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Proton exchange membranes based on sulfonated crosslinked polystyrene micro particles dispersed in poly(dimethyl siloxane)

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Abstract

Proton exchange membranes of sulfonated crosslinked polystyrene (SXLPS) particles dispersed in crosslinked poly(dimethyl siloxane) matrix were investigated. Three different sizes of particles—25, 8 and 0.08 μm—were used at loadings from 0 to 50 wt% and the influence of these variables on the water and methanol uptake and proton conductivity were observed. With the reduction in particle size in the composite membrane, more water or methanol uptake was observed. Three different states of water were revealed in the composite membranes by differential scanning calorimetry (DSC). The number of bound water molecules per SO_3H group was 11–15 in membranes with 8- and 25-μm SXLPS. The ratio of bound to unbound water molecules was more than one in these membranes, whereas it was less than one in membranes with 0.08-μm SXLPS. The proton conductivities of the membranes increased with the increase in particle loading. At particle loadings above 35 wt%, membranes containing 8-μm SXLPS had higher conductivity compared to 25-μm SXLPS at room temperature. The conductivity of membranes containing 0.08-μm SXLPS was restricted to 10^{-3} S/cm because of the inherently low IEC of the particles. Increasing the temperature from 30 to 80 °C drastically enhanced the conductivity of the composite membranes compared to Nafion® 112. At 80 °C, conductivities as high as 0.11 ± 0.04 S/cm were observed for membranes containing more than 30 wt% of 25-μm SXLPS particles.

Keywords: Polymer composite; PEM; Conductivity

1. Introduction

In recent years, proton exchange membranes (PEMs) have attained considerable importance due in large part to their application in fuel cells. Recently, there has been a shift in focus towards development of membranes for direct methanol fuel cells (DMFCs). Amongst the polymeric materials, perfluorosulfonate membranes (e.g. Nafion®) are dominant because of their high proton conductivity (0.08 S/cm at 25 °C in 100% humidity environment) [1]. However, these membranes exhibit very high methanol permeability compared to the membranes based on covalently crosslinked acid–base polymers or blends [2]. The term used in fuel cell technology is 'crossover' because the methanol fuel fed to the anode crosses the membrane, decreasing the cathode potential and the energy efficiency [3].

Sulfonated polystyrene, in the form of pure polymer, blends, composites and grafted polymer, has also been studied very widely for PEM application [4–7]. Sulfonated polystyrene and its blends have a limitation on the level of sulfonation because the polymer dissolves in water at high levels of sulfonation. Inorganic and hybrid organic–inorganic membranes are being studied, but none has shown particularly promising results [1,8]. Chen et al. [9,10] have developed proton exchange membranes using sulfonated crosslinked polystyrene (SXLPS) microspheres dispersed in various matrices like polystyrene–poly(ethylene oxide) and poly(vinyl pyrrolidone)–poly(vinylidene fluoride) blends. Whenever the percolation concentration of the membrane is surpassed, the blend can conduct ions. Hence, it is necessary to have a concentration of conducting particles above the percolation threshold to achieve high proton conductivity.

In this paper, we report on a study concerning the effect of SXLPS particle size and concentration on the properties of proton exchange membranes based on poly(dimethyl siloxane) (PDMS) matrix. PDMS was chosen as a model matrix because it has a low viscosity in the uncrosslinked state and spreads

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easily over most surfaces. Membrane preparation does not require any solvent and the crosslinking reaction takes place at room temperature. The crosslinked matrix has flexible structure, appropriate mechanical properties and is adequately resistant to acidic environment. Oren et al. [11] have studied a similar system, but with all characterizations done for the potassium salt of the sulfonated polystyrene. In our study, we have retained the sulfonic acid groups of SXLPS, as it is most logical to study the properties of PEMs in this form for potential application in fuel cells. The proton conductivity of the membranes was measured by impedance spectroscopy and the effect of temperature on the conductivity was determined. The water and methanol uptakes were also measured, with special emphasis on the determination of the state of water in the membrane at various loadings of particles. Strong hydrogen bonding interactions are present between the ‘bound’ water molecules and the sulfonic acid (SO_3H) groups of membranes. These can affect the transport of water and protons through the membrane. An attempt is made to correlate some of the properties to the size and ion exchange capacity (IEC) of the particles, as well as their concentrations.

2. Experimental

2.1. Materials

The SXLPS particles used were derived from Dowex Marathon C ion-exchange resin (Aldrich Chemical Company, Inc). The as-obtained beads were 380–500 μm in size, had divinyl benzene (DVB) content of 8–10 mol% and density of 1.2 g/cm^3. These beads were thoroughly washed with de-ionized (DI) water to remove any residual sulfuric acid. They were then ground in a Wiley mill and sifted with a 400-mesh sieve to obtain particles of average diameter of 25 μm. The particles of 8 μm size were obtained by cryogenic grinding in a shatterbox (SPEX certiprep). Smaller particles (80 nm) were synthesized using an emulsifier-free technique with 4 mol% DVB. A detailed procedure for the synthesis of these nanoparticles has been described previously [12]. The ion exchange capacity (IEC) of the particles was measured by titration and was found to be 4.76 meq/g for Dowex Marathon C resin and 2.19 meq/g for the synthesized nanoparticles. The vinyl-terminated PDMS used was DMS V25 (Gelest, Inc), which has 0.11–0.13 meq/g of vinyl groups and molecular weight of 17.2 kDa. The methyl hydrogen polysiloxane crosslinker used was Silopren U crosslinker 430 (GE Bayer silicones). It has 4.1 mol% hydride and a number average molecular weight of 13 kDa. The viscosities of DMS-V25 and Silopren U crosslinker 430 are 0.485 and 0.024–0.034 Pa s, respectively. A platinum carbonyl complex (Gelest, Inc) with 3–3.5% Pt concentration was used as a catalyst. The chemical structures of the SXLPS particles and the crosslinking reaction are shown in Fig. 1.

