

Fabrication and characterization of a PTFE-reinforced integral composite membrane for self-humidifying PEMFC

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Abstract

A novel PTFE-reinforced self-humidifying membrane based on low-cost sulfonated poly (ether ether ketone) (SPEEK) resin was fabricated. In the membrane a base layer and a thin protective layer were bonded by porous polytetrafluoroethylene (PTFE) film. The base layer, which is composed of silicon oxide supported platinum catalyst (abbreviated as Pt-SiO₂) dispersed in SPEEK resin, can suppress reactant crossover and achieve good membrane hydration due to the imbedded hygroscopic Pt-SiO₂ catalysts. The thin protective layer, which constitutes of H₂O₂ decomposition catalyst Pt-SiO₂ and high H₂O₂-tolerant Nafion resin, aims to prevent the SPEEK resin degradation by H₂O₂ produced at the cathode side by incomplete reduction of oxygen. The porous PTFE film tightly bonds with the SPEEK and the Nafion resins to form an integral membrane and accordingly to avoid delamination of the two different resins. The self-humidifying membrane was characterized by TEM, SEM and EDS, etc. The self-humidifying membrane exhibits higher open circuit voltage (OCV) of 0.98 V and maximum power density value of 0.8 W cm⁻² than 0.94 V, 0.33 W cm⁻² of SPEEK/PTFE membrane under dry condition, respectively. The primary 250 h fuel cell durability experiment was conducted and suggested that this low-cost self-humidifying membrane was durable both on fuel cell performance and the membrane structure under fuel cell operation condition with dry H₂/O₂.

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1. Introduction

Proton exchange membrane (PEM) fuel cells are very prospective alternative energy conversion devices for mobile and stationary application due to their high conversion efficiency from chemical energy to electric energy and environmental benefits [1–3]. The proton conductivity of the PEMs, such as Nafion or sulfonated poly (ether ether ketone) (SPEEK), depends on the water content of the membrane because of the hydrophilic nature of the sulfonic acid group attached to the polymer backbone and the necessity to hydrate the ionic clusters [4]. So far, to ensure good hydration of the membrane electrolyte, the reactant gases are usually humidified through an external humidification

system before entry into the fuel cells. However, the external humidifying subsystem brings complexity to the system. Therefore, operation of PEM fuel cells without humidification subsystems can greatly facilitate water and thermal management and reduce the system weight and complexity [5,6].

To operate the PEM fuel cells with dry reactants, Watanabe and co-workers firstly proposed a concept of self-humidifying composite membranes in which the nanometer-size Pt (suppressing reactant cross-over to generate water) and/or metal oxides (adsorbing and retaining water) were highly dispersed in the Nafion resin [7,8]. However, the composite membrane has the risk of formation electron-conducting path via the network of dispersed Pt particles in the whole membrane. In the latter papers, the researchers developed Pt-containing self-humidifying membrane mainly focusing on the following three directions: (1) decreasing the membrane thickness or incorporating some functional particles, such as SiO₂, ZrP, and Cs_{2.5}H_{0.5}

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PW₁₂O₄₀ to improve the cell performance under dry condition [9–11]; (2) designing new membranes of two-layered or three-layered structures to avoid short circuit through the membrane [12,13]; (3) using the hydrocarbon membrane which can decrease the cost of the PEM [14].

