

Investigation of self-humidifying membranes based on sulfonated poly(ether ether ketone) hybrid with sulfated zirconia supported Pt catalyst for fuel cell applications

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Abstract

A self-humidifying membrane based on sulfonated poly(ether ether ketone) (SPEEK) hybrid with sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$, SZ) supported platinum catalyst (Pt-SZ catalyst) was synthesized for fuel cell applications. The SZ, a solid state superacid with hygroscopic properties and proton-conductive properties, was employed to synthesize the Pt-SZ catalyst. The self-humidifying membrane (SPEEK/Pt-SZ) was characterized by TEM, FT-IR, TGA and SEM coupled with EDX. The SPEEK/Pt-SZ membrane exhibited higher water uptake and proton conductivity than the plain SPEEK membrane. Consequently, the SPEEK/Pt-SZ self-humidifying membrane under dry operation showed a higher open circuit voltage (OCV) of 1.015 V and a maximum power density of 0.95 W cm^{-2} , relative to 0.96 V and 0.54 W cm^{-2} for the plain SPEEK membrane. The incorporation of the catalytic, hygroscopic and proton-conductive Pt-SZ catalyst in the SPEEK matrix facilitated water balance and proton conduction, accordingly improved the single cell performance under dry operation. In addition, the enhanced OCV and the decreased area ohmic resistance confirmed the effect of Pt-SZ catalyst in the self-humidifying membrane on suppressing reactant crossover and the membrane self-humidification.

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Keywords: PEMFC; Self-humidifying membrane; Sulfated zirconia supported platinum catalyst; SPEEK; Proton conductivity

1. Introduction

Proton exchange membrane (PEM) fuel cells are promising alternative energy conversion devices for transportation and stationary applications due to their high energy conversion efficiency and environmental benefits [1–3]. Currently, PEM fuel cell systems are too complex and need to be simplified for mobile applications. For example, the operation of PEM fuel cells without external humidification subsystems is beneficial [4]. However, the proton conductivity of the PEMs, such as Nafion or sulfonated poly(ether ether ketone) (SPEEK) membranes, depend on the water content [5]. The unsaturated-humidification or non-humidification of reactant gases prior to entry into a

fuel cell may lead to the decreased water content, and accordingly reduced proton conductivity of the membranes [6,7]. The reduction in membrane thickness has facilitated water back-diffusion from the cathode to the anode, accordingly resulting in not significantly impaired proton conductivity of the operating membrane. However, this also accelerated the reactant crossover because of the membrane thinness, which may reduce the cell performance and accelerate the membrane degradation [8]. Therefore, there were two important issues in PEM fuel cell operating under dry conditions, namely, how to effectively suppress reactant crossover and how to keep a high membrane proton conductivity.

To suppress the mutual permeation of the reactant gases and realize the operation of the fuel cell under the dry condition, most literature focuses on development of self-humidifying PEMs. Watanabe et al. [9–12] proposed self-humidifying membranes with highly dispersed nanometer-sized Pt and/or hygroscopic oxides (e.g., SiO_2 or TiO_2). The Pt nanoparticles in the membrane could suppress the reactant crossover by catalytic

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recombination of the crossover H_2 and O_2 , and the hygroscopic oxides contributed to maintain the membrane water equilibrium. In addition, Lee et al. [13] impregnated nanometer-sized Pt crystallites into a Nafion® 112 membrane by reduction of $Pt(NH_3)_4^{2+}$, followed by in situ precipitation of zirconium phosphate in the Pt-Nafion membrane. The incorporation of zirconium phosphate in the membrane was expected to improve the cell performance under dry operation due to its high proton conductivity as well as the high water retaining properties. To meet the commercial demand of using low-cost membrane material, Xing et al. [14] investigated a self-humidifying composite membrane based on sulfonated poly(ether ether ketone) (donated as SPEEK). The membrane was prepared by firstly casting SPEEK solution onto porous PTFE film to obtain SPEEK/PTFE as a base layer, and then recasting the ink of SPEEK and Pt/C catalyst onto the SPEEK/PTFE base layer to form a Pt-C/SPEEK layer. It was noted that the above self-humidifying membranes were fabricated by separately incorporating Pt or Pt/C particles and inorganic particles in the base membrane to realize the effect of suppressing the gas crossover and membrane hydration. However, the presence of Pt or Pt/C particles in the whole membrane increased the risk of forming short circuit within the fuel cell due to electronic conduction of Pt and Pt/C.

