

# Preparation and evaluation of a novel self-humidifying Pt/PFSA composite membrane for PEM fuel cell

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## Abstract

A novel self-humidifying Pt/PFSA membrane for polymer electrolyte membrane (PEM) fuel cells has been developed. Platinum nanocrystals were dispersed gradationally in the membrane by equilibrium impregnation–reduction (I–R) method. The physical characteristics of the novel self-humidifying PEM were studied by those methods of XRD and XPS, and electrochemical Performances of the self-humidifying Pt/PFSA membrane and PFSA membrane compared in 5 cm<sup>2</sup> single cells with 0.3 Pt mg/cm<sup>2</sup> platinum loading. The results indicated that Pt distribution in the Pt/PFSA composite membrane was gradient degression from one side to the opposite side, and average size of Pt is about 6 nm. The peak power density of the Pt/PFSA cell reached over 1.2 W/cm<sup>2</sup> at 70 °C, 0.2 MPa with dry hydrogen and dry oxygen.  
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**Keywords:** Fuel cell; PEM; Self-humidifying; Composite membrane; Pt

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) show great promise for attaining high energy efficiencies and high power densities [1]. Such high power densities and high energy efficiencies are required for space, underwater and terrestrial applications. However, the industrialization hold-backs of PEMFC are not only high cost in fuel cells and infrastructures, but also the complexity of the peripheral operation systems. The self-humidifying operation of PEMFC is a most promising application technology. Recently, many groups attempt to remove the externally humidifying unit from PEMFC system by endowing the proton exchange membrane with self-humidifying ability [2,3]. Dhar [4] suggested the use of a very thin membrane, which allows the water molecule produced on the cathode surface to diffuse into the membrane, thereby humidifying the membrane. However, thin membrane is detrimental to the cell performance by increasing crossover of reactant gases. Furthermore durability of a cell is shortened by the insufficient structural robust-

ness. Watanabe et al. [5] invented a method to fabricate the self-humidifying electrolyte polymer, which involved uniform dispersion of Pt through out the membrane, as shown in Fig. 1(a). They proposed the higher performance of a single cell adopting the self-humidifying PEM to Pt dispersed uniformly throughout the membrane that acts as a recombination site for permeated hydrogen and oxygen to produce water molecules.

To cut off formation of an electron conducting path by the network of dispersed Pt particles, Yang et al. [6] suggested that a self-humidifying Pt-PEM was made by two membranes and fine Pt particles distributing between them. The Pt particles were coated onto the one side of the membrane by a sputtering method, and then followed by joining the Pt sputtered membranes, as shown in Fig. 1(b). However, the Pt particles layer lying two membranes and thick membrane electrolyte brought more resistance of proton transfer from anode to cathode in PEMFC.

The objective of this work is to provide a novel self-humidifying Pt/PFSA composite membrane with advantages such as nonexistence of an electron conducting path and low resistance of proton transfer in membrane electrolyte. For this purposes, the novel self-humidifying Pt/PFSA composite

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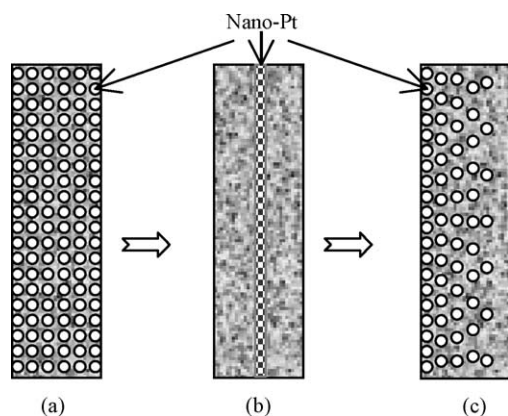


Fig. 1. Design concepts of self-humidifying Pt/PFSA composite membrane.

membrane, characterized by that Pt distribution in the membrane was gradient degression from one side to the other side, was fabricated using perfluorosulfonic acid (PFSA) copolymer membrane, which was deposited nano-Pt particles by equilibrium impregnation–reduction (I–R) method, as shown in Fig. 1(c).

