**Relationship between structure and mobility of proton carriers
injected by electrochemical substitution of sodium ions with protons
in 35NaO_{1/2}-1WO₃-8NbO_{5/2}-5LaO_{3/2}-51PO_{5/2}-based glasses**

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Abstract

Using Raman and ^{31}P magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopies, we studied the structural changes in $35\text{NaO}_{1/2}\text{-1WO}_3\text{-8NbO}_{5/2}\text{-5LaO}_{3/2}\text{-51PO}_{5/2}$ glass upon introducing Al_2O_3 and/or Y_2O_3 in order to understand the reduced mobility of proton carriers in glasses with Al_2O_3 and/or Y_2O_3 in which proton carriers were injected by alkali-proton substitution (APS). The Raman and ^{31}P MAS-NMR spectra showed that phosphate chains were shortened by the Al_2O_3 and/or Y_2O_3 introduced into 1W glass. This structural change increased the fraction of protons bound to oxygen atoms in the terminal PO_4 (*i.e.*, the Q^1 unit) of the phosphate chains. Because the protons bound to terminal Q^1 units in phosphate chains tightly bind to oxygen atoms, as opposed to the protons bound to inner Q^2 units in phosphate chains, we attributed the reduced mobility of proton carriers upon introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass to the shortening of phosphate chains. From these results we propose that to obtain a highly proton-conducting glass after APS, the glass must have a composition of $\text{O/P} < 3.5$ and thus a sufficiently high fraction of Q^2 units.

Keywords

proton conductor, alkali-proton substitution, glass structure, Raman, NMR

1. Introduction

Intermediate-temperature fuel cells (IT-FCs) operated at 300–500 °C have many advantages, such as their low material cost, rapid startup and shutdown, and greater energy efficiency than conventional solid-oxide and polymer-electrolyte fuel cells [1–3]. However, IT-FCs are not materialized for now because electrolytes applicable to IT-FCs have not yet been developed, despite intensive efforts to explore such materials.

Recently, we developed a new proton injection technique for sodium-containing phosphate glasses, termed alkali-proton substitution (APS), which we expect to be a powerful method to develop electrolytes applicable to IT-FCs. In this method, sodium ions are electrochemically substituted with protons, usually at ~250–400 °C [4,5], and the injected protons remain stable at lower temperatures than the temperature where APS is conducted. We have previously applied APS to $35\text{NaO}_{1/2}\text{-}1\text{WO}_3\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}51\text{PO}_{5/2}$ glass (1W glass) [6]. We attained a proton carrier concentration of $5 \times 10^{21} \text{ cm}^{-3}$ and a maximum proton conductivity of $4 \times 10^{-4} \text{ Scm}^{-1}$ at 250 °C. Based on its Arrhenius plot, the conductivity of this glass expected to be higher than $1 \times 10^{-2} \text{ Scm}^{-1}$ at >370 °C, but the glass softens and deforms at >250 °C. However, by introducing a small amount of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ instead of $\text{NaO}_{1/2}$ and/or $\text{PO}_{5/2}$, we increased its thermal stability up to 350 °C [7]. Unfortunately, in glasses with introduced $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$, their proton carrier mobility decreased to 1/20–1/50 of its original value. This reduction came from an increase in the concentration of protons tightly bound to oxygen, shown by the infrared (IR) absorption spectra in the region of the O–H stretching vibration (ν_{OH}). This change in the O–H bonds was related to the structural change in the glass upon the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$; however, the details of these structural changes and their influence on O–H bonds are not yet clear.

In the present study, we investigated the structures of glasses with and without $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. For this purpose, we prepared glasses with compositions of $35\text{NaO}_{1/2}\text{-}1\text{WO}_3\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}3\text{AlO}_{3/2}\text{-}48\text{PO}_{5/2}$ (1W-Al glass),

35NaO_{1/2}-1WO₃-8NbO_{5/2}-5LaO_{3/2}-3YO_{3/2}-48PO_{5/2} (1W-Y glass), and
30NaO_{1/2}-1WO₃-8NbO_{5/2}-5LaO_{3/2}-3AlO_{3/2}-3YO_{3/2}-50PO_{5/2} (1W-AlY glass) in addition to 1W
glass. Using Raman spectroscopy and ³¹P magic-angle spinning nuclear magnetic resonance
(MAS-NMR) spectroscopy, we studied their structures so as to better design glass that exhibits
high proton conductivity after APS.