In our previous work, a hygroscopic oxide (SiO_2) supported platinum catalyst as an additive was employed to fabricate the self-humidifying membrane [15]. The hygroscopic insulating oxides supported Pt catalyst can avoid electronic short circuit and keep good membrane hydration due to in situ adsorbing water produced at Pt particles on the surface of hygroscopic oxide particles. However, the hygroscopic inorganic oxides were not proton-conductive and mostly increased the membrane resistance.

In the present work, SPEEK/Pt-SZ self-humidifying membranes based on a sulfonated poly(ether ether ketone) (SPEEK) hybrid with sulfated zirconia supported Pt catalyst (abbreviated as Pt-SZ catalyst) was fabricated, on the basis of the low cost of SPEEK resin and the catalytic, hygroscopic and proton-conductive properties of the Pt-SZ catalyst. Here, the sulfated zirconia as the catalyst support, which is the strongest superacid among well known solid acids ($H_0 < -16$) [16], was widely studied as an additive to enhance the proton conductivity of the operating membranes at low humidities because of its hygroscopic and proton-conductive properties. The SPEEK matrix was chosen because of its better mechanical properties and much lower cost, as compared to perfluorosulfonated Nafion membrane. The SPEEK/Pt-SZ self-humidifying membrane was characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray detector (EDX) and thermo-gravimetric analysis (TGA). The water uptake and proton conductivity properties of the self-humidifying membrane were investigated, in comparison with the plain SPEEK membrane. The single cell performance employing the SPEEK/Pt-SZ membrane was evaluated and the resistance of the operating membrane under wet or dry H_2/O_2 operations was also investigated, in comparison with those of the plain SPEEK membrane.

2. Experimental

2.1. Preparation of the Pt-SZ catalyst and the membrane

The Pt-SZ catalyst was synthesized by impregnation of dried sulfated zirconia (SZ) particles with a solution of H_2PtCl_6 , the resulting mixture was dried at room temperature in air and subsequently reduced by hydrogen at $200^\circ C$ for 2 h. The designing loading of Pt on SZ particles was 2 wt.%. SZ particles (BET surface area of $128\text{ m}^2\text{ g}^{-1}$; average particle diameter of 10 nm) were prepared as following processes: The ZrO_2 particles obtained by supercritical drying method [17], were immersed in a 0.5 M H_2SO_4 solution for 60 min, followed by filtering and drying at 383 K for 24 h. After drying, the obtained solid particle was calcined at 873 K for 3 h under atmospheric conditions to form the SZ particles.

Sulfonated poly(ether ether ketone) (SPEEK) polymers with sulfonation degree of 67% were prepared following the procedure reported in the literature [18]. The degree of the sulfonation (DS) was determined by titration method described in elsewhere [19].

The SPEEK/Pt-SZ self-humidifying membrane was prepared by solution-casting method. The SPEEK was firstly dissolved in *N,N* dimethylacetamide (DMAc) at room temperature to prepare a 10 wt.% solution. Then the Pt-SZ catalyst was added to the above solution and stirred with a magnetic stirrer for 4 h to obtain a homogeneous mixture. The mass ratio of Pt-SZ catalyst and the SPEEK resin was 1:9. The resulting mixture was cast onto a clean flat glass, and then evaporated at $60^\circ C$ for 12 h till dry, followed by heat treatment at $120^\circ C$ under vacuum. For comparison, the plain SPEEK membrane was fabricated by the same way. The SPEEK/Pt-SZ membrane and the plain SPEEK membrane were designed as $24\ \mu\text{m}$ in thickness.