## 2. Experimental

### 2.1. Preparation of the Pt/PFSA membrane

All PFSA membranes, thickness of 50  $\mu\text{m}$  and EW value of 1000, were prepared by tape-casting method using perfluorosulfonylfluoride copolymer resin made in China. Pt/PFSA composite membranes were prepared according to the equilibrium I–R procedure presented below. Prior to impregnation of Pt(II), the PFSA membrane in the  $\text{H}^+$  form was vacuum dried and weighed to establish by difference the platinum loading. The PFSA membrane was boiled in 0.5 M NaCl for at least 30 min, and then soaked in 50  $^\circ\text{C}$  DI water overnight. In the impregnation step, the membrane in the  $\text{Na}^+$  form was equilibrated for 24 h at 50  $^\circ\text{C}$  with 640 ml solution of  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  which varied from 0.1 to 0.3 mM, with the resulting Pt loading varying from 0.02 to 0.06  $\text{mg}/\text{cm}^2$ . A co-solvent of  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (75%/25%) was used in this step. Following the impregnation, the membrane was exposed on one face to air and the other side to an aqueous reductant solution at 50  $^\circ\text{C}$ . The reductant of 0.1 M  $\text{NaBH}_4$  at pH 10 was used for 2 h. Following the reduction step, the Pt/PFSA membranes were equilibrated with 0.5 M  $\text{H}_2\text{SO}_4$  prior to drying for weighing.

### 2.2. Preparation of MEA for PEMFC

The membrane used in membrane electrode assembly (MEA) was Pt/PFSA composite membrane prepared according to the procedure presented in Section 2.1. The membrane was first subjected to a pretreatment in order to remove

organic and metallic impurities. Briefly, this pretreatment consists of heating the membrane in 10%  $\text{H}_2\text{O}_2$  to about 80  $^\circ\text{C}$  for ca. 1 h to remove organic impurities. This is then followed by treatment in 1 M  $\text{H}_2\text{SO}_4$  at 80  $^\circ\text{C}$  for 30 min to remove metallic ion impurities. Thereafter, the membrane is boiled in water several times before it is used in the PEMFC.

The electrodes with 5  $\text{cm}^2$  active area were prepared in same manner reported in our previous paper [7]. The content of electrocatalyst (20 wt.% Pt/C, Johnson–Matthey) loading was controlled to be 0.3  $\text{mg Pt}/\text{cm}^2$ . Especially, Nafion impregnation was carried out by brushing solubilized Nafion (5 vol.%, Aldrich) into the electrode structure. It has been found in previous studies that a Nafion content of 0.6  $\text{mg}/\text{cm}^2$  is optimal [8]. After Nafion impregnation, the electrodes were air-dried first at ambient temperature, and then in an oven at 70  $^\circ\text{C}$ . The electrodes were then hot-pressed to the Pt/PFSA membrane at a temperature of 135  $^\circ\text{C}$  for a period of 1 min and a pressure of 5 MPa.

### 2.3. Experiment measurement

To gather information on the Pt particles in the Pt/PFSA composite membrane, the X-ray powder diffraction (XRD) analysis was performed using a X-ray automated diffractometer (D/Max B, Japan) with Cu  $\text{K}\alpha$  radiation source. The  $2\theta$  Bragg angles were scanned between 10 $^\circ$  and 70 $^\circ$ , the diffraction patterns were analyzed by comparing them with standard diffraction patterns. To obtain information on the vertical distribution of Pt element within the Pt/PFSA composite membrane, we used X-ray photoelectron spectroscopy (XPS) (PHI-5300 ESCA system, Perkin-Elmer Corporation) depth profiling, in which the surface composition is monitored as the sample is eroded by an argon ion beam. XPS analysis was performed using the Al  $\text{K}\alpha$  X-ray source and a semispherical analyzer with a multi-channel detector.