Recently, many promising hydrocarbon polymers, such as SPEEK, sulfonated poly (ether sulfone) (SPES), etc., which have excellent chemical, mechanical and thermal stability and are low-cost, have been widely investigated. However, the durability of these hydrocarbon membranes is an urgent need to be resolved. It is known that a small amount of hydrogen peroxide produced by reactant crossover especially oxygen crossover at the anode side and by the incomplete reduction of oxygen at the cathode side is the potential factor for the oxidative degradation of the membrane [15–17]. Thus, suppressing the reactant crossover and enhancing the anti-oxidation ability of the membrane near the cathode side are the efficient ways to improve the long-term durability of the membrane. The high cross-linking/or thick membrane can mitigate the formation of H₂O₂ due to the low reactant crossover, but the membrane resistance is too high to achieve high power density for fuel cell [18]. Watanabe indicated that the thin membrane incorporated with the Pt particles and/or the hygroscopic oxides can achieve low reactant crossover and the resistance at once [19]. To prevent the membrane degradation from the H₂O₂ generated by incomplete reduction of oxygen at the cathode side, Yu et al. [20] developed a two-layer membrane by hot-pressing a thin Nafion membrane (as the protective layer) on a polystyrene sulfonic acid (PSSA) membrane. The experiment results indicated that the thin Nafion membrane located at the cathode side of the PEM fuel cells had improved the anti-oxidation ability of the PSSA membrane during the operation period for high H₂O₂-tolerant property of Nafion. However, the poor interlayer bonding between the hydrocarbon membrane and the Nafion membrane achieved by hot-pressing may lead to delamination of the two different resins because of their different chemical structure and dimension change under aqueous and thermal conditions [21,22]. The delamination leads to additional contact resistance at the interfaces between the layers and consequently the performance losses. Furthermore, the Nafion membrane located at the cathode can merely delay degradation of the PSSA membrane to some extent and cannot prevent degradation of the membrane, because the H₂O₂ tends to diffuse into the PSSA membrane under a concentration gradient.

In our previous researches, the insulated silicon oxide supported platinum catalyst (abbreviated as Pt-SiO₂) was investigated as an additive to fabricate self-humidifying membrane based on perfluorinated polymer and showed notable effect on suppressing the reactant crossover and membrane hydration [11,23,24]. In this work, we present a novel PTFE-reinforced integral Pt-SiO₂/SPEEK/PTFE/Nafion/Pt-SiO₂ self-humidifying membrane. The membrane constitutes of a base layer composed of Pt-SiO₂ dispersed low-cost SPEEK resin and a thin protective layer composed of Pt-SiO₂ dispersed Nafion resin, both of layers are bonded by porous polytetrafluoroethylene (PTFE) film. The base layer can suppress reactant crossover and achieve good membrane hydration due to the existence of Pt-SiO₂ catalyst. The thin protective layer, which constitutes

of Pt-SiO₂ catalysts for H₂O₂ decomposition and high H₂O₂-tolerant Nafion resin, can prevent the SPEEK resin degradation by H₂O₂ produced at the cathode side. The PTFE film in the self-humidifying membrane bonds and links the two resins together as an integral membrane to avoid the delamination of two layers. The physical and electrochemical properties of the self-humidifying membrane were investigated. The self-humidifying performance and the durability both on the performance and the structure of a single cell employing the self-humidifying membrane were also carried out.

2. Experimental

2.1. The preparation of the membranes

The Pt-SiO₂ catalyst was synthesized by the method reported in other literatures [11,24]. The silicon oxide (BET surface area 112 m² g⁻¹) were impregnated with aqueous solution of H₂PtCl₆ (3.7 mg Pt ml⁻¹) for 24 h. The resulting mixture was dried at room temperature in air and then reduced by H₂ at 200 °C for 3 h. The designing loading of Pt on SiO₂ was 1.5 wt.%.

The Pt-SiO₂/SPEEK/PTFE/Nafion/Pt-SiO₂ self-humidifying membranes were prepared by the following procedure. Firstly, the Pt-SiO₂ catalyst was first dispersed in the solution composed of 5% Nafion solution (DuPont Fluoroproducts) and dimethylsulfoxide (DMSO) (mass ratio, dry Nafion:Pt-SiO₂ = 15:1). The mixture was then poured onto a porous PTFE film (10 μm in thickness, ~85% in porosity, 0.3–0.5 μm in pore diameter) extended over a flat glass plate. The flat glass plate was heated at 75 °C until dryness. Secondly, the Pt-SiO₂ catalyst was dispersed in the SPEEK solution (mass ratio, SPEEK: Pt-SiO₂ = 15:1). Then a small quantity of the resulting mixture was cast on the upper PTFE film and subsequently dried at 75 °C. This process was repeated several times followed by treating the membrane at 120 °C for at least 10 h. The loading of the platinum in the membranes was 2.2 × 10⁻³ mg cm⁻². The self-humidifying membrane was about 24 μm in thickness, with 3 μm of Nafion/Pt-SiO₂ layer (protective layer) and about 21 μm of the SPEEK/Pt-SiO₂ layer (base layer). For comparison, the plain SPEEK/PTFE membrane was prepared by pouring SPEEK solution onto an extended porous PTFE film followed by drying at 75 °C and its thickness was also 24 μm.

