Proton conducting tungsten phosphate glass and its application in intermediate temperature fuel cells

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Abstract

High concentrations of proton carriers ($5.0 \times 10^{21} \text{ cm}^{-3}$) were injected into tungsten phosphate glass ($8\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}44\text{PO}_{5/2}$) by electrochemical substitution of sodium ions with protons at 345°C . The electromotive force of a hydrogen concentration cell that used the substituted glass as a solid electrolyte indicated a mixed conduction of protons and electrons in the glass with a mean proton transport number of 0.8 at 300°C . The partial conductivity of the protons was $8.0 \times 10^{-4} \text{ Scm}^{-1}$. The fuel cell generated electricity at a maximum power density of 1.3 mWcm^{-2} , even though its open circuit voltage was only 0.77 V because of the electronic contribution to the conductivity. Methods to increase the proton conductivity for improving fuel cell performance are discussed.

Keywords

Tungsten phosphate glass; Electrochemical substitution; Proton conductor; Intermediate temperature fuel cells;

1. Introduction

Solid electrolytes with high proton conductivity at 250~500 °C are critically needed for intermediate temperature fuel cells (IT-FCs). Such materials have yet to be established, although great effort has been devoted to developing highly conductive solid electrolytes [1-5]. Thus, new approaches are required to fabricate solid electrolytes with high stable concentrations of proton carriers at intermediate temperatures and that exhibit high proton conductivity.

Recently, we developed a new technique to inject protons into oxide glass that essentially substitutes alkali ions with protons [6]. As illustrated schematically in Fig. 1, it involves electrochemical oxidation of hydrogen at the palladium (Pd) anode and successive injection of protons, migration of protons and alkali ions in the glass to the cathode, electrochemical reduction of the alkali ions at the cathode, and successive discharge of the alkali atoms into a molten tin (Sn) cathode. The substitution of alkali ions with protons is performed at 300~500 °C in a hydrogen containing atmosphere, so the protons injected into the glass are stably maintained at these temperatures. Previously, we applied this technique to a $20\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}45\text{PO}_{5/2}$ glass. Very high proton concentrations ($4.3 \times 10^{21} \text{ cm}^{-3}$) were produced, and were stable up to 400 °C. Thus, electrochemical substitution can be used for fabricating proton-conducting solid

electrolytes for IT-FCs, despite the fact that simple annealing of alkali tungsten phosphate glass under a hydrogen atmosphere results in mixed conductors of alkali ions, electrons, and protons [7,8].

In our previous study, glass after electrochemical substitution exhibited considerable electronic conduction that reduced the mean transport number of protons to 0.3. This was because of the formation of W^{5+} by dissolution of hydrogen atoms from the Pd into the glass without transfer of electrons to the external circuit; i.e., the charge compensation pair of H^+/W^{5+} was formed, as described by the following reaction [9,10]:

In the present study, our goal is to increase the transport number of the protons. For this purpose, we changed the glass composition from $20WO_3$ - $35NaO_{1/2}$ - $45PO_{5/2}$ to $8WO_3$ - $35NaO_{1/2}$ - $8NbO_{5/2}$ - $5LaO_{3/2}$ - $44PO_{1/2}$. Although WO_3 -free glass is preferred to reduce electronic conductivity, we left a portion of WO_3 and added $NbO_{5/2}$ and $LaO_{3/2}$ in order to maintain a glass transition temperature $>450^\circ C$. We successfully increased the proton mean transport number of the glass after the electrochemical substitution, and demonstrated fuel cell operation at $300^\circ C$ using the glass as a solid electrolyte.

2. Experimental

2.1 Glass preparation

For comparison, sodium tungsten phosphate glasses with nominal compositions (cation mol%) of $8\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}44\text{PO}_{5/2}$ (8W-glass) and $20\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}45\text{PO}_{5/2}$ (20W-glass) were prepared by melt quenching. Mixtures of Na_2CO_3 , WO_3 , Nb_2O_5 , La_2O_3 and H_3PO_4 were melted in a platinum crucible at $1400\text{ }^\circ\text{C}$ for 45 minutes in air. The molten materials were poured into a carbon mold, annealed at $500\text{ }^\circ\text{C}$ for 30 minutes, and then cooled to room temperature at a slow rate of $20\text{ }^\circ\text{C h}^{-1}$. The resulting cylindrical glass blocks were cut into 1-mm-thick plates that were polished on both surfaces. The glass transition temperature was $466\text{ }^\circ\text{C}$, as determined by differential thermal analysis (SII, TG/DTA6300).