2.2. TEM analysis of the Pt-SZ catalyst

To study the morphology of the Pt-SZ catalyst, TEM (JEM-2000EX, JEOL, Japan) measurements were conducted. The Pt-SZ particles were dispersed in ethanol, using an ultrasonic bath, and then mounted on standard copper TEM grids.

2.3. FT-IR measurement of the SZ particles

To obtain structural information on the SZ particles, which acted as the catalyst support, the FT-IR measurement was conducted using a JASCO FT-IR 4100 spectrometer. The KBr pellet method was used to measure the IR spectrum of the SZ particles.

2.4. SEM and EDX analysis of the membranes

The morphology of the cross-sectional the plain SPEEK and SPEEK/Pt-SZ self-humidifying membranes was investigated by SEM (JEOL 6360LV, Japan) measurement. To determine the Pt-SZ catalyst distribution along the membrane cross-section, the signals of zirconia element were detected by EDX (Oxford Instruments Microanalysis 1350) mapping method.

2.5. Thermal analysis of the membranes

Thermogravimetric analysis (TGA) of the SZ particle and the membranes was performed by a TGA/DTA (Pyris Diamond TGA/DTA) system over a temperature ranging from 50 to 800 °C at the heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

2.6. Water uptake of the membranes

For measurement of the membrane water content, the membrane samples were immersed in deionized water at 20, 40, 60 and 80 °C for 4 h. The above-mentioned membranes were removed from liquid water, blotted dry to remove the excess surface water, and quickly weighed in a closed vessel. The membrane samples were then dried at 100 °C for 10 h under vacuum. The water content of the membranes was determined from the difference between wet and dry weights according to Eq. (1). Three repeat measurements were carried out for each membrane.

$$\Delta W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

2.7. Proton conductivity and areal resistance of the membrane measured by EIS

The proton conductivity of the membranes was determined from membrane resistance measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 mHz–100 kHz. The membrane samples were humidified by vapor water at each test temperature through the window [20]. A frequency response detector (EG&G model 1025, Princeton Applied Institute) and a potentiostat/galvanostat (EG&G model 273A, Princeton Applied Institute) were employed for the measurements. Moreover, resistances of the cells operated at the current density of 100 mA cm⁻² under dry or wet conditions were also measured by EIS. Three repeat proton conductivity and areal resistance measurements were carried out for each membrane.

2.8. The membrane electrode assemblies (MEAs) preparation and single PEM fuel cell evaluation

The MEAs with active area of 5 cm² were fabricated by hot-pressing method at 160 °C and 10 MPa for 2 min. The cathode were pre-fabricated using SGL carbon paper as the substrate and the 46.6 wt.% Pt/C (TKK, Japan) as the catalyst. The Pt loadings and Nafion loading in both the anode and the cathode were 0.4 mg cm⁻². The MEA was placed in a single cell using stainless steel as the end plates and stainless steel mesh as the current collectors.

Firstly, 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 operation with dry reactants, the cells were dried overnight by flowing dry N₂.

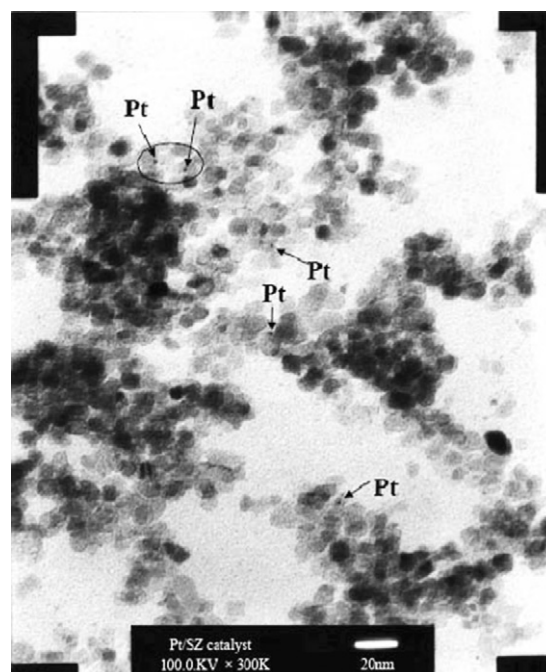


Fig. 1. TEM image of the nanosized Pt-SZ catalyst.