2. Experimental

2.1. Glass preparation

The glasses denoted 1W, 1W-Al, 1W-Y, and 1W-AlY were prepared by standard melt quenching.
The raw materials—Na₂CO₃, WO₃, Nb₂O₅, La₂O₃, Al₂O₃, Y₂O₃, and H₃PO₄—were weighed,
mixed, and then preheated at 450 °C in a platinum crucible for 30 min to degas the mixture. After
degassing, the mixture was melted at ~1400–1450 °C for 1 h in air. The molten materials were
poured into a cylindrical carbon mold with an inner diameter of 18 mm and annealed at
~420–450 °C for 10 min. It was then cooled to room temperature in the furnace at a cooling rate of
20 °C h⁻¹.

2.2. Alkali-proton substitution (APS)

The cylindrical glass block with a diameter of 18 mm was cut into disks, each with a thickness of
~0.8 mm. After polishing both surfaces of the glass disk, a palladium film with a thickness of ~0.2
μm was deposited on one surface by magnetron sputtering (JFC-1600, JEOL, Japan). The glass
disk was then loaded onto a specimen holder in the APS apparatus (KDK-800, Kenix Co., Japan)
with the Pd-deposited surface facing upwards. A detailed configuration of the APS apparatus can
be found elsewhere [5]. After elevating the furnace temperature as desired, the lower surface of the
glass disk was contacted with molten tin, and then a DC bias of 5.0 V was applied between the
Pd-film anode and the molten Sn cathode under a 5% H₂/95% N₂ atmosphere. The APS

temperatures and durations were 310 °C for 11 h, 345 °C for 4 h, 335 °C for 6 h, and 355 °C for 4 h for 1W, 1W-Al, 1W-Y, and 1W-AlY glasses, respectively.

2.3. Structural Characterization

Raman spectra of the glasses before and after APS were measured with a laser Raman spectrometer (NRS-3100, JASCO, Japan) at an excitation wavelength of 532 nm. ³¹P MAS-NMR spectra of the glasses before APS were measured by using Bruker Avance 600 spectrometer (Bruker BioSpin, Germany) operating at 14.1 T (Larmor frequency of 242.92 MHz) with a 2.5 mm magic-angle spinning probe operating at a spinning frequency of 30 kHz. These spectra were acquired using a pulse length of 4 μs (90° flip angle) and a recycle delay of 10 s; the spectra were referenced relative to 85% H₃PO₄ by setting the signal of solid (NH₄)₂HPO₄ to 1.33 ppm. The obtained signals were deconvoluted in the range of 20 to −60 ppm into two pseudo-Voigt functions using DMfit.

3. Results and discussion

Figure 1(a) shows Raman spectra of 1W, 1W-Al, 1W-Y, and 1W-Al-Y glasses before APS. The spectrum of 1W glass shows four characteristic bands at ~700, ~900, ~1165, and ~1250 cm^{−1}, similar to the previous report [15]. The bands at ~700, ~1165, and ~1250 cm^{−1} are associated with the phosphate framework [8–10], and the band at ~900 cm^{−1} is associated with MO₆ (*M* = Nb or W) octahedra [11–14]. The Raman shift of the stretching modes associated with the phosphate framework depends on the polymerization degree of the PO₄ tetrahedra, such as PO₄^{3−}, P₂O₇^{4−}, and (PO₃[−])_{*m*}. The PO₄ tetrahedra are generally classified using the number of bridging oxygen, *n*, of an individual PO₄ tetrahedron as Q^{*n*} (*n*=0, 1, 2, or 3). Using this classification, the bands associated with the phosphate framework are assigned as follows [8–10]. The bands at 700 cm^{−1} and 756 cm^{−1} are assigned to the symmetric stretching modes of the P–O–P bond for Q² [V_{P–O–P,sym}(Q²)] and

