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Effect of Phosphorus Ions on the Proton Conductivity in the Sol–Gel-Derived Porous Glasses

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The effect of phosphorus ions on the proton conductivity was examined for the sol–gel-derived glasses. The porous glasses were prepared through hydrolysis of $PO(OCH_3)_3$ and $Si(OC_2H_5)_4$, in which the phosphorus ions consisted of the POH bonds and were dissolved into the silica matrix without any P-O-Si bond. The electrical conductivity increased in a humid atmosphere and reached ~30 mS/cm at 50°C under 70% RH. High conductivity is achieved by both the POH bonds and the molecular water bonded to the POH bonds. The conductivity increased with a change in humidity from 40% to 80% RH. The phosphorus ions were selectively dissolved in water, resulting in a lower conductivity.

I. Introduction

Fuel cell systems, producing a direct electric current by the reverse chemical reaction of water electrolysis, have attracted much attention because of their ability to produce high energy without the emission of harmful pollutants. For this purpose, the membranes with high proton conductivity and high chemical and thermal durability are required as the electrolytes of the fuel cells. A series of perfluorosulfonic polymers such as Nafion^R have received much consideration as electrolyte separators operating at temperatures <100°C.[1–4] Although these ionomers exhibit high conductivity at low temperatures, they still have problems for practical use, because of their chemical and thermal degradation at temperatures higher than ~100°C. Stable inorganic membranes with high protonic conductivities, if developed, would extend beyond the limitation of the above compounds.

Recently, using a sol–gel method, fast proton conducting glasses were successfully prepared.[5] These glasses exhibit a conductivity of $\sim10^{-2}$ S/cm at room temperature,[6,7] which can function as membranes of the fuel cell electrolyte. The sol–gel-derived glasses are porous, and the pore surfaces are terminated with hydroxyl bonds and absorb water in a humid atmosphere. The proton conductivity in these glasses is promoted by the dissociation of protons from hydroxyl bonds in glass and the proton hopping between hydroxyl groups and water molecules.[7–9] The proton dissociation energy is primarily determined by the hydrogen bonding strength of the hydroxyl bonds. In this sense, the cations bound to hydroxyl with strong hydrogen bonding are favorable to increase the conductivity. Phosphorus ions were one candidate for the strong hydrogen bonding ions, and the P_2O_5–SiO_2 glasses exhibiting a high conductivity of 2.2×10^{-2} S/cm at 50°C were successfully prepared.[5–7] This is the highest conductivity, to our knowledge, for an inorganic glass, which is compared to that of the perfluorosulfonic polymers. However, it is not clear how the P^{5+} ions contribute to the proton conduction of glasses. Generally, phosphates are lacking in chemical durability and the water also lowers the chemical stability of glasses, despite the possibility of high conductivity. It is necessary to both determine the glass composition and manage the water content for the development of high-conducting glasses. Particularly, further research for the effect of the P^{5+} ions on the conductivity is required.

In this paper, we mainly report our studies on the effect of the P^{5+} ions on the proton conduction of the sol–gel-derived glasses. The effect of POH bonds to the electrical conductivity is also discussed from the experimental data on the chemical bonding of the POH in the P_2O_5–SiO_2 glasses.

II. Experimental Procedure

Sol–gel derived P_2O_5–SiO_2 glasses containing nominally 0–20 mol% P_2O_5 were prepared by the following process. Tetraethyl orthosilicate (99.9%, $Si(OC_2H_5)_4$, Colcote, Japan) was partially hydrolyzed at room temperature with a solution of H_2O, C_2H_5OH, and HCl in molar ratios of 1:1:0.01 per mol of $Si(OC_2H_5)_4$. After the solution was stirred for 30 min, trimethyl phosphate (>98%, $PO(OCH_3)_3$, Nacalai Tesque, Japan) was added, followed by stirring at room temperature for 1 h. The resultant solution was hydrolyzed by adding the mixed solution of $4H_2O$, $1C_2H_5OH$, and 0.04HCl per mol of the total amount of alkoxides for 1 h. After hydrolyzing, $HCONH_2$ was added in the solution, followed by stirring for 1 h. $HCONH_2$ is effective in changing the porosity of the glass, the amount of which was changed 1–3 mL for 5 g of oxide glass. The obtained solution was clear and was left for one week to form a stiff gel 0.1–0.5 mm thick. The gel was heated in air at 50°C/h to 600° or 700°C and held at that temperature for 2 h. The porous SiO_2 glass was prepared by the hydrolysis of 1 mol of $Si(OC_2H_5)_4$ with 4 mol H_2O and 1 mL $HCONH_2$ per 5 g of oxide glass. $5P_2O_5 \cdot 95SiO_2$ glass was also prepared from H_3PO_4 instead of $PO(OCH_3)_3$. No $HCONH_2$ was used because of the high reactivity of H_3PO_4.

