

SPES-SiO₂ Hybrid Proton Exchange Membranes from *In Situ* Sol–Gel Process of Negatively Charged Alkoxysilane

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ABSTRACT: One type of negatively charged alkoxysilane, that is, sulfonated 3-(mercaptopropyl)trimethoxysilane (SMPTS), has been developed from 3-(mercaptopropyl)trimethoxysilane (MPTS) and hydrogen peroxide. SMPTS is used to modify sulfonated poly(ether sulfone) (SPES) through *in situ* sol–gel process. The membranes with proper SMPTS dosage show enhanced ion exchange capacity (IEC), hydrophilicity, mechanical strength, chemical stability, and proton conductivity, which prove that SMPTS is an effective

modifier for preparing proton-exchange hybrid membranes. With MPTS of 5–20%, the hybrid membranes exhibit IEC 1.34–1.50 mmol g⁻¹, thermal stability 264–316°C, and proton conductivity 0.0015–0.0102 S cm⁻¹ and thus recommended for potential application in fuel cells. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 313–320, 2011

Key words: poly(ether sulfones); silicas; polyelectrolytes; thermogravimetric analysis; structure–property relations

INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) systems are gaining intensive attraction during the past decade owing to inherent advantages such as sustained operation at a high current density, low weight, compactness, long stack life, fast start-ups, and suitability for discontinuous operation.¹ The efficiency and durability of PEMFC systems depend much on the characteristics of the membranes. Accordingly, modifications of the conventional polymer membranes are under way, with focus on improvement of the chemical, thermal, and mechanical stabilities, restraint of swelling, decrease in the

dependence of the proton conductivity on the humidity.^{2,3} Among different modification methods, incorporation of inorganic components into organic polymers to get organic–inorganic hybrid membranes is an important means. In some cases, non-charged inorganic fillers such as silica,^{4,5} titania,⁶ and zeolite⁷ are incorporated into organic polymer electrolyte. The strength and stability of the obtained membrane can be improved and the methanol permeability be suppressed. Nevertheless, the membrane charge density is decreased, which generally leads to lower proton conductivity. For further improvement, proton conducting fillers are used, such as inorganic acid (H₃PO₄^{8,9}) and heteropolyacid,^{10–12} etc. Higher proton conductivity can be attained, because the fillers act as H⁺ conducting sites and contribute to the transport activity. However, stability of the membrane is restrained, and the long-time running persistence needs to be considered and improved.

For improving the maintenance of the proton conducting fillers, a different means is applied in the work of some other researchers,^{13–15} for example, inorganic particles [silica, clay, polyhedral oligosilsesquioxane (POSS), and etc] were functionalized with sulfonic acid groups and mixed with the organic polymer matrix. The inorganic network and the hydrogen bonding among sulfonic acid groups can enhance the stability and guarantee the maintenance of the fillers in the membrane matrix. Besides, –OH groups from the inorganic fillers (such as –SiOH) are located in the vicinity of acid groups

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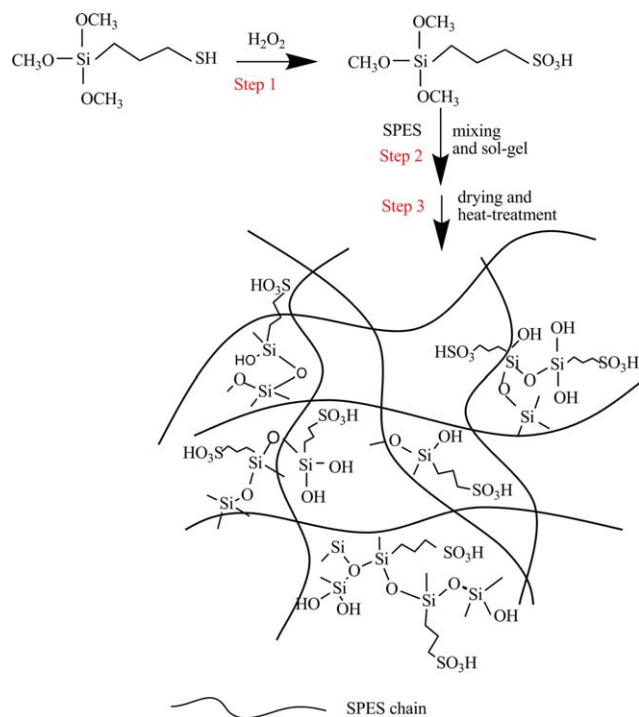
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Scheme 1 The preparation routes for sulfonated poly(ether sulfone) (SPES)-SiO₂ membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(-SO₃H) and can play an important role in increasing water content and capturing water due to their strong hydrogen bonding with water molecules.¹⁶