Q^1 [$\nu_{P-O-P, \text{sym}}(Q^1)$], respectively. The small band at 1007 cm^{-1} is assigned to the asymmetric stretching mode of the P–O–P bond for Q^2 , $\nu_{P-O-P, \text{asym}}(Q^2)$. The bands at $\sim 1050\text{--}1300 \text{ cm}^{-1}$ are attributed to the stretching modes of the bond between phosphorous and non-bridging oxygen, P–O[−]; the band at 1075 cm^{-1} is assigned to ν_{P-O^-} that of Q^1 , $\nu_{PO_3}(Q^1)$; the bands at 1161 and 1251 cm^{-1} are attributed to the symmetric and asymmetric stretching modes for Q^2 , $\nu_{PO_2, \text{sym}}(Q^2)$ and $\nu_{PO_2, \text{asym}}(Q^2)$, respectively. The band at 927 cm^{-1} associated with the MO_6 octahedron was assigned to the stretching mode of non-bridging $M\text{--}O^-$ bond, ν_{M-O^-} [11–14]. Table 1 summarizes all assignments of the observed Raman bands. The spectrum of 1W glass revealed no Q^0 or Q^3 units in it; thus, the phosphate framework in 1W glass consists mainly of Q^2 units and a small number of Q^1 units, *i.e.*, $(PO_3^-)_m$ chains, as we reported previously.

Upon introducing $AlO_{3/2}$ and/or $YO_{3/2}$ into 1W glass, significant decreases in intensities of the bands attributable to Q^2 units, $\nu_{PO_2, \text{sym}}(Q^2)$ around 1150 cm^{-1} and $\nu_{P-O-P, \text{sym}}(Q^2)$ around 740 cm^{-1} , were clearly observed. According to deconvolution of the P–O–P stretching band in $660\text{--}820 \text{ cm}^{-1}$, the intensity of the $\nu_{P-O-P, \text{sym}}(Q^1)$ increased upon $AlO_{3/2}$ and/or $YO_{3/2}$ addition while the intensity of the $\nu_{P-O-P, \text{sym}}(Q^2)$ decreased as indicated by thin solid lines in Fig. 1 and summarized in Table 2. Further, the $\nu_{P-O-P, \text{sym}}(Q^2)$ band shift to higher frequency upon $AlO_{3/2}$ and/or $YO_{3/2}$ addition. Taking into account that the phosphate framework of 1W glass consists mainly of $(PO_3^-)_m$ chains, these variations in band intensity indicate that introducing a small amount of $AlO_{3/2}$ and/or $YO_{3/2}$ in 1W glass decreased the average length of the $(PO_3^-)_m$ chains and resulted in formation of $P_2O_7^{4-}$ ions.

Figure 1(b) shows Raman spectra of the glasses after APS. The spectral shapes of 1W glass before and after APS are similar, but the band positions and intensities are slightly different. While the biggest change is the significantly reduced intensity of $\nu_{PO_2, \text{sym}}(Q^2)$ at $\sim 1160 \text{ cm}^{-1}$, this is not related to the structural variation in the phosphate framework during APS, but rather to the much smaller polarizability of injected protons compared with sodium ions [15–18]. The characteristic changes related to the structural change in 1W glass before and after APS are the shift to higher

frequency of the $\nu_{\text{P-O-P, sym}}(\text{Q}^2)$ band and the splitting of the $\nu_{\text{M-O-}}$ band. These changes are attributed to the shortening of the $(\text{PO}_3^-)_m$ chains and formation of new M-O-P bonds in 1W glass during APS, as we previously reported [15].