The surface area, pore volume, and pore size distribution of the sample were measured by a nitrogen gas sorption analyzer (Model NOVA-1000, Quantachrome Corp., Boynton Beach, FL). All the samples were heated in advance at 250°C in vacuum to remove the adsorbed water remaining in the glasses.

The content of P^{5+} and Si^{4+} ions in gel and glass was determined by inductively coupled plasma spectroscopy (Model ICPS-5000, Shimadzu, Tokyo, Japan). The powdered samples were dissolved in a KOH solution.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were collected using a NMR spectrometer (Model Unity 400, Varian Instruments, San Fernando, CA) operating at 161.906 MHz, with a spinning speed of 5 kHz, a delay time of 10 s, and pulse length of 8.8 μs. The chemical shifts were measured relative to 85% H_3PO_4 solution.

The electrical conductivity was determined from Cole–Cole plots by an ac method using an impedance analyzer (Model SI

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1260, Solartron,), where evaporated-gold electrodes were used. The samples were kept in a constant humidity chamber, in which the temperature and humidity were controlled to a constant 30°–90°C and 30%–90% RH, respectively. The Cole–Cole plot consisted of a single semicircle, and the electrical conductivity was obtained from the intersecting point of the semicircle with the real axis.

III. Results and Discussion

(1) Porous Properties and Electrical Conductivity of Glasses

The dried gels were transparent and porous, containing water and solvents incorporated during gel synthesis. The removal of physical adsorbed water and solvents started from room temperature, followed by the removal of water that was chemically bonded with hydroxyl groups on the pore surfaces. Further heating caused the dehydration–condensation reaction between the hydroxyl bonds. According to these reactions, the gels shrunk, resulting in the reduction of surface and volume of pores. The porous structure remained unchanged in glasses heated below ~800°C, the temperature at which porous glasses transform into nonporous ones. The specific surface area and pore volume for the SiO_2 and $5P_2O_5 \cdot 95SiO_2$ glasses prepared using different raw materials and heating at 700°C are summarized in Table I. It is apparent that properties strongly reflect the glass composition, the starting materials, and the amount of additives used in the gel synthesis.

When these glasses are exposed to an ambient air atmosphere, they absorb water, resulting in the increase of conductivity. It was previously reported that electrical charge carrier is proton-dissociated from the hydroxyl groups on the pore surfaces. The conductivity increases with an increase in the content of both the hydroxyl bonds and the adsorbed water.[7,9] In this sense, the glass with a large surface area and pore volume should exhibit high conductivity. However, that result is not necessarily the case; the $5P_2O_5 \cdot 95SiO_2$ glass exhibits higher conductivity than the SiO_2 glass (see Table I). Features of proton dissociation from the hydroxyl bonds can be studied using an infrared absorption spectroscope.[7] In the IR spectra, two absorption bands, peaking at 3680 and 3300 cm^{-1}, are observed, which are both assigned to OH bonds bound with Si^{4+} and P^{5+} ions, respectively. Compared with the SiOH bond, the proton in the POH bond is strongly hydrogen-bonded with water, indicating low activation energy for the dissociation of protons from the POH bonds. The lower activation energy allows the protons to be more mobile, resulting in an increase in the conductivity. The present results can be explained by our idea of proton conduction. However, as shown in Table I, the conductivity of the $5P_2O_5 \cdot 95SiO_2$ glass prepared using H_3PO_4 is $<10^{-5}$ S/cm at 30°C under 70% RH, which is too low, after due consideration of its small surface area and pore volume. This result strongly suggests that the chemical bonding of P^{5+} ions in glass structure is different from that in the glass prepared using $PO(OCH_3)_3$.

