Influence of silica content in sulfonated polysulfone/phosphotungstic acid hybrid membranes on properties for fuel cell application

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Abstract: The sulfonated polysulfone (SPSU)/phosphotungstic acid (PWA)/silica (SiO_2) hybrid membranes were researched for proton exchange membranes. The influence of silica content on the properties of composite membranes was studied in detail. The study displays that inorganic silica particles have a great influence on membrane properties, such as membrane durability, PWA extraction, proton and methanol transport behavior, thermal stability and water uptake. Interestingly, the hybrid membrane with 2 wt.% silica content showed the best results: low PWA extraction, long membrane life time under oxidative condition, high proton conductivity, and low methanol permeability. However, excessive silica content caused a large aggregation of SiO_2 particles, leading to the deterioration of membrane properties.

Introduction

Direct methanol fuel cells (DMFC) have attracted considerable attention for potential applications and advantages in view of their low weight, easy manipulation, high efficiency and low poison emission [1-4]. However, the current industry standard perfluorosulfonic polymers such as Nafion are limited by (a) high cost (b) high methanol permeability, and (c) loss of membrane performance at elevated temperatures. To overcome these drawbacks, in the past years, two classes of materials were investigated. One is polymeric material, including polysulfones [5-8], polyimides [9, 10], polybenzimidazoles [11-13] and poly(ether ether ketone) [14,15] with diverse mechanical and electrical properties, higher efficiency and low cost. The other is organic-inorganic composite material with special interactions between organic and inorganic parts, which offers exceptional opportunities to create materials with unique properties. Among them the incorporation of highly conductive ($0.02\text{-}0.1\text{ s}\cdot\text{cm}^{-1}$ at room temperature) heteropolyacid such as phosphotungstic acid (PWA) and silicotungstic acid (SiWA) has shown encouraging results [16-19]. However, PWA or SiWA itself is water soluble, and is easily extracted from the composite membranes in the presence of hot water, which would result in a decrease in proton conductivity and other desirable performance. To manage this drawback, one can immobilize PWA inside a silica matrix.

Therefore, in this paper, a kind of organic/inorganic composite membranes consisting of SPSU, PWA and SiO₂ have been researched for proton exchange membranes. The main goal of this study is to systematically investigate the influence of silica content on the nanostructures and properties of the SPSU/PWA/SiO₂ nanocomposite membranes and discuss the optimization of SiO₂ content in the composite membranes with superior properties.

Results and discussion

Thermal stability

The TGA curves of SPSU/PWA/SiO₂ composite membranes measured under flowing nitrogen are shown in Fig.1. Thermal stability of the composites is observed at around 250-300 °C where the first weight losses occur; the second weight loss are observed around 400 °C. The former is assigned to sulfonic acid groups' elimination, and the latter is identified as SPSU backbone degradation. In addition, the weight remaining after the polymer decomposition depends on the content of the inorganic component. That is, the weight residues of the composite membranes with 0 wt.%, 4.8 wt.%, 16.7 wt.% and 23 wt.% silica at T=700 °C is 27.2%, 32.2%, 39.4%, and 50%, respectively. The result suggests that the introduction of silica into the SPSU chains enhances the thermal stability of the given hybrid materials. The increase in the thermal stability may have resulted from the high thermal stability of silica and the crosslink point of the silica particles [23].

Fig. 1. TGA curves of SPSU/PWA/SiO₂ composite membranes. 1: SPSU; 2: SPSU/PWA; 3: SPSU/PWA/SiO₂-4.8%; 4: SPSU/PWA/SiO₂-16.7%; 5: SPSU/PWA/SiO₂-23%

Morphology studies

Fig. 2. displays the electron micrographs of SPSU/PWA/SiO₂ composite membranes with 1wt.%, 2wt.% and 4.8wt.% of silica content. From Fig. 2(a),(b), it can be seen that the SiO₂ and PWA particles are uniformly and well distributed over the membrane and do not form any agglomerations. The size of SiO₂ and PWA particles is observed to be around 30 nm. The silica particles in the composite membrane

containing 4.8 wt.% silica content show less uniformity in their distribution (Fig.2(c)). We can observe that the SiO_2 filler dispersion is not homogeneous, but aggregates of some micron are formed, which will become larger and more continuous by increasing the silica content.