Upon introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass, the changes in spectral shape after APS were not clear because the spectra of 1W-Al and 1W-Al-Y glasses were broader than that of 1W glass. We did not demonstrate peak deconvolution of the P-O-P stretching band, because the P-O-P stretching bands after APS were almost symmetric shapes and did not exhibit doublet or shoulder in contrast to the spectra before APS (Fig. 1 (a)). However, the $\nu_{\text{P-O-P, sym}}(\text{Q}^2)$ bands at $\sim 700 \text{ cm}^{-1}$ clearly shifted to higher frequencies after APS in 1W-Al, 1W-Y, and 1W-Al-Y glasses as summarized in Table 2, indicating that the $(\text{PO}_3^-)_m$ chains shortened, while splitting of the $\nu_{\text{M-O-}}$ band was not clearly observed in 1W-Al, 1W-Y, and 1W-Al-Y glasses after APS. Based on these observations, we summarize the structural changes caused by introducing a small amount of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass as follows: Introducing small amounts of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass shortens the $(\text{PO}_3^-)_m$ chains of the phosphate framework, and APS further shortens the $(\text{PO}_3^-)_m$ chains and forms new M-O-P bonds in $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ -introduced glasses.

Figure 2 shows ^{31}P MAS-NMR spectra of 1W, 1W-Al, 1W-Y, and 1W-Al-Y glasses before APS. All spectra show broadened and asymmetric signals, so we deconvoluted them into two signals at -9.9 and -20.8 ppm, as in our previous study [15]. The signals at -20.8 and -9.9 ppm are respectively assigned to ^{31}P in Q^2 and $\text{Q}^1_{(\text{M})}$ units [19–21]; in $\text{Q}^1_{(\text{M})}$ units, one of the three non-bridging oxygens in PO_4 bonds to Nb or W and forms a single P-O-M linkage [20,21]. Based on these assignments, we believe that the phosphate frameworks in 1W-Al, 1W-Y, and 1W-Al-Y glasses involve only Q^1 ($\text{Q}^1_{(\text{M})}$) and Q^2 units and consist of $(\text{PO}_3^-)_m$ chains, similar to the phosphate framework in 1W glass. This conclusion is consistent with the results obtained from the Raman spectra (Fig. 1). Assuming that the glasses contain no discrete pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$, the average formulas of the phosphate chains in the glasses before APS are $(\text{PO}_3^-)_{9.4}(\text{P}_2\text{O}_7^{4-})$ for

1W glass, $(\text{PO}_3^-)_{4.6}(\text{P}_2\text{O}_7^{4-})$ for 1W-Al glass, $(\text{PO}_3^-)_{2.4}(\text{P}_2\text{O}_7^{4-})$ for 1W-Y glass, and $(\text{PO}_3^-)_{2.4}(\text{P}_2\text{O}_7^{4-})$ for 1W-AlY glass, based on the intensity ratios of the Q^2 and $Q^1_{(M)}$ signals. Thus, we safely conclude that reduction in the average length of the $(\text{PO}_3^-)_m$ chains developed by introducing a small amount of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$.

Based on the structural features of the present glasses, we now discuss the reduction in mobility of proton carriers upon introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass. According to Naruse *et al.* [22], the proton that binds to the oxygen in the Q^1 unit that forms the terminal OH group in $(\text{PO}_3^-)_m$ chains tightly binds to oxygen, as opposed to the proton that binds to oxygen in the Q^2 unit, which forms the inner O–H group in $(\text{PO}_3^-)_m$ chains. Thus, introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass increases the fraction of protons tightly bound to oxygen; this occurs because introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass shortens the average length of $(\text{PO}_3^-)_m$ chains and increases the fraction of terminal Q^1 units in $(\text{PO}_3^-)_m$ chains.

