

Promotion of PEM Self-Humidifying Effect by Nanometer-Sized Sulfated Zirconia-Supported Pt Catalyst Hybrid with Sulfonated Poly(Ether Ether Ketone)

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A self-humidifying membrane based on low-cost 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 investigated for fuel cell applications. The SZ particle, a solid-state superacid with hygroscopic and high proton conductivity properties, was employed as the catalyst support. The SPEEK/Pt–SZ self-humidifying membrane was characterized by TEM and SEM coupled with EDX. FT-IR was conducted to verify the effect of SPEEK/Pt–SZ membrane on catalytic combination of crossover hydrogen and oxygen. To display the advantages of Pt–SZ catalyst as the additive, the IEC, water uptake, proton conductivity, single-cell performance, and areal resistance measurements were compared between the plain SPEEK membrane, SPEEK/Pt– SiO_2 membrane, and the SPEEK/Pt–SZ membrane. The SPEEK/Pt–SZ membrane exhibited the highest IEC value, proton conductivity, single-cell performance, and the lowest areal resistance relative to the plain SPEEK and SPEEK/Pt– SiO_2 membranes. The SPEEK/Pt–SZ self-humidifying membrane exhibited peak power density of 1.0 W/cm² under dry operation condition compared with 0.89 W/cm² and 0.58 W/cm² of SPEEK/Pt– SiO_2 and plain SPEEK membranes, respectively. The incorporation of the catalytic, hygroscopic and proton conductive Pt–SZ catalyst in the SPEEK/Pt–SZ self-humidifying membrane facilitated water balance and proton conduction, and accordingly improved its single cell performance under dry operation. In addition, the enhanced OCV and the decreased areal ohmic resistance confirmed the promotion effect of Pt–SZ catalyst in the self-humidifying membrane on suppressing reactant crossover and the membrane self-humidification.

1. Introduction

During the past several decades, much attention has been focused on the research and development of proton-exchange membrane fuel cells (PEMFCs) due to their advantages of high power density, simplicity of operation, high-energy conversion efficiency and lower harmful emissions.^{1–3} The markets and applications today and for the foreseeable future of the PEM fuel cell segment into three areas: automotive, stationary and portable.⁴ Each of these applications has different operating requirements, which in turn lead to different membrane needs. Currently, the PEMFC system is too complex and its weight and volume need to be further decreased to make this power generator suitable for portable applications. The operation of fuel cell with dry reactants is attractive for the portable applications due to its simplification and cost reduction to the PEMFC system as well as improvements to reduce the cell start-up time.^{5,6} However, the proton exchange membrane, such as Nafion or sulfonated poly (ether ether ketone) (SPEEK), has to be kept humid to obtain good ionic conductivity because of the hydrophilic nature of the sulfonic acid group attached to the polymer backbone and the necessity to hydrate the ionic clusters. Less than fully hydration results in a decrease in the proton conductivity of the membrane.^{7,8} It was reported that the reduction of PEM thickness can resolve the water management

problems to some extent due to the accelerated water back-diffusing from the cathode to the anode side.⁹ However, this method usually also accelerates the crossover of H_2 and O_2 because of the membrane thickness, which lowers the cell performance and accelerates the degradation of the PEMs.¹⁰ Hence, how to suppress reactants crossover and how to maintain enough proton conductivity are the two major issues to be considered under dry operation mode.

To suppress the reactants crossover and realize the operation of PEMFCs with dry reactants, several self-humidifying composite membranes were developed and showed effective improvement on fuel cell performance under dry condition. Watanabe et al.^{11–14} first proposed a concept of self-humidifying membrane fabricated by incorporating highly dispersed nanometer size Pt and/or hygroscopic oxides (e.g., SiO_2 or TiO_2) in Nafion membrane, which is shown in Figure 1a. The Pt nanoparticles were expected to suppress reactants crossover by catalytic recombination of crossover hydrogen with oxygen, and the hygroscopic oxides were expected to adsorb the water produced at Pt particles together with that produced at the cathode reaction to maintain water for appropriate proton conductivity in the membrane. However, the incorporation of non proton-conductive oxides mostly increases the resistance of the membrane and the presence of Pt particles through the whole membrane increases the risk of forming short circuit within the fuel cell. On the basis of the above problems, in the latter papers, the researchers developed self-humidifying membrane mainly focusing on the following three directions: (1)

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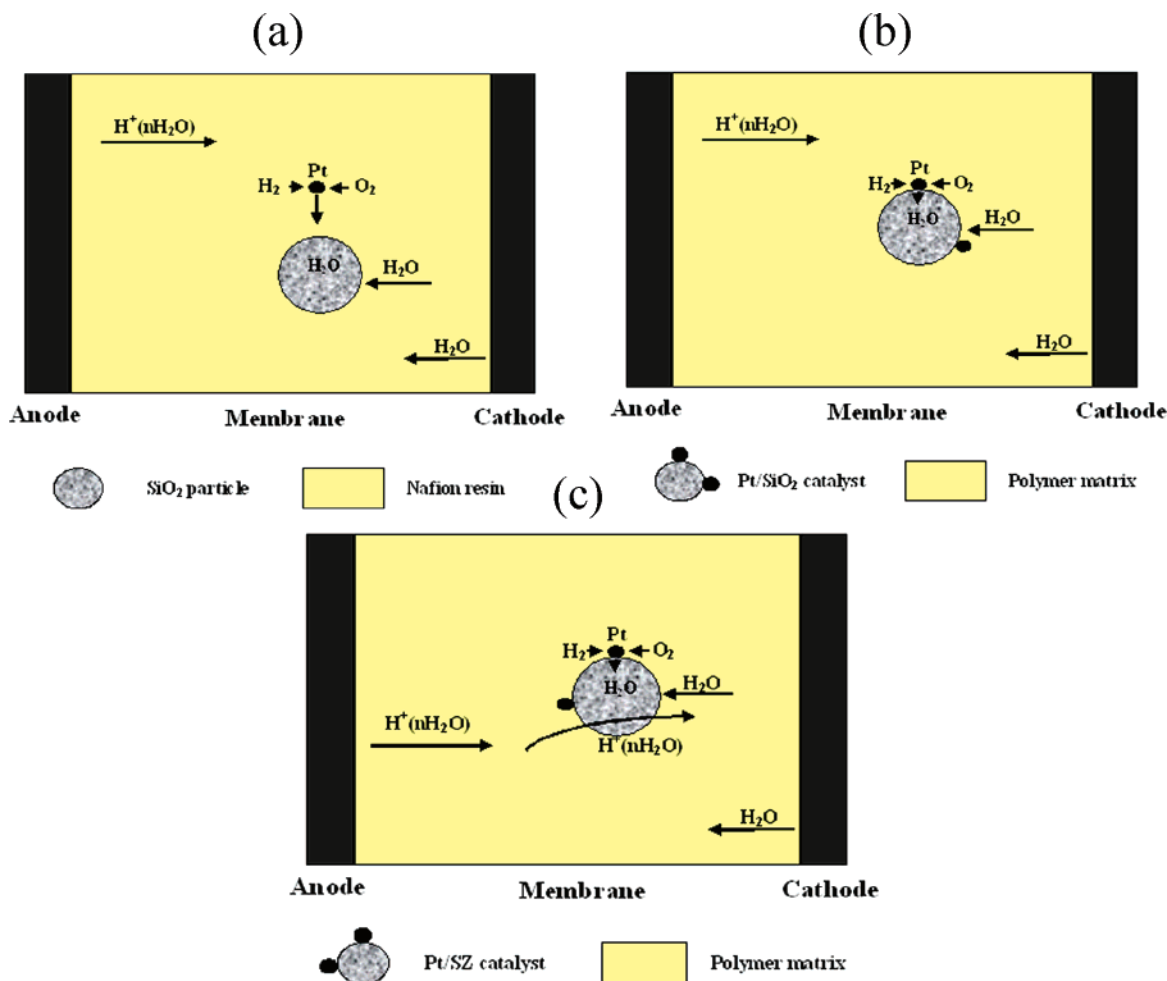