2.2. Membrane preparation

A typical formulation for crosslinked PDMS membrane consisted of 3.62 g of DMS V25, 0.37 g of U crosslinker 430 and 0.01 g of Pt catalyst. The SXLPS particles were added at various loadings to this formulation. Above 50 wt% of SXLPS particles, the membranes lost their mechanical integrity and were not suitable for measuring conductivity. Membranes with more than 50 wt% SXLPS were prepared only for studying their absorption characteristics. The components were mixed in a vial with the help of a spatula and then cast on a glass plate. The amount of formulation was maintained constant to obtain uniform thicknesses of about 0.5–0.6 mm in the final membranes. The cross linking reaction (at 28 °C) took approximately 3 h to complete.

The densities of the membranes were calculated from the weight and dimensions (length × width × thickness) of a rectangular sample.

3. Characterization

3.1. Optical micrographs

The dispersion of SXLPS particles in PDMS was viewed under a Nikon Lab Photo optical microscope. The surface of the membrane was viewed in reflectance mode.

3.2. Water uptake

Rectangular pieces of membrane of the size 2 mm × 3 mm were soaked and equilibrated in deionized water for approximately 2 days. A piece was removed, patted dry and then run in a Perkin–Elmer thermo gravimetric analyzer (TGA) to measure the water uptake. Nitrogen gas purge was maintained at a flow rate of 20 mL/min. In the TGA, the membrane sample was heated from 30 to 120 °C at 10 °C/min. The temperature was maintained at 120 °C for 10 min, during which the weight loss as a function of time was recorded. The total water lost along with the dry-final weight at the end of these steps was used to calculate the equilibrium water content on a dry basis. Several replicates of each membrane were run in the TGA. The water uptakes of the SXLPS particles were measured by keeping the particles in a Petri dish in a closed chamber maintained at 100% relative humidity for 2 days.

To evaluate the state of water in the membranes, a similar procedure as discussed for water-uptake measurements was followed for sample preparation. The surface of water-swollen membrane piece was patted dry and weighed prior to sealing the sample hermetically in an aluminum DSC pan. The sample was thin enough to ensure that the lid did not touch it. An empty sample pan with a lid was used as a reference. Thermograms were gathered using a TA Q100 differential scanning calorimeter. The samples were equilibrated at -30 °C (-40 °C for samples containing 25-μm SXLPS samples), then ramped at 3 °C/min up to 30 °C using the standard DSC mode. A nitrogen gas flow at 50 mL/min was maintained.

3.3. Methanol uptake

A 10 mm × 20 mm strip of membrane was dried in vacuum oven, weighed and soaked in 100% methanol. After 2 days,

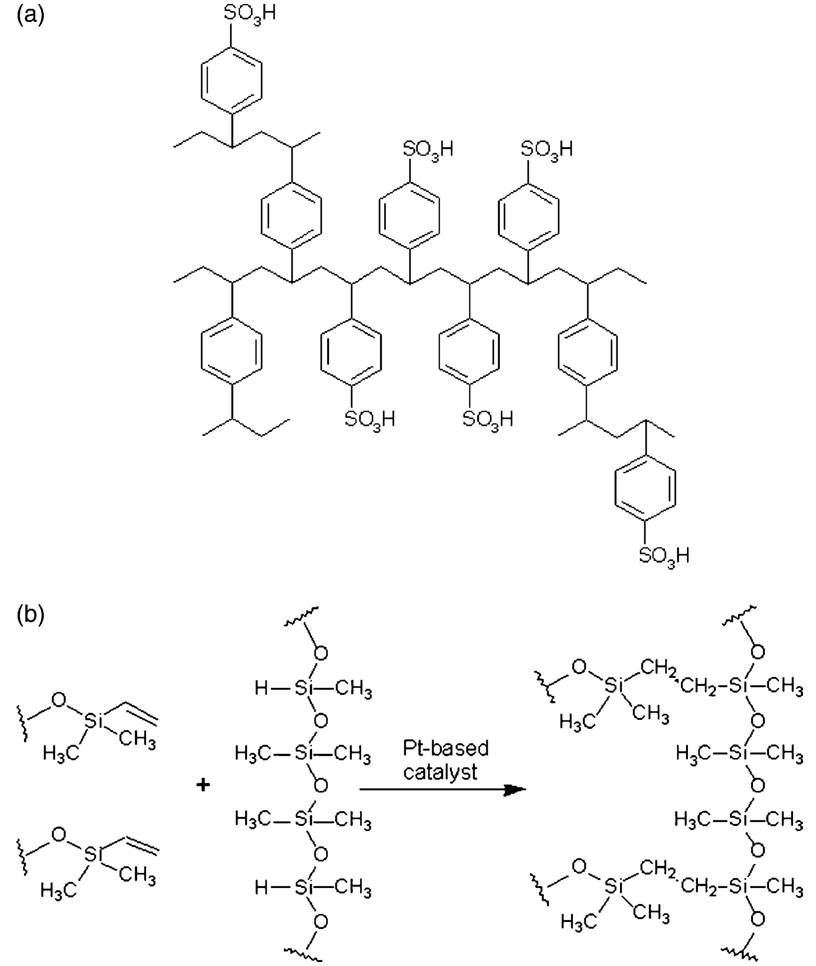


Fig. 1. Schematic of the (a) chemical structure of SXLPS particles and (b) PDMS crosslinking reaction.

the strip was removed, patted dry to remove surface methanol and immediately weighed.

