Evidence of water-cooperative proton conduction in silica glasses

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The effect of molecular water on proton conduction was quantitatively analyzed from conductivity measurements of silica glasses with and without water molecules. The activation energy for conduction linearly decreased with increasing logarithm of proton concentration for glasses containing only protons as charge carriers and as the logarithm of the product of proton and water concentration for glasses containing both proton and water. Electrical conduction in glasses containing both protons and water molecules is associated with proton hopping between hydroxyl and water molecules and its activation energy is related to the energy necessary for the dissociation of the proton from OH and H_2O. [S0163-1829(97)02418-1]

I. INTRODUCTION

Generally, electrical conductors of oxide glasses are divided into two types: ionic conduction for alkali-ion-containing glasses and electronic conduction for transition-ion-containing glasses. It has been believed that protons in glasses are not able to play a role as primary electrical charge carriers owing to strong OH bonding.[1] However, Abe and co-workers[2–4] measured high electrical conductivities for phosphate glasses containing protons, but not alkali ions, and concluded that protons are able to function as electrical charge carriers when they are strongly hydrogen bonded in oxide glasses. Protons are bound with oxygens to form hydroxyl groups attaching to network forming cations such as Si^{4+} and P^{5+} ions. The hydroxyl is hydrogen bonded with a counteroxygen, Si (or P-) OH $\cdots$ OSi, in which the hydrogen-bonding strength is strongly dependent on the bond strength between oxygen and Si^{4+} (or P^{5+}). Compared with silicate glasses, the hydroxyl groups in phosphate glasses are strongly hydrogen bonded with the counteroxygens. In certain compositions of calcium phosphate glasses, the mobility of the hydrogen-bonded protons is much higher than that of Na^+ and Ag^+ ions.[5] According to the criterion of Abe *et al.*, high electrical conductivities can be achieved for glasses containing a large amount of protons with strong hydrogen bonding (mobile protons).

The content of protons in glasses is apt to decrease with increasing the temperature of glass melting. Thus it is desired to prepare the glass with a large amount of protons at low temperature, e.g., by using a sol-gel method. Recently, we successfully prepared plates and films of alkali-free zirconium phosphate glasses containing molecular water, of which conductivities were approximately 10^{-2} S/cm at room temperature.[6] It was surprising that the conductivity of these glasses was much higher than those estimated for glasses containing protons, but not molecular water. The proposed mechanism for proton conduction in these glasses is that the dissociated protons move through molecular water so that the activation energy for proton transport is smaller than that in glass containing no molecular water.[6] However, the effect of molecular water was not clearly elucidated at that time. Molecular water acts sometimes in harmful ways to decrease the chemical durability of glasses. Therefore, it is important

to understand how molecular water affects proton conduction and to determine a truly effective molecular water for the development of high-proton-conducting glasses.

In this paper, we discuss how hydrogen-bonded molecular water contributes to proton conduction. Zirconium phosphate glasses are very sensitive to ambient air, which makes it difficult to determine the content of chemically and/or physically adsorbed waters. We used an amorphous porous silica glass prepared by the sol-gel method. Although proton mobility in silica glasses is small, the large amount of protons incorporated in sol-gel-derived glasses makes it possible to measure the conductivities. Furthermore, the structure and content of water in this glass have been investigated by many researchers[7] and can be changed by a careful heat treatment of the glass, which is favorable for discussing the above subjects. The water molecule bound with proton in SiOH bonds was determined using infrared spectroscopy and the effect of water on proton conduction was discussed from the measurement of direct-current conductivity.

II. EXPERIMENT

$Si(OC_2H_5)_4$ was hydrolyzed at room temperature with a solution of H_2O, C_2H_5OH, and HCl in molar ratios of 1:4:0.01 per mol of $Si(OC_2H_5)_4$. After the solution had been stirred for 1 h, it was left for about 2 weeks to form a stiff gel about 0.1–0.3 mm thick. The gel was heated in air at 50 °C/h to 600–800 °C and held at that temperature for 2 h.

