



Preparation and characterization of self-crosslinked organic/inorganic proton exchange membranes

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ABSTRACT

A series of silicon-containing sulfonated polystyrene/acrylate (Si-sPS/A) nanoparticles are successfully synthesized via simple emulsion polymerization method. The Si-sPS/A latexes show good film-forming capability and the self-crosslinked organic/inorganic proton exchange membranes are prepared by pouring the Si-sPS/A nanoparticle latexes into glass plates and drying at 60 °C for 10 h and 120 °C for 2 h. The potential of the membranes in direct methanol fuel cells (DMFCs) is characterized preliminarily by studying their thermal stability, ion-exchange capacity, water uptake, methanol diffusion coefficient, proton conductivity and selectivity (proton conductivity/methanol diffusion coefficient). The results indicate that these membranes possess excellent thermal stability and methanol barrier due to the existence of self-crosslinked silica network. In addition, the proton conductivity of the membranes is in the range of 10^{-3} – 10^{-2} S cm⁻¹ and all the membranes show much higher selectivity in comparison with Nafion[®] 117. These results suggest that the self-crosslinked organic/inorganic proton exchange membranes are particularly promising in DMFC applications.

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1. Introduction

The direct methanol fuel cells (DMFCs) using proton exchange membranes (PEMs) are promising energy conversion devices owing to their high energy efficiency, low emission, stable and simple operating conditions at a relatively low temperature, no requirement of fuel reforming process and environmentally friendly nature [1–3]. In DMFCs, the principal function of the PEMs is to allow the transport of protons from the anode to cathode, while prohibiting direct contact of the fuel and the oxidant. Thus, the performance of PEMs is crucial to the functioning of DMFCs. Currently, sulfonated perfluorinated polymers like Dupont's Nafion[®] are the most commonly available PEMs because of their excellent chemical and physical properties and high proton conductivity. However, the expensive cost, high methanol diffusion, loss of conductivity at high temperature (>80 °C) and difficulty in synthesis and processing have limited their wide commercialization [4,5]. In particular, the high methanol diffusion from the anode to the cathode across the PEM not only wastes fuel but also causes catalyst poisoning as well as energy efficiency and performance losses [6]. Thus, to improve the performance of DMFCs, especially to reduce the methanol dif-

fusion, considerable efforts have been devoted to modify Nafion[®] membrane or to develop alternative new nonperfluorinated PEM materials.

Crosslinking is an effective and simple method to enhance stability and mechanical property of membranes, in particular, to limit the overfull water swelling and methanol diffusion [7–10]. Therefore, for the PEMs used in DMFCs, crosslinking techniques have received extensive attention. In addition, organic/inorganic composites also constitute an emerging research field due to their advantages in improving mechanical and thermal properties as well as proton conductivity [11–14].

In this paper, we synthesize a series of silicon-containing sulfonated polystyrene/acrylate (Si-sPS/A) nanoparticles via emulsion polymerization. The incorporation of Si(OR)₃ groups in nanoparticles using vinyltriethoxysilicone as a functional (co)monomer during emulsion polymerization offers two functions: first, silicon-containing polymers could present high thermal and chemical stability [15]. Second, the hydrolysis and condensation reactions of Si(OR)₃ groups could lead to a self-crosslinked silica network in membranes [16,17]. The formation of self-crosslinked silica network not only can suppress the swelling and methanol diffusion but also can improve the stability, water retention and mechanical strength of PEM. Hence, the self-crosslinked organic/inorganic proton exchange membranes may have good potential in DMFC applications.

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Table 1
Recipes and properties of the Si-sPS/A latexes and membranes.

	Si-sPS/A-1	Si-sPS/A-2	Si-sPS/A-3
St (g)	1.8	1.8	1.8
BA (g)	7.2	7.2	7.2
MAA (g)	1.015	1.015	1.015
VTES (g)	1.84	1.84	1.84
TrEGDMA (g)	0.5	0.5	0.5
NaSS (g)	1.0	1.5	2.0
HEMA (g)	1.0	1.0	1.0
Solid content (%)	13.9	14.8	15.5
Conversion (%)	92.2	95.6	97.1
Particle size (nm)	141.6	117.1	105.9
Polydispersity	0.042	0.066	0.009
IEC ^a (mmol g ⁻¹)	0.35	0.50	0.65
IEC ^b (mmol g ⁻¹)	0.28	0.43	0.59

^a IEC obtained by calculation.

^b IEC obtained by titration.

sequently, the membrane was rinsed repeatedly with deionized water to remove any excess acid and stored in deionized water for further analysis. The surface morphology of the resulted PEMs was measured by SEM to characterize their roughness. No cracks were found on the surface of PEMs and the surface was smooth.