2.2. Characterization of the self-humidifying membrane

To study the morphologies of the SiO₂ supported Pt catalyst and SiO₂ particles, TEM (JEM-2000EX, JEOL, Japan) measurement was conducted. The cross-sectional morphology and the elemental distribution of the membrane were analyzed by scanning electron microscopy (SEM) attachment of energy dispersive spectroscopy (EDS) (JSM-6360LV model equipped with Oxford INCA X-sight) to characterize the self-humidifying membrane structure. The MEA images after 250 h fuel cell durability tests were also measured to characterize the stability of the membrane structure.

To test the dimensional stability of the membrane, the sample membranes were soaked in the deionized (DI) water, controlled

at each test temperature (40, 60, 80 °C) for 4 h, the dimension change (ΔL) was calculated from the following equation:

$$\Delta L (\%) = \frac{(L_2 - L_1)}{L_1} \times 100 \quad (1)$$

where L_1 and L_2 mean the distance before and after the samples soaked in DI water, respectively.

The membrane mechanical properties were measured using a tension tester AG-2000A (Shimadzu, AUTO graph) at room temperature, in accordance with China Standard QB-13022-91. Membrane specimens were tested using a programmed elongation rate of 50 mm min⁻¹.

The water uptake of the membrane was calculated from Eq. (2), W_1 is the weights of the wet membrane after immerse in water at 20, 40, 60, and 80 °C for 4 h and W_2 is the weight of the membrane dried under vacuum at 80 °C for 12 h

$$\Delta W (\text{wt.}\%) = \frac{(W_1 - W_2)}{W_2} \times 100 \quad (2)$$

Proton conductivity of the membranes was determined from membrane resistance measured by ac impedance spectroscopy over a frequency range of 100 mHz to 100 kHz. The ac impedance spectroscopy measurements were carried out using a frequency response detector (EG&G Model 1025) combined with a potentiostat/galvanostat (EG&G Model 273A). The resistance value was obtained at open circuit potential condition with gas pipeline dead end after cell performance testing with dry or fully humidified reactants. The results obtained in the form of resistance are normalized based on the geometric area and membrane thickness and reported as conductivity [25].

2.3. The membrane electrode assemblies (MEAs) preparation

The MEAs with active area of 5 cm² were fabricated by hot-pressing method at 160 °C and 10 MPa for 2 min. The anode and the cathode were prefabricated using SGL carbon paper as the substrate and the 46.6 wt.% Pt/C (TKK, Japan) as the catalyst. The Pt loadings of both the anode and the cathode were 0.4 mg cm⁻².

2.4. Single cell evaluation

The MEA was placed in a single cell using stainless steel as the end plates and stainless steel mesh as the current collectors. The single cells were operated at 60 °C with fully humidified H₂/O₂. The operation pressure was set at 0.20 MPa and the gas utilizations were fixed at 90% for H₂ and 50% for O₂. After stable performances were obtained, the cells were then operated with dry gases. Before the performance data were recorded, the cells were maintained at each experimental condition for 8 h.

The fuel cell durability test was performed by a 250 h continuous single cell operated at 500 mA cm⁻² and 50 °C with dry H₂/O₂. The cell potential versus current density date and OCV were measured every 10 h.

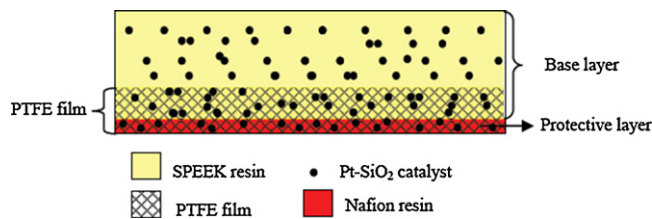


Fig. 1. Schematic diagram of the Pt-SiO₂/SPEEK/PTFE/Nafion/Pt-SiO₂ self-humidifying membrane.