Gold electrodes with a guard ring were evaporated onto the sample in order to avoid surface conduction due to water in ambient atmosphere. After exposing in air for 2 days, the sample was heated at 160–310 °C to control the adsorbed water content. Direct-current (dc) conductivity was measured with a vibrating reed electrometer over a temperature range 120–310 °C during cooling from the heat treatment temperature. The current was monitored under dc voltages of 5.0 V, and the steady-state current was measured to determine the dc conductivity. This method required the application of an electric field for period longer than about 30 min for the steady-state current so that there is a possibility of glass-electrode reactions and electrode polarization at high temperature.[8] In this experiment, we confirmed that the conductivity was independent of the voltages in the range of
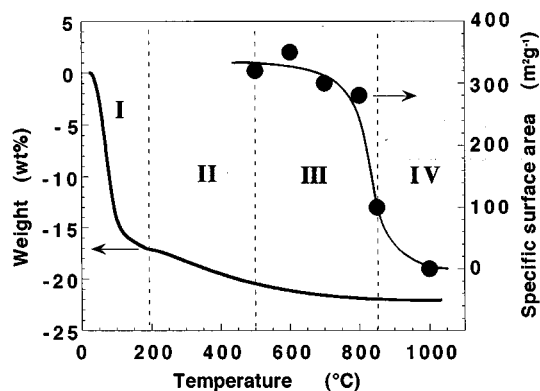
FIG. 1. TGA curve and specific surface area of synthesized silica gel.

3–10 V and no coloration due to the reaction between the glass and electrode was observed.

Infrared (IR) spectra were obtained between 4000 and 2000 cm^{-1} for the ~0.1 mm thick sample. Water content was determined by weighing the sample before and after heat treatment and the absorption intensity of IR spectra. The specific surface area was calculated by the Brunauer-Emmett-Teller (B.E.T.) equation using N_2 gas-adsorption isotherms. A thermal gravimetric analysis (TGA) curve was recorded with a heating rate of 5 °C/min.

III. RESULTS

A. Glass structure and nature of H_2O in glass

Synthesized silica gels are porous, containing a large amount of water incorporated during synthesis. The water in the gel is divided into four groups: physically adsorbed water in pores, water molecules bound with pore surface SiOH groups, surface OH groups bonded to Si ions, and finally OH bonds surrounded with SiO_4 tetrahedral silica networks. When heated, gels transform into glasses according to a dehydration, polycondensation reaction and by sintering. Figure 1 shows the TGA and specific surface area curves of gels, changes of which during heating are divided into four regions as shown in the figure, although the boundary between regions II and III is not clear. First, three regions are based on the removal of water due to the dehydration and condensation reactions, where the surface area remains unchanged. The sequence of dehydration is removal of physically adsorbed water at temperatures in region I, followed by the removal of water molecules bound with the surface SiOH groups (region II), and finally by loss of water produced by the dehydration condensation reaction between the surface SiOH bonds: SiOH+HOSi=Si-O-Si+H_2O (region III). The weight loss in regions I and II is up to ~90% of the total loss, which is restored by the adsorption of water in air humidity. On the other hand, the weight loss in region III is small and gradually proceeds with increasing temperature. The formed Si-O-Si bonds are stable, not to be ruptured by exposure to the ambient air humidity at room temperature. The abrupt decrease in surface area at around 850 °C is due to the sintering of particles promoted by the viscous flow of silica (region IV). The porous structure remains unchanged in glass heated below 800 °C, surfaces of which are terminated with SiOH bonds.
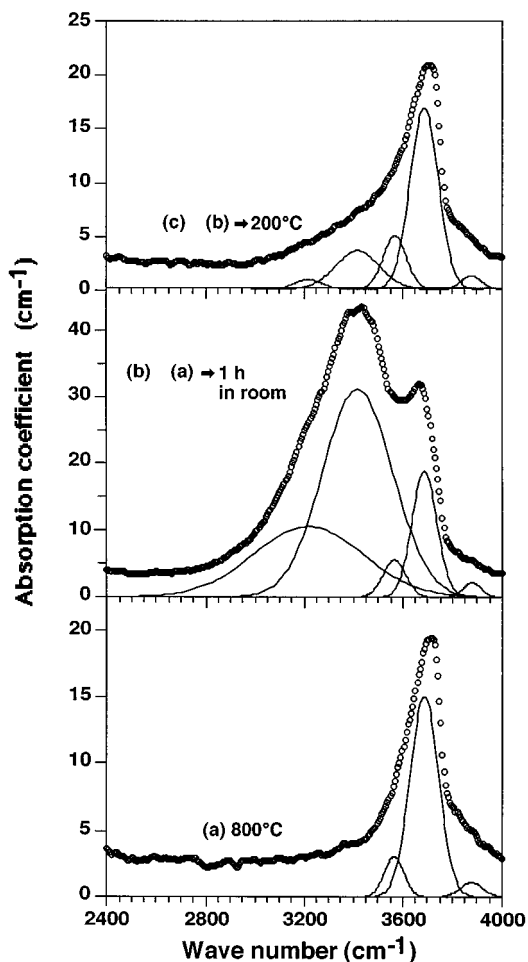

