Conductive Membranes

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Enhanced Proton Conduction in Polymer Electrolyte Membranes with Acid-Functionalized Polysilsesquioxane**

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Polymer electrolyte membranes are among important classes of polymeric materials as ion-exchangers, electrolytes for batteries and sensors, and dopants for electronic conductors.[1] In particular, recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton-conductive electrolyte membranes.[2] Mostly perfluorinated sulfonic acid ionomers have been studied as a proton-conductive membrane for PEMFCs. Their robust polytetrafluoroethylene (PTFE) backbone combined with strongly acidic perfluorosulfonic acid side chains affords very high proton conductivity and substantial durability. In terms of gas permeability, environmental friendliness, stability at high temperatures, and production cost, however, alternative proton-conductive membranes with non-fluorinated materials are in great demand.

A variety of alternative membranes have been proposed in the last decade.[3] Among them are aromatic hydrocarbon ionomers such as sulfonated polyimides (SPIs),[4] polyethers (SPEs)[5] and polyether sulfones (SPESs),[6] and phosphoric acid doped polybenzimidazoles (PBIs).[7] We have recently developed well-designed polyimide and polyether ionomers, membranes of which have shown 5000 h durability in hydrogen/air fuel cells.[8] One disadvantage yet to be overcome of these new membranes is insufficient proton conductivity, or more precisely, a heavy dependence of the proton conductivity on water activity. Proton conductivity generally drops several orders of magnitude upon decreasing the humidity from 100% to 20% RH (relative humidity). To ease the water management of fuel cells, a proton-conductive membrane that is less dependent on the humidity is mandatory.

For this and other purposes, it has been proposed to incorporate hygroscopic inorganic compounds such as silica,[9] titania,[10] zirconia,[11] tungsten oxide,[12] and others[13] into polymer electrolyte membranes. Some of these membranes show better mechanical properties and lower methanol permeability, however, the composite effect on the proton conductivity was not very distinctive or even negative in some cases. In addition to the chemical and physical state of the inorganic "fillers", the procedure for fabricating the membranes also seems crucial, as absorbed water can take part in proton conduction only when located in the vicinity of acid groups of matrix polymers.

The objective of the present research is to maximize the effect of incorporated inorganic compounds and thus to produce highly proton-conductive composite membranes. Our idea is to adopt 3-trihydroxysilyl-1-propanesulfonic acid (THOPS), which has a sulfonic acid group covalently bonded to a silicon atom through the alkylene group, as a precursor of the inorganic component. THOPS could be converted through a sol–gel process in the polymer electrolyte matrices into sulfopropylated polysilsesquioxane ($\{SiO_{3/2}$-$(CH_2)_3SO_3H\}_n$; SiOPS), which is expected to enhance the water absorbability and the proton conductivity in membranes.

As a matrix polymer, SPI (copolymer composition, $n = 0.5$) with an ion-exchange capacity (IEC) of 1.82 meq g^{-1} was chosen. Sol–gel processing of THOPS was carried out in a heated solution of the SPI in DMSO. Casting the resulting mixture gave composite membranes of SPI and SiOPS (Figure 1).

SPI/SiOPS composite membranes with a SiOPS content of up to 19 wt% were obtained. The brown composite membranes became stiffer with increasing SiOPS content but retained flexibility and transparency even under dry conditions. Formation of polysilsesquioxane was confirmed by ^{29}Si NMR spectra (see Figure S1 in the Supporting Information). In the spectrum of the THOPS used, four peaks were observed at $\delta = -42$, -51, -59, and -68 ppm, which are assignable to T^0, T^1, T^2, and T^3 (where T represents trifunctional silicon and the superscript number represents the number of siloxane bridges). There is some amount of oligomeric siloxane products (T^1, T^2, and T^3) included in the commercial THOPS aqueous solution as acknowledged by the supplier (Gelest, Inc.). In the ^{29}Si NMR spectrum of the resulting composite membrane, only one broad peak for T^3 silicon was observed, indicating a complete dehydration polycondensation reaction.