In electrochemical testing, the MEA assemblies were incorporated in the single cell test fixture with graphite blocks machined “series–parallel” flow field. The single cell was then installed in the fuel cell test station, which is equipped with adequate controls for temperature and pressure of the cell, and humidification and flow rate for the reactant gases. The test station was interfaced with a computer for data acquisition, plotting and analyses. All cells were operated with wet (RH = 100%) or dry  $\text{H}_2$  as fuel and with wet (RH = 100%) or dry  $\text{O}_2$  as the oxidant, a stoichiometry of pure hydrogen or oxygen is equal to 2. The cell was operated at 70  $^\circ\text{C}$  and 0.2 MPa. The performances of the single cells were evaluated when the hydrogen and the oxygen were in counter-flow.

## 3. Results and discussion

### 3.1. XRD analysis of Pt/PFSA composite membrane

XRD pattern for Pt/PFSA composite membrane was reported in Fig. 2. An average particle size of platinum can

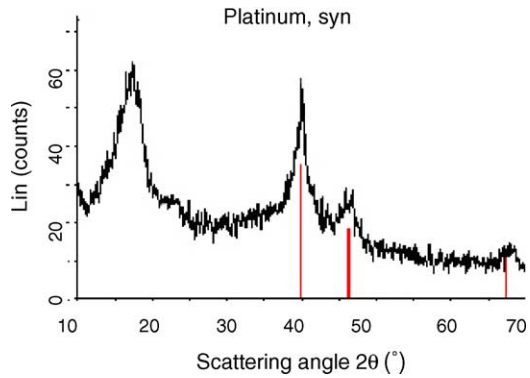


Fig. 2. XRD pattern of Pt/PFSA membrane, the vertical lines indicate the diffraction position of Pt.

be calculated from the broadening of peak (1 1 1) according to Debye–Scherrer equation:

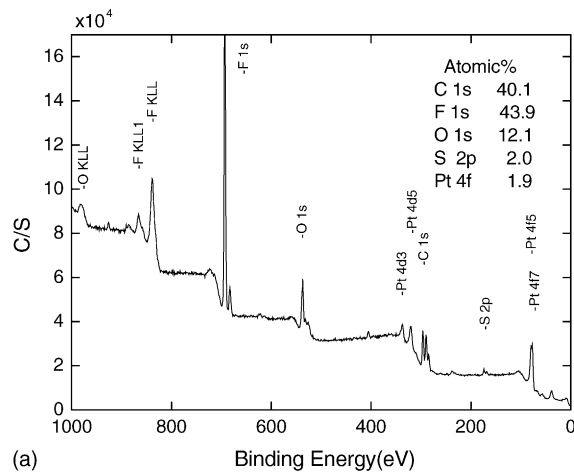
$$D_{hkl} = \frac{0.89\lambda}{B_{hkl} \cos \theta} B_{hkl}^2 = B_M^2 - B_S^2$$

Table 1  
Measurement parameters of XRD

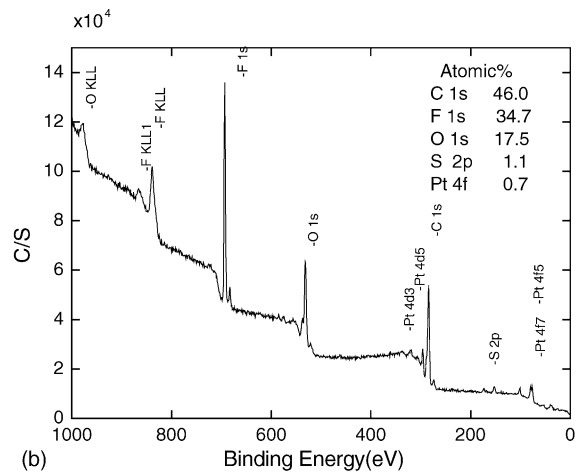
$hkl$	1 1 1
$\lambda$ (nm)	0.1541
$B_M$ (°)	1.312
Bragg, $2\theta$ (°)	39.891
$B_S$ (°)	0.104
Pt size (nm)	6

$B_M$  is the measured peak width at half peak intensity and  $B_S$  is the corresponding width for standard bulk materials.