The aim of our present work is to modify and improve the route above to develop SPES-SiO₂ membranes. One type of negatively charged alkoxy silane, that is, sulfonated 3-(mercaptopropyl)trimethoxysilane (SMPTS) will be prepared and used as an inorganic network precursor and proton conducting enhancer simultaneously for the modification of SPES. Because the silica network is grown *in situ* in the matrix of SPES, more homogeneous disperse can be expected than the system from the mixing of inorganic particles in the polymer.

Here, poly(ether sulfone) (PES) has been chosen as the starting polymer material due to its advantages such as relatively good stability, low price, and easiness of the chemical modification.¹⁷ PES has been widely used for membrane-based processes, including micro-, ultra-, and nanofiltration, reverse osmosis, and diffusion dialysis.^{17–20} Nevertheless, SPES has been less reported for PEMFC application due to the limitation in stability and water resistance. In the present work, the modification by SMPTS is expected to induce improvements of the membrane performances. The membranes characterizations relating the fuel cells applications will be investigated and discussed.

EXPERIMENTAL

Materials

Poly(ether sulfone) (PES) was purchased from Jida High-performance Material Co., of Changchun (China) and sulfonated according to conventional procedures.^{21,22} The ion exchange capacity (IEC) of the SPES is around 0.90 mmol/g. MPTS was from Nanjing Shuguang Chemical Group Co. (China). The other reagents, including toluene, dimethyl formamide (DMF), trimethylamine, ethanol, and hydrogen peroxide, were all of analytical grade and purchased from Shanghai Chemical Reagent Company (China). Deionized water was used all through.

Preparation of the hybrid membranes

The preparation of the hybrid membranes followed three steps:

Step 1: Sulfonation of MPTS.

Sulfonation of MPTS was conducted through the reaction with H₂O₂. Because the alkoxy silicon (-SiOR) groups in MPTS tend to undergo hydrolysis and condensation processes with acid as the catalyst, here, special attention was paid to prevent any undesirable aggregations. No aqueous solution of H₂O₂ was used. Different solvents (ethanol or DMF) were tried, as well as the variations of the reaction temperature, the molar ratio of the starting materials, and the solvent. The final reaction procedures were as following: MPTS (1 mL) was diluted with DMF (75 mL). Then, excessive H₂O₂ [H₂O₂ : MPTS (molar ratio = 20 : 1)] was added. After 10 min of mixing at room temperature, the solution was neutralized with aqueous ammonia (2 mL) and immediately taken for the next step of sol-gel process.

Step 2: *In situ* sol-gel process. SPES (1 g) was dissolved in DMF (2.5 mL) and then mixed with the product from Step 1. Subsequently, water (2 mL) was added, followed by further stirring for 24 h at 40°C.

Step 3: Drying and heat-treatment. The solution from Step 2 was cast onto Teflon plate and dried for 3 days. Then, it was heated from 60 to 120°C at the rate of 10°C/h and kept at 120°C for 3 h.

The above steps were illustrated in Scheme 1.

During the above preparation processes, mass ratio of MPTS to total mass of MPTS + SPES was changed from 5, 15, 20, 30, to 40%. The corresponding membranes obtained were denoted as A, B, C, D, and E (Table I). Pure SPES was also used for membrane preparation, without addition of MPTS.

Characterizations

FTIR spectra for the hybrid membranes and SPES membrane were recorded with a Vector 22 Fourier

TABLE I
The Dosage of MPTS for Preparation of Different Membranes and Their Thermal Degradation Temperature and Proton Conductivity

Membrane	SPES	A	B	C	D	E
Weight ratio of MPTS (%)	0	5	15	20	30	40
T_d (°C) ^a	440	316	308	264	289	252
Conductivity (S cm ⁻¹)	0.0011	0.0015	0.005	0.0102	0.0066	–

^a The thermal degradation temperatures (T_d) are defined as the temperature at which the weight loss reaches 5 wt % in TGA thermograms.

transform infrared spectrometer (Bruker). The thermal properties were investigated by the thermogravimetric analysis (Shimadzu TGA-50H analyzer) under air flow, with a heating rate of 10°C min⁻¹. Instron Universal Tester (Model 1185) was used to measure the tensile properties at 25°C. Dumbbell-shape specimens were used with an initial gauge length of 25 mm and the crosshead speed of 25 mm min⁻¹. The tensile strength (TS) and elongation at break (E_b) values were recorded. Morphology of the cross section of freshly fractured membranes was observed by scanning electron microscopy (XT30 ESEM-TMP PHILIP).