3. Results and discussion

3.1. Principle of the self-humidifying membrane

Fig. 1 shows the designing structure of our self-humidifying membrane. It can be seen that the major part of the membrane is the base layer and the other part is the protective layer, both of which are bonded by the PTFE film. The base layer consists of Pt-SiO₂ catalyst dispersed in the low-cost SPEEK resin. The Pt-SiO₂ catalyst were expected to chemically catalyze the mutually permeable H₂ and O₂, leading to a suppression of reactant crossover to the electrodes, while the hygroscopic Pt-SiO₂ catalyst were expected to absorb the water produced at Pt particles together with that produced at the cathode reaction to maintain water equilibrium in the membrane. Thus, the mitigation of hydrogen peroxide formation caused by reactants crossover and the membrane hydration can be solved at once. The thin protective layer is composed of Pt-SiO₂ catalyst dispersed in Nafion resin and aim to improve the anti-oxidation ability of the membrane near the cathode side. In the protective layer, the utility of Nafion resin is because of its excellent resistance to the hydrogen peroxide [20]. The Pt-SiO₂ catalyst can lower the activation energy for the disproportionation of hydrogen peroxide [26]. As a result, any hydrogen peroxide entering the protective layer can be decomposed by the Pt-SiO₂ catalyst, so that the SPEEK resin is protected from degradation by hydrogen peroxide.

The structural durability of composite membrane is very important for its application in fuel cells due to the fact that membrane is composed of different resins (Nafion and SPEEK), in two phases. Here, the PTFE film can not only enhance the mechanical property of the membrane, but also can mechanically bond with the SPEEK and Nafion resins and plays a role of linker that link the two resins together as an integral membrane [27]. In other words, the bonding and linking effect of the PTFE film avoids the delamination of the SPEEK resin from the Nafion resin which is caused by their different dimension change under the fuel cell condition.

In summary, this structural/chemical durable PTFE-reinforced self-humidifying membrane not only satisfies the requirement of membrane hydration, but also avoids short circuit because of insulated SiO₂ and prevents the oxidative degradation of the SPEEK membrane.

3.2. Characterizations of the self-humidifying membrane

Fig. 2 shows the TEM images of silicon oxide and Pt-SiO₂ catalyst. The images indicate that the diameter of SiO₂

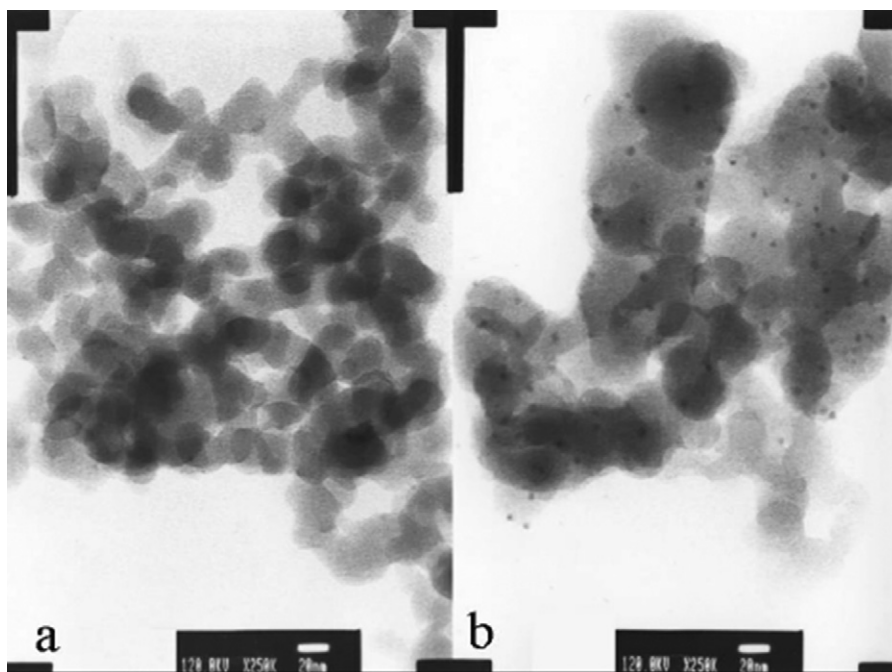


Fig. 2. TEM images of nanometer-sized SiO₂ particle (a), and Pt-SiO₂ catalyst particle (b).

particle is about 20 nm. The diameter of Pt crystallites on SiO₂ is 4–6 nm.