3. Results and discussions

3.1. TEM images of the Pt-SZ catalyst

Fig. 1 showed the TEM image of the Pt-SZ catalyst. The images indicated that the diameter of Pt-SZ particles was about 10 nm. It should be noted that there were a few Pt particles that can be seen clearly in the image, which was attributed to the combined result of low loading of Pt (2 wt.%) and the weak contrast between Pt particles and the sulfated zirconia in the TEM image mode. This phenomenon was consistent with that reported by Manoli [21]. The diameter of Pt crystallites on SZ particles was 1–2 nm.

3.2. FT-IR measurement of the SZ particle

To obtain the structure information of the SZ particles, which acted as the catalyst support, the FT-IR measurement was investigated and the results are shown in Fig. 2. From the Fig. 2, the peak at 1630 cm⁻¹ is attributed to the vibrations of acidic –OH groups, 748 cm⁻¹ to the vibrations feature of ZrO₂, and the peaks at 1240, 1141 and 1041 cm⁻¹ to the asymmetric stretching vibrations of sulfate groups binding via two oxygen atoms to the zirconium of support. All observed peaks were accordance with the reported literatures [22,23].

3.3. SEM-EDX measurements of membranes

To determine the morphology of the cross-sectional plain SPEEK and SPEEK/Pt-SZ membranes and the distribution of Pt-SZ catalyst in the membranes, the SEM-EDX measurements were conducted and the results were shown in Fig. 3. It was observed from Fig. 3(a and c) that the plain SPEEK mem-

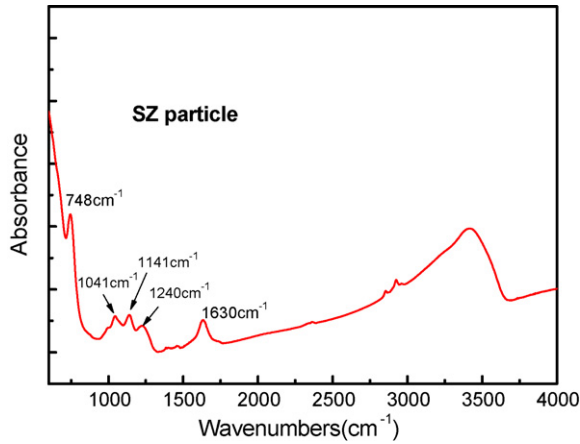


Fig. 2. FT-IR spectrum of the SZ particles.

brane and SPEEK/Pt-SZ membrane were both about $24\ \mu\text{m}$ in thickness. Furthermore, the cross-section of SPEEK/Pt-SZ membrane was smooth as the plain SPEEK membrane, and there was no conglomeration of Pt-SZ particles found in the whole cross-sectional SPEEK/Pt-SZ membrane. This is attributed to the nanometer-sized Pt-SZ particles and good compatibility between Pt-SZ particle and SPEEK matrix. Fig. 3(d) showed the zirconia element uniformly distributed along the cross-section

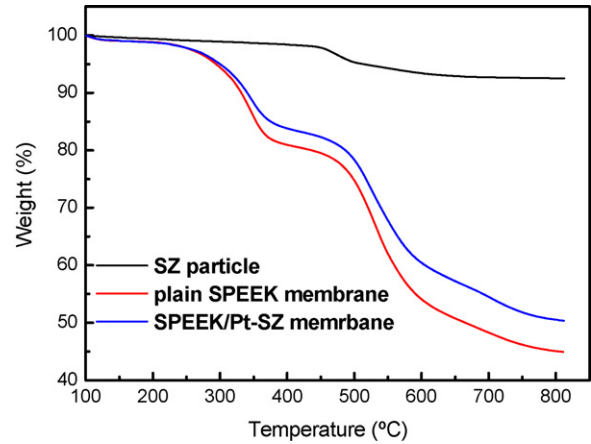


Fig. 4. TGA measurements of the SZ particle, SPEEK membrane and SPEEK/Pt-SZ self-humidifying membrane.

of the SPEEK/Pt-SZ membrane, indicating a good distribution of Pt-SZ particles in the SPEEK matrix.

