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Effects of hydrophobicity of the cathode catalyst layer on the performance of a PEM fuel cell

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ABSTRACT

The effects of hydrophobicity of the cathode catalyst layer on the performance of a PEM fuel cell are studied. The surface contact angle is measured to understand the changes of the hydrophobicity of the cathode catalyst layer upon the addition of hydrophobic dimethyl silicone oil (DSO). The results show that the contact angle increases with the DSO loadings in the cathode catalyst layer ranging from 0 to 0.65 mg/cm². The subsequent electrochemical measurements of the fuel cells with various cathodes reveal that the addition of DSO in the cathode catalyst layer can effectively prevent the cathode flooding at high current density, thus leading to a much higher limiting current density and the maximum power density when compared to the fuel cell with a normal cathode. An optimal DSO loading in the cathode catalyst layer is found to be around 0.5 mg/cm² under the testing conditions in this work. The fuel cell with cathode loaded with 0.5 mg/cm² can reach the maximum power density of 356 mW/cm² in H₂/air (or 709 mW/cm² in H₂/O₂) at room temperature, which is around 2.5 times in H₂/air (or 1.8 times in H₂/O₂) of that with normal cathode. All of the results indicate that the hydrophobicity of the cathode catalyst layer plays a crucial role in the water management of the fuel cell. The possible function of the DSO on improved oxygen solubility for the oxygen starved cathode during flooding warrants some further investigation.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are claimed to be highly efficient and environmentally friendly. In order to compete with the conventional energy conversion technologies, many efforts have been devoted to develop a high performance membrane-electrode-assembly (MEA) with improved durability and reduced precious metal loading [1–7]. To achieve these goals, two kinds of electrode design, i.e., PTFE-bonded [3] and thin-film electrode design [4–6], have been invented and widely employed in PEMFCs. For the PTFE-bonded catalyst layers, the PTFE can increase the diffusivity of gases and further provide hydrophobicity to open pores, thus avoiding water blocking, which is desirable for the gas diffusion. Although this property is uniquely desirable, the necessary heat treatment of the electrode at around 340 °C resulted in the agglomeration of the Pt/C catalyst and the consequent reduction of the catalyst utilization [1]. In addition, because Nafion was impregnated into the PTFE-bonded electrode, the catalyst utiliza-

tion and the cell performance are strongly dependent on the Nafion distribution within the catalyst layer [2]. A performance penalty is paid for the decrease in humidity of Nafion and possible blocking of the proton or electron pathway in the catalyst, which would lead to poor utilization of the catalyst [4]. Alternatively, thin-film catalyst layers were developed by using the hydrophilic perfluorosulfonate ionomer (Nafion) to bind carbon-supported catalyst particles which provides the necessary proton transport in the catalyst layer [6]. As a result, the thin-film catalyst layers, which are the most commonly used electrodes nowadays, have been found to achieve twice the power density output compared with that of the PTFE-bonded catalyst layers [7]. However, in the thin-film catalyst layer, the gas is not provided with a network of hydrophobic pores as in the PTFE-bonded catalyst layer; thus, gas diffusing through the catalyst layer must traverse pores filled with water and/or ionomer [6]. The cathode flooding is often a concern at high current density.

In practice, water is produced within the cathode via the oxygen reduction reactions and often carried in by humidified reactants. If the generation and removal of water inside of the cathode are not equilibrated, excessive water will fill up the pores in the catalyst layer (CL) and gas diffusion layer (GDL), leading to rapid cell voltage drop and immediate cell performance degradation due to flooding [8]. Proper cathode design and cell operation in mitigating flooding are essential to allow the fuel cells operating at their

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optimal performance and prolonged life span [9]. Water management is a complex subject, which has been widely studied through the numerical simulation and by the experimental optimization [10–12]. Intensive research activities have focused on investigating the effects of GDL and flow field design on the water management. Recently, a micro-porous layer (MPL) has been inserted in between the catalyst layer and the GDL and proved to be effective for water management in the cathode, although underlying physics in supporting the role of MPL on the water management is still controversial [13,14]. Cathode catalyst layer is the major contribution to the potential drop and thus losses of efficiency in PEM fuel cell because of the poor kinetics of the O_2 reduction and transport limitation. However, according to the literature, little attention has been paid to experimentally exploring the role of the cathode catalyst layer on the water management. Most of the numerical modeling works treated the cathode catalyst layer as an infinite thin layer without structural resolution [15]. However, our preliminary studies showed that the water balance and oxygen transport within the cathode can be significantly improved upon the addition of oxygen permeable and hydrophobic dimethyl silicone oil (DSO) into the catalyst layer [16].

