



Short communication

# Hydrophilic treatment poly(tetrafluoroethylene) reinforced sulfonated poly(ether ether ketone) composite membrane for proton exchange membrane fuel cell application

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## ABSTRACT

A reinforced composite membrane based on SPEEK (sulfonated poly ether ether ketone) and porous PTFE substrate (polytetrafluoroethylene) is fabricated and investigated for proton exchange membrane fuel cell application. In order to improve the combination between SPEEK polymer and PTFE matrix, PTFE substrate is hydrophilically pretreated by naphthalene sodium solution. The experimental results indicate that SPEEK can impregnate into treated PTFE substrate (abbreviated as trPTFE) more easily. The variation of PTFE surface property before and after treatment is characterized by water contact angle experiment and ATR-FTIR technique. The impregnated status of SPEEK polymer in PTFE matrix is also characterized by ATR-FTIR. According to the appearance photo of two composite membranes, it is showed that SPEEK/trPTFE composite membrane has more uniform and homogeneous morphology. Moreover, the mechanical property of SPEEK/trPTFE composite membrane also has an advantage over pristine SPEEK membrane. Due to the reinforced effect of trPTFE substrate, thinner composite membrane can be applied in single cell evolution and achieves better performance as a result.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical energy converters, which can transform chemical energy directly into electricity. Due to their high power density, convenient operation, high energy conversion efficiency and near zero harmful gas emissions, PEMFCs are one of the most ideal power sources in the future [1–3]. As one of the key components in PEMFCs, proton exchange membrane (PEM) has to possess excellent chemical, physical properties and high proton conductivity. Generally, in all of the candidates, perfluorosulfonic acid polymer membranes (e.g., Nafion<sup>®</sup>) have been perceived as the most suitable PEM materials at present [4]. However, a series of disadvantages, such as the expensive cost [5], high methanol permeability [6], loss of conductivity at high temperature (>80 °C) [7] and difficulty in synthesis and processing, have limited their further commercialization. So it is very necessary to develop the new generation membrane for PEMFC application.

In massive alternative membrane materials, sulfonated poly(ether ether ketone) (SPEEK) has attracted much more

attention due to their cheap cost, low methanol permeability [8], high thermal stabilities [9] and simplicity in synthesis and processing. However, this kind of membrane material not only becomes very brittle in dry state, but also bears excessively water swollen in wet state [10–12]. So it is difficult for SPEEK to meet the requirement of PEMFC application due to the disadvantages of mechanical property.

Porous PTFE reinforcement technique is considered as one of the most effective and common methods to increase membrane mechanical strength [13–17]. The reinforced composite membrane shows higher mechanical property, better dimensional stability and lower cost [13–17]. Higher membrane strength makes thinner membrane thickness possible (usually less than 50 μm), which will significantly reduce the areal resistance and increase the output performance of single cell [14–18]. However, the performance is strongly dependent on the combination status between polymer and porous PTFE substrate [17–19]. In most previous works, researchers had mainly focused on the preparation and the properties of PTFE reinforced Nafion<sup>®</sup> composite membrane due to their similar main-chain structure and better compatibility. Up to now, fewer papers had been mentioned PTFE reinforced hydrocarbon polymer composite membrane for PEMFC application, because the low surface energy and chemical inertness of PTFE inhibit the adhesion and impregnation of non-fluorinated main-chain poly-

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mer. Therefore, it is very important to solve the non-compatible property between hydrocarbon polymer and PTFE.

In order to improve interface compatibility, the hydrophobic PTFE usually needs to experience a hydrophilic surface treatment process [14,15,17,18]. This procedure will increase free surface energy of PTFE and promote its wetting property, so that the polymer can easily impregnate into the micro pores of PTFE matrix. It has been reported that the hydrophobic property of the PTFE can be modified by naphthalene sodium solution, ion beam irradiation, or chemical grafting [20–23].

