

Proton Conduction in Porous Silica Glasses with High Water Content

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Silica glasses with high surface area were prepared by the sol–gel method, the electrical conductivity of which was measured as a function of the content of adsorbed water. The glasses obtained by heating at 400–800 °C had specific surface areas of 700–900 m²/g glass and exhibited room-temperature conductivities of 10^{−6}–10^{−3} S/cm by absorbing the water in pores. The activation energy for conduction linearly decreased with increasing logarithm of the product of proton and water concentration. On the other hand, the increase in conductivity was represented to be proportional to the logarithm of water concentration. Electrical conduction in glasses containing a large amount of water is related to the dissociation of protons from the SiOH bonds and the proton hopping through water molecules in pores.

Introduction

Protons in glass are bound with oxygens to form hydroxyl groups attached to a network forming cations such as Si⁴⁺ and P⁵⁺ and are able to function as electrical charges when they are strongly hydrogen bonded in glasses.^{1–3} Fast proton-conducting glasses, if developed, have a high potential for use in clean energy fields, such as hydrogen gas sensors and hydrogen fuel cells. Recently, using a sol–gel technique, we succeeded in preparing P₂O₅-containing glasses with high conductivities of approximately 10^{−4}–10^{−2} S/cm at room temperature.^{4–6} These high conductivities are considered to be achieved by fast proton mobility in the coexisting adsorbed molecular water in samples. The question how the adsorbed waters contribute to the high proton conductivity was not clear at that time.

In the previous paper, we discussed the effect of molecular water on the proton conduction using sol–gel-derived porous silica glasses containing water molecules up to 2 wt %.⁷ Since the water content is less than 2 wt %, all the water molecules are strongly hydrogen-bonded with SiOH on the pore surface. The activation energy for conduction linearly decreased with increasing logarithm of the product of proton and water concentration. We concluded that the proton conduction is associated with proton hopping between SiOH and water molecules and its activation energy is related to the energy necessary for the dissociation of the proton from SiOH and H₂O. The dissociated proton from the hydroxyl groups moves between the SiOH and the H₂O bound with SiOH. However, the effect of the molecular water adsorbed in excess of the number of SiOH groups still remains unknown. Molecular water acts sometimes in harmful ways to decrease the chemical durability of glasses. The search for the effect of water on proton conduction is necessary for both an understanding of the mechanism of proton conduction in glass and the development of fast proton conducting glasses.

In this paper, we discuss how molecular water contributes to the proton conduction of water-containing glasses. Porous silica

glasses with high specific surface areas were prepared by the sol–gel method, the conductivities of which were measured under a controlled water vapor pressure. Although proton mobility in silica glasses is small owing to weak hydrogen bonding of the SiOH bond, the high surface area of our glasses makes it possible to contain a large amount of proton and water and to measure the conductivity by the alternating current method.

Experimental Section

Si(OC₂H₅)₄ (17.3 g) was hydrolyzed at room temperature with a solution of H₂O, C₂H₅OH, and HCl in molar ratios of 1:4:0.03 per mol of Si(OC₂H₅)₄. After hydrolyzing for 1 h, 3 mL NH₂CHO was added, followed by stirring for a further 1 h, and then the solution was left for 1 week to form a stiff gel about 0.1 mm thick. The gel was heated in air at 50 °C/h to 400–800 °C and held at that temperature for 2 h.

The conductivity was determined from Cole–Cole plots by an ac method using an impedance analyzer (Solartron SI 1260), where evaporated gold electrodes were used. The Cole–Cole plot consisted of a single semicircle, and the electrical conductivity was obtained from the point of the semicircle intersecting with the real axis. The samples for the measurement of conductivity were kept in a chamber controlled at constant temperature and constant water vapor pressure to absorb the water equal to the atmosphere. The mass of adsorbed water was determined by weighing the sample in the chamber.

The surface area, pore volume, and pore size distribution of the sample heated at 400–800 °C were measured by a nitrogen gas sorption analyzer (Quantachrome Corporation NOVA-1000). All the samples were heated in advance to 250 °C in a vacuum in order to remove the adsorbed-waters remaining in the glasses. The thermal analysis (DTA-TGA) curve was recorded with a heating rate of 5 °C/min using powdered samples.