A structure-based model developed by Eikerling and Kornyshev [17] revealed the water handling ability of the cathode catalyst layer and its effect on the cell performance. Kraytsberg and Ein-Eli [18] suggested that implementing cathode modified by oxygen permeable but water immiscible perfluorocarbons could help the water back diffusion to hydrate the membrane as well as repel water out of the cathode. Grot [19] coated some hydrophobic oxygen transport polymer such as perfluoropolyether (PFPE) on the cathode side of the MEA to facilitate water management in the PEMFC. Due to the fact that water is produced at the cathode catalyst layer, one would expect improved water management in the cathode by optimizing the hydrophobicity of the cathode catalyst layer. In this study, the hydrophobicity of the cathode catalyst layer is changed by adding the hydrophobic dimethyl silicone oil (DSO) into the catalyst ink mixture during the preparation. The motivation of this strategy is to combine the advantages of uniformly distributed Nafion in the Nafion-bonded electrode and the anti-flooding property in the PTFE-bonded electrode. Moreover, unlike the PTFE-bonded electrode, the fabrication of the DSO modified electrode does not require heat treatment, thus avoiding the agglomeration of the Pt/C catalyst. To explicitly demonstrate the effect of hydrophobicity of the cathode catalyst layer on the water management, no MPL is interposed between the CL and the GDL to avoid possible ambiguity. The loading of the DSO in the cathode catalyst layer is optimized experimentally to achieve the best fuel cell performance.

2. Experimental

The carbon-supported Pt catalyst is 50 wt.% Pt/C (Johnson Matthey) catalyst with the average Pt diameter of about 2 nm. Both anode and cathode are consisted of a wet-proofed carbon paper as the backing layer and a CL. Commercial TGP-H-090 carbon papers were impregnated with 15% PTFE to make it hydrophobic. The carbon paper was slowly dipped into a 10 wt.% PTFE suspension, and then dried at 80 °C to achieve uniform distribution of PTFE inside the carbon paper. The procedure was repeated until the desired weight gained. The PTFE-impregnated carbon paper was further heated at 250 °C for 0.5 h to remove the dispersant containing in the PTFE and finally sintered at 340 °C for another 0.5 h. The wet-proofed carbon paper can be directly used as a cathode GDL. An appropriate DSO (Shin-Etsu, Japan) was emulsified into a mixture of water and isopropanol by a highly intensive ultrasonic machine (Vcx 750, Sonics, USA) with appropriate loading. Then, the catalyst ink was prepared by ultrasonically dispersing the

carbon-supported Pt catalyst and Nafion solution into the emulsion. For the normal cathode, same procedure was applied to make the ink except that there is no DSO added into the mixture of water and isopropanol. The content of Nafion in the catalyst layer was 30 wt.%. Without any delay, the well dispersed ink was directly applied onto the PTFE-impregnated carbon paper by using a knife-blade. The electrodes were dried in an oven at 100 °C for 30 min. To better understand the effect of DSO on cathodic water management, no MPL was fabricated. The Pt and DSO loading were calculated from the total loading and from the weight percentage of Pt in the electrode. The loading of Pt in the CL with and without DSO was 0.35 mg/cm² and with a Nafion loading of 0.56 mg/cm². A commercial Nafion 112 membrane (EW1100, DuPont) was treated according to the recommended procedure by the supplier. A pair of the anode (without any DSO) and cathode was hot pressed on both sides of Nafion 112 membrane for 2 min at 135 °C and a pressure of 50 kg/cm² to form MEA.

MEAs were tested using an in-house made fuel cell fixture of approximately 4 cm² in geometric area with single-serpentine flow channel cut into the graphite bipolar plates. The channel is 0.8 mm wide and 1 mm deep, with 0.8 mm wide lands. Gases were humidified by passing through a temperature-controlled water bath. Hydrogen and air/ O_2 were fed into the anode and cathode, respectively, at a stoichiometry of 2.1 calculated at 1 A/cm². Without specifying, all tests were carried out at room temperature of around 22 °C and atmospheric pressure. The steady-state polarization and electrochemical impedance spectra (EIS) were measured using the Solartron Electrochemical Interface (1255B) in conjunction with a Solartron Frequency Response Analyzer (1287). Impedance spectra were recorded at frequencies range between 0.01 Hz and 10 kHz. The contact angles of water droplets in the cathode were measured using a contact angle measurement system (FTA32, Analytical Technologies). The cathodes were dried in the oven at 100 °C for 3 h before the contact angle measurement.

3. Results and discussion

Fig. 1 shows the SEM image of the cathode CL/GDL interface. The image revealed that the CL has a uniform thickness of around 10 μ m on the wet-proofed carbon paper. With experienced technique for ink painting onto the wet-proofed carbon paper, no obvious penetration of the catalysts into the carbon paper was found at the interface. This ensures similar properties of the wet-proofed carbon paper after treated with catalyst ink, so that the effect of the hydrophobicity of the cathode catalyst layer on the fuel cell performance can be investigated without any ambiguity.

