Improving thermal stability and its effects on proton mobility in proton-conducting phosphate glasses prepared by the electrochemical substitution of sodium ions with protons

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Abstract

We investigated electrochemical substitution involving the electrochemical oxidation of hydrogen with proton injection into an oxide glass. This was accompanied by the electrochemical reduction of sodium ions and the discharge of metallic sodium out of the glass. This is referred to as the alkali-proton substitution technique and we applied it to a sodium-containing phosphate glass. The thermal stability of the $1\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}51\text{PO}_{5/2}$ glass that previously deformed at $>250^\circ\text{C}$ improved to 350°C after alkali-proton substitution technique by the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. However, the mobility of the proton carriers decreased by $1/20\text{--}1/50$ by the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ while the thermal stability improved. Based on infrared absorption spectra the reduced mobility can be attributed to the increase in protons that are tightly bound to oxygen by weak hydrogen bondings.

Keywords

proton conductor, electrochemical process, alkali-proton substitution, FT-IR, fuel cells

1. Introduction

Intermediate temperature fuel cells (IT-FCs) that are operated at 300–500 °C have recently attracted much attention because they have advantages of cost, energy efficiency, and operating conditions compared with conventional solid oxide and polymer electrolyte fuel cells [1-3]. Many research groups have explored solid proton conductors applicable to electrolytes in IT-FCs. Electrical conductivity of $>1 \times 10^{-2} \text{ Scm}^{-1}$ at intermediate temperatures are required for the proton-conducting electrolytes in ITFCs; however, such a material has not been fully developed yet.

We recently developed a technique to inject carrier protons into oxide glass by the electrochemical substitution of alkali ions in the glass with protons at high temperatures. We refer to this as the alkali-proton substitution (APS) technique [4,5]. By applying this technique to 35NaO_{1/2}-1WO₃-8NbO_{5/2}-5LaO_{3/2}-51PO_{5/2} glass (1Wglass), we successfully injected proton carriers with a concentration higher than $5 \times 10^{21} \text{ cm}^{-3}$ and obtained a pure proton conductor [6]. However, the proton-conducting glass obtained (1W glass after APS) was not stable and underwent deformation at temperatures higher than 250 °C. Therefore, the maximum proton conductivity was limited to $4.0 \times 10^{-4} \text{ Scm}^{-1}$ at 250 °C. Extrapolation of the Arrhenius plot of its electrical conductivity suggests that the proton conductivity will reach $1 \times 10^{-2} \text{ Scm}^{-1}$ at 370 °C when the glass after APS becomes stable at $>370 \text{ °C}$ [6].

The temperature, where the glass underwent deformation during electrical conductivity measurement, of the 1W glass after APS is consistent with its glass transition temperature, T_g , of $\sim 200 \text{ °C}$ and its deformation temperature, T_d , of $\sim 250 \text{ °C}$. This indicates that the deformation was caused by the significant decrease in viscosity of the glass at $>250 \text{ °C}$. The reduction of viscosity of the glass induces the evaporation of H₂O and/or phosphoric acid, *i.e.*, deprotonation; and then, the proton conductivity of the glass is lost. One of the major advantages of glass electrolytes over crystal electrolytes is their compositional flexibility. This allows for an improvement in the thermal

stability, *i.e.*, suppression of the viscosity reduction and deprotonation, of the glass after APS upon optimizing the glass composition.

We thus studied three glasses, in which a portion of the $\text{NaO}_{1/2}$ and/or the $\text{PO}_{5/2}$ in the 1W glass were substituted with $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$, to increase the thermal stability of the glass. The compositions were: $35\text{NaO}_{1/2}\text{-}1\text{WO}_3\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}3\text{AlO}_{3/2}\text{-}48\text{PO}_{5/2}$ glass (1W-Al glass), $35\text{NaO}_{1/2}\text{-}1\text{WO}_3\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}3\text{YO}_{3/2}\text{-}48\text{PO}_{5/2}$ glass (1W-Y glass), and $30\text{NaO}_{1/2}\text{-}1\text{WO}_3\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}3\text{AlO}_{3/2}\text{-}3\text{YO}_{3/2}\text{-}50\text{PO}_{5/2}$ glass (1W-AlY glass). These were prepared and subjected to APS. Their deformation and deprotonation behaviors were studied by the thermal expansion and thermogravimetry (TG), respectively. The electrical conductivity after APS is discussed in terms of the mobility of the proton carriers.