3.4. TGA measurement of the membranes

Fig. 4 shows the TGA measurement of the SZ particle, the plain SPEEK membrane and the SPEEK/Pt-SZ self-humidifying

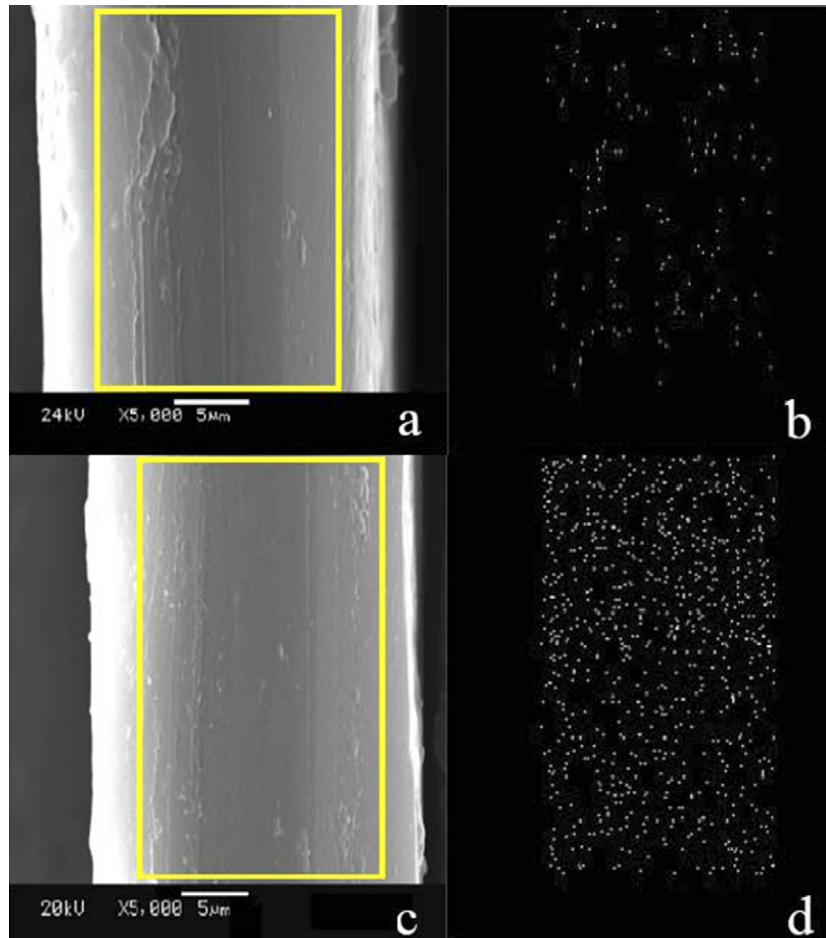


Fig. 3. SEM and EDX images of the plain SPEEK membrane (a and b) and SPEEK/Pt-SZ composite membranes (c and d).

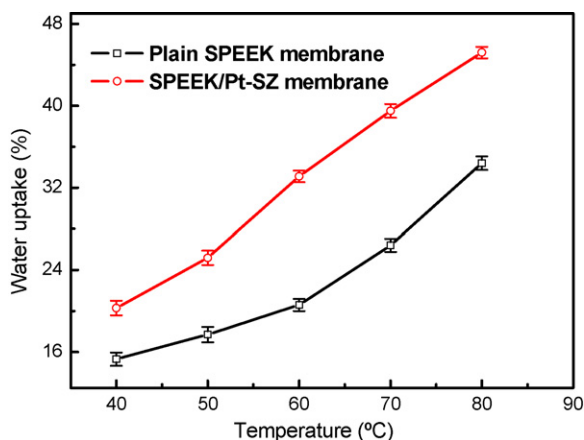


Fig. 5. Water uptake of plain SPEEK membrane and SPEEK/Pt-SZ self-humidifying membrane at various temperatures.