To characterize the morphology and the structure of the Pt-SiO₂/SPEEK/PTFE/Nafion/Pt-SiO₂ self-humidifying membrane, SEM attachment of EDS was employed and the images were showed in Fig. 3. Fig. 3a is the SEM micrograph of the surface of porous PTFE membrane. This micrograph shows there are fibers and knots in the membrane with enclosed micro-pores. It is observed in Fig. 2b that no micro-pore is observed through the whole membrane cross section. This indicated that the pores of porous PTFE film are fully impregnated by the SPEEK and the Nafion resins. To facilitate understanding the structure of the self-humidifying membrane, the cross section of the membrane is divided into three regions denoted as section I (3 μm), section II (5 μm) and section III (16 μm). It is observed from Fig. 3c that the sulfur (S) element distributed along the whole membrane cross section which indicates the SPEEK and Nafion resins have been impregnated in the porous PTFE film. To discern the distributions of the SPEEK and the Nafion resins in the cross section of the self-humidifying membrane, the membrane used Na-form Nafion resin, which was obtained by immersing the Nafion resin in 0.1 M NaOH solution for at least 24 h. By this treatment, the sodium (Na) ion was used as a signal of Na⁺-neutralized Nafion. Fig. 3d shows the sodium (Na) element distributed only in section I, which demonstrates the existence of Nafion resin in section I and the SPEEK resin in section II and section III. Fluorine (F) element is dispersed in the sections I and II, as it is shown in Fig. 3e, indicating that this region is the PTFE layer. Moreover, the section I shows higher fluorine element content than that in section II. This is ascribed to the perfluorinated Nafion resin in section I and non-fluorinated SPEEK resin in section II. The characteristic silicon (Si) element is distributed at the whole cross section due to the existence of the Pt-SiO₂

catalyst in Fig. 3f. Since the Pt loading in the self-humidifying membrane was too low to be analyzed quantitatively, the Pt element distribution was not given here. Therefore, the analysis by EDS is in good agreement with the design of self-humidifying membrane shown in Fig. 1.

The water uptake of the self-humidifying membrane and the plain SPEEK/PTFE membrane at different temperature are given in Fig. 4. From Fig. 4, it is clear that the water uptake of the self-humidifying membrane and the plain SPEEK/PTFE membrane increased with the increasing temperature. Moreover, the self-humidifying membrane exhibits more water uptake than that of the plain SPEEK/PTFE membrane at all test temperature. This is attributed to the existence of hygroscopic Pt-SiO₂ catalyst in the self-humidifying membrane. When the membrane absorbs higher amount of water, the number of exchange sites available per cluster increases; this results in the increase of the proton conductivity of the membrane. So the property of higher water uptake for self-humidifying membrane is expected to possess higher proton conductivity under dry condition.

Membrane proton conductivity was determined by measuring the membrane resistance by ac impedance. From Table 1, it can be seen that the proton conductivity of self-humidifying membrane is slightly lower than that of plain SPEEK/PTFE membrane under fully humidified condition. However, the self-humidifying membrane shows much higher proton conduc-

Table 1
The proton conductivity of the membranes under humidified and dry conditions

Membrane type	Proton conductivity (S cm ⁻¹)	
	RH (%) = 100	RH (%) = 0
SPEEK/PTFE membrane	2.2×10^{-2}	8.5×10^{-3}
Self-humidifying membrane	2.1×10^{-2}	2.0×10^{-2}