2. Experimental

2.1. Glass preparation

The glasses denoted 1W, 1W-Al, 1W-Y, and 1W-AlY were prepared by a conventional melt-quenching technique. The raw materials: Na_2CO_3 , WO_3 , Nb_2O_5 , La_2O_3 , Al_2O_3 , Y_2O_3 , and H_3PO_4 were weighed and mixed. They were then melted in a platinum crucible for 1 h at 1400–1450 °C in air. The molten materials were poured into a cylindrical carbon mold with an inner diameter of 18 mm. It was annealed at 420–450 °C for 10 min and subsequently cooled slowly to 350 °C at a cooling rate of 20 °C h⁻¹. It was then cooled to 100 °C at a cooling rate of 50 °C h⁻¹. The T_g and T_d of these glasses were determined using the thermal expansion curves recorded on a TMA/SS-6000 (SII, Japan).

2.2. Alkali-proton substitution (APS)

APS was applied to the prepared glasses using an APS apparatus (KDK-800, Kenix Co., Japan). The detailed configuration is described in our previous papers [4-6]. Disk-shaped glass

plates with a diameter of 18 mm and a thickness of 1 mm were sliced from the cylindrical glass block and both surfaces were polished. A thin film of metallic palladium (Pd) with a thickness of approximately 0.2 μm was deposited by magnetron sputtering onto one surface of the glass plate. The glass plate was then loaded into a holder made of quartz with the Pd-deposited surface facing upwards. The other face of the glass was positioned to enable contact with molten Sn under a 5% H_2 /95% N_2 atmosphere. A DC bias of 5.0 V was applied between the Pd anode and the molten Sn cathode. The APS temperature and duration was: 310 $^\circ\text{C}$ for 11 h, 345 $^\circ\text{C}$ for 4 h, 335 $^\circ\text{C}$ for 6 h, and 355 $^\circ\text{C}$ for 4 h, respectively, for the 1W, 1W-Al, 1W-Y, and 1W-AlY glasses.

2.3. Characterization

TG analyses of the glasses after APS were performed using a TG/DTA6300 (SII, Japan). The thermal expansion curves were measured using a TMA/SS-6000 (SII) to determine the T_g and the T_d . The sodium concentration in the glass was determined using an energy-dispersive X-ray spectrometer (EDX; JED-2300, JEOL, Japan) attached to a scanning electron microscope (SEM; JSM-6335F, JEOL, Japan). The concentration of protons that formed OH groups in the glass was determined by the absorbance of the O-H stretching vibration, ν_{OH} , as recorded by a Fourier transform infrared (FTIR) spectrometer (FT-IR6100, JASCO, Japan) with an infrared microscope (IRT-5000, JASCO, Japan). The OH concentration, n_{OH} in cm^{-3} , *i.e.*, the proton concentration, was calculated from the maximum absorption intensity of ν_{OH} , $\alpha(\nu_{\text{OH}})$ in cm^{-1} using the following equation[7]:

$$n_{\text{OH}} = 1.03 \times 10^{19} \times \alpha(\nu_{\text{OH}}) \quad (4)$$

Electrical conductivities at various temperatures were determined from the impedance spectra recorded using an impedance analyzer (HP4192A) under a dry 5% H_2 /95% N_2 atmosphere. Both surfaces of the glass plate after APS were polished again, because the glass surfaces were slightly roughed during APS. Then, Pd films were deposited again for the electrical conductivity and

electromotive force (emf) measurements. The mean transport number of the protons was calculated from the emf of the hydrogen concentration cell with a structure of gas (I), Pd | glass | Pd, gas (II). Gas (I) was constant at 5% H₂/95% N₂ and gas (II) was a mixture of H₂ and N₂ with various H₂ concentrations from 0.2% to 5%. The partial pressure of water, $P_{\text{H}_2\text{O}}$, of gases (I) and (II) was fixed at 1.7×10^3 Pa and this was achieved by passing water at 15 °C to define the P_{H_2} and P_{O_2} in the atmosphere.

