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**Binary blends and ternary composites as proton exchange
membranes**

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ABSTRACT

Naphthalene-containing blend membranes, comprising sulfonated polyaryletherketone (SPAEK) as the primary matrix, and basic component polyazomethine (PAM), which has a chemical structure partially similar with SPAEK, were investigated as proton exchange membranes (PEM)s. Further, a ternary-composite membrane was successfully prepared by introducing acid-functionalized polysilsesquioxane (POSS-SO₃H) into SPAEK/PAM composite using a sol-gel process. The relevant properties of the PEMs, such as proton conductivity, methanol permeability, water uptake, and morphology were determined, and it was shown that the ternary-composite membrane, SPAEK/PAM/POSS-SO₃H, showed a superior combination of properties for proton conductivity and methanol resistance. Its selectivity was 7.5 times higher than Nafion.

Keywords: Poly(aryl ether ketone); Proton exchange membranes; Composites; Sol-gel; Fuel cells

1. Introduction:

In the 21st century, as easily recoverable fossil fuel resources diminish further, convenient alternative power sources are being urgently sought. Fuel cells, which transform chemical energy directly into electricity, have advantages such as environmental friendliness, high efficiency and quiet operation, and are widely regarded as promising clean energy sources [1]. Proton exchange membranes (PEM)s are the central components of membrane electrode assemblies (MEAs), the electrochemical heart of the fuel cell. Important properties such as high proton conductivity, limited fuel diffusion and chemical, and dimensional stability are required for use in these applications [2].

Nafion[®] membranes are commercial products manufactured by DuPont[™]. Although perfluorosulfonic acid structures in Nafion-type PEMs impart exceptional oxidative and chemical stability and high proton conductivity [3], these materials have some drawbacks such as high cost, low operating temperature, and high fuel permeability, which are limitations to widespread adoption. Alternative inexpensive proton-conducting materials with superior properties are required, such as sulfonated polyaryletherketones (SPAEEKs), which are being investigated due to their higher temperature capability and overall thermooxidative and chemical stability performance [4].

It should be noted that most newly developed proton conducting materials have a typical profile of exhibiting unilateral improvements in properties, but fall short in integrated performance compared with Nafion [5,6]. Composite membranes (e. g.

acid-base enhanced type PEMs), which have certain molecular interactions between different polymeric materials, can make multi-improvements for fuel cell applications. For example, most binary composite membranes have obvious improvements in dimensional stability and methanol resistance due to strong molecular interactions, such as hydrogen bonding between particular functional groups [7-11], but the proton conductivity is usually lower than that of the corresponding unitary membranes owing to decreased effective ion exchange capacity (IEC) values.

Sulfonated inorganic compounds introduced into PEMs to form organic-inorganic hybrid membranes have been shown to have some attractive membrane properties relevant to direct methanol fuel cells, since the sulfonic acid functionalization somewhat compensates for the lower IEC value of the added inorganic component (DMFCs) [12-17]. Recently, 3-trihydroxysilyl-1-propanesulfonic acid (THOPS) was used to form a multi-acid-functionalized polysilsesquioxane (POSS-SO₃H) via a sol-gel process, which was incorporated into polyarylether-type matrix. It was found that POSS-SO₃H containing hybrid membranes were highly proton conductive with enhanced water-holding capability [18,19]. In the present study, sulfonated poly(aryl ether ketone) (SPAEEK) [11,15] was used as the primary PEM matrix, with 0 – 10% of a molecular-enhancing polyazomethine (PAM); each polymer contained naphthalene, ether and ketone structural units common to both [20]. A series of binary component composite SPAEK/PAM PEM films was prepared by solution casting and the properties were compared with a ternary-component composite

(SPAЕК/PAM/POSS-SO₃H) membrane.

2. Experimental

2.1 Materials

Sodium 6,7-dihydroxynaphthalene-2-sulfonate was purchased from Rintech Inc., and was recrystallized twice from a mixture (50:50 in volume) of water and ethanol. 1,4-Bis(4-fluorobenzoyl)benzene was obtained from Jilin University, China. Bisphenol AF was obtained from Sigma-Aldrich, and was recrystallized from toluene before use. 1,5-Bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was synthesized via a Friedel-Crafts acylation reaction followed by an aromatic nucleophilic substitution reaction [20]. Terephthalaldehyde (Sinopharm Chemical Reagent Co., Ltd.) and anhydrous lithium chloride (Tianjin North Union Fine Chemicals Development Co., Ltd.) were used without purification. 3-Trihydroxysilyl-1-propanesulfonic acid (THOPS) was purchased from ABCN chemical company from Germany. All other chemicals were reagent grade and obtained from commercial sources and used without further purification.

