Preparation of highly proton-conductive and thermoplastic composites was successfully pursued from H3PO4-doped silica gel and organic polymers with sulfo groups. The sulfo groups and polystyrene blocks in the organic polymers were found to improve the proton conductivity and molding characteristics of the resultant composite, respectively. The composite composed of H3PO4-doped silica gel with a molar ratio of 0.5 of H3PO4/SiO2 in 80 mass% and sulfonated styrene-isoprene-styrene (SIS-SO3H) block copolymer in 20 mass% showed a high electrical conductivity of 10^-4 S·cm^-1 at 25°C in dry N2 atmosphere and good molding characteristics. The temperature dependence of the electrical conductivity of the composite was of the Vogel-Tamman-Fulcher type, indicating that proton transferred through a liquid-like phase present in the composites consisting of silica gel and organic polymer. The elastic modulus of the composite was larger by one to two orders of magnitude than that of the SIS-SO3H elastomer. The thermoplastically deforming temperature of the composite was around 130°C, which was higher by 50°C than that of the SIS elastomer itself. The capacitance of a totally solid state electric double-layer capacitor, which was fabricated using the composite as an electrolyte and activated carbon powders as polarizable electrode, was comparable to those of the conventional capacitors with liquid electrolytes.

Key-words : Sol-gel method, Proton conductivity, Phosphoric acid, Elastomer, Sulfo group, Electric double layer capacitor

1. Introduction

Recently electrochemical devices which convert chemical energy directly to electrical one have been extensively studied from a viewpoint of environment protection since they are expected as clean power sources to reduce the amounts of air pollutants and hazardous substances generated from the combustion of fossil fuels.2) Solid state proton conductors are key materials for the electrochemical power devices such as fuel cells, metal hydride batteries, and supercapacitors.2)–5) The gel materials, which are apparently “solid,” prepared by the sol–gel method contain a large number of micropores and mesopores filled with “liquid.” The gel materials are thus expected to be fast proton conductors by doping an electrolyte into the pores.6) On the basis of the expectation above, we prepared the silica gels containing several kinds of acids and salts as an electrolyte by the sol–gel method and demonstrated that protonic acids with hydrated water acted as effective proton donors to improve the conductivity.7)–9) Moreover we have applied the proton-conducting gels to the electrochemical devices such as electrochromic cells10) and capacitors.11) Very recently we have fabricated composites composed of H3PO4-doped silica gel and styrene-ethylenylene-butylenestyrene (SEBS) elastomer for the improvement of the molding properties12) and for the application to the totally solid-state electric double-layer capacitors as a solid electrolyte.13)

In the preceding work,12),13) we selected SEBS elastomer as a binder to fill up the voids between the silica grains, and we found that SEBS elastomer provided the resultant composites with good molding characteristics. In the present work, we have designed the sulfonated organic polymer, which is expected to assist the proton conduction in the composite as well as good molding characteristics due to the thermoplasticity. This paper reports the proton conductivity and thermoplastic properties of the composites composed of H3PO4-doped silica gel and sulfonated organic polymer. In addition, characteristics of the totally solid state electric-double-layer capacitor fabricated using the composite as an electrolyte and activated carbon powders as polarizable electrode are reported.

2. Experimental procedure

2.1 Preparation of composites

Silica sols were prepared from tetraethoxysilane (Si(OEt)4), ethanol (EtOH), H2O containing HCl as a catalyst, and [C6H5CH2]3NBF4 in a molar ratio of Si(OEt)4 : EtOH : H2O : HCl : [C6H5CH2]3NBF4 = 1 : 4 : 8 : 0.01 : 0.01. The [C6H5CH2]3NBF4 was used to shorten the gelation time. After mixing these components at room temperature, H3PO4 was added to the mixture. The resultant solution was stirred continuously at room temperature until gelation occurred. The H3PO4/SiO2 molar ratio was fixed to be 0.5. H3PO4-doped silica bulk gels obtained were dried in vacuo at 60–80°C for 8 h and heat-treated at 150°C for 1 h. The dried gels were ground to be powders of 10 to 80 μm.