Liquid water transport through catalyst layer relies strongly not only on the pore structure, porosity and permeability but also on the degree of hydrophobicity. In this study, the hydrophobicity of the cathode catalyst layer was varied by adding hydrophobic DSO into the cathode catalyst layer during the catalyst ink preparation stage. The images of the water droplet on the two kinds of cathodes, i.e., normal cathode and cathode with DSO loading of 0.5 mg/cm², were taken and compared in Fig. 2. Initially, the surface contact angles for both cathodes are almost same at around 130° (shown in Fig. 2a and b). However, after 1 h incubation of the water droplet on the CL, the surface contact angle of the normal cathode significantly decreased from 130° to around 70°, which was much smaller than the value of 101° of the cathode with DSO loading of 0.5 mg/cm². Nafion comprises of hydrophobic reticulated structure and percolated hydrophilic regions, which becomes hydrophobic when it is dry [20]. As a result, the normal cathode initially exhibited hydrophobic property when water droplet was just applied onto the cathode catalyst layer (Fig. 2b). However, because water gradually hydrates the hydrophilic regions, the cathode CL finally turns to be hydrophilic (Fig. 2c). The surface contact angles of var-

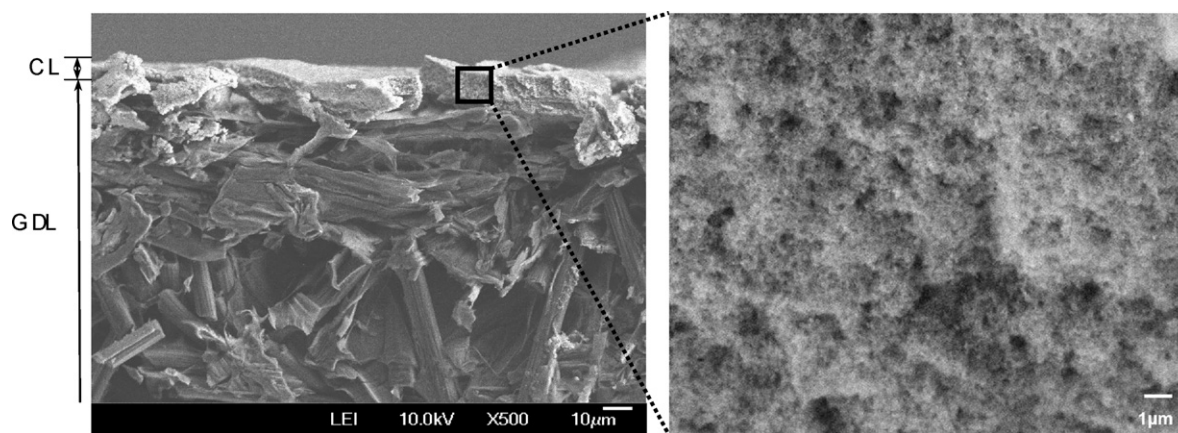


Fig. 1. SEM image for the cross-section of the interfacial region between the catalyst layer and GDL.

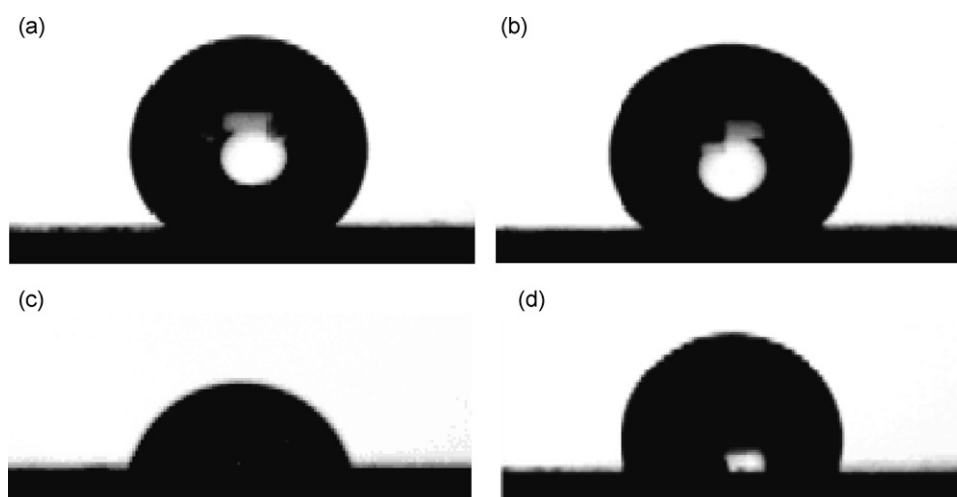


Fig. 2. Images of water droplet: initial water droplet on (a) normal cathode catalyst layer and (b) 0.5 mg/cm² DSO loaded cathode catalyst layer; water droplet after 1 h on (c) normal cathode catalyst layer and (d) 0.5 mg/cm² DSO loaded cathode catalyst layer.

ious cathodes with different DSO loadings of 0, 0.25, 0.40, 0.50 and 0.65 mg/cm² were summarized in Fig. 3. The error bar in Fig. 3 was based on the surface contact angles measured from three cathodes with same DSO loading. Initially, the measured contact angles for all of the cathodes are similar to be around 130°. After 1 h incubation of

the water droplet on the cathode catalyst layer, the surface contact angle significantly decreased with the reduction of the DSO loading in the cathode catalyst layer. The results in Fig. 3 clearly revealed that the addition of DSO significantly enhances the hydrophobicity of the cathode catalyst layer.

