Spinodal-type phase separation and proton conductivity of Al_2O_3 -doped porous glasses

Shin-ichi MINAMIYAMA, Yusuke DAIKO, Atsushi MINESHIGE, Masafumi KOBUNE and Tetsuo YAZAWA[†]

Department of Materials Science and Chemistry, University of Hyogo, Shosha, Himeji, Hyogo 671–2201

Porous glasses with the surface area of $\approx 300 \text{ m}^2/\text{g}$ were prepared utilizing the spinodal-type phase separation of Al_2O_3 -doped $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses. The proton conductivity under humidified conditions and their relations to the amount of doped Al_2O_3 were investigated. The proton conductivity of the glass doped with 2 mol % of Al_2O_3 was about 6 times higher than that of the undoped glass. Fourier transform infrared (FT-IR) measurements revealed that the absorption by the strongly hydrogen-bonded OH groups increased with increasing the amount of Al_2O_3 . Bond overlap populations (BOPs), which are directly related to the strength of the covalent bond, between the surface OH groups and an absorbed water molecule were calculated based on a first-principles theory (DVX α). The BOP values between O and H of the surface OH groups decreased by the Al_2O_3 doping. Substitution of Si atoms of the Si–O–Si silica networks with Al atoms, and formation of the Al–OH–Si bonds effectively improved the proton conductivity under humidified conditions.

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1. Introduction

Fast-proton-conducting materials have attracted considerable attention and have been widely studied to apply for protonic devices such as sensors and fuel cells.^{1)–3)} Perfluorosulfonate ionomers such as Nafion[®] have been used as fuel cell electrolytes since the first development.⁴⁾ Although these perfluorosulfonate ionomers exhibit a high proton conductivity of $\approx 0.1 \text{ S/cm}$ and chemical stability compared with polymer electrolytes based on hydrocarbon structures, their disadvantages such as high cost, low operation temperature, and unsatisfied electrochemical stability (e.g. for the radical attack) limit their industrial applications.^{5),6)} This has prompted a great interest in developing a new electrolyte with high proton conductivity and stabilities.

We have studied the proton conductivity of sodium borosilicate-based nanoporous glasses.^{7),8)} Sodium borosilicate ($\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$) glasses show spinodal-type phase separation to $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and SiO_2 phases when they are heated above glass transition temperature.^{9),10)} Since the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ phase dissolves almost completely in acid solution, as shown in Fig. 1, continuous nanopores with a few nanometer can be easily obtained. The nanoporous glasses modified with 3-mercaptopropyltrimethoxysilane $[(\text{OCH}_3)_3\text{SiC}_3\text{H}_6\text{SH}]$ and subsequent oxidation of thiol groups ($-\text{C}_3\text{H}_6\text{SH}$) to sulfonic acid groups ($-\text{C}_3\text{H}_6\text{SO}_3\text{H}$) was found to show a high proton conductivity of $\sim 1 \times 10^{-2} \text{ S/cm}$ at 90% of relative humidity.⁷⁾

Compared with porous glasses modified with *organic groups* such as $-\text{C}_3\text{H}_6\text{SO}_3\text{H}$, we anticipate that a fast-proton-conducting *all-inorganic-electrolyte* such as $\text{SiO}_2-\text{Al}_2\text{O}_3$ composite oxides will be more suitable as a possible electrolyte due to its chemical/thermal stabilities as well as low fabrication cost. Aluminosilicate zeolite shows Brønsted acidity. Also, Aoki et al. reported applicable proton conductivity of $\text{SiO}_2-\text{Al}_2\text{O}_3$ composite oxides.¹¹⁾

Fig. 1. Schematic illustration of the preparation procedures for the porous proton conducting electrolyte having continuous nanochannels.

In this paper, we discuss on the structure and proton conductivity of Al_2O_3 -doped porous glasses. Hydrogen bonding strength was monitored by Fourier transform infrared (FT-IR) spectroscopy. The hydrogen bonding strength was calculated based on a first-principles theory (DVX α). Proton conductivities of glasses are discussed in relation to the calculation results.

