

## Pt/SiO<sub>2</sub> catalyst as an addition to Nafion/PTFE self-humidifying composite membrane

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### Abstract

A novel self-humidifying reinforced composite membrane for the proton exchange membrane fuel cell (PEMFC) was developed. Pt/SiO<sub>2</sub> catalyst particles were dispersed uniformly into the Nafion resin, and then Pt–SiO<sub>2</sub>/Nafion/PTFE reinforced composite membrane was prepared using solution-cast method. Compared with the performance of the fuel cell with commercial Nafion<sup>®</sup> NRE-212 membrane, the cell performance with the self-humidifying composite membrane was obviously improved under both humidified and dry conditions at 80–120 °C. The self-humidifying composite membrane could minimize membrane conductivity loss under dry conditions due to the presence of catalyst and hydrophilic Pt/SiO<sub>2</sub> particles.

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**Keywords:** Fuel cell; Self-humidify; Composite membrane; Pt/SiO<sub>2</sub> catalyst

### 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as a suitable alternative to internal combustion and diesel engines because of their high power density, high energy conversion efficiency and low emission level [1]. The proton exchange membranes (PEMs) currently used in fuel cells, such as Nafion<sup>®</sup> membranes, require adding water to humidify the fuel and oxygen in order to maintain the membrane's proton conductivity. The humidifying system of the reactant gases is a

burden for the PEMFC. The reduction of PEM thickness reduces the water management problems due to the water back-diffusing from the cathode [2]. However, this usually also accelerates the crossover of H<sub>2</sub> and O<sub>2</sub> because of the thin membranes [3], which lowers the cell performance and accelerates the degradation of the PEMs [4].

Another major issue limiting the application of PEMFCs is the poisoning of the platinum-based anode catalysts by trace amounts of CO which are inevitably present in reformed fuels. In order to increase CO tolerance and to improve the thermal utilization rate of the fuel cell system, the operating temperature should be maintained at 120–150 °C [5–7]. However, the membranes currently used for PEMFCs, such as the Nafion<sup>®</sup> membrane of DuPont, shown significant loss in conductivity and mechanical stability at elevated temperatures.

Therefore, management of the water content in PEMs is recognized as a key requirement for PEMFCs. Attempting to overcome these problems, one method is to develop self-humidifying proton exchange membranes. In previous work, many kinds of composite membranes have been developed to modify Nafion<sup>®</sup> to achieve suitable operation at elevated temperatures. One of

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the approaches is to add hydrophilic materials to the membranes. Such hydrophilic materials are heteropolyacides, i.e. ZrP, ZrSPP, etc., and oxides, i.e. zirconium dioxide, titanium dioxide and silicon dioxide [8–12]. These compounds display high water retention capability that is crucial for the proton conductivity of membranes at elevated temperatures. The experimental data have shown that the addition of inorganic hydrophilic materials substantially extend the working temperature range.

Another approach is to develop a typical inorganic/organic composite self-humidifying polymer electrolyte membrane such as developed by Watanabe et al. [13–15]. In this kind of self-humidifying composite membrane, the nanometer-size Pt and/or hygroscopic materials are dispersed into the Nafion resin. The Pt particles can catalyze the oxidation of crossover hydrogen with oxygen to generate water to humidify the membrane. When hygroscopic materials, such as SiO<sub>2</sub> or TiO<sub>2</sub> were added to the membranes, the water produced at the Pt particles was adsorbed by these metal oxides [16–22]. Recently, Zhu et al. [23] prepared a self-humidifying membrane with a sandwich structure with Nafion-impregnated porous PTFE composite as the central layer and nanosized SiO<sub>2</sub> supported Pt catalyst imbedded into the Nafion as the two side layers. Up to now, no self-humidifying membrane which was filled with Pt/SiO<sub>2</sub> in the whole membrane has been reported.