Water uptake (W_R) was measured according to the following procedure²³: the samples were dried in vacuum oven at 80°C until a constant mass m_1 was attained. Then, they were immersed in distilled water for 2 days. Afterward, the surfaces were dried, and the samples were weighed as m_2 . The W_R was calculated according to the equation: $W_R = (m_2 - m_1)/m_1 \times 100\%$.

IEC was measured according to our previous work.²⁴ The samples were first dried to constant mass and then converted to H⁺ form by immersing in 1 mol/L HCl for 2 days. Excess HCl was washed off and then immersed in 0.04 mol/L KOH. Then, the concentration of KOH was back titrated with 0.04 mol/L HCl.

The chemical stabilities of the membranes were investigated by immersing 0.3 g sample in 80-mL H₂O₂ solution (3% mass percent) for 36 h at 30°C. The H₂O₂ solution was renewed every 6 h. The samples were taken out every 6 h, wiped carefully to remove excess liquid, and weighed.

The proton conductivity of the membrane was measured using the normal four-point probe technique according to our previous work.²⁵ The measuring cell in Teflon material consisted of two stainless steel flat outer current-carrying electrodes (2 cm apart) and two platinum wire inner potential-sensing electrodes (1 cm apart). Membrane in 1 cm wide and 4 cm long was fully hydrated and mounted on the cell. The impedance was determined using an Auto lab PGSTAT 302 (Eco Chemie, Netherlands) at galvanostatic mode with ac current amplitude of 0.1 mA over frequency range from 1 MHz to 50 Hz.

The proton conductivity (κ) is calculated according to the following expression:

$$\kappa = \frac{L}{RWd}$$

where R is the obtained membrane resistance, L is the distance between potential-sensing electrodes, and W and d are the wide and thickness of the membrane, respectively.

RESULTS AND DISCUSSION

FTIR spectra

The FTIR spectra of SPES and hybrid membranes A–E are shown in Figure 1. All the hybrid membranes contain the characteristic spectra of SPES including: the bands between ~ 2850 and ~ 3030 cm⁻¹ are from the stretching of CH₃, CH₂, and CH groups²⁶; the bands at ~ 1575 cm⁻¹, ~ 1486 cm⁻¹, and ~ 700 cm⁻¹ are attributed to the phenyl groups (stretching vibration of C=C, in-plane bending vibration of CH₂=, and out-of-plane bending vibration of Ar–H). The intensities of these bands in

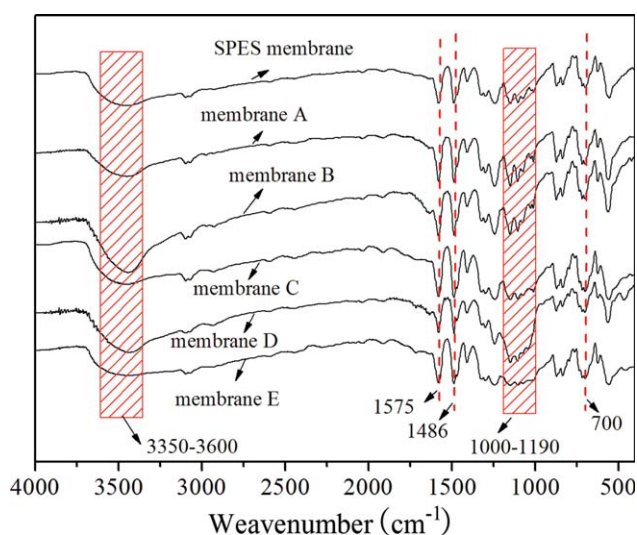


Figure 1 The FTIR spectra of the SPES membrane and the hybrid membranes A–E. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