FIG. 2. Infrared spectra for glasses heated at 800 °C (a), followed by exposing to an air atmosphere at room temperature for 1 h (b), and then heated at 200 °C for 1 h (c).

The SiOH groups on pore surfaces are sensitive to air humidity, and the adsorption-desorption reaction is reversible. Figure 2(a) shows the IR spectrum of sample heated at 800 °C: an absorption band at around 3700 cm^{-1} with shoulders at high- and low-wave-number sides of the main band, which is deconvoluted into three bands at 3550, 3680, and 3830 cm^{-1} using a Gaussian function as shown in Fig. 2(a). These are all assigned to the OH stretching modes of Si-OH bonds.[9] On heating in region III the absorption intensities of these bands decreased according to the dehydration-condensation reaction of SiOH bonds. Intensities for glass obtained by heating at 800 °C were about 10 times higher than those for dense glass heated at 900 °C. Porous glass, heated at 800 °C, was exposed into ambient air for 1 h at room temperature, the spectrum of which is shown in Fig. 2(b); pronounced broadbands around 3200 and 3400 cm^{-1}, which are assigned with the free and hydrogen-bonded molecular water, respectively. The intensities of the 3200 and 3400 cm^{-1} bands increase with increasing the exposing time, indicating large quantities of absorbed waters. These adsorbed waters were reversibly removed by heating above 100 °C as shown in Fig. 2(c). On the other hand, the intensity of bands at 3550, 3680, and 3830 cm^{-1} remains unchanged during these treatments.

TABLE I. Water content, electrical conductivity at 150 °C, and activation energy for conduction of glasses heated at 600, 700, and 800 °C, followed by exposing to an air ambient for 2 days, and then heated at 160–300 °C for 2 h.

	H$_2$O/wt. %			$\log_{10}(\sigma/\text{S cm}^{-1}$ at 150 °C)			Activation energy (kJ/mol)		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
160 °C	1.62	1.29		−12.0	−13.1		62	76	
210 °C	1.09	1.07		−12.8	−13.4		69	79	
250 °C	0.63	0.61	0.57	−13.3	−13.6	−14.6	75	87	103
310 °C	0.38	0.35	0.29	−13.5	−14.4	−15.1	82	96	111
[a]	1.19	0.62	0.27				115	129	136

[a]Numbers in the bottom row are for glasses heated at 600, 700, and 800 °C.

These experimental results indicate that the amount of water bound with Si-OH groups of pore surfaces can be determined by exposure in air, followed by heating at temperatures in the region II. In this experiment, water contents were determined by weighing the sample before and after heating at 150–350 °C, which are summarized in Table I.