The ^{31}P-MAS-NMR spectra were measured to investigate the structure of the glasses prepared using $PO(OCH_3)_3$ and H_3PO_4. The spectra for glasses heated at 600°C are shown in Fig. 1, where the chemical shifts are recorded relative to H_3PO_4 solution. The sharp resonance signal at ~0 ppm, with a small signal at approximately -10 ppm, is observed in the glass prepared using $PO(OCH_3)_3$. The signal at 0 ppm is assigned to the P^{5+} ions bound with four nonbridging oxygens and/or hydroxyl bonds such as H_3PO_4.[10] As discussed later, because of the low reactivity of $PO(OCH_3)_3$, it does not react either with water or the hydrolyzed $Si(OC_2H_5)_4$. $PO(OH)_3$ remains unchanged in the gel and thermally decomposes to form PO_4^{3-} and/or $PO(OH)_3$. On the other hand, in the glass prepared using H_3PO_4, relatively strong signals are also observed at -10 and ~-30 ppm, in addition to the signal at 0 ppm, which are attributed to the P^{5+} ions bonded with one and two bridging oxygens, respectively.[10] This result indicates that H_3PO_4 easily reacts with the hydrolyzed $Si(OC_2H_5)_4$ to form P-O-Si or P-O-P bonds. The formation of these bonds causes the content of hydroxyl bonds to decrease, which results in a lower conductivity of the glass. Thus, the choice of the starting chemicals is important for the preparation of glasses exhibiting high conductivity.

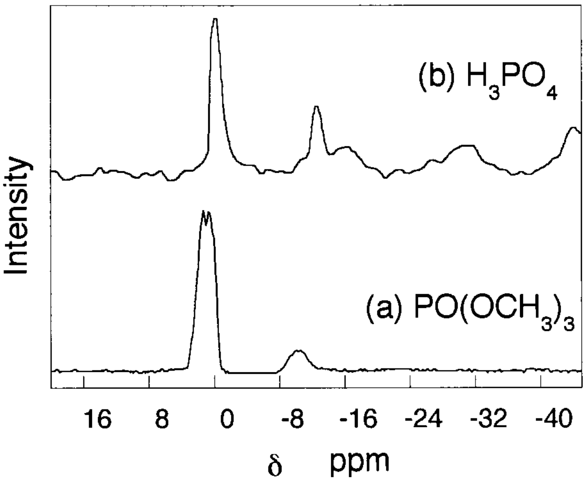

Fig. 1. P-MAS-NMR spectra of the $5P_2O_5 \cdot 95SiO_2$ glasses obtained by heating at 600°C using $PO(OCH_3)_3$ and H_3PO_4.

(2) Chemical Bonding of Phosphorus Ions in Glass

It is evident that the P^{5+} ions can function to increase the conductivity of glass. From this point of view, we can expect much higher conductivity by increasing the P_2O_5 content. It is generally known that the $PO(OCH_3)_3$ scarcely forms a Si-O-P bond.[11,12] The concentration of the phosphorus and silicon ions was determined by an ICP analyzer for gels dried at 45°C and glasses heated at 600°C. The concentration of silicon ions in both the gel and the glass was equal to the nominal composition, whereas the concentration of phosphorus ions decreased. The concentration ratio of the phosphorus ions to silicon ions is shown in Table II for the glasses containing P_2O_5 up to nominally 20%. Note that the phosphorus ions selectively decrease, and the degree of decrease is pronounced as the nominal content of P_2O_5 increases.

