Short communication

Proton conducting composite membranes from sulfonated polyethersulfone Cardo and phosphotungstic acid for fuel cell application

Lei Li [a,b,*], Yuxin Wang [b,*]

[a] *School of Chemistry and Chemical Technology, Shanghai Jiaotong University, Shanghai 200240, China*
[b] *Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

Abstract

A new kind of inorganic–organic composite membranes based on sulfonated polyethersulfone Cardo (SPES-C) with embedded phosphotungstic acid (PWA) was prepared. The composite membranes were characterized by using FT-IR, XRD, TGA and SEM techniques. FT-IR and XRD measurements confirmed the presence of PWA particles into the polymer matrix. FT-IR spectra indicated the existence of a specific interaction between PWA particles and SPES-C polymer. TGA results showed that the composite membranes were thermally stable up to approximately about 200 °C. SEM micrographs verified that nano-scale PWA particles were homogeneously distributed into the polymer matrix. By incorporation PWA into SPES-C polymer the proton conductivity of the composite membranes was enhanced. It was 4.5×10^{-2} S cm^{-1} at 90 °C and 6.7×10^{-2} S cm^{-1} at 110 °C, while the conductivity of Nafion® 115 membrane was 4.1×10^{-2} S cm^{-1} and 4.7×10^{-2} S cm^{-1} at 90 °C and 110 °C, respectively.
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1. Introduction

Fuel cells have been attracted considerable attention as electrical power sources due to their high efficiency and low pollution levels. Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) using proton conducting polymer membranes are the most promising candidates for transportation, residential and portable applications. For these applications, it is important to develop new membranes capable of operating at intermediate temperature (90–130 °C) to enhance fuel oxidation kinetics and reduce heat exchange requirements [1].

As a proton conducting membrane, now perfluorinated ionomers have been the best available materials. However, the presently available perfluorinated ionomers are not suitable for high temperature applications due to the decrease in the proton conductivity and mechanical strength, and the increase in the methanol cross-over for DMFC. In addition, their high cost

and environmental inadaptability are also other serious drawbacks. Therefore, there has been a great demand for alternative proton conducting membranes for high temperature PEMFC and DMFC. Several methods have been proposed to increase the performance of proton conducting membranes at intermediate temperature, and promising results have been obtained with the use of composite membranes, where inorganic particles are embedded into a conducting polymer matrix [2–13].

In the present work a similar approach was followed and the inorganic material was chosen as heteropoly acids (HPAs). HPAs are known to be the most conductive solids among the inorganic solid electrolytes at room temperature, and they are considered as a new kind of electrolyte for fuel cell applications. However, the HPAs are water-soluble materials. Electrochemically produced water may dissolve HPAs and the acids may leak out through the gas outlet holes, which would result in declining cell performance. Consequently, a major research objective is to fix the HPAs in stable structures and maintain its high proton conductivity. It is interesting to note that some inorganic–organic membranes, which HPAs were well dispersed into hydrophilic polymer matrix, have been promising for PEMFC and DMFC applications [6–13]. When HPAs were embedded in hydrophilic polymer matrix, they were expected to endow the composite

* Corresponding authors. Tel.: +86 21 34202613; fax: +86 21 54742567.
E-mail addresses: lilei0323@yahoo.com.cn (L. Li),
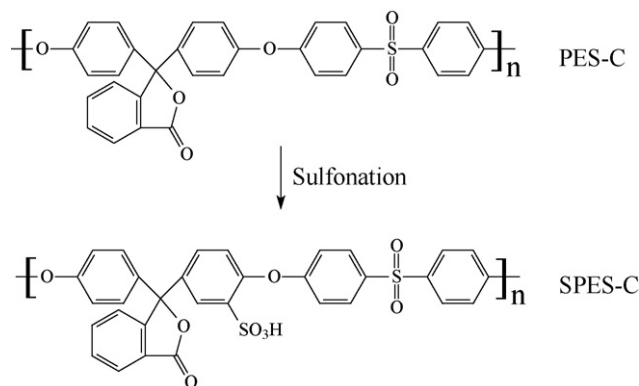yxwang@tju.edu.cn (Y. Wang).

