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Citation	Journal of the Ceramic Society of Japan, 110(1278), 131-134 https://doi.org/10.2109/jcersj.110.131
Issue Date	2002-02-01
Doc URL	http://hdl.handle.net/2115/73943
Rights(URL)	https://creativecommons.org/licenses/by-nd/4.0/deed.ja
Type	article
File Information	JCS110.131-134.pdf



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Phosphosilicate Gels as a Solid State Proton Conductor at Medium Temperature and Low Humidity

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中温低湿度におけるプロトン伝導性固体としてのホスホシリケートゲル

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Phosphosilicate (P_2O_5 - SiO_2) gels with a P/Si molar ratio of 1.0 heat-treated at 150°C were found to retain a high conductivity of $1.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ even after holding at a temperature of 130°C at a relative humidity of 0.7% for about 400 min. On the other hand, the conductivity of the porous silica gels impregnated with 5 M H_3PO_4 largely decreased from 1×10^{-2} to $6 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ during holding under the same conditions for about 400 min. The difference in the changes of conductivities between phosphosilicate gels and H_3PO_4 -impregnated porous silica gels with holding time indicates that the former can retain larger amounts of adsorbed water at 130°C than the latter. Condensed structural units with Si-O-P-OH groups in the phosphosilicate gels are expected to enhance the retention of the adsorbed water in the gels and improve the proton conductivity even at relatively high temperatures and low humidity conditions.

[Received August 22, 2001; Accepted November 16, 2001]

Key-words: Proton conduction, Phosphosilicate gel, Phosphoric acid, Medium temperature range, Low humidity

1. Introduction

In recent years, solid state proton conductors which show high conductivities in the medium temperature range (100–200°C) with low humidity have been required as an electrolyte for direct methanol fuel cells and fuel cells for electric vehicles.^{1)–4)} The efficiency of modification of methanol is improved and the poisoning of Pt catalysts with CO is depressed at medium temperatures. In addition, the weight and volume of humidifiers, which are indispensable for the operation of the polymer electrolyte fuel cells, must be reduced for the practical application to the electric vehicles. These situations described above are the background for the requirement of the highly proton conductive solid state materials in the medium temperature range with low humidities.

Proton conductive organic polymers with functional groups or containing proton donors like acids and salts tend to degrade at temperatures higher than 100°C.¹⁾ Some proton donors like heteropolyacids and protonic acids are dehydrated or thermally decomposed at temperatures in the medium range with relatively low humidity.⁵⁾ Therefore, the selection of matrices with sufficient thermal stability and proton donors which have good affinity with hydrated water and with the matrices is very important^{6),7)} to satisfy the requirements for solid state proton conductors employed in that temperature range with low humidity.

Phosphosilicate, i.e., P_2O_5 - SiO_2 , gels which were prepared from alkoxy silane and H_3PO_4 by the sol-gel method are a promising candidate of the solid state proton conductors in the low and medium temperature ranges.^{8),9)} Since the phosphosilicate gels consist of thermally stable silica networks and phosphate which has a strong affinity with adsorbed water molecules, the gels can be expected to show high proton conductivities at medium temperatures even with low humidity.

We have so far reported the proton conductivities of phosphosilicate gels in a low temperature range around room

temperature and effects of phosphorous-containing starting materials on the conductivity of the resultant gels.^{10),11)} In the present work, changes in proton conductivity of the phosphosilicate gels, which have been prepared by the sol-gel method, with holding time at a temperature higher than 100°C with low humidity have been examined. In addition, we have compared the conductivities of the phosphosilicate gels and porous silica gels impregnated with phosphoric acid to clarify the characteristics of the sol-gel derived phosphosilicate gels.

2. Experimental procedure

The preparation procedures of the phosphosilicate gels were essentially the same as described in the previous paper.¹¹⁾ Tetraethoxysilane (TEOS) and H_3PO_4 were used as the starting materials. In this study, the molar ratio of TEOS/ H_3PO_4 was varied to be 0.5, 1.0 or 1.5. The phosphosilicate gels were obtained at 50°C in a vessel open to the air. The dry gels, which were pulverized into powders with an agate mortar and a pestle, were heat-treated at 150°C for 5 h. On the other hand, porous silica gels were prepared from tetramethoxysilane (TMOS), which was hydrolyzed with ammonia water of pH=9.8 in methanol (MeOH) at room temperature for 10 min; the molar ratio of TMOS/MeOH/ H_2O was 1/2/10. Poly(ethylene glycol) (PEG) was added to the above solution. The average molecular weight of PEG used in this study was 600 and the molar ratio of PEG to TMOS was 0.3. The transparent and homogeneously PEG-containing gels were obtained under the same conditions for the phosphosilicate gels described above. The dry gels obtained were pulverized into powders and heat-treated at 600°C for 5 h to burn out PEG added. The specific surface area and pore volume of the resultant porous silica gels were $671 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.35 \text{ ml} \cdot \text{g}^{-1}$, respectively. The porous silica gel powders were immersed into 5 M H_3PO_4 aqueous solution and impregnated with H_3PO_4 by stirring the solution at room temperature for 3 h. The H_3PO_4 -impregnated porous

silica gels were filtrated and subsequently dried *in vacuo* (the pressure of about 100 Pa) at room temperature.