3. Results and discussion

Figure 1(a) shows TG analyses of the glass after APS together with those of the 35NaO_{1/2}-20WO₃-45PO_{5/2} (20W) and 8WO₃-35NaO_{1/2}-8NbO_{5/2}-5LaO_{3/2}-44PO_{1/2} (8W) glasses after APS [4,5]. The weights of the glasses began to decrease at >300 °C. These weight decreases can be attributed to deprotonation caused by the evaporation of H₂O and/or phosphoric acid from the glasses. The temperatures indicated by the arrows in Fig. 1(a) are defined as the on-set temperature of deprotonation. Figure 1(b) shows the relationship between the on-set temperature of deprotonation and the T_g of the glasses before APS. As shown in the figure, the deprotonation starts at a higher temperature when the T_g of the glass before APS is higher. The T_g and T_d of the glasses before and after APS are summarized in Table 1. Both T_g and T_d increase upon the addition of AlO_{3/2} and/or YO_{3/2} compared with the 1W glass. The T_g and T_d of the 1W-AlY glass after APS were 80–90 °C higher than those of the 1W glass. These results indicate that high thermal stability can be attained for the glass after APS when APS is applied to the glass with a high T_g before APS.

Figure 2 shows Arrhenius plots of the electrical conductivity of the glasses after APS. Electrical conductivity could be measured for the 1W-Al, 1W-Y, and 1W-AlY glasses after APS up to 350 °C without softening and deformation as expected from their T_g and T_d values, whereas it could not be measured for the 1W glass at >250 °C because of softening and

deformation. The thermal stability of the 1W glass was successfully improved by $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ addition. The mean proton transport number for those glasses was found to be unity from the emf measurements. However, their proton conductivities were 1–2 orders of magnitude lower than that of the 1W glass [5]. The highest conductivity was $\sim 1 \times 10^{-3} \text{ Scm}^{-1}$ at 350 °C for the 1W-Al glass after APS, and we did not achieve the expected conductivity of $> 1 \times 10^{-2} \text{ Scm}^{-1}$ despite the thermal stability being successfully improved.

Table 2 summarizes the sodium and OH concentrations of the glasses before and after APS. The absolute values of the decreasing sodium concentration, Δn_{Na} , and the increasing OH concentration, Δn_{OH} , agree well with each other. This indicates that the sodium ions in the glass before APS were successfully substituted with protons after APS. The OH concentration after APS was $6\text{--}8 \times 10^{21} \text{ cm}^{-3}$ for 1W-Al, 1W-Y, and 1W-AlY, and this value is slightly higher than that of the 1W glass after APS of $5 \times 10^{21} \text{ cm}^{-3}$. Therefore, the decrease in proton conductivity that was induced by $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ addition can be attributed to the reduced mobility of the proton carriers in the 1W-Al, 1W-Y, and 1W-AlY glasses after APS. Table 3 summarizes the mobility of the proton carriers at 250 °C in the glasses after APS. These values were calculated assuming that all the protons that form OH groups at room temperature, as detected by IR spectroscopy, become carriers at high temperature. It is evident that the mobility of the proton carriers is reduced by 1/20–1/50 by the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into the glass.

The following discussion explains the reason for the mobility of the proton carriers being reduced by the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ into the 1W glass, based on the IR spectra in ν_{OH} region as shown in Fig. 3. For the 1W glass that is before the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$, an intense and broad ν_{OH} band centered at $\sim 2900 \text{ cm}^{-1}$ is observed. The broad band is slightly asymmetric and deconvoluted into an intense 2900 cm^{-1} band and a weak 3300 cm^{-1} band. Both these bands are present at a lower frequency than the ν_{OH} band for the free H_2O molecule at 3690 cm^{-1} [8]. Therefore, the protons in the OH groups form hydrogen bonds with the adjacent

oxygen [8]. For the glasses containing $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$, the intensity of the band at 3300 cm^{-1} obviously increases compared with the glass without $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. The mobility of the proton carriers decrease with an increase in the intensity ratio of the band at 2900 cm^{-1} to the band at 3300 cm^{-1} , I_{3300}/I_{2900} , as indicated in Table 3. This reduced mobility of the proton carriers can be attributed to the increase in protons that are tightly bound to oxygen, *i.e.*, the formation of weak hydrogen bondings, as follows: When the concentration of protons that are tightly bound to oxygen is small, the protons can move without passing through the proton site, where the protons are tightly bound to oxygen. Therefore, the macroscopic proton mobility is determined by the protons that are loosely bound to oxygen. When the concentration of protons that are tightly bound to oxygen is large, the tightly bound proton site is involved in the conduction path, *i.e.*, the protons cannot move over a long distance without passing through the tightly bound proton site. In this case, the macroscopic proton mobility is determined by the protons that are tightly bound to oxygen; as a result, the observed mobility of protons decreases as indicated in Table 3. The mechanism for the strength of O-H bonding being significantly affected by the introduction of a small amount of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$ is not clear. However, this change must come from a change in the glass structure upon the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. Because there is no precedent for a glass containing such a high proton concentration at high temperatures, as is the case for the studied glasses, an understanding of the mobility of the proton carriers in these glasses is deficient at present. The relationship between the mobility of the proton carriers and the glass structure in the electrochemically proton-injected glasses will provide valuable information for the design of an optimal glass composition to achieve a simultaneous high protonic conductivity and high thermal stability.