Polyisoprene (PI) and styrene-isoprene-styrene block copolymer (SIS) were selected as the base polymers to be sulfonated (Scheme 1). The average molecular weights of PI and SIS were 40000 and 220000, respectively. The styrene/isoprene mole ratio in SIS was 1.2/78. The specific gravity of the SIS was 0.90. Sulfonation ratios were varied from 0 to 50% for PI and from 0 to 20% for SIS (Table 1), where the ratio was defined as a percentage of the amount of SO3H groups to the total amounts of hydrogens and SO3H groups represented as X in Scheme 1. PI without sulfonation was used as a dioxane solution. Sulfonated polyisoprene (PI-SO3H) with the ratio of 5 and 10% was dissolved in toluene and PI-SO3H with the ratio of 30 and 50% in water. SIS and sulfonated styrene-isoprene-styrene block copolymer (SIS-SO3H) were dissolved in toluene.
Proton-Conductive Composites Composed of Phosphoric Acid-Doped Silica Gel and Organic Polymers with Sulfo Groups

The solutions containing polymers above were mixed with H₃PO₄-doped silica gel powders using an agate mortar in ambient air. The mixing was continued until the solvent completely evaporated. The composites composed of H₃PO₄-doped silica gel and the organic polymer above were subsequently pressed at 400 MPa to be a pellet of 13 mm in diameter and about 1 mm in thickness. The amount of the organic polymer in the composites was varied from 5 to 20 mass%. All the composites were dried in vacuo at room temperature for 1 h before electric and thermo-mechanical measurements.

2.2 Characterization of composites

Solid-state ³¹P NMR spectra were obtained with magic angle spinning (MAS) on a Varian Unity Inova 300 NMR spectrometer operating at 121.419 MHz at a spinning rate of about 5000 Hz to be a pellet of 13 mm in diameter and about 1 mm in thickness. The amount of the organic polymer in the composites was varied from 5 to 20 mass%. All the composites were dried in vacuo at room temperature for 1 h before electric and thermo-mechanical measurements.

2.3 Fabrication of totally solid electric double-layer capacitor

Totally solid state electric double-layer capacitors were fabricated using the composite composed of H₃PO₄-doped silica gel and SIS-SO₃H as an electrolyte and the composite hybridized with activated carbon powders, ACP, as a polarizable electrode. The sulfonation ratio of SIS-SO₃H was 20% and the amount of the SIS-SO₃H blended was 20 mass%. The capacitor fabricated had a three layered structure of polarizable electrode part/electrolyte part/polarizable electrode part and was 13 mm in diameter and about 3 mm in thickness. The preparation process was essentially the same as described in the preceding paper. The feature of the capacitor to be noted is that the large surface area of ACP is covered with the H₃PO₄-doped silica gel because ACP were mixed homogeneously with the sol and then gelatinized.

Cyclic voltammetry of the capacitors was carried out to evaluate the capacitor performance using a Hokuto Denko HA-501 potentiostat and a Hokuto Denko HB-301 function generator. The dc resistance of the capacitors fabricated was calculated from an initial voltage drop when the capacitors were discharged. Discharge properties of the capacitors fabricated were also investigated and the capacitance was determined from the discharge curves. The influence of water adsorption to the composites in an ambient atmosphere on the characteristics of the capacitors was also investigated.

3. Results and discussion

3.1 Properties of H₃PO₄-doped silica gel

Preliminary experiment showed that the protonic acids with hydrated water like H₃PO₄ acted as an effective proton donor and increased the resultant acid-doped silica gels. The H₃PO₄-doped silica gel with a H₃PO₄/SiO₂ molar ratio of 0.5 was amorphous when the gel was heat-treated at 150°C. The heat treatment higher than 180°C was found to cause the formation of crystalline phases such as Si(HPO₄)₂·H₂O and Si₆(PO₄)₄, and to decrease the proton conductivity of the gel.

Figure 1 shows ³¹P MAS-NMR spectrum of H₃PO₄-doped silica gel with a H₃PO₄/SiO₂ molar ratio of 0.5 heat-treated at 150°C. The spectrum was obtained in ambient air at room temperature. A peak of strong intensity at 0 ppm is assigned to H₃PO₄ (Q₀ species), indicating that H₃PO₄ added is present mainly as orthophosphoric acid in the silica gel. A small peak can be seen at −11 ppm, which is assigned to Q₁ species with a P–O–P bond. From the IR absorption spectra it was found that an absorption peak at 1020 cm⁻¹ due to P–O–Si bond was clearly observed in the H₃PO₄-doped silica gels heat-treated at 150°C.
3.2 Properties of organic polymers

The frequency-dependent complex impedance plots were obtained for PI-SO$_3$H with a sulfonation ratio of 50% and SIS-SO$_3$H with a sulfonation ratio of 20% at room temperature. The ionic conductivities of the PI-SO$_3$H and SIS-SO$_3$H were respectively $1.2 \times 10^{-3}$ and $3.2 \times 10^{-4}$ S cm$^{-1}$ in an ambient atmosphere. The conductivities of PI-SO$_3$H and SIS-SO$_3$H decreased by about two orders of magnitude in a dry N$_2$ atmosphere than those in an ambient atmosphere.