2.2 Polymer Synthesis

2.2.1 Synthesis of the Naphthylated Sulfonated PAEK

Naphthalene-containing sulfonated poly(aryl ether ketone) (SPAЕК) was synthesized from sodium 6,7-dihydroxynaphthalene-2-sulfonate, 1,4-bis(4-fluorobenzoyl)benzene, and bisphenol AF, following a previously reported procedure [11,15]. The SPAЕК (IEC~ 1.30 meq g⁻¹) structure is shown in Scheme 1.

The inherent viscosity measured at 25.0 °C using a Ubbelohde viscometer and a polymer concentration of 0.5 g/dL in DMAc was 1.08 dL/g.

FTIR (KBr, cm^{-1}): 1032, 1103 ($-\text{SO}_3$); 1660 ($\text{C}=\text{O}$).

^1H NMR (DMSO-d_6 , ppm): 8.21 (s, 0.7 H); 8.01-7.73 (m, 10.6 H); 7.45-7.07 (m, 6.6 H).

Scheme 1 Synthesis of a naphthylated SPAEK as a matrix.

2.2.2 Synthesis of the Naphthylated PAM Containing Ether and Ketone Linkages

Naphthalene-containing polyazomethine (PAM) was synthesized according to a previously reported procedure [20]. The PAM structure is shown in Scheme 2. The inherent viscosity in DMAc at 25.0 °C was 0.13 dL/g.

FTIR (KBr, cm^{-1}): 1610 ($\text{C}=\text{N}$); 1670 ($\text{C}=\text{O}$).

^1H NMR (DMSO-d_6 , ppm): 8.74 (s, 1 H); 8.06 (s, 2 H); 7.78-7.05 (m, 10 H); 3.70 (s, 3 H).

Scheme 2 Synthesis of a naphthylated PAM containing ether and ketone linkages.

2.3 Membrane Preparation

Powdered SPAEK in sodium form (5 g) was stirred overnight in 500 mL of 2 M H_2SO_4 , then washed with water until it was neutral. The resulting SPAEK was dried at 120 °C in vacuum for 4 hours before use. Different samples of SPAEK/PAM in the relative weight proportions of 1/0, 0.98/0.2, 0.95/0.05, 0.92/0.8 and 0.9/0.1 (0.5 g in total weight) were separately dissolved in 5 mL of N,N-Dimethylacetamide (DMAc). After 6 h of stirring, the solutions were filtered and cast onto 10 cm × 10 cm glass plates and then dried at 60 °C for 24 hours and at 100 °C, 120 °C for 12 hours separately. The resulting films were immersed in deionized water and separated from the glass.

The ternary-composite membrane, SPAEK/PAM/POSS- SO_3H , was cast from SPAEK/PAM/THOPS (0.75/0.1/0.15 in weight). Two drops of concentrated hydrochloric acid were added before stirring. It was fabricated in the same way mentioned above. All the samples could be cast into transparent membranes. The

thickness of the PEM samples was in range of 30~60 μm .

3. Measurements

3.1 Characterization

The ^1H NMR spectra were obtained on a Bruker 510 spectrometer operating at a proton frequency of 500 MHz. DMSO- d_6 was selected as solvent. FT-IR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer.

3.2 Water Uptake and Swelling Ratio Measurements

Membrane samples were vacuum dried at 120 $^{\circ}\text{C}$ until constant weight and measured as W_{dry} . Then the membranes were soaked in deionized water at different temperatures of 20 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, 80 $^{\circ}\text{C}$ and 100 $^{\circ}\text{C}$ for 2.5 hours separately. After each procedure, the wet membranes were quickly weighed with surface water removed by filter paper and noted as W_{wet} . Water uptake was calculated by:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

Where W_{wet} and W_{dry} are the weights of wet and dry membrane samples, respectively.

