

Proton Incorporation, Mixed Alkaline Effect and H⁺/e⁻ Mixed Conduction of Phosphosilicate Glasses and Glass-ceramics

Yusuke DAIKO,^{a,*} Takeshi YAMADA,^b Satoshi YAMANISHI,^b Atsushi
MINESHIGE,^b and Tetsuo YAZAWA^b

^a *Department of Materials Science and Chemistry, University of Hyogo, 2167 Shosha,
Himeji, Hyogo 671-2280, Japan*

^b *Department of Frontier Materials, Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya, Aichi 466-8555, Japan*

* Corresponding author: Fax: +81 52 735-5614, Email: daiko.yusuke@nitech.ac.jp

Abstract

Ionic conduction and proton transport number (t_H) of various glass-electrolytes were measured at 500°C for intermediate temperature fuel cells. A borosilicate glass (Na₂O-B₂O₃-SiO₂) shows $t_H = 0.04$, which increases to 0.2 by doping 3 mol% of P₂O₅ component. A phosphosilicate glass (Na₂O-P₂O₅-SiO₂) shows $t_H = 0.6$ at the same condition. A glass with $t_H = 1.0$ can be obtained for a mixed alkali glass (Na₂O-K₂O-P₂O₅-SiO₂). It was found that the Al₂O₃ doping is indispensable in order to improve the chemical durability of the phosphosilicate glasses. On the other hand, in the case of non-alkali glass (SnO-B₂O₃-P₂O₅-SiO₂), SnP₂O₇ single phase dispersed dense glass-ceramics was obtained with Sn/P = 0.52, and the glass ceramic shows $t_H = 1.0$. By increasing the amount of SnO₂ and decreasing P₂O₅, Sn-rich Sn_{2.5}P₃O₁₂ phase was observed, and the glass-ceramics show a possibility of proton/electron mixed conductivity.

Key-words:

Glass, Fuel Cell, Proton Conduction, Mixed Alkali Effect

1. Introduction

Fuel cells have attracted much attention owing to their high energy conversion efficiency with very a few CO₂ emissions.¹² Although perfluorosulfonate ionomers (e.g. Nafion®) exhibit high proton conductivity (approximately 0.1 S/cm), their industrial applications are limited by their high cost, low operation temperatures (<100 °C), and insufficient electrochemical stability.³ Fuel cell operation higher than 100 °C in dry conditions is desired to improve the total efficiency and CO tolerance of Pt electrodes, increase the electrode reaction rate, and simplify system integration. This has prompted a great interest in developing a new electrolyte with high proton conductivity and stabilities.

We have studied about proton conducting glasses and those applications for an intermediate temperature fuel cell.⁴⁵⁶ Some glasses show very high ionic conductivity including Na⁺,⁷ Li⁺,⁸ Cu⁺,⁹¹⁰ Ag⁺,¹¹¹² F⁻ and so on.¹³ However, preparation of a fast proton conducting glass is far difficult due to mainly following two reasons. The protons in glasses exist mainly as OH groups. For typical oxide glasses, the melting temperatures of glasses are higher than 1000 °C and such OH groups evaporate during the melting procedure. Thus, there are very a few protons inside melting-glasses. Furthermore, the remaining -O⁻ and H⁺ ionic pairs are strongly bonded to each other, leading to a very high dissociation energy of the proton. Doremus estimated that in silicate glass the mobility of Na⁺ ions is 10⁴ times that of protons.¹⁴ Ernsberger suggested in 1980 that proton cannot move inside glasses.¹⁵¹⁶

On the other hand, Namikawa and Asahara suggested in 1965 based on a study of water content and electrical conductivity, that the electrical carriers in barium phosphate glasses are protons.¹⁷ In the 1980s and 1990s, Abe and co-workers reported the

electrical properties of more than 100 types of phosphate glasses.¹⁸¹⁹ They proved that the protons in some phosphate glasses are mobile when they have strong hydrogen bonds, and proton conductivity is proportional to the square of the concentration of mobile protons, as follows:

$$\sigma = A_H [H^+]^2 \quad (1)$$

where A_H is a constant determined from the peak wavenumber of the OH stretching vibrations in the infrared (IR) absorption spectra.