The morphology of the composite membrane and the distribution of SiOPS was investigated by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). In the SEM image of the cross-section of the membrane (Figure 2a), no particles of SiOPS were confirmed. As confirmed by energy-dispersive X-ray (EDX) analyses,[14] silicon was present relatively uniformly through-

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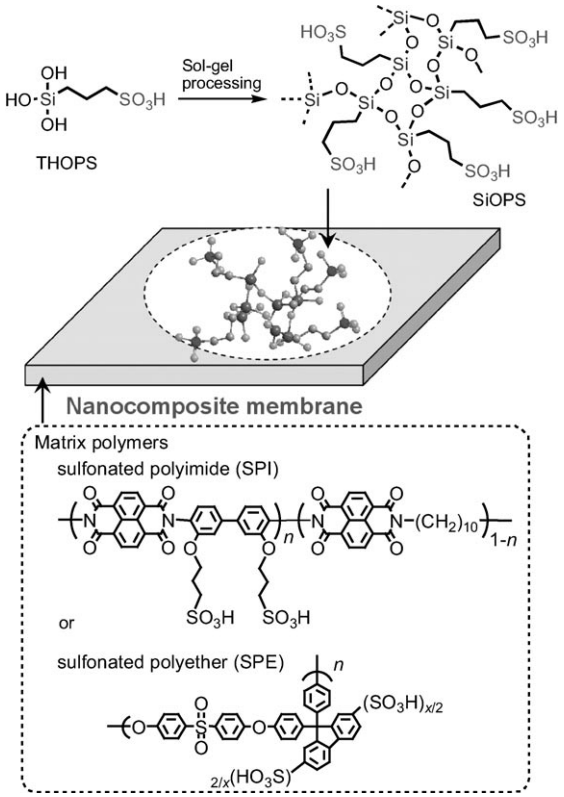

Figure 1. Representation of proton-conductive nanocomposite membranes composed of a polymer electrolyte (matrix) and sulfopropylated polysilsesquioxane (SiOPS).

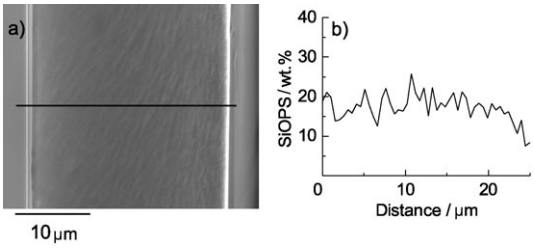

Figure 2. a) Electron microscopy image and b) distribution of SiOPS at the cross-section of the SPI/SiOPS nanocomposite membrane. The average loading of SiOPS was 16 wt%. The SiOPS distribution was calculated from the Si/S atomic ratio obtained by EDX analysis of the sample marked by a black line in part (a).

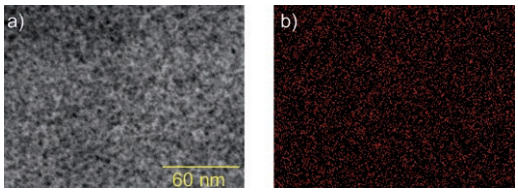

Figure 3. a) STEM image and b) Si elemental distribution of the SPI/SiOPS nanocomposite membrane (average SiOPS loading: 16 wt%). The sample was stained with silver by ion exchange of sulfonic acid groups. The stained membrane was embedded in epoxy resin and sectioned to yield 30-nm thick samples using a microtome. Silicon is represented in red in part (b).

out the membrane which enabled us to calculate the average loading amount of SiOPS (16 wt% in Figure 2b).

The STEM image of the Ag-stained membrane sample revealed that the ionic domains of approximately 5 nm diameter (represented by dark areas) were present and well-connected to each other (Figure 3a). The connectivity of the ionic domains was significantly better than that of the parent SPI membrane, while the size of the spherical ionic clusters was comparable.[8a] It is believed that the ionic domains result from the aggregation of sulfonic acid groups both from the polymer electrolyte and SiOPS. Elemental analyses of the SPI/SiOPS sample shown in the STEM image of higher magnification further support highly dispersed SiOPS (Figure 3b). These results suggest that SPI and SiOPS form a well-dispersed nanocomposite membrane.