To investigate the effect of the DSO in the cathode catalyst layer on the polarization behaviors of a single fuel cell, MEAs with same anode but different cathodes (with DSO loadings of 0, 0.25, 0.40, 0.50 to 0.65 mg/cm² in the catalyst layer) were fabricated and tested. A normal cathode, which is without DSO in cathode catalyst layer, was used for comparison. Fig. 4 shows the effects of DSO loading in the catalyst layer on the polarization curves, obtained at room temperature and atmospheric pressure under humidified hydrogen and dry air. To understand the operational stability of the fuel cells under testing conditions, the polarization behaviors right after half hour gas purging and the polarization behaviors right after running at constant voltage of 0.4 V for 3 h were recorded and compared for all fuel cells with different MEAs. During the *I*–*V* sweeping right after half hour gas purging, the CL and the membrane are under dry condition. Meanwhile, the cathodes are expected to be in an under-saturation condition. As a result, two phenomena can be observed from the polarization curves shown in Fig. 4a. One is the low output current density at voltage of 0.8 V for all the MEAs, which could be due to the low ionic conductivity of the Nafion cluster in the CL right after half hour gas purging. More specifically, the output current densities at 0.8 V were found to be 56, 50, 41, 26, 12 mA/cm² for

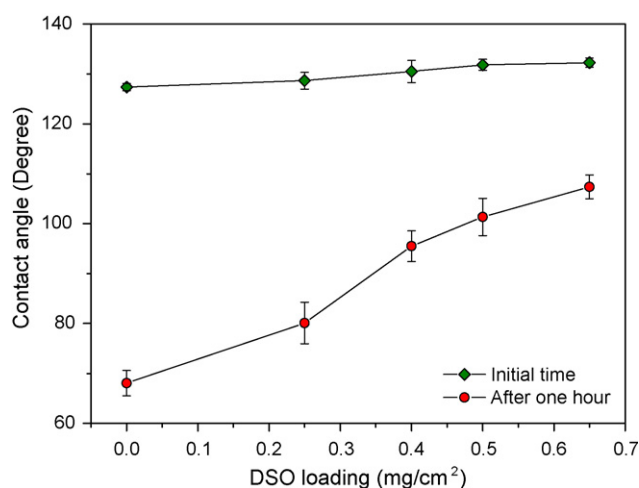


Fig. 3. Contact angles of the cathode catalyst layers with different DSO loadings measured at initial time and after 1 h.

