JOURNAL OF
Materials
CHEMISTRY

Nafion-bifunctional silica composite proton conductive membranes†

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Received 20th August 2001, Accepted 4th January 2002
First published as an Advance Article on the web 1st March 2002

Sol–gel derived sulfonated phenethylsilica with hydrophilic –Si-OH and proton conductive –SO_3H functional groups was used as a bifunctional additive to improve the proton conductivity and water uptake characteristics of Nafion. Nafion-bifunctional silica (NBS) composite membranes were prepared by casting Nafion–ethanol solutions mixed with sulfonated phenethylsilica sol. The ion exchange capability of NBS composite membranes increases linearly with the amount of bifunctional silica incorporated, and is about 1.9×10^{-3} mol SO_3H g^{-1} for NBS with 7.5 wt% silica. Liquid water uptake measurements showed that NBS composite membranes have higher water uptake (g H_2O g^{-1} composite membrane) than bare recast Nafion while the degree of hydration (*i.e.*, $n$$H_2O$–$SO_3H$) remains fairly constant. The NBS composite membranes showed improved proton conductivity when compared with bare recast Nafion and Nafion 117 membranes at 80 °C and over a range of relative humidity.

Introduction

Proton conductive polymer membranes have attracted much attention because of their applications in electrochemical devices such as proton-exchange-membrane fuel cells (PEM-FC). At present, perfluorosulfonic polymers such as Nafion (DuPont) are most extensively studied because of their outstanding chemical, mechanical and thermal stability and high proton conductivity.[1–5] However, Nafion membranes tend to significantly dehydrate at high temperature or low relative humidity leading to low proton conductivity and poor PEM-FC performance. As a result, water management problems have been widely investigated to improve Nafion's high temperature performance and avoid cathode flooding and dehydration from the anode side (due to electro-osmotic drag).[6–11] One promising strategy is to incorporate nanometer-sized particles of hygroscopic metal oxides (silica, titania, and zirconia phosphate) into Nafion[6–12] to improve the hydration characteristics of Nafion. This approach also makes it possible to eliminate gas humidification significantly simplifying fuel cell design.[8–10]

The hygroscopic nanoparticles (*e.g.*, silica and titania) used in most of the previous studies are single functional (hydrophilic) even though nanoparticles that are both hydrophilic and proton conductive (bifunctional) would have been preferred. In the present study, we attempt to incorporate a bifunctional sulfonated phenethylsilica into Nafion to improve its proton conductivity and water uptake characteristics. Sulfonated silica has been demonstrated to have proton conductivity comparable to water saturated Nafion.[13,14] Preliminary results of ion exchange capacity, water uptake, degree of hydration, and proton conductivity of Nafion-bifunctional silica (NBS) composite membranes will be reported.

Experimental

Preparation of composite membranes

The preparation protocol of NBS composite membranes is shown in Fig. 1. Sulfonated phenethyltrimethoxysilane (PETMS) was obtained by sulfonating PETMS with chlorosulfonic acid. A stoichiometric amount of chlorosulfonic acid (99%, Alfa) was dropwise added into PETMS (98%, Alfa) under rigorous stirring. The solution mixture was then stirred at room temperature for 2 to 3 h to ensure complete sulfonation of phenethyl groups.[13] After sulfonation, measured amounts of absolute ethanol and deionized (D.I.) water were added to give a molar ratio of the final mixture of sulfonated PETMS–H_2O–ethanol = 1 : 6.39 : 18.68. Hydrolysis of sulfonated PETMS was carried out under self-acid-catalysis of the sulfonic groups under stirring for 1 day. The final sulfonated silica sol (bifunctional silica sol) has 5 wt% silica.

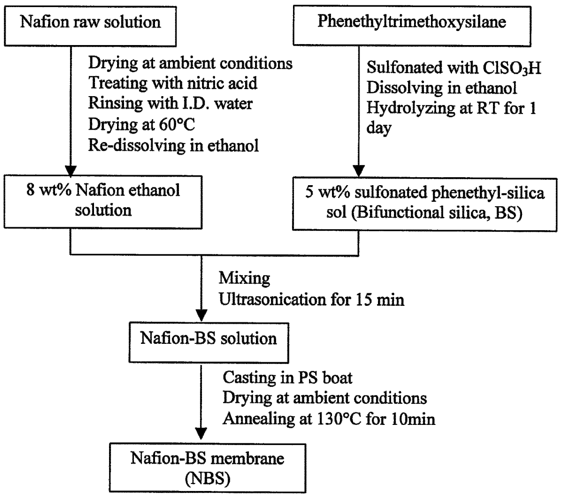

Fig. 1 Preparation protocol of NBS composite membranes.