The nanocomposite membrane was subjected to stability tests under dry and wet conditions. With thermogravometric (TG)/differential thermal analysis (DTA) under dry nitrogen, the membrane showed four-step weight losses (Figure 4a). By

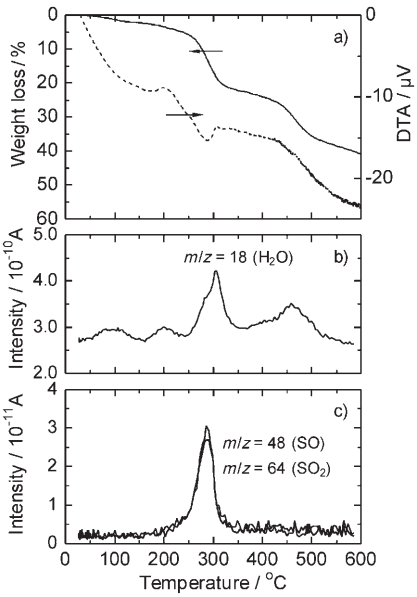

Figure 4. a) TG/DTA curves and b), c) mass spectrometry chromatograms of the SPI/SiOPS nanocomposite membrane in dry nitrogen (average SiOPS loading: 16 wt%).

using mass spectroscopy (Figure 4b and c), the first (RT to 150 °C) and the second (150 to 230 °C) steps were assigned to the loss of absorbed water, while the third (230 to 350 °C) and the fourth (above 350 °C) steps were attributed to the loss of sulfonic acid groups and the degradation of the main chain, respectively. The absorbed water in the second weight-loss step is assigned to the water absorbed by SiOPS, as revealed by comparison with the TG/MS spectra of bare SPI.[15] Note that SiOPS has a stronger water-holding capability than the SPI matrix.[16]

The nanocomposite membrane was substantially stable in wet conditions. After treatment with Fenton's reagent at 80 °C for 1 h or with pressurized steam at 140 °C for 24 h, the

membrane was intact without observable losses of incorporated SiOPS from the membranes, indicating high oxidative and hydrolytic stability (Table 1). The results are surprising given the fact that SiOPS alone dissolves immediately in hot water. There seems to be a strong interaction between SiOPS and SPI (possibly hydrogen bonding among sulfonic acid groups) to stabilize SiOPS in the composite membranes.

Table 1: Oxidative and hydrolytic stability of SPI, SiOPS, and SPI/SiOPS membranes.

Membrane	Oxidative stability [wt%][a]	Hydrolytic stability [wt%][b]
SPI	98	100
SiOPS	0	0
SPI/SiOPS	98	99

[a] Residue after treatment with Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80°C for 1 h. [b] Residue after treatment with pressurized steam (100% RH) at 140°C for 24 h.

The humidity dependence of the water uptake and the proton conductivity of the nanocomposite membranes with different loadings of SiOPS are summarized in Figure 5. As

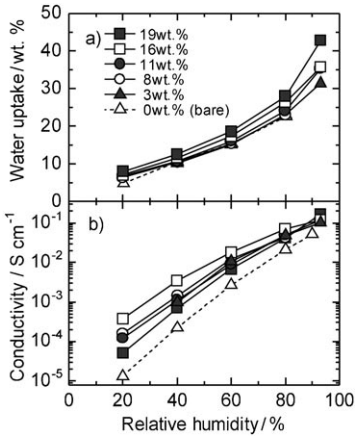

Figure 5. Humidity dependence of a) the water uptake and b) the proton conductivity of SPI/SiOPS nanocomposite membranes at 80°C (average SiOPS loading was 0–19 wt% as indicated in part (a)).

SiOPS with its very high IEC value of 5.71 meq g^{-1} is highly hygroscopic, the composite membranes showed a higher water uptake than the bare SPI membrane. The water uptake increased as the loading of SiOPS increased. While this effect was observed at wide humidity range (20–90% RH), it was more pronounced at higher humidity conditions. The composite membranes showed higher proton conductivity than the bare SPI membrane. In particular, the conductivity at low humidity was significantly improved. The highest conductivity at 20% RH was obtained for the 16 wt% SiOPS sample (3.7×10^{-4} S cm^{-1}) which is about 30 times higher than that of the bare SPI membrane. The higher conductivity of the composite membranes results from the increased IEC value (e.g., 2.43 meq g^{-1} for the 16 wt% SiOPS sample) and the improved water-holding capability (the latter was confirmed by TG analyses in Figure 4). The result is consistent with the above-mentioned microscopic analyses (Figure 3a) in which were observed well-connected ionic domains as a proton-transporting pathway. It seems that the number and connectivity of the ionic clusters are more crucial than their size for a better proton conduction. The higher water uptake and higher proton conductivity of the composite membranes were also confirmed at 100°C (Figure S2 in the Supporting Information) to reveal their good thermal stability. The 19 wt% SiOPS sample showed a lower conductivity at low humidity than the other composite membranes despite its higher water-uptake properties. It is presumably because excess SiOPS molecules could aggregate to form larger particles that are less miscible with the matrix polymer.