3.4. Proton conductivity

The proton conductivity along the plane of the membranes was measured by Impedance Spectroscopy using a Solartron 1260 impedance analyzer over a frequency range of 0.1–10^6 Hz. The applied voltage was 50 mV. A Bekktech cell was used to measure conductivity of the hydrated membrane. The high frequency data from impedance spectroscopy was fitted with a semicircle, with its diameter associated to the resistance, R. The conductivity, was calculated as $\sigma = l/RA$, where σ is the conductivity, l is the length of membrane between the electrodes and A is the area of the cross section perpendicular to the current flow.

To measure conductivity at higher temperatures, the cell was connected to a humidifier and a temperature controller. The hydration was controlled by a constant flow of nitrogen gas through the humidifier to the cell at the flow rate of 176 mL/min. Before each reading, the membrane was allowed to equilibrate for at least 1 h. To attain the maximum humidity level in the cell, the humidifier and the cell were maintained at the same temperature.

4. Results and discussion

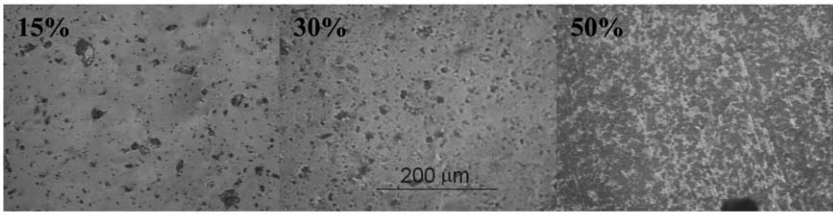
The membranes containing 0.08-, 8- and 25-μm SXLPS are denoted as M0.08, M8 and M25. For ease of comparison of the data of different particle sizes, the membranes with various loadings of SXLPS are represented in terms of their IEC. The IEC of each membrane was calculated on the basis of the IEC of particles used in the membrane and the weight fraction of the same using Eq. (1):

$$\mathrm{IEC_M} = \frac{\mathrm{IEC_P} W_\mathrm{P}}{W_\mathrm{M}} \tag{1}$$

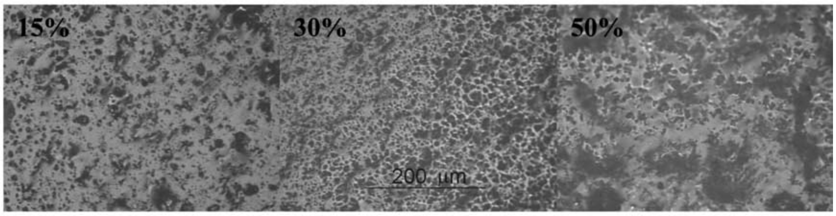
where $\mathrm{IEC_M}$ and $\mathrm{IEC_P}$ are the IECs of the membrane and particles, respectively; W_P is the weight of particles in a membrane with total weight of W_M.

The density of PDMS with 0% SXLPS was found to be 1.26 ± 0.73 g/cm^3. The variation in the weight fraction of particles was found to have no significant effect on the densities of M0.08 ($p = 0.32$ for the null hypothesis) and average density of the membrane

(a) 0.08-µm SXLPS in PDMS



(b) 8-µm SXLPS in PDMS



(c) 25-µm SXLPS in PDMS

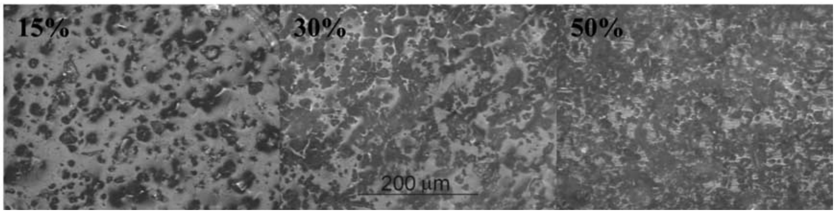


Fig. 2. Optical micrographs showing dispersion of (a) 0.08-, (b) 8- and (c) 25-µm SXLPS particles at 15, 30 and 50 wt% loading in PDMS membranes.

was 0.93 ± 0.02 g/cm^3. For M8 and M25, the densities decreased with the weight fraction of SXLPS ($p = 0.073$ and 0.104, respectively, for null hypothesis on the negative slope) and they ranged from 0.71 to 1.05 g/cm^3. The lower density values of composite membranes compared to the particles and PDMS indicates that there was some void volume in the mixture.

The optical micrographs of PDMS membranes containing 0.08-, 8- and 25-µm SXLPS are shown in Fig. 2(a)–(c), respectively. The micrographs indicate that the SXLPS particles were well-dispersed in PDMS; however, with increasing weight fraction the particles formed agglomerates.