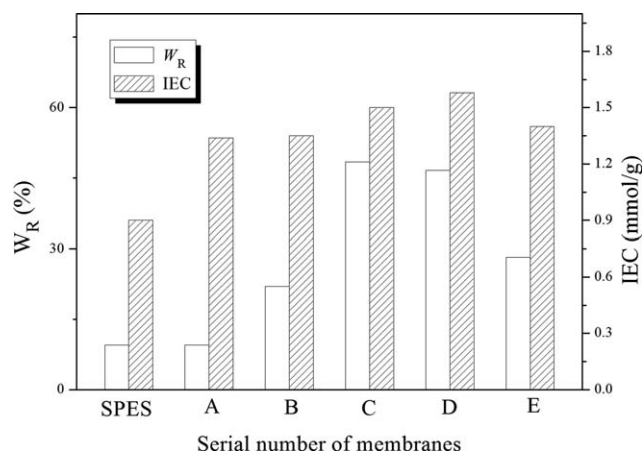


Figure 2 IEC and W_R of the SPES membrane and the hybrid membranes A–E.

different membranes remain similar to each other, because SMPTS makes no contribution to adsorption in these areas. Nevertheless, the bands in the range of 1100–1190 cm^{-1} follow an increasing trend from pure SPES membrane, hybrid membrane A–D. This should be due to the increasing dosage of SMPTS, which contains $-\text{SO}_3\text{H}$ and $-\text{Si}-\text{O}-\text{Si}-$ groups and makes contribution to adsorption in this area, including $-\text{S}=\text{O}$ stretching (~ 1030 and ~ 1180 cm^{-1})²⁷ and $-\text{Si}-\text{O}-\text{Si}-$ stretching (~ 1070 cm^{-1}).²⁸ Besides, the wide adsorption band in the area of 3350–3600 cm^{-1} also gradually becomes more intense. Stretching of $-\text{OH}$ groups from $-\text{SO}_3\text{H}$, $-\text{SiOH}$, and adsorbed H_2O molecules are responsible for the band, and the increase of its intensity indicates the increase of $-\text{SO}_3\text{H}$ group content and hydrophilicity of the membranes. For membrane E, the bands in the area of 1100–1190 cm^{-1} and 3350–3600 cm^{-1} are somehow less intense than membrane D. Hence the content of $-\text{SO}_3\text{H}$, $-\text{Si}-\text{O}-\text{Si}-$, and $-\text{SiOH}$ groups is lower than membrane D. This change trend will be discussed more in the next section.

IEC and water uptake (W_R)

The ion exchange capacity (IEC) and W_R values of SPES and hybrid membranes are collected in Figure 2. The IEC values of the hybrid membranes are in the range of 1.34–1.58 mmol g^{-1} , higher than the value of SPES (0.90 mmol/g). This indicates that SMPTS has a higher charge density than that of SPES.

As SMPTS content increases from membrane A to D, the IEC values increase. Nevertheless, membrane E shows lower IEC than membrane D. This is in accordance to the FTIR observation result but not as expected. For confirmation, we have repeated the membranes preparation processes, and the measured

IEC results still follow the same trend. The abnormally lower IEC of membrane E may be due to loss of the charged component. That is, $-\text{SO}_3\text{H}$ groups may be degraded partially during the heat treatment process (at 120°C for 3 h). For membrane E in which the inorganic–organic phase separation becomes more serious (as will be discussed in SEM section (Morphology Section)), the degradation of $-\text{SO}_3\text{H}$ groups is more serious, leading to its lower IEC.

The hybrid membranes generally exhibit higher W_R values than the SPES membrane. Increase of the hydrophilicity should be due to the increase of $-\text{SO}_3\text{H}$ and $-\text{SiOH}$ groups, both of which exhibit high hydrophilicity. Interestingly, hybrid membrane A has similarly low W_R (9.5%) as SPES membrane, though the IEC of membrane A is obviously higher. Microstructure of the membrane should be the main reason: organic–inorganic interpenetrated network can be formed when low content of silanes is used for sol–gel process in the presence of polymer matrix.¹⁶ Hence the membrane structure is more compact, and the adsorption of water becomes more difficult.