Figure 2 illustrates the ^{31}P-NMR spectra for the $5P_2O_5 \cdot 95SiO_2$ glasses heated at 50° to 600°C. The dried gel exhibits one resonance signal at ~3 ppm, the same as that of $PO(OCH_3)_3$, indicating that $PO(OCH_3)_3$ does not react but remains unchanged in the gel. Similar spectra were observed for the samples heated at 100°C. On heating, this signal shifts into a negative ppm, and appears at ~1 ppm at 300°C. The signal ~0 ppm is also assigned to the phosphorus ion in the PO_4^{3-} monomer such as H_3PO_4. Moreover, a small signal appeared at -10 ppm, which is attributed

Table I. Porous Properties and Electrical Conductivity for Glasses Prepared using Different Materials

Sample No.	Glass composition (mol %)	Chemicals for P_2O_5	Heating temperature (°C)	Formamide (mL)	Surface area (m^2/g)	Pore volume (cm^3/g)	Conductivity[†] (S/cm)
1	$100SiO_2$		700	1	7.5×10^2	0.48	5.5×10^{-3}
2	$5P_2O_5 \cdot 95SiO_2$	$PO(OCH_3)_3$	700	1	5.2×10^2	0.37	3.0×10^{-2}
3	$5P_2O_5 \cdot 95SiO_2$	H_3PO_4	700	0	1.3×10^2	0.20	5.5×10^{-6}

[†] Conductivities were measured at 30°C under 70% RH.

Table II. Glass Composition of Gel Dried at 45°C and Glasses Heated at 600°C

Nominal glass composition		Analyzed P/Si ratio	
P_2O_5 (mol%)	P/Si ratio	45°C	600°C
5	0.105	0.075	0.068
10	0.222	0.134	0.103
15	0.353	0.176	0.132
20	0.500	0.169	0.144

to the phosphorus ions bound to one bridging and three nonbridging oxygens.[10] This result suggests that the decomposed $PO(OCH_3)_3$ is partially polymerized or reacted with SiO_4 network structure, forming P_2O_7 or P-O-Si bonds, respectively. Comparing the peak intensity of these species, it is apparent that most of the phosphorus ions form the $PO(OH)_3$ such as phosphoric acid.

(3) Electrical Conductivity and P_2O_5 Content

On exposing the glasses to a humid atmosphere, they absorb the water. Correspondingly, the conductivity increases and reaches a constant level within a few tens of minutes. Figure 3 shows the relation between the conductivity, measured at 30°C, and the relative humidity for the $5P_2O_5{\cdot}95SiO_2$ glasses heated at various temperatures. It is evident that the conductivity increases with increasing humidity and reaches a constant value above ~70% RH. The electrical charge carrier is only proton-dissociated from the POH and SiOH bonds on the pore surfaces, and the conductivity is determined by the amount of both the hydroxyl bonds and the adsorbed water. It is interesting to note in Fig. 3 that the $5P_2O_5{\cdot}95SiO_2$ glasses heated >300°C exhibit a similar dependence of conductivity on the humidity, whereas the conductivities for the dried gel and glasses heated <200°C are low, and less sensitive to the humidity change. This dependence of the conductivities on the heating temperature reflects the glass structure, especially the chemical bonding of the P^{5+} ions. In the glass heated <300°C, as mentioned above, the $PO(OCH_3)_3$ remains unchanged and does not form POH bonds. The protons in the $POCH_3$ bonds do not contribute to the electrical conductivity. It is apparent that the change of the $POCH_3$ into POH makes the conductivity increase. This result again indicates that the protons from the POH bonds are electrical charge carriers and their mobility is enhanced by the adsorbed water molecules.

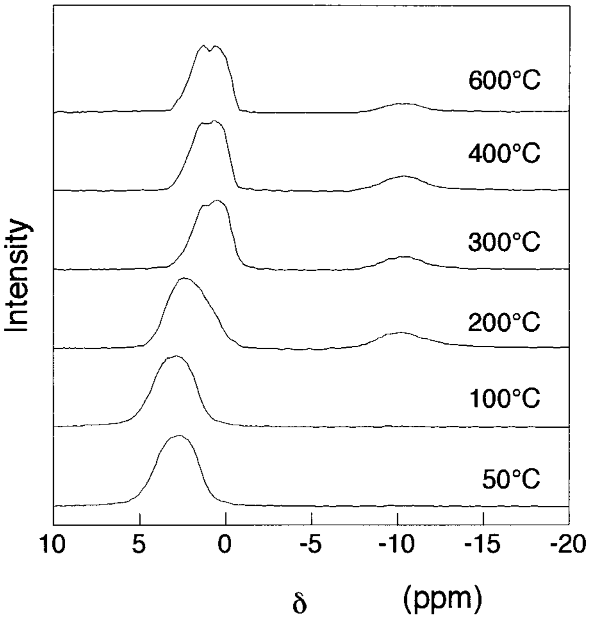

Fig. 2. P-MAS-NMR spectra of the $5P_2O_5{\cdot}95SiO_2$ glasses obtained by heating at 50° to 600°C using $PO(OCH_3)_3$.