membrane. Here, the TGA of the SZ can denote the thermal behavior of the Pt-SZ catalyst due to no weight change of the Pt particle at test temperature in nitrogen atmosphere. It can be seen that the SZ has a weight loss of about 1.0% at 250 °C and about 4.8% at the temperature ranging from 450 °C to 800 °C. The two weight loss regions were attributed to the water evaporation from the SZ surface and the decomposition of the SO_4^{2-} bounded at the surface of the ZrO_2 , respectively [22]. The SO_4^{2-} content in SZ was estimated from weight loss to be about 4.8 wt.%. The plain SPEEK membrane exhibited two weight loss regions for decomposition of sulfonic acid groups at 250–370 °C and decomposition of the polymer chain occurs at above 500 °C. For the SPEEK/Pt-SZ self-humidifying membrane, the TGA curve showed similar behavior with that of the SPEEK membrane except the weight loss value, indicating the existence of the Pt-SZ catalyst in the self-humidifying membrane.

3.5. Water uptake of the membranes

For the PEMs, water uptake is an important property because of its direct relation to the proton conductivity. According to cluster network model [24], it was proposed that when the single cell was operated with low-humidified and non-humidified reactant gases, the PEM was of low hydration, which resulted in the shrunken available clusters and thus the elongation in the interconnecting channels [25]. The enhancement of hygroscopic properties for the PEM could offset the disadvantage of shrunken clusters, according increase the proton conductivity of the membrane. Fig. 5 shows the water uptake data of the plain SPEEK membrane and the SPEEK/Pt-SZ self-humidifying membrane in the temperature ranging from 40 to 80 °C. From Fig. 5 it can be seen that the water uptake of the SPEEK/Pt-SZ membrane and the plain SPEEK membrane increased with the temperature. Moreover, the SPEEK/Pt-SZ self-humidifying membrane exhibited higher water uptake than the plain SPEEK membrane at all test temperatures, indicating the better hygroscopic property of SPEEK/Pt-SZ membrane relative to that of the plain SPEEK membrane. This was due to the incorporation of hygroscopic Pt-SZ catalyst in the membrane, which can provide additional

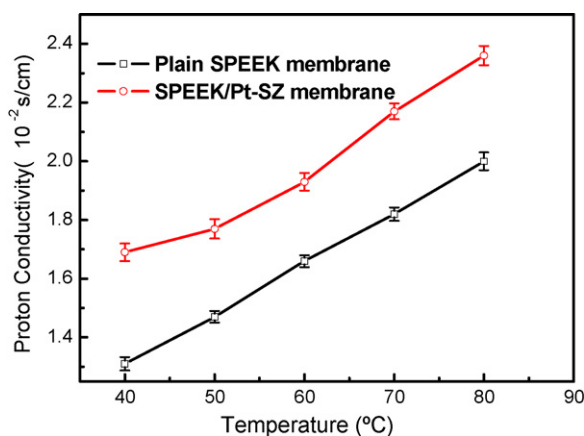


Fig. 6. Proton conductivity of plain SPEEK membrane and SPEEK/Pt-SZ self-humidifying membrane at various temperatures.

hydrogen bonding sites and new acid sites for water absorption [26].

3.6. Proton conductivity of the membranes

Membrane proton conductivity was determined by measuring the membrane resistance by EIS. Fig. 6 shows the proton conductivity of the plain SPEEK membrane and SPEEK/Pt-SZ self-humidifying membrane at various temperatures in a 100% relative humidity (RH) atmosphere. It was observed that the proton conductivity of the SPEEK/Pt-SZ self-humidifying membrane and the plain SPEEK membrane increased with the temperature, and the SPEEK/Pt-SZ self-humidifying membrane showed higher proton conductivity values than those of plain SPEEK membrane, which was consistent with the results of water uptake measurement. The increase in proton conductivity of the SPEEK/Pt-SZ self-humidifying membrane relative to that of SPEEK membrane was ascribed to the combined result of the enhanced water uptake as well as the additional acidity sites provided by Pt-SZ particles. The structure formula when SZ adsorbs water to generate Bronsted acid site for proton transport is shown in Fig. 7 [27,28]. The Pt-SZ particles in the SPEEK/Pt-SZ membrane should be a useful bifunctional additive embedded into SPEEK matrix for promotion of water adsorbing as well as proton-conductive properties.