2. Experimental procedure

The glass was prepared by melting the mixture of the analytical grade reagents Na_2CO_3 , SiO_2 , H_3BO_3 and Al_2O_3 at 1500°C for 2 h in a platinum crucible and then casted on a carbon plate. The composition of mother glass was $9.4\text{Na}_2\text{O} \cdot 25.4\text{B}_2\text{O}_3 \cdot 65.2\text{SiO}_2$ (mol %), and the amount of Al_2O_3 as dopant was varied from 0 to 3 mol %. Hereafter, the n mol % of Al_2O_3 doped glass is denoted as *Al-n* (e.g. *Al-1* corresponds 1 mol % Al_2O_3 -doped $9.4\text{Na}_2\text{O} \cdot 25.4\text{B}_2\text{O}_3 \cdot 65.2\text{SiO}_2$ glass). For the phase separation procedure, the obtained glass was heat-treated at 585°C for 72 h. The phase-separated borosilicate glass was then immersed into 1 mol/L of HNO_3 solution at 98°C for 24 h to leach out the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ phase (50 mL HNO_3 solution for 1 g glass). Finally, the resultant glass was rinsed with ion exchange water.

Specific surface area, pore volume and pore diameter of the samples were calculated from the nitrogen adsorption–desorption isotherms measured at 77 K (Belsorp mini; Bel Japan, Inc.). The pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) method.¹²⁾ Fourier transform infrared (FT-IR)

[†] Corresponding author: T. Yazawa; E-mail: yazawa@eng.u-hyogo.ac.jp

Fig. 2. Pore size distribution curves calculated using the results of nitrogen desorption isotherms.

spectrometer (FT/IR-480 plus; JASCO Corp.) was used to monitor the hydrogen bonding state. Prior to the FT-IR measurements, glass samples were dried at 120°C for 2 h to remove the absorbed water molecules.

The electrical conductivity was determined from Cole-Cole plots by an AC method using an LCR meter (HIOKI 3532-50LCR) with frequencies ranging from 50 Hz to 5 MHz. The size of glass plate samples for conductivity measurements were 1 cm × 1 cm with 0.5 mm thickness, and silver paste electrodes (Dotite® D-362, Fujikura Kasei Co., Ltd.) with 5 mm in diameter were used.

²⁷Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) measurements were carried out using a Varian Unity 400 plus instrument. The NMR spectra were measured at 104.2 MHz, a 90° pulse length of 2.0 μs and a spinning rate of 4000 Hz. The same glass piece was used for all the measurements (BET, conductivity, FT-IR, NMR).

For theoretical calculations, molecular structures were optimized by using MOPAC software (method AM1). The optimized coordinate of elements were then used for the calculation of bond overlap population (BOP) between oxygen and proton of the surface OH group using the DVXα method.¹³⁾

3. Results and discussion

3.1 Structure of the porous glasses

X-ray diffraction analysis revealed that no crystals were observed for all the glasses. The glasses with more than Al₂O₃ of 3 mol % were broken into pieces during the acid treatment. Pore size distributions calculated using the desorption branches of Al-0, Al-1 and Al-2 glasses are shown in Fig. 2. Average pore radius was calculated to be approximately 2 nm. Table 1 summarizes the specific surface area and pore volume for these glasses. The specific surface area increased with increasing the amount of Al₂O₃ up to 2 mol %.

Figure 3 shows the ²⁷Al MAS NMR spectra for the Al-3 glass. A single peak around 50 ppm attributed to the four-coordinated Al atoms was clearly observed. Similar peak position was also observed for Al-1 and Al-2 glasses. In the case of pure Al₂O₃, six-coordinated Al atoms were also observed around 0 ppm. These XRD and NMR results suggest that the Al

Table 1. Specific surface area and pore volume of Al-0, Al-1, Al-2 and Al-3 glasses

	Al-0	Al-1	Al-2	Al-3
Surface area (m ² g ⁻¹)	288	304	330	185
Pore volume (mm ³ g ⁻¹)	145	100	172	9.3

Fig. 3. ²⁷Al MAS NMR spectra of the Al-3 glass (* marks represent the spinning sideband).

Fig. 4. FT-IR spectra of Al-0, Al-1, Al-2 and Al-3 glasses. Each spectrum was normalized to the absorbance of Si-O stretching band at 1100 cm⁻¹.

atoms in glasses were substituted with Si, and Al-O-Si bonds are considered to be formed via the substitution.

FT-IR spectroscopy is useful to investigate the relationship between the hydrogen-bond strength and proton conductivity.^{14),15)} The position of OH absorption bands depends on the hydrogen bond strength. It was reported that oxide glasses with OH stretching band of lower wavenumber show higher proton conductivity.^{14),15)} FT-IR spectra of glasses are shown in Fig. 4. Each spectrum was normalized to the absorbance of Si-O stretching band at 1100 cm⁻¹. Note the absorbance for OH

Fig. 5. Temperature dependences of proton conductivity of *Al-0*, *Al-1* and *Al-2* glasses measured at 90% of relative humidity.

groups ($3000\text{--}3800\text{ cm}^{-1}$) increase clearly with increasing the amount of Al_2O_3 . Furthermore, the peak shifts to a lower wavenumber with increasing the amount of Al_2O_3 , suggesting the decrease of the O–H bonding strength after the Al_2O_3 doping.