4.1. Water uptake

The water uptake of membrane was calculated from Eq. (2):

$$\text{Water uptake, \%} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad (2)$$

and the mass fraction of water was calculated from Eq. (3):

$$m_{\text{w}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \qquad (3)$$

where W_{wet}, weight of membrane after soaking in water for 2 days; W_{dry}, weight of membrane at the end of the TGA run and m_{w}, mass fraction of the water in the membrane.

The water uptake of the three types of membranes—M0.08, M8 and M25—is shown in Fig. 3 as a function of the IEC of the membranes. The water uptake of 8- and 25-µm SXLPS particles without PDMS matrix is plotted at an IEC of 4.76 meq/g. Similarly, the value at 2.19 mequiv/g corresponds to 100% particles of 0.08-µm SXLPS. In these membranes, the SXLPS is the only component capable of absorbing water; the PDMS matrix as such does not have any significant water uptake. The data were fitted using a continuous kink function [13]. We can hypothesize that the kink in the curve separates the two distinct morphologies of the composite membrane. The initial higher slope region of the curve represents a composite system in which the matrix forms the major phase. As expected, the water uptake of the membrane increased linearly with increasing amounts of SXLPS in the membranes, up to a point after which the

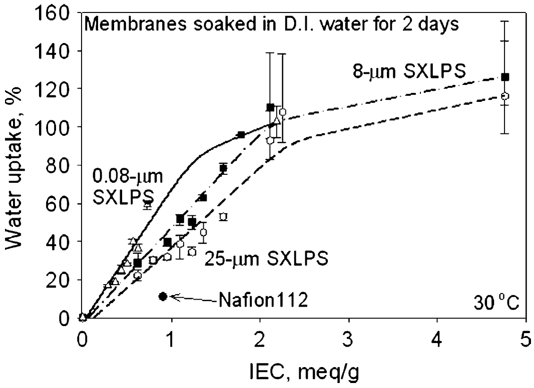


Fig. 3. Water uptake of membranes with 25-, 8- and 0.08-µm SXLPS particles dispersed in a PDMS matrix. Open hexagons, filled squares and open triangles represent the average water uptake of membranes with 25-, 8- and 0.08-µm SXLPS particles, respectively. The filled circle represents Nafion112. The error bracket represents the range of replicates from the same membrane and is not an estimate of the total variance at that IEC.

particles impinge and form continuous regions. This hypothesis was substantiated by optical microscopy as shown in Fig. 2. The initial slopes of M25, M8 and M0.08 were 23.3 ± 6.8, 27.8 ± 5.3 and 38.9 ± 12.8 moles of water per mole of SO_3H group. We can further hypothesize that the water taken up by the membranes is present as bound water near the sulfonic acid groups of the particles and as water channels or free water in the interfacial area between the particles and the matrix. (A more detailed analysis of the state of water in the membrane is presented in the subsequent Section 4.2.) When the weight fraction of particles is increased, there should be a strictly proportional increase in the amount of sulfonic acid groups and interfacial area if the particles are separated. However, when SXLPS particles impinge to form continuous domain, there should be a much lower increase in the interfacial area between particles and matrix. The second region of lower slope represents a system in which the particles form the major phase and the addition of PDMS has little effect. In the first region, the effect of particle size on the water uptake of the membranes is evident. Membranes with smaller SXLPS particles take up more water compared to membranes with larger particles due to high interfacial area at same weight fraction. However, all membranes take up about 50 wt% water at higher SXLPS loading irrespective of the particle size (Fig. 3).

The water uptake of Nafion® 112 membranes was measured to be about 10 wt% at room temperature which is comparable to the results reported by Cappadonia et al. [14], but much lower than the results reported by Zawodzinski et al. [15]. This difference could be due to the acid pretreatment used by Zawodzinski et al. [15] before measuring the water uptake. In our experiments, the Nafion® 112 was used as received.

4.2. State of water in the membrane

The water absorbed by ionomers or charge-containing composite polymeric membranes has been described to be present in three distinguishable forms [16–19]. In present context, water taken up initially is closely bound to the sulfonic acid groups and is known as 'bound water.' The water taken up thereafter is present as 'loosely bound water' and 'free water.' It has been shown that the bound water that forms a true solution with the polymer does not freeze at 0 °C and the melting endotherm observed in a DSC thermogram at that temperature is due to the free and loosely bound water [19]. The knowledge of the state of water in PEMs may be important, as it has been hypothesized that though the bound water promotes proton conductivity, it is the free water that enhances it most by forming a network of continuous hydrated material [20]. In the following discussion, freezable water will be liberally denoted as free or loosely bound water and non-freezable water will be denoted as bound water.