We previously reported proton conductivity of borosilicate and phosphosilicate glasses.⁴⁻⁶ By adding network modifiers of monovalent cation such as alkali metal and Ag^+ ions, these ions migrate in addition to proton, resulting into decrease proton transport number (t_H). Also, proton conductivity of glasses decreases significantly by adding network modifiers of bivalent cation (Mg^{2+} , Ca^{2+} , Zn^{2+} etc.).

In this paper, composition of glasses and its relation with both t_H and ionic conductivity are overviewed based on our recent results. Crystallization of non-alkali glasses (SnO-doped phosphosilicate glass) and those t_H are also discussed.

2. Borosilicate and phosphosilicate glasses

Borosilicate and phosphosilicate glasses were prepared using conventional melting method using an alumina crucible (SSA-H). Appropriate amounts of the materials were melted at 1600°C for 2 h, and then cast on a carbon plate. The glasses were then annealed from 600°C down to room temperature. Proton transport number was estimated by using hydrogen concentration cell, and conductivity was calculated based on the result of two-probe AC impedance method. The t_H was determined from the electromotive force (EMF) using a hydrogen concentration cell. The detailed

preparation/analysis methods are given in our previous papers.⁴⁻⁶

Fig. 1 shows the temperature dependences of ionic conductivity of 9.4Na₂O·25.4B₂O₃·65.2SiO₂ (mol%) glasses doped with xP₂O₅ (mol%) glasses ($x = 0, 1$ and 3). Conductivity was measured under both Ar (dry) and humidified conditions (**Fig. 1d**). The activation energy of all glasses was estimated to be 88~92 kJ/mol. Note that there are no difference in conductivity under Ar and humidified conditions for the borosilicate glasses with $x = 0$ and 1, whereas conductivity improves under humidified condition for the glass with $x = 3$. Proton transport numbers (t_H) of glasses are summarized in **Table 1**. The borosilicate glasses with $x = 0$ and 1 show $t_H \approx 0$, indicating no proton conduction, and the conductivities shown in **Figs. 1a-b** are attributed to the motion of Na⁺ ion. On the other hand, t_H increases to $t_H = 0.2$ for the borosilicate glass with $x = 3$ under humidified condition, suggesting a part of carrier (20 %) is proton. It is evident that P₂O₅ component effectively increases the t_H value. However, glasses with $x > 3$ were not obtained due to very high viscosity of these melts, and we changed the composition of mother glass from borosilicate to phosphosilicate.

The t_H of the 15Na₂O·35P₂O₅·50SiO₂ phosphosilicate glass increases up to 0.58 at the same temperature. Still, Na⁺ ions migrate in addition to protons, and the glass cannot be applied for fuel cell electrolytes.

Pronounced changes in properties can be seen by adding a second alkali oxide (so called mixed-alkali effect, MAE).²⁰²¹²² In the case of ionic conductivity, conductivity of alkali metal ions decreases significantly due to the MAE. In order to decrease the Na⁺ ion conductivity of the phosphosilicate glass, we prepared a mixed-alkali glass with both sodium and potassium ions. **Fig. 2** shows the temperature dependences of conductivities of (15- x)Na₂O· x K₂O·35P₂O₅·50SiO₂ (mol%) glasses with $x = 0$ and 9.

Note the conductivity shown in **Fig. 2** is attributed to not proton but alkali metal ions (Na^+ , K^+) since the measurement was performed under *Ar* atmosphere. (We will show about the proton incorporation under H_2 atmosphere in the following session). It is clear from **Fig. 2** that the conductivity decreases approximately one order of magnitude by co-adding Na_2O and K_2O owing to the MAE.

As mentioned in introduction, there are very a few protons inside melting-glasses. On the other hand, we previously reported that protons dissociated on a Pt electrode under H_2 atmosphere are incorporated into glasses due to the electrochemical potential difference between anode and cathode. **Fig. 3** shows cole-cole plots of the mixed alkali glass ($7.5\text{Na}_2\text{O}\cdot 7.5\text{K}_2\text{O}\cdot 35\text{P}_2\text{O}_5\cdot 50\text{SiO}_2$ (mol%)) measured under *Ar* and hydrogen gas atmosphere. 100% of H_2 gas was exposed to a side of the glass and 1% H_2 (99% *Ar*) was exposed to the other side as shown in the inset of **Fig. 3**. Note that the electrical resistance measured under hydrogen atmosphere was approximately one order of magnitude lower than that measured under *Ar* owing to increase the number of carrier by the incorporation of protons. Furthermore, the t_{H} of the mixed alkali glass reached to $t_{\text{H}} \sim 1.0$ (**Table 1**), suggesting the main carrier in the glass is proton, and the transport of protons in the glass is independent from that of alkali ions. The relation between the amount of proton incorporated $[\text{H}^+]$ and conductivity can be expressed by the eq. (1).⁵

