Remarkable High Proton Conducting $\text{P}_2\text{O}_5-\text{SiO}_2$ Glass as a Fuel Cell Electrolyte Working at Sub-Zero to 120°C

Yusuke DAIKO, Tomoko AKAI,* Toshihiro KASUGA and Masayuki NOGAMI
Nagoya Institute of Technology, Showa-ku, Nagoya-shi 466-8555
*National Institute of Advanced Industrial Science and Technology, Midorigaoka, Ibaraki-ku 563-8577

Abstract

Proton conductivity of the $\text{P}_2\text{O}_5-\text{SiO}_2$ glasses was investigated at sub-zero to 120°C. The glasses prepared by a sol-gel method are porous, pore diameters in which are smaller than 5 nm with an average diameter of 2.5 nm. The electrical conductivities, measured under 100% RH, follow the Arrhenius equation with the activation energy of 10 kJ/mol in the temperature between 120 and -20°C. Below -20°C, the adsorbed-water molecules are frozen to increase the activation energy and decrease the proton conductivity. We could conclude that our $\text{P}_2\text{O}_5-\text{SiO}_2$ glasses, exhibiting high protonic conductivity of ~30 mS/cm at 120°C, have potential for the electrolyte of the fuel cell operating at sub-zero to 120°C.

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Fuel cell system using proton-conducting electrolyte has attracted much attention because of its ability to produce high energy without the emission of harmful pollutants. A series of perfluorosulfonate ionomers such as Nafion® currently serve as electrolyte membrane in the fuel cell due to their high proton conductivity at around room temperature.1)-4) The conductivity of these ionomers is largely depending on their water content. Adequate water content of the ionomers is essential to maintain the conductivity of the polymer electrolyte membrane. However, the conductivity unfortunately decreases at temperatures higher than ~80°C because of their inability to retain water. The conductivity also decreases below 0°C due to freezing of water, which limits the fuel cell operation to the narrow temperature range. In addition, they have still many problems for practical use because of their chemical and thermal degradation during use over long periods of time. Stable membranes with high protonic conductivities in the wide temperature range from sub-zero to ~100°C, if developed, would extend beyond the limitation of the above compounds and have potential for various applications, but few reports are available on the materials with thermal stability.5)-7)

Recently, using a sol-gel method, we succeeded in the preparation of $\text{P}_2\text{O}_5-\text{SiO}_2$ glasses exhibiting high conductivity of ~10-2 S/cm at room temperature.5)-13) Our glasses, prepared by heating the gels at temperature above 600°C, are porous and contain water molecules in the pores. We discussed that the proton conduction is promoted by the dissociation of protons from hydroxyl bonds on the pore surfaces and the proton hopping between hydroxyl groups and water molecules.10)-13) The conductivity increases with increasing the content of the adsorbed water. In this view, the sol-gel-derived glasses have potential for the fuel cell operating at higher temperature and could substitute for perfluorinated ionomers as the electrolyte. In the previous papers, however, our research is limited to the glass preparation and the conductivity measurement between 25 and 70°C. An information on the conductivity at the temperatures ranging from sub-zero to over 100°C is essential for the practical application to the fuel cell.

Here, we report the conductivities of the sol-gel-derived glasses over a wide temperature range from -100 to 120°C and show that the glasses exhibit high conductivities at temperature ranging from -20 to 120°C. Our fast proton-conducting glasses at temperature from sub-zero to 120°C could substitute for perfluorosulfonate ionomers as the electrolyte.

5P2O5•95SiO2 (mole %) glasses were prepared by the sol-gel method using Si(OC2H5)4 and PO(OCH3)3. HCONH2 was used to change the porosity of the glass. A detailed explanation of the gel preparation is given elsewhere.10) The gels were heated in air at 600°C for 5 h to form glasses 0.2-0.6 mm thick. The glasses are porous, the surface area and pore volume of which are determined to be 534 m²/g and 0.34 cm³/g, respectively, by a nitrogen gas sorption analysis. Pore diameters in the sample are smaller than 5 nm with an average diameter of 2.5 nm. Pore surfaces are terminated with hydroxyl bonds, POH and SiOH, are sensitive to humidity. Upon exposing the glass to humid atmosphere, it absorbed the water on the pore surfaces, and consequently electrical conductivity increased. The electrical conductivity was determined from Cole–Cole plots by an ac method using an impedance analyzer, where evaporated-gold electrodes were used. The electrical charge is only proton dissociated from the hydroxyl groups on the pore surfaces and the conductivity increases with increasing relative humidity, reaching a constant value at >70% RH.10) The measurement system for conductivity at high temperatures with high water vapor pressure was designed with a stainless vessel. Water pressure was controlled by pressure of a separate vapor source.15)

The conductivity ($\sigma$), measured under 100% RH, is shown in Fig. 1 as a function of the reciprocal of temperature ($1/T$), indicating the data follow the Arrhenius equation, $\sigma = \sigma_0 \exp (-E/RT)$, where $\sigma_0$ is a preexponential term, $R$ gas constant, and $E$ activation energy. It is apparent that the dependence of conductivity on temperature is divided into two regions with different activation energy ($E$) 10 and 72 kJ/mol at higher and lower than -20°C, respectively. It is most interesting to notice that the glass does not exhibit
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The decreased conductivity above 80°C but exhibits the increased conductivity with increasing temperature, reaching ~30 mS/cm at 120°C. Thus, our fast protonic-conducting glass would extend functionality beyond the limitation of perfluorosulfonate ionomers and is expected to have potential for the electrolyte of the fuel cell operating above 100°C. The conductivities above 120°C are not measured at present, the reason why is that the electrode is separated from the sample in the high humid atmosphere and at high temperature. However, no change was observed in the sample itself, suggesting that high conductivities can be measured at higher temperatures by the development of better electrode.

