



Full length article

Dense proton injection into phosphate glasses using corona discharge treatment



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ARTICLE INFO

Article history:

Received 7 May 2017

Received in revised form 27 August 2017

Accepted 21 September 2017

Available online 23 September 2017

Keywords:

Proton conduction

Ion exchange

DC voltage

Fuel cell

Hydrogen

ABSTRACT

Sodium ions in 25NaO_{1/2}-6LaO_{3/2}-6GeO₂-63PO_{5/2} (mol%) glasses were substituted with protons using corona discharge treatment (CDT) under a H₂ atmosphere. The substitution of sodium ion to proton proceeded from the anode side to the cathode side with constant current flow during the CDT. A crystalline free and transparent glass plate of 0.3 mm thickness was obtained after CDT for 96 h. The maximum decrease rate from sodium ion to proton was 78 ± 10%. The proton conductivity of 8.5 × 10⁻⁴ S/cm was attained at 400 °C.

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1. Introduction

Oxide materials containing dense mobile protons are anticipated for use as a thermally and chemically durable proton conductor. For example, proton conductivity higher than 10⁻³ S/cm with low activation energy (0.1–0.25 eV) has been reported in several phosphate glasses containing H₂O molecules [1,2]. Solid acids such as CsHSO₄ and CsH₂PO₄ are also studied extensively as proton conductors [3–5]. A distinctive characteristic of these materials is the strong hydrogen bonding between OH function and next neighbor oxygen. However, the upper temperature limit to maintain the conductivity of these oxides was approximately 200 °C because of desorption of H⁺ from the matrix. By contrast, the aluminosilicate thin films synthesized using sol-gel processes were examined as host materials of thermally durable proton conductor [6]. The proton is located near four-fold coordinated Al³⁺ as a charge compensator. Actually, H⁺ remains in the matrix even if the film is heated to temperatures higher than 400 °C. However, the proton

conductivity was limited to less than 10⁻³ S/cm⁻¹ because of the low concentration of H⁺ and weak hydrogen bonding between OH functions and next-neighbor oxygens.

On the other hand, the alkali ions contained in oxide glasses can be substituted to protons using the corona discharge treatment (CDT) [7–9]. Corona is a non-disruptive electrical discharge created at the anode needle tip under application of high DC voltage. We recently reported that CDT can be used to form a substitution layer on the anode side of a soda-lime silicate glass [7]. The concentration of OH groups in the alkali deficient layer is balanced with the amount of the excluded Na⁺. Furthermore, the H₂ atmosphere is effective to accelerate the substituted layer formation [8]. However, it was impossible to increase the substitution layer thickness to more than 15 μm because the H⁺ mobility of in the soda-lime silicate glass was three orders of magnitude lower than that of Na⁺ [10].

This study was conducted to pass the substitution layer of Na⁺ to H⁺ completely from the anode side to the cathode side of the oxide glass using CDT. The base glass system used for this study was LaO_{3/2}-PO_{5/2}, which has been reported as a host candidate for the optical fiber amplifier [11]. The proton conductivity in phosphate glasses is generally higher than that in silicate glasses because

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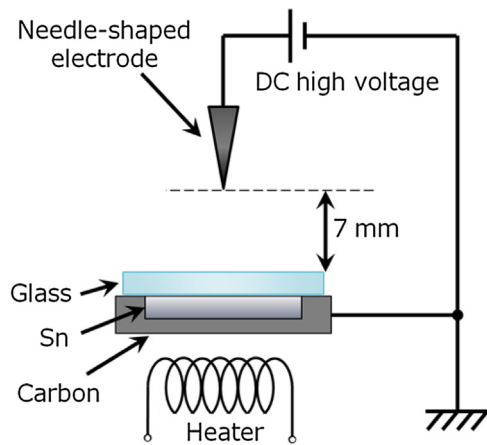


Fig. 1. Experimental setup of CDT.

hydrogen bonded protons are much more mobile in the matrix than those localized as the free OH function [2,12,13]. Recently, the substitution method of H^+ for Na^+ in phosphate glasses was reported using the Pd thin film catalyst as the anode side contact electrode, which is designated as APS [14–19]. Non-contact and Pd free are notable benefits of the CDT, which is expected to be used for dense proton injection to phosphate thin glass films.

2. Experimental

Glass composition that is stable against the CDT was investigated based on the quaternary system of $NaO_{1/2}-LaO_{3/2}-GeO_2-PO_{5/2}$, in which the Na^+ is necessary for substitution to H^+ . The addition of GeO_2 was indispensable to inhibit surface crystallization of the glass during the substitution of Na^+ to H^+ [19]. Glasses were fabricated using a conventional melt-quenching method with raw reagents of Na_2CO_3 , La_2O_3 , GeO_2 , and H_3PO_4 . The mixed reagents were melted in a platinum crucible for 2 h at $1350^\circ C$ in air; then they were poured into a cylindrical carbon mold of 10 mm diameter. After annealing from the glass transition temperature (T_g) to $25^\circ C$, the glass rod was cut and polished to 10 mm diameter and 0.3 mm thickness. The T_g and the deformation temperature (A_t) were estimated using thermomechanical analysis (TMA/SS–6000; Seiko Instruments Inc.) under applied weight of 20 mN/mm^2 .