Fig. 1. Chemical structure of PES-C and sulfonated PES-C polymers.

membranes with their high proton conductivity, while retaining the desirable mechanical properties of the polymer membranes.

Polyethersulfone with Cardo (PES-C) synthesized from phenolphthalein is a novel kind of thermoplastics engineering material [14], and has high mechanical, thermal and chemical resistance. In the PES-C structure, there is a carton atom involved in a five-member lactone ring of a phenolphthalein moiety (Fig. 1). Sulfonation of PES-C can be directly carried out in concentrated sulfuric acid [15,16]. Recently, we found that the methanol permeability of SPES-C membranes was about an order of magnitude lower than that of Nafion® membrane, which will be a better candidate for DMFC application [16]. However, the conductivity of SPES-C polymer is strongly dependant on the degree of sulfonation. At reduced levels of sulfonation the aromatic polymers have lower water uptake and lower conductivity ($\sigma < 10^{-2}$ S cm^{-1}), which is not acceptable for use in fuel cell. Conversely, if the degree of sulfonation is increased to improve conductivity, the mechanical properties of the membrane deteriorate. In this paper, this drawback can be overcome through preparing inorganic–organic hybrid membranes, which inorganic conductor particles are embedded into polymer matrix. The polymer matrix used was partially sulfonated PES-C polymer, and the inorganic conductor phosphotungstic acid (PWA) powders. The structural and electrochemical performances of the composite membranes prepared were investigated.

2. Experimental

2.1. Membrane preparation

PES-C was obtained from Engineering Plastics of Suzhou (Jiangsu, China). The weight-averaged and number-averaged molecular weights as obtained with a size exclusion chromatograph (pL Gel mixed type C 5 μm column, Touzart et Matignon) calibrated with polystyrene as molecular weight standards were 117,000 and 65,000 g mol^{-1}, respectively. Sulfonated polyethersulfone Cardo with degree of sulfonation (DS) 70% was prepared as described elsewhere [15,16]. The degree of sulfonation of SPES-C polymers was determined by back-titration method.

The composite membranes were prepared by solution casting the acid form of SPES-C and PWA. PWA was dried at 100 °C

in an air circulating oven for 24 h before use (the number of hydrated water molecules per PWA ≈ 6). The SPES-C polymer was first dissolved (10 wt.%) in dimethylformamide (DMF) and weighted amount of PWA was then added into the solution. The weight ratio of PWA to SPES-C was 40 wt.% in our experiments. The clear homogeneous yellow solution was stirred for 24 h at room temperature. The color of this solution was not found any change in the experiments. Then the mixture was cast onto a clean glass plate by casting knife. The cast membranes were dried at 60 °C for 6 h to remove the solvents, and annealed at 100 °C for 4 h. After drying the membranes at 60 °C, it was found that the color was changed from the yellow solution to the highly transparent, slight red membranes. However, there was no change of the membrane color in the annealing process at 100 °C. After cooling to room temperature, the resultant membranes were spontaneously peeled from the glass plate in deionized water. Finally, the membranes were treated with 1 M sulfonic acid solution for 24 h at room temperature and subsequently rinsed with deionized water for several times. All the membranes were kept in deionized water before testing.

2.2. Structural characterization

FT-IR spectra were measured in absorbance mode by using a FT-IR spectrometer (BIO-RAD FTS3000) in the range of wave numbers 4000–600 cm^{-1}. Before FT-IR measurement, the samples were dried at 80 °C for 24 h. TGA was carried out using a thermal balance (LCT-2, Beijing Optical Instruments Co.). Samples of approximately 15–20 mg were first dried at 80 °C for 24 h, and then programmed from 30 to 900 °C at a rate of 10 °C min^{-1} under nitrogen atmosphere. The crystalline structure of samples was characterized by the X-ray diffractometer (Rigaku D/max-2500) using Cu Kα ($\lambda = 1.54056 \times 10^{-10}$ m) radiation. Data were collected by the step-scanning mode with steps of 0.05° (time per step: 1 s). The morphology of the composite membranes was investigated using a scanning electron microscope (PHILIPS XL-30). Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Au prior to SEM examination.

2.3. Water uptake

The membranes were dried in an oven at 60 °C for 48 h, weighed, soaked in deionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighted. Water uptake was calculated from:

$$\text{water uptake} = \frac{G_w - G_d}{G_d} \times 100\%$$

Here, G_w is the weight of the wet membranes and G_d the weight of the dry membranes.