Figure 1. Schematic diagram of self-humidifying membranes: (a) membrane designed by Watanabe; (b) polymer matrix/Pt-SiO₂ membrane; (c) polymer matrix/Pt-SZ membrane.

incorporating some functional particles of high proton conductivity, such as Cs_{2.5}H_{0.5} PW₁₂O₄₀, ZrP to improve the membrane proton conductivity under dry condition;^{15,16} (2) designing new membranes of two-layered or three-layered structures to avoid short circuit through the membrane;^{17–19} (3) using the low-cost hydrocarbon membrane for the considering of the commercialization requirement of the fuel cells.^{20,21}

Note that, until now, most of the self-humidifying membranes have been fabricated by separately incorporating Pt particles and functional inorganic particles in the base membrane to realize the effect of suppressing the gas crossover and membrane hydration. However, the problems of forming electron circuit through the membrane and not efficiency and timely adsorbing water produced at the Pt particles on functional inorganic particles are still existed. Fabricating the self-humidifying membrane based on polymer matrix hybrid with appropriate nonelectron-conducting inorganic materials supported platinum catalyst may offset above disadvantages. In our previous work, the silicon oxide-supported platinum catalyst (abbreviated as Pt-SiO₂) was investigated as an additive to fabricate self-humidifying membrane.²² The Pt-SiO₂ catalyst can avoid the short circuit through the whole membrane due to the insulated property of SiO₂ particle and can achieve good membrane hydration for in-situ adsorbing the water produced at Pt particles on hygroscopic SiO₂ particle, which is showed in Figure 1 b. Unfortunately, the SiO₂ as the catalyst support is not a proton conductor and thus limits further improvement of cell performance under dry condition.

Sulfated zirconia was recognized as the strongest solid acid among all known solids with Hammett acid strength H_0 of -16.03 ²³ and studied by many researchers as an additive to fabricate composite membrane for higher temperature/lower humidity fuel cell application.²⁴ Sulfated zirconia supported platinum catalyst (abbreviated as Pt-SZ catalyst), which owns the catalytic, hygroscopic, and proton conductive properties, was widely studied as the bifunctional metal-acid catalyst for skeletal isomerization of alkanes in recent years.^{25,26} By far, there is no application report of Pt-SZ catalyst in self-humidifying composite membranes for PEM fuel cells.

The development of cost-effective PEMs is greatly needed for the fuel cell commercialization, especially if fuel cells are to be utilized in portable electronics.²⁷ Currently, perfluorosulfonic acid (PFSA) membranes, in particular Nafion, are a favorable option and are commonly used in fuel cell stacks, but they are difficult to be synthesized, and their capital cost still remains high. Furthermore, the mechanical property and reactant permeability become problematic when thinner membranes are used to reduce the membrane resistance. Recently, the sulfonated polyether ether ketone (SPEEK) has been considered as a promising candidate for fuel cell application because it possesses good thermal stability, mechanical property, proton conductivity and low cost. Several studies have been reported on SPEEK used as a PEM material in both hydrogen and direct methanol fuel cells.^{28–30} Compared with Nafion membrane, the SPEEK membrane has narrower clusters, larger average separation of neighboring sulfonic acid functional

groups, more branched with more dead-end “pockets”, which resulted in lower proton conductivity.³¹ Thus, until now, the cell performance using the plain SPEEK membrane in fuel cell condition especially under dry conditions was too low to satisfy the real application as PEM in fuel cell for its low proton conductivity.

In the present study, based on the work of Pt/SiO₂-contained self-humidifying membrane, SPEEK/Pt-SZ self-humidifying membranes were developed for the targets of improving the cell performance under dry operation condition and decreasing the membrane cost. As displayed in the Figure 1c, the Pt-SZ not only has the properties similar to Pt-SiO₂ catalyst, avoiding the electron circuit through the whole membrane and hydrating the membrane more effectively by in-situ adsorbing the water produced at Pt particles, but also can improve membrane proton conductivity by providing new acid site and bridging neighboring shrunken clusters to effectively shorten the distance of proton transport. The structure of the SPEEK/Pt-SZ self-humidifying membrane was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray detector (EDX). To understand the advantages of promoted self-humidification effect of the Pt-SZ catalyst, the physicochemical and electrochemical properties, such as IEC, water uptake, gas permeability, and proton conductivity, between the SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ self-humidifying membranes, were compared. The single cell performances and the areal resistances under wet and dry condition of the plain SPEEK membrane and two self-humidifying composite membranes were also investigated in the present study.

2. Experimental

2.1. Preparation of the Catalysts and the Self-Humidifying Membranes. Sulfonated poly(ether ether ketone) (SPEEK) polymers were prepared following the procedure reported in the literature.³² The PEEK supplied by Vitrex was dried overnight at 110 °C under vacuum before it was used in the reaction.