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†Electronic supplementary information (ESI) available: SEM images of the surface of a NBS composite membrane (a) and a Nafion 117 membrane (b). Inset: A NBS composite membrane at high magnification. See http://www.rsc.org/suppdata/jm/b1/b107498a/

DOI: 10.1039/b107498a

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Nafion solution (DuPont, SE-5112, equivalent weight (E.W.) = 1100 g mol^{-1} SO_3H) was processed as follows to avoid membrane cracking during casting. Nafion solution was first dried at ambient conditions overnight. Nafion solids obtained were treated with 50% concentrated nitric acid followed by washing with D.I. water until pH = 7, and drying at 60 °C overnight. The treated Nafion solids were dissolved in absolute ethanol to obtain 8 wt% Nafion in ethanol solution.

Measured amounts of bifunctional silica sol and Nafion solution were mixed, and the resultant mixture was ultrasonicated for 15 min to ensure complete mixing. The NBS composite membranes were obtained by casting the mixture into polystyrene boats (Fisher) followed by drying at ambient conditions for 3–4 h, and annealing at 130 °C for 10 min.[15] As a comparison, pure Nafion membranes (recast membrane) were prepared using the above procedure without the addition of bifunctional silica sol. Based on SiO_2 content in the composite membrane, 1.0 wt% BS-Nafion, 2.5 wt% BS-Nafion, 5 wt% BS-Nafion and 7.5 wt% BS-Nafion composite membranes (denoted as 1NBS, 2.5NBS, 5NBS and 7.5NBS, respectively) were obtained. Membrane thickness was measured with a micrometer at several locations on the membrane sample and the average was used for the proton conductivity measurement.

Characterization

The bifunctional silica structure was examined by Fourier transform infrared spectroscopy (FT-IR, Bruker Equinox 55, 0.5 cm^{-1} resolution). A small amount of sulfonated silica sol was dried at 100 °C overnight, ground and compressed into KBr-based wafers for IR analysis. The NBS composite membrane and commercial Nafion 117 membrane were examined with a scanning electron microscope operated at 5 kV (SEM, Philips XL30-FEG). A low voltage (5 kV) was used to avoid electron beam damage to Nafion. Ion-exchange capacity (IEC) was defined as the accessible number of sulfonic groups (in moles) in 1 g dry NBS composite membrane, and was measured by titration with 0.1 M NaOH (phenolphthalein as indicator). Water uptake was calculated by taking the difference between the wet weight and dry weight of a composite membrane sample. To obtain the wet weight, a membrane sample was equilibrated with distilled water at room temperature or 80 °C overnight. The wet sample was then removed and blotted dry with a Kimwipe (Fisher) before being transferred to a capped weighing bottle for weighing. The dry weight was also measured in a capped weighing bottle after the sample was dried at 100 °C for 1 day.

Membrane proton conductivity was measured using a four-electrode ac impedance method.[16,17] All the membrane samples were in their protonated state and immersed in room temperature water overnight prior to measurement. The experimental setup used (similar to the one reported in ref. 16) consisted of a sample fixture in an environmental chamber where temperature and humidity can be controlled. The impedance measurements were conducted using an impedance/gain-phase analyzer (Solartron SI 1260) and a potentiostat (Solartron SI 1287). The conductivity of the membrane was calculated using the equation[16]

$$\sigma = l/RS$$

where σ, l, R, and S were the ionic conductivity, distance between electrodes, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

Results and discussion

1. Bifunctional silica structure

Fig. 2 shows a FT-IR spectrum of bifunctional silica. The bands at 1601 cm^{-1} (ν(C=C)), 1492 and 1453 cm^{-1} ($\delta(CH_2)$,ν(C=C)), 739 cm^{-1} (γ(=CH)), 699 cm^{-1} (δ'(ring)) are attributed to characteristic vibrations of the benzene group.[18] The band at 3389 cm^{-1} is ascribed to a hydrated sulfonic group. The bands at 1201 and 1034 cm^{-1} are assigned to the asymmetric and symmetric stretching of a sulfonic group.[19] The band at 918 cm^{-1} is ascribed to terminal SiOH groups. The band at 1112 cm^{-1} is assigned to Si–O–Si asymmetric stretching.[20] The bifunctional silica structure (with sulfonated phenethyl groups) was clearly verified.