2.4. Measurements

The particle size and polydispersity of the latex particles were measured using ZetaPALS dynamic light scattering (DLS) detector (BI-90Plus, Brookhaven Instruments Corporation, Holtsville, NY, 15 mW laser, incident beam = 660 nm) at 25 °C. The scattering angle was fixed at 90°. The samples were highly diluted ($C < 0.01$ wt.%) before testing to prevent multiple scattering.

The Fourier transform infrared (FTIR) measurement was performed on a Nicolet Instruments Research Series 5PC Fourier Transform Infrared Spectrometer. For all samples, KBr pellets were prepared and measured in the range from 4000 to 400 cm⁻¹.

The thermal stability of membranes was investigated through the thermogravimetric analysis (TGA) experiment using a Pyris 1TGA (PerkinElmer) at a heating rate of 10 °C min⁻¹ in N₂ flow.

The theoretical IEC value was calculated as the quotient of the molar content of the sulfonic acid groups and the membrane weight in feed. The titrated IEC value was determined as follows. The membrane in acid form was immersed in 1.0 M NaCl solution for 24 h to replace the protons of sulfonic acid groups with sodium ions. Then the replaced protons were titrated using 0.01 M NaOH solution. The IEC was calculated according to the equation:

$$\text{IEC} = \frac{C \times V}{M} \times 100$$

where C and V are the normality and the volume of NaOH solution, respectively. M is the weight of membrane.

Before measuring the water uptake, the membrane was vacuum-dried at 100 °C until constant weight was obtained. The dried membrane was immersed in deionized water for 24 h at different temperatures. Subsequently, the membrane was taken out and immediately weighed after wiping out the surface water. The water uptake was calculated as the percent of weight increase in the membrane with respect to the weight of the original membrane.

The methanol diffusion coefficient was determined using a glass diffusion cell as described elsewhere [18]. This cell consisted of two compartments and membrane was clamped between the two compartments. Prior to testing, the membrane was hydrated in deionized water for at least 24 h. 2 M methanol was placed on one compartment and water was placed on the other one. Both closed compartments were magnetically stirred during the measurement. The increases in concentration of methanol in the water

compartment with time were measured using a SHTMADU GC-8A gas chromatograph. The methanol diffusion coefficient was calculated as follows:

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

where A , L and V_B are the effective area, the thickness of membrane and the volume of permeated compartment, respectively. C_A and C_B are the methanol concentration in feed and in permeated compartments, respectively. DK is the methanol diffusion coefficient.

Proton conductivity measurement was carried out using an SI 1260+SI 1287 impedance analyzer over the frequency range of 10–10⁶ Hz. The conductivity cell composed of two stainless steel electrodes. Before measurement, the membrane was hydrated in distilled deionized water for at least 24 h. Then the hydrated membrane was sandwiched between two electrodes and placed in a temperature-controlled cell containing distilled deionized water. The impedance measurement was performed at desired temperature and the proton conductivity was determined by

$$\sigma = \frac{d}{Rtw}$$

where d is the distance between the electrodes, t and w are the thickness and width of the membrane, respectively. R is the resistance value from the impedance data.

3. Results and discussion

3.1. Latex particles analysis

To obtain latex particles capable of forming the proton exchange membrane with suitable mechanical strength, a variety of monomers including St, BA, TrEGDMA, VTES, MAA and HEMA were copolymerized with NaSS in this study. The monomer conversion, particle size and polydispersity of the resulting latex particles are listed in Table 1. It is clear that the Si-sPS/A latexes showed high monomer conversion (>92.2%) that was determined gravimetrically via the solids content. Furthermore, DLS measurement exhibited that the particle sizes of the Si-sPS/A particles decreased from 141.6 to 105.9 nm as increasing the amount of NaSS in the feed. The decrease in diameter is due to the well-known surfactant effect. The charged monomer NaSS acted as a polymerizable surfactant tends to locate on the surface of polymer particles and provides stability to the particles in the polymerization. Therefore, the colloidal stability increased and particles sizes decreased with increasing amount of NaSS [19].