2.4. Conductivity measurements

The proton conductivity of these composite membranes in the traverse direction was measured by locating the samples in a measurement cell using a frequency response analyzer (FRA)
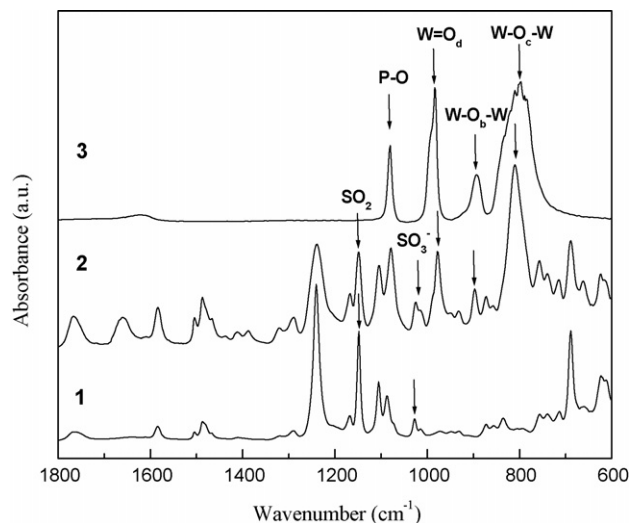
Fig. 2. FT-IR spectra of the SPES-C membrane with 70% DS (line 1); PWA/SPES-C composite membrane (line 2) and pure PWA powders (line 3).

Fig. 3. TGA curves of the SPES-C membrane with 70% DS (line 1) and PWA/SPES-C composite membrane (line 2).

(Autolab PGSTAT20) [17]. Two stainless steel electrodes with a contacting area of 28.8 mm^2, connected from the FRA, pressed the membrane to be tested in between horizontally. The measured temperature was controlled from room temperature to 110 °C. The conductivity σ was calculated from the impedance data, using the relation $\sigma = l/RS$ where l and S was the thickness and area of the membranes, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the $Re(z)$ axis.

3. Results and discussion

The physical and chemical properties of SPES-C depend on the degree of sulfonation and the nature of counter ions. In our experiments, we found that SPES-C membrane with 70% DS had low degree of swelling in water, even boiled in 1 M aqueous methanol solution for 10 h. Therefore, SPES-C with 70% DS was used as the polymer matrix in our experiments.

FT-IR spectra of the PWA/SPES-C composite membrane, SPES-C membrane with 70% DS and pure PWA powders were shown in Fig. 2. The symmetric stretching band of SO$_3^-$ was observed at 1028 cm^{-1} in pure SPES-C and red shifted to 1024 cm^{-1} when doped with PWA. On the other hand, the symmetric stretching band of SO$_2$ observed at 1149 cm^{-1} was insensitive to incorporation of PWA (see Fig. 2 and Table 1). This means that the PWA particles primarily interact with the sulfonic acid moiety as opposed to some other functional unit in the backbone of polymer. In the IR spectrum of the pure PWA
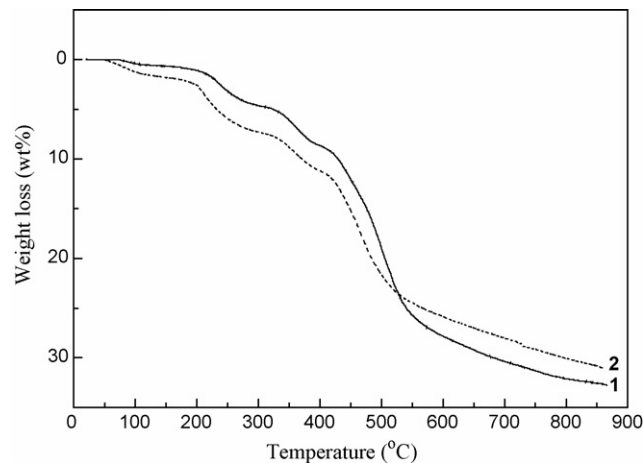
powders, there are four characteristic peaks of the Keggin structure: the P–O stretching band at 1080 cm^{-1}, the terminal oxygen band at 986 cm^{-1}, the bridging oxygen bands at 887 cm^{-1} and 797 cm^{-1}, respectively. In the IR spectrum of the PWA/SPES-C composite membranes, these characteristic peaks of the Keggin anion were also observed. Compared to that of pure PWA, the terminal oxygen band in the PWA/SPES-C composite membrane was red shifted to 977 cm^{-1}, and the bridging oxygen bands were blue shifted to 896 and 810 cm^{-1}. The P–O stretching band at 1078 cm^{-1} observed in the composite membrane was relatively broad, which indicates that the local interaction of P–O is similar to that of the pure PWA powders. These frequency shifts clearly demonstrate that there is the specific interaction between Keggin structure of PWA molecules and SPES-C polymer, which is probably both the terminal oxygen and the bridging oxygen interact with the sulfonic acid groups of polymer in connection with protonated water molecules. In addition, it was observed that the intensity of the carbonyl group at 1750 cm^{-1} in the PWA/SPES-C composite membrane was higher than that of the pure SPES-C membrane. Maybe it is related to the interaction between the carbonyl group of SPES-C polymer and PWA molecules.