In this study, a self-humidifying reinforced composite membrane (25 μm) was developed. Pt/SiO<sub>2</sub> particles which are expected to catalyze the recombination of H<sub>2</sub> and O<sub>2</sub> and suppress the chemical short-circuit reaction at the electrodes, were dispersed into this type of membrane. The water produced at Pt/SiO<sub>2</sub> sites can be absorbed by the SiO<sub>2</sub> particles without any migration. At the same time, the water produced at the cathode can be absorbed by the SiO<sub>2</sub> particles as well to increase the hydration of the membrane. A porous PTFE film was used to reinforce the membrane, so that a thinner membrane can be made with enough mechanical strength and large gas permeation. The single cell (electrode area = 5 cm<sup>2</sup>) with these PEMs exhibited better performance than that with the commercial Nafion<sup>®</sup> NRE-212 membrane under fully humidified and dry conditions.

## 2. Experiment

### 2.1. Catalyst and membrane preparation

The Pt/SiO<sub>2</sub> catalyst was prepared from H<sub>2</sub>PtCl<sub>6</sub> and silicon dioxide (with an average particle size of 20 nm, manufactured in Zhejiang, China) via microwave-assisted polyol process [24]. The loading of Pt on SiO<sub>2</sub> was about 2 wt.%.

Composite membranes were prepared by the following procedure: the Nafion<sup>®</sup> resin was obtained from Nafion<sup>®</sup> dispersion (Nafion<sup>®</sup> R-1100 resin, DuPont Fluoroproducts, USA). The Nafion<sup>®</sup>/DMAC solution and Pt/SiO<sub>2</sub> catalyst made above were mixed ultrasonically to form a catalyst ink. The microporous PTFE films (manufactured in Shanghai, China) with pore diameter 0.3–0.5 μm and thickness 15 μm was used as a support to make composite membranes. The amount of Pt/SiO<sub>2</sub> in the composite membranes was controlled at 5 wt.%. The thickness of the composite membranes was about 25 μm. For simplification, this

composite membrane was denoted as Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM.

### 2.2. XRD analysis

To gather information on the Pt/SiO<sub>2</sub> catalyst, the X-ray powder diffraction (XRD) analysis was performed using a Panalytical X'pert PRO diffractometer (Philips X'pert PRO) with Cu Kα radiation source. The X-ray diffractogram was obtained for 2θ varying between 20 and 90°.

### 2.3. SEM analysis

A JEM-1200EX microscope was used to observe the surface and cross-section morphology of the composite membrane. Then, an Oxford Instruments X-ray Microanalysis 1350 was used to analyze the elemental distribution through the cross-section of the composite membrane. The composite membranes were cut in liquid nitrogen (77 K) to expose their cross-sections.

### 2.4. Water uptake and swelling

Samples of the membranes were weighed (*W*<sub>1</sub>) after immersion in deionized water for 8 h at controlled temperature. Then, samples were weighed (*W*<sub>2</sub>) after drying in a vacuum oven at 80 °C for 12 h. Water content (Δ*W*) was calculated from Eq. (1).

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

where *W*<sub>1</sub> and *W*<sub>2</sub> are the wet mass and dry mass of the sample expressed in gram, respectively.

Membranes specimens (size 4 cm × 5 cm) were stored in the a vacuum oven at 80 °C for 12 h and the distance between specified positions was measured before (*L*<sub>1</sub>) and after (*L*<sub>2</sub>) the samples were soaked in deionized water controlled at 40, 60 and 80 °C for 8 h. Dimensional change (Δ*L*) was calculated by using the following equation:

$$\Delta L (\%) = \frac{L_2 - L_1}{L_1} \times 100 \quad (2)$$

### 2.5. Mechanical strength

Samples of the membranes were dried in a vacuum oven at 80 °C for 12 h. The maximum strength was measured with a tension tester AG-2000A (Shimadzu, AUTOgraph) at room temperature. Tensile conditions were based on Chinese Standard QB-13022-91 and the samples were measured using a programmed elongation rate of 50 mm min<sup>−1</sup>.

### 2.6. Gas permeability

An electrochemical method (Chrono-coulometry) was used to measure the hydrogen crossover through the membranes. The electrochemical method is described elsewhere [25]. The CHI 660 Electrochemical Station (CH Corporation, USA) was used for this test. The fuel cell hardware was operated with hydrogen at the anode, and nitrogen at the cathode. A 0.5 V voltage was

applied across the cell, so that the hydrogen permeating through the membrane was oxidized electrochemically at the cathode. The flow rate of H<sub>2</sub> and N<sub>2</sub> was controlled at 10 and 30 ml min<sup>-1</sup>, respectively.