Thermal stability

The TGA and DrTGA diagrams, as shown in Figures 3 and 4, demonstrate that there are three weight loss peaks for all the membranes in the area of 50–120°C, 270–420°C, and 500–600°C, respectively. Because the membranes have been heated at 120°C for 3 h during the preparation process, the first weight loss peak should be mainly due to the evaporation of absorbed water. The second and third weight loss peaks in the range of 270–420°C and 500–600°C are due to the decomposition of the $-\text{SO}_3\text{H}$ groups¹⁶ and the degradation of the main chains of the

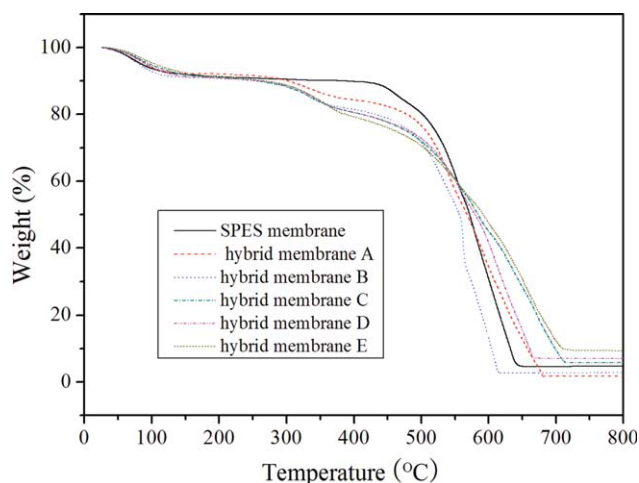


Figure 3 TGA diagrams of the SPES membrane and the hybrid membranes A–E. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

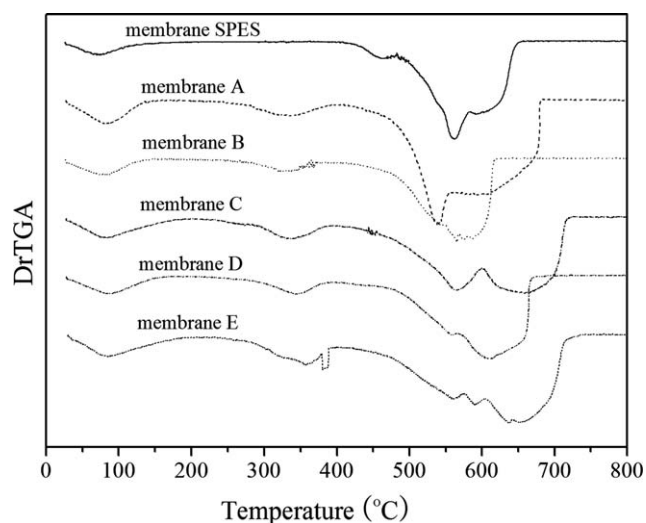


Figure 4 DrTGA diagrams of the SPES membrane and the hybrid membranes A–E.

membranes. The first and second weight loss peaks of SPES membrane are the least significant among all the membranes, indicating its lowest hydrophilicity and $-\text{SO}_3\text{H}$ content and confirming further the IEC and W_R results.

The thermal degradation temperatures (T_d , defined as the temperature at 5% weight loss) are determined (Table I) with neglect of weight loss before 100°C. Comparison of the T_d values of the different membranes indicates that the introduction of SMPTS has induced decrease of the SPES membrane thermal stability because of the increase of the less stable $-\text{SO}_3\text{H}$ groups. Nevertheless, the membrane thermal stability is acceptable when compared with some reported hybrid membranes, such as the sulfonated poly(arylene ether sulfone)-silica membrane, which decomposes at around 250°C,²⁹ and the poly(vinyl alcohol)-silica membrane, which degrades at temperature before 200°C.³⁰

Morphology

For investigating the hybrid membranes microstructure and the compatibility between different components, SEM micrographs of the SPES membrane and hybrid membranes B and D are shown in Figure 5.

Figure 5 shows that the pure SPES membrane is compact and smooth. With 15% MPTS, the membrane B is still compact and generally smooth, though some roughness can be observed. Hence the *in situ* sol-gel process has rendered relatively homogeneous disperse of the silica component in the membrane. With further increase of MPTS, membrane D becomes highly microporous. Aggregation of the silica particles (several micrometers) can be observed. Therefore, the incorporation of high content of SMPTS will decrease the membrane homogeneity.

Proper content of MPTS (<30%) is suggested for maintaining the membrane homogeneity and compactness.

