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Electrical and mechanical properties of $Na_{2.8}Ca_{0.1}Al_2Ga_{0.5}P_{2.7}O_{12}$ glass based electrolyte materials: Influence of Ag^+ ion-exchange

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ABSTRACT

Sodium super ionic conductor (NASICON) based glass is emerging as solid electrolyte material for Na-ion batteries. In the present study, we report the influence of $Ag^+ \rightarrow Na^+$ ion-exchange process on the electrical, optical, structural and mechanical properties of NASICON type glass with a chemical formula of $Na_{2.8}Ca_{0.1}Al_2Ga_{0.5}P_{2.7}O_{12}$ (NCAGP). Ag^+ ion exchange process was carried out by dipping NCAGP glass in $AgNO_3$ molten salt at 300 °C for 15 min (IE15min) and 30 min (IE30min). The diffusion depth of Ag^+ ions was measured to be about ~7 μm and ~25 μm for IE15min and IE30min samples, respectively. The dc conductivity values were obtained from base (NCAGP), IE15min and IE30min bulk glass samples through the complex impedance plots at a temperature range of 75 °C–200 °C. With the increase in ion-exchange time, the dc conductivity slightly diminished on account of marginally increase in activation energy (E_a) values. Optical absorption spectra for 30 min ion-exchanged glass revealed the localized surface plasmon resonance (LSPR) band, confirming the reduction of Ag^+ ion to Ag^0 metal with an increase in ion-exchange time from 15 min to 30 min. Presence of Raman vibrational peak at 233 cm^{-1} has also confirmed the formation of Ag—O bonds. The mechanical hardness values obtained through Vickers indentation method reveal enhanced hardness and crack resistance of bulk glasses with the ion-exchange treatment by causing compressive stress on the surface of NCAGP glass. The threshold load for the crack generation is increased from 0.5 kgf (4.9 N) to 2 kgf (19.6 N) after the ion-exchange treatment. Overall, improved mechanical and good electrical properties reveal the applicability of IE15min NCAGP glass as an electrolyte material for Na-ion batteries.

1. Introduction

Sodium in comparison with lithium is economical and relatively abundant. Therefore, the research and development on Na-ion batteries, which are deemed as an alternative to the Li-ion batteries, and gathering momentum in recent years [1]. In the development of Na-ion batteries, a critical challenge lies in identifying a highly suitable and efficient electrolyte material. Among the various types of commercially available electrolyte materials like organic polymer, solid- and gel-polymer electrolytes, solid-type electrolyte material is considered ideal in view of energy efficiency and safety issues [1,2]. In addition, the mechanical stability plays a key role in the process of developing a solid electrolyte material because the active electrode materials expand and contract while charging and discharging of battery [3]. Any change in volume may create cracks, which are responsible for the improper functioning of solid electrolyte material [4,5]. The good processability and low elastic moduli of solid electrolyte materials define the capacity of batteries; therefore, the above-mentioned aspects should be considered in developing solid based electrolyte materials.

Sodium super ion conductor (NASICON) based phosphate glasses, with better processability and suitable ionic conductivity (2.2×10^{-6} $S{\cdot}cm^{-1}$ at 423 K), are regarded as suitable solid electrolyte materials [6]. Nevertheless, high elastic moduli (~50 GPa) of phosphate glasses limit its usage in the commercial application [4,7]. It should be highlighted that various techniques to strengthen glass have been employed over the last few decades, which include thermal treatment, chemical treatment and crystallization process [8]. In general, cracks in bulk materials may be due to stress created on the surface [9]. It is known that in ion-exchange chemical treatment, cations on the surface of the material are exchanged with the cations available in the molten salt, generating compressive stress on the thin surface layer and enhancing the fracture toughness of brittle material [8,10]. It has been further described that ion-exchange chemical treatment, has the potential to produce new materials with high ion conductivity, an essential parameter for electrolyte materials [11]. Therefore, mechanically and electrically improved NASICON based phosphate glasses can

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be generated through the ion-exchange process and thereby utilized in Na-ion batteries as electrolyte materials. However, producing glass materials with high ionic conductivity with improved mechanical properties after the implementation of the ion - exchange process still remains a challenge.