### 2.7. Membrane electrode assembly preparation and single cell test

The membrane electrode assembly (MEA) was prepared by a hot pressing process. The 20 wt.% Pt/Vulcan XC-72 (Pt/C) catalyst from E-TEK, carbon paper from Toray, PTFE suspension and Nafion solution (DuPont) were used in electrode preparation. The loading of Pt/C catalyst on the anode and cathode were both 0.5 mg Pt cm<sup>-2</sup>. Two electrodes with effective area 5 cm<sup>2</sup> were hot-pressed onto one piece of membrane to form an MEA. The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors.

The performance of the fuel cell was evaluated by *I*–*V* curves in the temperature range 80–120 °C. The fuel and oxidant were fed in co-flow to the fuel cell. When the cell was operated with H<sub>2</sub>/O<sub>2</sub> fully humidified gases, the flow rates of inlet gases were controlled to keep a constant utilization of H<sub>2</sub> at 70% and O<sub>2</sub> at 40% for various current densities. And when the cell was operated with dry H<sub>2</sub>/O<sub>2</sub> gases, the fluxes of inlet gases were controlled at a fixed rate (H<sub>2</sub> 10 ml min<sup>-1</sup> and O<sub>2</sub> 15 ml min<sup>-1</sup>). The cell was started by increasing the cell temperature set point to 80 °C and raising the saturator temperatures to their respective values. Similarly, the H<sub>2</sub> and O<sub>2</sub> pipeline temperatures were also maintained 5 °C higher than the saturators to prevent water condensation in the lines. All data were obtained at an absolute pressure of 0.3 MPa.

When the cells were operated with humidified reactant gases, the conditions were as following: humidifier temperature *T*<sub>H<sub>2</sub>/T<sub>O<sub>2</sub></sub> = 80/80 °C; cell temperature *T*<sub>cell</sub> = 80 °C; gas pressure *P*<sub>H<sub>2</sub>/P<sub>O<sub>2</sub></sub> = 0.30/0.30 MPa. The data were recorded after stable performance was obtained. When the cells were operated with dry gases, the cells were dried overnight with dry N<sub>2</sub> before test.</sub></sub>

## 3. Results and discussion

### 3.1. XRD and SEM study

In the self-humidifying composite membrane, the catalyst particles catalyze the chemical reaction of hydrogen and oxygen but do not transmit electrons [20]. The catalyst particles should be isolated and dispersed in the composite membrane. Therefore, we hope that the catalyst particles are as fine as possible.

Fig. 1 shows the XRD patterns of our Pt/SiO<sub>2</sub> catalyst made via microwave-assisted polyol process.

The average platinum particle size can be calculated from the width of peak (1 1 1) according to Debye–Scherrer formula (3) [26].

$$D_{hkl} = \frac{0.89\lambda}{B_{hkl} \cos\theta} \quad (3)$$

*B*<sub>*hkl*</sub> is the measured peak width at half peak intensity.

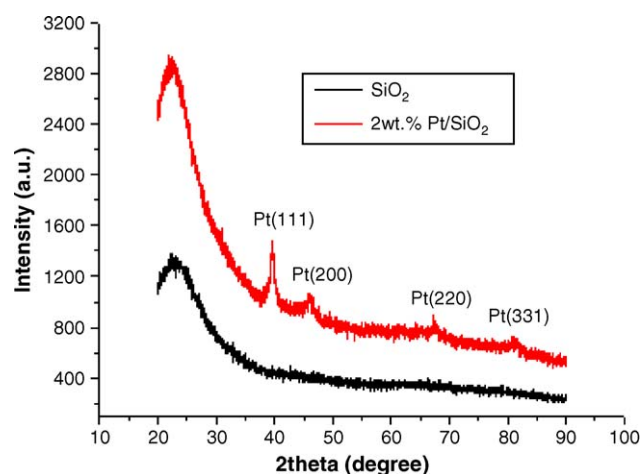


Fig. 1. X-ray diffraction patterns of SiO<sub>2</sub> and Pt/SiO<sub>2</sub> catalyst particles.