In this paper, a novel composite membrane based on porous PTFE reinforced SPEEK is fabricated and investigated for PEMFC application. The main innovation of this work is to develop an advanced technique to decrease the chemical inertia of PTFE substrate and enhance the combination status between hydrophilic hydrocarbon polymer and hydrophobic PTFE substrate. And the paper is based on the following two points: on the one hand, SPEEK is chosen as the proton conductivity polymer due to its cheap cost, easy synthesis method and promising development in PEMFC field; on the other hand, PTFE is hydrophilically modified by naphthalene sodium solution to improve its wetting and adhesion property. To characterize hydrophilic-hydrophobic state of PTFE, the water contact angle experiment was applied. ATR-FTIR technique was used to compare PTFE surface variation before/after hydrophilic treatment, and confirm the impregnated status of SPEEK in PTFE substrate. The experimental results show that SPEEK prefers to spread on hydrophilic treated PTFE surface. The reinforced effect of PTFE substrate has been tested by tensile experiment. Single cell evaluation indicates that thinner membrane exhibits lower areal resistance and better cell performance.

## 2. Experiment

### 2.1. Sulfonation of PEEK

SPEEK was prepared by the post-sulfonation method. Firstly, 150 ml 98%  $\text{H}_2\text{SO}_4$  was transferred to the reaction flask with a mechanical stirrer. And then, 8 g dried PEEK (Victrex, PEEK, 450 PF, MW = 38,300) was slowly added to the flask under stirring. The polymer was completely dissolved for 2 h under 35 °C. After that, the reaction system was heated up to 50 °C and kept it for 1 h. The solution was dropped into deionized water and washed the fibers until the neutral PH. At last, the polymer was dried at 120 °C for 24 h. The sulfonation principle is schemed in Fig. 1. The extent of sulfonation of SPEEK is 37%, which is determined by titration.

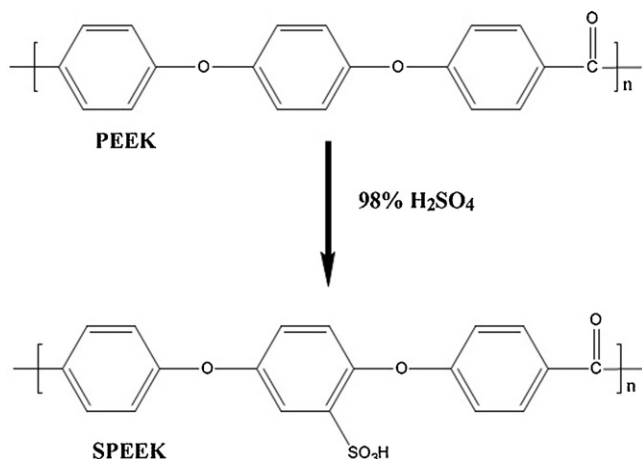


Fig. 1. Sulfonation principle diagram of PEEK.

### 2.2. Pretreatment of porous PTFE film

The porous PTFE film (thickness 15  $\mu\text{m}$ , mean pore size 0.3–0.5  $\mu\text{m}$ , porosity >90%, Dagong New Mater. Co., Shanghai, China) was hydrophilically pretreated by naphthalene sodium solution. Naphthalene sodium solution was prepared as follows: 3.25 g naphthalene was first dissolved in 50 ml THF at room temperature. And then, 0.65 g sodium was added into the above solution under  $\text{N}_2$  atmosphere. The solution was refluxed until the color changed from colorless to black. At last, the PTFE film was immersed in naphthalene sodium solution for 5 s, followed by washing with deionized water until fully removing residual solvent and impurity.

### 2.3. Preparation of composite membranes

SPEEK was dissolved in a mixed solvent containing dimethyl sulfoxide (DMSO) and ethanol (volume ratio 1:1) at 50 °C in a closed vessel, and treated PTFE or untreated PTFE film was preliminarily extended on a stainless steel frame. Then, SPEEK polymer solution was poured into the steel frame. The solvent was evaporated at 75 °C until dry, and followed by heat-treatment at 120 °C. The treated PTFE composite SPEEK membrane was abbreviated as SPEEK/trPTFE, and the untreated PTFE composite SPEEK membrane was abbreviated as SPEEK/PTFE. We also defined the air side of composite membranes as upper surface and the glass side as lower surface.

### 2.4. Characterization of membranes

#### 2.4.1. Water contact angle experiment

The water contact angle experiment was conducted on two porous PTFE films before and after treatment by naphthalene sodium solution. The samples were extended on glass sheets to avoid significant changes of the film surface, and then tested with a sessile drop method (JC2000A, POWEREACH®, Shanghai Zhongchen Digital Technic Apparatus Co. Ltd., China). A syringe was employed to make a 10  $\mu\text{L}$  DI water droplet close to the surface of the samples.