\In view of the above, an effort has been made to study the influence of ion-exchange process on the mechanical and electrical properties of Ga_2O_3 contain (mol.%) $34.1Na_2O$-$2.5CaO$-$24.3Al_2O_3$–$6.1Ga_2O_3$–$33.0P_2O_5$ (designed from Sodium superionic conductor (NASICON) based $Na_{2.8}Ca_{0.1}Al_2P_{2.7}Ga_{0.5}O_{12}$ chemical formula) phosphate glasses. The ion-exchange process was performed after immersing the glass material in $AgNO_3$ molten salt at 300 °C for 15 min and 30 min. The electron microscopic technique was utilized to identify the presence and distribution of Ag^+-ion in the ion-exchange surface area. In addition, the structural modifications with the ion-exchange process have been elucidated using micro-Raman spectroscopy. The electrical conductivity and mechanical hardness of the base glass and its influence on the ion exchange process were systematically investigated in the present work.

2. Experimental

2.1. Material preparation

The bulk glass having new chemical composition was prepared by melt quenching technique using high purity powder chemicals $(NH_4)H_2PO_4$, Na_2CO_3, $CaCO_3$, Al_2O_3, and Ga_2O_3. Homogeneous mixture of batch, obtained by hand grinding in agate motor, was preheated in an alumina crucible for decarbonisation using the following heat treatment schedule: (i) RT to 350 °C at a heating rate (β) of $1\,K\,min^{-1}$followed by a dwell at 350 °C for 6 h; (ii) from 350 °C to 600 °C at $\beta = 1\,K\,min^{-1}$ followed by a dwell at 600 °C for 3 h and (iii) from 600 °C to 900 °C at $\beta = 4\,K\,min^{-1}$ followed by a dwell at 900 °C for 1 h. The decarbonized batch mixture was first melted in alumina crucible and then re-melted again in Pt-crucible for better homogeneity at 1350 °C for 2 h, in air atmosphere with intermediate stirring using thin platinum rod. Glass in bulk form was obtained by quenching of melt onto a pre-heated (400 °C) stainless-steel mould followed by annealing at temperatures around the glass transition temperature 350 °C [6].

For Ag^+ ion exchange process samples were cut into 6 × 6 mm square with the thickness of 6 mm and polished to an optical grade quality. The glass samples were immersed in molten salt of $AgNO_3$, kept in an alumina crucible inside a box type muffle furnace, at 300 °C (well below the glass transformation temperature ~350 °C) for 15 min and 30 min. After the prescribed time (15 min and 30 min), the ion exchanges glasses were taken out and washed several times under normal tap water followed by lukewarm water and ultra-sonication for 5 min in distilled water. The ion-exchanged glasses hereafter described with “IE15min” indicate 15 min of the ion-exchange time and “IE30min” indicates 30 min of ion-exchange time at 300 °C. The $6 \times 6 \times 6\,mm^3$ samples were used for optical, spectroscopic, and mechanical studies.

2.2. Material characterization

For AC conductivity measurements, as per instrument requirement glass samples were uniformly cut to 8 × 8 mm square with the thickness of 1.5 mm and polished to optical grade quality. The ion - exchange process was also followed for this dimension glass samples as mentioned earlier. All three glass samples namely Base glass (NCAGP), IE15min and IE30min were then hand coated with high conductivity (volume resistivity = 0.0174 Ω·cm) silver paint (CAT. No. 8331-14G) procured from MG Chemicals Ltd., Canada. The silver coated glass samples were cured overnight at RT in the air atmosphere. The conductivity measurements were carried out in the frequency range 55 Hz to 1 MHz with 3 V rms using LCR Hi Tester (Model HIOKI-3532-50, Japan). Two-probe setup with test leads connected to a Test Fixture HIOKI-9262 was used to acquire the data. The real-time data was acquired through HIOKI LCR sample program version 4.03E software by HIOKI, Japan. The temperature-dependent frequency characteristics of the glass samples were measured from room temperature to 200 °C with 25 °C interval using dry high-temperature calibrator (model: DPI-1200, supplied by local vendor) with the temperature accuracy of ± 1 °C. The DC conductivity (σ_{dc}) of the samples was measured from the estimated values of bulk resistance of the samples derived from impedance plots.

