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Journal of Power Sources 63 (1996) 141–144

JOURNAL OF POWER SOURCES

Short Communication

Ionic transport and battery characterization studies in $(30\text{–}x)Na_2O-xNaF\text{–}60B_2O_3\text{–}10Tl_2O$ glasses

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Received 17 May 1996; accepted 1 July 1996

Abstract

The results from measurements of the d.c. electrical conductivity of the $Na_2O\text{–}NaF\text{–}B_2O_3\text{–}Tl_2O$ glass system and the transference number are reported. Electrochemical cells with the configuration $Na/(30Na_2O\text{–}60B_2O_3\text{–}10Tl_2O)/(\text{graphite}+\text{iodine}+\text{electrolyte})$ have been fabricated and the discharge characteristics examined. The open-circuit voltage and the short-circuit current (maximum) are 2.27 V and 2.19 mA, respectively. Several other cell parameters are reported.

Keywords: Oxide glasses; Ionic transport; Transference numbers; Electrochemical cells; Short-circuit current; Specific energy

1. Introduction

There has been considerable interest in fast-ion conduction in alkali haloborate glasses [1–3]. Most of this work deals with the lithium chloroborate system with very few studies of alkali fluoroborate glasses. While a few of these papers [4–6] discuss $NaF\text{–}B_2O_3$ and $NaF\text{–}Na_2O\text{–}B_2O_3$ glasses, only one of them [6] discloses the effect of composition on the physical properties of these glasses in some detail.

Shelby and Ortolano [7] reported the results of a study of the properties of binary $NaF\text{–}B_2O_3$ glasses and ternary glasses in the $NaF\text{–}Na_2O\text{–}B_2O_3$ system. The results indicate that these glasses exhibit property/composition behaviour similar to that of sodium borate glasses. A structural model was proposed and it suggests that the fluorine ions enter the structure via BO_3F groups, with three bridging oxygen ions and one non-bridging fluorine ion per group.

Thallium ions are known to contribute to electrical conductivity in silicate and borate glasses in a way similar to alkali ions [8]. Sakka et al. [9] reported that the electrical conductivities of mixed cation glasses of the $Na_2O\text{–}Tl_2O\text{–}B_2O_3$ system are identical to those of $Tl_2O\text{–}B_2O_3$ glasses at the same Tl_2O content. Kamiya et al. [10] studied the distribution of Tl^+ ions in $Tl_2O\text{–}B_2O_3$ and $Na_2O\text{–}Tl_2O\text{–}B_2O_3$ glasses by X-ray diffraction based on electron radial distribution analysis.

The present work examines the electrical conductivity of quarternary glasses in the $(30-x)Na_2O-xNaF\text{–}60B_2O_3\text{–}10Tl_2O$ system. An electrochemical cell with configuration Na/glass/(graphite + iodine + electrolyte) is fabricated and its discharge characteristics determined.

2. Experimental

2.1. Sample preparation

Five samples of $Na_2O\text{–}NaF\text{–}B_2O_3\text{–}Tl_2O$ glasses (various compositions) were prepared by the melt quench technique. For this purpose, high purity NaF, Na_2CO_3 (Merck, GR grade), boric acid (certified grade) and thallium oxide (Fluka) were melted in a silica crucible at a temperature in the 950 to 1050 °C range (depending on the composition) for about 1 h. Glass that contained H_3BO_3 lost approximately 2 wt.% during melting. This is due primarily to loss of absorbed water from the raw materials. Since the weight loss was independent of the NaF content, it does not appear likely that any significant deviations from desired fluorine contents occurred. Such a conclusion is supported by the work of Hunter and Ingram [4] who found that very little fluorine loss occurred from similar melts. The melts were agitated frequently to ensure a homogeneous mixture. The melt was then quenched rapidly by pouring into a stainless-steel mould and pressed with another steel rod to yield disc-shaped samples. No traces of attack on the crucibles by the melts was detected. The mould and the steel rod were pre-heated to 150 °C in order to avoid shattering of the quenched disc under thermal stress. The samples were then annealed at the quench-

0378-7753/96/$15.00
PII S0378-7753(96)02453-6

Table 1
Glass composition, compositional variable, activation energy and pre-exponential factor of the system $(30-x)Na_2O-xNaF-60B_2O_3-10Tl_2O$

Glass no.	Glass composition	$R=Na_2/O(Na_2O+NaF)$	Activation energy (eV)	$\log \sigma_o$
G1	$30Na_20\text{–}60B_2O_3\text{–}10Tl_2O$	1.0	0.88	3.1
G2	$24Na_2O\text{–}6NaF\text{–}60B_2O_3\text{–}10Tl_2O$	0.8	0.89	2.5
G3	$18Na_2O\text{–}12NaF\text{–}60B_2O_3\text{–}10Tl_2O$	0.6	0.86	1.4
G4	$12Na_2O\text{–}18NaF\text{–}60B_2O_3\text{–}10Tl_2O$	0.4	0.90	2.5
G5	$6Na_2O\text{–}24NaF\text{–}60B_2O\text{–}10Tl_2O$	0.2	0.87	2.7
G6	$30NaF\text{–}60B_2O_3\text{–}10Tl_2O$	0.0	0.87	2.3

ing temperature for about 4 h. All the glass samples were clear and transparent with no visible evidence of either phase separation or crystallization.