Chemical stability

For simulating the fuel cell operating conditions, the oxidative stability of proton exchange membranes has often been evaluated in strong oxidative circumstances such as 3% H_2O_2 ³¹ or hot Fenton's reagent as an accelerated testing.^{32,33} The former method is also adopted here, and results of hybrid membranes

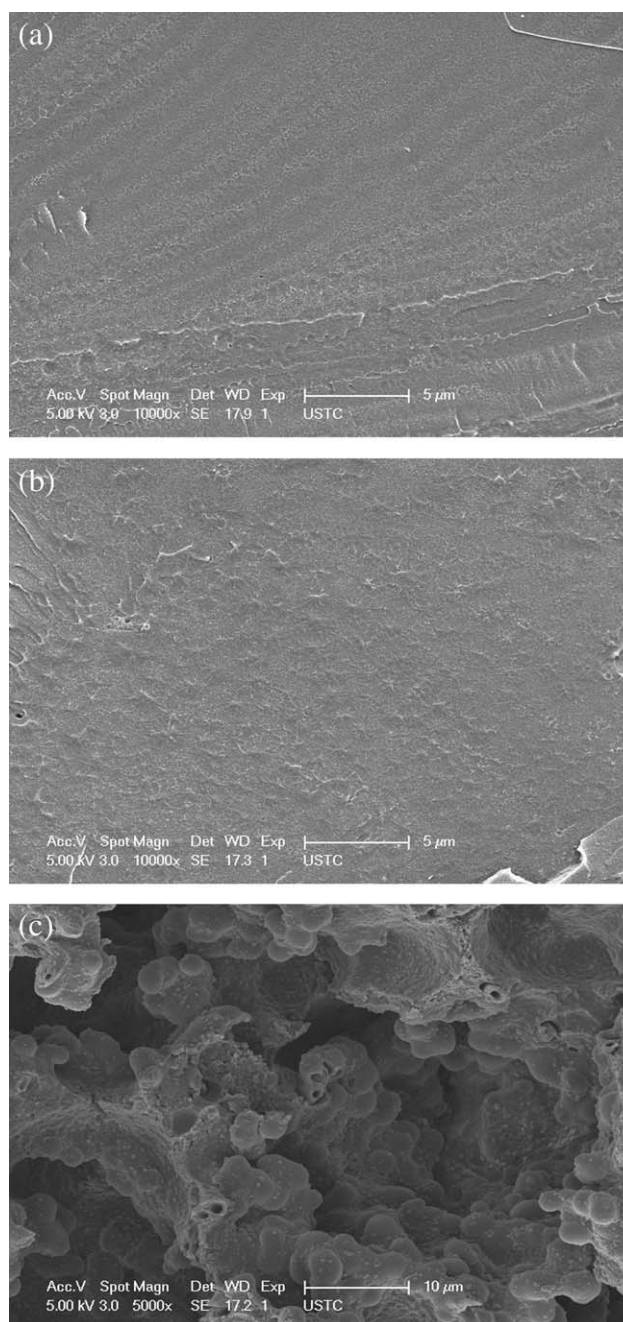


Figure 5 SEM micrographs of (a) the SPES membrane, (b) the hybrid membrane B, and (c) the hybrid membrane D.

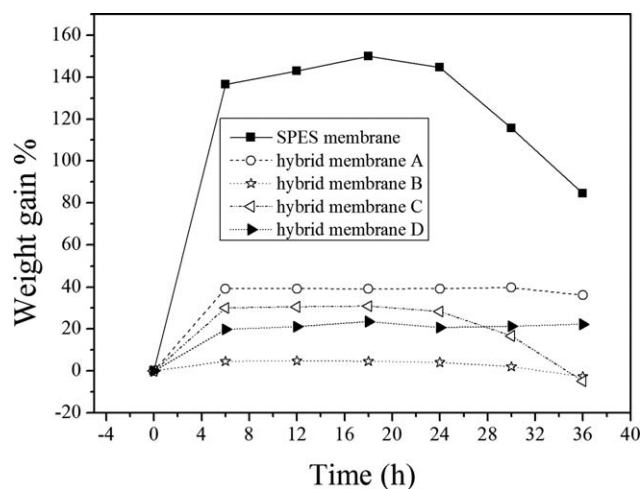


Figure 6 Chemical resistances of the SPES membrane and the hybrid membranes A–D.

A–D, together with the SPES membrane, are shown in Figure 6. The hybrid membrane E becomes brittle when treated with the 3% H_2O_2 solution and therefore no data can be obtained.