2.2 Electrochemical substitution of sodium ions with protons

Electrochemical substitution was carried out using the experimental apparatus (Kenix Corp. KDK-800) depicted in Fig. 2. A Pd thin film was deposited by magnetron sputtering on one surface of a glass plate that was then loaded on the holder with the Pd film facing up. The other glass face was in contact with molten Sn heated to $345\text{ }^\circ\text{C}$ in a 5% H_2 –95% N_2 atmosphere. A 5.0 V DC bias was applied between the Pd-anode and the molten Sn-cathode, and the electrochemical substitution was performed for 10 h. In

order to monitor its progress, current flowing through the external circuit was recorded.

The concentrations of sodium ions and protons that form OH groups in the glass were respectively determined from energy-dispersive X-ray (EDX) spectroscopy (EDAX, CDU-S; on a JEOL JSM-5600 scanning electron microscope) and Fourier transform infrared spectroscopy (FT-IR, JASCO FT-IR610 spectrometer) for the O-H stretching vibration (ν_{OH}). The OH, *i.e.*, proton, concentration (C_{OH} in cm^{-3}) was calculated from the maximum absorption intensity $\alpha(\nu_{OH})$ of ν_{OH} , using: [11]

$$C_{OH} = 1.03 \times 10^{19} \times \alpha(\nu_{OH}) \quad (2).$$

The concentration of W^{5+} in the glass was determined with Vis-NIR absorption spectra (Hitachi U-4100 spectrophotometer), by using the optical absorption cross section $2.1 \times 10^{-18} \text{ cm}^2$ per W^{5+} ion, at 1300 nm, determined by Tawarayama *et al.* [9].

2.3 Electrical conductivity and fuel cell tests

After electrochemical substitution, both surfaces of the glass plates were polished again and Pd-film electrodes were deposited. Electrical conductivity was determined from the impedance spectrum recorded with an impedance analyzer (HP4192A) in a 5% H_2 –95% N_2 atmosphere. The mean transport number of protons was obtained from the electromotive force (emf) of the hydrogen concentration cell, denoted by gas (I),

Pd|glass|Pd, gas (II). Gas (I) was fixed at 5% H₂–95% N₂, and gas (II) was a mixture of hydrogen and nitrogen with various hydrogen concentrations in the range 0.6 –5%. The partial pressure of water in both gases (I) and (II) was fixed at 1.7×10^3 Pa by bubbling the gases through 15 °C water.

Fuel cell tests for 0.45-mm thick, substituted 8W-glass were performed at 300 °C. Pd electrodes were deposited on both surfaces of the glass, and 5% H₂–95% N₂ and air (21% O₂–79% N₂) were respectively supplied to the anodes and cathodes at a flow rate of 50 mLmin⁻¹. Both gases were humidified by bubbling through 15 °C water.

3. Results and Discussion

3.1 Electrochemical substitution of sodium ions with protons

Progress of the electrochemical substitution in the 8W-glass was monitored by the current flowing through the external circuit, and by sodium carbonate deposition on the surface of the Sn cathode, which indicates external discharge of sodium ions from the glass. EDX analysis indicated that the sodium concentration in the glass following the substitution was reduced by a factor of 1/23 relative to the initial glass. The EDX spectra also indicated that X-ray intensities for other elements did not change after electrochemical substitution.

FT-IR spectra in the ν_{OH} region for the glasses before and after electrochemical substitution are shown in Fig. 3 (a). The ν_{OH} absorption coefficient after the substitution was 75 times higher than that in the glass before substitution. From this data, C_{OH} in the glass after the treatment was determined to be $5.0 \times 10^{21} \text{ cm}^{-3}$, while it was $6.6 \times 10^{19} \text{ cm}^{-3}$ before the processing. Therefore, we conclude that approximately all sodium ions in the 8W-glass ($9.1 \times 10^{21} \text{ cm}^{-3}$) were substituted with protons during the electrochemical substitution taking that the intense ν_{OH} absorption in the glass after substitution was close to the detection limit of the spectrometer into account. The glass after electrochemical substitution was stable in the atmosphere and no hygroscopicity was observed.

