Preparation of Proton-Conductive Inorganic−Organic Hybrid Films from 3-Glycidoxypropyltrimethoxysilane and Orthophosphoric Acid

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Proton-conductive inorganic−organic hybrid films, which can be used as an electrolyte for polymer electrolyte-type fuel cells at temperatures higher than 100 °C with low humidification, have been prepared from 3-glycidoxypropyltrimethoxysilane, tetramethoxysilane, and orthophosphoric acid by the sol−gel method. Self-supporting, flexible, and brownish transparent films with a thickness of about 200 to 300 μm were obtained. Differential thermal analysis and thermogravimetric measurements revealed that the films were stable up to about 200 °C. The ionic conductivity of the films increased with an increase in the content of phosphoric acid in the films. The films with a molar ratio of P/Si = 1.5 kept a high conductivity of about 7×10^{-4} S cm^{-1} even after holding for 6 h under 0.7% relative humidity at 130 °C.

Introduction

Recently, solid materials with high proton conductivity have attracted much attention for application in a variety of electrochemical devices.[1−3] Among these electrochemical devices, polymer electrolyte-type fuel cells (PEFCs) are being extensively studied as a new energy-conversion device. The PEFCs are at present used at temperatures lower than 100 °C because the proton conductive membranes used for the fuel cells lose their conductivity at temperatures higher than 100 °C. To improve energy conversion efficiency and to avoid CO poisoning of catalysts, PEFCs that can operate at temperatures higher than 100 °C are strongly desired.[3] The high production cost of the membranes formed from perfluoroalkyl sulfonates has motivated the development of a new type of low cost membrane.[3]

We have reported the preparation of proton-conductive solid electrolytes by the sol−gel method,[4−11] and recently found that phosphosilicate gels prepared from tetraethoxysilane and orthophosphoric acid showed high proton conductivity at room temperature and also at temperatures higher than 100 °C with low relative humidity.[10,11] The use of an organic polymer component should allow the formation of flexible proton conducting membranes from these gel powders. The simplest way to form such membranes is the formation of inorganic−organic composites, where pulverized inorganic gel powders are dispersed in a polymer matrix. Another way is the formation of inorganic−organic hybrids, where inorganic and organic components are chemically bonded. Proton-conductive inorganic−organic hybrid membranes have been reported more than 10 years ago by Sanchez and Poinsignon[12] and recently by many researchers.[3,13−19] However, at temperatures higher than 100 °C, these hybrid membranes usually show high proton conductivity only with high humidity.

In the present study, we have prepared proton-conductive inorganic−organic hybrid films, which show high proton conductivity at temperatures higher than 100 °C with very low relative humidity, from 3-glycidoxypropyltrimethoxysilane (GPTMS), tetramethoxysilane (TMOS), and orthophosphoric acid by the sol−gel method.

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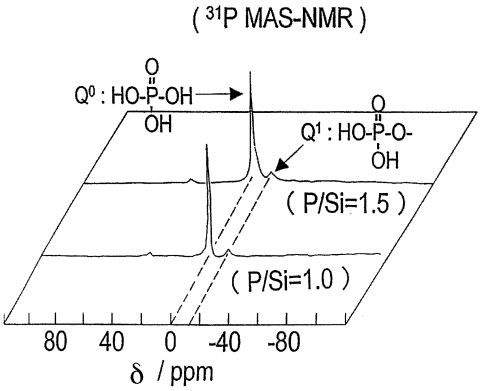

Figure 1. ^{31}P MAS NMR spectra of the inorganic−organic hybrid films with the P/Si molar ratios of 1.0 and 1.5.

Experimental Section

GPTMS and TMOS were dissolved in ethanol, and aqueous orthophosphoric acid was added to the solution to hydrolyze the silanes. After the solution was stirred for 2 h, a precursor sol was obtained. The sol was poured into Petri dishes and gelled at room temperature. The gel films obtained were then dried at 50 °C for 1 day. The films obtained were then dried at 50 °C for 1 day, and consecutively at 100 °C for 5 h and at 150 °C for 5 h.