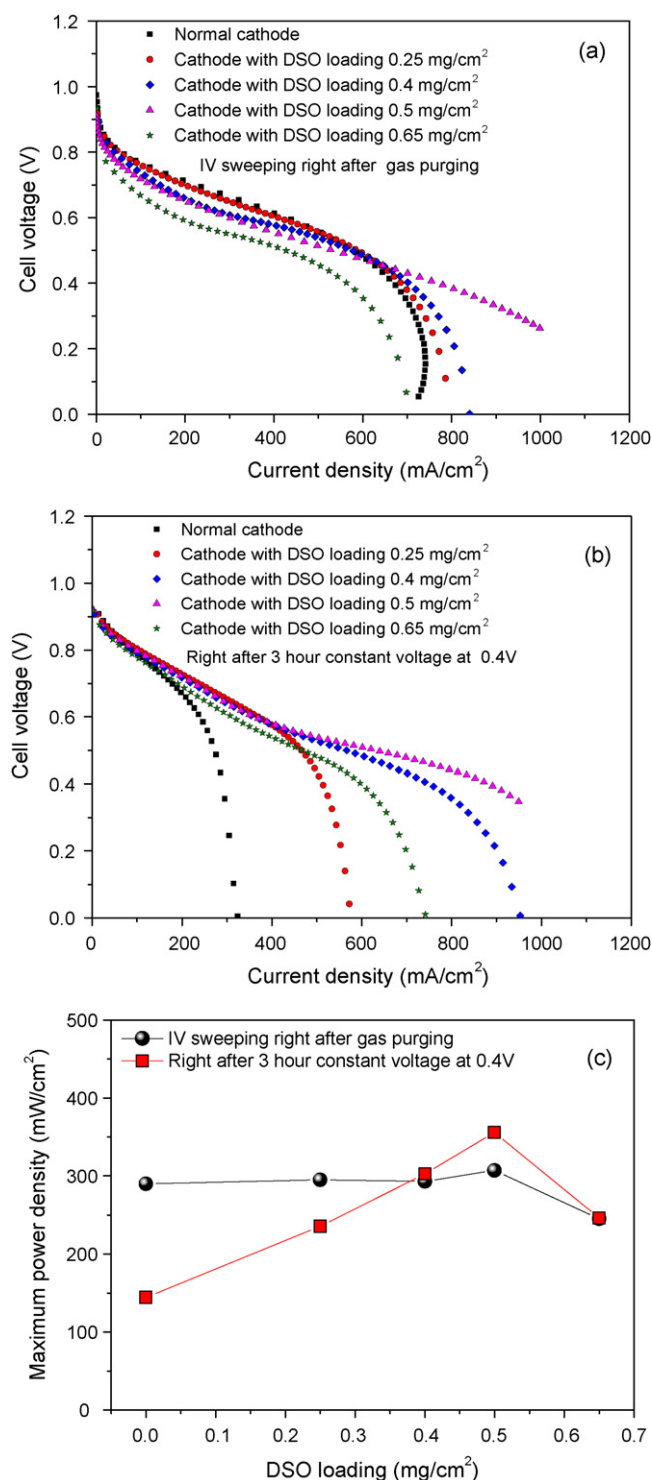


Fig. 4. Polarization V - I curves obtained at room temperature and atmosphere pressure with humidified hydrogen and dry air (a) I - V sweeping right after 30 min gas purging; (b) I - V sweeping right after the fuel cell running at a constant voltage of 0.4 V for 3 h and (c) corresponding maximum power density.

the MEAs with DSO loadings of 0, 0.25, 0.40, 0.50 to 0.65 mg/cm² in the catalyst layer, respectively. With the loading of DSO increasing, the current densities at 0.8 V decrease significantly. The other phenomenon is the similar limiting current densities observed for the MEAs except for the one with 0.5 mg/cm² DSO loaded cathode. This could be attributed to the optimized balance between the improved cathode hydrophobicity for water expelling and the blocking effect

of the liquid DSO within the cathode for the fuel cell with cathode loaded with 0.5 mg/cm² DSO.

As shown in Fig. 4b, after running the fuel cells at a constant voltage of 0.4 V for 3 h, the kinetic polarization of the fuel cells has been greatly improved due to the enhanced Nafion conductivity and catalyst utilization by opening many “dead” regions in the CL when some water has been presented in the pores of CL [17,21]. However, fast drop of the I - V curve at the high current density was observed for the normal cathode after 3 h of constant voltage polarization. During the I - V sweeping right after gas purging, the fuel cell with normal cathode showed a limiting current density of 741 mA/cm², which significantly dropped to ~320 mA/cm² after further polarization at a constant voltage of 0.4 V for 3 h. The surface contact angle measurement shown in Fig. 3 revealed that the normal cathode turns to be hydrophilic after 1 h incubation in water due to the gradual hydration of the Nafion clusters in the catalyst layer. As a result, more and more liquid water produced during the constant voltage polarization, which would occupy all the pores in the CL, thus causing serious flooding in the normal cathode, and preventing the oxygen transport from bulk into the cathode catalyst layer [22]. The addition of DSO increases the hydrophobicity of the cathode catalyst layer, which is believed to be able to help expel water from the voids of the CL and facilitate the hydration of PEM [10]. This was confirmed by the polarization curves for the fuel cells with DSO loaded cathodes shown in Fig. 4b. It was found that the limiting current densities of the cathodes with DSO loading higher than 0.4 mg/cm² will kept almost unchanged before and after 3 h of constant voltage polarization, which were significantly different from those cathodes with DSO loading of less than 0.4 mg/cm². The comparative results in Fig. 4a and b together with the contact angle results in Fig. 3 clearly indicated that the flooding phenomenon in the cathode could be effectively prevented by increasing the hydrophobicity of the cathode catalyst layer.

Fig. 4c compares the maximum power densities of the fuel cells with different DSO loadings in the cathode catalyst layer for I - V sweeping right after half hour gas purging and polarization after 3 h of constant voltage running at 0.4 V. The results show that the maximum power densities measured in the I - V sweeping right after gas purging are slightly different. However, the maximum power densities of the fuel cells with normal cathode and cathode loaded with 0.25 mg/cm² DSO significantly dropped from 290 to 144 and 295 to 201 mW/cm², respectively, after 3 h of constant voltage polarization. It can be observed that obvious increment in the maximum power densities for the fuel cell with cathodes loaded with 0.50 mg/cm² of DSO after 3 h constant voltage polarization. As a result, an optimal DSO loading was found to be 0.50 mg/cm² with the maximum power density of 356 mW/cm², which is the highest maximum power density among the fuel cells in this study. Referring back to the polarization curves in Fig. 4a and b, one can understand that the changes of the maximum power densities of the fuel cells are mainly attributed to the water condition in the cathode. For the normal cathode, the serious flooding in the cathode led to the drop of the power density. With excessive DSO loading in the cathode catalyst layer (e.g. the case of 0.65 mg/cm² in this study), even though no flooding phenomenon was observed after activation, a lower limiting current density of ~750 mA/cm² was found when compared to that with optimal loading of 0.50 mg/cm². This indicated that the excessive DSO content in the cathode catalyst layer would result in some voids blockage and hence a restricted surface area for reactant transport, which causes lower limiting current density [14].

