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Short Communication

Ionic transport and battery characterization studies on NaI–Na_2O–B_2O_3 ternary glassy system

Md. Jamal, Md. Shareefuddin, M. Narasimha Chary

Department of Physics, Osmania University, Hyderabad 500 007, India

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Abstract

Glasses in the ternary system xNaI–$y$$Na_2O$–$[100-(x+y)]B_2O_3$ prepared by a melt quenching method are characterized by using different experimental techniques such as X-ray diffraction, ionic transference number and conductivity. The conductivity is found to vary in a non-linear manner with change in the NaI/Na_2O ratio. The highest conductivity glass composition is used as an electrolyte in the fabrication of a solid-state electrochemical cell. A decomposition potential of 2.5 V is determined for the electrolyte. The discharge characteristics of the cell are investigated at ambient temperature and various cell parameters are determined. The open-circuit voltage and short-circuit current of the cell are 2.7 V and 1600 μA, respectively.

Keywords: Glass electrolytes; Electrochemical cells; Open-circuit voltage; Short-circuit current

1. Introduction

Solid-state batteries [1–3] have been investigated for many years because of their advantages in terms of operation over a wide temperature range, rugged structure, and long storage life. For most microelectronic circuits with power requirements of only a few milliwatts, it is necessary to opt for miniaturized solid-state batteries. Superionic glasses are of technological interest because of their application to micro-batteries [4–6]. Besides having high ionic conductivities, the glass electrolytes have several advantages such as isotropic properties, absence of grain boundaries, ease of preparation and greater stability to moisture and iodine diffusion. In particular, alkali-ion conducting glasses are used mostly as solid electrolytes [7–11]. Apart from scientific interest, sodium-based battery systems have advantages over their lithium counterparts. Sodium is much more abundant and lower priced than lithium. Moreover, it forms no alloy with aluminium and this metal can therefore be used for current collectors instead of the more expensive and heavier nickel.

In the present paper, studies are reported on the sodium-ion conducting glass system: xNaI–$y$$Na_2O$–$[100-(x+y)]B_2O_3$. The influence of variation of doping salt (NaI) and glass modifier (Na_2O) on the transport properties are discussed. A solid-state cell is fabricated with the highest conducting glass composition (10NaI–10Na_2O–80B_2O_3) as the solid electrolyte and its discharge characteristics are investigated at room temperature.

2. Experimental

Glasses with the composition (mol%) xNaI–$y$$Na_2O$–$[100-(x+y)]B_2O_3$ were prepared by a melt quenching method. Stoichiometric quantities of the starting materials, namely, sodium iodide, sodium carbonate and boric acid (analar grade), were weighed to get 5 g of the required composition, and then mixed and ground to obtain homogeneous mixtures. These mixtures were melted at 900–950 °C in a platinum crucible for 30 min. The homogeneous melt was quenched rapidly on to a pre-heated stainless-steel plate that was maintained at a temperature of 373 K. The glasses were annealed at this temperature for 24 h to relieve the mechanical stresses. The glasses so obtained are colourless and transparent. The glass compositions are given in Table 1. All the glass samples were characterized by X-ray diffractometry, using a Philips X-ray diffractometer (Model PW

Table 1
Activation energies of different glasses

Glass	Composition	Activation energy (eV)	σ_{RT} $(\Omega\ cm)^{-1}$	t_{ion}
G1	8NaI–12Na_2O–80B_2O_3	0.79	5.33×10^{-9}	0.92
G2	10NaI–10Na_2O–80B_2O_3	0.68	5.20×10^{-5}	0.95
G3	12NaI–8Na_2O–80B_2O_3	0.72	1.26×10^{-6}	0.93
G4	14NaI–6Na_2O–80B_2O_3	0.74	5.76×10^{-6}	0.92
G5	15NaI–5Na_2O–80B_2O_3	0.63	4.32×10^{-5}	0.95

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1710). The ionic transference number was determined by the polarization technique. The ionic conductivity measurements were performed on glass samples using the experimental technique described elsewhere [12].

With $10NaI–10Na_2O–80B_2O_3$ as the solid electrolyte, a solid-state cell was fabricated in the configuration Na/electrolyte/(I_2+C+electrolyte). Metallic sodium was used as the negative electrode [8]. The anode was made by mixing iodine, graphite and electrolyte in the ratio 5:5:1. The discharge characteristics of this cell were monitored for a load of 10 KΩ by means of a Keithley electrometer (Model 614).

3. Results and discussion

The recorded X-ray diffractograms of all the glass samples were featureless and exhibited no peaks that indicated an amorphous nature. The ionic transference number was measured from the polarization current versus time plot using the equation [13]:

$$t_{ion} = \frac{I_i - I_f}{I_i} \quad (1)$$

where I_i is the initial current and I_f is the final residual current. Fig. 1 presents the polarization current versus time plot for $10NaI–10Na_2O–80B_2O_3$ glass. The transference number values for all the samples are found to be close to unity and this indicates that the glasses are principally ionic conductors. The electronic contribution to the charge transport is small. The ionic conductivity has been measured as a function of both temperature and salt:glass-modifier [NaI/Na_2O] ratio. The data plots of log σ against $10^3/T$ are shown in Fig. 2 for different NaI/Na_2O ratios. The variation was found to follow the Arrhenius relation:

$$\sigma = (\sigma_0/T)\exp(-E_a/kT) \quad (2)$$

where σ_0 is the pre-exponential factor, T is the absolute temperature, k is the Boltzmann constant, and E_a is the activation energy for migration of Na^+ ions. The activation energies of different glass compositions are given in Table 1. The variation of log σ with (NaI/Na_2O) ratio at four different temperatures is shown in Fig. 3. It can be observed that conductivity increases in a non-linear manner and attains a maximum for $NaI/Na_2O = 1.0$. For $NaI/Na_2O > 1.0$, the conductivity decreases. The maximum conductivity was observed for the $10NaI–10Na_2O–80B_2O_3$ glass composition. The incorporation of Na_2O in B_2O_3 modifies the boron–oxy-

