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Inorganic−Organic Hybrid Membranes with Anhydrous Proton Conduction Prepared from 3-Aminopropyltriethoxysilane and Sulfuric Acid by the Sol−Gel Method

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Polymer electrolyte fuel cells (PEFCs) are attractive power devices because of high-energy conversion efficiency and no pollutant emission. At present, proton exchange membranes used for PEFCs are perfluorosulfonated membranes represented by Nafion. These membranes have some limitations such as use at temperatures lower than 100 °C because of low thermal stability and under high humidity to achieve high proton conductivity.[1] These limitations are disadvantages for higher PEFC performance. Operation of PEFCs at intermediate temperatures (100−200 °C) avoids CO poisoning of the Pt catalyst and accelerates the electrode reactions.[2,3] Therefore, membranes which are suited for use at intermediate temperatures are desired. In this temperature range water absorbed in membranes is removed easily, so that a proton conduction mechanism without the participation of water is favorable. Blends of polymers bearing basic sites such as amine and strong acids such as H_2SO_4 and H_3PO_4 are known to show anhydrous proton conduction.[4,5] In such acid−polymer blends, protons transfer between protonated and nonprotonated basic sites and/or along a hydrogen bond formed among oxoacid anions. Most of these acid−polymer blends, however, have been characterized at temperatures below 100 °C, probably owing to low thermal stability of the organic polymers.[5−10] On the other hand, proton conductive inorganic−organic hybrid membranes prepared by the sol−gel method show thermal stability in the intermediate temperature range because of a presence of polysiloxane backbone.[11−15] It is considered that inorganic−organic hybrid membranes bearing an acid−base pair must be appropriate for use in intermediate temperatures because they possess the properties of both anhydrous proton conduction and thermal stability. In this Communication, we have reported that preparation and characterization of novel inorganic−organic hybrid membranes by the sol−gel method from 3-aminopropyltriethoxysilane (APTES) and sulfuric acid as anhydrous and thermally stable proton conductors.

Mixtures of APTES and water with a molar ratio of 1:100 were stirred for 1 day at room temperature (rt). Concentrated H_2SO_4 was added dropwise to the mixtures cooled in an ice water bath, followed by stirring for 1 day at rt. The molar ratio of H_2SO_4 to APTES was fixed to be 0 or 1.0. Then the sol was poured to Petri dishes and stood without sealing until gelation at rt. The membranes obtained were dried at 50 °C for 1 day and then heat-treated at 100, 150, and 200 °C for 3 h at each temperature. Membranes prepared from only APTES are referred to as poly(3-aminopropylsilsesquioxane) (PAPS) membranes, and ones from APTES and H_2SO_4 are referred to as poly(3-aminopropylsilsesquioxane hydrogensulfate) (PAPS-HSO_4) membranes. For IR measurements, PAPS and PAPS-HSO_4 films on Si substrates were prepared by coating of the precursor sol followed by the same drying and heating process as the membrane preparation. The conductivities of the membranes were determined from impedance data obtained by using an impedance analyzer (Solartron SI 1260) in a frequency range of 10 to 8×10^6 Hz. Gold was sputtered on both sides of the membranes as the electrodes.

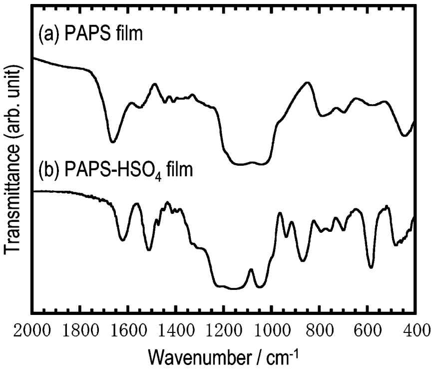

Figure 1. IR spectra of (a) the PAPS film and (b) the PAPS-HSO_4 film coated on Si substrate.

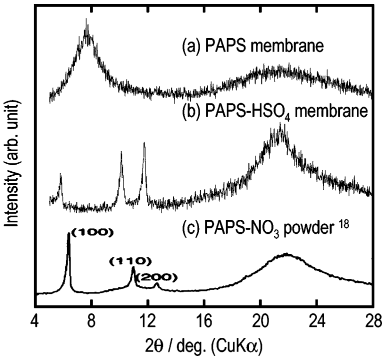

Figure 2. XRD patterns of (a) the PAPS membrane and (b) the PAPS-HSO_4 membrane. XRD pattern of (c) the PAPS-NO_3 powder[18] is also shown for comparison.

Membranes with a thickness of several hundreds of micrometers were obtained. The PAPS-HSO_4 membranes were flexible, whereas the PAPS membranes were stiff and brittle. From the results of DTA-TG measurements, the PAPS-HSO_4 membranes were confirmed to be thermally stable up to 300 °C (see Supporting Information).