3.2. FTIR study

The chemical structures of Si-sPS/A membranes with different IEC values were characterized by FTIR. It can be seen from Fig. 1 that all the samples exhibit the characteristic stretching peaks of C–H (CH₂) at 2959 and 2873 cm⁻¹, stretching vibration of C=O at 1735 cm⁻¹, and distortion vibration of CH₂ at 1457 and 1392 cm⁻¹. Moreover, the peak at 1114 cm⁻¹ corresponded to the Si–O–Si asymmetric stretching [20]. The existence of Si–O–Si peak proved the occurrence of hydrolysis and condensation reactions (crosslinking) of Si(OR)₃ groups and suggested the formation of crosslinked silica network structure in the membranes. The characteristic peaks at 1034 and 1004 cm⁻¹ represented the symmetric stretching vibration of SO₃⁻ and in-plane bending of para-substituted phenyl ring [21,22], respectively. The intensities of these two peaks increased with the increment of IEC. Furthermore, the broad peak at around 3440 cm⁻¹ corresponded to –OH stretching vibration owing to the presence of SO₃H groups and absorbed water, and this peak also showed an increasing tendency as the IEC increased. The

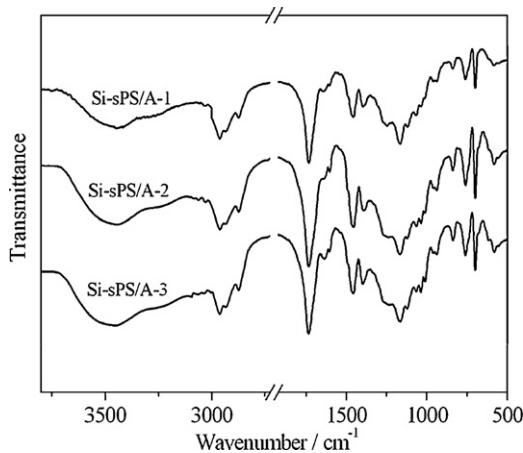


Fig. 1. FTIR spectra of Si-sPS/A membranes with different IEC values.

FTIR spectra study clearly indicated that the polymerization and hydrolysis-condensation reactions were carried out successfully. That is, the self-crosslinked organic/inorganic proton exchange membranes were fabricated as desired.

3.3. Thermal stability

The TGA measurement was conducted to evaluate the thermal stability of the membranes. Prior to testing, all the samples were preheated to 150 °C and kept at this temperature for 20 min to remove moisture, followed the samples were cooled to 100 °C and then reheated to 700 °C at 10 °C min⁻¹ under nitrogen atmosphere. The TGA curves of the Si-sPS/A membranes are shown in Fig. 2. It was obvious that all the membranes exhibited a two-step degradation curve. The first weight loss occurring at around 260–400 °C was attributed to the splitting-off of sulfonic acid groups, and the mass losses at this temperature range increased with the rise of IEC. Above 400 °C, the membranes underwent the second degradation step, which corresponded to the decomposition of the main chain and crosslinking bridge. The inspections of the thermograms suggested that the Si-sPS/A membranes had good thermal stability, which could be explained as follows. First, the Si–O bond energy was higher than that of C–C bond [23]. Second, the hydrolysis and condensation reactions of Si(OR)₃ groups in membrane led to the formation of crosslinked silica network structure, which made the membrane more compact and hence improved the thermal stability [24].

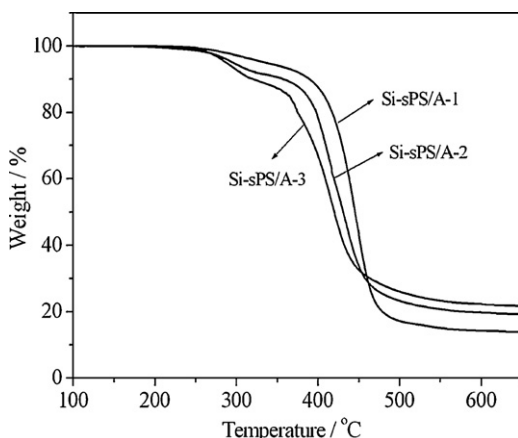


Fig. 2. TGA curves of Si-sPS/A membranes.

3.4. Ion-exchange capacity (IEC)

IEC provides an indication of the content of exchangeable acid groups in the membranes and is known to have the profound effects on many important properties of PEMs, such as the water uptake and proton conductivity [25]. Table 1 lists the calculated and titrated IEC values of Si-sPS/A membranes. It is found that both IEC values increases with increasing weight fraction of NaSS added in the feed because the increase in NaSS content led to the incorporation of more sulfonic acid groups. In addition, the IEC values observed by titration method were lower than the corresponding theoretical values. This discrepancy could be explained by two facts in our system. On the one hand, the amount of NaSS in the final polymer maybe less than the value in the feed due to part of NaSS monomers or oligomers from the solution were not incorporated in the final particles. On the other hand, the hydrolysis and condensation reactions of Si(OR)₃ groups in membrane led to the formation of crosslinked silica network structure. The crosslinked network decreased chain mobility and made the membrane denser and free volume depressed, which may result in less and smaller hydrophilic channels for proton mobility, and perhaps some of the groups buried inside the particles were not accessible to the reagent. Hence the exchangeable –SO₃Na groups were reduced and IEC values decreased.