The TGA curves of SPES-C membrane and PWA/SPES-C composite membrane were shown in Fig. 3. It is evident that there are five weight loss steps for SPES-C polymer. After two weight loss due to evaporation of residual DMF and the crystal water molecules of PWA particles, which ended at about 210 °C, a third step was observed. This step can be attributed to the splitting-off of sulfonic acid groups. It is interesting to

Table 1
Infrared assignments of PWA, SPES-C and PWA/SPES-C composite membrane

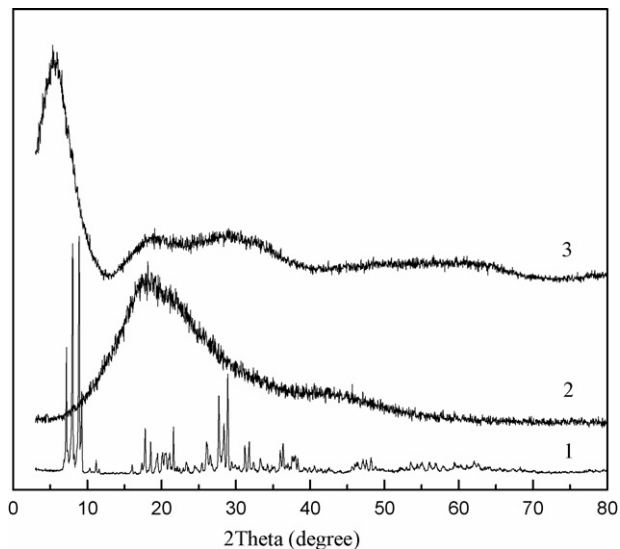| Sample	Wave number (cm^{-1})					
	$-SO_3^-$	$-SO_2$	P—O	W=O$_d$	W—O$_b$—W	W—O$_c$—W
SPES-C	1028	1149	–	–	–	–
PWA/SPES-C	1024	1150	1078	977	896	810
H$_3$PW$_{12}$O$_{40}$·6H$_2$O	–	–	1080	986	887	797

Fig. 4. XRD patterns of the samples. Line 1: pure PWA powders; line 2: SPES-C membrane with 70% DS and line 3: PWA/SPES-C composite membrane.
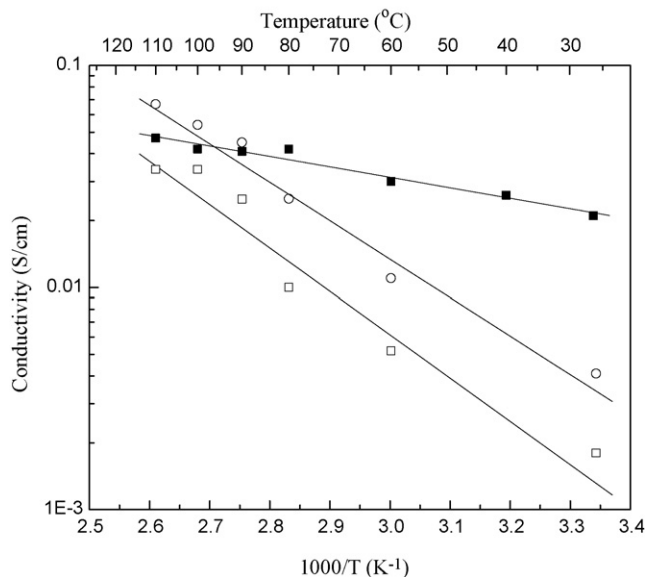