The main parameters of Pt X-ray diffraction and calculation result are listed in Table 1. In the diffraction gram of Pt, the peaks at 2θ of about 40, 46.5, 68 and 82° are relative to Pt fcc lattice. The whole set of observed reflections was found to match closely in intensities with the expected reflections for the pure Pt [27] and the Pt particles with average size of about 8nm.

The SEM photomicrographs of the surface and cross-section of the composite Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM are shown in Fig. 2. The SEM picture (Fig. 2a) reveals a rough surface of the self-humidifying membrane due to existence of Pt/SiO<sub>2</sub> catalyst particles. It can be seen that the Pt/SiO<sub>2</sub> particles are uniformly and well-distributed at the surface (Fig. 2a) and through the cross-section (Fig. 2b) of the membrane. Fig. 3 shows the distribution of the Pt/SiO<sub>2</sub> particle size based on Fig. 2b. From the statistical result, the size of the particles was mostly in the range between 200 and 400 nm. This dimension is much larger than the size of Pt and SiO<sub>2</sub> particles due to the congregation of SiO<sub>2</sub> particles during the membrane preparation.

Fig. 4 shows the EDX results of the cross-section of Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM. It can be seen that the Si and S elements were dispersed homogeneously along the cross-section of the membrane (Fig. 4a and c). It means that the Pt/SiO<sub>2</sub> catalyst particles and Nafion resin were uniformly dispersed in the membrane. From the EDX analysis result of the F element (Fig. 4b), the PTFE porous film was asymmetrically positioned in the composite membrane, and the Nafion layer on each side of it. It is due to the gravitation of the PTFE which is located at the bottom of the membrane when it is being prepared by solution casting method.

Table 1  
Measurement parameters of XRD

<i>hkl</i>	1 1 1
λ	0.1541
<i>B</i> <sub>111</sub> (°)	1.0015
Bragg, 2θ (°)	39.625
Pt size (nm)	8.4

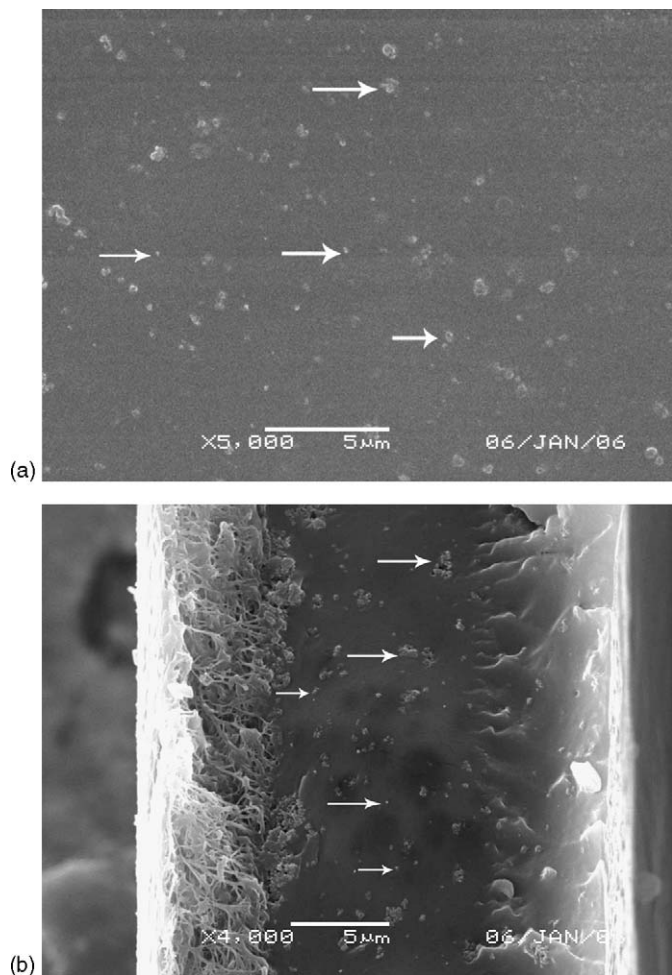


Fig. 2. SEM photomicrographs: (a) surface of Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM; (b) cross-section of the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM.