Temperature dependences of proton conductivities for *Al-0*, *Al-1* and *Al-2* glasses are shown in Fig. 5. As expected from the FT–IR results, the proton conductivity increased significantly with increasing the amount of Al_2O_3 . Note that the 2 mol % Al_2O_3 -doped porous glass shows about six-fold increase in proton conductivity.

In the case of $\text{Na}_2\text{O–B}_2\text{O}_3\text{–SiO}_2$ glasses without Al_2O_3 , Na^+ ions are mainly placed around the four-coordinated boron due to the charge compensation. We previously reported that the number of the four-coordinated boron decreased by the doping of Al_2O_3 .¹⁶⁾ This indicates that a part of Na^+ ions in the Al_2O_3 -doped glasses should be placed around not only B but also Al atoms due to the charge compensation (Fig. 6). During the acid treatment, the $\text{Na}_2\text{O–B}_2\text{O}_3$ phase dissolves in acid solution and the porous glass is obtained. On the other hand, as shown in Fig. 6, the Na^+ ions placed around Al atoms exchange with H^+ ions, and OH groups are newly generated after the ion-exchange reaction. It was reported that oxides with Al–OH–Si bond show Brønsted acidity.¹¹⁾ It is thus considered that the OH groups for *Al-1*, *Al-2* and *Al-3* glasses shown in FT–IR spectra are attributed to the newly formed Al–OH–Si hydroxyl groups. In the following section, we discuss the theoretically calculated O–H bonding strengths and their relations to the proton conductivity.

3.2 Hydrogen bonding strength and proton conductivity

As shown in Fig. 5, proton conductivity of the porous glass increased by the Al_2O_3 doping, and Al–OH–Si hydroxyl groups were considered to be formed on pore surfaces after the acid treatment. Effect of the substituted Al atoms on the proton dissociation was also studied using the first-principles calculation (DVX α method). Simplified molecular models of Si–OH and Al–OH–Si networks shown in Fig. 7, in which a water molecule was hydrogen-bonded with a surface OH group, were used for the calculations. The bond overlap population (BOP) is directly related to the strength of the covalent bond.

Fig. 6. Schematic illustration of the ion-exchange reaction for Al_2O_3 -doped glasses during the acid treatment.

Fig. 7. Calculation models for Si–OH and Al–OH–Si hydrogen bond networks and bond overlap populations calculated using DVX α calculation.

The calculated BOP values are also shown in Fig. 7. In the case of the Si–OH bond, the BOP value between $\text{O}_{(1)}$ and $\text{H}_{(1)}$ was calculated to be 0.6179. Note that the corresponding value for Al–OH–Si [$\text{O}_{(2)}$ and $\text{H}_{(2)}$] decreased significantly to 0.5696, suggesting that the dissociation energy of proton decreased by the formation of Al–OH–Si network. These calculation results are in good agreement qualitatively with the FT–IR data (the peak shifts to a lower wavenumber after the doping of Al_2O_3).

Proton concentrations in glasses were estimated from the FT–IR spectra shown in Fig. 4 using the Lambert–Beer equation:

$$E = \varepsilon C d \quad (1)$$

where E is the absorbance, ε is the molar absorption coefficient, C is the concentration and d is the thickness of the sample. We assumed that ε did not change by the addition of small amount of Al_2O_3 , and thus the C was proportional to the E . The proton concentration of *Al-0* was previously estimated to be $\approx 5\text{ }\mu\text{mol/m}^2$.⁷⁾ From the FT–IR spectra shown in Fig. 4, the ratio of the peak area for OH groups ($3000\text{--}3800\text{ cm}^{-1}$) of *Al-0*, *Al-1* and *Al-2* glasses were estimated to be 1.0:2.1:3.0. From the peak area, proton concentrations of *Al-1* and *Al-2* glasses were roughly estimated to be 10.5 and $15\text{ }\mu\text{mol/m}^2$, respectively. For the borosilicate-based porous glasses (*Al-0*), pore surfaces are terminated with surface OH groups (Si–OH group). Owing to the increase of the surface area from $288\text{ m}^2/\text{g}$ (*Al-0*) to $330\text{ m}^2/\text{g}$ (*Al-2*) as well as the newly formed OH groups, proton concentrations increased from 5 to $15\text{ }\mu\text{mol/m}^2$.

Fig. 8. Relationship between the proton concentration and the corresponding proton conductivity at 40 and 80°C for Al-0, Al-1 and Al-2 glasses.