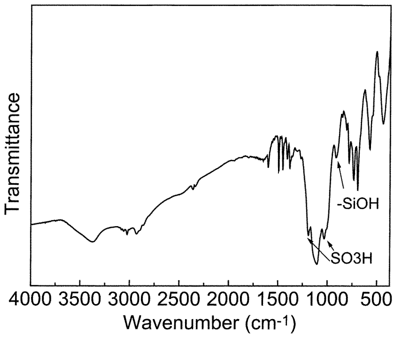

Fig. 2 IR spectrum of bifunctional silica.

2. Morphology of membranes

SEM images of the top surface of the 5NBS composite membrane and Nafion 117 membrane are shown in the ESI.† The surface of the NBS composite membrane is generally smooth and comparable to that of Nafion 117. The minor surface defects on NBS composite membranes (ESI†) may be due to fast ethanol (solvent) evaporation during recasting and can be eliminated by controlled drying during recasting. NBS composite membranes are very uniform confirming that no phase separation has occurred during the casting and drying process. Similar cross-section images were obtained (not shown).

3. Ion-exchange capacity (IEC)

Ion exchange capacities of recast bare Nafion membranes and NBS composite membranes as measured by NaOH titration are shown in Fig. 3. The number density of sulfonic groups increases significantly from 9.0 × 10^{-4} to 1.9 × 10^{-3} mol SO_3H g^{-1}as more bifunctional silica is incorporated. The number density of accessible sulfonic groups measured with NaOH titration agrees with the value calculated based on 1100 E.W. of Nafion and by assuming complete sulfonation of phenethyl groups, suggesting that bifunctional silica particles have stayed inside the hydrophilic ionic cluster channels within Nafion and are easily accessible. This is consistent with the fact that –SiOH groups and –SO_3H groups are more compatible with hydrophilic ionic clusters than with the hydrophobic Teflon-like backbone of Nafion.

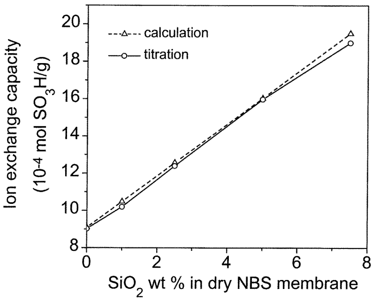

Fig. 3 Ion exchange capacity of recast Nafion and NBS composite membranes with different SiO_2 content.

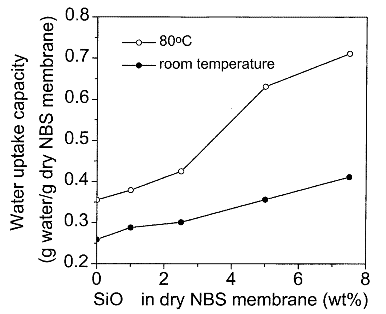

Fig. 4 Water uptake capacity of recast Nafion and NBS composite membranes.

3. Water uptake capability

Water uptakes at room temperature and 80 °C as a function of silica amount in the composite membranes are shown in Fig. 4. Water uptake of the membranes increases as the silica amount increases. This result is reasonable if one considers that sol–gel derived bifunctional silica without high-temperature calcination has a high concentration of –SiOH groups, which are highly hydrophilic. The membrane absorbs more water at 80 °C than at room temperature because the Nafion network is more swollen at high temperature. This is consistent with the results reported in the literature.[21]

The degree of hydration (expressed as nH$_2$O/SO$_3$H) is shown in Fig. 5. It was calculated from the data shown in Fig. 4 based on a Nafion E.W. of 1100 and by assuming 100% sulfonation of phenethyl groups in the bifunctional silica sol. At room temperature, n slightly decreases from 16.5 to 13.5 with increased silica content in the membrane. At 80 °C, n remains at about 21 ± 2, which is very close to the value of 22.08H$_2$O–SO$_3$H obtained from Nafion 117. This shows clearly that the NBS composite membranes can be effectively hydrated for sulfonic groups from both Nafion and bifuctional silica, which is essential to proton conduction.