Results

Porous Properties. It is well-known that gels synthesized through the hydrolysis of metal alkoxides contain a large amount of water incorporated during gel synthesis. The water in the

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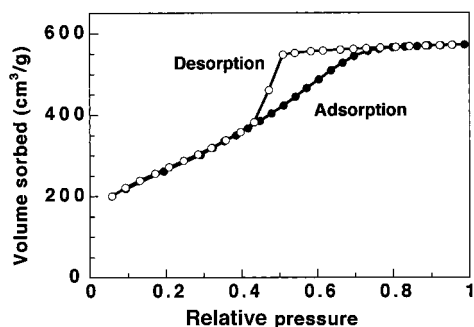


Figure 1. N₂ adsorption–desorption isotherm for silica porous glass heated at 400 °C.

TABLE 1: Porosity and Water Content of Silica Glasses Heated at 400–800 °C

temperature (°C)	surface area (m ² /g)	pore volume (mL/g)	average pore radius (nm)	water content (wt %)	content of surface OH bonds (mol/L), (number/nm ²)	
400	959	0.88	1.8	3.2	7.8	2.2
500	936	0.74	1.6	2.3	5.7	1.7
600	898	0.72	1.6	1.6	3.9	1.2
700	858	0.75	1.7	1.1	2.6	0.8
800	690	0.54	1.6	0.6	1.6	0.6

gel is divided into four types: physically and chemically adsorbed waters in pores, surface OH groups bonded with Si⁴⁺ ions, and OH groups surrounded with silica glass network structure. Heating removes water and formamide and causes polycondensation between the surface SiOH groups. The samples heated above 400 °C are colorless and transparent. A typical adsorption–desorption isotherm for a sample heated at 400 °C is shown in Figure 1. It is of type 4, which has a hysteresis that is normally attributed to the existence of pore cavities larger than the opening, the so-called ink-bottle pores. Pore surface area, pore volume, and the average pore size of glasses heated at 400–800 °C are summarized in Table 1. The specific surface area and volume of pores decreases as the heat treatment temperature increases, which is due to the polycondensation reaction between the surface SiOH bonds: SiOH + HOSi → Si–O–Si + H₂O. The content of OH bonds, shown in Table 1, was determined from the TG curve, assuming that the weight loss was the removal of water produced by the polycondensation of SiOH bonds. Characteristic of these sol–gel-derived glasses is the fact that a large amount of water is left in the glass compared with melt-quenched glasses.

Water Adsorbed in the Porous Glass. Pore surfaces of the porous glass are terminated with hydroxyl bonds and sensitive to air humidity. On exposing the glasses to ambient air, they absorb water, which is hydrogen-bonded with SiOH of the pore surfaces. This reaction is monitored by following the sample weight, which increases with time and approaches a saturated level after several hours. Figure 2 shows the relation between the content of adsorbed water and the partial vapor pressure of water at 30 °C. The water content increases with the water vapor pressure in the atmosphere. After a rapid increase in the water content at the water vapor pressure between ~0.5 and 0.8, the water content reaches a constant value, which is compared to that of the pore volume, indicating that the pores in the glass are filled with water.

Electrical Conductivity. Cole–Cole plots of the frequency-dependent complex impedance show a single semicircle, and electrical conductivity can be determined from the intersecting point of the semicircle with a real axis. Figure 3 shows the relation between conductivity and temperature, measured at

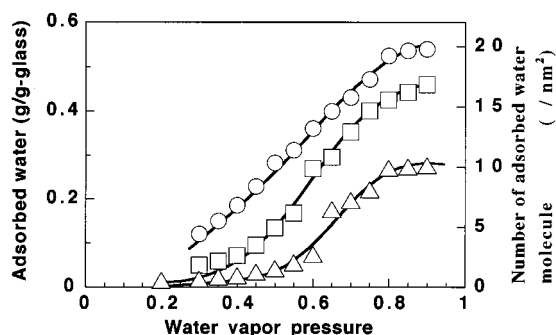


Figure 2. Change in weight of glasses heated at 400 °C (○), 600 °C (□), and 800 °C (△), with exposing in water vapor at 30 °C. The number of adsorbed water molecules per 1 nm² surface area, shown on the right, was determined from the water content and surface area.