4. Summary

In this study, we improved the thermal stability of the 1W glass after APS by the introduction

of a small amount of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. The obtained 1W-Al, 1W-Y, and 1W-AlY glasses are stable at 350 °C, which is 100 °C higher than the stability limit of the 1W glass. However, the mobility of the proton carriers in the 1W-Al, 1W-Y, and 1W-AlY glasses are 1/20–1/50 lower than that of the 1W glass. This reduced mobility is attributed to an increase in the protons that are tightly bound to oxygen leading to the formation of weak hydrogen bonding. This change in O-H bond strength must come from a structural change in the glass, which is induced by the introduction of $\text{AlO}_{3/2}$ and/or $\text{YO}_{3/2}$. Understanding the relationship between the glass structure and proton mobility will provide information about the glass compositions required to achieve a simultaneous high proton carrier mobility and high thermal stability in these glasses.

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Figure captions

Figure 1.(a) TG curves of the glass after APS together with those of the 20W and 8W glasses after APS. (b) On-set temperatures for the deprotonation of the glasses after APS as a function, and the T_g of the glasses before APS.

Figure 2. Arrhenius plots of the electrical conductivity of the glasses after APS. The mean proton transport numbers of the glasses were determined from the emfs of hydrogen concentration cells and are unity.

Figure 3.IR spectra of the OH stretching vibration, ν_{OH} , region of the glasses after APS. The thin lines are deconvoluted curves.

Table 1 Glass transition temperatures, T_g , and deformation temperatures, T_d , of the glasses before and after APS.

Glass	Before APS		After APS	
	$T_g / ^\circ\text{C}$	$T_d / ^\circ\text{C}$	$T_g / ^\circ\text{C}$	$T_d / ^\circ\text{C}$
1W	407	453	196	247
1W-Al	457	499	224	290
1W-Y	448	487	228	284
1W-AlY	476	520	281	339

Table 2 Sodium and OH concentrations, n_{Na} and n_{OH} , of the glasses before and after APS and differences, Δn , in n_{Na} and n_{OH} before and after APS.

Glass	Sodium concentration / cm^{-3}			OH concentration / cm^{-3}		
	$n_{\text{Na}}(\text{before APS})$	$n_{\text{Na}}(\text{after APS})$	Δn_{Na}	$n_{\text{OH}}(\text{before APS})$	$n_{\text{OH}}(\text{after APS})$	Δn_{OH}
1W	9×10^{21}	3×10^{21}	-6×10^{21}	4×10^{19}	5×10^{21}	5×10^{21}
1W-Al	9×10^{21}	2×10^{21}	-7×10^{21}	3×10^{19}	6×10^{21}	6×10^{21}
1W-Y	9×10^{21}	1×10^{21}	-8×10^{21}	4×10^{19}	6×10^{21}	6×10^{21}
1W-AlY	8×10^{21}	1×10^{21}	-8×10^{21}	4×10^{19}	8×10^{21}	8×10^{21}

Table 3 Proton conductivity, σ_{H} , proton carrier concentration, n_{H^+} , and mobility of the proton carriers, μ_{H^+} , at 250 $^\circ\text{C}$ in the glasses after APS. All the protons that form OH groups at room temperature are assumed to be proton carriers at 250 $^\circ\text{C}$. I_{3300}/I_{2900} indicates the intensity ratio between the ν_{OH} band at 2900 cm^{-1} and the ν_{OH} band at 3300 cm^{-1} in IR spectra shown in Fig. 3.

Glass	$\sigma_{\text{H}} / \text{Scm}^{-1}$	$n_{\text{H}^+} / \text{cm}^{-3}$	$\mu_{\text{H}^+} / \text{cm}^2\text{V}^{-1}\text{s}^{-1}$	I_{3300}/I_{2900}
1W	3×10^{-4}	5×10^{21}	4×10^{-7}	0.24
1W-Al	2×10^{-5}	6×10^{21}	2×10^{-8}	0.40
1W-Y	8×10^{-6}	6×10^{21}	9×10^{-9}	0.72
1W-AlY	9×10^{-6}	8×10^{21}	8×10^{-9}	1.1

Figure 1a

Figure 1b

Figure 2

Figure 3