

Short communication

Improvement of low-humidity performance of PEMFC by addition of hydrophilic SiO₂ particles to catalyst layer

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Abstract

Hydrophilic SiO₂ particles are added to the catalyst layer of a fuel cell membrane–electrode assembly (MEA) to improve wettability and performance at low-humidity conditions. The SiO₂ added MEAs are prepared by spraying technique and the contact angle is measured by the sessile drop method. The effects of SiO₂ additions of 0, 20, 40 and 60 wt.% (based on Pt/C) are investigated for various relative humidity levels in the anode and the cathode. The increased wettability of the cathode catalyst layer exerts an adverse effect on cell performance by causing flooding; this result demonstrates the hydrophilicity of SiO₂. With 40 wt.% addition of SiO₂ to the anode catalyst layer, the current density at 0.6 V and 0% relative humidity of the anode is 93% of that at 100% relative humidity. By comparison, the performance of a cell using a MEA with no added SiO₂ is only 85% of that at 0% relative humidity. A MEA with SiO₂ addition in the anode gives a higher performance at 60% relative humidity of the cathode than one with an undoped MEA. Increased wettability of the anode catalyst layer caused by SiO₂ addition renders it easy to absorb water from back diffusion.

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1. Introduction

During the past several decades, much attention has been focused on the research and development of proton-exchange membrane fuel cells (PEMFCs) as power sources for stationary and portable application. This is because of their attributes of high power density, low weight, simplicity of operation, high-energy conversion efficiency and zero harmful emissions. The membrane in the PEMFC system requires water to maintain its proton conductivity during operation. In order to retain the optimum hydration level, water has to be supplied to the membrane by a humidifying system. On the other hand, a high humidity of the inlet reactant gases may lead to cathode flooding, which limits the access of oxygen to the active surface of the catalyst particles. Thus, proper hydration is critical to maintaining membrane conductivity and performance [1,2].

Most PEMFC studies have been performed under near-saturated operating conditions at various temperatures and pres-

sure, but several studies have been undertaken at low-humidity conditions. Ge et al. [3] used a water-absorbing sponge made of polyvinyl alcohol to develop an internally humidified system. The water sponge was advantageous for humidification of the dry inlet air and for removal of liquid water from the cell. Williams et al. [4] modified the gas diffusion layer (GDL), and thereby improved cell performance under low and no external humidification conditions. Other studies [5–8] include self-humidifying membranes prepared by embedding catalyst particles into membrane [5–8]. The catalyst particles act as water-generation sites by recombination of permeated hydrogen and oxygen. This does, however, give rise to the problem of short-circuits due to the electrical conductivity of the embedded particles. Other researchers [9–11] have prepared Nafion/SiO₂ composite membranes to improve cell performance at high temperatures. The SiO₂ serves to increase the uptake of water.

In this work, hydrophilic SiO₂ particles are used to control the wettability and performance of a membrane–electrode assembly (MEA) at low-humidity conditions. Adding SiO₂ to the catalyst layer is very simple due to its good dispersion in isopropyl alcohol. The wettability of the SiO₂-doped MEA differs from that of the undoped MEA and is related to the concentration of SiO₂.

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The in-cell performances of MEAs are evaluated at different relative humidity levels of the anode and the cathode.

2. Experimental

2.1. Preparation of membrane–electrode assemblies (MEAs)

2.1.1. Standard MEA

A 40 wt.% Pt/C (Johnson Matthey) catalyst, a 5 wt.% Nafion[®] solution (Dupont) and isopropyl alcohol were mixed, sprayed on to a Nafion[®] 112 membrane and dried at 50 °C for 3 h. Dried MEAs were pressed for 2 min at 10 MPa. A Nafion[®] 112 membrane was pretreated with 5 wt.% H₂O₂, de-ionized water, 1.0 M H₂SO₄ and de-ionized water at 80 °C for 30 min, respectively. The Pt loading at both the anode and the cathode was 0.4 mg Pt cm⁻² and the effective area of the MEA was 25 cm² (5 cm × 5 cm). Carbon paper (GDL 10BC, SGL) was used as gas-diffusion layer.

2.1.2. SiO₂-doped MEA

SiO₂ (7 nm, Aldrich) was added to isopropyl alcohol and the mixture was placed under sonication for 10 min to achieve for good dispersion. The SiO₂-doped MEAs were prepared by the same method as that described above for the undoped counterpart. The compositions of the MEAs are listed in Table 1.