The phosphosilicate gel powders and H_3PO_4 -impregnated porous silica gel powders were pressed to be a rectangular rod (3 mm \times 3 mm \times 10 mm) in a mold. Silver paste was painted on both end faces of the rod as the electrodes and the faces were attached with gold wires. In the molding with press, polyvinyl alcohol (PVA) of 0.1 g was added to the phosphosilicate gels or the H_3PO_4 -impregnated silica gels (1 g each) to improve the molding properties of the gels. The conductivities of the gels were determined by the impedance data obtained using an impedance analyzer in a frequency range of 10 Hz to 8 MHz.

The sample rods mounted on the holder for conductivity measurements were kept at 30°C and 60% relative humidity (R.H.) for 3 h in a temperature- and humidity-controlled chamber and consecutively inserted into a glass tube which was kept at a given temperature in an electric furnace for the measurement of the electric conductivities of the rods. Changes in the conductivity and temperature of the rods with holding time were continuously measured in the glass tube. The measuring temperature was 130°C. The R.H. of the measuring atmosphere in the glass tube was varied from 0 to 1.4% at 130°C by changing the partial pressure of water vapor in the N_2 gas which was introduced into the glass tube. The values of R.H. at 130°C were calculated from the partial pressure of water vapor in the introduced water vapor-containing N_2 gas and the saturated water vapor pressure (2026 mmHg) at 130°C. For example, the partial pressure of water vapor in the water vapor-containing N_2 gas at 25°C and 60% R.H. becomes 14.3 mmHg. Therefore, the relative humidity in the glass tube at 130°C with the partial pressure of water vapor of 14.3 mmHg is calculated to be 0.7% R.H. Similarly, the partial pressure of water vapor in the water vapor-containing N_2 gas at 30°C and 90% R.H. becomes 28.6 mmHg, which can be achieved by using a humidifier. In this case, the pressure of 28.6 mmHg corresponds to 1.4% R.H. at 130°C. When dry N_2 gas is introduced into the glass tube at 130°C, R. H. in the tube is estimated to be 0%.

X-ray diffraction and ^{31}P , ^{29}Si MAS NMR were measured for the gel powders. An energy dispersive X-ray (EDX) microanalyzer was used for the elemental analysis of phosphorus and silicon in the gels.

3. Results and discussion

Figure 1 shows changes in conductivities of the phosphosilicate (open circles) with a P/Si molar ratio of 0.5 and

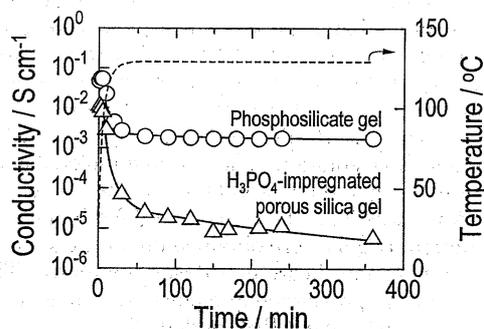


Fig. 1. Variations in conductivities of the phosphosilicate (open circles) and H_3PO_4 -impregnated porous silica (open triangles) gels with holding time at 130°C for 400 min. The R.H. of the measuring atmosphere was 0.7%. The temperature profile for the samples is shown by the broken line.