4. Proton conductivity

The proton conductivities of Nafion 117, recast Nafion, 2.5NBS, 5NBS were measured at different temperatures and relative humidities (RH). At room temperature and 100% RH, the proton conductivities for the Nafion 117, recast Nafion, 2.5NBS, and 5NBS are 0.0308, 0.0235, 0.0383, and 0.0774 S cm^{-1}, respectively. This clearly shows that the proton conductivity of the membrane increases with the incorporation of bifunctional silica. It is emphasized that NBS composite membranes have higher proton conductivity than both Nafion 117 and recast Nafion membranes. Nafion based PEM-FC are commonly operated at 80 °C, therefore the proton conductivity of the commercial Nafion 117, recast Nafion and NBS composite membranes were measured at 80 °C and different RH (Fig. 6). NBS composite membranes possess higher proton conductivity than pure Nafion membranes (Nafion 117 and recast Nafion) over the whole RH range. The improvement of ion conductivity is more significant at higher RH. For example, at 100% RH the proton conductivities for Nafion 117, recast Nafion, 2.5NBS, and 5NBS are 0.0394, 0.0258, 0.1059, and 0.2274 S cm^{-1}, respectively. This clearly shows that at 100% RH, 2.5NBS and 5NBS composite membranes have much higher proton conductivities than Nafion 117 (2.7 and 5.8 times, respectively).

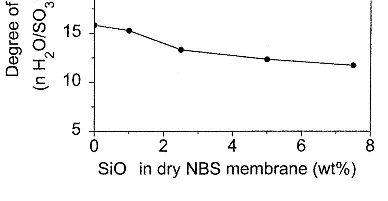

Fig. 5 Degree of hydration of recast Nafion and NBS composite membranes.

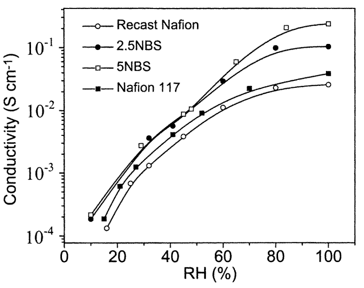

Fig. 6 Proton conductivity of Nafion 117, recast Nafion, NBS composite membrane measured at 80 °C *versus* relative humidity.

Studies reported in literature[11,16] showed that proton conductivity is directly correlated with sulfonic number density (mole SO$_3$H$^+$ g^{-1}) and degree of hydration (mol H$_2$O/mol SO$_3$H). NBS composite membranes have a higher number density of sulfonic groups due to the incorporation of bifunctional silica, and this has led to an increased proton conductivity even though the degree of hydration of NBS composite membranes is almost the same as that of pure Nafion membranes.

It is known that Nafion 117 in different physical states can possess different proton conductivities.[16,17] The Nafion 117 sample in this experiment was measured at 80 °C, and the proton conductivity obtained is quite comparable to the value of heat-treated Nafion (called N-form) in ref. 16. The proton conductivity of the NBS composite membrane is also higher than that reported for the Nafion–SiO$_2$ composite membrane where single functional silica was used.[22] This further indicates that the bifunctional silica within the network of recast Nafion is more efficient at improving the proton conduction than the single functional silica.[22] It is important to point out that the proton conductivity of NBS composite membranes increases significantly with temperature. For example, at 100% RH the proton conductivity increases from 0.0383 to 0.1059 S cm^{-1} for 2.5NBS, and from 0.0774 to 0.2274 S cm^{-1} for 5NBS when the temperature increases from room temperature to 80 °C. A similar result was reported for the Nafion–SiO$_2$ composite membrane.[22] The temperature dependence may be associated with the activation process of proton conduction in a composite membrane. It can be seen from Fig. 6 that the difference of proton conductivity between 2.5NBS and 5NBS composite membranes decreases at RH $<$ 50% and this is possibly because the ionic clusters and ionic channels for proton migration in the composite membrane shrink at lower relative humidity leading to lower proton mobility.

Conclusions

Sulfonated phenethylsilica appears to be a useful bifunctional additive to a Nafion membrane, improving its water uptake capacity and proton conductivity. The water uptake as well as the ion exchange capacity of the NBS composite membrane increases with the amount of silica incorporated. The degrees of hydration (nH$_2$O/SO$_3$H) of recast Nafion and NBS composite membrane with SiO$_2$ contents of 0–7.5 wt% are similar, and are 21 ± 2 after the membrane is saturated in 80 °C liquid water, and 16.5–13.5 after saturation in room temperature water. The proton conductivity of the composite membranes at 80 °C and

100% RH with 2.5–5.0 wt% SiO_2 is 2.7–5.8 times higher than the Nafion 117 membrane.

Acknowledgements

This work was supported in part by The Ford Motor Company Endowment Fund to CE-CERT, California Energy Commission, Riverside Public Utilities, UC-EI, UC-SMART, Honeywell, US-EPA, and UC-TSR&TP. We thank Dr Stan F. Simpson of Honeywell for providing commercial Nafion 117 membrane samples.

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