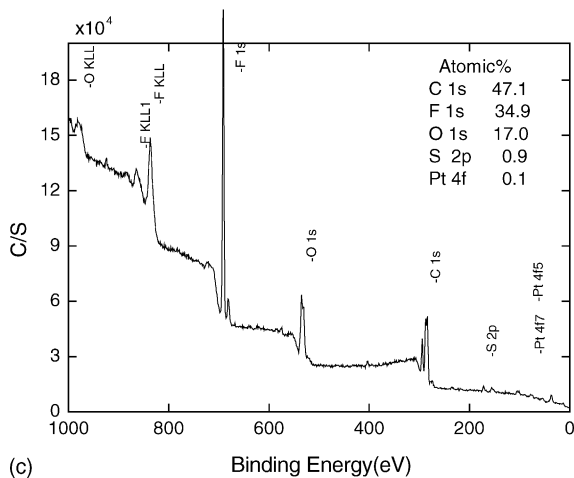
The main parameters of Pt X-ray diffraction and calculation result were listed in Table 1. In the diffractogram of Pt, the peaks at  $2\theta$  of about  $40^\circ$ ,  $46.5^\circ$  and  $68^\circ$  are relative to Pt fcc lattice. It also showed that the broad amorphous features peak of PFSA copolymer is about  $18^\circ$ , and full crystalline peaks of PFSA copolymer did clearly not occur. From these results it seemed the Pt/PFSA composite membrane is made up of amorphous PFSA copolymer and Pt particles with average size of 6 nm.



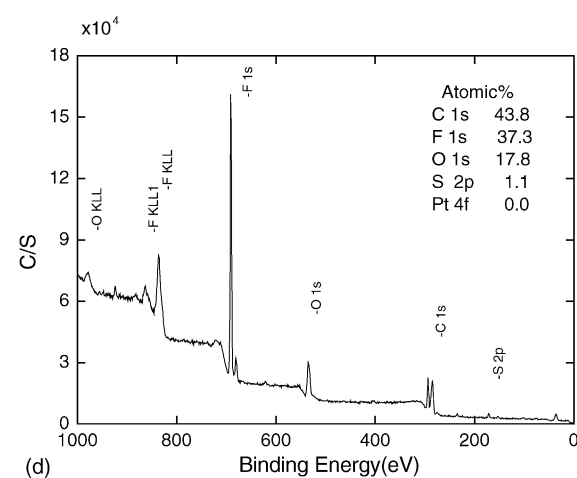
(a)



(b)



(c)



(d)

Fig. 3. XPS patterns and elements distribution in different thickness of Pt/PFSA composite membrane: (a)  $0 \mu\text{m}$  (in the face of reductant  $\text{NaBH}_4$ ); (b)  $10 \mu\text{m}$ ; (c)  $40 \mu\text{m}$ ; (d)  $50 \mu\text{m}$ .

### 3.2. XPS analysis of Pt/PFSA composite membrane

The intensity versus binding energy profiles in different thickness of the Pt/PFSA composite membrane obtained from XPS analysis using ion (argon) bombardments were shown in Fig. 3(a)–(d). The F 1s and C 1s signals represent the main chain of PFSA; the O 1s and S 2p signals represented the branch chain of PFSA. Pt crystallites were in turn symbolized by the Pt 4f signal. Comparing the relative intensities of Pt 4f, C 1s, F 1s and O 1s signals for different thickness surfaces of Pt/PFSA composite membrane, the at.% of elements were also reported in Fig. 3(a)–(d). The Pt at.% decreased gradually from 1.9 to 0% when the thickness of the membrane varies with 0–50  $\mu\text{m}$ .

The distribution of Pt particles in the equilibrium I–R method was dependent upon both the concentration distribution of Pt(II) in membrane at the onset of the reductant step and the concentration of the reductant. The Pt(II) concentration profile was steep at the beginning of the impregnation step and was flat at equilibrium. It was observed from XPS that the Pt/PFSA membrane which was equilibrium impregnated has Pt particles deposited deep as 40  $\mu\text{m}$  in the membrane.