Fig. 6. Conductivity of membranes as a function of temperature. □: SPES-C membrane with 70% DS; ○: PWA/SPES-C composite membrane; and ■: Nafion® 115 membrane.

observe that the temperature at which the splitting-off of the sulfonic acid groups increased from 269 °C of SPES-C membrane to 278 °C of PWA/SPES-C composite membrane. Since it was shown that the specific interactions occurred between the sulfonic acid groups and the PWA particles, this result reveals that the specific interactions contribute to enhance the thermal stability of composite membrane. The similar results were also observed in the HPAs or tungsten oxide doped into sulfonated copolymer composite membranes [4,11]. The fourth step was end at 420 °C, which is due to the degradation of lactone rings. And the decomposition of the polymer was above 420 °C. From the TGA measurements, it can be found that the PWA/SPES-C composite membrane is thermally stable up to approximately about 200 °C, which should be enough stable for the fuel cell operation at intermediate temperature (90–130 °C)

The XRD patterns of pure PWA powders, SPES-C membrane and the PWA/SPES-C composite membrane were shown in Fig. 4. The XRD pattern of SPES-C membrane is typical of an amorphous structure. In the XRD pattern of the PWA/SPES-C composite membrane, two broad amorphous peaks were observed at $2\theta = 5$–$6°$ and $2\theta = 28$–$30°$, which are attributed to the PWA powders. Compared with the pattern of pure PWA powders, the peak at $2\theta < 10°$ in the composite membrane had

a small blue shift. Maybe it is due to the specific interaction between PWA particles and SPES-C polymer.

Fig. 5 shows the cross-sectional morphology of the pure SPES-C and PWA/SPES-C composite membranes. It can be found that the solid PWA particles were well mixed with SPES-C matrix and showed no agglomeration after membrane preparation. From the micrograph, the PWA particles were observed to be about 50–80 nm and homogeneously distributed within the SPES-C matrix. This result supports the specific interaction between PWA and SPES-C polymer. This homogeneous distribution will be favorable for proton transport as it minimizes the distance between particles.

Prior to conductivity measurements all the membranes were soaked in water for hydration. Fig. 6 shows the Arrhenius plots of the proton conductivity as a function of temperature at 100% RH (relative humidity) for the PWA/SPES-C membrane compared with SPES-C membrane with 70% DS and Nafion® 115 membrane. It can be clearly seen that the conductivity of pure SPES-C membrane was lower than that of Nafion® 115 in the whole range of temperature. When PWA particles were doped into pure SPES-C membrane, the conductivity was improved
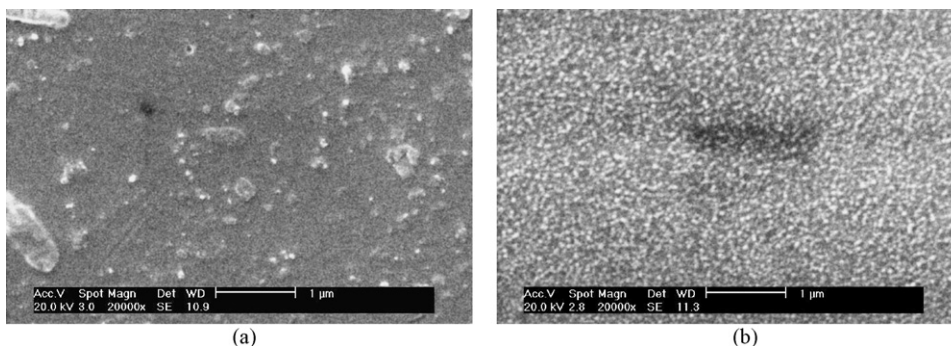

Fig. 5. SEM micrographs of the SPES-C (a) and PWA/SPES-C composite membrane (b).