H_3PO_4 -impregnated porous silica (open triangles) gels with holding time at 130°C for about 400 min. The R.H. of the measuring atmosphere in the glass tube was 0.7%. The P/Si molar ratio of the H_3PO_4 -impregnated porous silica was found from EDX analysis to be about 0.5. The broken line in Fig. 1 is the temperature profile for the gel samples in the glass tube. At the beginning of the sample setting (0 min), the conductivities of the phosphosilicate gel and H_3PO_4 -impregnated porous silica gel were 5×10^{-2} and 1×10^{-2} $\text{S} \cdot \text{cm}^{-1}$, respectively. The conductivity of the phosphosilicate gel decreases by 1.0 to 1.5 orders of magnitude in 20 min and then tends to level off. The initial decrease in conductivity with an increase in the temperature of the gel is caused by a decrease in the amounts of adsorbed water due to evaporation. The phosphosilicate gel shows a conductivity of 2×10^{-3} $\text{S} \cdot \text{cm}^{-1}$ even in about 400 min. On the other hand, the conductivity of the H_3PO_4 -impregnated silica gel largely decreased in 50 min from 1×10^{-2} to 2×10^{-5} $\text{S} \cdot \text{cm}^{-1}$ and then gradually to 6×10^{-6} $\text{S} \cdot \text{cm}^{-1}$ in about 400 min. The P/Si molar ratio of the H_3PO_4 -impregnated silica gel was about 0.5, which was almost the same as that of the phosphosilicate gel. Therefore, the difference in the changes of conductivities between phosphosilicate gel and H_3PO_4 -impregnated silica gel with the holding time indicates that the former can retain larger amounts of adsorbed water at temperatures in the medium range than the latter. The presence of adsorbed water which strongly interacted with phosphosilicate matrix was confirmed from thermal analyses. The results will be reported in detail elsewhere.

Variations in conductivities of the phosphosilicate gels containing various amounts of phosphorus with holding time at 130°C are shown in Fig. 2. Open circles, closed circles and open diamonds represent phosphosilicate gels with the P/Si molar ratios of 0.5, 1.0 and 1.5, respectively. The initial conductivities were 5×10^{-2} $\text{S} \cdot \text{cm}^{-1}$ for the gel with the P/Si molar ratio of 0.5 and about 10^{-1} $\text{S} \cdot \text{cm}^{-1}$ for the gels with the ratios of 1.0 and 1.5. Although the conductivities of all the gels decrease with holding time from 0 to 20 min due to a decrease in the amounts of the adsorbed water by evaporation, the value of each gel tends to level off in 20 min. The conductivities of the gels with the P/Si molar ratios of 1.0 and 1.5 are about 10^{-2} $\text{S} \cdot \text{cm}^{-1}$ even in 400 min, which is much higher than those of the gel with the molar ratio of 0.5. The optimum P/Si molar ratio of the gel to enhance the conductivity of that temperature is probably around unity.

Humidity of the measuring atmosphere was changed to

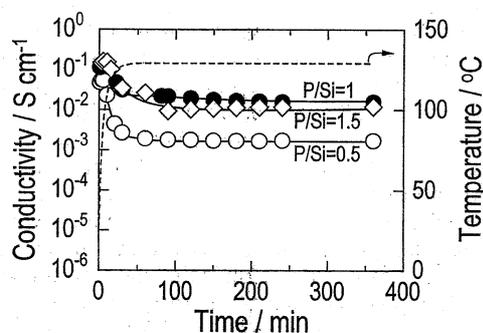


Fig. 2. Variations in conductivities of the phosphosilicate gels containing various amounts of phosphorus with holding time at 130°C for 400 min. The R.H. of the measuring atmosphere was 0.7%, and the broken line has the same meaning as in Fig. 1. Open circles, closed circles and open diamonds represent phosphosilicate gels with the P/Si molar ratios of 0.5, 1.0 and 1.5, respectively.

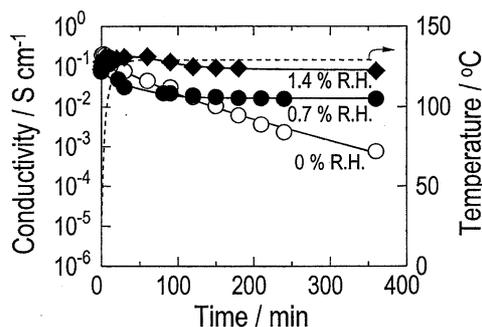


Fig. 3. Variations in conductivities with holding time under 0 (open circles), 0.7 (closed circles) and 1.4 (closed diamonds) % R.H. at 130°C for the gels with the P/Si molar ratio of 1.0. The broken line has the same meaning as in Fig. 1.

evaluate the influence of small amounts of water vapor on the conductivity of the gels; the gels with the P/Si ratio of 1.0 were used. Figure 3 shows variations in conductivities with holding time under 0 (open circles), 0.7 (closed circles) and 1.4 (closed diamonds) % R.H. at 130°C for the gels with the P/Si molar ratio of 1.0. The broken line shows the temperature profile for the gel samples. It can be seen that the conductivity of the gel monotonically decreases from 10^{-1} to 8×10^{-4} S·cm $^{-1}$ while the gel was kept in the atmosphere of 0% R.H. The conductivity of the gel decreases in 20 min and tends to level off at around 10^{-2} S·cm $^{-1}$ during holding under 0.7% R.H. It is noteworthy that the decrease in conductivity of the gel is so small during holding under 1.4% R.H.; the conductivity is as high as 8×10^{-2} S·cm $^{-1}$ even after holding for about 400 min. These results indicate that a very small amount of water vapor is sufficient for the gels to retain a high conductivity of about 10^{-1} S·cm $^{-1}$ at temperatures in the medium range.