### 3.2. Membrane characterization

Table 2 shows the comparison of the water uptake and swelling of Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM and NRE-212. The water uptake measured for the commercial membrane is lower than that declared by the producer DuPont (45–50%). This difference is due to the different test methods. In our test, the temperatures: 40, 60 and 80 °C were used instead of 100 °C. In any case, when we compare the results obtained in the same experimental conditions, Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM had much higher water uptake than the NRE-212 membrane in spite of the lower content of Nafion resin. This is due to the water absorbency of SiO<sub>2</sub> in the composite membranes. Moreover, the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM shows lower swelling, which

Table 2  
Water uptake and swelling of the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion® NRE-212 membranes

Temperature (°C)	Water uptake (%)		Swelling (%)	
	NRE-212	Pt–SiO <sub>2</sub> /Nafion/PTFE-PEM	NRE-212	Pt–SiO <sub>2</sub> /Nafion/PTFE-PEM
40	10.71	34.15	6.3	1.5
60	21.08	38.73	10.0	2.5
80	26.16	53.54	25.2	6.7

Table 3  
Mechanical property of membranes

	Nafion® NRE-212 (dry)	Pt–SiO <sub>2</sub> /Nafion/PTFE-PEM (dry)
Thickness (μm)	50	25
Maximum strength (MPa)	26.60	32.25

means that composite membrane could increase dimension stability [28].

The maximum strengths of Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion® NRE-212 membranes are shown in Table 3. The maximum strengths measured for the NRE-212 is similar to that declared by the producer DuPont. The mechanical strength of the composite membrane was a little better than NRE-212 in spite of its thinness. Good mechanical strength will make it possible for the thinner composite membrane to be used in fuel cell and improve the cell performance meanwhile.

The hydrogen permeation rate of the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM and the Nafion® NRE-212 membrane are shown in Fig. 5. The hydrogen permeation rate of the two membranes had the same dependency on temperature and increased as the temperature increased. This result is in accordance with the result that Liu et al. gained [28]. It can be found that the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM had a larger hydrogen permeation rate than the Nafion membrane. This high gas permeability of the composite membrane is helpful to self-humidification. The greater gas crossover can generate more water in the composite membrane which makes the cell with a composite membrane show a better performance than an unmodified membrane.

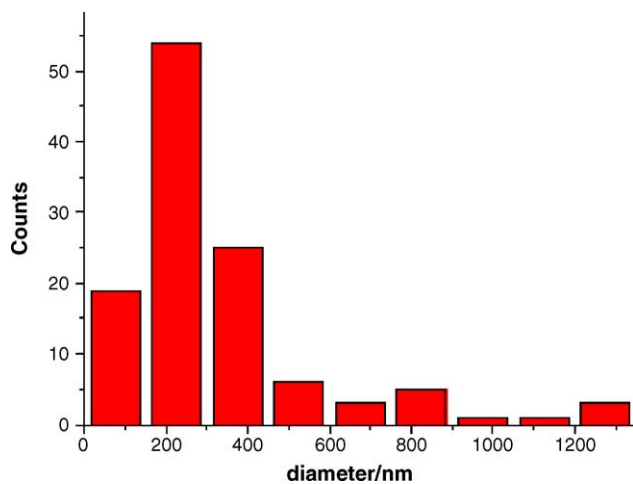


Fig. 3. Distribution of SiO<sub>2</sub> particle size in the composite membrane obtained from the cross-section image of SEM photomicrograph.