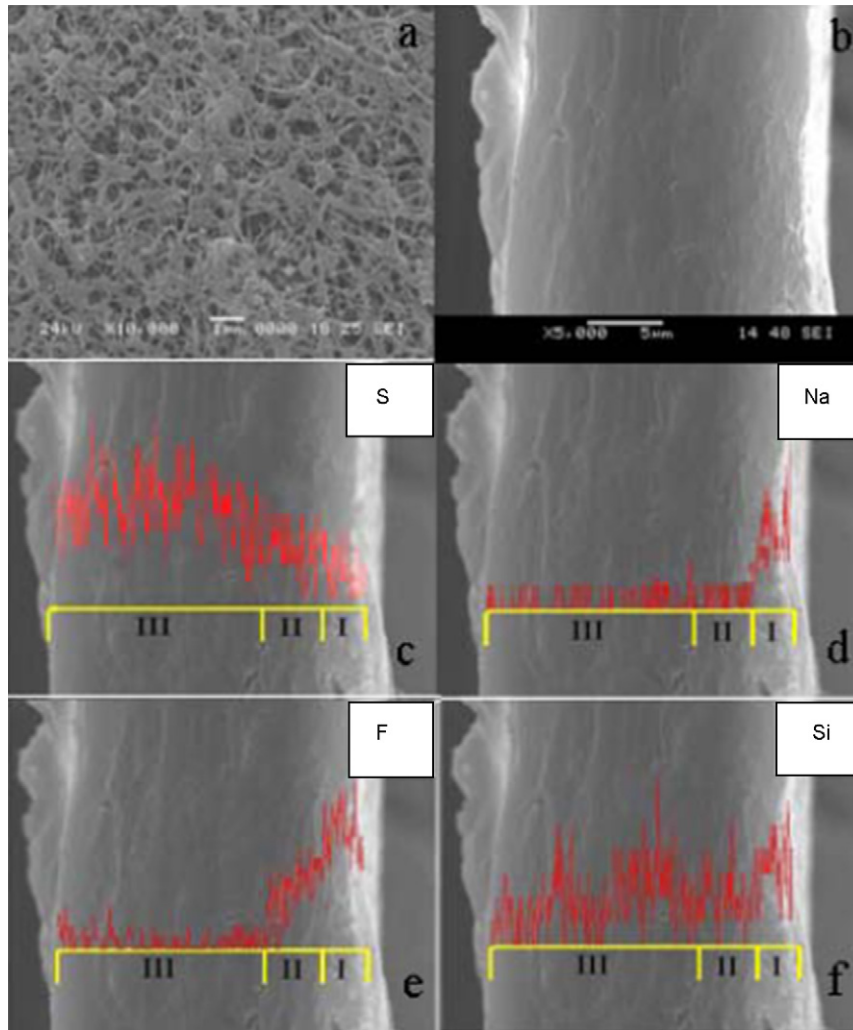


Fig. 3. SEM and EDS images of self-humidifying membrane along the cross section (a) surface of PTFE membrane, (b) cross section of self-humidifying membrane, (c) the distribution of sulfur element, (d) the distribution of sodium element, (e) the distribution of fluorine element and (f) the distribution of silicon element.

tivity ($2.0 \times 10^{-2} \text{ S cm}^{-1}$) than that of the plain SPEEK/PTFE membrane ($8.5 \times 10^{-3} \text{ S cm}^{-1}$) under dry condition. This can be explained by the fact that the more water content of the self-humidifying membrane under dry condition due to the strong

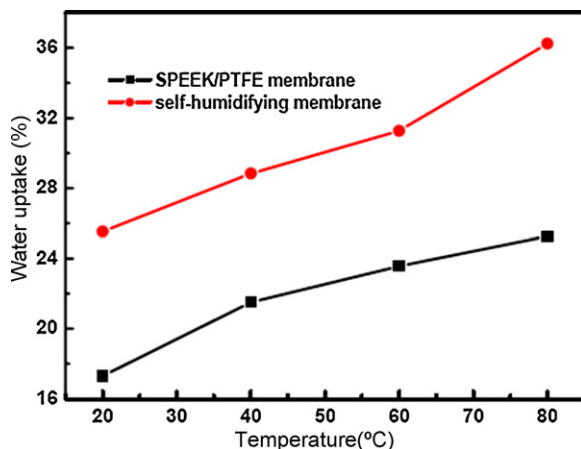


Fig. 4. Comparison of water uptake of plain SPEEK/PTFE membrane and the self-humidifying membrane at different temperature.

interaction between hygroscopic Pt-SiO₂ particles and the water produced at the Pt particles and diffused from the cathode side.

Table 2 shows the mechanical property and dimensional changes of the tested membranes. It is observed that all the PTFE-containing membrane show enhanced mechanical property and thus allows thin membrane feasible to be employed in PEM fuel cells, which accelerates the water back-diffusion from the cathode to the anode and accordingly do benefit to the membrane self-humidification. The dimensional changes of the two pure ionomer (SPEEK and Nafion) remarkably increase as the increasing temperature and show obviously different values with each other. In this situation, delamination phenomenon often occurs between the two different resins and accordingly results in the increasing contact resistance. The three PTFE-containing membranes exhibit decreased dimensional change values than those of the pure ionomer membranes in all tested temperature due to the effect of PTFE-reinforcement. Furthermore, the dimensional changes of the three PTFE-containing membranes are insensitive to the temperature change and almost similar to each other at each test temperature. The PTFE film in our self-humidifying membrane bonds and links the two resins together