The CDT was performed in H_2 atmosphere. Fig. 1 presents the experimental setup of CDT. The glass plate was placed on the grounded carbon cathode. The molded tin was placed between the glass and the carbon to absorb the discharged Na. The DC voltage of 4.0–4.5 kV was applied with an increasing rate of 1 kV/min to the anode of Pt coated steel needle using a DC voltage supplier (AKTB–010K1PN/S; Touwakeisoku Co. Ltd.). The end point of the needle was located 6 mm above the glass surface. The current flow in the circuit during CDT was monitored using a data logger (midi Logger GL220; Graphtec Corp.).

The glass composition before and after CDT was analyzed using an energy dispersive X-ray spectrometer (EDS; JED–2300, JEOL Ltd.). The measurement area was $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ square in the control software of JED–2300. The Na concentration, [Na], was estimated by its integrated $NaK\alpha$ peak intensity, which was normalized by the $GeL\alpha$ peak. The OH concentration [OH] in the glass was estimated by absorbance of the O–H stretching vibration using a Fourier transform infrared spectrometer (FT-IR, Affinity-1; Shimadzu Corp.). Before measurements, the specimen surfaces after CDT were polished evenly from both surfaces to a thin plate less than $50\text{ }\mu\text{m}$ thickness, which was required to obtain an unsaturated OH absorption peak. The [OH] was calculated from the maximum

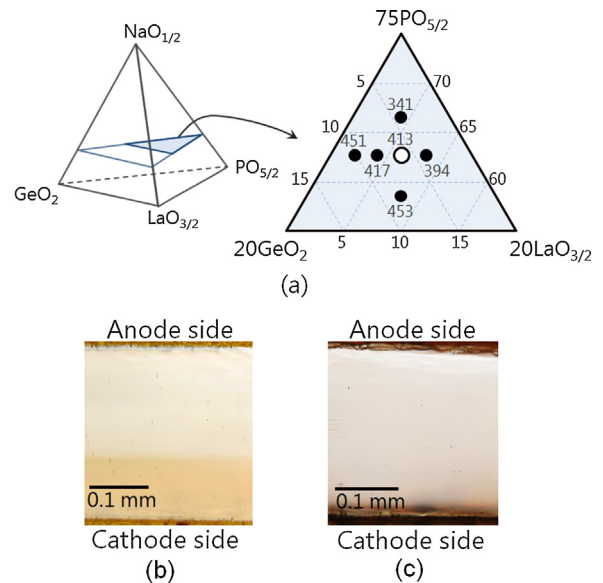


Fig. 2. (a) Glass compositions investigated in this study, in which the stable composition against crystallization during CDT is denoted by open circle. (b) and (c) are cross sections of glasses after CDT for 8 h and 48 h at $370^\circ C$, 4.5 kV in H_2 atmosphere. The distance between the glass and anode needle tip is 6 mm. The number in (a) is T_g of each glass. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

absorption intensity (α) at 2800 cm^{-1} using the following equation: $[OH] = 1.03 \times 10^{19} \times \alpha$ [20]. The structural change of the glass network before and after CDT was investigated using a Raman spectrometer (in Via Reflex; Renishaw Plc.). The precipitated crystals during CDT and the heat treatment were analyzed using an X-ray diffractometer (Smart Lab; Rigaku Corp.). The weight loss during heating ($5^\circ C/h$) in a N_2 atmosphere using a thermogravimetry-differential thermal analysis (TG-DTA) (EVO2; Rigaku Corp.).

The electrical conductivity was measured using an impedance analyzer (HP4192A; Hewlett Packard Co.) under 5% H_2 and 95% N_2 with a 20 cc/min flow rate and a constant heating rate of $5^\circ C/h$. Before the measurement, the Pd film of 500 nm thickness was deposited on both sides of the polished specimen of 0.2 mm thickness using rf-sputtering deposition (RSP-4-RF5 \times 2; Cryovac Corp.). The DC polarization characteristics were measured using a DC voltage application. The mean transport number of the protons was obtained from the electromotive force (emf) measured by the hydrogen concentration cell, where the anode side was 100% H_2 and the cathode side was a mixture of H_2/N_2 with H_2 concentration between 100 vol.% - 4.0 vol.%.

3. Results and discussion

3.1. (1) glass composition and CDT condition

Fig. 2(a) shows the as-melted glass compositions examined for CDT. The T_g of these glasses are shown in the figure. When the CDT temperature was higher than $400^\circ C$, the anode side surface was crystallized, as confirmed from microscope observations and X-ray diffraction. The CDT below $340^\circ C$ generated the small cracks on the anode side surface. Therefore, the onset temperature of CDT was found at $370^\circ C$. The most stable glass composition against crystallization after CDT was $25NaO_{1/2}-6LaO_{3/2}-6GeO_2-63PO_{5/2}$ (mol%, abbreviated as LGP-0), which is indicated by the solid circle in the figure. Fig. 2(b) shows the cross section of the LGP glass after CDT for 8 h. A color change was found in the middle of the cross section, which is the boundary of substituted and unsubstituted regions. Such a boundary can be recognized by the refractive index

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