In practice, the Pt 4f signal decreased from one side to opposite side of the Pt/PFSA membrane, as indicated in Fig. 4, especially, XPS spectra only showed very weak and noisy signals at 40  $\mu\text{m}$  of membrane thickness, and majority of the platinum was embedded within the first half of the membrane, which verified our new design of self-humidifying platinum composite membrane.

### 3.3. Electrochemical testing

Electrochemical characterizations in single cells were carried out both two operation modes of external-humidification and self-humidification. Performances of single cells using the Pt/PFSA composite membrane and the PFSA membrane (same as copolymer substrate of the Pt/PFSA com-

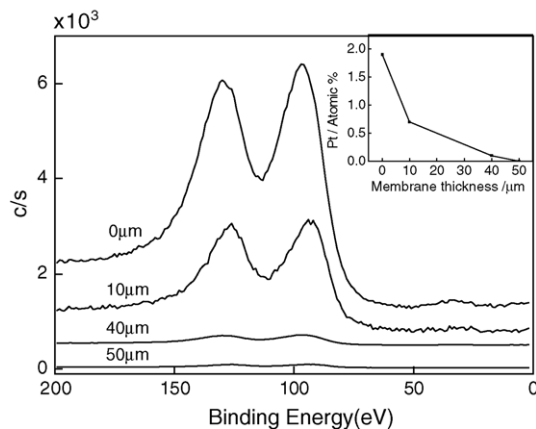


Fig. 4. Relative signal intensities and at.% concentration for Pt element in different thickness of Pt/PFSA composite membrane.

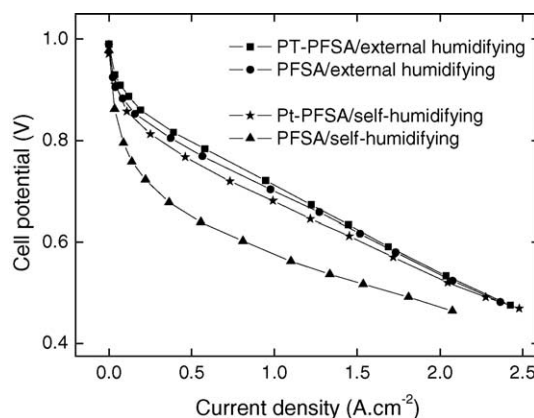


Fig. 5. Current–voltage curves of cells operation in  $\text{H}_2/\text{O}_2$ . The operations are according to Section 2.3.

posite membrane) were presented in Fig. 5. The external-humidification cell showed better performance than that of self-humidifying cell. This indicated that the rate of proton conduction through the external-humidification membrane exceed that through the self-humidifying membrane. Considering the result in terms of water content in the membrane again, the water content in the self-humidifying membrane seemed to be lower as compared to that in the case of external-humidification.

However, regardless of the external-humidification or self-humidification, the Pt/PFSA membrane cell exhibited better performance than PFSA membrane cell. The reason was that the more water was produced by the chemical reaction of  $\text{H}_2$  and  $\text{O}_2$  on Pt catalysts in electrolyte membrane, so the Pt/PFSA membrane had better conductivity than the PFSA membrane at the same operation mode. The self-humidifying process of Pt particles includes at least three steps. The first step is permeation of  $\text{H}_2$  and  $\text{O}_2$  through the membrane, the second is internal adsorption of reactant gases on Pt particles embedded and the final step is the recombination of internally adsorbed  $\text{H}_2$  and  $\text{O}_2$  on the Pt particles.