Shore hardness and tensile stress of SIS base polymer were 52 and 204 kg/cm$^2$, respectively.

3.3 Proton conductivity of composite of H$_3$PO$_4$-doped silica gel and PI-SO$_3$H

Figure 2 shows an example of the frequency-dependent complex impedance plot measured for the composite composed of H$_3$PO$_4$-doped silica gel and PI-SO$_3$H. The plots were obtained at 23 and 45°C in an N$_2$ atmosphere. The sulfonation ratio of the PI-SO$_3$H was 50%. The composite was dried in vacuo at room temperature for 1 h just before the measurement and the amount of the PI-SO$_3$H blended was 5 mass%. A part of semicircle and a straight line are observed in the plot at 23°C and a straight line at 45°C. It can be seen that bulk resistance of the composite corresponding to the intersection of plots with the real axis decreases with an increase in the measurement temperature.

We have showed in the preceding work that the conductivity of the composites composed of H$_3$PO$_4$-doped silica gels and an organic polymer significantly increased with an increase in the amount of H$_3$PO$_4$ added. This result indicates that the charge carrier of the composites must be proton dissociated mainly from the H$_3$PO$_4$, whereas the transport number of proton in the composites is probably smaller than unity.

Figure 3 shows the temperature dependence of ionic conductivities of composites composed of H$_3$PO$_4$-doped silica gel and PI-SO$_3$H with different sulfonation ratios. Closed diamonds, open squares, closed squares, open circles and closed circles represent the composites containing PI-SO$_3$H with sulfonation ratios of 0, 5, 10, 30 and 50%, respectively. The amount of the PI-SO$_3$H blended was 5 mass% for all the composites. The conductivity of composites was measured in a dry N$_2$ atmosphere during both heating and cooling runs in a temperature range from room temperature to 100°C after the composites were dried in vacuo at room temperature for 1 h.

3.4 IR spectra of PI-SO$_3$H with adsorbed water

Figure 4 shows IR absorption spectra of PI without sulfonation (a) and PI-SO$_3$H with a sulfonation ratio of 50% (b). In Fig. 4(a), absorption peaks at 1650 and 2900 cm$^{-1}$ are assigned to stretching vibrations of C=C bonds and C-H bonds, respectively. The doublet peaks at around 850 and 1400 cm$^{-1}$ are assigned to deformation vibrations of C-H bonds. On the other hand, peaks due to –SO$_3$H bonds are
seen at around 1050 and 1200 cm\(^{-1}\) in Fig. 4 (b). Peaks at 1700 and 3500 cm\(^{-1}\) are assigned to the deformation vibration of H–O–H bonds and the stretching vibration of O–H bonds in H\(_2\)O. In addition, a peak at 2300 cm\(^{-1}\), which is not observable for PI in Fig. 4 (a), is clearly seen. The similar peak was also observed at around 2300 cm\(^{-1}\) for sulfuric acid, so that this peak must be due to S–O–H bonds. When the PI-SO\(_3\)H was dried in vacuo at room temperature, the intensity of the peaks at 1700 and 3500 cm\(^{-1}\) due to H\(_2\)O did not change. This result indicates that H\(_2\)O is strongly adsorbed to PI-SO\(_3\)H. The increase in conductivity of the composites with an increase in sulfonation ratio of PI and with storage in an ambient atmosphere can be ascribed to the increase in the amount of hydrated water, which probably forms liquid paths suitable for proton conduction.

3.5 Proton conductivity of composite of H\(_3\)PO\(_4\)-doped silica gel and SIS-SO\(_3\)H

It was found from Fig. 2 that the conductivity of the composite containing PI-SO\(_3\)H increased with increasing the sulfonation ratio. The molding characteristics of the composite were, however, not so good, and the composite tore when a tensile stress was applied to the composite for the measurement of the thermomechanical properties. For the practical application of proton-conductive composites to electrochemical devices such as fuel cells, metal hydride batteries and supercapacitors, the improvement of molding properties to form sheet of membrane is indispensable. We have shown so far that SEBS elastomer provided the resultant composites with good molding characteristics due to its polystyrene part as a hard segment. In the present work, we have designed the SIS-SO\(_3\)H, which is expected to assist the proton conduction in the composite as well as good molding characteristics due to the thermoplasticity.