Figure 1 shows IR spectra of PAPS and PAPS-HSO_4 films coated on Si substrate. The bands assigned to Si−O−Si are observed for both films at 1150 cm^{-1} and 1050 cm^{-1}.[16] This indicates that ethoxy groups of APTES are hydrolyzed and condensed to form siloxane backbone. For the PAPS films, the band at 1660 cm^{-1} is attributable to $-NH_2$.[16] The weak band at 1530 cm^{-1} ascribed to $-NH_3^+$ is also observed because a part of amino groups is protonated by

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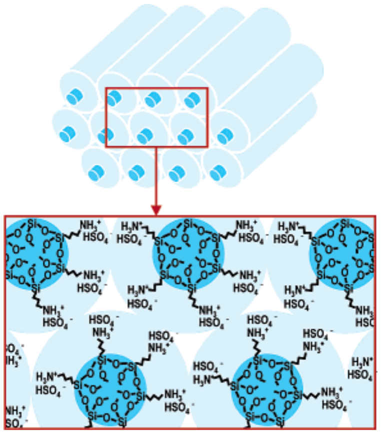

Figure 3. Illustration of supposed nanostructure of the PAPS-HSO$_4$ membrane.

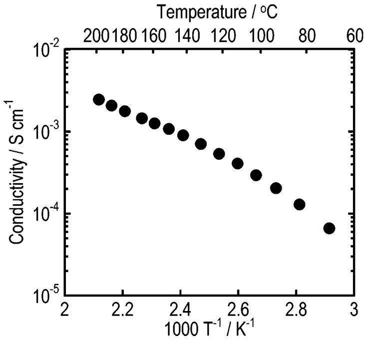

Figure 4. Temperature dependence of conductivity of the PAPS-HSO$_4$ membrane.

residual silanol groups.[16] For the PAPS-HSO$_4$ films, the band assigned to $-NH_3^+$ appears more strongly, indicating that the amino groups are protonated by H_2SO_4. The bands at 580 cm^{-1} and 870 cm^{-1} due to HSO_4^-[17] are observed for the PAPS-HSO$_4$ films. These results suggest that ion complexes were formed by the reaction of amino groups and H_2SO_4 in the PAPS-HSO$_4$ films.

Figure 2 shows XRD patterns of the PAPS membrane and the PAPS-HSO$_4$ membrane. The XRD pattern of a poly(3-aminopropylsilsesquioxane nitrate) (PAPS-NO$_3$) powder sample prepared from 3-aminopropyltrimethoxysilane (APTMS) and HNO_3[18] is also shown for comparison. For the PAPS-HSO$_4$ membrane, three sharp peaks are observed in the small angle region, although there are no sharp peaks for the PAPS membrane. These sharp peaks have a d-value ratio of about 1:0.577:0.5, which is similar to that of the PAPS-NO$_3$ powder. The PAPS-NO$_3$ powder is reported to form a hexagonal phase by the stacking of rodlike polysiloxanes with ion complexes of ammonium groups and NO_3^- extruded outside.[18] Thus, the PAPS-HSO$_4$ membrane was expected to have a similar structure with HSO_4^- as counter anions instead of NO_3^- as illustrated in Figure 3.

Figure 4 shows the temperature dependence of conductivities of the PAPS-HSO$_4$ membrane. The membranes were kept at 200 °C for 2 h under dry N_2 flow to remove absorbed water. Then measurements were carried out at each temperature after they were held for 30 min in a cooling regime from 200 °C. The PAPS-HSO$_4$ membrane shows high conductivity of 2×10^{-3} S cm^{-1} at 200 °C, although the PAPS membrane showed the conductivity of less than 10^{-9} S cm^{-1} at the same temperature. In the PAPS-HSO$_4$ membrane the conductivities probably originated from proton transfer along hydrogen-bond chains formed among HSO_4^- themselves, which is in the same manner as other acid-polymer blends.[4] In the PAPS-HSO$_4$ membranes protons probably migrate through the ion complexes existing outside of the rodlike polysiloxanes. Such conduction paths are different from those in conventional polysiloxane-based hybrid polymers where protons migrate through a three-dimensional random network. It is known that the proton conductivity of an ordered arrangement of proton conductive nanodomain is higher than that of a randomly arranged one.[19] Thus, the ordered arrangement of the ion complexes among the rodlike polysiloxanes would contribute to fast proton transfer by forming a continuous conduction path.

In summary, we have successfully prepared the PAPS-HSO$_4$ inorganic–organic hybrid membranes with high thermal stability. IR spectra of the films show that H_2SO_4 reacts with amino groups to form ion complexes. XRD patterns suggest that the PAPS-HSO$_4$ membranes have a hexagonal structure formed by the stacking of rodlike polysiloxanes with the ion complexes extruded outside. For the PAPS-HSO$_4$ membranes, high conductivity of 2×10^{-3} S cm^{-1} at 200 °C under dry conditions is achieved by the formation of hydrogen-bond chains among HSO_4^- anions, which act as a proton conduction path. Ordered arrangement of the ion complexes would contribute to fast proton transfer by the formation of a continuous conduction path.

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Supporting Information Available: DTA-TG curves of the PAPS membrane and the PAPS-HSO$_4$ membrane. This material is available free of charge via the Internet at http://pubs.acs.org.

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