As concerning Pt/PFSA membrane cell, it was observed that the discharge performance of the external-humidification was slightly better than the self-humidification in the range of 0–2.0  $\text{A}/\text{cm}^2$ . However, higher than 2.0  $\text{A}/\text{cm}^2$ , the performance of the self-humidification was almost equivalent to the external-humidification, the peak power density reached 1.2  $\text{W}/\text{cm}^2$ . This novel phenomenon indicates that the self-humidifying cell had excellent performance at high current density, because at low current density, the most water generated at the cathode was discharged out of the cell, and the water supplied to the PEM was little, on the other hand, water produced by electrochemical reaction from the cathode could balance water transport by electro-osmotic drag from anode at high current density. Fig. 6 showed that the power density of Pt/PFSA membrane cell was higher than the PFSA membrane cell at operation mode of self-humidification; moreover, the self-humidifying power density of Pt/PFSA membrane cell was close to the external-humidifying power densities of

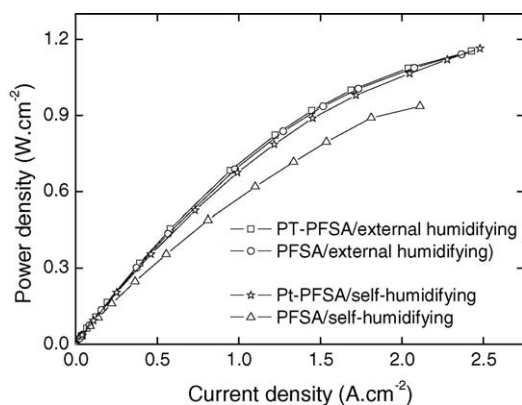


Fig. 6. Power density curves of cells operation in  $H_2/O_2$ . The operations are according to Section 2.3.

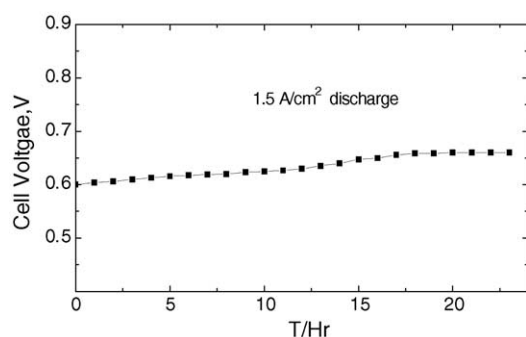


Fig. 7. Stability of the  $H_2/O_2$  fuel cell with Pt/PFSA. The operations are according to Section 2.3.

Pt/PFSA and PFSA membranes. The stability of the self-humidifying single cell using Pt/PFSA membrane was examined for 24 h under application of a constant current density  $1.5 \text{ A/cm}^2$  at  $70^\circ\text{C}$ . The cell voltage initially increased slowly with increasing time and finally reached a steady state value about  $0.66 \text{ V}$  at  $1.5 \text{ A/cm}^2$ , as shown in Fig. 7. The results obtained shows that the stability of the Pt/PFSA membrane is excellent.

#### 4. Conclusion

In this work, a novel preparation method of a self-humidifying membrane for the PEMFC was presented,

using homemade perfluorosulfonic acid (PFSA) copolymer membrane and depositing nano Pt particles by equilibrium impregnation–reduction (I–R) method. Based on the results of the XRD and XPS analyses, the Pt/PFSA membrane was characterized by that distribution of  $6 \text{ nm}$  Pt particles was gradient degression from one side to the opposite side of the membrane and Pt loading varies from  $0.02$  to  $0.06 \text{ mg/cm}^2$ . The results of electrochemical testing showed that the power density of the Pt/PFSA membrane cell reached  $1.2 \text{ W/cm}^2$  at  $0.5 \text{ V}$ ,  $70^\circ\text{C}$ , with  $0.2 \text{ MPa}$  dry hydrogen and dry oxygen, which were higher performance than that of PFSA membrane cell. The excellent self-humidifying performance of Pt/PFSA membrane was attributed to the fact that the gradient presence of Pt particles in the membrane increases the proton conductivity of the membrane, due to the generation of water molecules on the Pt particles by the recombination of permeated hydrogen and oxygen. Especially, the novel Pt/PFSA membrane cut off an electron conducting path by gradient distribution of Pt particles.

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