B. Electrical conductivities of glasses treated in ambient air humidity

The direct-current conductivities were measured for samples containing the water molecule bound with the surface SiOH groups, but not physically adsorbed water in pores. Generally, the conductivity varied exponentially with reciprocal temperature over the temperature range measured:

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

where E is an experimental activation energy, T temperature, R the gas constant, and σ_0 a preexponential term called the frequency factor. Figure 3 shows the conductivity vs temperature plot based on Eq. (1) for glasses heated at 160–310 °C. Prior to the conductivity measurement, samples were heated at 600 °C, followed by exposure to air for 2 days to absorb water. It is evident that the sample heated at high temperature exhibits low conductivity and high activation
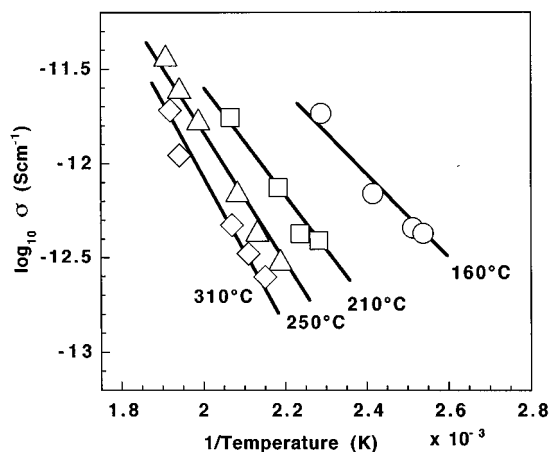

FIG. 3. Relation between electrical conductivity and reciprocal temperature for glasses heated at 600 °C, followed by exposing to an air ambient for 2 days, and then heated at 160, 210, 250, and 310 °C for 2 h.

energy. Similar changes were observed for samples heated at 700 and 800 °C. Table I summarizes the experimental results of activation energies and the electrical conductivities at 150 °C.

The electrical conductivity was also measured for glasses, heated at 600–800 °C, containing no molecular water, although these data have somewhat large experimental errors owing to the measuring limits of our equipment. These data are listed in Table I.

IV. DISCUSSION

One possible mechanism for proton conduction in materials with hydrogen bonding is a cooperative proton transfer along a linked chain of hydrogen bonds. This involves the dissociation of protons, their orientation along the conducting direction, and tunneling.[10] Protons are rapidly transferred from one site to the other site. Abe *et al.* assert that protons in glasses are divided into two main types of mobile and immobile protons according to the strength of the XOH $\cdots$ OX hydrogen bonding, and the mobility of protons increases with the strength of hydrogen bonding.[4] The OH bond in phosphate glasses is generally weak owing to the formation of hydrogen bonding, and the mobility of dissociated protons into the glasses is much higher than that of the alkali ions. In contrast with such phosphate glasses, when water is incorporated in silica glasses, it forms a silanol bond, in which the OH bond is very strong (weak hydrogen bonding) and the protonic electrical conductivity is very low. This is true for full density silica glasses containing impurity water. The present glasses are porous and contain a large amount of OH bonds on pore surfaces. For example, a glass heated at 800 °C exhibited a high OH content of about 0.3 wt. % in water and an electrical conductivity of 1.5×10^{-16} S/cm at 150 °C. Thus the measured high conductivities can be attributed to the high proton content.

As shown in Figs. 1 and 2, glasses heated at a temperature above 600 °C contain SiOH bonds, but not molecular water, in which SiOH bonds are concentrated on the pore surfaces to form weakly hydrogen bonding with the neighboring SiOH. Therefore, it is considered that the electrical conductivity is associated with proton dissociation from SiOH bonds under an electrical field and the subsequent hopping of protons from the initial site to a neighboring site. The activation energies for conduction are plotted in Fig. 4 as a function of the logarithm of proton concentration
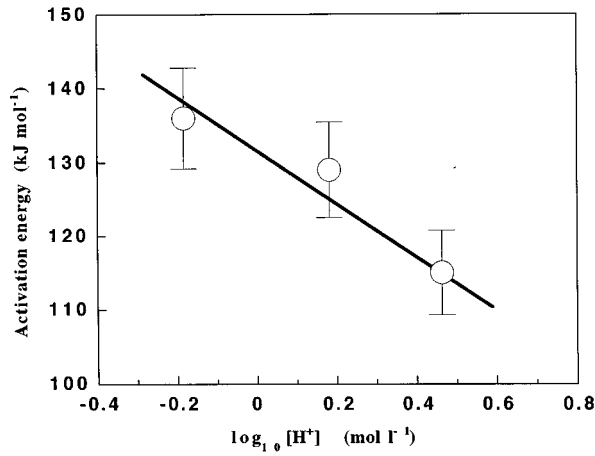
FIG. 4. Relation between activation energy for conduction and the proton concentration in glasses heated at 600, 700, and 800 °C for 2 h. The content of molecular water is zero or negligibly small.