^{31}P MAS NMR spectra were measured with a Varian Unity Inova 300 spectrometer at 121.42 MHz with a sample spinning rate of about 5000 Hz, and chemical shifts were measured with reference to 85% aqueous H_3PO_4. The proton conductivity of the films was determined from the impedance data obtained using an impedance analyzer (Solartron SI 1260) in a frequency range of 10 Hz to 8 MHz. For the measurement of the conductivity at low relative humidity (RH) at 130 °C, hybrid films on a holder for the conductivity measurements were first kept at 30 °C and 60% RH for 3 h in a temperature- and humidity-controlled chamber, and then inserted into a glass tube which was kept at a given temperature in an electric furnace. The relative humidity was controlled by changing the partial pressure of water vapor in the introduced N_2 gas. Also, dried N_2 gas was introduced into the glass tube at 130 °C.

Results and Discussion

Self-supporting, flexible, transparent, and brownish films with a thickness of about 200−300 μm were obtained in the composition of P/Si ranging from 0 to 1.5 (molar ratio). From the nitrogen adsorption measurements, the hybrid films were found to have almost no pores, and BET surface areas were estimated to be less than 0.5 m^2g^{-1}, indicating that the films were dense. Figure 1 shows the ^{31}P MAS NMR spectra of the hybrid films with P/Si molar ratios of 1.0 and 1.5. The films were dried in a vacuum for 1 h before the measurements. A sharp and intense band is observed at around 0 ppm in both spectra. This band is assigned to isolated phosphoric acid (Q^0 units). A small band at around −15 ppm, which is assigned to condensed phosphoric acid with a bridging oxygen, is also observed. The NMR spectra thus indicate that phosphorus is mainly present as isolated phosphoric acid in the hybrid and only a small portion of phosphoric acid made P−O−P or Si−O−P bonds, which should be observed as Q^1 units. It is confirmed that almost all of the phosphoric acid remained in the films after keeping the hybrid films in the chamber at 30 °C under 60% RH for 3 h. Because the epoxy groups in GPTMS are cleaved under acidic conditions to form hydroxy groups as indicated by FTIR spectroscopy, the hydroxy groups formed are suggested to have a strong interaction with phosphoric acid, which may explain the fact that almost all of the phosphoric acid remains in the films after being kept at 30 °C under 60% RH for 3 h.

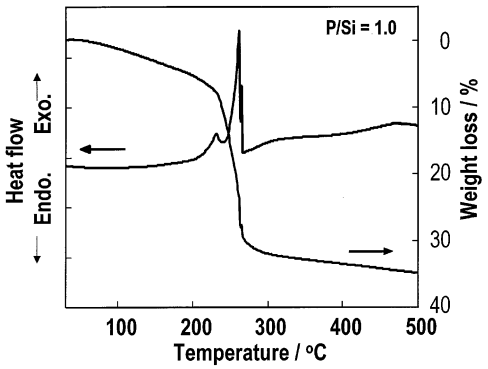

Figure 2. DTA−TG curves for the inorganic−organic hybrid film with P/Si of 1.0.

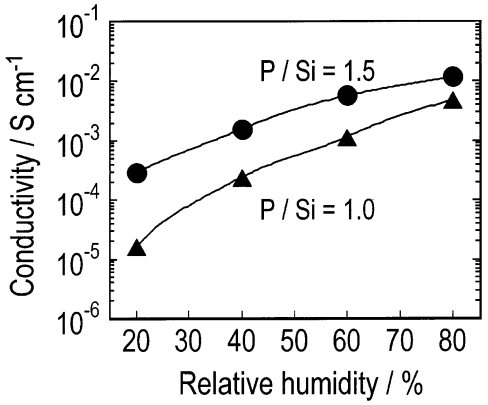

Figure 3. Proton conductivity of the hybrid films as a function of RH at 30 °C.

Figure 2 shows the differential thermal analysis (DTA) and thermogravimetry (TG) curves for the hybrid film with a P/Si molar ratio of 1.0. The small weight loss up to 200 °C is due to the loss of adsorbed water. Exothermic peaks with a decrease in weight at around 200−250 °C are due to combustion of the organic groups in GPTMS. DTA−TG curves reveal that the hybrid films prepared in this study are thermally stable up to about 200 °C.

Figure 3 shows proton conductivity of the hybrid films as a function of RH at 30 °C. The conductivities of all the hybrid films slightly increase with an increase in RH from 60 to 80%, and increase with increased phosphoric acid content of the films. These results indicate that the amount of adsorbed water in the gels must increase with an increase in the RH or the content of phosphoric acid, and the adsorbed water contributes to the increase in conductivity. Although nitrogen adsorption measurements showed that the hybrid films had a dense structure, paths suitable for fast proton conduction must be formed in the hybrid films by the adsorption of water.