Doping of Al_2O_3 component affects significantly both on the MAE and on the durability of glass. Since glasses above mentioned were prepared by using an alumina crucible, these glasses should contain a few mol% of Al_2O_3 component. In order to understand the effect of Al_2O_3 , we varied the amount of doped Al_2O_3 . Here, a Pt crucible was used to prepare these glasses.

Fig. 4 shows the relationship between the amount of Al_2O_3 and t_{H} measured at

500°C. It was found that the t_H of the glass without Al₂O₃ is approximately 0.6, and the t_H reached to ~1.0 for glasses with Al₂O₃ > 5 mol%.

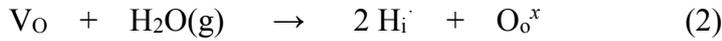
In general, phosphate glasses are hygroscopic and deliquescent. In order to check the chemical durability, glasses were immersed into water (room temperature), and the weight change was measured. Changes in weight % with the immersion time for the mixed alkali glass with 5 mol% Al₂O₃ (Al-5) and without Al₂O₃ (Al-0) are shown in **Fig. 5**. The Al-0 glass dissolves rapidly in water and the value of pH decreases from 7 to 1 due to the phosphoric acid. On the other hand, the weight and pH value of Al-5 remain unchanged even after 7 days. It is evident that the Al₂O₃ doping is indispensable in order to improve both the t_H (~1.0) and chemical durability of the phosphosilicate glasses.

Fuel cell test was also performed using the mixed alkali glass at 500°C. Pt electrodes for anode and cathode were sputtered on both side of glass (~1 mm), and pure hydrogen and oxygen gasses were used for the measurement. As shown in **Fig. 6**, the open circuit voltage (OCV) was approximately 1.2 V, and no significant degradation was observed for 1000 h, suggesting the glass is thermally/chemically stable at 500°C under a fuel cell condition. The maximum power density was 0.2 mW/cm², which improved to ~5 mW/cm² by using Ni and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (BSCF) electrodes for anode and cathode, respectively. However, a serious crack was observed between glass and electrodes after a few hour fuel-cell-operations when Ni and BSCF electrodes were used, which may be due to the difference in their thermal expansion coefficients. Further studies about these issues are in progress in order to improve the fuel cell powder density.

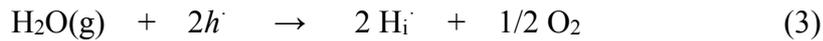
3. SnP₂O₇ dispersed glass-ceramics

In the above session, we show proton conduction of borosilicate and phosphosilicate glasses. The MAE is a crucial aspect in order to decrease Na⁺ ion conductivity and to obtain $t_H = 1.0$. In this session, we report about the proton conduction of non-alkali SnO-B₂O₃-P₂O₅-SiO₂ glass-ceramics.

Hibino et al. have reported that SnP₂O₇ shows high proton conductivity ($> 10^{-2}$ S/cm) around 150 ~ 300°C.²³ SnP₂O₇ has a cubic structure with SnO₆ octahedron and PO₄ tetrahedron units at the corners and edges, respectively.²⁴ Such closely packed PO₄ tetrahedron units can provide many proton-bonding sites. Oxygen vacancy and hole are formed by substitution. For example, H₂O(vapor) and the vacancy reacts as the eq. (2), resulting into produce proton (H_i[·]).



where V_O, H_i[·] and O_o^x denote oxygen vacancy, newly generated interstitial proton and lattice oxide ion, respectively. In the case of the reaction of hole(*h*[·]) and H₂O(g), the following eq. (3) is proposed.



Proton conductivity of non-doped SnP₂O₇ was 60 mS/cm at 200°C. Thus, we prepared non-alkali SnO-B₂O₃-P₂O₅-SiO₂ glasses with various Sn/P ratios.