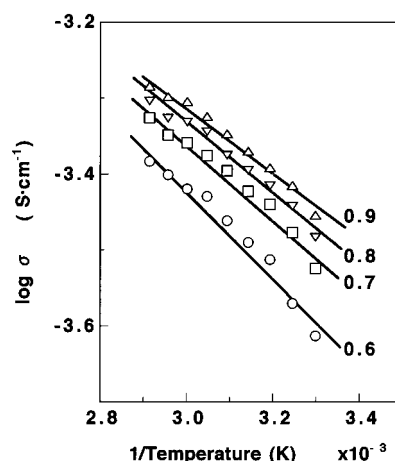


Figure 3. Relation between electrical conductivity and reciprocal temperature for glass heated at 400 °C with exposing in water vapor pressure at 0.6–0.9.

constant water vapor pressure, for glass heated at 400 °C. Note that the conductivity varies exponentially with reciprocal temperature over the temperature range 30–90 °C

$$\sigma = \sigma_0 \exp(-E/RT) \quad (1)$$

where E is an activation energy, T temperature, R the gas constant, and σ_0 a preexponential term. It is evident that the sample treated under high humidity exhibits low activation energy.

The conductivity of samples heated at 400–800 °C, measured at 30 °C in the various water vapor pressures, is plotted in Figure 4 as a function of the water vapor pressure. It is apparent that the conductivity rapidly increases with increasing water vapor pressure and reaches an approximately constant value at the water vapor pressure above 0.8.

Discussion

In a previous paper, we reported the electrical conductivity of porous silica glasses containing both protons and water, the content of which was changed by a careful heat treatment in air and ambient atmosphere.⁷ The activation energy for conduction linearly decreased with increasing logarithm of proton concentration for glasses containing only protons as charge carriers. The porous silica glasses heated at high temperature contain SiOH bonds, but not molecular water, in which OH bonds are concentrated on the pore surfaces to form weak hydrogen bonds with the neighboring SiOH bond. When an electrical field is applied to the glass, the protons are

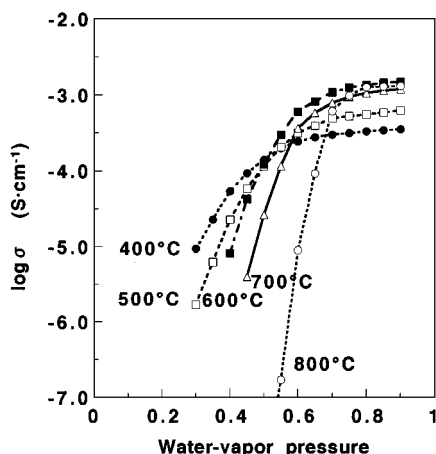
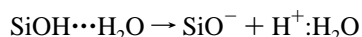


Figure 4. Conductivity, measured at 30 °C, of glasses heated at various temperatures with exposing in water vapor pressure at 0.3 to 0.9.

dissociated from SiOH bonds and subsequently move from the initial site to a neighboring site, resulting in the electrical conductivity. In the glasses heated at high temperature, the number of SiOH bonds decreases according to the dehydration condensation reaction between the surface SiOH bonds. This reaction reduces the proton concentration as a charge carrier, resulting in the decrease in the conductivity. On the other hand, in glasses containing both protons and water, the activation energy for conduction decreased with increasing the logarithm of the product of proton and water concentration:

$$E = E_0 - k \log\{[H^+][H_2O]\} \quad (2)$$

where $[H^+]$ and $[H_2O]$ are contents of proton and water and E_0 is the activation energy independent of the content of water. We concluded from this relation that the activation energy for conduction in glasses containing water molecules bound with SiOH bonds is related to the dissociation of the proton from the SiOH bond and the dissociation equilibrium between the proton and water molecule. The first term in eq 2 corresponds to the energy required to dissociate a proton from the SiOH bond. The dissociated proton moves to a water molecule bound with the SiOH bond, forming the activated $H_2O:H^+$ state:



where the dotted line represents the hydrogen bonding between the proton and water molecule. The second stage of the proton hopping is the dissociation of the proton from the activated $H_2O:H^+$ state.

The second term in eq 2 is considered to be due to the dissociation of the proton from the activated $H^+:H_2O$ state. Since the number of water molecules is limited by the number of SiOH bonds and all the water molecules are linked into the SiOH bond, the dissociated proton moves by hopping between SiOH and H_2O .