We found in the previous works that the proton conduction favors proton hopping between hydroxyl bonds and water molecules.10,13,14) The activation energy for proton conduction is primarily related to the dissociation of protons from the hydroxyl groups on the pore surfaces. The dissociated protons move to a neighboring water molecule, forming the activated H2O:H+ state. The second stage of the proton hopping is the dissociation of the proton from the activated H2O:H+ state and forming the activated state with the neighboring water molecule. Thus, the protons are hopping between the adsorbed water molecules. In Fig. 1, the activation energy was calculated to be 10 kJ/mol from the slope of the linear relation at 120 to -20°C, which is similar to that for proton conduction in perfluorosulfonate ionomers and liquid water. This low activation energy indicates again that the protons transfer by hopping through the water molecules in the pores. Of further interest in Fig. 1 is that the conductivities are well represented in one Arrhenius equation with the activation energy of 10 kJ/mol at temperature down to -20°C. This result indicates the possibility of glasses used in the fuel cell at low temperature. The freezing temperature of the adsorbed-water was determined to be -20°C from the differential scanning calorimetry trace of the water-absorbed glass, which is much lower than that of bulk water. It is well known that the freezing temperature decreases with decreasing the size, which is recognized as the quantum size effect of the matters.16,17) Our glass has the pores with the average size of 2.5 nm and the motion of water molecules are restricted by the small-sized pores in the cross section, though free in the vertical direction. Thus, the restricted motion of the water confined in the small pores brings the freezing temperature to lower than 0°C.

When the temperature decreased below -20°C, the conductivities deviated from the linear relation to follow to the different Arrhenius equation with the activation energy of 72 kJ/mol. This behavior suggests that the frozen-water molecules exert a different effect on the proton conduction in glass. The proton motion was studied in detail by the 1H NMR spectra. In the previous paper, we discussed the local motion of protons from the relaxation process of the 1H NMR signal, which was related to the proton conduction.10) The spectra are dominated by a peak at ~7 ppm, which are assigned to the protons in the hydroxyl and adsorbed water but not separated into the bands of each protons due to the thermal vibration. In order to obtain more detailed information on the proton interaction between the hydroxyl and the adsorbed water molecules, 1H combined rotation and multiple pulse spectroscopy (CRAMPS) spectra were recorded at 200 MHz with a BR-24 pulse sequence at various temperatures. Figure 2 shows the 1H CRAMPS spectra measured at various temperatures down to -110°C. A signal around 7 ppm exhibits the decreased intensity and the broadened line width as the temperature decreases. Note that the sample cooled at -90°C has the broadened band peaking around 9 ppm with two shoulders in both sides. This spectrum feature has become apparent with decreasing temperature. These broadened spectra were well fitted using three Gaussian bands peaking at ~7, ~9 and ~14 ppm, which are tentatively assigned to the protons of SiOH, water molecules and POH, respectively, from the polarizability of the hydroxyl bonds. These NMR features strongly suggest that no chemical exchange of proton is taken place between the hydroxyl and the adsorbed water molecules at -90°C or below, which results in low conductivity. The activation energy for proton conduction is estimated to be 72 kJ/mol in this water-frozen temperature region. The appar-

Fig. 1. Relationship between electrical conductivity and reciprocal temperature for 5P2O5-95SiO2 glass. The sample was obtained by heating the gel at 600°C for 5 h, then kept in a chamber to absorb an amount of water equal to humid atmosphere at 100% RH.

Fig. 2. 1H CRAMPS spectra, recorded at 200 MHz with a BR-24 pulse sequence at various temperatures, for 5P2O5-95SiO2 glass. Arrows indicate the deconvoluted-peak positions.
A large value of the activation energy indicates the disordered motion between the hydroxyl and the frozen water molecules.

In summary, we have presented protonic conductivities at temperatures of −100 to 120°C of the sol-gel-derived P2O5–SiO2 glasses. The conductivities follow the Arrhenius equation with the activation energy of 10 kJ/mol in the temperature range of −20 to 120°C and no degradation in the conductivity is observed even high temperatures above 100°C. Below −20°C, the adsorbed-water molecules are frozen to increase the activation energy and decrease the proton conductivity. It is concluded that our P2O5–SiO2 glasses, exhibiting high protonic conductivity of ≈30 mS/cm at 120°C, have potential for the electrolyte of the fuel cell operating at high temperatures.

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