3.5. Water uptake behavior

Water assists the transportation of protons from the anode to the cathode. Hence, proton exchange membranes should absorb sufficient water, whereas excessive water absorption will induce the loss of the dimensional stability and mechanical properties. Therefore, maintaining appropriate water uptake level is crucial for proton exchange membranes. The water uptake of Si-sPS/A membranes was measured at different temperature and the results were presented in Fig. 3. Obviously, the water uptake of membranes had an increasing tendency with increment of IEC. It can be understood based on the fact that as the IEC increased, the hydrophilicity of membranes increased and the larger ion clusters could be formed due to the incorporation of more hydrophilic sulfonic acid groups, which led to more absorption of water. Hence, the Si-sPS/A-3 membrane possessed the highest water uptake owing to its most sulfonic acid content.

The effect of temperature on water uptake of the membranes was also investigated. As illustrated in Fig. 3, the water uptake had an increasing trend with the increment of temperature. Take Si-sPS/A-3 for example, its water uptake sharply increased from 49.0

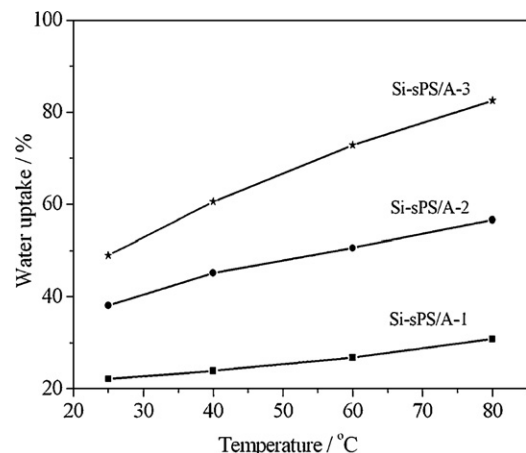


Fig. 3. Water uptake of Si-sPS/A membranes at different temperatures.

Table 2
Proton conductivity, methanol diffusion coefficient and selectivity of Si-sPS/A and Nafion® 117 membranes at 25 °C.

Membranes	Methanol diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	Proton conductivity (S cm^{-1})	Selectivity (Ss cm^{-3})
Si-sPS/A-1	1.82×10^{-8}	2.18×10^{-3}	1.20×10^5
Si-sPS/A-2	4.49×10^{-8}	5.78×10^{-3}	1.29×10^5
Si-sPS/A-3	9.46×10^{-8}	1.56×10^{-2}	1.65×10^5
Nafion® 117	2.36×10^{-6}	5.02×10^{-2}	2.13×10^4

to 82.5% as the temperature varied from 25 to 80 °C. This is because that at elevated temperature, the polymer chain mobility and the free volume for water adsorption increased, hence water molecules could penetrate the membrane more easily and the water uptake increased. In addition, due to the hydrophilic property of sulfonic acid groups, the water uptake increased more quickly with temperature in higher IEC membrane than in lower IEC membrane.

3.6. Methanol diffusion coefficient measurement

In DMFCs, the methanol diffusion not only wastes fuel but also results in the significant loss of fuel cell performance. Hence the PEMs used in DMFCs should possess low methanol diffusion coefficient. Table 2 lists the methanol diffusion coefficient of Si-sPS/A and Nafion® 117 membranes. It can be seen that similar to the water uptake behavior, the methanol diffusion coefficient of the Si-sPS/A membranes increased as the IEC values increased. It is well-known that methanol transports through the hydrophilic ionic channels for a fully hydrated membrane. When more hydrophilic sulfonic acid groups were incorporated into the membranes, more and larger water absorption channels could be formed. Hence methanol could relatively easily go through the channels and methanol diffusion coefficient was enhanced correspondingly.

The notable feature is that all of the Si-sPS/A membranes exhibited better methanol barrier property compared with the Nafion® 117. The low methanol diffusion coefficient of the Si-sPS/A membranes could be attributed to the formation of crosslinked silica network. As mentioned in previous section, the crosslinking in membranes might make the membranes more compact, which reduced chain mobility, free volume and water uptake. Hence the channels which the penetrant molecules could permeate were restricted and the methanol diffusion through the membranes decreased. In this study, the maximum methanol diffusion coefficient obtained from Si-sPS/A-3 was $9.46 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which was only approximately 1/25 of that of Nafion® 117 ($2.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, measured in this work). This indicated that methanol diffusion may significantly be reduced if these membranes are used in DMFCs.