Fig. 2. SEM of composite membranes: (a) 1% silica; (b) 2% silica; (c) 4.8% silica.

Water uptake

The room temperature water uptake of SPSU/PWA/ SiO_2 composite membranes as a function of silica content is shown in Fig. 3.

Fig. 3. Influence of silica content on the water uptake of composite membranes.

As expected, the water uptake of the composite membrane increases as the silica particles content increase. For example, the water uptake of the film containing 2 wt.% silica is 21.3%, while the film loaded with 33.3 wt.% silica showed a water uptake of 31.6%. The introduction of silica enhances the membrane hydrophilicity due to the presence of numerous $\equiv\text{SiOH}$ groups in the composites, which can form strong bonding with H_2O molecules.

PWA extraction

The extraction of PWA is detected by UV-Vis recording spectrophotometer as mentioned after treatment in water and given in Table1. Differing from the general expectation that an increasing quantity of silica leads to a consecutive decrease of PWA extraction from the SPSU/PWA/ SiO_2 composite membranes, a peculiar PWA extraction behavior is observed at SiO_2 content above 2 wt.%. When SiO_2 content is below 2 wt.%, PWA is stabilized within the silica skeleton, and the PWA extraction leaked out from the composites is negligible. However, it weakens the PWA stability of the corresponding composite membranes when SiO_2 content above 2 wt.%. This phenomenon can be well interpreted by morphology of composite membranes with different SiO_2 content. The more well-dispersed SiO_2 nanoparticles, the more PWA molecules were fixup tightly. However, SiO_2 nanoparticles begin to aggregate over 2 wt.%, that is why the stabilization of PWA within the silica skeleton is weakened.

Tab. 1. PWA extraction from composite membranes in water.

Membranes	PWA extraction (%)		
	24h	48h	72h
SPSU/PWA	2.00	3.52	4.65
SPSU/PWA/ SiO_2 -1.0%	1.10	1.49	2.05
SPSU/PWA/ SiO_2 -2.0%	0.15	0.26	0.33
SPSU/PWA/ SiO_2 -4.8%	0.33	0.52	0.62
SPSU/PWA/ SiO_2 -9.0%	2.00	3.22	5.53
SPSU/PWA/ SiO_2 -16.7%	2.65	4.20	5.54
SPSU/PWA/ SiO_2 -23%	2.61	3.40	5.06

Chemical stability and mechanical properties

Table 2 gives examples for improvement of the oxidative stability of SPSU/PWA composite membranes via the incorporation of SiO_2 particles. Hydrophilic silica particles seem to be effective in enhancing the tolerance of a radical attack dependent of SiO_2 particles dispersion. This trend could be clearly observed in Table 2. Furthermore, the highest tolerance to free radical attack is observed in the composite membrane with 2 wt.% silica content. The addition of silica above 2 wt.% induces irregular aggregation of silica particles within the SPSU matrix, which is consistent with its nanostructure in SEM picture (Fig.3c), and weakens the chemical stability of the corresponding composite membranes.

The mechanical properties in Table 2 list physical parameters important in investigating optimal SiO_2 content. The SiO_2 particles act as reinforcing agents improving the tensile strength of SPSU/PWA/ SiO_2 composite membranes, but decreasing the elongation at break. However, adding excessive SiO_2 content weakens both its tensile strength and elongation. In particular, the worsening of mechanical properties is visible at SiO_2 content over 4.8 wt.%.

Tab. 2. Oxidative stabilities and mechanical properties of composite membranes.

