Preparation of Proton Conductive Phosphosilicate Gels Derived from 2-(Diethoxyphosphoryl)ethyltriethoxysilane

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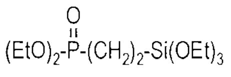
The phosphosilicate gels derived from the mixture of 2-(diethoxyphosphoryl)ethyltriethoxysilane (DPTS) and tetraethoxysilane (TEOS) showed a high proton conductivity after a heat treatment at 450 °C. The high conductivity was brought by the generation of large amounts of isolated orthophosphoric acid in the gels due to the thermal decomposition of DPTS.

Highly proton-conductive gels have a great potential for the application to the total solidification of electrochemical power devices.[1–5] Phosphosilicate gels prepared by the sol–gel method are one of the most promising proton-conductive materials.[6,7] The proton conductivities of the phosphosilicate gels are governed by the amount of phosphorus atoms in the gels, the structure of which is changed with the selection of starting materials containing phosphorus atoms and the heat treatment temperatures. We have prepared phosphosilicate gels from the mixture of tetraethoxysilane (TEOS) and orthophosphoric acid or of TEOS and triethyl phosphate by the sol–gel method and discussed the relationship between the proton conductivity and structure of the gels.[8] We have found that the phosphosilicate gels containing larger amounts of isolated orthophosphoric acid led to higher proton conductivities. On the other hand, it is necessary to develop the silica network of phosphosilicate gels in order to keep the structure stable when they are used at temperatures over 100 °C as electrochemical power devices. However, when the phosphosilicate gels were heat-treated at higher temperatures, e.g., at a temperature in a range of 150–600 °C, for the further development of silica network, the amount of isolated orthophosphoric acid in the gels decreased due to condensation. It is thus important to prepare the phosphosilicate gels consisting of a large amount of isolated orthophosphoric acid and a developed silica network structure for the application to the electrochemical power devices of high reliability.

In this study, we have prepared proton-conductive phosphosilicate gels derived from the mixture of tetraethoxysilane (abbreviated as TEOS; 95%, Wako) and 2-(diethoxyphosphoryl)ethyltriethoxysilane (abbreviated as DPTS; 95%, Gelest) by



$(EtO)_2\text{-}\overset{\overset{\displaystyle O}{\|}}{P}\text{-}(CH_2)_2\text{-}Si(OEt)_3$

DPTS

the sol–gel method. We have also prepared phosphosilicate gels derived from the mixture of TEOS and orthophosphoric acid for comparison. DPTS is a compound with a phosphorus atom combined with a silicon atom through an ethylene group. Therefore, it is expected that phosphosilicate gels derived from DPTS would keep the atomic ratio P/Si constant during the heat treatment and the heat treatment would lead to the thermal decomposition of ethoxy or ethylene groups in the gels to generate much isolated orthophosphoric acid.

TEOS was diluted with ethanol (EtOH) and hydrolyzed with hydrochloric acid at room temperature for 10 min. An appropriate amount of DPTS was added to the hydrolyzed solution and then the solution was stirred at room temperature for 3 h. The solution was kept at 50 °C for 1 week to form stiff gels. The molar ratio of $TEOS/EtOH/H_2O/HCl/DPTS$ was 1/8/8/0.01/1. The dry gels, which were pulverized into powders with an agate mortar and a pestle, were heat-treated at a given temperature in a range of 150–600 °C for 5 h. Phosphosilicate gels derived from the mixture of TEOS and orthophosphoric acid were prepared in the same manner described in a previous paper.[8] The powder samples were pressed into a pellet of 13 mm in diameter and 0.4 mm in thickness, and then gold circular electrodes were evaporated on both sides of the pellet. Ionic conductivities were determined from Cole–Cole plots by an ac method using an impedance analyzer. The resultant gels were characterized by performing the measurements of Fourier transformed infrared spectroscopy (FT-IR), ^{29}Si and ^{31}P solid state magic angle spinning nuclear magnetic resonance (MAS-NMR), X-ray diffraction and specific surface area.

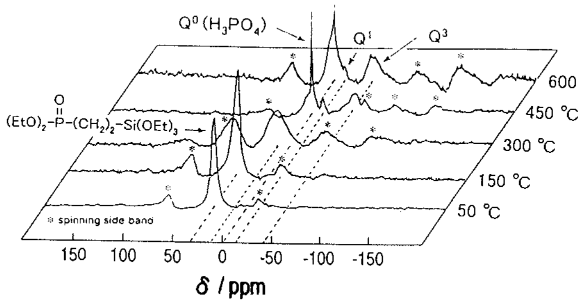


Figure 1. ^{31}P MAS-NMR spectra of TEOS and DPTS-derived phosphosilicate gels heat-treated at various temperatures.