The Pt-SZ catalyst with the Pt loading of 2 wt.% was synthesized by impregnation of the sulfated zirconia (BET surface area of 128 m²/g; average particle diameter of 10 nm) with aqueous solution of H₂PtCl₆ (3.7 mgPt/mL, A.P., Sino-Platinum Metals Co. Ltd.) for 24 h. The resulting mixture was dried at room temperature in air and reduced by H₂ at 200 °C for 3 h. The SZ particles were synthesized by the following procedure: The ZrO₂ particles obtained by supercritical drying method,³³ were immersed in a 0.5 M H₂SO₄ solution for 60 min, followed by filtering and drying at 383 K for 24 h. After drying, the obtained solid particles were calcined at 873 K for 3 h under atmospheric conditions to form the SZ particles. The Pt-SiO₂ catalyst with the Pt loading of 2 wt.% was obtained by the same procedure of Pt-SZ catalyst. The SiO₂ particles were 112 m²/g in BET surface area and 20 nm in average particle diameter.

The SPEEK/Pt-SZ membrane was prepared by solution-cast method. The SPEEK was first dissolved in *N,N* dimethylacetamide (DMAc) at room temperature to prepare a 10 wt.% solution. Then required quantity of 5.0 wt.% Pt-SZ catalyst was added to the polymer solution and stirred with a magnetic stirrer for 4 h. The resulting solution was cast onto a clean flat glass and then removed the solvents at 60 °C for 12 h followed by further drying at 120 °C under vacuum. For comparison, the SPEEK/Pt-SiO₂ membrane was fabricated with the same method and the Pt-SiO₂ content was also 5 wt.%.

2.2. Characterization of the Self-Humidifying Membranes.

2.2.1 TEM, SEM-EDX, FT-IR Analyses of the Pt-SZ Catalyst,

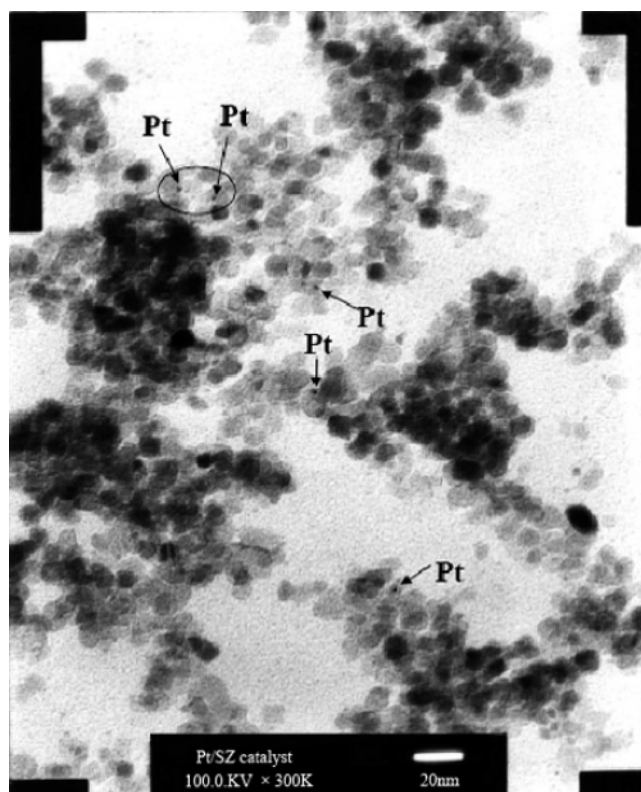


Figure 2. TEM image of the Pt-SZ catalyst.

and the Self-Humidifying Membranes. TEM (JEM-2000EX, JEOL, Japan) micrographs were taken on Pt-SZ catalyst particle. The samples were dispersed in ethanol, using an ultrasonic bath, and then mounted on standard copper TEM grids.

The cross sectional morphology of the SPEEK/Pt-SZ self-humidifying membrane was investigated by SEM (JEOL 6360LV, Japan). The distribution of zirconia element along the membrane cross-section was detected by EDX (Oxford Instruments Microanalysis 1350).

FTIR spectra of the plain SPEEK membrane, SPEEK/SZ membrane and SPEEK/Pt-SZ membrane were recorded on a JASCO FT-IR 4100 spectrometer to verify the effect Pt-SZ catalyst on catalytic combination of crossover hydrogen and oxygen.

2.2.2. Physicochemical Characterizations of the Self-Humidifying Membranes. The ion exchange capacity (IEC) values of plain SPEEK membrane, SPEEK/Pt-SZ and SPEEK/Pt-SiO₂ membranes were determined by titration method: 2–3 g of the samples was placed in 1 M aqueous NaOH and kept for 24 h. The solution was then back-titrated with 0.1 M HCl using phenolphthalein as an indicator.

The total water uptake of the membrane was calculated from eq 1, 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 100 °C for 12 h:

$$\Delta W(\text{wt.}\%) = (W_1 - W_2)/W_2 \times 100\% \quad (1)$$

For measurement of the bound water content, the membrane samples (after immersed in water at 20 °C for 4 h) were heated in a high-resolution thermo-gravimetric analyzer (TGA, Perkin-Elmer Instruments) at a rate of 10 °C min⁻¹ from 30 to 200 °C with nitrogen as carrier gas. The weight loss percentage of the membranes in the temperature range from 100 to 150 °C, which indicates the bound water content, was recorded.³⁴