The mass of SPES membranes increases first, but then decreases as the time prolongs. Especially, after 24 h, the membrane mass decreases rapidly. When the membrane was soaked in the oxidative solution, there exist two contrary effects—membrane degradation and membrane swelling.³⁴ The predominance of the latter effect brings an increase in membrane mass and vice versa.

For hybrid membranes A–D, mass gains during first 6 h are much slighter (4.6–39.2%) than the SPES membrane (136.5%). After 6 h, mass of hybrid membranes A, B, and D remains almost unchanged. Therefore, the chemical stability has been significantly increased when compared with SPES membrane. This should be due to the incorporation of the silica network in the membranes. Besides, the interaction between SPES and SMPTS components through hydrogen bonding among sulfonic acid groups can also help stabilize the different contents in the membranes. Among different hybrid membranes, the membrane B shows the least significant mass gains as the time prolongs, indicating proper dosage of SMPTS is more favorable for membrane chemical stability. Excessive SMPTS will damage the membrane homogeneity and decrease the chemical stability, as proved by the brittleness of membrane E in 3% H_2O_2 solution.

Tensile properties

The TS and E_b values of hybrid membranes are collected in Figure 7. The pure SPES membrane has relatively poor mechanical properties, with TS of 3.47 MPa and E_b of 2.58%. After 5 and 15% addition of

MPTS (the membranes A and B), the mechanical strength and the flexibility are enhanced significantly (18.0 MPa and 10.3% for the membrane A and 22.7 MPa and 12.1% for the membrane B). The TS value is comparable with the value of Nafion membrane (21.04 MPa),¹⁶ indicating the excellent strength of the hybrid membranes A and B. With further increase of MPTS for membrane C and D, nevertheless, TS and E_b values decrease. Membrane E is brittle and not suitable for the measurement.

Different effects should be considered to understand the above change trend of the mechanical properties: the content of $-\text{SO}_3\text{H}$ group increases after incorporation of SMPTS. The hydrophilic character of sulfonic groups can allow water to act as an external plasticizer, and, accordingly, polymer chain mobility is increased.¹⁷ Besides, interpenetrated organic–inorganic network can be formed at low-SMPTS content. Therefore, both flexibility and strength of the membranes are improved. At higher SMPTS content, the homogeneity of the membranes decreases. Inorganic aggregations and particles are formed, rather than the interpenetrated organic–inorganic network.¹⁶ Therefore, the mechanical strength and flexibility both decrease.

Membrane conductivity

The proton conductivity values of the SPES and hybrid membrane A–D are listed in Table I. No conductivity value can be obtained for membrane E due to its brittleness. The SPES membrane has a low conductivity of 0.0011 S cm^{-1} , and the proton conductivity of hybrid membranes is improved to the values $0.0015\text{--}0.0102 \text{ S cm}^{-1}$. Therefore, the addition of SMPTS is advantageous for conductivity of the protons.

Up to now, there are intensive debates as for the H^+ transport mechanisms in the proton conducting

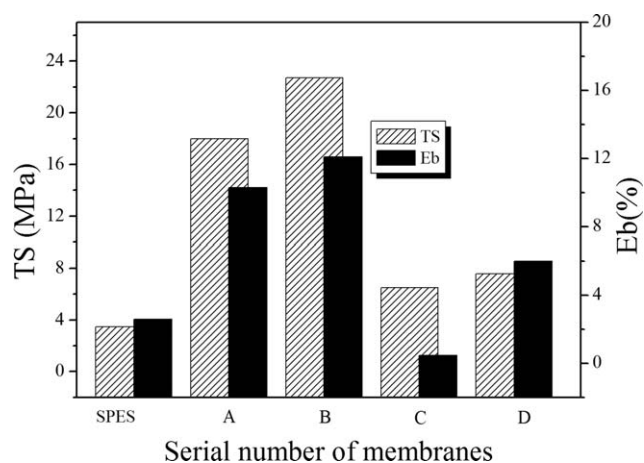


Figure 7 TS and E_b of the SPES membrane and the hybrid membranes A–D.