Figure 5 shows an example of the frequency-dependent complex impedance plots measured for the composite composed of H\(_3\)PO\(_4\)-doped silica gel and SIS-SO\(_3\)H with a sulfonation ratio of 20% at 32, 48, and 80°C in an N\(_2\) atmosphere. The amount of SIS-SO\(_3\)H blended was 20 mass%. The measurement was carried out in the frequency range from 10 Hz to 8 MHz. A semicircle and a straight line are observed in the plot at 48°C. A part of semicircle is observable for the plot at 32°C and a straight line for 80°C. The bulk resistance of the composite was obtained from the intersection of the semicircle with the real axis at a lower frequency and the intersection of the straight line with the real axis. It can be seen that the bulk resistance of the composite decreases with an increase in the measurement temperature.

Figure 6 shows the temperature dependence of ionic conductivities of the composites composed of H\(_3\)PO\(_4\)-doped silica gel and SIS-SO\(_3\)H. The amount of SIS-SO\(_3\)H was fixed to be 20 mass%. In this figure, x represents the sulfonation ratio in % of SIS-SO\(_3\)H. The conductivity of composites was measured in a dry N\(_2\) atmosphere during both heating and cooling runs immediately after the composites were dried in vacuo at room temperature for 1 h.
of all the composites is roughly the Vogel–Tamman–Fulcher type\textsuperscript{15)} as well as that of the composite with PI-SO\textsubscript{3}H. This result reflects the fact that most of H\textsubscript{3}PO\textsubscript{4} added to silica gels is present as a liquid-like phase in pores filled with adsorbed water in silica gel as shown in Fig. 1.

### 3.6 The thermomechanical properties of the composites

When a tensile stress was applied to the composite containing PI-SO\textsubscript{3}H for the measurement of the thermomechanical properties, the composite tore due to its poor molding characteristics. On the other hand, the composites containing SIS-SO\textsubscript{3}H exhibited a thermoplastic elasticity and good molding characteristics, so that sheets of the highly proton conductive composite were obtained. The elastic modulus of the composites was measured to discuss the influence of the blend of the elastomer to the H\textsubscript{3}PO\textsubscript{4}-doped silica gel.

Figure 7 shows temperature dependence of thermomechanical properties of SIS itself (a) and composite containing SIS-SO\textsubscript{3}H in 20 mass\% (b). The sulfonation ratio of the SIS-SO\textsubscript{3}H was 20\%. Open and closed circles represent the elastic modulus and loss energy, respectively. The elastic modulus and loss energy of SIS-SO\textsubscript{3}H at room temperature are respectively $2.7 \times 10^6$ Pa and $2.1 \times 10^{-7}$ J, whereas those of the composite are $4.6 \times 10^9$ Pa and $4.1 \times 10^{-5}$ J. The temperature dependences of the modulus and loss of the composite were similar to those of the SIS-SO\textsubscript{3}H. For the SIS-SO\textsubscript{3}H, a drop of modulus and a peak in loss energy are seen at around 80°C, which corresponds to the thermoplastically deforming temperature of the elastomer. The drop of modulus is observed around 130°C for the composite, indicating that the thermoplastically deforming temperature is increased by 50°C due to the homogeneous blending of the gels with SIS-SO\textsubscript{3}H. The inorganic gel grains must prevent the softening of SIS-SO\textsubscript{3}H at higher temperatures than its intrinsic thermoplastically deforming temperature. Large fluctuation is seen in loss energy for the composite and the peak corresponding to thermoplastically deforming temperature is not clearly observed. This large fluctuation is probably caused by the energy loss due to heat of vaporization of adsorbed water.

### 3.7 Electric double-layer capacitor using composites as a solid electrolyte

The cyclic voltammogram of the capacitor fabricated using the composite composed of H\textsubscript{3}PO\textsubscript{4}-doped silica gel and SIS-SO\textsubscript{3}H as an electrolyte and ACP as a polarizable electrode showed the typical capacitive current curve in a sweep region of +0.4 to −0.4 V. This result demonstrates that electric charge was stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte in spite of its totally solid state structure. No redox peaks were observed in the sweep region and the cyclic voltammogram was unchanged with repeated runs.