The DSC thermograms of M0.08, M8 and M25 with varying amounts of particles are shown in Fig. 4(a)–(c), respectively. The thermograms of 0.08-, 8- and 25-μm SXLPS particles, measured after equilibrating them in a 100% relative humidity chamber, are shown in Fig. 4(d). For most membranes, two closely spaced melting peaks are observed near 0 °C. On heating, the first peak is sharp and the second peak is broad. According to Tasaka et al. [16] the first peak belongs to the free water and the second peak belongs to loosely bound water, which has partially restricted movement. Fig. 4(a)–(c) illustrate the melting behavior for membranes with different SXLPS particle sizes. In the DSC thermograms of the 8- and 25-μm SXLPS particles, no freezable water was observed; however, for 0.08-μm SXLPS particles, an endothermic peak corresponding to free water was observed near 0 °C. This could be due to the agglomeration of the 0.08-μm particles, which can also entail entrapment of free water within the agglomerates. This is also possible with particles in the membrane. As PDMS is a hydrophobic matrix and the SXLPS particles are highly hydrophilic, some agglomeration of particles is expected in the membrane, which can entrap some free water. The absence of melting peaks for 8- and 25-μm SXLPS indicates that all the water absorbed by the particles is bound to sulfonic acid groups. As the wt% of SXLPS in the membranes was increased, the water uptake increased and the area of the endothermic peak at 0 °C, which corresponds to the melting enthalpy of water, was also found to increase. The free-water content in the membrane was defined using:

$$m_{\mathrm{w,f}} = \frac{\text{Melting enthalpy, J/g}}{\text{Heat of fusion of pure water, J/g}} = \frac{\text{Peak area at }0^{\circ}\text{C, J/g}}{334\text{ J/g}} \tag{4}$$

where $m_{\mathrm{w,f}}$, mass fraction of freezable water.

The mass fraction of bound water was calculated from:

$$m_{\mathrm{w,uf}} = m_{\mathrm{w}} - m_{\mathrm{w,f}} \tag{5}$$

where m_{w}, total mass fraction of water in membrane calculated from Eq. (3), and $m_{\mathrm{w,uf}}$, mass fraction of unfrozen water.

The peak area was calculated by the TA Universal Analysis® software. The weight fractions of frozen and unfrozen water in the membranes with varying amounts of SXLPS particles are shown in Fig. 5. The moles of bound water per SO_3H group (λ_{bound}) were calculated from the weight fractions and IECs of the membranes. These are listed in Table 1. From the mean values of λ_{bound}, it appears that all the three types of samples have roughly the same amount of bound water per SO_3H group. Our values are also close to those reported by Gupta et al. [20]. However, the relative amounts of bound and unbound waters are different. This is elucidated in Fig. 5 where bound- and unbound-water weight fractions are plotted as a function of IEC of membranes. It is clearly evident that out of the entire amount of water taken up by M8 and M25, relatively higher fractions were present as bound water compared to unbound-freezable water, whereas in M0.08, a higher fraction of water was present in the unbound state compared to bound state. Clearly, this difference could be due to the difference in the IEC and