#### 2.4.2. ATR-FTIR spectra analysis

ATR-FTIR spectra of SPEEK, trPTFE, PTFE, SPEEK/trPTFE, and SPEEK/PTFE surface were carried out on a JASCO FT-IR 4100 spectrometer to further verify the structure variation. An ATR accessory containing a Ge crystal was used and the ATR-FTIR spectra were recorded in the wave number range from 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### 2.4.3. Mechanical property

The mechanical property of the membranes was measured with a tension tester GMT 4503 (SANS, AUTO graph) at room temperature. The membrane specimens were of 4 mm width and tested using a programmed elongation rate of 50  $\text{mm min}^{-1}$ .

#### 2.4.4. Single PEM fuel cell tests

The membrane electrode assemblies (MEAs) were fabricated by hot-pressing the anode and the cathode to the membrane at 160 °C and 1 MPa for 2 min. The Pt loading in the anode and the cathode were 0.3 and 0.7  $\text{mg cm}^{-2}$ , respectively. The Nafion® loading in both the anode and the cathode were 0.4  $\text{mg cm}^{-2}$ . The active area of MEAs was 5  $\text{cm}^2$ . The MEA was placed in a single cell using stainless steel as the end plates and stainless mesh as the current collectors. PEMFC single cell was operated at 80 °C and 0.2 MPa with fully humidified  $\text{H}_2/\text{O}_2$ . During single cell evaluation, the ohmic resistance was also measured by electrochemical impedance technique. The IR-free corrected polarization curves, based on original

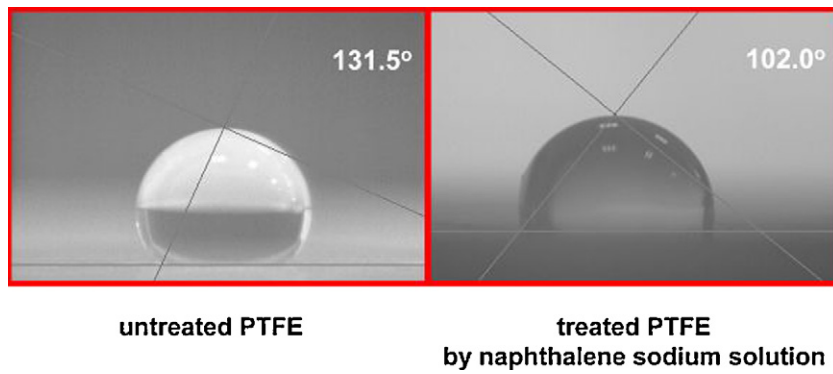


Fig. 2. Contact angle of PTFE films before and after treatment by naphthalene sodium solution for 5 s.

polarization curves, were conducted by compensating voltage loss caused by ohmic resistance at different current density.

### 3. Results and discussion

#### 3.1. The surface property variation of PTFE film before and after treatment by naphthalene sodium solution

##### 3.1.1. Water contact angle experiment

The surface property is very important for the combination relation between polymer and PTFE substrate. Lower water contact angle and more hydrophilic surface usually bring better impregnation state [15,17,18]. To compare the difference of surface property before and after hydrophilic treatment, the water contact angle experiment of PTFE film was conducted and the image was shown in Fig. 2. It is observed that the contact angle of PTFE film treated by naphthalene sodium solution is 102.0°, which is about 30° lower than 131.5° of untreated PTFE film. According to the Kelvin equation shown as follows, the reduced contact angle will increase the capillary pressure difference and improve surface wetting property. Finally, the increased pressure difference will enhance capillary force, which is more favorable to make hydrophilic polymer impregnate into PTFE micro pores [15,17–19].

$$\Delta P = \frac{4\tau \cos \theta}{d}$$

where  $\Delta P$  is the difference in capillary pressure (kPa),  $\tau$  is the surface tension of the liquid ( $\text{N m}^{-2}$ ),  $\theta$  is the contact angle (°) and  $d$  is the size of the pore (m).

##### 3.1.2. ATR-FTIR spectra analysis

To research the modified effect of PTFE by naphthalene sodium solution, the ATR-FTIR technique was utilized. In Fig. 3, it is clearly shown the differences before and after treatment by naphthalene sodium solution. Compared to the untreated PTFE, the absorption intensity of C–F bonds of treated PTFE (from 1100 to 1300  $\text{cm}^{-1}$ ) becomes weak and some new absorption peaks appear. Timmons and Hess [21] used XPS spectrum to investigate the surface variation of PTFE before and after treatment. They found that the treatment process will induce a defluorinated reaction and the concentration of carbon and oxygen on trPTFE surface significantly increased. As a result, the modified fluorocarbon surface is expected to have more improvement in adhesion, bonding ability and wetting property.