($\log_{10}[H^+]$), satisfying the linear relation between E and $\log_{10}[H^+]$ within the experimental errors:

$$E_1 = E_{10} - n_1 \log_{10}[H^+]. \tag{2}$$

A similar relation has been found in alkali-free phosphate glasses containing protons.[2–4] In Eq. (2) the value of E_{10} is an activation energy at $[H^+]=1$ (mol/l); it is 130 kJ/mol, somewhat smaller than that obtained for dense silica glass containing impurity water (~ 150 kJ/mol). Such a small energy is reasonably explained as follows: E_{10} energy is considered to be term of the energy required to dissociate protons from SiOH bonds overcoming the binding force of OH bonds. The formation of hydrogen bonding makes the energy for proton dissociation lower, resulting in small activation energy. On the other hand, the constant n_1 is considered to be related to the proton-jumping process from a given site to a next site and depends on the host-glass compositions. The hopping distance to protons decreases with increasing proton concentration, which also results in a lower activation energy for hopping.

Next, we will discuss the effect of water molecules on proton conduction. The water contents of SiOH groups of pore surfaces were changed between 0.2 and 1.5 mol/l by exposure in air followed by heating at 160–310 °C. These water contents are compared with the number of protons of the surface SiOH groups (0.6–2.9 mol/l in H^+), meaning that all the adsorbed water are hydrogen bonded with SiOH groups and there is no free molecular water in pores. The dependence of proton conductivity on water content is evident from data shown in Fig. 3 and Table I. Activation energies are plotted in Fig. 5 as a function of the logarithm of water content. It is evident that the relation is expressed by the similar formula as Eq. (2) applied for the proton conduction of glasses containing no molecular water:

$$E_2 = E_{20} - n_2 \log_{10}[H_2O], \tag{3}$$

where the values of E_{20} and n_2 have same meanings as Eq. (2). The experimentally obtained activation energy depends linearly on the logarithm of water content, and the slope of the line is almost the same within experimental error for
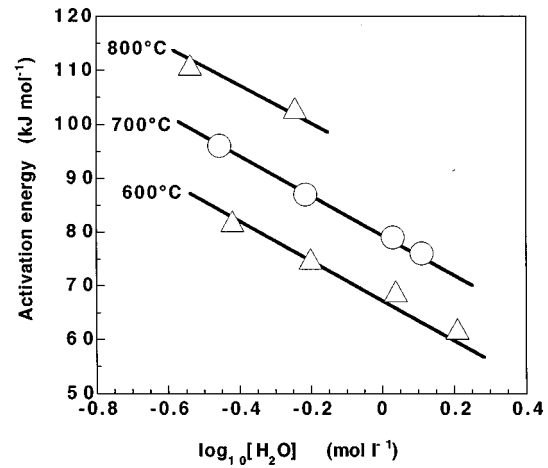

FIG. 5. Relation between activation energy for conduction and water content. Glasses shown in this figure were treated by heating at 600, 700, and 800 °C, followed by exposing to an air ambient for 2 days, and then heated at 160, 210, 250, and 300 °C for 2 h.

glasses heated at different temperatures. When compared at the same content of molecular water, the magnitude of the activation energy increases with increasing the heat-treatment temperature. These results strongly suggest that the dissociated protons from SiOH bonds can move from an initial site to a neighboring site through molecular water. Molecular water makes it possible to decrease the distance for hopping of protons, resulting in accelerating cooperative proton transfer by water molecules. To examine quantitatively the role of water molecule to the proton transfer, the activation energies are replotted as a function of $\{\log_{10}[H^+] + \log_{10}[H_2O]\}$ in Fig. 6. Note that three separate lines shown in Fig. 5 are well represented in one straight line:

$$E = E_0 - n \log_{10}\{[H^+] \cdot [H_2O]\}, \tag{4}$$

where E_0 is 85 kJ/mol and n is about 30. It is interesting to point out that the activation energy decreases with logarithm of the product of $[H^+]$ and $[H_2O]$. Although the physical meaning for this mechanism is not clear yet, we consider that
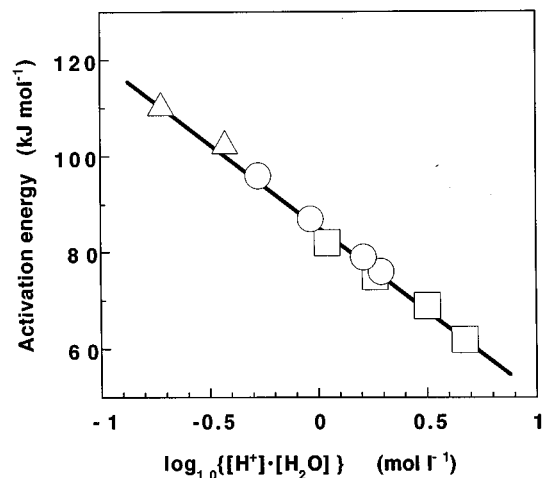

FIG. 6. Plotting of the activation energy shown in Fig. 5 against logarithm of product of concentration of proton and water molecule. Marks correspond to those in Fig. 5.
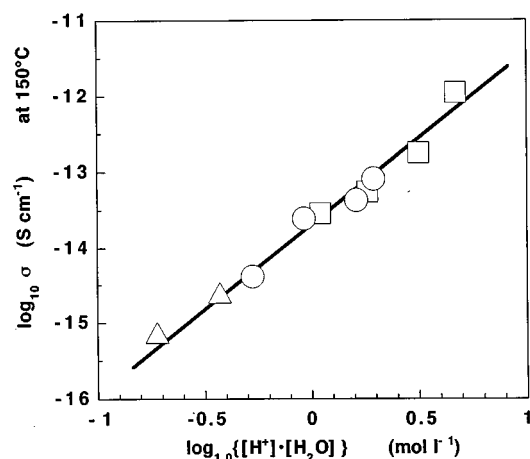
FIG. 7. Relation between electrical conductivity at 150 °C and the product of concentration of proton and water molecule. Marks correspond to those in Fig. 5.

proton conduction in glasses containing water molecules bound with SiOH bonds is based on the dissociation of proton from the SiOH bond and the dissociation equilibrium between the proton and water molecule. The first term in Eq. (4) corresponds to the energy required to dissociate a proton from the OH bond, which is reduced by the strong hydrogen bonding between the proton and water molecule. The dissociated proton moves to a water molecule forming the activated $H_2O:H^+$ state. The second term is due to the dissociation of the proton from this activated $H_2O:H^+$:

$$H_2O:H^+ = H_2O + H^+.$$
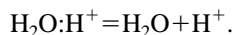
The dissociation energy ΔG is related to the dissociation constant K, which is given by

$$\Delta G \propto -\ln K \propto -\ln\{[H^+]\cdot[H_2O]\}. \tag{5}$$

Thus the activation energy for proton conduction is reduced markedly with increasing water content. On the other hand, the energy for the proton hopping is small because of the very short hopping distance between SiOH and H_2O. The electrical conductivities at 150 °C are shown in Fig. 7, which are also well represented to be proportional to $\log_{10}\{[H^+]\cdot[H_2O]\}$. In the present glasses, since the number of water molecules linked into the SiOH bond is limited by the number of SiOH bonds, the dissociated protons move by hopping between the SiOH and H_2O. When molecular water greater than the number of SiOH groups is absorbed into the glasses, different effects can be expected. Those will be discussed in another paper.

V. CONCLUSIONS

Silica glasses prepared by the sol-gel method were favorable for examining the effect of the water molecule on proton conduction in glasses containing both protons and molecular water. The content of protons and water in glass was changed by both exposure in an air ambient and heat treatment. The electrical conduction process is rate controlled by the dissociation of proton from OH and H_2O and its activation energy decreased with the logarithm of the product of $[H^+]$ and $[H_2O]$.

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