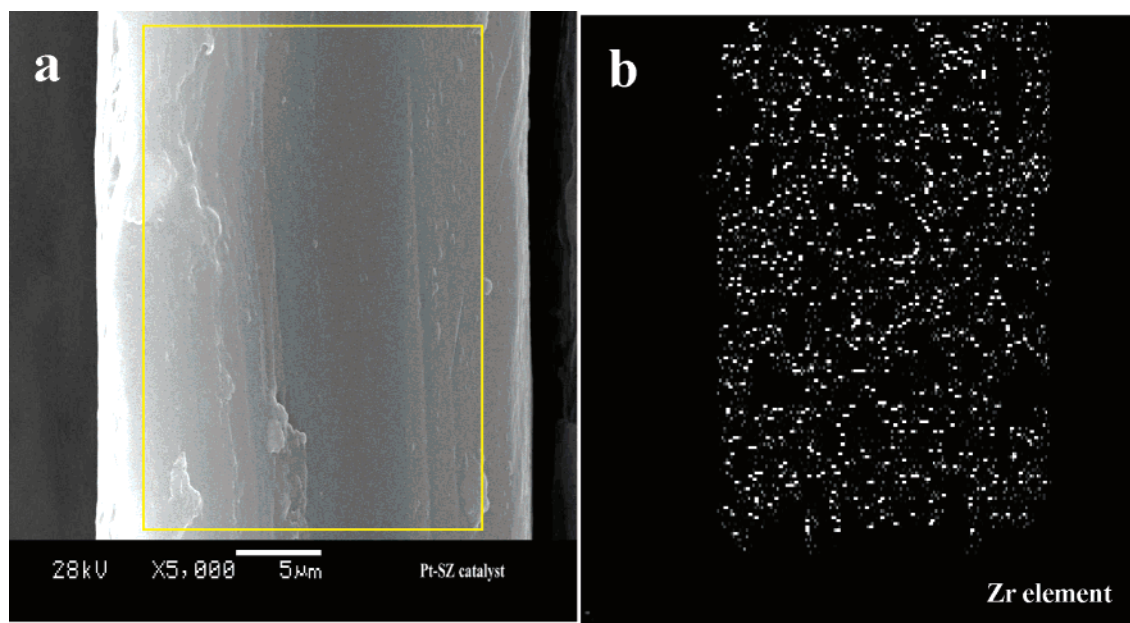


Figure 3. SEM-EDX image of the SPEEK/Pt-SZ composite membrane.

TABLE 1: Comparison of IEC Values and H₂ Permeability Properties of Membranes

membrane	thickness (μm)	IEC (mmol g^{-1})	H ₂ crossover current density (mA cm^{-2})
SPEEK	25	1.81	1.1
SPEEK/Pt-SiO ₂	25	1.73	0.98
SPEEK/Pt-SZ	25	1.94	1.0

An electrochemical method (Chrono-coulometry) was used to measure the hydrogen permeability through the membranes followed the process described elsewhere.³⁵ The CHI 660 Electrochemical station (CH Corporation, USA) was used for this test. The fuel cell hardware was maintained at 60 °C with dry hydrogen at the anode and the nitrogen at the cathode, respectively. A 0.3 V voltage was applied across the cell and the flow rates of hydrogen and the nitrogen were controlled at 10 and 30 mL min⁻¹, respectively.

2.2.3. Proton Conductivity and Areal Resistance Measurements by EIS. Electrochemical impedance spectroscopy (EIS) were performed on the MEAs using a frequency response detector (EG&G model 1025, Princeton Applied Institute) and a potentiostat/galvanostat (EG&G model 273A, Princeton Applied Institute) over a frequency range of 100 mHz to 100 kHz. The nitrogen as the carrier gas was used at both anode and cathode. The membrane resistance was measured at 60 °C with the relative humidity (RH) of 10%, 50%, 75%, and 100%. The different RH condition was obtained by controlling the anode and cathode humidifier temperatures. The results obtained in the form of resistance are normalized based on the geometric area and membrane thickness and reported as proton conductivity.³⁶ Moreover, areal resistances of the cells operating at the current density of 100 mA cm⁻² under dry or wet conditions were also measured by EIS.

2.2.4. 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 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 and Nafion loadings of both the anode and the cathode were 0.4 mg/cm².

The MEA was placed in a single cell using stainless steel as the end plates and stainless steel mesh as the current collectors.

First, 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. The primary 50 h fuel cell stability test was performed by an intermittent process. The single cell was operated at 500 mA/cm² with dry H₂/O₂ during the day and left off during the night.

3. Results and Discussions

3.1. TEM, SEM-EDX Measurements of the SPEEK/Pt-SZ Membrane. **3.1.1 TEM Images of the Pt-SZ Catalyst.** To study the morphology of the Pt-SZ catalyst, TEM measurement was conducted, and the image was shown in Figure 2. It was observed that the Pt-SZ catalyst was uniform in particle size with diameter of 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 Jean-Marie Manoli.³⁷ From the Figure 2, it can be seen that the diameter of Pt crystallites on SZ particles was 1–2 nm.

3.1.2. SEM-EDX Measurement of the SPEEK/Pt-SZ Membrane. To determine the cross-sectional morphology of the SPEEK/Pt-SZ membrane and the distribution of the Pt-SZ catalyst in the membrane, the SEM-EDX measurement was conducted and the results were shown in Figure 3. It was observed from Figure 3a that the cross section of the SPEEK/Pt-SZ membrane was very dense and smooth, with no congregative Pt-SZ particles found in the whole cross section. The analysis of zirconium elemental on the cross-section of the membrane can facilitate to well estimate the distribution of Pt-SZ catalyst in the composite membrane. Figure 3b showed the zirconium element had a very uniform distribution along the cross section of the SPEEK/Pt-SZ membrane, which indicated a good distribution of Pt-SZ particles in the membrane. The

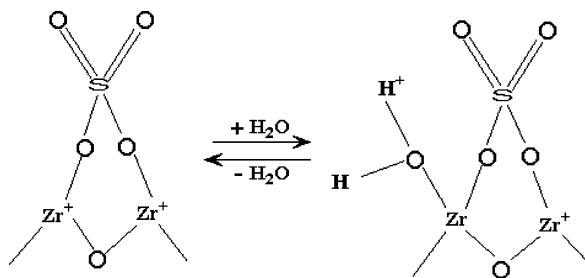


Figure 4. Structure of the sulfated zirconia (SZ) adsorbed/desorbed water.

high-uniformly dispersion of the Pt–SZ catalyst could increase the interface between the Pt–SZ catalyst and the SPEEK matrix and increase the possibility of their synergism. Since the Pt loading in the SPEEK/Pt–SZ membrane was too low to be analyzed quantitatively, the Pt element distribution was not given here.

3.2. IEC Value and H₂ Permeability Measurement of the Membranes. Table 1 listed the IEC values and the H₂ permeability of the plain SPEEK membrane, SPEEK/Pt–SiO₂ membrane and SPEEK/Pt–SZ membrane. It was observed that the SPEEK/Pt–SZ membrane was the most acid membrane, having the highest IEC value of 1.94 mmol·g⁻¹. The incorporation of superacid SZ particles increased the membrane acid property for providing new strong acid site and was expected to enhance the membrane proton conductivity. The structure of SZ has been studied extensively and many surface models have been proposed.^{38,39} Figure 4 shows the interconversion of Lewis acid site into Brønsted acid sites by the presence of water molecules, which was observed by IR spectra of pyridine adsorption.^{40,41} The SPEEK/Pt–SiO₂ membrane showed the lower IEC value of 1.73 mmol·g⁻¹ than the plain SPEEK membrane of 1.81 mmol·g⁻¹, which was due to the existence of non proton-conductive SiO₂ particles.