Figure 8 shows the comparison of discharge curves measured in (a) dry N\textsubscript{2} and (b) ambient air atmospheres at room temperature for the capacitor fabricated. The capacitor was charged by applying a constant dc voltage of 0.5 V for 30 min at room temperature before the measurement. Both in (a) dry N\textsubscript{2} and (b) ambient air atmospheres the voltage drop during discharge of the capacitor increases with an increase in the discharge current. It can be seen that voltage drop during discharge in ambient air (b) is
smaller than that in dry N\textsubscript{2} (a). This result corresponds to the drastic decrease in the resistance of the capacitors due to the water adsorption to the composite in an ambient atmosphere. Voltage drops by 1\% and 20\% in 1200 s under a discharge current of 0 A are observed in (a) dry N\textsubscript{2} and (b) ambient air atmospheres, respectively. One of the most important factors which cause these voltage drops should be a leak current through the side area of the three layered tablet capacitor. Perfect insulation between a pair of polarizable electrode layers in capacitors is, thus, required to diminish the current leakage. The increase in the amount of adsorbed water in the capacitor in an ambient atmosphere might facilitate the formation of paths for leakage.

The dc resistance of a capacitor can be estimated by voltage drop, IR-drop, at the beginning of discharge process of the capacitors. Since IR-drop was proportional to the discharge current $I$, $R$(IR-drop) of the capacitor can be obtained. The capacitance, $C$, of capacitors can also be given by $(\frac{I}{V})$, where $I$ is the constant discharge current, $t$ is the time for discharge, and $V$ is the potential change of the capacitor caused by discharge.\(^{17}\) The values of $R$(IR-drop) and $C$ calculated are listed in Table 2 together with resistance obtained from complex impedance plot, $R$(imp.), in a dry N\textsubscript{2} atmosphere and in an ambient air atmosphere at room temperature. Both in dry N\textsubscript{2} and in ambient air atmosphere, the values of $R$(imp.) are comparable to those of $R$(IR-drop). The value of $C$(gram of total ACP) of the capacitor in an ambient atmosphere is four times larger than that of the capacitor in dry N\textsubscript{2} and comparable to those of the conventional capacitors with liquid electrolytes.\(^{18}\) The large capacitance of the totally solid double-layer capacitors fabricated is attributable to the sufficient formation of electric double-layer at the interface between the highly proton conductive silica gel and ACP.

### Table 2. Resistances Calculated from Complex Impedance and IR-Drop and Capacitances (a) in Dry N\textsubscript{2} and (b) in Air of the Electric Double-Layer Capacitor with ACP and the Composite Composed of H\textsubscript{3}PO\textsubscript{4}-Doped Silica Gel and SIS-SO\textsubscript{3}H at Room Temperature

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>$R$(imp.) / Ω</th>
<th>$R$(IR-drop) / Ω</th>
<th>$C$/Fg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Dry N\textsubscript{2}</td>
<td>2530</td>
<td>2710</td>
<td>3</td>
</tr>
<tr>
<td>(b) Air</td>
<td>48</td>
<td>53</td>
<td>12</td>
</tr>
</tbody>
</table>

4. Conclusion

We have prepared composites composed of H\textsubscript{3}PO\textsubscript{4}-doped silica gel and sulfonated organic polymers and investigated the proton conductivity and thermoelastics properties of the composites. The conductivities of the composites containing PI-SO\textsubscript{3}H and SIS-SO\textsubscript{3}H increased with an increase in the sulfonation ratio, so that sulfo groups must assist the proton transfer in the composites. The temperature dependence of conductivity of all the composites was not the Arrhenius type but the Vogel–Tamman–Fulcher type, indicating that proton transferred through a liquid-like phase present in micro pores of the H\textsubscript{3}PO\textsubscript{4}-doped silica gels and/or between the gel granules.

From the IR absorption spectra, the increase in conductivity of the composites with an increase in sulfonation ratio was ascribed to the increase in the amount of hydrated water, which forms the liquid paths suitable for proton conduction.

The composites containing SIS-SO\textsubscript{3}H exhibited not only a high proton conductivity but also good molding characteristics due to its thermoplastic elasticity, so that sheets of the highly proton conductive composite were obtained. For the composite, thermoplastically deforming temperature was observed around 130°C, indicating that the thermoplastic property was improved by 50°C due to the homogeneous blending of the gel with SIS-SO\textsubscript{3}H.

We have succeeded in fabrication of the totally solid electric-double layer capacitors using the composite as an electrolyte and ACP as polarizable electrode. The value of capacitance of the capacitor in an ambient atmosphere was 12 F/(gram of total ACP), which was four times larger than that of the capacitor in dry N\textsubscript{2}. The large capacitance in an ambient atmosphere should be attributable to the formation of electric double-layer with sufficient electricity at the interface between the composite and ACP due to the water adsorption, which allowed the interface to form paths suitable for fast proton transport.

The composite fabricated in the present study is promising as a proton conductive solid electrolyte not only for electric double-layer capacitors but also for fuel cells and metal hydride batteries. The fundamental characteristics of the composites are now under study aiming at the application to the above electrochemical power devices.

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