To further confirm the effect of SiOPS in the polymer electrolyte membranes, SPE[8d] (IEC = 1.63 meq g^{-1}; degree of sulfonation, $x = 1.1$; Figure 1, bottom) was adopted as a matrix. Unlike SPI, SPE gave opaque white composite membranes regardless of the loading of SiOPS (SPE alone gave transparent colorless membranes). In the SEM and STEM images of SPE/SiOPS composite membranes, ellipsoidal particles of SiOPS with diameters of several hundred nanometers were clearly observed. We have not well understood as yet the origin of the differences in the miscibility (or compatibility) with SiOPS between the two polymer electrolytes. The higher polarity of SPI owing to its imide linkages could be responsible for its better miscibility with SiOPS. The SPE/SiOPS composite membranes showed a similar trend in water-uptake behavior to the SPI composites (Figure 6). Higher SiOPS loadings resulted in higher water uptake. The proton conductivity also increased as the loading of SiOPS increased. At 20% RH, a composite membrane containing 9 wt% SiOPS showed 10 times higher proton conductivity than that of the bare SPE membrane. From these results, it is clear that the incorporation of SiOPS evokes a significant improvement in proton-conducting behavior in the polymer electrolyte membranes.

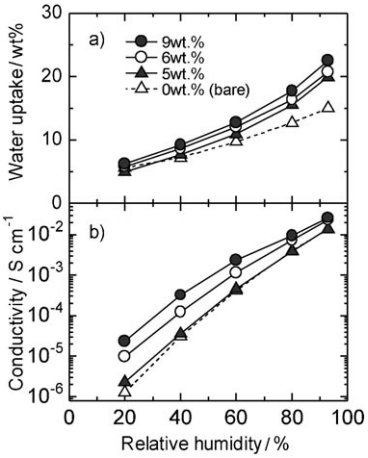

Figure 6. Humidity dependence of a) the water uptake and b) the proton conductivity of SPE/SiOPS composite membranes at 80°C (average SiOPS loading was 0–9 wt% as indicated in part (a)).

In summary, we have developed an effective approach to improving the proton conductivity of polymer electrolyte membranes by simply incorporating acid-functionalized polysilsesquioxane (SiOPS). Nanocomposite membranes prepared by in situ sol–gel processing showed much higher proton conductivity (up to 30 times) than that of the original membranes and accordingly less dependence of the conductivity on the humidity. The methodology is likely to be versatile as confirmed by the preparation of two different series of polymer electrolytes, although the miscibility with SiOPS depends on the matrix polymer. The nanocomposite membranes are expected to have an impact in the field of solid electrolyte science, especially conductive membrane materials.

Experimental Section

Sulfonated polyimide (SPI) was synthesized as described.[8a] An aqueous solution of 3-trihydroxysilyl-1-propanesulfonic acid (THOPS; 0.2526 g, 35 wt%) was added to a solution of SPI (0.25 g) in DMSO (10 mL), and the mixture was stirred at 60 °C for 1 h. It was then cast onto a flat glass plate and dried at 60 °C at atmospheric pressure and at 100 °C under vacuum. The obtained membrane was washed with ethanol containing 1N HNO_3 for 12 h. The acidification procedure was repeated three times and was followed by washing the sample with pure ethanol to obtain a composite membrane.

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[14] The fluctuation in Figure 2b is due to the low intensity (low signal-to-noise ratio) of sulfur as a light element in the EDX analyses but not to the actual variation of the loading amount of SiOPS.
[15] The first weight loss step was assigned to the evaporation of water absorbed by the sulfonic acid groups of SPI. See Ref. [8a].
[16] The higher water-holding capability of SiOPS compared to that of SPI is thermodynamic as the TG curves are independent of the heating rate.