Figure 1 shows ^{31}P MAS-NMR spectra of TEOS and DPTS-derived phosphosilicate gels heat-treated at various temperatures. The peaks at 33 ppm in the gels heat-treated at 50 and 150 °C are attributed to phosphorus atom in DPTS. An intense peak at 0 ppm in the gels heat-treated at temperatures over 450 °C can be ascribed to isolated orthophosphoric acid (Q^0 unit)[9–11], which was generated from the thermal decomposition of DPTS. In the gel heat-treated at 300 °C, a broad peak is observed at 12 ppm. From the changes in IR absorption bands of the gels with heat treatment, the methoxy and dimethylene groups in DPTS were found to thermally decompose at temperatures from 150 to 300 °C and from 300 to 450 °C, respectively. Therefore, a broad peak at 12 ppm in the gel heat-treated at 300 °C is probably due to an intermediate formed by the decomposition from DPTS to orthophosphoric acid. The peaks at –10 ppm due to Q^1 units and at around –44 ppm due to Q^3 units are seen in the spectra of the gels heat-treated at temperatures from 450 to 600 °C. ^{29}Si MAS-NMR spectra of the DPTS-derived gels indicate that six-coordinated silicon atoms which coexisted with four-coordinated phosphorus atoms in the gels were not present for all the gels heat-treated at temperatures in the range from 50 to 600 °C. Thus, the peaks at –44 ppm can be assigned to Q^3 units.[8]

Figure 2 shows the variation of ionic conductivities with relative humidity at 25 °C for the TEOS and DPTS-derived phosphosilicate gels which were heat-treated at various temperatures. The conductivity of the DPTS-derived phosphosilicate gels heat-treated at 150 °C was too low to be measured. IR absorption spectra showed that the ethoxy groups in gels burned out with a heat treatment at 300 °C. Therefore, the increase in the proton conductivity of the gels after a heat treatment at 300 °C should be mainly caused by the generation of P–OH groups due to the combustion of ethoxy groups. It is worth noting that the conductivity of the DPTS-derived phosphosilicate gel drastically increases with a heat treatment at 450 °C. This result must be originated by the formation of isolated orthophosphoric acid in the gel due to the thermal decomposition of DPTS as comfirmed from ^{31}P MAS-NMR spectra and IR spectra. The DPTS-derived gels heat-treated at 450 °C show high conductivities, e.g., 3×10^{-4} S cm^{-1} under 80% relative humidity at 25 °C. The specific surface area (ca. 20 m^2g^{-1}) of the gels and the atomic ratio P/Si (0.5) remained constant during the heat treatment from 150 to 600 °C. It has been found from Figure 1 that the relative peak area at 0 ppm due to Q^0 unit to the total peak area due to the condensed units decreased during the heat treatment in the temperature range from 450 to 600 °C. The decrease in conductivity of the gels during the heat treatment is thus probably attributed to the decrease in the amount of isolated orthophosphoric acid due to the condensation. Proton conductivities of all the DPTS-derived phosphosilicate gels heat-treated at various temperatures are increased with an increase in relative humidity, whereas the difference between conductivities of the gels becomes small. The amounts of absorbed water in the gels must increase with an increase in the relative humidity, so that continuous paths suitable for fast proton conduction are formed in the gels due to the adsorption of water.

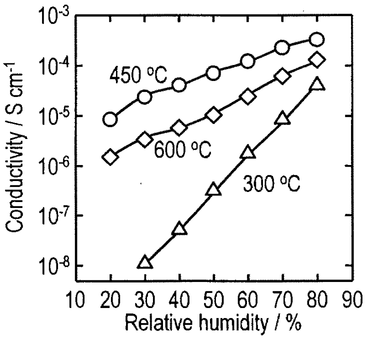


Figure 2. Variation of ionic conductivity with relative humidity at 25 °C for TEOS and DPTS-derived phosphosilicate gels heat-treated at various temperatures. Triangles, circles, and diamonds represent the phosphosilicate gels heat-treated at 300, 450, 600 °C, respectively, for 5 h.

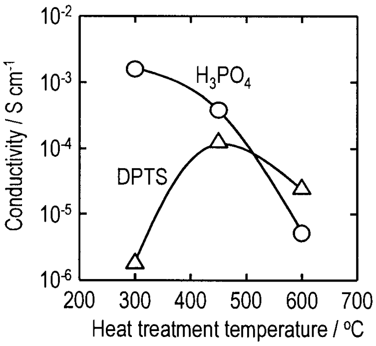


Figure 3. Variation of ionic conductivity under 60 % relative humidity at 25 °C for phosphosilicate gels heat-treated at various temperatures. Circles and triangles represent the phosphosilicate gels derived from TEOS and orthophosphoric acid or TEOS and DPTS, respectively.

Figure 3 shows the comparison of ionic conductivities under 60% relative humidity at 25 °C of TEOS and orthophosphoric acid-derived gels and TEOS and DPTS-derived gels as a function of heat treatment temperature. The molar ratio of P/Si was fixed to be 0.5 for both gels. The conductivity of orthophosphoric acid–derived phosphosilicate gels monotonically decreases with an increase in the heat treatment temperature. On the other hand, the conductivity of DPTS-derived ones is maximized at a heat treatment temperature of 450 °C. Although orthophosphoric acid-derived phosphosilicate gels show higher conductivities than DPTS-derived gels in the heat treatment temperature range up to 450 °C, the proton conductivity (2×10^{-5} S cm^{-1}) of DPTS-derived gels is higher than that (5×10^{-6} S cm^{-1}) of orthophosphoric acid-derived ones in the case of heat treatment at 600 °C. The higher conductivity of DPTS-derived gels after a heat treatment at 600 °C may be caused by the fact that the DPTS-derived gels contained larger amounts of Q^0 unit, namely isolated orthophosphoric acid, than the orthophosphoric acid-derived ones. The ratio (0.63) of the amount of Q^0 unit to the total amounts of the condensed units in the DPTS-derived gels was found to be larger than that (0.53) in the orthophosphoric acid-derived ones from the comparison of their NMR spectra.[8] In conclusion, DPTS is a useful starting material to design phosphosilicate gels with high proton conductivities and a developed network structure for the electrochemical devices with high reliability.

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