SnO₂ doped phosphosilicate glasses were prepared by the melting method using the

alumina crucible (SSA-H). The starting materials were analytical grade reagents SnO₂, Al₂O₃, P₂O₅, SiO₂ and B₂O₃. Materials were melted in the alumina crucible at 1600°C for 2 h, and then cast on a carbon plate. The glasses were then annealed from 600°C down to room temperature.

Various glasses with the Sn/P ratio from 0.15 to 1.53 were prepared. These glasses obtained were X-ray amorphous. XRD patterns after heat-treated at 900°C for 15 h are shown in **Fig. 7**. Note that SnP₂O₇ single-phase dispersed glass-ceramic can be successfully obtained with Sn/P = 0.52 after the heat treatment. On the other hand, by increasing the amount of SnO₂ and decreasing P₂O₅, Sn-rich Sn_{2.5}P₃O₁₂ phase was observed.

Fig. 8 shows the relationship between Sn/P ratio and alternate current conductivity (σ_{AC}) before and after the heat-treatment. In the case of glass with Sn/P = 0.52, conductivity increases more than one order of magnitude after the heat treatment. On the other hand, no significant changes were observed for Sn_{2.5}P₃O₁₂-dispersed glasses.

To ensure the carrier species, proton transport number (t_H) was measured using the hydrogen concentration cell, and the relationship between the EMF and hydrogen partial pressure is shown in **Fig. 9**. It is immediately apparent that the SnP₂O₇-dispersed glass shows $t_H = 1$ at 500°C, suggesting the main carrier is proton. Proton transport number decreases significantly with increasing Sn/P ratio.

Ion blocking electrode (sputtered Au) was used for both the σ_{AC} and σ_{DC} measurements, and thus we obtained electron (or hole) conductivity from the σ_{DC} measurement, whereas σ_{AC} includes the information about both ion and electron conductivities. Proton conductivity of SnO₂-doped phosphosilicate glass increases clearly after the deposition of SnP₂O₇ phase based on the result of σ_{AC} . On the other

hand, in the case for Sn-rich glasses, it seems electron may also migrate. Note in **Fig. 10** that the glasses with $\text{Sn/P} > 0.52$ decrease the t_{H} value may be due to the electron conduction, however the EMF of $\text{Sn}_{2.5}\text{P}_3\text{O}_{12}$ -dispersed sample still increase with increasing the hydrogen partial pressure. These results suggest that proton can also move inside the Sn-rich glass-ceramics.

One serious problem of SnP_2O_7 is that the sintered density is less than 90 %, and cross-over of hydrogen and oxygen gasses through SnP_2O_7 decreases fuel cell power density. Single gas permeation through the glass-ceramics was measured using He and N_2 gasses. He or N_2 gas at 0.1 MPa was provided to a side of the sample with 1 mm thickness, and the flow rate of the permeated gas to a opposite side was measured at room temperature. No leakage for both He and N_2 was confirmed. This should be owing to a amorphous glass matrix which effectively densifies and prevents gas permeation.

4. Conclusion

Proton transport number and conductivity of phosphosilicate glasses and glass-ceramics were investigated. The MAE is a crucial aspect in order to decrease Na^+ ion conductivity and to obtain $t_{\text{H}} = 1.0$. It was found that the Al_2O_3 doping is indispensable in order to improve both the t_{H} (~ 1.0) and chemical durability of the phosphosilicate glasses. We also successfully prepared SnP_2O_7 dispersed glass-ceramics by conventional melting method. In this case, the glass-ceramics with $\text{Sn/P} = 0.52$ shows $t_{\text{H}} = 1$ at 500°C , whereas those with $\text{Sn/P} > 0.52$ have Sn-rich $\text{Sn}_{2.5}\text{P}_3\text{P}_{12}$ phase, and these glass-ceramics show proton/electron mixed conduction. Although the conductivity of these glasses is not enough, these new materials are a promising candidate for a new type of electrolyte or electrode which can be for intermediate

temperature fuel cell.

Acknowledgement

The author, Y. Daiko, is deeply grateful to Dr. T. Yazawa and Dr. A. Mineshige (*Univ. Hyogo*), Dr. T. Minami (Osaka Prefecture Univ.) for their kind support and fruitful discussions. The works described in this paper were partially supported by the Adaptable and Seamless Technology Transfer Program (A-STEP, JST no. AS221Z03900C).