Membranes	Dissolving time(min)	Tensile strength(Mpa)	Elongation(%)
SPSU/PWA	420	49.2	10.9
SPSU/PWA/SiO ₂ -1.0%	900	66.7	10.6
SPSU/PWA/SiO ₂ -2.0%	1410	66.9	8.3
SPSU/PWA/SiO ₂ -4.8%	1200	49.6	6.5
SPSU/PWA/SiO ₂ -9.0%	1020	43.7	3.7
SPSU/PWA/SiO ₂ -16.7%	600	29.5	2.6
SPSU/PWA/SiO ₂ -23%	510	16.4	1.8

Proton conductivity

Fig. 4 shows the proton conductivities of SPSU/PWA/SiO₂ composite membranes with various content of SiO₂ content at 30°C and 80°C. In region I, it is apparent that the addition of silica below 2 wt.% seems to be somewhat effective in increasing the proton conductivity. This phenomenon is consistent with those reported by others [24, 25]. However, in region II, an excess of the silica phase could result in a counter effect. It is considered that an excess of the silica phase inhibits proton conduction in the membrane [26, 27]. With the silica content 2 wt.%, the proton conductivity of the composites at 80 °C is 0.134 s·cm⁻¹, which is comparable to the result of Nafion 117 at the same test conditions.

Fig. 4. Effect of SiO₂ content on proton conductivity in the composite membranes.

Methanol permeability

Fig.5(a) shows the methanol permeability of the SPSU/PWA/SiO₂ composite membranes. In region I, for these membranes, the values decrease with the existence of SiO₂. In particular, the lowest methanol permeability is also observed in the composite with 2 wt.% SiO₂ content and its methanol permeability, at 30 °C and 80 °C, is $3.46 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ and $7.5 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively, which is about an order of magnitude lower than Nafion 117. The well-dispersed SiO₂ nanoparticles play an

important role in decreasing permeability via reduction of free volume within the SPSU matrix. However, in region II, the excess addition of silica content results in aggregation of silica particles within the SPSU matrix, also resulting in a counter effect. An agglomeration of the SiO_2 nanoparticles physically hinders interaction among SPSU chains, and their average interchain distance increases, which results in low methanol barrier properties. These analyses imply that the composites with higher content of SiO_2 do not always show better cell performance.

Fig. 5. (a) Effect of SiO_2 content on methanol permeability in the composite membranes; Fig. 5(b) Proton conductivities versus methanol permeabilities (1: 0% silica content; 2: 1% silica content; 3: 2% silica content; 4: 4.8% silica content; 5: 9% silica content; 6: 16.7% silica content)

Fig. 5(b) shows the proton conductivities and methanol permeabilities of hybrid membranes and Nafion 117 at 30°C and 80°C . Generally, the proton conductivity has a strong trade-off relationship with the methanol permeability [28]. A target membrane would be located in the upper left-hand corner. From the picture, we can see that the optimum silica content in the composite membranes is about 2 wt.%. The membranes with above 2 wt.% silica content (from point 4 to 6) show a very vertical trend. That means the methanol permeability of membranes with above 2 wt.% silica remains unchanged, while the proton conductivity decreases abruptly.

Conclusions

SPSU/PWA/ SiO_2 composite membranes with different SiO_2 weight content were researched for DMFC. The study showed that SiO_2 content plays an important role in microstructures and membrane properties. The results showed that well-dispersed SiO_2 nanoparticles is effective in lowering PWA extraction and methanol permeability and enhancing proton conductivity in nanocomposite membranes. PWA stability within the silica skeleton increased up to 2 wt.% SiO_2 , but rapidly decreased above about 5 wt.%. The trends in methanol barrier property, chemical stability and mechanical properties were very similar to those of the PWA stability within the SPSU matrix. The composite membrane with 2 wt.% silica content showed the best

results, whereas excessive silica content caused a large aggregation of SiO₂ particles, leading to the deterioration of membrane properties. In the present study, the optimum silica content in the nanocomposite membranes is about 2 wt.%.

Experimental

Materials

Sulfonated polysulfone was prepared via a direct sulfonation method as described in our previous work [20]. The chemical structure and the preparation of SPSU are shown in Scheme 1. PWA was obtained from chemical plants in Shanghai, China and was used as received. Silica gel was obtained from Qingdao Haiyang Chemical Group Company.

Scheme 1. The preparation of SPSU.

Preparation of the composite membrane

PWA supported on silica gel was prepared by using PWA and silica gel. An appropriate amount of PWA was mixed with silica gel in a water solution. Subsequently, it was stirred in an ultrasonic bath for 30 min. Then the suspension was dried at room temperature. The resulting solid material was crushed in an agate-mortar to obtain a fine powder and then it was further dried at 50 °C for 2 h.