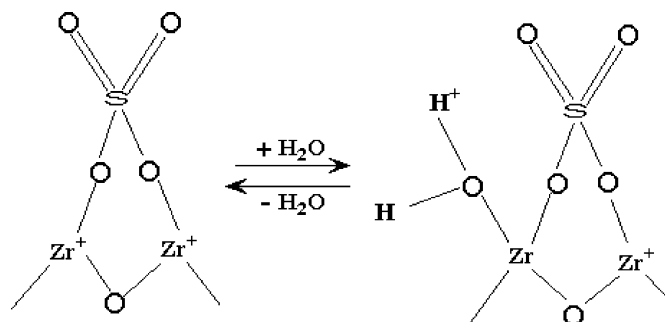


Fig. 7. Structure formula of the sulfated zirconia (SZ) adsorbed/desorbed water.

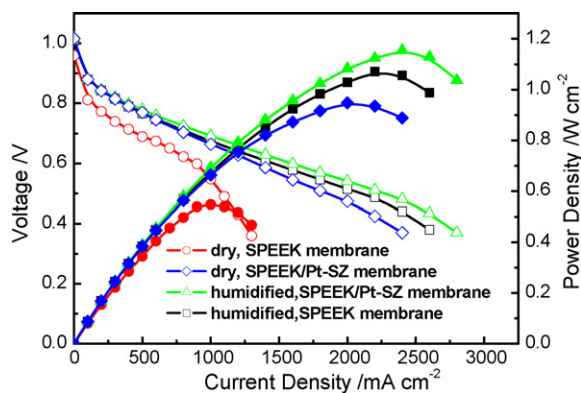


Fig. 8. Single cell performances of SPEEK/Pt-SZ self-humidifying membrane with fully humidified H_2/O_2 (Δ , \blacktriangle), dry H_2/O_2 (\diamond , \blacklozenge) and plain SPEEK membrane with fully humidified H_2/O_2 (\square , \blacksquare), dry H_2/O_2 (\circ , \bullet) operated at 60°C . $P_{H_2} = P_{O_2} = 0.2\text{ MPa}$.

3.7. Single cell evaluation

To verify the self-humidification effect of SPEEK/Pt-SZ self-humidifying membrane, the single cell performances of the plain SPEEK membrane and SPEEK/Pt-SZ membrane with dry H_2/O_2 at $T_{\text{cell}} = 60^\circ\text{C}$ and with fully humidified H_2/O_2 at $T_{H_2} = T_{\text{cell}} = T_{O_2} = 60^\circ\text{C}$ were evaluated, as shown in Fig. 8. The single cell employing the SPEEK/Pt-SZ self-humidifying membrane outperformed those of the plain SPEEK membrane under wet or dry operation conditions. The peak power densities of the single cells employing the SPEEK/Pt-SZ membrane under wet and dry operations are 1.15 , 0.95 W cm^{-2} compared with the plain SPEEK membrane of 1.07 , 0.54 W cm^{-2} , respectively. The performance of the cell employing the SPEEK/Pt-SZ self-humidifying membrane was slightly influenced by humidification conditions. The SPEEK/Pt-SZ membrane under dry operation condition showed much better performance than that of plain SPEEK membrane. For example, the cell voltage at 1000 mA cm^{-2} for the SPEEK/Pt-SZ membrane was 0.664 V , 116 mV higher than 0.548 V of the plain SPEEK membrane. This better performance was attributed to the incorporation of the hygroscopic Pt-SZ catalyst, which could adsorb the water produced on the Pt particle as well as the water back-diffused from the cathode side when the membrane needed it. Furthermore, the Pt-SZ catalyst could provide the additional acid groups for proton transport due to its proton-conductive properties.