2.2. Measurement of contact angle of MEAs

The sessile drop method is the most common means of measuring the contact angle of a liquid on a solid surface. In this technique, a droplet of water was set on the surface and the contact angle was measured by fitting a tangent to the three-phase point where the liquid surface touched the solid surface. To characterize the wetting property of MEAs, the contact angle of a water drop on the catalyst layer was determined experimentally by direct image analysis of the shape of the drop at room temperature. Catalyst ink (Mixture of Pt/C, 5 wt.% Nafion[®] solution, SiO₂ and isopropyl alcohol) was sprayed on to one side of an aluminium foil, dried at 50 °C for 3 h, and then pressed for 2 min at 10 MPa. Samples of the catalyst layers were fixed on glass plate and water was dropped on to them.

Table 1
Composition of membrane–electrode assemblies

MEA	Weight fraction based on Pt/C			SiO ₂ addition
	Pt/C	SiO ₂	Nafion [®] ionomer	
S0	1	0	0.33	None
SC20	1	0.2	0.4	Cathode
SC40	1	0.4	0.47	Cathode
SA20	1	0.2	0.4	Anode
SA40	1	0.4	0.47	Anode
SA60	1	0.6	0.53	Anode

SC20 means that SiO₂ was added to the cathode at 20 wt.% based on Pt/C. SA20 means that SiO₂ was added to the anode at 20 wt.% based on Pt/C.

2.3. Measurement of polarization

Several different humidifier temperatures were tested to study the influence of inlet humidification. The anode and cathode gases were humidified by passage through bubbler-type humidifiers. The fuel was pure hydrogen and the oxidant was air. The cell temperature was fixed at 70 °C and the gas flow of air/H₂ was in a stoichiometric ratio of 1.5 for the anode and 3.0 for the cathode. All experiments were conducted at atmospheric pressure. The temperatures of the gas lines to the anode and the cathode were always set at 5 °C above the cell temperature to prevent water condensation.

To investigate the influence of anode humidification, the anode humidifier was set at 70, 65, 58, 50 and 37 °C. These temperatures are equivalent to relative humidities of 100, 80, 60, 40 and 20%, respectively. To maintain 0% relative humidity, the hydrogen was not humidified and the temperature of cathode humidifier was set at 65 °C during measurement. To investigate the effect of cathode humidification, the temperature was set at 70, 65, 58 and 50 °C, and that of the anode humidifier was maintained at 70 °C.

3. Results and discussion

3.1. Contact angle of MEA

An image of the water droplet on each MEA is given in Fig. 1. The samples S0, S20, S40 and S60 have SiO₂ particles in the catalyst layer at levels of 0, 20, 40 and 60 wt.% (based on Pt/C), respectively. As the concentration of SiO₂ is increased, the contact angle becomes smaller. Thus, the results show that the wettability of the catalyst layer is improved by the addition of hydrophilic SiO₂ particles to the catalyst layer. The optimum amount of SiO₂ has, however, to be determined by single-cell tests, because too much addition of SiO₂ to the catalyst layer may exert an adverse on the ionic or electrical conductivity of the catalyst layer.

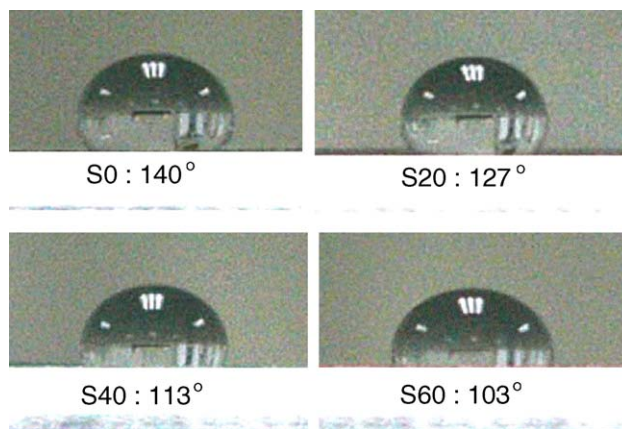


Fig. 1. Contact angles of MEAs measured by water droplet. (S0: no SiO₂ addition, S20: 20 wt.% SiO₂ addition to catalyst layer, S40: 40 wt.% SiO₂ addition to catalyst layer, S60: 60 wt.% SiO₂ addition to catalyst layer. Weight fraction of SiO₂ is based on Pt/C.)