The synthesized SPSU with a degree of sulfonation (DS) of 53% was used for preparing all the composites. An appropriate amount 20% SPSU solution was mixed with PWA or PWA/SiO₂ powders (weight ratio, SPSU: PWA=8:2) in an ultrasonic bath for 30 min. The composite membranes were prepared by solution casting. The resulting films were transparent with a yellowish color and a thickness of about 50~150 μm.

Characterization

The degradation process and the thermal stability of the samples were investigated using thermogravimetry analysis (TG 209 F1 Iris). The TGA measurements were then carried out under a nitrogen atmosphere using a heating rate of 10 °C·min⁻¹ from 30 °C to 700 °C.

SEM imaging was done to evaluate the uniformity of the dispersion of additives in the membrane and the additive particle/agglomerate size. The imaging was done using a S-3000N SEM. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Au prior to SEM examination.

Water uptake experiment was carried out by immersing the dried membranes in de-ionized water at room temperature for 24 h in order to understand the amount of water uptake before and after treatment. For measurement, the membranes were taken out, wiped with filter paper, and immediately weighed. The amount of water-uptake, W_{H_2O} , was calculated using following equation:

$$W_{H_2O}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where W_{wet} is the mass of the membrane in grams after absorption and W_{dry} is the mass of the dried membrane in grams.

The amount of PWA extracted from the composite membranes in water was determined with UV-Vis recording spectrophotometer. Before immersing in 30 mL de-ionized water at 60 °C for some time, the prepared dry composite films were weighed. The solvent with extracted PWA was put into a quartz cell and then measured at 260 nm, which shows the maximum absorption spectrum. We can get the extracted PWA concentration (C) from the concentration-absorption UV-Vis spectrum graph and the PWA extraction (%) was determined from:

$$PWA \text{ extraction } (\%) = \frac{C \times 30\text{mL}}{\text{weight of PWA in sample}} \times 100 \quad (2)$$

The resistance to hydrogen peroxide radical was examined in Fenton's reagents (a 3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C. The anti-oxidative stability was characterized by the expended time that the membrane started to break into pieces and disappear into solution. Each measurement was carried out repeatedly at last five times to ensure good reproducibility.

Mechanical properties test was measured using an Universal Materials Testing Machine at strain rate of $10 \text{ mm} \cdot \text{min}^{-1}$ on 4 mm wide×15 mm long samples.

Membranes equilibrated during immersion in water at room temperature were investigated through determining impedances of SPSU membrane samples to evaluate the proton conductivity (σ). The impedances were determined by using the self-made equipment by alternating current [21], The proton conductivity was calculated from following equation:

$$\sigma = \frac{l}{R \times S} \quad (3)$$

where σ is proton conductivity ($\text{s} \cdot \text{cm}^{-1}$); R is the ohmic resistance of membrane sample (Ω); l is the distance between the electrodes (cm); S is the face area of membrane sample (cm^2).

The methanol permeability of the composite membranes was determined through a glass diffusion cell [22]. The glass cell consisted of two compartments. One compartment (V_A) was filled with a 10 M methanol solution. The other (V_B) was filled with de-ionized water. The membrane was clamped between the two compartments and these kept under stirring during the experiment. A flux of methanol penetrates across the membrane as a result of the concentration difference between the two compartments. Under pseudo steady-state condition, which prevailed during the experiment and for $c_B \gg c_A$, the methanol concentration in the receiving compartment as a function of time is given by following equation:

$$Dc_B = \frac{A}{V_B} \times \frac{DK}{L} c_A \times Dt \quad (4)$$

where c is concentration, $A(\text{cm}^2)$ and $L(\text{cm})$ the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The assumptions are made in this study that D inside the membrane is constant and K does not depend on concentration. The product DK is the membrane permeability (P).

$$P = \frac{L}{A} \times \frac{Dc_B}{c_A Dt} \times V_B \quad (5)$$

where c_B was measured several times during the experiment and the permeability is calculated from the slope of the straight line. The methanol concentrations with time were measured using a gas chromatograph. The temperature was kept constant in a thermostatic water bath.

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