The effects of hydrophobicity of the cathode catalyst layer on the fuel cell performance were also investigated using humidified hydrogen and dry oxygen as the oxidant at room temperature (Fig. 5). The fuel cells with cathodes loaded with 0, 0.25, 0.40, 0.50 and 0.65 mg/cm² DSO showed current densities of 613.5, 785.8,

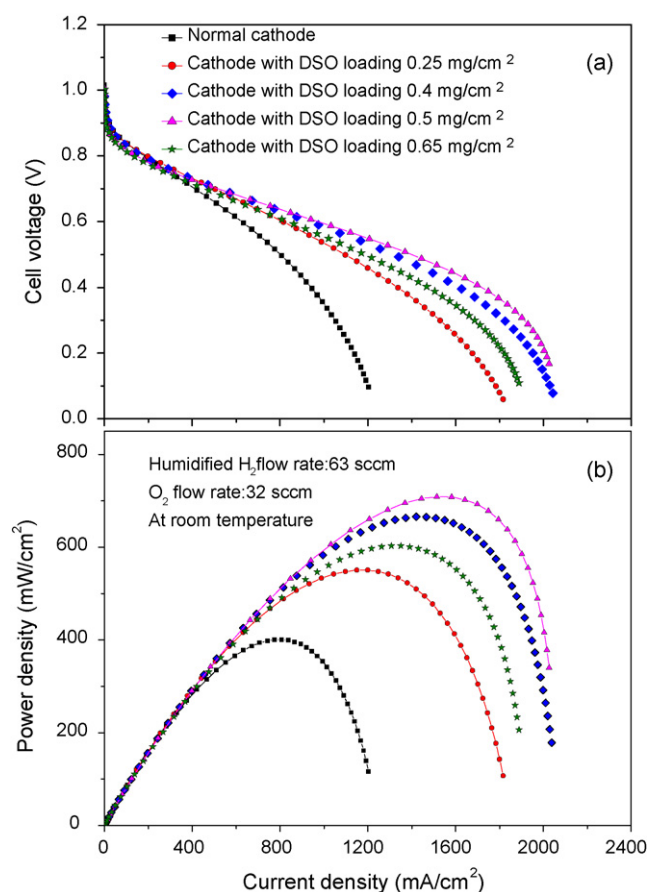


Fig. 5. Polarization V - I curves and power densities of the single PEMFCs with normal cathode and cathodes with different DSO content in humidified hydrogen and dry oxygen at room temperature and atmosphere pressure.

936.2, 961.1, 830.5 mA/cm² at 0.6 V, respectively. An improvement of 80% in current density at 0.6 V for the fuel cell with DSO loading of 0.50 mg/cm² in cathode catalyst layer has been achieved as compared to that of a normal cathode. Moreover, the fuel cells with DSO loaded cathodes showed a limiting current density close to ~2000 mA/cm², which is around 1.7 times of the fuel cell with a normal cathode. To make the results comparable, all fuel cells have been tested at a stoichiometry of 2.1 calculated at 1 A/cm². The obvious exhibition of limiting current for fuel cell with 0.50 mg/cm² loaded cathode is due to the low stoichiometry number of oxygen, which means almost all oxygen provided has been consumed. Those results indicated that not only the flooding problem could be avoided but the catalyst utilization was also improved, if the hydrophobicity of the cathode catalyst layer was carefully optimized. The maximum power densities at room temperature were found to be 400, 551, 666, 709, 602 mW/cm² for the fuel cells with cathodes loaded with 0, 0.25, 0.40, 0.50 and 0.65 mg/cm², respectively.

To better understand the above observations, impedance spectra were taken at different voltages for the fuel cells with normal cathode and with DSO loaded cathodes running in dry air/humidified hydrogen system. The results are collectively presented in Fig. 6. The Nyquist plots for all the fuel cells in Fig. 6a with different cathodes showed a kinetic loop under low overpotential condition (i.e., at output voltage of 0.8 V). With further reducing the output voltage, i.e., higher current was generated, more water was produced within the cathode catalyst layer. If the produced water cannot be effectively removed from the catalyst layer, cathode flooding will happen. When the fuel cells operated at a much