Table 2
Mechanical property and dimensional change of the tested membranes

Membrane	SPEEK	Nafion	SPEEK/PTFE	Nafion/PTFE	Self-humidifying membrane
Thickness (μm)	24	24	24	24	24
Maximum strength (MPa)	47.06	21.43	54.43	37.23	49.57
Dimensional change (%)					
40 °C	25	17	7.5	6.8	7.2
60 °C	32	20	8.4	7.8	8.1
80 °C	40	25	12	10	11

as an integral membrane and accordingly improves the interface durability with non-delamination between the two resins.

3.3. Fuel cell performance

To verify the self-humidification effect of the self-humidifying membrane, the single cell performances of the plain SPEEK/PTFE membrane and the self-humidifying membrane under dry and fully humidifying conditions were measured and the results are shown in Fig. 5. The performance of the cell with the self-humidifying membrane is similar to that with the plain SPEEK/PTFE membrane under humidified condition. This is consistent with their similar proton conductivity in Table 1. However, the cell with the self-humidifying membrane outperforms that of the plain SPEEK/PTFE membrane at all current density with their peak power density of 0.8 and 0.33 W cm^{-2} under dry condition, respectively. The plain SPEEK/PTFE membrane has almost reached its limit current density at the 1000 mA cm^{-2} , while the self-humidifying membrane still has a power density of 0.64 W cm^{-2} at the same condition. The better performance is attributed to the hygroscopic Pt-SiO₂ particles inside the self-humidifying membrane, which can absorb water at low current density and release water at high current density to maintain the water balance in the membrane. In addition, from Fig. 5 it can be seen that the performance of the cell employing the self-humidifying membrane is slightly influenced by humidification as compared to that of the SPEEK/PTFE membrane.

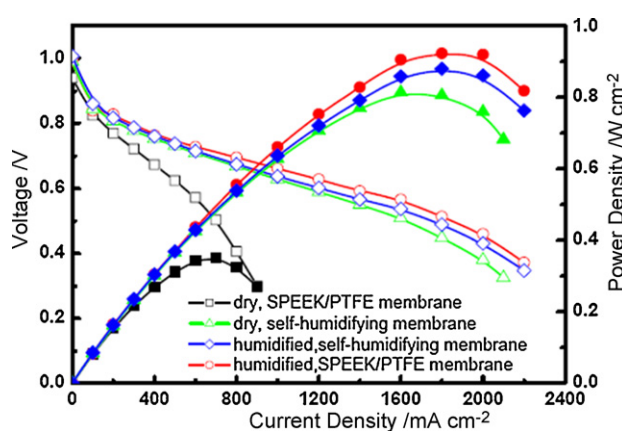


Fig. 5. Comparison of the single cell performance of plain SPEEK/PTFE membrane and the self-humidifying membrane with fully humidified and dry H_2/O_2 operated at 60 °C with the gas pressure of 0.2 MPa.

The OCV is a good measurement of hydrogen or oxygen crossover through the PEMs to the cathode or anode during the operation of fuel cell. In the dry condition, the self-humidifying membrane shows higher OCV (0.98 V) than that of plain SPEEK/PTFE membrane (0.94 V). The reactant crossover was suppressed by the chemically catalyzing recombination at Pt-SiO₂ catalyst inside the self-humidifying membrane and according resulting in a higher OCV value. The low reactants cross-over significantly reduce the cathode polarization and the amount of H_2O_2 formation caused by reactant crossover.

3.4. Durability of fuel cell performance and membrane structure

The fuel cell performance durability of the self-humidifying membrane had been examined by operating a single cell at 500 mA cm^{-2} for 250 h with dry reactants. From Fig. 6 it is found that during 250 h operation, the single cell shows no obvious degradation both on OCV and the cell performance under dry condition. The primary results indicated that the durability of the self-humidifying membrane under fuel cell operation condition was satisfactory. Both the suppressed reactants crossover due to the imbedded Pt-SiO₂ catalyst and protective layer located at the cathode of the membrane contribute to ensure the stability of the membrane under fuel cell operation condition. However, the long term durability of self-humidifying membrane still needs to be investigated in the future.

