プロトンの浸入、混成アルカリ効果及びH⁺/e⁻混成拡散挙動のリン酸塩ガラス及びガラスセラミックス

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Proton Incorporation, Mixed Alkaline Effect and
H\(^+\)/e\(^-\) Mixed Conduction of Phosphosilicate Glasses
and Glass-ceramics

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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 (Na$_2$O-B$_2$O$_3$-SiO$_2$) shows $t_H = 0.04$, which increases to 0.2 by doping 3 mol% of P$_2$O$_5$ component. A phosphosilicate glass (Na$_2$O-P$_2$O$_5$-SiO$_2$) shows $t_H = 0.6$ at the same condition. A glass with $t_H = 1.0$ can be obtained for a mixed alkali glass (Na$_2$O-K$_2$O-P$_2$O$_5$-SiO$_2$). It was found that the Al$_2$O$_3$ 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-B$_2$O$_3$-P$_2$O$_5$-SiO$_2$), SnP$_2$O$_7$ 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 SnO$_2$ and decreasing P$_2$O$_5$, Sn-rich Sn$_{2.5}$P$_3$O$_{12}$ 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. 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. 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. Some glasses show very high ionic conductivity including Na⁺, Li⁺, Cu⁺, Ag⁺, F⁻ and so on. 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. Ernsberger suggested in 1980 that proton cannot move inside glasses.

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. In the 1980s and 1990s, Abe and co-workers reported the
electrical properties of more than 100 types of phosphate glasses. 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:

$$\sigma = A_H [H^+]^2$$  \hspace{1cm} (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. 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.

**Fig. 1** shows the temperature dependences of ionic conductivity of $9.4\text{Na}_2\text{O} \cdot 25.4\text{B}_2\text{O}_3 \cdot 65.2\text{SiO}_2$ (mol%) glasses doped with $x\text{P}_2\text{O}_5$ (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 $\text{Na}^+$ 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 $\text{P}_2\text{O}_5$ 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 $15\text{Na}_2\text{O} \cdot 35\text{P}_2\text{O}_5 \cdot 50\text{SiO}_2$ phosphosilicate glass increases up to 0.58 at the same temperature. Still, $\text{Na}^+$ 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)\textsuperscript{20,21,22}. In the case of ionic conductivity, conductivity of alkali metal ions decreases significantly due to the MAE. In order to decrease the $\text{Na}^+$ 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 $(15-x)\text{Na}_2\text{O} \cdot x\text{K}_2\text{O} \cdot 35\text{P}_2\text{O}_5 \cdot 50\text{SiO}_2$ (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\(_2\)O and K\(_2\)O 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 (7.5Na\(_2\)O·7.5K\(_2\)O·35P\(_2\)O\(_5\)·50SiO\(_2\) (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 \(t_H \sim 1.0\) (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 [H\(^+\)] and conductivity can be expressed by the eq. (1).

Doping of Al\(_2\)O\(_3\) 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\(_2\)O\(_3\) component. In order to understand the effect of Al\(_2\)O\(_3\), we varied the amount of doped Al\(_2\)O\(_3\). Here, a Pt crucible was used to prepare these glasses.

Fig. 4 shows the relationship between the amount of Al\(_2\)O\(_3\) and \(t_H\) measured at
500°C. It was found that the $t_H$ of the glass without Al$_2$O$_3$ is approximately 0.6, and the $t_H$ reached to ~1.0 for glasses with Al$_2$O$_3 > 5$ 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% Al$_2$O$_3$ (Al-5) and without Al$_2$O$_3$ (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 Al$_2$O$_3$ 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/cm$^2$, which improved to ~5 mW/cm$^2$ by using Ni and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (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. SnP$_2$O$_7$ 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 $t_{li} = 1.0$. In this session, we report about the proton conduction of non-alkali SnO-B$_2$O$_3$-P$_2$O$_5$-SiO$_2$ glass-ceramics.

Hibino et al. have reported that SnP$_2$O$_7$ shows high proton conductivity ($> 10^{-2}$ S/cm) around 150 ~ 300°C.$^{23}$ SnP$_2$O$_7$ has a cubic structure with SnO$_6$ octahedron and PO$_4$ tetrahedron units at the corners and edges, respectively.$^{24}$ Such closely packed PO$_4$ tetrahedron units can provide many proton-bonding sites. Oxygen vacancy and hole are formed by substitution. For example, H$_2$O(vapor) and the vacancy reacts as the eq. (2), resulting into produce proton (H$_i$).

$$\text{V}_0 + \text{H}_2\text{O}(g) \rightarrow 2\text{H}_i^+ + \text{O}_o^x$$  \hspace{1cm} (2)

where V$_0$, 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 H$_2$O(g), the following eq. (3) is proposed.

$$\text{H}_2\text{O}(g) + 2h^- \rightarrow 2\text{H}_i^+ + 1/2\text{O}_2$$  \hspace{1cm} (3)

Proton conductivity of non-doped SnP$_2$O$_7$ was 60 mS/cm at 200°C. Thus, we prepared non-alkali SnO-B$_2$O$_3$-P$_2$O$_5$-SiO$_2$ glasses with various Sn/P ratios.

SnO$_2$ doped phosphosilicate glasses were prepared by the melting method using the
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 Sn₂.₅P₃O₁₂ phase was observed.

Fig. 8 shows the relationship between Sn/P ratio and alternate current conductivity (σₐc) 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 Sn₂.₅P₃O₁₂-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 σₐc and σₐc measurements, and thus we obtained electron (or hole) conductivity from the σₐc measurement, whereas σₐc 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 σₐc. 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 Sn/P > 0.52 decrease the $t_{H}$ value may be due to the electron conduction, however the EMF of Sn$_{2.5}$P$_3$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$_2$O$_7$ is that the sintered density is less than 90 %, and cross-over of hydrogen and oxygen gasses through SnP$_2$O$_7$ 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 $t_{H} = 1.0$. It was found that the Al$_2$O$_3$ 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$_2$O$_7$ dispersed glass-ceramics by conventional melting method. In this case, the glass-ceramics with Sn/P = 0.52 shows $t_{H} = 1$ at 500$^\circ$C, whereas those with Sn/P > 0.52 have Sn-rich Sn$_{2.5}$P$_3$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.

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Table 1

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<tr>
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<td>7.5Na$_2$O·7.5K$_2$O·35P$_2$O$_5$·50SiO$_2$</td>
<td>dry</td>
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(* doped with $x$ mol% P$_2$O$_5$, -: no significant changes in EMF)