The molar ratios of P/Si obtained with EDX for phosphosilicate gels almost agreed with the nominal values of 0.5, 1.0 and 1.5 and unchanged even after a heat treatment at 150°C for 5 h.

All the gels with the P/Si molar ratios of 0.5, 1.0 and 1.5 dried at 50°C were found to be amorphous from the XRD measurements. Whereas the gel with a molar ratio of 0.5 was amorphous after a heat treatment at 150°C for 5 h, the gels with molar ratios of 1.0 and 1.5 formed crystalline $\text{Si}_5\text{O}(\text{PO}_4)_6$ after the heat treatment.

Figure 4 shows ^{31}P MAS NMR spectra of phosphosilicate gels with the P/Si molar ratios of 0.5, 1.0 and 1.5 heat-treated at 150°C for 5 h. A sharp and intense peak is observable at 0 ppm for all the gels, which is assigned to the isolated orthophosphoric acid (Q^0 unit). A small peak due to condensed phosphoric acid with a bridging oxygen (Q^1 unit)¹² is seen at -10 ppm for the gel with a ratio of 0.5. On the other hand, the peaks due to Q^1 unit, Q^3 unit with three bridging oxygens, and fully condensed Q^4 unit¹² are respectively observed at -10 , -31 , and -44 ppm for the gels with ratios of 1.0 and 1.5.

In ^{29}Si MAS NMR spectra of the gels with molar ratios of 1.0 and 1.5, the presence of six-coordinated silicon, which coexists with Q^4 unit due to four-coordinated phosphorus, was confirmed from a peak at around -213 ppm.^{12,13}

The phosphosilicate gels containing condensed phosphorous units maintained higher conductivities than the H_3PO_4 -impregnated porous silica gels as shown in Fig. 1. In all the phosphosilicate gels with the P/Si molar ratios of 0.5, 1.0 and 1.5, the presence of phosphorus Q^1 units as well as Q^0 units was found from MAS NMR spectra as shown in

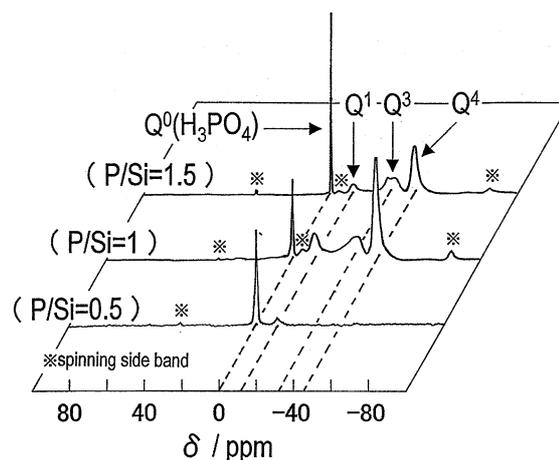


Fig. 4. ^{31}P MAS NMR spectra of phosphosilicate gels, which were heat-treated at 150°C for 5 h, with the P/Si molar ratios of 0.5, 1.0 and 1.5.

Fig. 4. Therefore, phosphorus Q^1 units which should have Si-O-P-OH groups are expected to enhance the retention of the adsorbed water in the phosphosilicate gels and thus improve the proton conductivity of the gels even in a low humidity atmosphere in the medium temperature range.

4. Conclusions

Proton conductivity of the phosphosilicate gels increased with an increase in the P/Si molar ratio from 0.5 to 1.0 and tended to level off at 1.0 to 1.5. The conductivity of the phosphosilicate gel with a P/Si molar ratio of 1.0 decreased and tended to level off at 1.5×10^{-2} S·cm $^{-1}$ in 20 min during holding at 130°C and 0.7% R.H. for about 400 min. The gel showed a high conductivity of 8×10^{-2} S·cm $^{-1}$ during holding under 1.4% R.H. at 130°C. These results indicate that a very small amount of water vapor is sufficient for phosphosilicate gels to retain a high proton conductivity of about 10^{-1} S·cm $^{-1}$ at temperatures in the medium range. The condensed structural units with Si-O-P-OH groups are expected to enhance the retention of the adsorbed water and thus improve the proton conductivity of the gels even in a low humidity atmosphere at relatively high temperatures. Sol-gel derived phosphosilicate gels are thus promising candidates as solid state proton conductors for the electrochemical devices used in the medium temperature range with low humidity.

Acknowledgment This work has financially been supported by the "Research for the Future" Program from the Japan Society for the Promotion of Science and by the Grant-in-Aid for Scientific Research on Priority Areas (B) No. 740 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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