The dimensional swelling ratio was measured in the same way of water uptake as the following formula:

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100$$

Where L_{wet} and L_{dry} represented the lengths of wet and dry membrane samples (approximate dimensions were 1 cm $\times$ 3 cm), respectively.

3.3 Proton Conductivity

Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&GPARC, Princeton, NJ) was applied to measure proton conductivity by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0V dc rest voltage. The film samples were fixed in a measuring cell which was made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. The specimens were immersed in deionized water for at least 24 h prior to measurement. The proton conductivity of membranes was tested at different temperatures, and values were obtained via following formula:

$$\sigma = \frac{L}{R \times A}$$

Where R is the membrane resistance, L is the distance between the electrodes and A is the cross-sectional area of membrane.

3.4 Methanol permeability

Methanol diffusion coefficient was measured using a two-compartment cell separated by a membrane sample (2.5 cm × 2.5 cm), which was placed between two silicone rubber gaskets and clamped together. One side of the cell was filled with 100 mL methanol solution (10 mol/L), and 100 mL of pure deionized water was placed in the other compartment. Each side of the cell was magnetically stirred for 2.5 h before measurement. Methanol concentration in the water compartment was determined by a GC-14C gas chromatograph (SHTMADU, Tokyo, Japan). Peak area was converted into methanol concentration after it was corrected by a calibration curve, and methanol permeability was calculated using the following equation:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0)$$

Where A, L and V_B are the diffusion area, membrane thickness, and the permeated water volume separately. C_B and C_A are methanol concentration in water compartment and methanol compartment, respectively and DK is the methanol diffusion coefficient.

3.5 Oxidative Stability

Dry membrane samples were cut into 1 cm × 2 cm rectangle pieces and weighed before immersion in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The relative oxidative stability was evaluated by recording the retained weights of vacuum dried membranes after (a) soaking in Fenton's reagent for 1 h and (b) the time when the membranes dissolved.

3.6 Morphology

The morphology of the membranes was observed by a scanning electron microscope (Shimadzu SSX-550 superscan SEM) in order to investigate the molecular interaction and the homogeneity of the phase distribution in composite membranes. The samples were fractured in liquid nitrogen after dried. And the fractured sections of the samples were vacuum sprayed with a layer of Au before SEM examination.

4. Results and Discussions

4.1 Binary Blend and Ternary Composite Membranes

Sulfonated polyaryletherketones (SPAEEKs) having numerous structural varieties

are among the most studied types of hydrocarbon proton exchange membranes [4,21-23]. However, in order to achieve high proton conductivity, high sulfonation contents is required, which often leads to poor oxidative and dimensional stability under the fuel cell operating conditions, especially in a humidified environment at elevated temperatures [6,21]. In attempts to mitigate the conductivity – dimensional swelling trade-off, blend membranes and composites containing SPAEK and other molecular enhancers have been investigated. For example, Manthiram reported acid–base blend binary membranes consisting of an acidic sulfophenylated poly(ether ether ketone ketone) (Ph-SPEEKK) matrix polymer with minor amounts of basic polysulfone tethered with 5-amino-benzotriazole [8]. The blend membranes were shown to have higher proton conductivity and lower liquid uptake and dimensional swelling compared with single-component Ph-SPEEKK or sulfonated poly(ether ether ketone) (SPEEK) membranes. As a result of the low dimensional swelling and suitable proton conductivity properties of these blend membranes, they out-performed Nafion membranes in DMFC tests at high methanol concentrations. Most recently, a series of acid–base molecule-enhanced composite membranes were reported by us [9]. The composite membranes, composed of sulfonated poly(aryl ether ketone) (6FSPEEK) as the acidic primary matrix component, and aminated poly(aryl ether ketone) containing naphthyl units as the minor basic component, exhibited obviously improved thermal, oxidative and dimensional stability while maintaining acceptable proton conductivity.

Fig. 1. Schematic diagram of the ternary-composite: SPAEK/PAM/POSS-SO₃H.