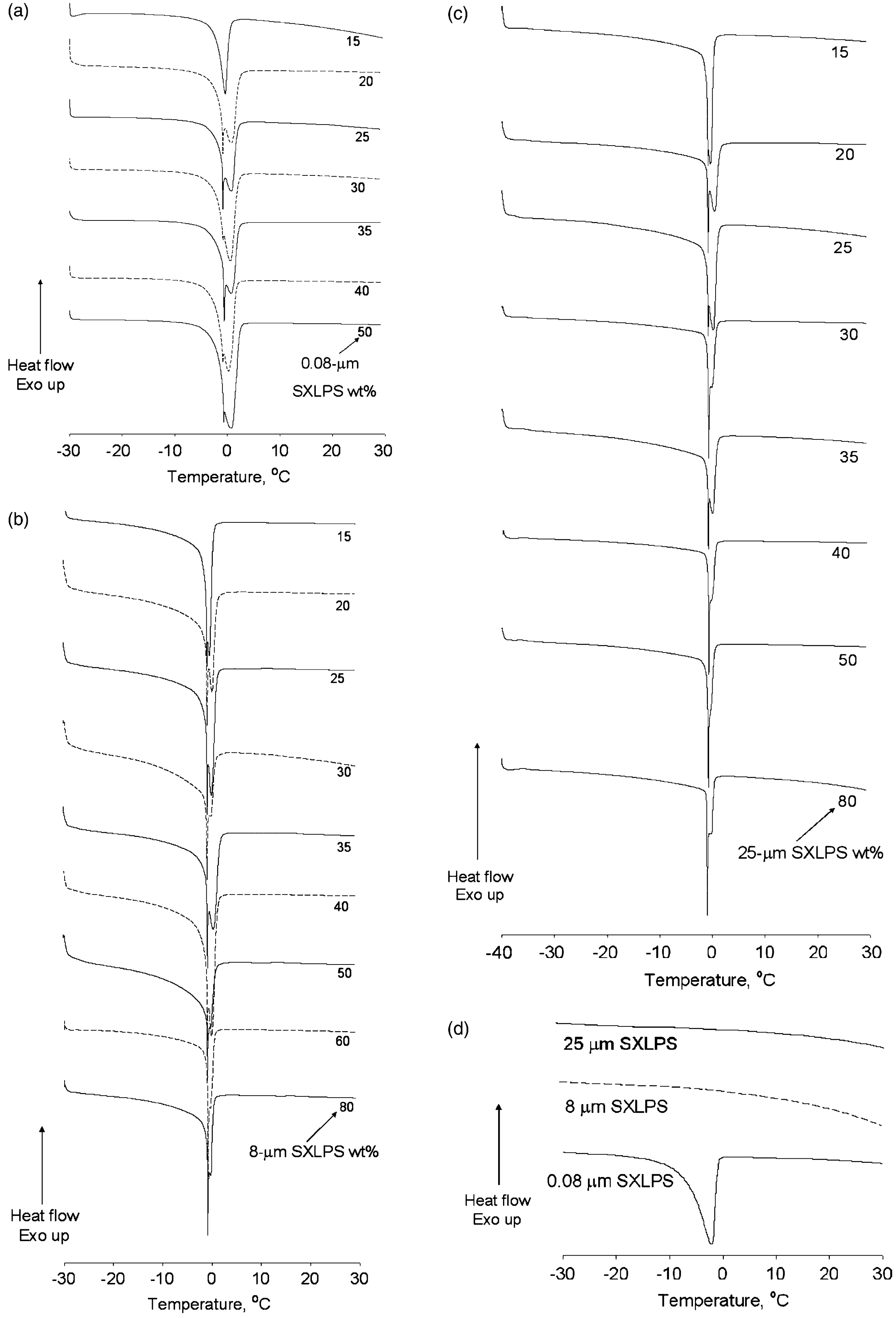


Fig. 4. (a) DSC thermograms of PDMS membranes containing (a) 0.08-, (b) 8- and (c) 25-μm SXLPS particles after soaking in water for 2 days, (c) DSC thermograms of PDMS membranes containing 25-μm SXLPS after soaking in water for 2 days, (d) DSC thermograms of SXLPS particles after equilibrating in a 100% relative humidity chamber.

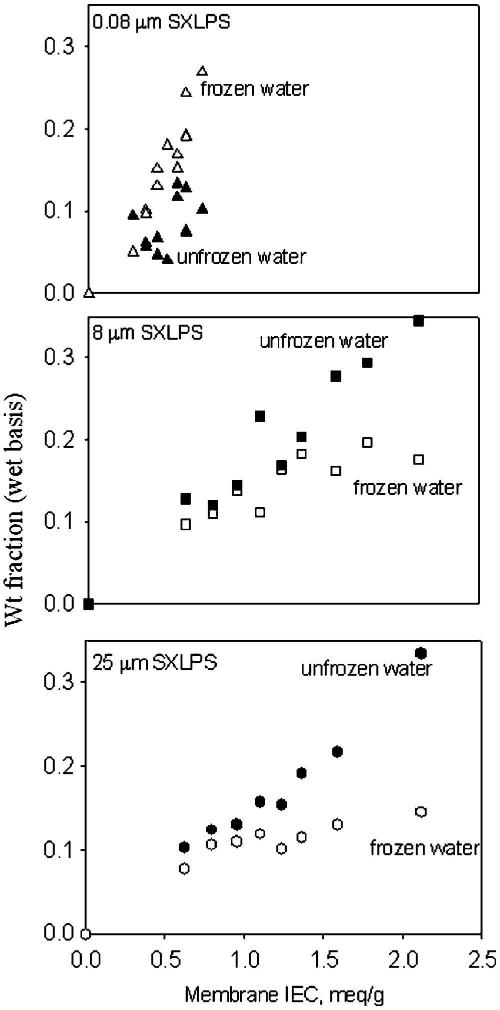


Fig. 5. The relative amounts of frozen and unfrozen water in the membranes as a function of the IEC of the membrane, evaluated from the DSC data. Filled symbols represent unfrozen water and open symbols represent frozen water.

size of the particles. The higher IEC (4.76 meq/g) of the larger particles in the M8 and M25 membranes is expected to result in more water in non-freezable state than in the freezable state. As M0.08 has much smaller particles with lower IEC, higher fractions of absorbed water remain in the unbound state. The data of M8 and M25 also suggest that as the SXLPS wt% in membrane was increased, the bound water content increased; however, the unbound water content did not increase proportionally. This is in accordance with the kink function used to describe the water uptake behavior shown in Fig. 3. As the SXLPS wt% was increased, particles formed the major phase and impinged on each other. As a result, the bound water content increased whereas the unbound water remained almost constant as there was virtually no more increase in interfacial area between particles and matrix.

Table 1
Melting peak positions and amount of water bound to SO_3H groups in PDMS membranes with SXLPS

Size of SXLPS particles in membrane (µm)	Average moles of bound water/SO_3H group (λ_{bound})
0.08	12.43 ± 3.1
8	14.9 ± 2.4
25	11.63 ± 1.89
SXLPS-*g*-FEP (Gupta et al.)	8–9

The moles of bound water are expressed as average with 95% confidence interval.

4.3. Methanol uptake

The methanol uptake of the membranes was calculated on dry membrane basis from:

$$\text{Methanol uptake, } \% = \frac{W_{\text{MeOH}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{6}$$

where W_{MeOH} is the weight of membrane after soaking in 100% methanol for 2 days, and W_{dry} is the weight of dry membrane. The equilibrium mass fraction m_{MeOH} was calculated from:

$$m_{\text{MeOH}} = \frac{W_{\text{MeOH}} - W_{\text{dry}}}{W_{\text{MeOH}}} \tag{7}$$

The plot of the methanol uptake as a function of IEC and SXLPS size is shown in Fig. 6. It is evident that PDMS without any particles did not have any significant methanol uptake. As the weight fraction of the particles, and correspondingly the IEC increased, the methanol uptake was found to increase. The linear model used to examine the methanol uptake as a function of particle diameter, surface area and IEC was:

$$\text{Methanol uptake, } \% = a_1X_1 + a_{12}X_1X_2 \tag{8}$$

where X_1 = IEC of membrane, meq/g and $X_2 = 1/d = A_{\text{sp}}\rho/6$, cm^{-1}, where d = number average diameter of particles, cm, A_{sp} = specific surface area, cm^2/g and ρ = density of particles, g/cm^3. The first term of the model represents methanol uptake into the particle volume, while the second term represents methanol adsorbed on the surface of the particle.