Table 2
Water uptake and conductivity of the membranes

Membrane	Thickness (μm)	Water uptake (%)	E_a (kJ mol^{-1})	Conductivity (S cm^{-1})	
				25 °C	110 °C
SPES-C	90	15	35.87	1.8×10^{-3}	3.4×10^{-2}
PWA/SPES-C	90	52	32.90	4.1×10^{-3}	6.7×10^{-2}
Nafion® 115	152	32	9.04	2.1×10^{-2}	4.7×10^{-2}

to a certain extent. The conductivity of the composite membrane was 4.5×10^{-2} S cm^{-1} at 90 °C and 6.7×10^{-2} S cm^{-1} at 110 °C, while the conductivity of Nafion® 115 membrane was 4.1×10^{-2} S cm^{-1} and 4.7×10^{-2} S cm^{-1} at 90 °C and 110 °C, respectively. These results reveal that the PWA/SPES-C composite membrane had higher conductivity than that of Nafion® 115 at high temperature, which should be a better candidate for PEMFC application at intermediate temperature. The apparent activation energy of Nafion® 115 was 9.04 kJ mol^{-1}, which is in agreement with the literature value of 9.4 kJ mol^{-1} [18]. The apparent activation energies for our membranes were higher than that of Nafion® 115 membrane (see Table 2). Maybe there are other variables affecting the measured activity energy in the experiments, besides the temperature factor. The first variable is the ion content of the polymers. The dissociation constants of weak acids vary with the temperature, so the ion contents in SPES-C polymer will also vary. This will affect the conductivity measurements, and therefore the measured activation energy. However, this behavior probably did not influence the activation energy determined for Nafion® membrane. Nafion® 115 membrane was fully ionized at room temperature, so an increase in temperature will not influence the ion content. The second is water uptake. Because the dissociation constant of SPES-C polymer increases with the temperature, water uptake of pure SPES-C and PWA/SPES-C membranes also vary with the temperature. However, Nafion® 115 membrane was pretreated in boiling H_2SO_4 solution, so water uptake likely did not increase with increasing in temperature [19]. In addition, the aqueous disperse phase in Nafion® and our membranes are also different. In the case of Nafion® membranes which are described as nanoporous inert "sponges" for water of hydration, this water shows little interaction with the polymer chains and forms hydration shells around the sulfonic acid groups [20]. In PWA/SPES-C composite membranes, the homogeneous nano-scale distribution of PWA particles within the polymer matrix will make aqueous phase in the composite membrane more continuous. It also leads to increasing conductivity to certain extent.

It is important to mention that the conductivity of the composite membrane was not affected by storage in water at room temperature for 3 months. This reveals that PWA particles can be stable in the SPES-C matrix for a long term. Maybe there are two factors affecting the stability of PWA particles into polymer matrix. One is the SPES-C polymer matrix. In our experiments, SPES-C polymer used has lower water uptake and lower swelling, even at high temperate. Therefore, it will effectively reduce the extraction of PWA particles, and make them be stable in the polymer matrix. Another is the size

and distribution of PWA particles in the polymer matrix. It was shown in SEM micrograph that nano-scale PWA particles were homogeneously separated from polymer matrix, whereas PWA particles in the sulfonated polymer remained in the matrix.

4. Conclusions

In this paper the inorganic–organic composite membranes have been prepared by incorporation of phosphotungstic acid into partically sulfonated PES-C polymer. The membranes were characterized using FT-IR, XRD, TGA and SEM techniques. FT-IR and XRD confirmed there was the specific interaction between PWA particles and sulfonated polymer matrix. TGA measurements showed that the composite membrane has a good thermal stability. SEM micrograph showed that nano-scale PWA particles were homogenously distributed within the polymer matrix. The incorporation of PWA into SPES-C polymer not only enhanced the thermal stability of composite membrane, but also improved the conductivity at intermediate temperature. Compared with Nafion® 115 membrane, the PWA/SPES-C composite membrane exhibits higher conductivity at intermediate temperature. The PWA/SPES-C composite membranes are easy to prepare and much less expensive than the commercial perfluorinated membranes. Their high conductivity and long-term stability qualify the PWA/SPES-C composite membranes to be considered for use in PEMFC and DMFC as alternative to Nafion® based membranes.

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