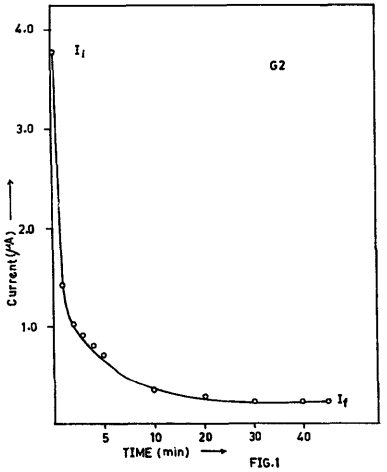

Fig. 1. Polarization current as a function of time for $10NaI–10Na_2O–80B_2O_3$ glass sample.

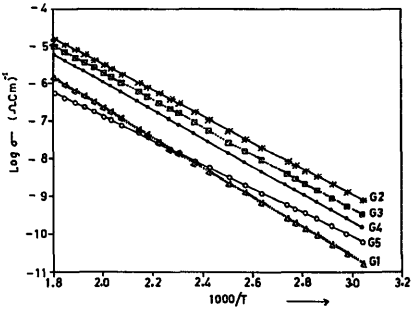

Fig. 2. Variation of log σ vs. $10^3/T$ for different glasses G1, G2, G3, G4 and G5

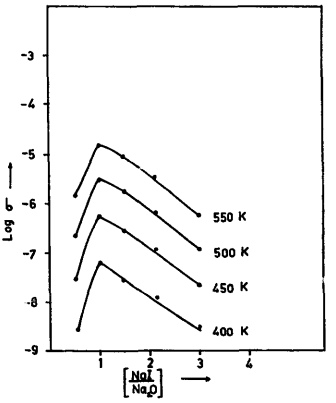

Fig. 3. Variation of log σ vs. (NaI/Na_2O) ratio at different temperatures.

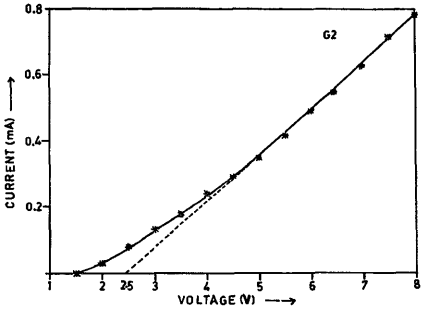

Fig. 4. Variation of current vs. applied voltage for cell with $10NaI–10Na_2O–80B_2O_3$ glass as the electrolyte.

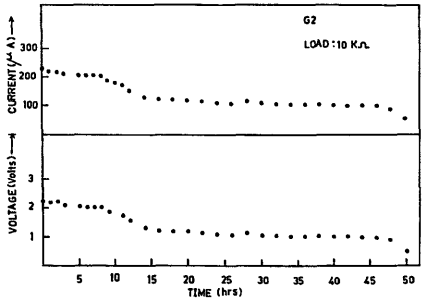

Fig. 5. Cell discharge characteristics of $10NaI–10Na_2O–80B_2O_3$ glass for a load of 10 kΩ.

gen network by converting some of the BO_3 units in BO_4 units. This allows dissolution of NaI salt in the glass matrix and provides more Na^+ ions for the charge transport. In the present system, conductivity maxima is envisaged by the incorporation of NaI. Further increase in NaI decreases the value of conductivity probably due to the smaller number of lattice sites available for cation movement [5,14].

Using the highest conducting glass $10NaI–10Na_2O–80B_2O_3$ as the solid electrolyte, a cell with the configuration Na/glass electrolyte/(I_2+C+electrolyte) was used for the determination of electrochemical decomposition potential of the electrolyte. A stabilized external voltage was applied. The voltage was changed at a rate of 10 mV s^{-1} and the corresponding current was measured. Fig. 4 shows the plot of current against the applied voltage for this cell. From the intercept of this curve with the electrochemical decomposition potential (x-axis), the value of the applied voltage for which there is a significant passage of current in the cell can be fixed at 2.5 V [5].

A solid-state cell was fabricated using $10 NaI–10Na_2O–80B_2O_3$ as the solid electrolyte and its discharge characteristics were studied at 303 K by connecting a load of 10 kΩ. Fig. 5 shows the discharge characteristics of the cell. The open-circuit voltage (OCV) for the cell was found to be 2.7 V and the short-circuit current (SCC) was 1600 μA. The initial drop in the voltage may be attributed to ohmic polarization which is followed by gradual drop with time. The cell parameters were as follows:

cell weight (g)	1.210
effective area of cell (cm^2)	1.314
discharge time from OCV to 1.0 V (h)	48
current density (μA cm^{-2})	76
power density (mW kg^{-1})	82.6
energy density (Wh kg^{-1})	3.97
discharge capacity (mAh)	4.8

4. Conclusions

The glasses investigated were principally ionic conductors and variation of the composition has considerable influence on the transport properties of the glass system. A decomposition potential of 2.5 V is determined for the glass electrolyte $10NaI–10Na_2O–80B_2O_3$ which is found to possess the highest ionic conductivity. The solid-state cell fabricated with this electrolyte has an OCV of 2.7 V and an SCC of 1600 μA.

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