The hydrogen permeability was measured by electrochemical method and the data were obtained as the form of H₂ crossover current density. From Table 1 it can be seen that the H₂ crossover current density of two self-humidifying membrane

were very close to that of the plain SPEEK membrane. In the operating fuel cell with plain SPEEK membrane, the crossover H₂ and O₂ permeated through the membrane and reacted at the cathode and the anode, respectively, and accordingly increased the cathode polarization and anode membrane degradation.^{13,42} However, in the situation of operating the two self-humidifying membranes, the crossover H₂ and O₂ could be chemically catalyzed into H₂O by Pt–SiO₂ or Pt–SZ catalyst inside the membrane, which in turn can decrease the cathode polarization and anode membrane degradation caused by reactants crossover.

3.3. IR Spectrum of the Self-Humidifying Membrane. To examine whether the SPEEK/Pt–SZ membranes has the catalytic property of recombination hydrogen and oxygen forming water by experimental method, IR absorbance measurements was conducted⁴³ for the plain SPEEK membrane, SPEEK/SZ membrane and SPEEK/Pt–SZ membrane. Before measurements, all membranes were initially completely dried in the vacuum oven for 2 days at 120 °C. After been dried completely, the membrane samples were mounted in a single cell without electrodes and operated with dry hydrogen and oxygen at 0.2 MPa for 2 days at 60 °C. Figure 5 showed the IR spectra of the above membranes after exposure in the dry hydrogen and oxygen at 0.2 MPa for 2 days. As shown in the Figure 5, it was obviously that the absorbance peak of the OH stretching at 3450 cm⁻¹ is observed only in the SPEEK/Pt–SZ membrane after exposure in the dry H₂/O₂, indicating the validity of the catalytic property of the Pt particles existence in the membrane. In the SPEEK/Pt–SZ or SPEEK/Pt–SiO₂ self-humidifying membranes, the Pt–SZ or Pt–SiO₂ catalysts acted the catalytic recombination center for suppressing the crossover H₂ and O₂, forming water inside and thus humidifying the membrane.

3.4. Water Uptake of the Membranes. For the PEMs, water uptake is an important property for its direct relation to the proton conductivity. Particularly, under low humidification or non-humidified operation, the technique for adsorption and retention of water to prevent the membrane from drying out is needed to be improved. To verify the effect of Pt–SiO₂ or Pt–SZ catalysts on improving the membrane hygroscopic property, water uptake measurement was conducted. According to the

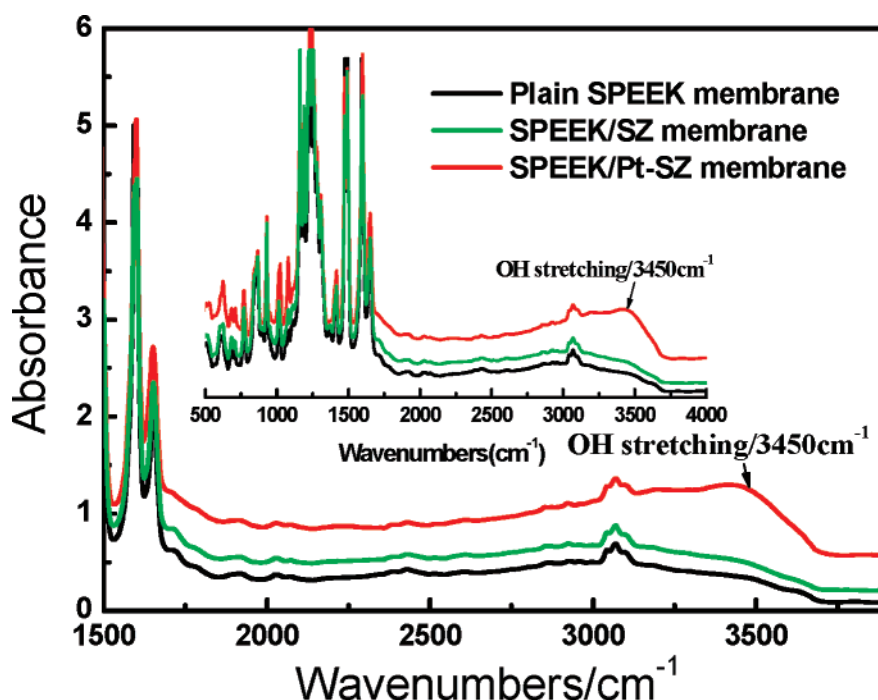


Figure 5. IR spectra of the membranes after exposure in dryH₂/O₂ condition.

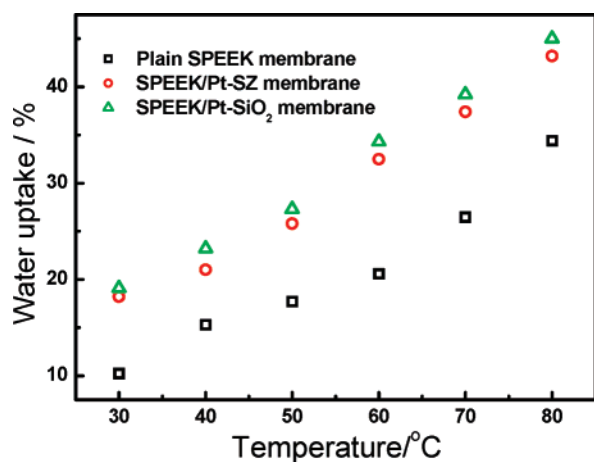


Figure 6. Water uptake measurement of the membranes at various temperatures.

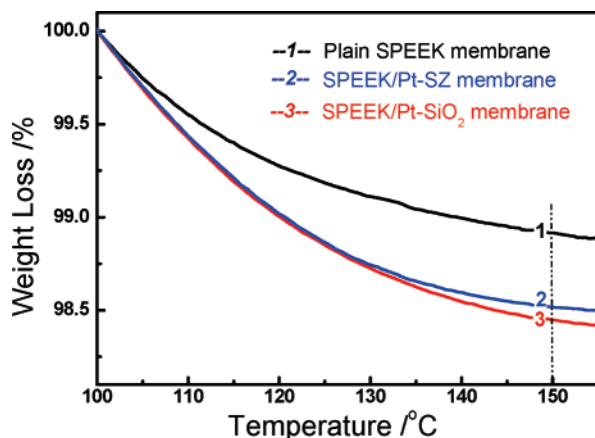


Figure 7. The bound water content comparison of the plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes measured by TGA.