In the present study, polyazomethine, also named as poly(schiff base), was employed as the molecular-enhancer minor basic component of the blend in a sulfonated poly(aryl ether ketone) primary matrix. The acid-base interactions between azomethine and sulfonic acid groups of the two polymers were expected to enhance some properties. The shared features in chemical structure, such as phenyl ether, phenyl ketone, and naphthalene units, contribute towards compatibility in the blend system. Recently, Miyatake et al reported the enhancement in the proton conductivity of aromatic polymer membranes by incorporating acid-functionalized polysilsesquioxane ($\text{IEC} \sim 5.71 \text{ meq g}^{-1}$), whereby the conductivity at low humidity

was significantly improved. The higher conductivity of the composite membranes was believed to be highly relevant with increased IEC value and the improved water-holding capability [18].

The interactions between the N-containing groups and $-\text{SO}_3\text{H}$ groups allows the construction of a ternary system, which is composed of a continuous primary matrix, a molecular-enhancement component and a multi-acid inorganic unit (Figure 1). In this system, DMAc was selected as the solvent to prepare binary blend and ternary composite membranes, and a sol-gel process was adopted to prepare ternary-composite. All the membranes cast from SPAEK/PAM binary-blends at any proportion and from SPAEK/PAM/POSS- SO_3H ternary-composite were uniform and transparent, and their photos are shown in Figure 2.

Fig. 2. Photos of the membranes. (A) Pure SPAEK; (B) Binary blend: PAEK/PAM (90:10); (C) Binary blend: PAEK/PAM (95:5); (D) Ternary composite: SPAEK/PAM/POSS- SO_3H .

4.2 Water Uptake and Swelling Ratio of Membranes

Membranes water uptake is an important PEM property, which is inter-related with proton conductivity and mechanical integrity. While high water uptake generally

leads to high proton conductivity, excessive amounts result in unacceptable levels of dimensional swelling that degrade the mechanical properties and increase methanol diffusion [21]. An optimum water content, which balances high proton conductivity with dimensional stability of the membranes, is a requirement [6]. The temperature dependant water uptake and dimensional swelling ratio of the membranes are shown in Figure 3 and 4.

Fig. 3. Water uptake of the membranes at different temperatures.

For the binary SPAEK/PAM blends, it is clearly observed that water uptake and swelling ratio decreased obviously with increasing the content of PAM, which can be explained by a decrease in the relative non-interacting content of sulfonic acid groups in the blend membranes. The blend membranes exhibited improved dimensional stability in comparison with the pure SPAEK membrane sample. As expected, both

values of water uptake and swelling ratio increased with 15 wt% of THOPS incorporated into the ternary (SPAEK/PAM/POSS-SO₃H) composite membrane, since it contains a multiple sulfonic acid groups. Importantly, the dimensional swelling ratio was maintained at ~22%, which was similar to that of Nafion [24]. Thus, both the binary blend and the ternary composite membranes exhibited good dimensional stability.

Fig. 4. Swelling ratio of the membranes at different temperatures.

4.3 Oxidative Stability of the Membranes

The relative oxidative stability of pure, blend and composite membranes were compared by challenging them with Fenton's Reagent at 80 °C. While hydrocarbon PEMs have been successfully operated in a fuel cell environment for multiple hours, they are known to be very sensitive to the Fenton's test, so the information the test

provides is that of relative oxidative stability. The weight of pure SPAEK membrane retained 88% after treatment in Fenton's reagent for 1 hour, and was completely dissolved within 7 hours. All the blend membranes exhibited improved oxidative stability compared with the primary SPAEK matrix. The retained weight of SPAEK/PAM (90:10) was 97% after treatment in Fenton's reagent for 1 hour and it remained undissolved at 20 hours. The ternary composite SPAEK/PAM/POSS-SO₃H also exhibited much better oxidative stability compared with the pure SPAEK membrane, remaining undissolved at 15 hours. A possible explanation is that the stronger inter-chain interactions induced by acid-base strengthen the polymer matrix, impeding access of the Fenton's reagent to attack the polymer chains within the membrane.

4.4 Proton Conductivity of Pure and Composite Membranes

Proton conductivities of pure SPAEK and the blend and composite membranes were measured at 100% RH and estimated using impedance diagrams. The temperature-dependent conductivity results in Figure 5 show that the conductivities increased with temperature, and decreased with increasing content of PAM. However, the proton conductivity of the ternary membrane was significantly higher than all the other membranes, including the pure SPAEK, membrane at every temperature. For example, at 80 °C, the proton conductivity of the ternary-composite membrane was 0.031 S/cm, which was higher than all the SPAEK/PAM membranes (0.012-0.025 S/cm) and pure SPAEK membrane (0.028 S/cm). This is attributed to the incorporation of the multi-acid POSS inorganic component.