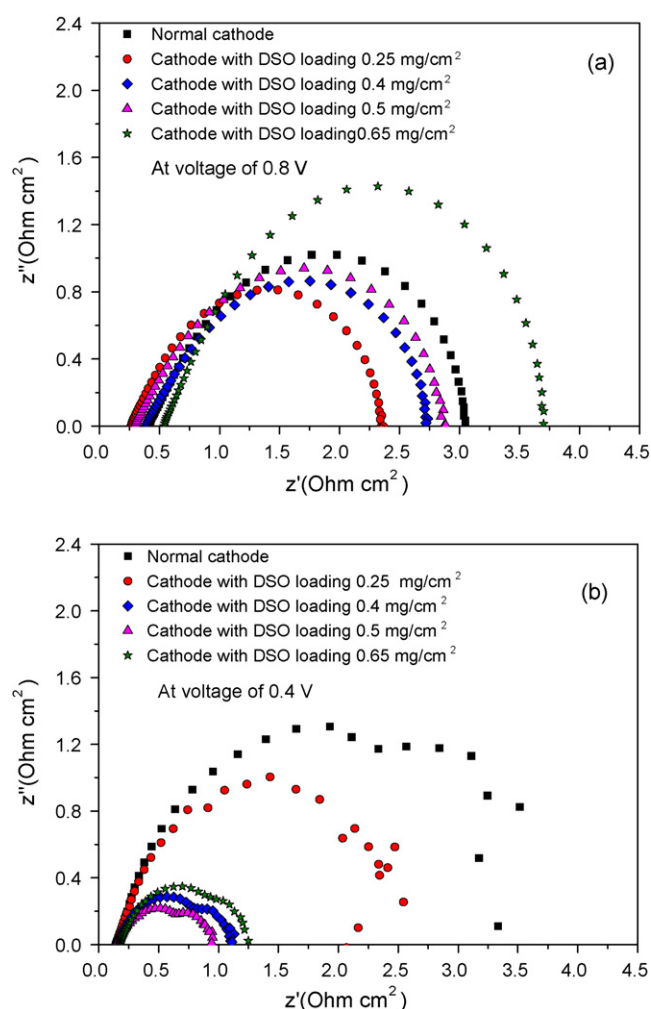


Fig. 6. Impedance spectra obtained at 0.8 V (a) and 0.4 V (b) for the fuel cells with a normal cathode and different DSO loaded cathodes.

lower voltage of 0.4 V (Fig. 6b), the mass transport resistance of the fuel cell with normal cathode was around 3 times larger than that of the fuel cell with cathode loaded with 0.5 mg/cm² DSO. As can be seen in Fig. 6b, the impedance arc of the fuel cell with normal cathode started to distort at lower output voltage due to excessive water produced in the cathode [23]. This indicated that the fuel cell with a normal cathode would suffer from serious flooding problem under this operating condition, which is consistent with the low limiting current density observed in Figs. 4b and 5b.

In order to further understand the effects of hydrophobicity of the cathode catalyst layer on the fuel cell performance, the start-up behaviors of the fuel cells with normal cathode and cathode loaded with DSO 0.5 mg/cm² were investigated under dry hydrogen and dry air condition at room temperature. The fuel cells operated at 0.4 V, and the output currents of the fuel cells were recorded for comparison. Because dry hydrogen and dry air were fed into the fuel cell, the Nafion membrane and the Nafion clusters in the electrodes showed extreme low ionic conductivity due to the dehydration, leading to negligible initial output currents (shown in Fig. 7). For the fuel cell with a normal cathode, the current density increased significantly to a maximum value of 600 mA/cm² within 1 min, then it gradually dropped to around 450 mA/cm². However, quite different start-up behavior was observed for the fuel cell with a cathode loaded with 0.5 mg/cm² DSO, i.e., (i) it required around 5 min to reach a maximum current of 750 mA/cm² each a maximum current of 750 mA/cm² and (ii) no obvious current dropped was observed

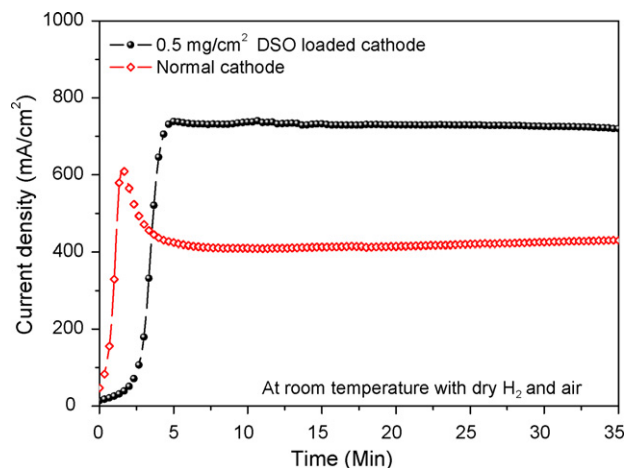


Fig. 7. Effect of DSO in the cathode catalyst layer on the start-up behaviors of the fuel cells in dry hydrogen and dry air at room temperature (at 0.4 V).