It is quite reasonable that the mobility of proton carriers decreases upon introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass because of the increase in proton carriers tightly trapped by non-bridging oxygens. Naruse *et al.* also found in the IR spectra of $\text{MgO-H}_2\text{O-P}_2\text{O}_5$ glasses that those two kinds of OH groups are clearly distinguished by the position of ν_{OH} ; ν_{OH} appears at $\sim 3300 \text{ cm}^{-1}$ for terminal OH groups in $(\text{PO}_3^-)_m$ chains, where protons bind to oxygens in Q^1 units, and appears at $\sim 2900 \text{ cm}^{-1}$ for inner OH groups in $(\text{PO}_3^-)_m$ chains, where protons bind to oxygens in Q^2 units [22]. Based on this finding, upon introducing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into 1W glass, the relative intensities of the ν_{OH} band at $\sim 3300 \text{ cm}^{-1}$ and $\sim 2900 \text{ cm}^{-1}$ should increase and decrease, respectively. This situation completely agrees with the IR spectra in the ν_{OH} region of 1W, 1W-Al, 1W-Y, and 1W-AlY glasses, as shown in Fig. 3 in ref. 7. Thus, we conclude that the reduced mobilities in 1W-Al, 1W-Y, and 1W-AlY glasses come from the increased fraction of protons binding to oxygens in Q^1 units, which in turn comes from the increased fraction of Q^1 units in the

PO₄ tetrahedra caused by the shortening of the (PO₃⁻)_m chain upon introducing AlO_{3/2} and/or YO_{3/2} into 1W glass. Figure 3 gives a schematic of this situation.

This new understanding shows that to obtain a glass that has high proton mobility after APS, it must have a sufficient number of Q² units compared to Q¹ units; that is, it must have a highly polymerized (PO₃⁻)_m chain. The polymerization degree of phosphate ions in glasses is generally described by the ratio of oxygen atoms to phosphorous atoms: the O/P ratio. For example, the metaphosphate composition, where infinite (PO₃⁻)_∞ chains are formed, corresponds to O/P=3.0; the pyrophosphate composition, where P₂O₇⁴⁻ dimers are formed, corresponds to O/P=3.5; the orthophosphate composition, where PO₄³⁻ monomers are formed, corresponds to O/P=4.0. Assessing the O/P ratio, glass compositions with O/P>3.5 are not expected to have proton carriers with high mobility because the pyrophosphate and orthophosphate ions involve no Q² units. The glass must have a composition with O/P<3.5 to generate proton carriers with high mobility.

Returning to the glasses discussed here, they contain some intermediate components between glass former and modifier, such as WO₃, NbO_{5/2}, and AlO_{3/2}; thus, oxygen atoms that do not bond to phosphorous atoms should exist [20,21]. In this situation, the O/P ratio does not indicate the exact polymerization degree of the PO₄ tetrahedra. However, the O/P ratio in 1W-Al, 1W-Y, and 1W-AlY glasses are 3.59, while that in 1W glass is 3.44. These O/P ratios describe well the high proton mobility in 1W glass and the low proton mobility in 1W-Al, 1W-Y, and 1W-AlY glasses. Consequently, the O/P ratio acts as a good reference index to predict the mobility of proton carriers. Thus, we conclude that, to obtain a highly proton-conductive glass after APS, the glass must have a composition with O/P<3.5.

4. Summary

Using by Raman and ³¹P MAS-NMR spectroscopies, we investigated the structural changes in 1W-glass induced by adding Al₂O₃ and/or Y₂O₃. The Raman and ³¹P MAS-NMR spectra showed

1 that introducing Al_2O_3 and/or Y_2O_3 into 1W glass shortened its $(\text{PO}_3^-)_m$ chains. This increased the
2 fraction of protons bound to oxygen atoms in the terminal PO_4 (*i.e.*, the Q^1 unit) of the phosphate
3 chains. Because the protons bound to terminal Q^1 units in phosphate chains bind tightly to oxygen
4 atoms, as opposed to the protons bound to inner Q^2 units in phosphate chains, introducing $\text{AlO}_{3/2}$
5 and/or $\text{YO}_{3/2}$ into 1W glass decreased the mobility of the proton carriers. Because pyrophosphate
6 and orthophosphate ions that consist of only Q^1 units generate protons that tightly bind to oxygen
7 atoms, glasses with compositions of $\text{O/P} > 3.5$ are not expected to have proton carriers with high
8 mobility and thus high conductivity. Consequently, we conclude that to obtain a glass with high
9 proton conductivity after APS, it must have a composition with $\text{O/P} < 3.5$ and thus a sufficiently
10 high fraction of Q^2 units.
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Table

Table 1. Assignment of Raman bands observed in the spectra of the glasses before and after APS