Fig. 5. Proton conductivities of the membranes.

4.5 Methanol Permeability and Selectivity of the membranes

Fig. 6. Methanol permeability of the membranes.

Low methanol permeability is required for the efficient use of PEMs in direct methanol fuel cells (DMFCs) [25]. Membranes should be effective barriers since high diffusion of methanol transported from the anode to the cathode compartment leads to power loss and mixed potentials. One of the most significant drawbacks of Nafion is its high methanol crossover. As shown in Figure 6, the incorporation of minor amounts of PAM component into SPAEK improves the methanol resistance. The methanol permeabilities of the binary blend membranes were in the range of $0.49\text{--}1.19 \times 10^{-7} \text{ cm}^2/\text{s}$, which are over an order of magnitude lower than the value of Nafion 117 ($2.94 \times 10^{-6} \text{ cm}^2/\text{s}$). With the incorporation of the multi-acid POSS component, the methanol permeability increased, but still had a low value of $0.74 \times 10^{-7} \text{ cm}^2/\text{s}$, which was much lower than that of pure SPAEK membrane ($2.65 \times 10^{-7} \text{ cm}^2/\text{s}$) and Nafion.

Fig. 7. Selectivity (proton conductivity/methanol permeability) of the membranes.

PEMs with high proton conductivity and low methanol permeability are preferred for use in DMFCs. The selectivity values shown in Figure 7 are reported as the quotient of proton conductivity at 80 °C divided by methanol permeability. Although the proton conductivities of pure SPAEK and blend/composite membranes were lower than Nafion 117, selectivity values were significantly higher. The ternary-component composite membrane had the highest selectivity of $4.1 \times 10^5 \text{ S} \cdot \text{s} \cdot \text{cm}^{-3}$, which was 7.5 times higher than the value of $5.43 \times 10^4 \text{ S} \cdot \text{s} \cdot \text{cm}^{-3}$ for Nafion 117, which suggest this was the most favorable PEM composition for DMFC applications.

4.6 Morphology of the membranes

(A) Pure SPAEK

(B) Binary blend

(C) Ternary composite

(D) Ternary composite

Fig. 8. SEM photographs of the membranes. (A) Cross-section view of pure SPAEK; (B) Cross-section view of SPAEK/PAM (90:10); (C) Cross-section view of SPAEK/PAM/POSS-SO₃H; (D) Surface view of ternary composite.

Since polymers microstructure influences several aspects of the membrane properties, internal morphology of the membranes was studied by SEM. Figure 8 (A), (B) and (C) are the cross-section photographs of the pure SPAEK, binary blend and ternary composite membranes, which were fractured after treatment in liquid nitrogen. In comparison with pure SPAEK, SPAEK/PAM blend and SPAEK/PAM/POSS-SO₃H composite membranes had more tearing belts, which is believed to be caused by the introduction of the molecular-enhancement PAM component. In the cross-section of the SPAEK/PAM/POSS-SO₃H, a more

1 complicated morphology was observed. Small particles formed by inorganic clusters
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3 were uniformly dispersed throughout the continuous polymer matrix, which are more
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6 clearly seen on the surface of a ternary composite membrane, shown in Figure 8 (D).
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10 11 12 **5. Conclusions**

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14 The properties of PEM membranes based on single component SPAEK,
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16 acid-base binary blends of SPAEK/PAM, and a ternary PEM containing
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18 multi-sulfonated POSS were compared. The introduction of small amounts of
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20 nitrogen-containing PAM into the primary SPAEK primary membrane resulted in
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22 blend membranes having reduced methanol permeability and improved dimensional
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24 and oxidative stability. The ternary composite membrane, wherein sulfonated POSS
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26 was incorporated into the blend membrane by the sol-gel process, exhibited the
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28 highest proton conductivity in comparison with pure SPAEK and binary blend
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30 membranes. The latter membrane also had the highest methanol selectivity,
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32 suggesting this approach may be useful for improving PEM properties for fuel cell
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34 applications.
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