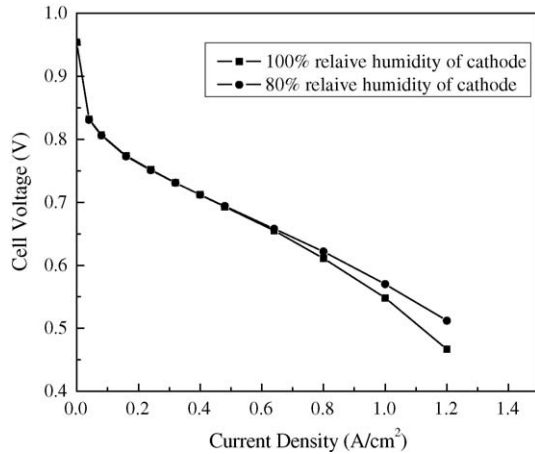


Fig. 2. Polarization curves of MEA S0 at 100% relative humidity of the anode and 70 °C. (S0: no SiO₂ addition.)

3.2. SiO₂ addition to cathode

If the temperature of the cathode humidifier is too high, there will be excess water in the cathode and flooding will occur at high currents, as shown in Fig. 2. It is seen that the cell performance of a cathode with 100% relative humidity is lower than that of one with 80% relative humidity for the MEA S0 sample. Under flooding conditions, liquid water prevents oxygen from accessing the catalyst layer and this causes a fall in voltage. The MEAs SC20 and SC40 have hydrophilic SiO₂ particles in the cathode catalyst layer and give rise to more severe flooding than the MEA S0, as shown in Fig. 3. A high concentration of SiO₂ also causes a large drop in voltage by flooding. In this case, flooding occurs not in the GDL or the channels but in the catalyst layer. MEA SC40 in Fig. 3 shows a very poor performance compared with the other MEAs. This indicates that less water is produced in the cathode catalyst layer, but more severe flooding occurs because the water produced resides mainly in the cathode catalyst layer. Thus, it is not desirable to add hydrophilic SiO₂

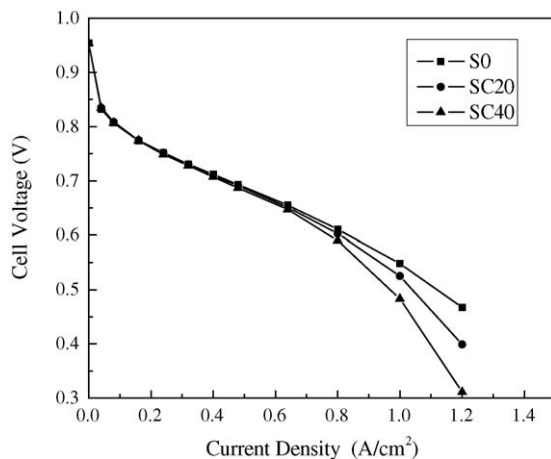


Fig. 3. Polarization curves of MEAs at 100% relative humidity of the anode and cathode and 70 °C. (S0: no SiO₂ addition, SC20: 20 wt.% SiO₂ addition to cathode, SC40: 40 wt.% SiO₂ addition to cathode. Weight fraction of SiO₂ is based on Pt/C.)

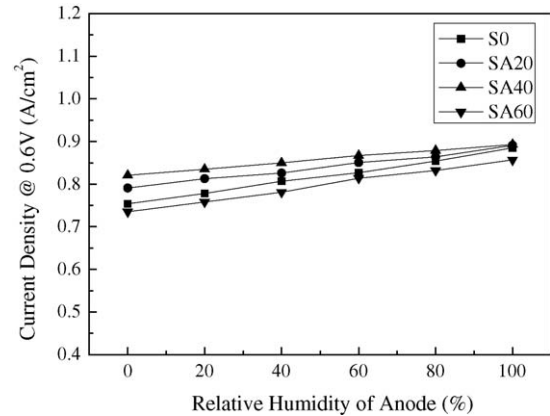


Fig. 4. Current density at 0.6 V at various relative humidities of anode and 70 °C. (S0: no SiO₂ addition, SA20: 20 wt.% SiO₂ addition to anode, SA40: 40 wt.% SiO₂ addition to anode, SA60: 60 wt.% SiO₂ addition to anode, relative humidity of cathode is 80%. Weight fraction of SiO₂ is based on Pt/C.)

particles to the cathode catalyst layer because it causes flooding. On the other hand, these results confirm that there is an increase in wettability of catalyst layer on the addition of SiO₂.