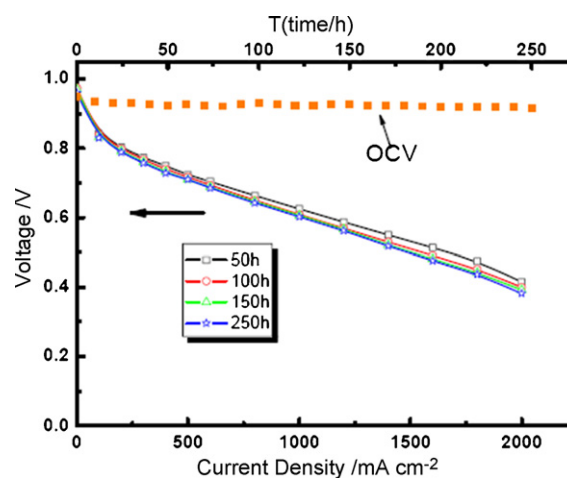


Fig. 6. Polarization curves and the OCV value employing self-humidifying membrane during the fuel cell durability test operated at 50 °C with dry H_2/O_2 . $P_{\text{H}_2} = P_{\text{O}_2} = 0.2$ MPa.

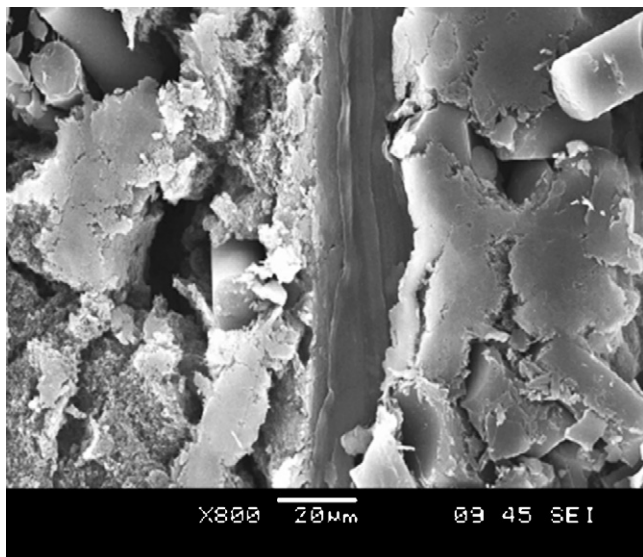


Fig. 7. SEM image of the cross-section of a MEA with self-humidifying membrane after 250 h fuel cell test under dry conditions.

To check the structural durability of the self-humidifying membrane, Fig. 7 shows the SEM images of cross-section of MEAs with self-humidifying membrane after fuel cell durability tests. From Fig. 7, it can be seen that the MEA employing our PTFE-reinforced self-humidifying membrane did not undergo appreciable delamination phenomenon after 250 h fuel cell operation. During the operation of a fuel cell, the temperature and the humidity change frequently. The PTFE membrane can tightly bond both the Nafion and SPEEK resins to ensure non-delamination of two resins and accordingly improve the durability of the membrane structure.

4. Conclusions

A novel PTFE-reinforced integral self-humidifying membrane Pt-SiO₂/SPEEK/PTFE/Nafion/Pt-SiO₂ was fabricated. The membrane structure was confirmed by TEM, SEM, EDS, etc. The self-humidifying membrane show enhanced water uptake and decreased dimensional change at all test temperature and higher proton conductivity under dry condition compared to the plain SPEEK/PTFE membrane. The single cell performance with the self-humidifying membrane is much better than that of plain SPEEK/PTFE membrane with the peak power density of 0.8 W cm⁻² for the former and 0.33 W cm⁻² for the latter under dry operation condition due to the hygroscopic Pt-SiO₂ catalyst in the self-humidifying membrane. This new

self-humidifying membrane did not show obvious degradation on fuel cell performance and membrane structure after 250 h fuel cell durability tests. Both the low reactant crossover due to the imbedded nano-scale Pt-SiO₂ catalyst and the effect of protective layer contribute to ensure the performance durability of self-humidifying membrane under fuel cell operation condition. The PTFE film ensures the stability of membrane structure by a tight bond between Nafion and SPEEK resin. We believe that this novel low-cost self-humidifying membrane is promising for application in PEM fuel cells.

Acknowledgements

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