3.8. OCV and areal resistance analysis

To elucidate the effect of the Pt-SZ catalyst on the contribution of suppressing the reactant crossover and improvement of performance, the open circuit voltage (OCV) values and the resistance values of single cells employing the SPEEK/Pt-SZ membrane and the plain SPEEK membrane under dry and wet conditions were analyzed. The OCV is a good measurement of hydrogen or oxygen crossover through the PEMs during the operating fuel cell. The cell with less hydrogen and oxygen crossover will lead to a higher OCV value. Table 1 shows the OCV values of the SPEEK/Pt-SZ self-humidifying membrane

Table 1

OCV values of single cells employing different membranes under dry and wet operation

| Membrane | OCV (V) | |
|-------------|---------------|---------------|
| | Wet operation | Dry operation |
| SPEEK | 1.008 | 0.96 |
| SPEEK/Pt-SZ | 1.018 | 1.015 |

Table 2

Ohmic resistances of single cells operated at 0.1 A cm^{-2} under dry and wet operation

| Membrane | Ohmic resistance ($\text{m}\Omega\text{ cm}^2$) | |
|-------------|---|---------------|
| | Wet operation | Dry operation |
| SPEEK | 95 ± 2 | 180 ± 6 |
| SPEEK/Pt-SZ | 85 ± 2 | 100 ± 4 |

and the SPEEK membrane under dry and wet operation conditions. It is obvious that the single cell with the self-humidifying membrane exhibited higher OCV values than those of SPEEK membrane both under dry or wet conditions. The presence of the Pt sites after incorporation of the Pt-SZ catalyst in the self-humidifying membrane can effectively suppress the reactants crossover by chemically catalyzing the reaction between the permeable H_2 and O_2 , and result in a higher OCV value.

Table 2 shows the ohmic resistance values of the cells employing the SPEEK/Pt-SZ self-humidifying membrane and the plain SPEEK membrane at the current density of 100 mA cm^{-2} under wet and dry operation conditions. It was found that the ohmic resistance value of the plain SPEEK membrane under dry operation was much larger than under wet operation with the values of 180 ± 6 , $95 \pm 2\text{ m}\Omega\text{ cm}^2$, respectively. In contrast, the SPEEK/Pt-SZ self-humidifying membrane exhibited close ohmic resistance under both the dry operation condition and wet operation condition. The lower resistance of the self-humidifying membrane under dry conditions, compared with that of the plain SPEEK membrane, was ascribed to the incorporation of catalytic, hygroscopic, and proton-conductive Pt-SZ particles. The existence of Pt-SZ catalyst can in situ adsorb the water produced on the Pt particles by chemical catalytic reaction of permeating H_2 and O_2 to rehydrate the membrane, and meanwhile provide new acid sites for proton transport. The lower resistance of the SPEEK/Pt-SZ self-humidifying membrane contributed to the higher performance relative to the plain SPEEK membrane.

4. Conclusion

A sulfated zirconia supported platinum catalyst (Pt-SZ) and a self-humidifying membrane based on the Pt-SZ catalyst and low-cost SPEEK resin were synthesized. The supported catalyst and the self-humidifying membrane were investigated by the TEM, FT-IR, SEM-EDX, TGA, water uptake and proton conductivity measurements. The SPEEK/Pt-SZ self-humidifying membrane exhibited higher water uptake and proton conductivity

ity than the plain SPEEK membrane due to the existence of the hygroscopic and proton-conductive Pt-SZ catalyst. A single cell employing the SPEEK/Pt-SZ membrane exhibited higher cell OCV values and performance than the plain SPEEK membrane cell under both dry and wet conditions. Furthermore, the performance of the single cell with a SPEEK/Pt-SZ membrane was only slightly influenced by the humidification conditions compared with that of plain SPEEK membrane. The higher OCV values and the lower resistance for the SPEEK/Pt-SZ membrane under dry operation, as compared to of the plain SPEEK membrane, were attributed to the incorporation of catalytic, hygroscopic and proton-conductive Pt-SZ catalyst inside the self-humidifying membrane. Therefore, our novel low-cost self-humidifying membrane could be very promising for application in PEM fuel cells.

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