#### 3.2. The property comparisons of SPEEK/trPTFE and SPEEK/PTFE composite membranes

##### 3.2.1. ATR-FTIR spectra analysis at upper and lower surface

To confirm the impregnated status of SPEEK polymer in porous PTFE matrix, the ATR-FTIR technique was employed. As we know,

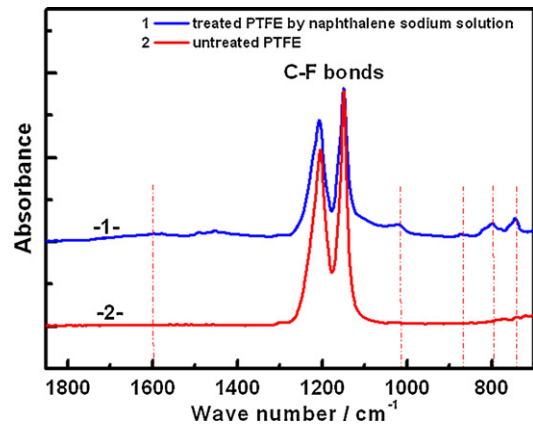


Fig. 3. ATR-FTIR spectra of PTFE films before and after treatment by naphthalene sodium solution for 5 s.

ATR-FTIR is an attractive tool and a non-invasive surface-sensitive technique to study polymer surface state, and can help to provide a wealth of useful interface information [24]. So, in this study, we employ this technique as a valuable analysis tool to research both upper and lower surface of SPEEK/trPTFE and SPEEK/PTFE, so as to evaluate the quality of polymer infiltration in PTFE matrix [25]. From Fig. 4, it is obvious to see that, at upper surface, both SPEEK/trPTFE and SPEEK/PTFE show the same characteristic peaks just like pristine SPEEK. For example, the absorption peaks at 1250, 1078 and 1021  $\text{cm}^{-1}$  are assigned to the sulfonic acid group of SPEEK, and the absorption at 1646  $\text{cm}^{-1}$  is assigned to the carbonyl band of SPEEK. The result indicates that the upper surfaces of two composite membranes are covered with a SPEEK layer.

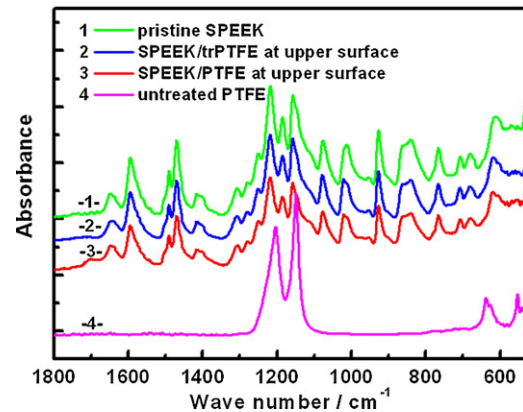
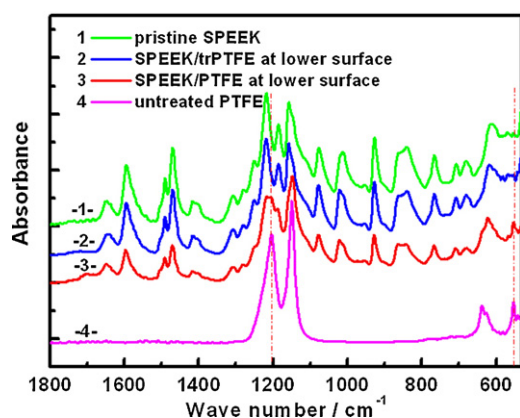


Fig. 4. ATR-FTIR spectra of upper surface of SPEEK/trPTFE and SPEEK/PTFE composite membranes.