3.7. Proton conductivity

One of the most essential properties of proton exchange membranes is proton conductivity. In this section, the proton conductivity was determined at 100% relative humidity and the results are shown in Table 2 and Fig. 4, respectively. For comparison, the proton conductivity of Nafion® 117 membrane was also measured under the same experimental conditions.

It is found that the proton conductivity of these membranes depended on various factors. First, it can be noted that proton conductivity increased with increasing IEC and water uptake. It is because that protons transferred between ionic clusters consisting of polar groups such as $-\text{SO}_3\text{H}$ and the number of ionic clusters was related to the number of $-\text{SO}_3\text{H}$ groups and water content in the membrane [26]. More sulfonic acid groups and water absorption could lead to the formation of more free protonic ions, ionic clusters and larger free volume in the membrane, which made the free protons more mobile and the protons in the form of hydro-

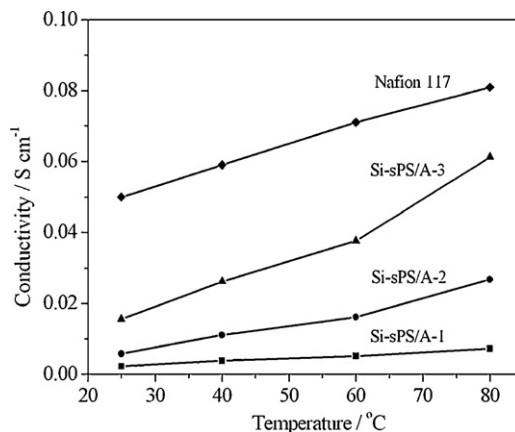


Fig. 4. Proton conductivities of Si-sPS/A and Nafion® 117 membranes at different temperatures.

nium ions probably pass through the ionic clusters more easily, the proton conductivity therefore was improved [27]. In addition, it is apparent that the proton conductivity of all the membranes increased with the increment of temperature. This trend was the same as that observed for water uptake behavior. For example, the proton conductivity of Si-sPS/A-3 membrane gradually increased from 0.015 to 0.061 S cm^{-1} with increasing temperature from 25 to 80 °C. The positive temperature-conductivity dependency suggested a thermally activated process. Elevating temperature could increase structural reorientation, water uptake and mobility of water and proton, which facilitated the transport of proton and hence contributed to the improvement of proton conductivity [24].

Although the proton conductivities of Si-sPS/A membranes were lower compared with that of Nafion® 117, they were acceptable for DMFC applications. Thus, the polymers described here remain potentially viable PEM materials, especially for small portable devices.

3.8. Comparison of selectivity

The integrated property of proton exchange membranes is usually characterized by the selectivity (the ratio of proton conductivity to methanol diffusion coefficient). The higher the selectivity value, the better the membrane performance is [28]. Table 2 exhibits the selectivity of Si-sPS/A and Nafion® 117 membranes at 25 °C. It can be noted that though the Si-sPS/A membranes displayed lower proton conductivity, they offered higher selectivity in comparison with Nafion® 117 membrane due to tremendous reduction in methanol diffusion coefficient. The highest selectivity value ($1.65 \times 10^5 \text{ Ss cm}^{-3}$) could be observed in the Si-sPS/A-3 membrane, which was approximately eight times of that of Nafion® 117 membrane ($2.13 \times 10^4 \text{ Ss cm}^{-3}$).

4. Conclusion

The silicon-containing sulfonated polystyrene/acrylate (Si-sPS/A) nanoparticles were successfully synthesized via convenient emulsion polymerization method. DLS analysis showed that

the average diameters of the synthesized particles with different IEC ranged from 105.9 to 141.6 nm. The self-crosslinked organic/inorganic proton exchange membranes (Si-sPS/A membranes) were also prepared and their suitability as proton exchange membranes for DMFC applications was investigated preliminarily. FTIR spectroscopy clearly indicated the existence of crosslinked silica network structure in the membranes and the Si-sPS/A membranes were found to have good thermal stability up to 260 °C by TGA analysis. In addition, the methanol diffusion coefficients of all Si-sPS/A membranes were significantly lower meanwhile their selectivity was higher than those of Nafion® 117 membrane. This is a significant advantage for membrane materials used for DMFCs. Furthermore, the development of Si-sPS/A membranes via eco-friendly route provided cost effective process for PEM preparation since the use of inexpensive chemicals and also the process was relatively simpler. Based on these results, it could be concluded that the Si-sPS/A membranes had good potential as PEMs for DMFC applications.

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