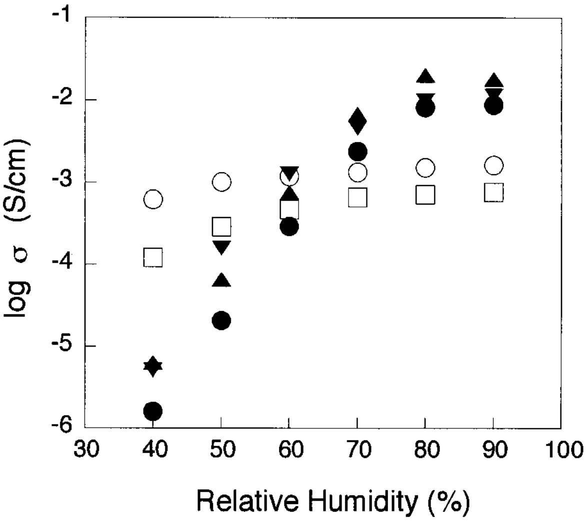

Fig. 3. Relation between the conductivity, measured at 30°C, and the relative humidity for the $5P_2O_5{\cdot}95SiO_2$ glasses heated at 50° (○), 100° (□), 300° (●), 400° (▲), and 500°C (▼).

Figure 4 shows the relation between the conductivity, measured at 90°C under 70% RH, and the content of P_2O_5 in the glasses heated at 600°C, where the P_2O_5 concentration is analyzed. It is interesting to note how the P_2O_5 affects the increase in the conductivity of glasses.

(4) Chemical Durability and Conductivity

Another important feature in increasing the conductivity is that the POH bonds are isolated but do not to react with the silica network structure. However, the lack of the formation of chemical bonding between the P^{5+} and Si^{4+} ions might decrease the chemical durability of the glass. The $5P_2O_5{\cdot}95SiO_2$ glass heated at 600°C was immersed in water and the dissolved elements were analyzed by ICP, the result of which was shown in Fig. 5. In this figure, the contents of the dissolved phosphorus and silicon ions are plotted as a function of immersion time at room temperature. It is evident that the P^{5+} ions are easily dissolved in water and the dissolved phosphorus ions go up to >80% after a long immersion

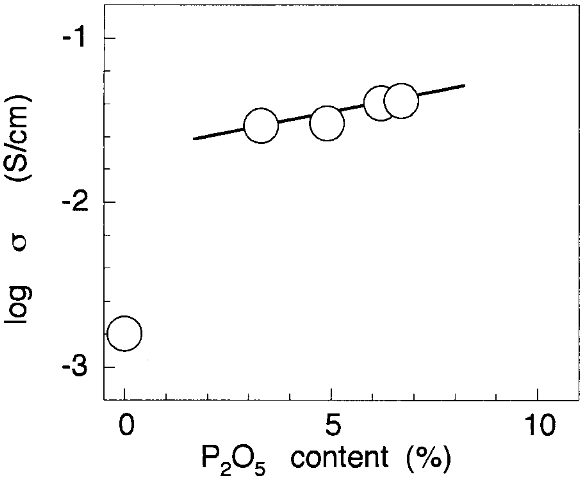

Fig. 4. Relation between the conductivity, measured at 30°C under 70% RH, and the content of P_2O_5 in the glasses heated at 600°C.