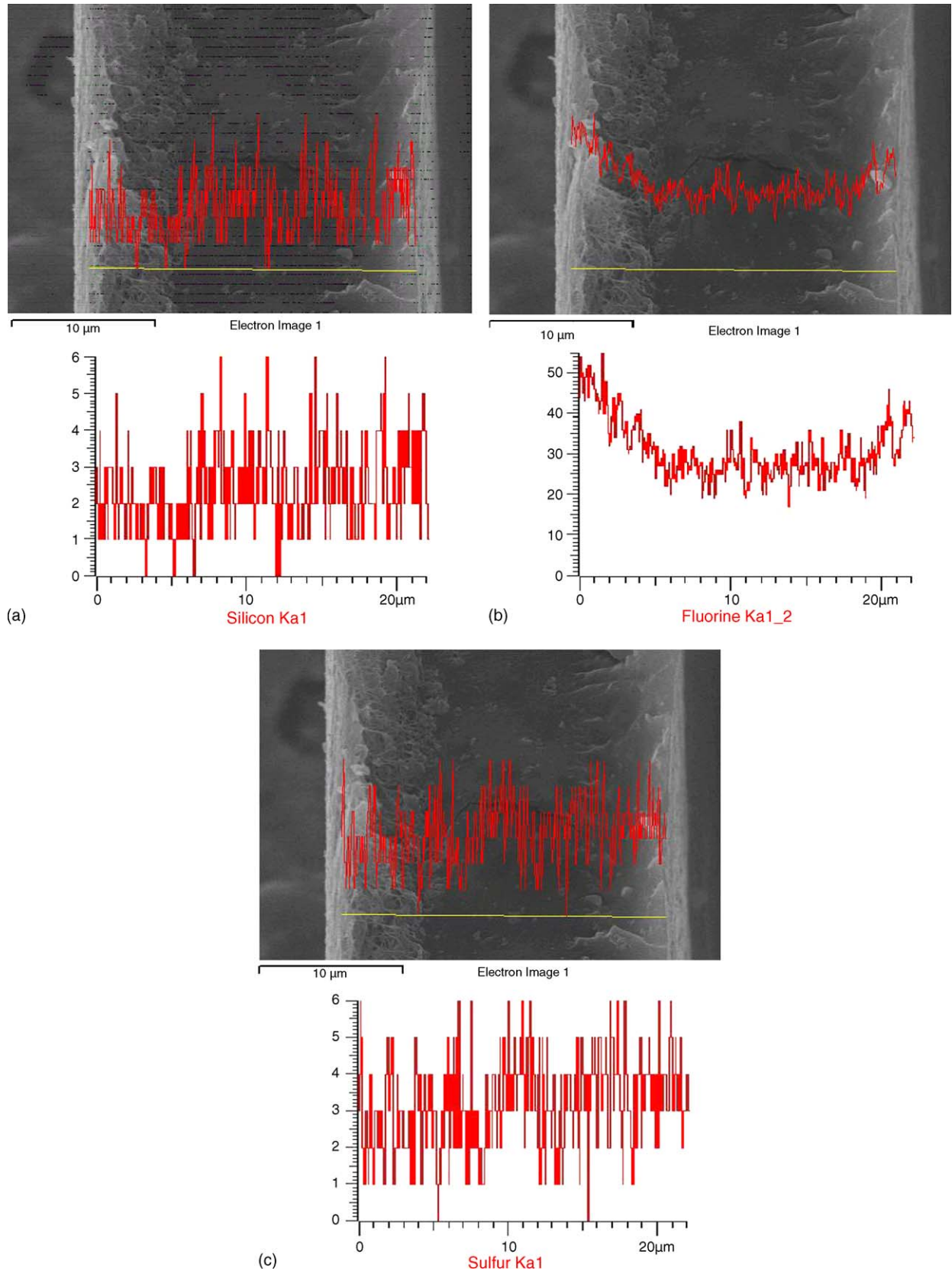


Fig. 4. EDX analysis result of Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM: (a) Si element; (b) F element; (c) S element.