TABLE 2: Comparison of Total/Bulk/Bound Water Content of the Plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ Membranes

membrane	thickness (μm)	water uptake (%)		
		total water	bulk water	bound water
SPEEK	25	10.23	9.13	1.1
SPEEK/Pt-SiO ₂	25	19.1	17.5	1.6
SPEEK/Pt-SZ	25	18.2	16.7	1.5

Eikerling's theory, there are two different types of water in PEMs.⁴⁴ One type of water is needed for the solvation of the sulfonic groups, and the other type of water fills the micropores and behaves like bulk water. In this article, the two kinds of distinguished water are defined as the bound water and the bulk water. The total water and the bound water were measured by weighting and TGA methods,⁴⁵ and then the bulk water was obtained by subtracting of the bound water content from the total water.

Figure 6 showed the total water uptake of the plain SPEEK membrane, SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes as the function of temperature. It was observed that the water uptake for all the membranes increased with the temperature. Furthermore, two self-humidifying membranes exhibited higher water uptake values than that of plain SPEEK membrane, indicating the enhanced adsorbing water ability. The higher water uptake was due to the incorporation of hygroscopic Pt-SiO₂ and Pt-SZ catalysts in the membrane.

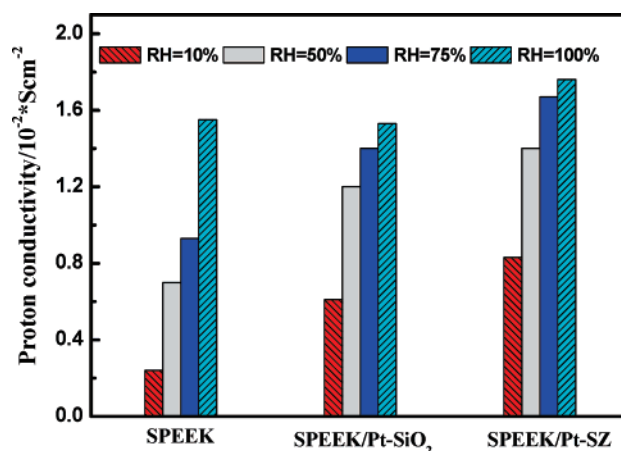


Figure 8. Proton conductivity of the plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes at 10% RH, 50% RH, 75% RH, and 100% RH at 60 °C.

For measurement of the bound water content, the TGA measurement, as an excellent method to characterize the membrane water retention capability was used. For easy comparison of weight loss characteristics, the weight percentages of the three membrane samples at 100 °C were all fixed at 100%. Figure 7 showed the bound water contents of the plain SPEEK membrane, SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membrane. It can be seen that the SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes showed enhanced water retaining ability, having the higher bound water content of 1.6 and 1.5 wt. % relative to the 1.1 wt. % for the plain SPEEK membrane.

Table 2 compared the contents of total/bulk/bound water of plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes after immersed in water 20 °C for 4 h. It was observed that SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes showed the total/bulk/bound water content of 19.1/17.5/1.6 and 18.2/16.7/1.5 wt.%, respectively, which was almost twice of those plain SPEEK membrane.

The higher total/bulk/bound water of SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ self-humidifying membranes indicated improved water adsorbing and retaining ability and it was attributed to the existence of hygroscopic property of Pt-SiO₂ or Pt-SZ catalyst. This property was expected to improve the membrane proton conductivity under dry operation conditions.

3.5. Proton Conductivity of the Membranes. Membrane proton conductivity was determined by measuring the membrane resistance by EIS. Figure 8 showed the proton conductivity results of the plain SPEEK membrane, SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ self-humidifying membranes measured at 10% RH, 50% RH, 75% RH, and 100% RH at a temperature of 60 °C. It was observed that two self-humidifying membranes showed higher proton conductivity values relative to the plain SPEEK membrane at unsaturated RH conditions. The SPEEK/Pt-SZ self-humidifying membrane exhibited the highest proton conductivity values among three membranes. For example, the SPEEK/Pt-SZ membrane showed proton conductivity of 1.4×10^{-2} S/cm at RH = 50%, which was higher than SPEEK/Pt-SiO₂ membrane of 1.2×10^{-2} S/cm and the plain SPEEK membrane of 0.61×10^{-2} S/cm. At present, there are two predominant proton transport mechanism called vehicle mechanism (movement of hydrated protons) and Grotthus mechanism (proton hopping) in the PEM. According to the cluster network model, 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

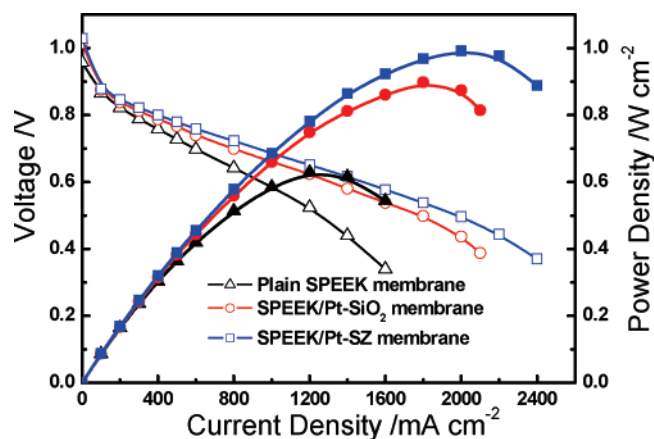


Figure 9. Performance comparison of single cell employing the plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes with dry H₂/O₂ at 60 °C.