Table 1

glass / mol%	condition	t_H
9.4Na ₂ O·25.4B ₂ O ₃ ·65.2SiO ₂ $x=0$ *	dry	-
	humidify	-
9.4Na ₂ O·25.4B ₂ O ₃ ·65.2SiO ₂ $x=1$ *	dry	-
	humidify	-
9.4Na ₂ O·25.4B ₂ O ₃ ·65.2SiO ₂ $x=3$ *	dry	0.04
	humidify	0.2
15Na ₂ O·35P ₂ O ₅ ·50SiO ₂	dry	0.58
7.5Na ₂ O·7.5K ₂ O·35P ₂ O ₅ ·50SiO ₂	dry	1.0

(* doped with x mol% P₂O₅, -: no significant changes in EMF)

-
- ¹ B. H. Steele and A. Heinzl, *Nature*, **414**, 345 (2001).
 - ² Q. Li, R. He, J. O. Jensen and N. J. Bjerrum, *Chem. Mater.* **15**, 4896 (2003).
 - ³ T. Norby, *Solid State Ionics*, **125**, 1 (1999).
 - ⁴ Y. Daiko, T. Yamada, A. Mineshige, M. Kobune and T. Yazawa, *Electrochem. Solid-State Lett.*, **14**, B63 (2011).
 - ⁵ Y. Takamatsu, Y. Daiko, S. Kohara, K. Suzuya, A. Mineshige and T. Yazawa, *Solid State Ionics*, **245-246**, 19 (2013).
 - ⁶ Y. Daiko, T. Yamada, A. Mineshige and T. Yazawa, *MRS Proceedings*, **1495**, mrsf12-1495-i14-05 doi:10.1557/opl.2013.9.
 - ⁷ F. A. Fusco and A. L. Tuller, *Superionic Solid and Solid Electrolytes*, Academic Press, Boston, 43 (1989).
 - ⁸ A. Pradel and M. Ribes, *Mater. Sci. Eng.*, **B3**, 45 (1989).
 - ⁹ C. Liu and C. A. Angell, *Solid State Ionics*, **13**, 105 (1984).
 - ¹⁰ N. Machida and T. Minami, *J. Am. Ceram. Soc.*, **71**, 784 (1988).
 - ¹¹ J. O. Malugani, A. Wasniewski, M. Doreau, G. Rikabi and A. A. Robert, *Mat. Res. Bull.*, **13**, 427 (1978).
 - ¹² L. Changle, S. H. G. K and A. C. A, *Solid State Ionics*, **18-19**, 442 (1986).
 - ¹³ J. M. Reau and M. Poulain, *Mater. Chem. Phys.* **23**, 189 (1989).
 - ¹⁴ R.H. Doremus, *J. Electrochem. Soc.*, **115**, 181 (1968).
 - ¹⁵ F.M. Ernsberger, *Phys. Chem. Glass*, **21**, 146 (1979).
 - ¹⁶ F.M. Ernsberger, *J. Non-Cryst. Solid*, **38-39**, 557 (1980).
 - ¹⁷ H. Namikawa and Y. Asahara, *J. Ceram. Assoc. Japan*, **74**, 205 (1965). [in Japanese]
 - ¹⁸ Y. Abe, H. Hosono, O. Akita and L.L Hench, *J. Electrochem. Soc.*, **141**, L64 (1994).
 - ¹⁹ Y. Abe and M. Takahashi, *Chem. Phys. Lett.*, **411**, 302 (2005).
 - ²⁰ J. O. Isard, *J. Non-Cryst. Sol.*, **1**, 235 (1969).
 - ²¹ D. E. Day, *J. Non-Cryst. Sol.*, **21**, 343 (1976).
 - ²² M. D. Ingram, *Phys. Chem. Glasses*, **28**, 215 (1987).
 - ²³ M. Nagao, T. Kamiya, P. Heo, A. Tomita, T. Hibino and M. Sano, *J. Electrochem. Soc.*, **153**, A1604 (2006).
 - ²⁴ R. K. B Gover, N. D. Withers, S. Allen, R. L. Withers and J. S. O. Evans, *J. Sol. Stat. Chem.*, **166**, 42 (2002).