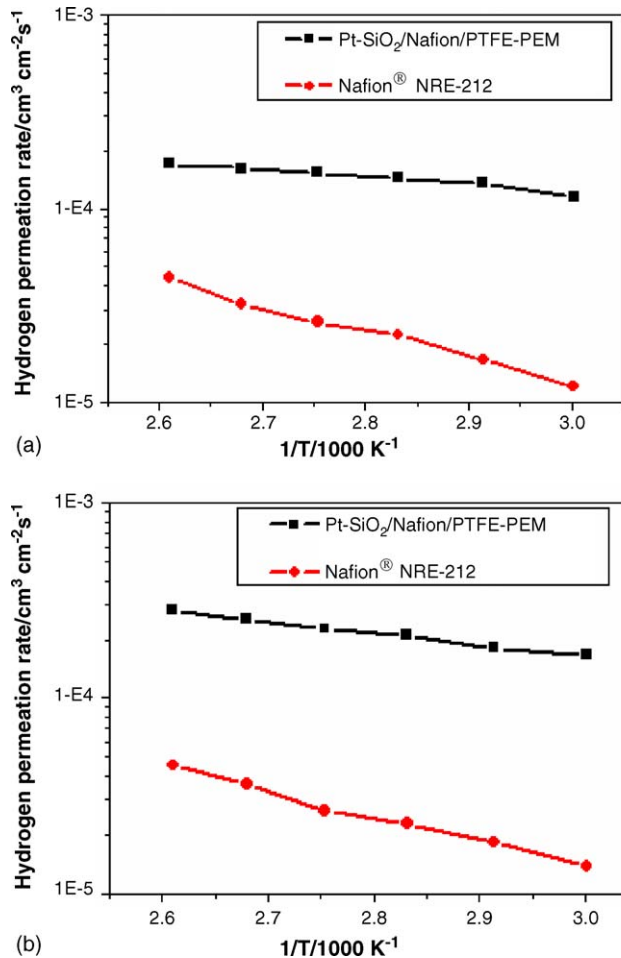


Fig. 5.  $H_2$  permeation rate of the composite membrane and the Nafion NRE-212 membrane with: (a) humidified gas and (b) dry gas.

### 3.3. Performance of PEMFCs operated under fully humidified and dry conditions

Fig. 6 shows the polarization curves of cells with Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion<sup>®</sup> NRE-212 membrane operated under fully humidified conditions with the cell temperature at 80, 110 and 120 °C, respectively. The cell performance with the Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM was better than that with the NRE-212. The best performance and the maximum power density values were obtained for both the membranes at 80 °C (1.65 and 1.21 W cm<sup>-2</sup> for Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and NRE-212, respectively). When the temperature was above 100 °C, the performance of the cells decreased. It is suspected that the membrane hydration ratio per sulfonyl group decreases as the cell temperature increases. A maximum power density of 0.945 W cm<sup>-2</sup> for Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM at 0.58 V against to 0.59 W cm<sup>-2</sup> for NRE-212 at 0.49 V were recorded at 120 °C. The decrease of the cell performance with the Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM at higher temperature was less than that of Nafion<sup>®</sup> NRE-212, which means that the addition of Pt particles can produce water effectively and SiO<sub>2</sub> as the hygroscopic material in the membrane can retain water at high temperature. Though the composite membranes had a higher

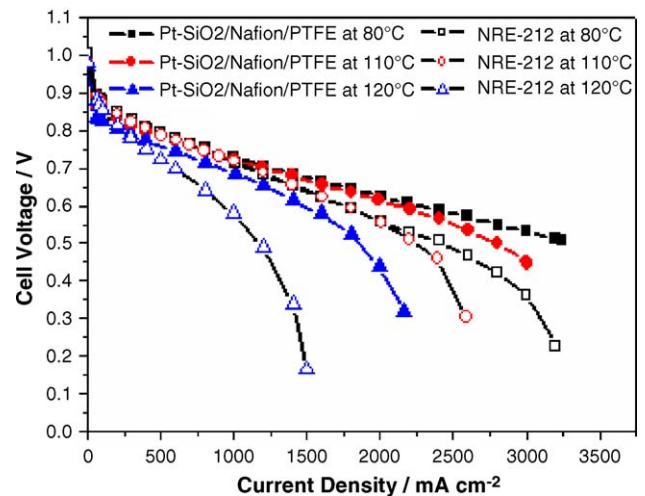


Fig. 6. Performance of  $H_2/O_2$  fuel cells with Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion<sup>®</sup> NRE-212 membrane under humidified conditions.

PTFE content than the Nafion membrane, the composite membranes are much thinner than the NRE-212 membrane and the additive silica made it more hydrophilic. The lower membrane thickness is also sufficient to compensate for its low conductivity so that the area resistance [28] of the composite membrane is lower than that of NRE-212 membrane. We concluded that addition of the Pt/SiO<sub>2</sub> effectively suppressed  $H_2$  and  $O_2$  crossover and retained water more effectively than other self-humidified membranes mentioned above.