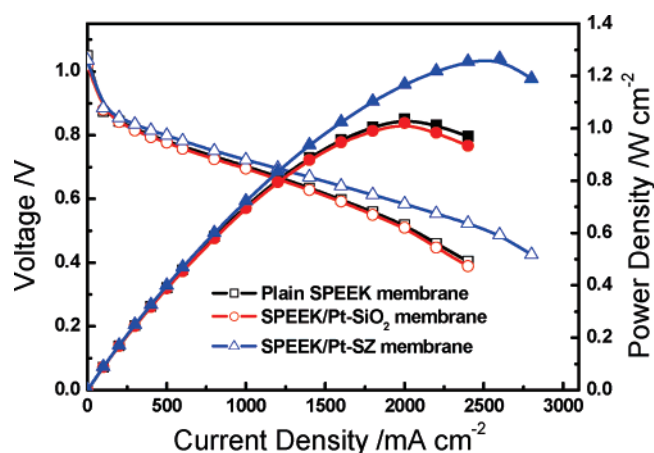


Figure 10. Performance comparison of single cell employing the plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes with fully humidified H₂/O₂ at 60 °C.

channels.⁴⁶ This phenomenon would get worse for the plain SPEEK membrane because of its natural microstructural deficiency (narrower channel and more branched with more dead-end “pockets”). However, for the self-humidifying membranes, the nanometer-sized hygroscopic Pt-SZ or Pt-SiO₂ catalyst in the SPEEK matrix can easily interact with the sulfonic acid groups of SPEEK, increasing the number of available proton exchange site of SPEEK and enlarging the diameter of the clusters for their hygroscopic property, and accordingly increased the membrane proton conductivity as the vehicle mechanism. Hiroki Hagihara⁴⁷ etc had found that the hydrophilic clusters size increased after the incorporation of hygroscopic SiO₂ particle through the SAXS measurement. In addition, besides the effect similar to Pt-SiO₂ catalyst, the Pt-SZ particle in the SPEEK/Pt-SZ membrane can provide additional strong acid group for proton transport and bridge neighboring shrunken clusters to effectively shorten the distance of proton hopping transport, and thus increasing the membrane proton conductivity as the Grotthuss mechanism. In other words, Pt-SZ particle not only transfer proton by its strong acidity, but also can assist sulfonic acid group of the SPEEK to transfer proton. The similar inorganic-assisted proton transport mechanism was proposed by V. Ramani on the study of the Nafion/HPA composite membrane.⁴⁶ As a consequence, the SPEEK/Pt-SZ membrane had the highest proton conductivity at low RH for its hygroscopic and proton conductive property, which in turn contributed to the good single cell performance.

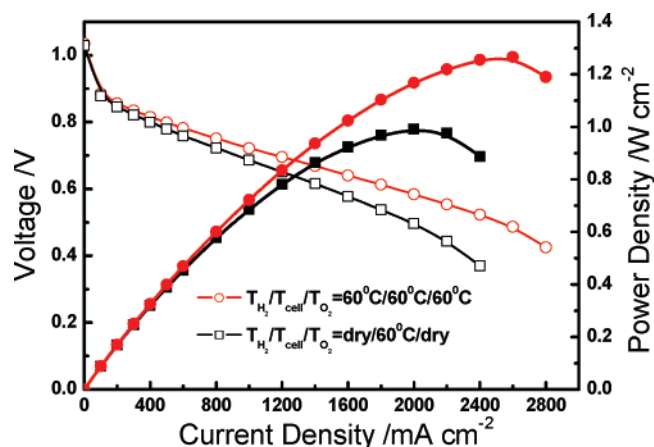


Figure 11. Performance comparison of single cell employing of SPEEK/Pt-SZ membranes with dry H₂/O₂ at 60 °C and with fully humidified H₂/O₂ at $T_{H_2}/T_{cell}/T_{O_2} = 60/60/60$ °C.

TABLE 3: Comparison of the Fraction of Current Density Delivered by a PEMFC Employing the Plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ Membranes on Operating with Dry H₂/O₂

membrane	fraction of current density at different voltages (%)				
	0.8 V	0.7 V	0.6 V	0.5 V	0.4 V
SPEEK	61	60	59	62	62
SPEEK/Pt-SiO ₂	97	81	82	90	90
SPEEK/Pt-SZ	80	82	79	80	82

3.6. Single Cell Evaluation. Figure 9 showed single cell performance employing with the plain SPEEK membrane, SPEEK/Pt-SiO₂ membrane and SPEEK/Pt-SZ membrane with dry H₂/O₂ at $T_{cell} = 60$ °C. From the Figure 9, it was observed that the plain SPEEK membrane exhibited poor output performance, for example, 0.585 W/cm² at 1000 mA/cm². Compared with the plain SPEEK membrane, the single cell performances of two self-humidifying membranes were dramatically improved, with the improvement order of SPEEK/Pt-SiO₂ membrane < SPEEK/Pt-SZ membrane. The peak power density values of SPEEK/Pt-SiO₂ membrane and SPEEK/Pt-SZ membrane are 0.89 and 1.0 W cm⁻², respectively. The trend of cell performance was incorporate with previous proton conductivity measurement and was in accordance with our design concept. The extreme improvement of the performance for SPEEK/Pt-SZ membrane was in association with its high IEC value, high proton conductivity, and high water content.

Figure 10 showed the single cell performances of the three membranes with fully humidified H₂/O₂ at $T_{cell} = 60$ °C. The plain SPEEK membrane exhibited similar cell performance with the SPEEK/Pt-SiO₂ membrane, which was consistent with the proton conductivity results at RH = 100%. The SPEEK/Pt-SZ membrane showed the highest output performance than the plain SPEEK membrane and SPEEK/Pt-SiO₂ membrane due to the increased acid property after incorporation of Pt-SZ catalyst.

Figure 11 compared the performances of the single cell employing the SPEEK/Pt-SZ membrane under fully humidified and dry conditions. As indicated in Figure 11, the SPEEK/Pt-SZ membrane exhibited close cell performances under fully humidified and dry conditions with their peak power densities of 1.26 and 1.0 W cm⁻², which manifested the self-humidification effect of the membrane. To compare the influence of humidification condition on the cell performance employing the three membranes, Table 3 listed the fractions of current density

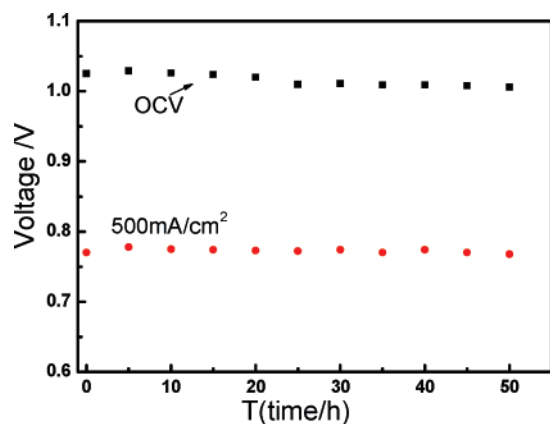


Figure 12. 50 h fuel cell test of a single cell with SPEEK/Pt-SZ self-humidifying membrane with dry H_2/O_2 operated at 60 °C. $P_{\text{H}_2} = P_{\text{O}_2} = 0.2 \text{ MPa}$.