The glass after the electrochemical substitution was black because some of the W^{6+} ions were reduced to W^{5+} ions that have a $d-d$ electronic transition [12] in the visible region as shown in Fig. 3 (b). The concentration of W^{5+} ions in the 8W-glass after substitution was calculated to be $5.4 \times 10^{19} \text{ cm}^{-3}$, while that of the 20W-glass was $2.3 \times 10^{20} \text{ cm}^{-3}$. In addition, the concentration of W^{5+} ions that supplies the electron carriers decreased by one-quarter because of the reduction of the WO_3 concentration in the glass from 20 to 8 %.

3.2 Electrical conductivity and fuel cell tests

Figure 4 (a) shows the emfs of the hydrogen concentration cell at 300 °C using the substituted 8W-glass as a solid electrolyte as a function of the log of the hydrogen concentration $P(\text{H}_2)$ ratio for gases (I) and (II). As expected, the emfs increased with increasing $P(\text{H}_2)$ ratio; although the values were slightly smaller than the theoretical values obtained from the Nernst equation. The mean transport number of the protons was calculated to be 0.8, which is almost threefold greater than that for the 20W-glass and twofold greater than that for the $10\text{WO}_3\text{-}33\text{NaO}_{1/2}\text{-}10\text{BaO}\text{-}20\text{NbO}_{5/2}\text{-}27\text{PO}_{5/2}$ glass [6, 13]. According to the Vis-NIR absorption spectra (Fig. 3 (b)), the concentration of W^{5+} ions in the 8W-glass was reduced to one-quarter of that in the 20W-glass. The increasing transport number of the protons is attributed to the decreasing electronic carrier concentration caused by the reduced WO_3 concentration in the 8W-glass. However, the 8-mol% WO_3 concentration was not sufficiently low enough to eliminate electronic conduction. The reduced WO_3 concentration lowers the glass transition temperature and thus decreases the thermal stability of the glass. Thus designing a glass composition that has both a low WO_3 concentration and a high thermal stability is a key challenge in the fabrication of a pure proton conductor applicable to IT-FCs.

Figure 4 (b) is an Arrhenius plot of the partial conductivities of protons in the

8W-glass after electrochemical substitution. They were calculated from the total conductivity, assuming that the mean transport number of the protons is 0.8 and is not temperature-dependent over this range. The proton conductivity was $8.0 \times 10^{-4} \text{ Scm}^{-1}$ at 300 °C, which was 3–4 times larger than that of the substituted 20W-glass [6]; however, the conductivity is at least an order of magnitude smaller than the value applicable to the thick solid electrolyte in the fuel cell system. The proton-conducting glass fabricated by substitution already contains a proton carrier density $>5 \times 10^{21} \text{ cm}^{-3}$ that cannot be increased significantly. Based on the Arrhenius plot, the proton conductivity of the 8W-glass can be extrapolated to $\sim 1 \times 10^{-2} \text{ Scm}^{-1}$ at 400 °C. This indicates that the concentration and the mobility of proton carriers are sufficiently high for use as an electrolyte in an IT-FC operating at temperatures >400 °C, if the glass is stable at those temperatures. Therefore, increasing the thermal stability of the glass is a viable approach to achieve proton conductivity $>1 \times 10^{-2} \text{ Scm}^{-1}$, and is a key goal in the future.

According to previous work [14], the activation energy of proton conduction in glass can be evaluated by the concentration and strength of hydrogen bonding. For the substituted glass here, it was calculated to be 0.91~0.95 eV, which is close to the observed activation energy of 0.76 eV based on the Arrhenius plot of $\ln(\sigma T)$. This suggests that proton conduction in the substituted glass can be described by a hopping

mechanism that was applied to previous glasses having much lower proton concentrations of $4 \times 10^{19} \sim 3 \times 10^{20} \text{ cm}^{-3}$.