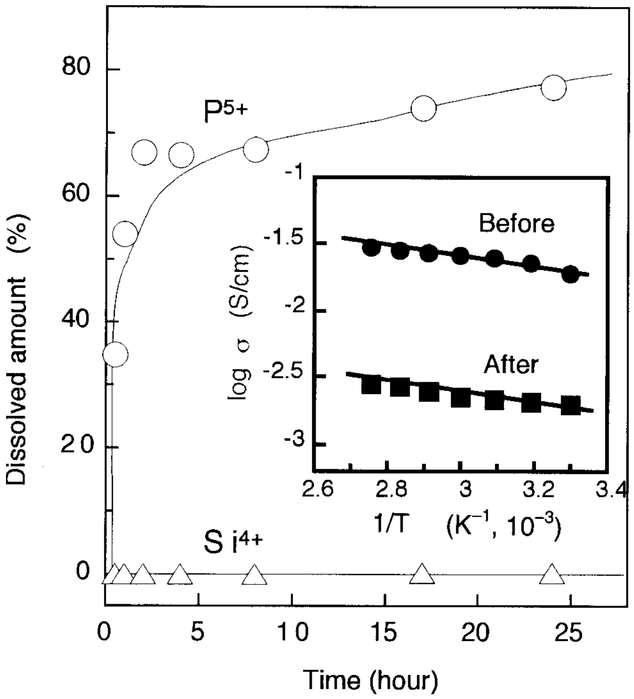

Fig. 5. Dependence of the dissolved amount of P^{5+} and Si^{4+} ions on the immersion time in water for the $5P_2O_5{\cdot}95SiO_2$ glasses heated at 600°C. Inset indicates the temperature dependence of conductivity of the glass before and after immersion for 24 h.

period. Contrarily, the Si^{4+} ions are hardly dissolved. This result strongly suggests that the P^{5+} ions are not chemically bonded to the silica network. The POH bonds are weakly bound with the silica particles consisting of the core structure and are concentrated on the pore surfaces. The change in the conductivity before and after immersion in water is also shown in the inset of Fig. 5, where the conductivities, measured under 80% RH, are plotted as a function of the reciprocal temperature. It is evident that immersion in water causes the conductivity to drastically decrease to values similar to those of the SiO_2 glass.

In the actual fuel cell experiment, the glasses are kept in ambient air <90% RH so as not to solve in liquid water. The conductivity measurement was repeated under high humidity. Figure 6 shows the time dependence of conductivity measured at 50°C under 40% and 80% RH. It is evident that within the experimental conditions, the conductivity is dependent upon the change in the humidity. No decrease in the conductivity was observed within the experimental period.

IV. Conclusions

$P_2O_5{\cdot}SiO_2$ glasses with a high proton conductivity of $\sim 2.2 \times 10^{-2}$ S/cm at 50°C under 70% RH were successfully prepared using the sol–gel method. The phosphorus ions consist of the POH bonds and are dissolved into the silica matrix. Protons in the POH bonds are easily dissociated and transferred between the POH bonds and the adsorbed water, resulting in high conductivity.

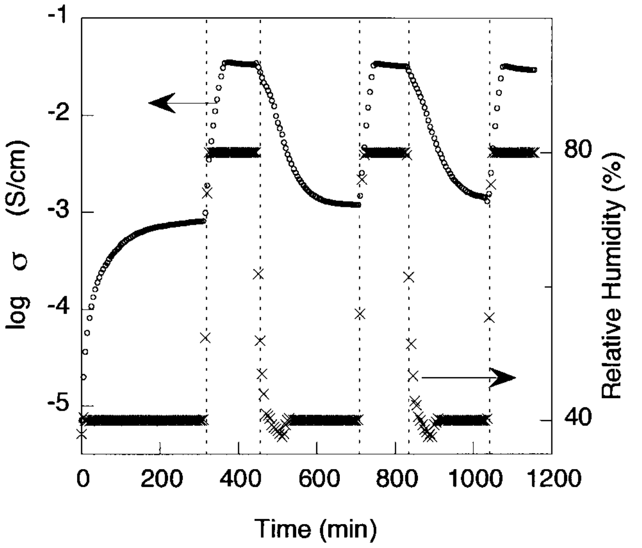

Fig. 6. Change in conductivity, measured at 50°C, on exposure to humid atmospheres of 40% and 80%.

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