3.3. SiO₂ addition to anode catalyst layer

3.3.1. Effect of relative humidity of anode

Cell performance is represented by the current density at 0.6 V, as shown in Fig. 4. The performance of MEA S0 at 0% relative humidity of the anode is 85% of that at 100% relative humidity. Similarly, MEA SA20 and SA40 show 90 and 93%, respectively. By contrast, MEA SA60 reports a very low performance at all relative humidity values of the anode. This result may be due to an excess of SiO₂ particles that cover active sites of the Pt catalyst.

If too much water is produced in cathode, i.e. sufficient to cause a difference in water concentration between the cathode and the anode, water will move from the cathode to the anode. This phenomenon is called ‘back diffusion’. If performance enhancement is due only to water uptake from external humidification, there must be no difference at 0% relative humidity of anode. There is, however, a large difference in performance and indicates the effect of back diffusion of water. Thus, it may be possible for SiO₂ to assist the absorption of water by simultaneous external humidification and back diffusion.

3.3.2. Effect of relative humidity of cathode

The cell performance of each MEA, as represented by the current density at 0.6 V, is given in Fig. 5 for various relative humidities of the cathode. All of the MEAs exhibit maximum performance at 80% relative humidity. Excess water occurs in the cathode at 100% relative humidity and results in flooding. At 40 and 60% relative humidity of the cathode, there is rapid decrease in performance due to drying out of both the membrane and the catalyst layer. Water in the cathode is supplied by external humidification and by water production from the oxygen reduction reaction. In addition, proton transfers the pulls water molecules from the anode to the cathode during operation. This

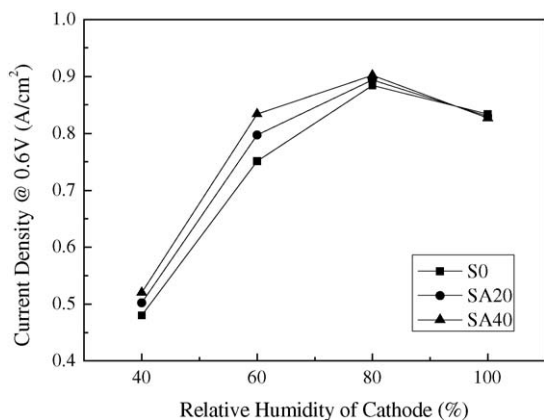


Fig. 5. Current density at 0.6 V at various relative humidities of cathode and 70 °C. (S0: no SiO₂ addition, SA20: 20 wt.% SiO₂ addition to anode, SA40: 40 wt.% SiO₂ addition to anode, relative humidity of anode is 100%. Weight fraction of SiO₂ is based on Pt/C.)

process is sometimes called ‘electro-osmotic drag’. At high current densities, the anode can dry out even if the cathode is well hydrated. Thus, water must diffuse from the cathode to the anode to prevent drying out of anode catalyst layer and to maintain cell performance. High wettability of the anode may help to absorb water from back diffusion so that MEA SA20 and SA40 both exhibit higher performance than MEA S0 at 40 and 60% relative humidity of the cathode.

4. Conclusions

Hydrophilic SiO₂ particles are added to the catalyst layer to improve its performance at low relative humidities of the anode and the cathode. The contact angles of SiO₂-doped MEA are measured from the images of a water droplet on the respec-

tive catalyst layer at room temperature. As the concentration of SiO₂ is increased, the contact angle becomes smaller and wettability is increased. Thus, adding SiO₂ to the cathode causes flooding and represents the effect of the hydrophilicity of SiO₂ particles.

For SiO₂ addition to the anode catalyst layer, the current density of 0.6 V and 0% relative humidity of the anode is 93% of that at 100% relative humidity of the anode. Under the same conditions, undoped-MEA provides only 85% of the current density. With respect to the relative humidity of the cathode, SiO₂-doped MEA gives a higher performance at 60% relative humidity than that of undoped MEA. The high wettability of MEA facilitates the absorption of water from back diffusion.

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