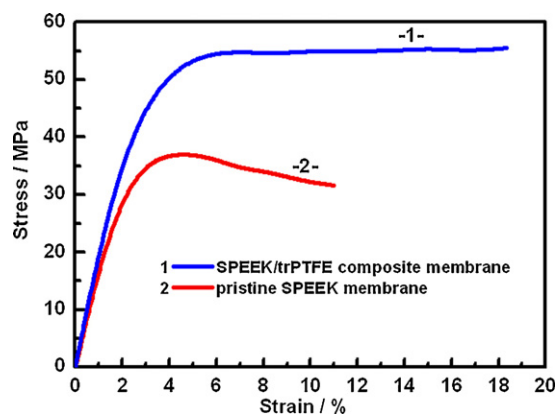


**Fig. 5.** ATR-FTIR spectra of lower surface of SPEEK/trPTFE and SPEEK/PTFE composite membranes.

However, in Fig. 5, the absorption spectra of lower surface of two composite membranes are completely different. For instance, at lower surface of SPEEK/trPTFE, it shows the same absorption peaks just like its upper surface and hardly finds the vibration peak of PTFE. But, a new peak has been found at  $1204\text{ cm}^{-1}$  at the lower surface of SPEEK/PTFE, which can be attributed to the  $\text{CF}_2$  stretching vibration of PTFE. The different experimental phenomenon suggests that SPEEK polymer can form a continuous layer at lower surface of hydrophilic treated PTFE and difficultly spread at lower surface of hydrophobic untreated PTFE. The above results suggest that SPEEK polymer can infiltrate into hydrophilic treated PTFE more easily than hydrophobic untreated PTFE.

### 3.2.2. The appearance morphology difference

To further indicate the hydrophilic treatment process could help polymer impregnate into the PTFE matrix, the photograph of three membranes is shown in Fig. 6. From left to right, the sample is SPEEK/trPTFE, SPEEK/PTFE and porous PTFE film. On the one hand, it is visually seen that the color of SPEEK/trPTFE is dark yellow, which is different from SPEEK/PTFE and porous PTFE film. The darker color represents the color of trPTFE, which was also observed by Timmons and Hess [21]. This phenomenon indicates that the carbon–fluorine surface layer of trPTFE has been defluorinated and original carbon–fluorine bonds are replaced by new generating carbon–carbon bonds [21]. Obviously, the carbon–carbon surface is easier to be wetted than carbon–fluorine surface, so trPTFE shows lower water contact angle and more new absorption peaks in above experiments. On the other hand, the two composite membranes in the photograph show different appearance morphology. The SPEEK/trPTFE composite membrane is uniform and homogeneous. However, SPEEK distributes inhomogeneously on untreated PTFE

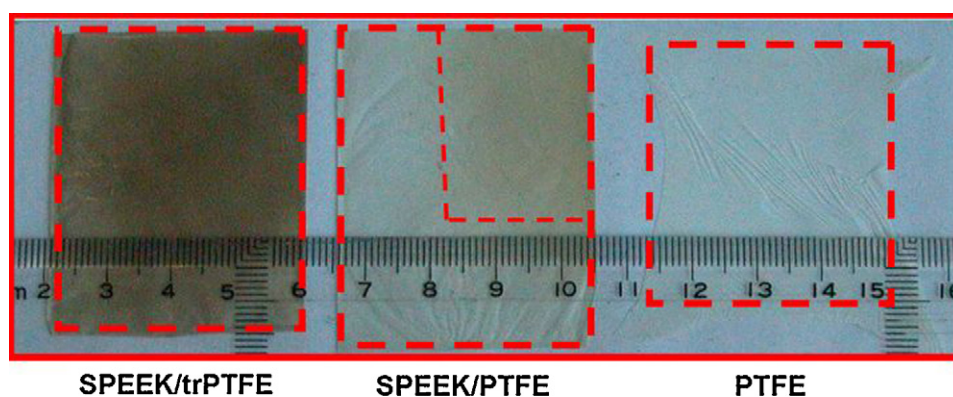


**Fig. 7.** The mechanical property of SPEEK/trPTFE composite membrane and pristine SPEEK membrane.

surface and the aggregative phenomenon is very evident. For example, in the right top corner of SPEEK/PTFE membrane, it can easily observe the aggregative SPEEK polymer on the surface (yellow part). On the contrary, lesser polymer appears in the left down corner and the light PTFE substrate is even exposed (white part). The different morphology indicates that SPEEK polymer hardly spreads on untreated PTFE surface, and cannot completely impregnate into the untreated PTFE matrix.