over a period of more than 30 min. The different start-up behaviors of the fuel cells with normal and with DSO loaded cathodes are caused by the different hydrophobicity of the cathode catalyst layers (shown in Fig. 3). Because of the hydrophilic property of the normal cathode, the Nafion in the normal cathode is easier to be hydrated by the water produced during operation than that of the hydrophobic DSO loaded cathode [24]. As a result, the fuel cell with a normal cathode can reach a maximum current within much shorter time than that with DSO loaded cathode. However, the hydrophilic property of the normal cathode at the same time causes it to be easily flooded during operation, which is reflected by the drop of the current after 1 min of operation shown in Fig. 7. Thus, although the fuel cell with DSO loaded cathode showed slower start-up in dry hydrogen and dry air, it demonstrated excellent anti-flooding ability at high current condition.

4. Conclusions

In this study, the effects of the DSO loadings in the cathode catalyst layer on the performance of a PEM fuel cell at room temperature were investigated and characterized systematically. The cathodes with DSO loadings of 0, 0.25, 0.4, 0.5 to 0.65 mg/cm² in the catalyst layer were fabricated by adding hydrophobic DSO into the cathode catalyst layer during the catalyst ink preparation step. The

contact angle measurement indicated that the hydrophobicity of the catalyst layer increased with the increase of the DSO loading. The single cell test results showed that the addition of the DSO into the cathode catalyst layer can prevent cathode flooding effectively at high current density. An optimal DSO loading was found to be 0.5 mg/cm². The fuel cell with this DSO loading at the cathode catalyst layer has achieved the highest maximum power density of 356 mW/cm² in H₂/air (or 709 mW/cm² in H₂/O₂) at room temperature. This was a significant improvement from 144 mW/cm² in H₂/air (or 400 mW/cm² in H₂/O₂) of the fuel cell with a normal cathode. Excessive DSO loading, i.e., 0.65 mg/cm² in this study, may block the pores of catalyst layer, leading to a lower limiting current density and a maximum power density. The experimental results clearly revealed that the cathode catalyst layer with optimized hydrophobicity is effective in expelling excessive water from the voids/pores of the catalyst layer, thus preventing the flooding and improving the fuel cell performance.

References

- [1] X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qiao, J. Yu, J. Power Sources 79 (1999) 75.
- [2] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, Electrochim. Acta 46 (2001) 799.
- [3] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 4143.
- [4] E.A. Ticianelli, C.R. Derouin, A. Redondo, S. Srinivasan, J. Electrochem. Soc. 135 (1988) 2209.
- [5] M.S. Wilson, J.A. Valerio, S. Gottesfeld, Electrochim. Acta 40 (1995) 355.
- [6] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
- [7] S. Litster, G. McLean, J. Power Sources 130 (2004) 61.
- [8] U. Pasaogullari, C.Y. Wang, J. Electrochem. Soc. 152 (2005) A380.
- [9] W. Schmittinger, A. Vahidi, J. Power Sources 180 (2008) 1.
- [10] K. Jiao, B. Zhou, J. Power Sources 169 (2007) 296.
- [11] M. Han, S.H. Chan, S.P. Jiang, Int. J. Hydrogen Energy 32 (2007) 385.
- [12] K. Jiao, B. Zhou, J. Power Sources 175 (2008) 106.
- [13] Z. Qi, A. Kaufman, J. Power Sources 109 (2002) 38.
- [14] C. Lim, C.Y. Wang, Electrochim. Acta 49 (2004) 4149.
- [15] M. Eikerling, J. Electrochem. Soc. 153 (2006) E58.
- [16] A. Li, S.H. Chan, N.T. Nguyen, Electrochem. Commun. 11 (2009) 897.
- [17] M. Eikerling, A.A. Kornyshev, J. Electroanal. Chem. 453 (1998) 89.
- [18] A. Kravtsov, Y. Ein-Eli, J. Power Sources 160 (2006) 194.
- [19] S.A. Grot, in US patent 6,740,445.
- [20] H.P. Brack, M. Slaski, L. Gubler, G.G. Scherer, S. Alkan, A. Wokaun, Fuel Cells 4 (2004) 141.
- [21] Z. Qi, A. Kaufman, J. Power Sources 111 (2002) 181.
- [22] H. Li, Y. Tang, Z. Wang, Z. Shi, S. Wu, D. Song, J. Zhang, K. Fatih, J. Zhang, H. Wang, Z. Liu, R. Abouatallah, A. Mazza, J. Power Sources 178 (2008) 103.
- [23] X. Yuan, J.C. Sun, M. Blanco, H. Wang, J. Zhang, D.P. Wilkinson, J. Power Sources 161 (2006) 920.
- [24] D.R. Sena, E.A. Ticianelli, V.A. Paganin, E.R. Gonzalez, J. Electroanal. Chem. 477 (1999) 164.