Raman spectra for bulk glass samples were obtained using a Horiba LabRam HR 800 Evolution confocal Raman microscope, with a 478 nm argon ion laser source (10 mW) focused with a 100× objective lens having the spot size of $\sim 3.14\,\mu m^2$ on to the surface of glass samples. The collected Raman radiation was dispersed with a $600\,lines{\cdot}mm^{-1}$ grating and focused on a Peltier-cooled charge-coupled device (CCD) detector allowing a spectral resolution of $2\,cm^{-1}$. The instrument was calibrated with intense Raman signal for crystalline silicon at $520.7\,cm^{-1}$. All spectra were recorded in the range $100–1500\,cm^{-1}$ with an integration time of 5 s and 20 accumulations per spectrum.

Optical absorption, transmission and reflection spectra of the base glass and ion exchanges glasses were recorded at room temperature in the wavelength region of 200–850 nm (slit width of 2 nm) using UV–VIS-NIR absorption spectrophotometer (Model: UV-3101PC, Shimadzu, Japan). Baseline has been corrected with respect to air by placing standard external slits in the reference and sample beam paths constant while recording absorption and transmission of spectra in case of specular reflection; moreover, highly reflecting mirror supplier along with the instrument was used at the reference side.

Ag^+ ion diffusion studies were carried out through line profile analysis by (EDS) Energy Dispersive X-ray spectroscopy using Oxford instrument (Model: INCA-250, UK equipped with SDD $50\,mm^2$ detector) attached with FE-SEM instrument (Model: SIGMA, Carlzeiss, Germany). For EDS analysis, the ion-exchanged IE15min and IE30min 6 × 6 × 6 mm square samples were cut in to half and polished to optical grade quality and etched with HF on the cross-section side.

Mechanical properties of the glass samples were obtained using Vikers indentation test method in a microhardness tester model, MMT-X7 made by Clemex CMT, Canada under different loads starting from 0.1 kgf (0.98 N) to 2.0 kgf (19.6 N). The surface texture of the base glass, IE15min, and IE30min glass samples were taken with an optical microscope model, BX51 made by Olympus, Japan under 100× objective lens.

3. Results and discussion

3.1. Impedance, EDS and optical spectral analysis

The AC conductivity studies of all the three glass samples i.e., base glass, IE15min, and IE30min were measured over 55 Hz to 1 MHz frequency range at different temperatures with the interval of 25 °C starting from 75 °C up to 200 °C. The complex impedance plots (cole-cole plot), which represent real impedance (Z′) versus imaginary impedance (Z″) in a semi-circle plot, were utilized to determine the bulk resistance, R, which is equal to Z′ when Z″ = 0 at lower frequency region, for all the samples in the specified temperature range. Fig. 1 shows such cole-cole plot for all the three glass samples at 100 °C. The diameter of semi-circle increased in case of “IE15min” and “IE3 0 min” glass samples indicating the enhanced bulk resistance of the glass after the ion-exchange treatment. The bulk resistance was then used to calculate the dc conductivity, σ_{dc}, of the samples using the relation $\sigma_{dc} = (t/(R \times A))$, where t = thickness of the sample, R is the bulk resistance and A is the applied electrode area of the cross-section.

Fig. 2 (a-e) shows the measured dc conductivity of the base and the ion-exchanged glasses at different temperatures. It is interesting to note that the difference in dc conductivity between the base glass and the ion-exchanged glasses gradually increases with increasing temperature (a considerable difference can be seen at temperature ≥150 °C) might