Figure 4 shows the variations in conductivities with time for the hybrid films with P/Si of 1.5 kept at 130 °C in dry N_2 and under 0.7 and 1.4% RH. The broken line shows the temperature profile around the sample. In dry N_2, the conductivity of the hybrid films monotoni-

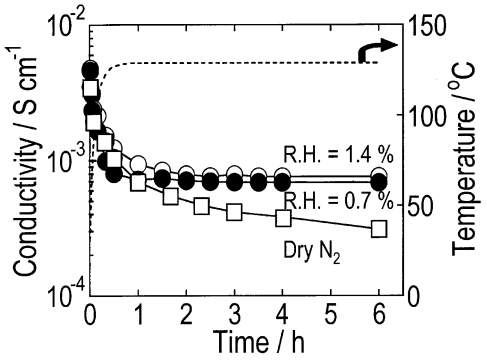

Figure 4. Variations in conductivities with time for the hybrid films with P/Si of 1.5; the films were kept at 130 °C in dry N_2 and under 0.7 and 1.4% R. H.

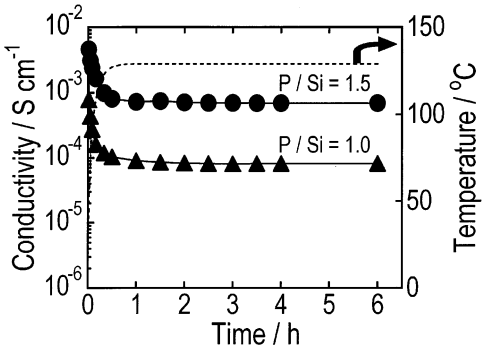

Figure 5. Variations in conductivities with time for the hybrid films with P/Si of 1.5 and 1.0, kept at 130 °C under 0.7% RH.

cally decreases with time. At 0.7 or 1.4% RH, the conductivity slightly decreases and becomes constant after about 1 h, which must be due to the decrease in the amount of the adsorbed water in the film kept at 130 °C. After 1 h, the amount of the adsorbed water continuously decreased in dry N_2. Because more water should be adsorbed in hybrid films under 1.4% RH than in the film under 0.7% RH, the conductivity tends to increase with increasing water content. The conductivities of the hybrid films were lower by one or two orders of magnitude than those of phosphosilicate gels at the same conditions.[11] Phosphosilicate gels, which are hydrophilic and porous, can easily adsorb much water, and exhibit high conductivity even at temperatures higher than 100 °C. In the hybrid films, an organic component, which should be hydrophobic, was introduced. In addition, the hybrid films had a dense structure. Thus, the hybrid films are expected to show much lower conductivity. However, the hybrid films show high proton conductivity at temperatures higher than 100 °C even at low RH, suggesting that the epoxy groups in GPTMS play a very important role in the hybrid films: the epoxy groups in GPTMS were cleaved under the acidic condition to form hydroxy groups, and the hydroxy groups formed must have strong interaction with phosphoric acid and also with water.

Figure 5 shows the variations in conductivities with time for the films with P/Si of 1.5 and 1.0 after being kept at 130 °C under 0.7% RH. The conductivities of the hybrid films become constant after 1 h, and increase with an increase in the content of phosphoric acid in the films. The film with P/Si of 1.5 keeps a high conductivity of about 7×10^{-4} S cm^{-1} even after holding for 6 h. It is reported that H_3PO_4-doped polymers such as polybenzimidazole show high proton conductivity at anhydrous state[1,20,21]. The conduction mechanism of the hybrid films would be very similar to that of the H_3PO_4-doped polymers, but we have proposed here a new class of proton-conducting materials based on organic−inorganic hybrids. The inorganic−organic hybrid showed high proton conductivity both at room temperature with humidification and at temperatures higher than 100 °C with low relative humidity. This indicates that these proton-conductive inorganic−organic hybrid films are very promising as an electrolyte for PEFCs which can operate at temperatures higher than 100 °C with low humidification.

Conclusions

We have prepared proton-conductive inorganic−organic hybrid films from GPTMS, TMOS, and orthophosphoric acid by the sol−gel method. The conductivity of the films increased with an increase in the content of phosphoric acid in the films. The films with P/Si of 1.5 kept a high conductivity of about 7×10^{-4} S cm^{-1} even after holding for 6 h under 0.7% RH at 130 °C. The hybrid films have high potential for use as an electrolyte for polymer electrolyte-type fuel cells at temperatures higher than 100 °C.

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