All the parameters of the model were significant at the 95% probability level or above and were estimated as $a_1 = 24.9 \pm 1.54$, $a_{12} = 2.36 \pm 0.6$, where the indicated errors are the 95%

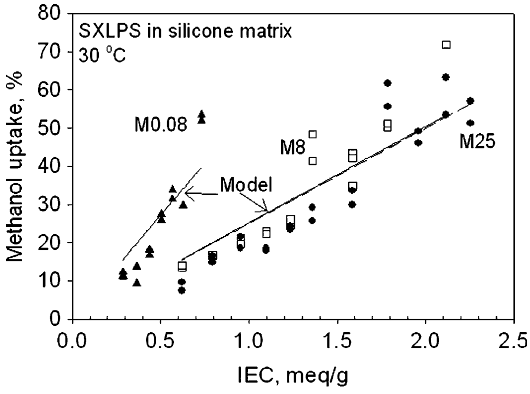


Fig. 6. Methanol uptake of composite membranes prepared with different sizes of SXLPS particles at different loadings. The circles, squares and triangles represent membranes with 25-, 8- and 0.08-µm SXLPS, respectively. See text for details concerning the model.

confidence intervals of the parameters, and the units compared to those assigned to the variables.

From this model, it is clear that the methanol uptake of the composite membranes increases with increase in IEC and decrease in particle diameter. The smaller particles have higher specific surface area; hence the methanol uptake is increased. Compared to the composite membranes, Nafion® 112 exhibited much higher methanol uptake of 50.7±11.8% (dry weight basis) at the same IEC. This peculiarly high methanol absorption of Nafion® has been reported by several other workers [21,22]. Due to the crosslinked nature of the matrix, the uptake of methanol by PDMS membranes was much reduced. Also, as is evident from Fig. 6, the crosslinked membrane will not dissolve in methanol at any concentration.

4.4. Proton conductivity

The proton conductivities of hydrated membranes as a function of particle loading (expressed here as IEC) for M0.08, M8 and M25 are shown in Fig. 7. For comparison, the conductivity of Nafion® 112 was measured in similar way. It has been hypothesized that hydrated Nafion® has isolated clusters of SO_3H groups that are connected by water channels [23–25]. Compared to the homogenous morphology of Nafion® at the micron scale, the composite membranes have a heterogeneous structure. As a result, conductivity values comparable to Nafion® 112 are obtained at very high loading of 40–50 wt% of 8- and 25-μm SXLPS. The restriction on the conductivities of M0.08-membranes is due to the lower IEC of particles and limitation on the maximum loading of particles. Our results are comparable with results reported by Carretta et al. [26] for membranes based on sulfonated polystyrene and with other similar particles-in-matrix composite systems reported by Chen et al. [27]. The conductivity values reported by Oren et al. [11] are much lower compared to our results. This could be due to the difference in the measurement procedure and due to the fact that they were measuring K^+ conductivities instead of proton conductivity.

To assess the temperature dependence, the conductivity was measured in the temperature range of 30–80 °C at 100% humidity. The results are shown in Fig. 8. The conductivities of all the membranes increased with increasing temperature. Nafion® 112 showed a steady increase in conductivity from 0.04 S/cm at 30 °C to 0.105 S/cm at 80 °C. Compared to this, the composite membranes displayed a drastic rise in conductivity with temperature. Although the conductivities of membranes with 30 and 40 wt% SXLPS were much lower than Nafion® 112 at room temperature, at higher temperatures similar values were obtained. When the SXLPS content in the membrane was increased to 50 wt%, the conductivity was more than 0.1 S/cm at temperature above 60 °C. One of the possible reasons for this difference in temperature dependence of composite membranes and Nafion® 112 could be the higher water content in the composite membranes. At high temperatures, the mobility of water molecules increases, which in turn improves the transport of protons through the membrane. Our results show lower conductivity values compared to those reported by Chen et al. [28] for membranes with SXLPS in sulfonated polystyrene matrix with similar IEC. An easier route for percolation is expected in sulfonated matrices, and hence they could obtain higher conductivities at similar IECs. However, the unsulfonated matrix has the advantage of independent control of swelling and mechanical properties.

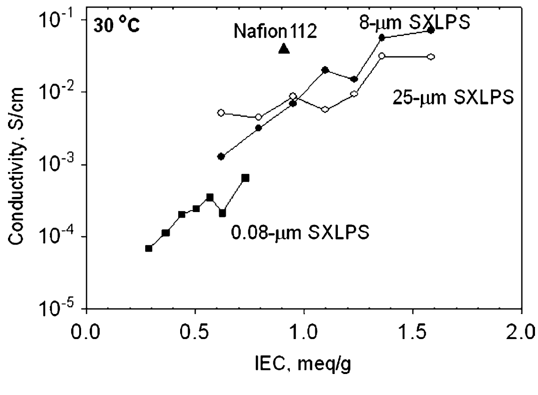


Fig. 7. Conductivity of PDMS membranes containing 25-, 8- and 0.08-μm SXLPS as a function of the particle loading (expressed here as ion exchange capacity). All the membranes were soaked in DI water prior to measurement.

