct}$ results for the cells are listed in Table 3. As it is known, the diameter of the semicircle depends on the $R_{ct}$. The diameter of the semicircle is related with the $R_p$ for the oxygen reduction reaction and the catalyst layer capacitance (C) [34–36]. Here, $C$ is replaced with a constant phase element (CPE), defined as $Z(CPE) = 1/(Q(j\omega)^{-n})$, where $Q$ has the numerical value of the admittance ($1/|Z|$) at $\omega = 1$ rad s\textsuperscript{-1} and $n$ is the exponent value) because the capacitance due to the double layer charging is distributed along the length of the pores in the porous electrode [37]. The ZSimpWin fitting soft is used to fit the data by applying the EC mentioned above, and the $R_{ct}$ results for the cells are listed in Table 3. As it is known, the diameter of the semicircle depends on the electrode potential. The two investigated current densities result in two $R_{ct}$ values. Since there is only one loop in the EIS, the diameter may also be caused by the mass transport through the pores and the Nafion\textsuperscript{®} polymers in the CL [38,39]. This contribution should be more obvious at a higher current density.

Comparing with CCM0 (Table 3), there are no obvious changes in $R_{ct}$ at 0.1 A cm\textsuperscript{-2} of CCM1–CCM7. This means the PTFE addition to the CL does not affect the charge transfer process in the catalyst/

### Table 2
The fitting parameters of the polarization curves.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$C$ (mV)</th>
<th>$I_{0,c}$ (A cm\textsuperscript{-2})</th>
<th>$r$ (Ω cm\textsuperscript{2})</th>
<th>$l_{0,c}$ (A cm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCM0</td>
<td>881.4</td>
<td>874.3</td>
<td>0.224</td>
<td>0.489</td>
</tr>
<tr>
<td>CCM1</td>
<td>845.7</td>
<td>841.8</td>
<td>0.255</td>
<td>0.736</td>
</tr>
<tr>
<td>CCM3</td>
<td>837.3</td>
<td>864.8</td>
<td>0.222</td>
<td>0.108</td>
</tr>
<tr>
<td>CCM5</td>
<td>856.9</td>
<td>863.2</td>
<td>0.263</td>
<td>0.640</td>
</tr>
<tr>
<td>CCM7</td>
<td>839.7</td>
<td>860.3</td>
<td>0.271</td>
<td>0.735</td>
</tr>
</tbody>
</table>

Here, $C$, $I_{0,c}$, $I_{l,c}$, and $r$ are the parameters to be estimated. $\alpha$ is assumed to be 0.5 [31]. The exchange current density is mainly a function of the electrode characteristics and the limiting current density is a parameter linked to the concentration overpotential which is generally caused by a change in porosity, tortuosity in the diffusion layer (DL) and the presence of water droplets or films. $r$ represents the total contribution of the linear polarization components including the ohmic losses, the charge transfer resistance ($R_{ct}$) of the hydrogen oxidation reaction. The $l_{0,c}$ shows the smallest value with the concentration polarization. Thus, the last column of Table 2 indicates that adding a certain PTFE can improve the concentration polarization of the thin film CL.

**Fig. 6. Cyclic voltammogram curves of different CCMs.**

**Fig. 7. EIS of the fuel cells at 0.1 A cm\textsuperscript{-2} and 0.5 A cm\textsuperscript{-2}.**

**Fig. 8. The applied equivalent circuit for fitting the EIS.**
electrolyte interface. On the other hand, the $R_\text{p}$ reflected by the semicircle at 0.5 A cm$^{-2}$ obviously improved after adding PTFE to the CL. When the content is 5 wt.%, $R_\text{p}$ at 0.5 A cm$^{-2}$ decreases by 44.3% compared with that without PTFE. From the different changing rate of $R_\text{p}$ at the two current densities, it is confirmed that $R_\text{p}$ is related with the mass transport in the CL. And it is concluded that the addition of an appropriate amount of PTFE in the CCM can decrease the diffusion resistance in the CL. This means that the hydrophobic thin film CL can favor the mass-transport process.

4. Conclusions

A new hydrophobic thin film catalyst layer was fabricated by decal method. By introducing the Nafion® hyperdispersant to the PTFE solution, the aggregation of PTFE in the ink was improved. Due to the addition of PTFE, the hydrophobicity of the CL was enhanced and the pore volume of the CL was expanded. The cell performance of the CCMs proved that the optimal PTFE content was 5 wt.%. The EIS results at 0.1 A cm$^{-2}$ and 0.5 A cm$^{-2}$ showed that adding PTFE to the CL did not affect the charge transfer resistance, while the internal mass diffusion of the CL was improved.

Acknowledgement

This work was financially supported by the National High Technology Research and Development Program of China (No. 2007AA05Z123) and the National Natural Science Foundations of China (No. 20636060, No. 20876154). We also appreciate Kikusui Electronics Corp. for supplying the electronic load.

References


Table 3
The fitting results of the charge transfer resistance for the cells.

<table>
<thead>
<tr>
<th>CCMs</th>
<th>$R_\text{p}$ at 0.1 A cm$^{-2}$/Ω cm$^2$</th>
<th>$R_\text{p}$ at 0.5 A cm$^{-2}$/Ω cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCM0</td>
<td>0.493</td>
<td>0.264</td>
</tr>
<tr>
<td>CCM1</td>
<td>0.498</td>
<td>0.242</td>
</tr>
<tr>
<td>CCM3</td>
<td>0.521</td>
<td>0.176</td>
</tr>
<tr>
<td>CCM5</td>
<td>0.473</td>
<td>0.147</td>
</tr>
<tr>
<td>CCM7</td>
<td>0.536</td>
<td>0.191</td>
</tr>
</tbody>
</table>