Figure 5 plots the I-V and the power density curves of the fuel cell operated at 300 °C that used the substituted 8W-glass as a solid electrolyte. The data indicates that the fuel cell worked successfully and generated significant power. The open circuit voltage was only 0.77 V because of the electronic contribution to the conductivity. The maximum power density was 1.3 mWcm^{-2} , which is not sufficient for practical use. The configuration of our test fuel cell was of course primitive in point of that dense Pd cathode with 0.2 μm of thickness was used. Since we did not observe obvious peeling off the Pd cathode film from the electrolyte caused by water vapor formation at the interface between the electrolyte and cathode, the water vapor formation suggested to be occurred at the surface of cathode; however, the details were not clear at the present. Also, the Pd is not suitable as a cathode because it is easy to oxidize in air at high temperatures, although obvious palladium oxide formation was not detected in the present condition. Therefore, to improve the fuel cell performance, suitable electrode materials must be developed in addition to increasing the proton conductivity and transport number of the glass electrolyte.

4. Conclusions

We fabricated proton-conducting oxide glass at intermediate temperatures by using electrochemical substitution of sodium ions with protons. The proton carrier was injected with a high density of $5.0 \times 10^{21} \text{ cm}^{-3}$ into $8\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}8\text{NbO}_{5/2}\text{-}5\text{LaO}_{3/2}\text{-}44\text{PO}_{5/2}$ glass at 345°C . The resulting proton conductivity was $8.0 \times 10^{-4} \text{ Scm}^{-1}$ at 300°C , although the electron conductivity was $2.0 \times 10^{-4} \text{ Scm}^{-1}$ due to W^{5+} formation during electrochemical substitution. The 0.8 of mean transport number for the protons was significantly higher than that (0.3) observed for electrochemically proton-injected $20\text{WO}_3\text{-}35\text{NaO}_{1/2}\text{-}45\text{PO}_{5/2}$ glass. The reduced WO_3 concentration in the glass effectively reduced the electronic contribution to the conductivity, and fabrication of a pure proton conductor is expected to have a further reduction in the WO_3 concentration.

The fuel cell successfully generated electricity at 300°C with a maximum power density of 1.3 mWcm^{-2} . The results indicate that electrochemical substitution of alkali ions with protons in glass is a promising way to fabricate proton conductors for IT-FCs.

Acknowledgement

This work was supported in part by the Advanced Low Carbon Technology Research

and Developing Program of Japan Science and Technology Agency (JST-ALCA).

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Figure captions

Fig. 1. Schematic of electrochemical substitution of sodium ions with protons.

Fig. 2. Schematic of apparatus for electrochemical substitution. 1: Gas inlet, 2: Thermocouple, 3: Gas outlet, 4: Contact electrode, 5: Thin-film Pd anode on the glass sample, 6: Glass sample, 7: Glass sample holder made of SiO₂-glass, 8: Tungsten lead wire, 9: Molten Sn cathode, 10: SiO₂-glass pan, and 11: SiO₂-glass tube.

Fig. 3. (a) FT-IR spectra in the ν_{OH} absorption region of the 8W-glass before (blue dashed line, magnified 30 times) and after (red solid line) electrochemical substitution. (b) Optical absorption spectra from the visible to the near infrared of the 8W-glass before (blue dashed line) and after (red solid line) electrochemical substitution, together with the spectrum of the 20W-glass after electrochemical substitution (black line).

Fig. 4. Electrical properties of 8W-glass after electrochemical substitution. (a) Emfs of the hydrogen concentration cell at 300 °C as a function of the log of the $P(H_2)$ ratio in gases (I) and (II), using the substituted 8W-glass as a solid electrolyte. The slopes of theoretical emfs for the pure proton conductor are indicated. (b) Arrhenius plot of the

partial proton conductivity in the 8W-glass after electrochemical substitution, assuming that the mean transport number of the protons is 0.8 and is constant over the temperature region. The dashed line is an extrapolation of the conductivity, assuming that activation energy is the same as that for temperatures $< 300\text{ }^{\circ}\text{C}$.

Fig. 5. I-V and power density curves for the fuel cell, 5% H_2 –95% N_2 , Pd|electrolyte|Pd, 21% O_2 –79% N_2 , operated at $300\text{ }^{\circ}\text{C}$. The electrolyte was the 8W-glass after electrochemical substitution. The inset is a schematic of the fuel cell configuration.

Figure(s)-fig1

Figure(s)-fig2

Figure(s)-fig3 a,b

Figure(s)-fig4 a,b

Figure(s)-fig5