Figure 8 shows the relationship between the proton concentration on pore surfaces and the corresponding proton conductivity at 40 and 80°C for Al-0, Al-1 and Al-2 glasses. Proton conductivity is proportional to the concentration (n) and mobility (μ) as:

$$\sigma = ne\mu \quad (2)$$

where e is the elementary electric charge. The electrical carriers are only protons dissociated from the hydroxyl groups on the pore surfaces, however, it is important that Al-0 glass has only Si-OH group while Al-1 and Al-2 have both the Si-OH and Al-OH-Si groups. Note that the Al-1 and Al-2 glasses show higher proton conductivities than the expected ones from Eq. (2) (shown as dotted lines). As discussed from the DVX α calculations and FT-IR results, the proton dissociation energy of hydroxyl groups decreased after the formation of Al-OH-Si bonds. Proton conductivity shown in Fig. 8 is thus consistent with the DVX α calculation results. The substitution of Si atoms of Si-O-Si silica networks with Al atoms, and the formation of Al-OH-Si bonds improve effectively the proton conductivity under humidified conditions. Further studies about the hydrogen bonding networks and glass compositions are in progress to prepare an *all-inorganic electrolyte* with high proton conductivity.

4. Conclusions

Porous glasses (PGs) with 4 nm in diameter pores were prepared utilizing a spinodal-type phase separation of Na₂O-B₂O₃-SiO₂ glass, and effect of Al₂O₃ doping on proton conductivity was studied. The proton conductivity of glasses increased with increasing the amount of Al₂O₃, and the 2 mol %

Al₂O₃-doped glass showed about six times higher proton conductivity compared with the undoped one. Fourier transform infrared (FT-IR) measurements revealed that the absorbance for OH groups (3000–3800 cm⁻¹) increased clearly with increasing the amount of Al₂O₃. First-principles calculations (DVX α) suggested that the bonding strength between O and H atoms of surface OH groups decreased significantly by the doping of Al atoms. The substitution of Al atoms (Al-O-Si bonds) enhances proton conductivity. The nanoporous glasses have good shapability and thermal/chemical stabilities, and the surface-modified glasses thus prepared have a potential as practical proton conducting materials.

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References

- 1) B. H. Steele and A. Heinzel, *Nature*, **414**, 345–352 (2001).
- 2) C. Heitner-Wirguin, *J. Membr. Sci.*, **120**, 1–33 (1996).
- 3) B. Smitha, S. Sridhar and A. A. Khan, *J. Membr. Sci.*, **259**, 10–26 (2005).
- 4) K. A. Mauritz and R. B. Moore, *Chem. Rev.*, **104**, 4535–4585 (2004).
- 5) J. Wu, X. Yuan, J. J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu and W. Merida, *J. Power Sources*, **184**, 104–119 (2008).
- 6) N. Yousfi-Steiner, P. Moçotéguy, D. Candusso, D. Hissel, A. Hernandez and A. Aslanides, *J. Power Sources*, **183**, 260–274 (2008).
- 7) Y. Daiko, H. Katayama, T. Araki, A. Mineshige, M. Kobune, S. Yusa, T. Yazawa, K. Nagasaka, S. Murata, S. Matsumoto, A. Koiwai and I. Konomi, *J. Phys. Chem. C*, **113**, 1891–1895 (2009).
- 8) T. Araki, Y. Daiko, A. Mineshige, M. Kobune, N. Toyoda, I. Yamada and T. Yazawa, *J. Am. Ceram. Soc.*, **93**, 127–131 (2010).
- 9) T. Yazawa, K. Kuraoka and W.-F. Du, *J. Phys. Chem. B*, **103**, 9841–9845 (1999).
- 10) W.-F. Du, K. Kuraoka, T. Akai and T. Yazawa, *J. Phys. Chem. B*, **105**, 11949–11954 (2001).
- 11) Y. Aoki, E. Muto, A. Nakao and T. Kunitake, *Adv. Mater.*, **20**, 4387–4393 (2008).
- 12) E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373–380 (1951).
- 13) H. Adachi, M. Tsukada and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875–883 (1978).
- 14) Y. Abe, H. Hosono, Y. Ohta and L. L. Hench, *Phys. Rev. B*, **38**, 10166–10169 (1988).
- 15) M. Nogami and Y. Abe, *Phys. Rev. B*, **55**, 12108–12112 (1997).
- 16) W.-F. Du, K. Kuraoka, T. Akai and T. Yazawa, *J. Mater. Sci.*, **35**, 4865–4871 (2000).
- 17) H. P. Boehm, “Advances in Catalysis,” Academic press, New York and London (1966).