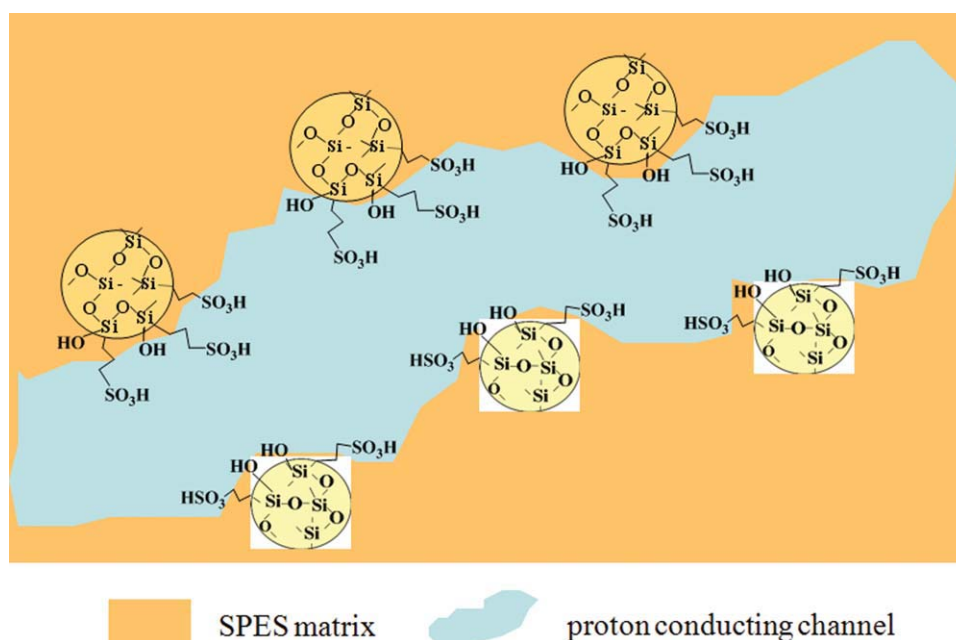


Figure 8 Illustration of the disperse of the silica component in the SPES matrix to form proton-conducting channels. The contribution from SPES is not shown for simplification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membranes. Different mechanisms are suggested, including Grotthuss, en masse diffusion, migration, surface site hopping, convective processes, or their combinations.^{35–38} Nevertheless, it is agreed that the Grotthuss mechanism, that is, proton transfer through H-bond breaking and forming process, is at least a contributing mechanism at higher membrane water contents.³⁹ Besides, the importance of some vital properties of the polyelectrolyte membrane, such as the content of the charged groups, the hydrophilicity, the formation, and connection of proton transfer channel, is agreed by most literature. With these understanding, the influence of SMPTS on the membrane conductivity can be well appreciated: the membrane IEC as well as the hydrophilicity is increased, and hydrogen bonding between Si–OH and H⁺ is introduced. These are all favorable for membrane conductivity. Another peculiarity of our membranes lies in that the proton conducting –SO₃H groups from SMPTS are covalently cross-linked with the inorganic silica component. Hence the highly hydrophilic channels from –SiOH groups are located in the vicinity of the proton conducting acid clusters (as illustrated by Fig. 8), which can facilitate the proton transport and help in decreasing the negative effect of the silica aggregation on the membrane conductivity. For instance, membrane D, which contains silica particles of several micrometers, behaves conductivity lower than membrane C, but obviously higher than SPES membrane and hybrid membranes A–B. Therefore, the particle size of the fillers has not significantly hindered the proton transport in the hybrid membranes, which is

in accordance with the conclusion of previous research.¹⁷

CONCLUSIONS

Negatively charged alkoxy silane, that is, SMPTS, has been prepared and used as both an inorganic filler and charge density enhancer for SPES through *in situ* sol–gel process. The hybrid membranes with proper dosage of SMPTS can exhibit higher mechanical strength and chemical stability when compared with SPES membrane. Hybrid membrane A with 5% shows TS value of 18.0 MPa and E_b value of 10.3%, while hybrid membrane B with 15% MPTS shows TS of 22.7 MPa and E_b of 12.1%. Excessive SMPTS decreases the homogeneity of the membranes and induce decrease of the membrane performances.

When compared with conventional noncharged fillers, the merit and peculiarity of SMPTS lie in that the proton-conducting –SO₃H groups are covalently crosslinked with the alkoxy silane [–Si(OR)] groups. Hence, the IEC is increased, and the highly hydrophilic channel by –SiOH groups is located in the vicinity of the proton-conducting acid clusters. Both can facilitate proton transfer in the membrane, and thus the proton conductivity is increased.

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