In contrast, the present glasses are obtained using NH_2CHO during the gel synthesis to form a high surface area and contain a large amount of OH groups on pore surfaces. For example, a glass heated at 400 °C has a surface area of 960 m²/g and H_2O content of about 3.2 wt %, indicating that the pore surface of 1 nm² contains on the average 2.3 OH bonds. The number of the OH bonds decreases with increasing the heat treatment temperature (see Table 1). On exposing the glasses to ambient air, they absorb a large amount of water in the pores. The absorbed waters, shown in Figure 2, are calculated as the number

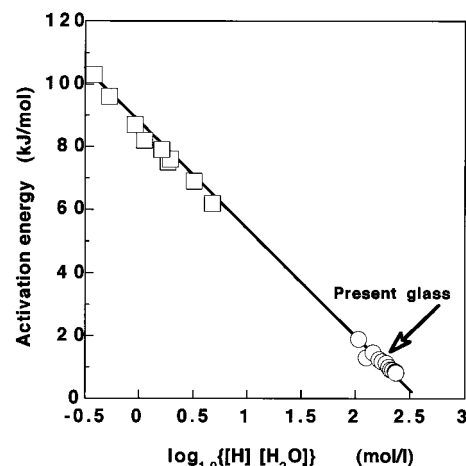
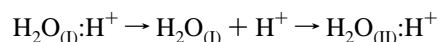


Figure 5. Relation between activation energy for conduction and concentration of protons and water. Activation energy was determined from Arrhenius plots in Figure 3. Data for glasses containing a small amount of water are from ref (7).

of H_2O molecules per 1 nm² surface area, which is shown on the right axis in Figure 2. It is interesting to notice that the number of adsorbed water molecules rapidly increases above the pressure at which the surface SiOH bonds are covered with one water molecule. Among the water molecules adsorbed in the pores, the water molecules in the first layer are strongly hydrogen-bonded with the SiOH groups and the residual H_2O molecules form a liquid state in the pores.

Figure 5 shows the relation between the activation energy and the concentration of proton and water together with the data of the previous study. Note that the activation energy decreases with the logarithm of the product of $[H^+]$ and $[H_2O]$, and a formula similar to eq 2 can be applied. This strongly suggests that the proton conduction in glasses containing a large amount of water is basically controlled by the same mechanism as for glasses containing a small amount of adsorbed water; namely, the charge carrier in these glasses is the proton dissociated from the SiOH bonds. The dissociated proton moves to a neighboring H_2O molecule, forming the activated $H_2O:H^+$ state. The second stage of the proton hopping is the dissociation of the proton from the activated $H_2O:H^+$ state, forming the activated state with the neighboring H_2O :



where $H_2O_{(I)}$ and $H_2O_{(II)}$ represent the water molecules that the proton is hopping between. In this dissociation equilibrium, the dissociation energy decreases with increasing $[H^+]$ and $[H_2O]$. Thus, it is concluded that the activation energy for proton conduction is reduced as the water content increases. The protons transfer by hopping through water molecules in pores.

Next we consider the conductivity of glasses containing a large amount of water. Previously we found that the electrical conductivities linearly increase with the logarithm of the product of protons and water. On the other hand, the present glasses exhibit different dependencies of conductivity on the water concentration. As shown in Figure 6, the conductivities are well represented to be proportional to the logarithm of the water concentration rather than the product of proton and water concentrations. In this figure the conductivities of glasses containing a small amount of water are also shown as a function of the logarithm of water concentration.⁷ It is evident that the conductivities of the present glasses are much higher than those

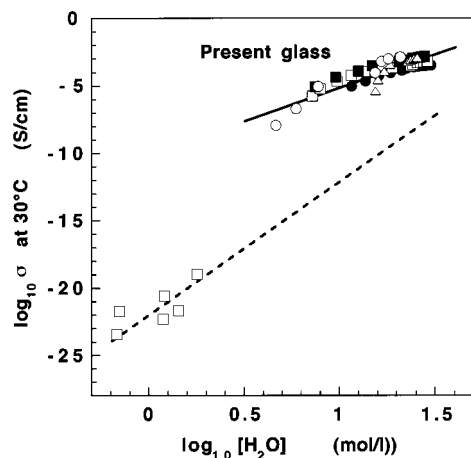


Figure 6. Plotting of electrical conductivity shown in Figure 4 against logarithm of concentration of water. Data for glasses containing a small amount of water are from ref 7. Marks correspond to those in Figure 4.

calculated by extrapolating the relation for the low water-containing glasses. These results also indicate that the protons as the charge carriers transfer by hopping through water molecules in the pores, which is a mechanism similar mechanism to that for proton transfer in liquid water.

Conclusion

The effect of water on proton conduction in glass has been successfully studied in porous silica glasses prepared by the sol-gel method. Silica glasses obtained by heating at 400–800 °C had specific surface areas of 700–900 m²/g glass and exhibited room-temperature conductivities of 10⁻⁶–10⁻³ S/cm by absorbing the water in the pores. The electrical conductivity increased with increasing the logarithm of water concentration. The electrical conduction process was associated with the dissociation of a proton from SiOH bonds and proton hopping through water molecules in the pores.

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