Fig. 7 shows the polarization curves of  $H_2/O_2$  fuel cells with Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion<sup>®</sup> NRE-212 membranes operated under un-humidified conditions at 80–120 °C. The best performance and the maximum power density values were also obtained for both the membranes at 80 °C (1.29 and 0.88 W cm<sup>-2</sup> for Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and NRE-212, respectively). A maximum power density of 0.77 W cm<sup>-2</sup> for Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM at 0.48 V against to 0.28 W cm<sup>-2</sup> for NRE-212 at 0.55 V was recorded at 110 °C. At 120 °C,

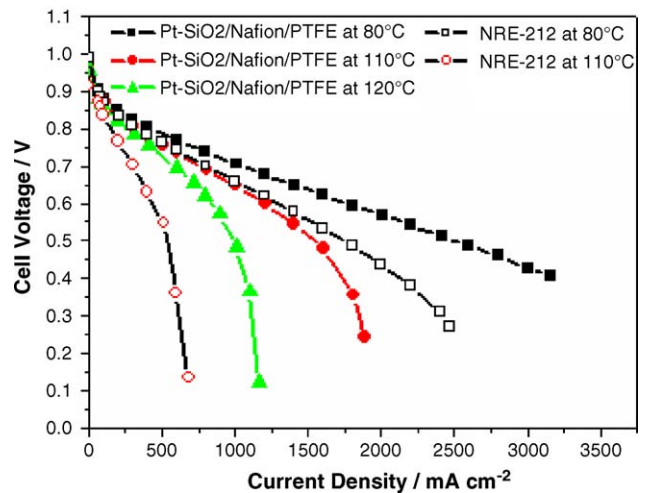


Fig. 7. The polarization curves of un-humidified  $H_2/O_2$  cell with the Pt-SiO<sub>2</sub>/Nafion/PTFE-PEM and Nafion<sup>®</sup> NRE-212 membrane operated at 80–120 °C.

NRE-212 could not have steady performance while the Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM could work at 120 °C reaching a power density of about 0.51 W cm<sup>-2</sup> at 0.572 V. The cell performance with Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM under dry gas conditions was obviously improved, and is due to the addition of Pt/SiO<sub>2</sub> as the hygroscopic material dramatically increased the water content in the membrane, and increased the proton conductivity as well.

These results mean that the proton conductivity of Pt–SiO<sub>2</sub>/Nafion/PTFE-PEM exceeds that of the Nafion membrane under all conditions especially above 100 °C. This high proton conductivity is due to the addition of the Pt/SiO<sub>2</sub> catalyst particles into the membrane. The Pt/SiO<sub>2</sub> particles which were embedded in the membrane effectively catalyze the chemical reaction of the H<sub>2</sub> and O<sub>2</sub> crossover through the membrane to generate water. Meanwhile, the SiO<sub>2</sub> particles play an important role in maintenance of the water produced in the self-humidifying membrane in situ at high temperature due to their hygroscopic properties and they release the water once the PEM needs it. In our experiments, a very thin (about 25 μm thick) composite reinforced membrane was used, which generated more water for self-humidification due to the higher gas permeation rate.

#### 4. Conclusions

The Pt–SiO<sub>2</sub>/Nafion/PTFE self-humidified composite membrane was made via a solution casting method. The results of the XRD and SEM studies showed that the Pt/SiO<sub>2</sub> particles were homogeneously dispersed within the membrane. Comparison investigation between the H<sub>2</sub>/O<sub>2</sub> fuel cells with Pt–SiO<sub>2</sub>/Nafion/PTFE and Nafion® NRE-212 membranes were performed. The cell performance with the self-humidifying composite membrane was obviously improved under both humidified and dry conditions at 80–120 °C. The self-humidifying composite membranes could minimize membrane conductivity loss under dry conditions. This is due to the presence of Pt/SiO<sub>2</sub> in the membrane. In view of the simplification of the control system, the self-humidification performance is particularly important for PEMFCs for vehicles and various electronic devices. In the future work, further uniform self-humidifying composite membranes for high temperature fuel cell applications will be studied.

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