Position (cm ⁻¹)	Assignment ^a	Notation	Ref.
703~709	Symmetric stretching mode of P-O-P bond for Q ² units	$\nu_{\text{P-O-P, sym}}(\text{Q}^2)$	8-10
752~757	Symmetric stretching mode of P-O-P bond for Q ¹ units	$\nu_{\text{P-O-P, sym}}(\text{Q}^1)$	8-10
909~946	Stretching mode of M-O ⁻ bond of MO ⁶ octahedron	ν_{MO^-}	11-14
988~1012	Asymmetric stretching mode of P-O-P bond for Q ² units	$\nu_{\text{P-O-P, asym}}(\text{Q}^2)$	8,10
1073~1093	Symmetric stretching mode of P-O ⁻ bond for Q ¹ units	$\nu_{\text{PO}_3}(\text{Q}^1)$	8,10
1146~1168	Symmetric stretching mode of P-O ⁻ bond for Q ² units	$\nu_{\text{PO}_2, \text{sym}}(\text{Q}^2)$	8-10
1249~1278	Asymmetric stretching mode of P-O ⁻ bond for Q ² units	$\nu_{\text{PO}_2, \text{asym}}(\text{Q}^2)$	8-10

^a M denotes Nb or W.

Table 2. Results of deconvolution of the P-O-P stretching bands before APS, positions of $\nu_{\text{P-O-P, sym}}(\text{Q}^1)$ and $\nu_{\text{P-O-P, sym}}(\text{Q}^2)$ and their ratios of integrated intensity Q¹/Q², and peak positions of $\nu_{\text{P-O-P, sym}}$ after APS.

	Position (cm ⁻¹)							
	Before APS				After APS			
	1W	1W-Al	1W-Y	1W-Al-Y	1W	1W-Al	1W-Y	1W-Al-Y
$\nu_{\text{P-O-P, sym}}(\text{Q}^1)$	738	746	743	749	---	---	---	---
$\nu_{\text{P-O-P, sym}}(\text{Q}^2)$	696	700	699	703	711	727	728	730
Integrated intensity ratio of Q ¹ /Q ²	1.82	2.31	2.45	2.97	---	---	---	---

Figures

Fig. 1 Raman spectra of 1W, 1W-Al, 1W-Y, and 1W-AlY glasses (a) before and (b) after APS. Thin solid lines in (a) indicate the results of deconvolution of P-O-P stretching bands into two Gaussian peak.

Fig. 2 ^{31}P MAS-NMR spectra of 1W, 1W-Al, 1W-Y, and 1W-AlY glasses before APS. The thin solid lines indicate the deconvoluted NMR signals assigned to $\text{Q}^1_{(\text{M})}$ and Q^2 units.

(a) 1W glass

(b) 1W-Al, 1W-Y and 1W-AlY glasses

Fig. 3 Schematic of the proton conduction mechanism in 1W glass and in 1W glasses with added $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$: (a) 1W glass and (b) 1W-Al, 1W-Y, and 1W-AlY glasses. This figure only shows the phosphate framework consisting of PO_4 tetrahedra (blue and green polygons) and protons bound to oxygen in the PO_4 tetrahedra (red circles). Other components—such as WO_3 , $\text{NbO}_{5/2}$, $\text{LaO}_{3/2}$, $\text{AlO}_{3/2}$, and $\text{YO}_{3/2}$ —are ignored for simplicity. Orange arrows indicate the proton-hopping pathways. The fraction of protons bound to Q^1 units, which tightly bind to oxygen atoms, is small in 1W glass, so the protons can move without passing through the proton site in the Q^1 units. In this case, the macroscopic proton mobility is determined by the protons bound to the Q^2 units, which bind loosely to oxygen atoms. In 1W-Al, 1W-Y, and 1W-AlY glasses, the fraction of protons bound to Q^1 units is very high, so protons cannot move over a long distance without passing through the proton site in the Q^1 units. In this case, the macroscopic proton mobility is determined by the protons bound to the Q^1 units, so the observed mobility of its proton carriers is smaller than that in 1W glass.