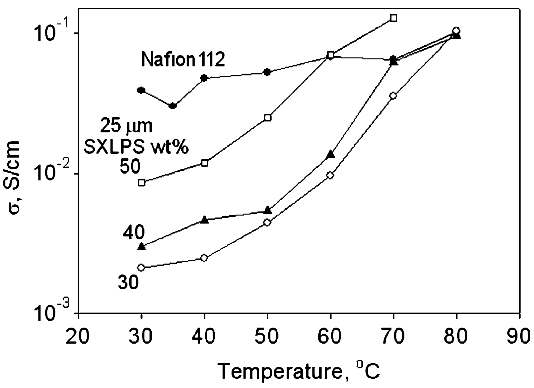


Fig. 8. Conductivity of 25-μm SXLPS containing membranes with various loadings of particles and Nafion® 112 at different temperatures. The humidity of cell was maintained at its maximum by maintaining equal temperature with the humidifier.

5. Conclusions

We studied the properties of composite ion exchange membranes made by dispersion of SXLPS particles in a crosslinked PDMS matrix. The size of particles and their ion exchange capacity had significant effect on the water uptake, methanol uptake and proton conductivities of the membranes. The state of water in composite membranes was determined by DSC. The molar ratio of water to $-SO_3H$ group varied from 11 to 15. The relative amounts of bound and unbound water were found to depend on the size, IEC and concentration of the particles in the membrane. The methanol uptake in these membranes was restricted by the crosslinked matrix, and methanol contents comparable to Nafion® 112 were observed only at more than 50 wt% loading of particles. A linear model was used to correlate the methanol uptake of the membranes with the IEC of membranes and surface area of the particles.

The proton conductivities of the composite membranes were enhanced by higher loading of particles with values of more than 0.01 S/cm above 35 wt% loading. Increasing temperature drastically increased the conductivities of the composite membranes, whereas a relatively lower increase was observed for Nafion® 112.

References

[1] Dimitrova P, Friedrich KA, Stimming U, Vogt B. Solid State Ionics 2002;150:115.

[2] Walker M, Baumgärtner K-M, Kaiser M, Kerres J, Ullrich A, Räuchle E. J Appl Polym Sci 1999;74:67.

[3] Ren X, Zawodzinski Jr TA, Uribe F, Dai H, Gottesfeld S. Proc Electrochem Soc 1995;95-23:284.

[4] Carretta N, Tricoli V, Picchioni F. J Membr Sci 2000;166:189.

[5] Chen N, Hong L. Polymer 2004;45:2403.

[6] Ding J, Chuy C, Holdcroft S. Macromolecules 2002;35:1348.

[7] Bae B, Kim D. J Membr Sci 2003;220:75.

[8] Damay F, Klein LC. Solid State Ionics 2003;162–163:261.

[9] Chen N, Hong L. Solid State Ionics 2002;46:377–85.

[10] Hong L, Chen N. J Polym Sci, Part B: Polym Phys 2000;38:1530.

[11] Oren Y, Fregen V, Linder C. J Membr Sci 2004;239:17.

[12] Brijmohan S, Swier S, Weiss RA, Shaw MT. Ind Eng Chem Res 2005;44:8039.

[13] Shaw MT, Cua EMC. Annual Meeting—The Society of Rheology 2001 P04 Hilton Head Island, SC.

[14] Cappadonia M, Wilhelm Erning J, Saberi Niaki SM, Stimming U. Solid State Ionics 1995;77:65.

[15] Zawodzinski Jr TA, Derouin C, Radzinski S, Sherman RJ, Smith VT, Springer TE, et al. J Electrochem Soc 1993;140:1041.

[16] Tasaka M, Suzuki S, Ogawa Y. J Membr Sci 1988;38:175.

[17] Ping ZH, Nguyen QT, Chen SM, Zhou JQ, Ding YD. Polymer 2001;42:8461.

[18] Kim YS, Dong L, Hickner MA, Glass TE, Webb V, McGrath JE. Macromolecules 2003;36:6281.

[19] Tranoudis I, Efron N. Contact lens and anterior eye 2004;27:193.

[20] Gupta B, Buechi FN, Staub M, Grman D, Scherer GG. J Polym Sci, Part A: Polym Chem 1996;34:1873.

[21] Nandan D, Mohan H, Iyer RM. J Membr Sci 1992;71:69.

[22] Skou E, Kauranen P, Hentschel J. Solid State Ionics 1997;97:333.

[23] Gierke TD, Munn GE, Wilson FC. J Polym Sci, Polym Phys Ed 1981;19:1687.

[24] Fujimura M, Hashimoto T, Kawai H. Macromolecules 1982;15:136.

[25] Orfino FP, Holdcroft S. J New Mater Electrochem Syst 2000;3:285.

[26] Carretta N, Tricoli V, Picchioni F. J Membr Sci 2000;166:189.

[27] Chen N, Hong L. Solid State Ionics 2002;46:377–85.

[28] Chen S-L, Krishnan L, Srinivasan S, Benziger J, Bocarsly AB. J Membr Sci 2004;243:327.