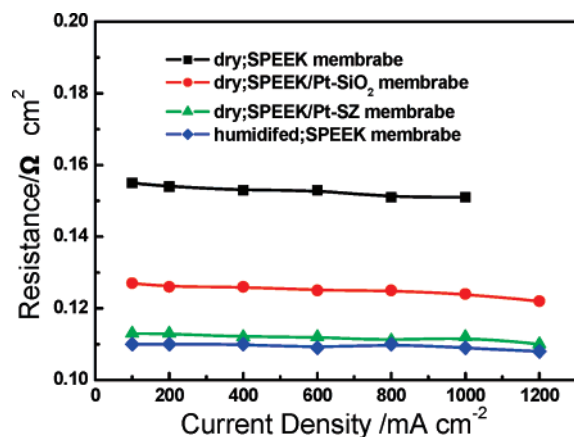


Figure 13. Comparison of the areal resistances of the plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ membranes as a function of current density operated with dry H_2/O_2 at 60 °C.

TABLE 4: The OCV Values of the Plain SPEEK, SPEEK/Pt-SiO₂, and SPEEK/Pt-SZ Membranes at the Dry and Humidified Operation Conditions

membrane	open-circuit voltage (V)	
	wet mode	dry mode
SPEEK	1.005	0.958
SPEEK/Pt-SiO ₂	1.020	1.015
SPEEK/Pt-SZ	1.035	1.029

at different voltages for plain SPEEK membrane and two self-humidifying membranes, which were calculated by comparing the currents generated under dry H_2/O_2 with those obtained under fully humidified H_2/O_2 . The fractions of current density delivered by the PEMFC with the two self-humidifying composite membrane are higher than those delivered by the PEMFC with the plain SPEEK membrane. For example, the cells with SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membrane generate 82% and 79% of the current generated with humidified reactants at the cell voltages of 0.7 V, compared with 59% for the plain SPEEK membrane. This indicated that the incorporation of nanometer-sized functional Pt-SiO₂ or Pt-SZ catalysts in the SPEEK membrane represented pronounced effect on humidifying the membrane and improving the cell performance under dry condition. Here, although the SPEEK/Pt-SiO₂ membrane showed higher fractions of current density than SPEEK/Pt-SZ membrane, the cell performances employing with SPEEK/Pt-SiO₂ membrane under both humidified and dry conditions were lower than those of SPEEK/Pt-SZ membrane.

To determine the stability of the fuel cell performance employing the SPEEK/Pt-SZ self-humidifying membrane, primary 50 h fuel cell operation test with dry H_2/O_2 was conducted and the results were shown in Figure 12. It was observed that the performance with the SPEEK/Pt-SZ membrane does not exhibit obvious drop in both open circuit voltage (OCV) and the voltage at 500 mA/cm² after 50 h operation at 60 °C with dry reactants. The long-term operation of fuel cell with SPEEK/Pt-SZ membrane would be investigated in the future work.

3.7. OCV Analysis of the Single Cells. 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 4 showed the OCV values of the plain SPEEK membrane, SPEEK/Pt-SiO₂ membrane, and SPEEK/Pt-SZ self-humidifying membrane under dry and wet operation conditions. It was obvious that the single cells with the SPEEK/Pt-SiO₂ membrane and SPEEK/Pt-SZ self-humidifying membrane exhibited higher OCV values than those of SPEEK membrane both under dry and wet conditions. Although the SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes showed the close hydrogen permeability compared to the plain SPEEK membrane, the crossover hydrogen and oxygen of the two self-humidifying membranes were effectively chemically catalyzed into H_2O by Pt-SiO₂ or Pt-SZ catalyst inside the membrane, thus decreased the amount of crossover-gas in the electrodes, which in turn resulted in higher OCV values of the fuel cells.

3.8. Areal Resistance of the MEAs. The areal resistance values of the single cells employing the plain SPEEK membrane under dry and wet conditions and those of the SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membrane under dry condition as a function of current density were obtained by EIS measurements and displayed in Figure 13. The resistance of the plain SPEEK membrane was 0.153 Ω cm² at 400 mA/cm², and slightly decreased with the increasing current density due to the humidification by back-diffused water from the cathode. The resistances of the two self-humidifying membranes were obviously lower than those of plain SPEEK membrane at all tested current density. The order of areal resistance is, SPEEK membrane > SPEEK/Pt-SiO₂ membrane > SPEEK/Pt-SZ membrane. The resistance of the SPEEK/Pt-SZ membrane was 0.112 Ω cm² at 400 mA/cm², which was almost coincided with that of plain SPEEK membrane operated with fully humidified H_2/O_2 at 60 °C. This indicated the remarkable self-humidification effect of Pt-SZ catalyst in the membrane.

Conclusion

A self-humidifying membrane based on sulfonated poly (ether ether ketone) (SPEEK) hybrid with sulfated zirconia supported platinum catalyst (abbreviated as Pt-SZ catalyst) was synthesized by solution-casting method. The membrane structure was characterized by TEM, SEM and EDX. The comparisons of physical-chemical properties between the plain SPEEK membrane, the SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes, such as IEC value, H_2 permeability, water uptake, proton conductivity, were investigated. The SPEEK/Pt-SZ membrane exhibited higher IEC value, water uptake and proton conductivity relative to the plain SPEEK membrane, which is due to the incorporation of hygroscopic and proton conductive Pt-SZ catalyst in the membrane. Furthermore, compared with the SPEEK/Pt-SiO₂ membrane, the SPEEK/Pt-SZ membrane behaved more advantages on improving membrane proton conductivity and single cell performance under dry condition

for the acid property of Pt–SZ particles and its assistance effect on proton transfer by bridging pathway between clusters. The SPEEK/Pt–SZ self-humidifying membrane exhibited the highest cell performance under dry condition with its peak power density of 1.0 W/cm², compared with 0.89 and 0.58 W/cm² of SPEEK/Pt–SiO₂ and plain SPEEK membranes, respectively. Furthermore, the OCV values and areal resistances analysis confirmed the effect of hygroscopic, proton conductive and catalytic Pt–SZ catalyst in the SPEEK/Pt–SZ membrane. The low-cost SPEEK/Pt–SZ self-humidifying membrane is promising for application in PEM fuel cells.

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