### 3.3. The mechanical property of SPEEK/trPTFE and SPEEK membranes

The mechanical property of membrane is an important factor for its dimensional stability and durability, especially under fuel cell operation conditions [26,27]. To test the mechanical property of membranes, tensile characteristics SPEEK/trPTFE and pristine SPEEK membrane are measured. From Fig. 7, it could be seen that the order of tensile strength of two membranes is SPEEK/trPTFE > pristine SPEEK. For example, the tensile strength of SPEEK/trPTFE composite membrane is 55.48 MPa, higher than 36.98 MPa of pristine SPEEK. The improved mechanical property is attributed to the reinforced effect of porous PTFE substrate. In addition, the elongation at break of SPEEK/trPTFE composite membrane is also nearly two times higher than pristine SPEEK membrane due to the toughening effect of porous PTFE film. According to Tang et al.'s work [26], the reinforced membrane is of advantage to avoid MEA mechanical damage including membrane cracks, tears, punctures, and pinholes. So, under the same condition, the reinforced SPEEK/trPTFE composite membrane is expected to have more favorable mechanical stability.



**Fig. 6.** The appearance morphology of SPEEK/trPTFE and SPEEK/PTFE composite membranes.



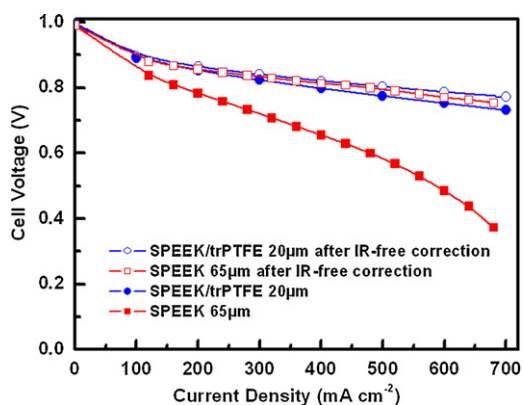


Fig. 8. Single cell performance comparisons before and after IR-free correction by employing SPEEK/trPTFE composite membrane (20  $\mu\text{m}$ ), pristine SPEEK membrane (65  $\mu\text{m}$ ) with fully humidified  $\text{H}_2/\text{O}_2$  at 80 °C.

### 3.4. Single PEM fuel cell evaluation

Fig. 8 shows us the single cell performance of SPEEK/trPTFE composite membrane and pristine SPEEK membrane with fully humidifying  $\text{H}_2$  and  $\text{O}_2$  at 80 °C. From this figure, it is found that SPEEK/trPTFE composite membrane (20  $\mu\text{m}$ ) has better single cell performance than pristine SPEEK membrane (65  $\mu\text{m}$ ). And we have also noticed that the open circuit voltage (OCV) of thinner composite membrane is comparable to thicker pristine membrane, this phenomenon is similar with Liu et al.'s result [28]. The reason of OCV degradation of pristine SPEEK membrane is possibly attributed to the excessive swell under fuel cell operation condition. Moreover, in ohmic polarization zone, the voltages of composite membrane fall slower than pristine membrane when current density increases. Generally, ohmic resistance of membrane represents the major part of voltage losses in ohmic polarization zone [29]. So the improved cell performance can be ascribed to thinner membrane thickness, the lower areal resistance and shorter proton transport pathway of SPEEK/trPTFE. In order to obtain more electrochemical information and eliminate membrane thickness influence, IR-free corrected polarization curves are also drawn in Fig. 8. After IR-free correction, the composite membrane and pristine membrane almost show the same cell voltages at different current densities, because the compensated cell voltages only reflect the state of catalyst and electrodes and do not depend on membrane. Even if the thinner membrane has an advantage over thicker membrane, but it is hard to make an ultra-thin membrane for pristine hydrocarbon polymer due to the brittle and crack property [14]. So, compared with pristine SPEEK membrane, trPTFE reinforced SPEEK composite membrane can bring better performance and show more potential in PEM fuel cell application.

## 4. Conclusions

In this paper, a novel porous PTFE reinforced SPEEK composite membrane was prepared and investigated. The porous PTFE

substrate film was hydrophilically treated by naphthalene sodium solution. According to the experimental results, treated PTFE film showed lower water contact angle and more hydrophilic surface, which enhanced the combination between SPEEK polymer and PTFE matrix. The mechanical property of SPEEK/trPTFE composite membrane was also improved such as tensile strength and elongation at break. Based on the analysis of experimental results, the reinforced effect of treated PTFE made thinner membrane possible and accordingly led to a better single cell performance. As a promising candidate, SPEEK/trPTFE composite membrane could be applicable in PEMFCs field for its lower cost and relatively higher performance.

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