2.2. *Chemical analysis of Tl_2O*

The concentration of Tl_2O was detected by X-ray fluorescence analysis. Each glass sample was dissolved in nitric acid with a known amount of $Sr(NO_3)_2$ and the X-ray emission spectra of the solution was taken with a Rigaku–Denki spectrometer. A comparison of the intensity ratio I_{Tl}/I_{Sr}, where I_{Tl} and I_{Sr} are the peak intensities of the Tl $L\alpha$ and Sr $K\alpha$ lines, was used to determine the concentration of Tl_2O from the calibration curves.

2.3. *Electrical conductivity*

Suitable glass samples of about 1 mm thick for electrical conductivity measurements were prepared by grinding and polishing the surfaces. Silver electrodes were deposited by a thermal evaporation technique under a vacuum of better than 10^{-5} torr. The d.c. electrical conductivity of the glass sample was measured as a function of temperature between 90 and 300 °C by measuring the current through the sample for a known voltage applied for very short time. This was achieved with a Keithly 616 digital electrometer picoammeter with a sensitivity of 10^{-14} A.

The compositional variable used to specify the glasses is described as follows

$$R=Na_2O/(Na_2O+NaF) \quad (1)$$

The composition and compositional variable of the glass system is given in Table 1. The amorphous nature of the samples was investigated by X-ray diffraction analysis using a Philips X-ray diffractometer.

3. Results and discussion

The chemical analysis results for thallium suggest that about 2% of Tl_2O is lost by evaporation during melting. A loss of about 10% of Tl_2O during melting has been reported for glasses of the $Tl_2O\text{–}SiO_2$ [11] and $Ag_2O\text{–}Tl_2O\text{–}B_2O_3$ systems [9] when the Tl_2O content is higher than 20 mol%.

The glass composition discussed in this paper is based on the general formula $xNa_2O-yNaF\text{–}(90-x-y)B_2O_3\text{–}10Tl_2O$. This basis is used so that glasses containing a constant value of $x+y$ will have a constant Na/B ratio. Consideration of any possible mixed-anion effect involves variations in properties as a function of $x/(x+y)$ with constant boric oxide and thallium oxide content.

Plot of the logarithm of electrical conductivity of $Na_2O\text{–}NaF\text{–}B_2O_3\text{–}Tl_2O$ glasses as a function of reciprocal absolute temperature (drawn by using a least-squares fit) exhibit straight lines, see Fig. 1. The temperature dependence of the d.c. electrical conductivity for the glass system follows the Arrhenius equation

$$\sigma=\sigma_0 \exp(-E_s/KT) \quad (2)$$

where E_s is the activation energy for conduction, K the Boltzmann constant, T the Kelvin temperature, and σ_0 is the pre-exponential factor. The activation energy E_s and the logarithm of the pre-exponential factor σ_0 were calculated from the conductivity plots and are summarized in Table 1.

The electrical conductivity at 100, 200 and 300 °C of $Na_2O\text{–}NaF\text{–}B_2O_3\text{–}Tl_2O$ glasses as a function of the compositional variable R is given in Fig. 2. The minimum conductivity is found around an $Na_2O/(Na_2O+NaF)$ ratio of 0.6. A minimum in conductivity corresponds to a maximum in activation energy. The maximum activation energy is found for an $Na_2O/(Na_2O+NaF)$ ratio of 0.4.

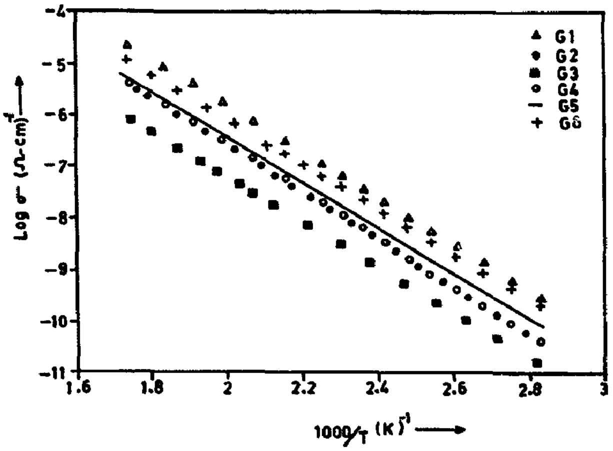

Fig. 1. Temperature dependence of d.c. electrical conductivity of $(30-x)Na_2O-xNaF\text{–}60B_2O_3\text{–}10Tl_2O$ glasses.

Table 2
Characteristics and performance of Na/glass(G1)/cathode cell at room temperature

Cell weight (g)	0.64
Electrolyte thickness (cm)	0.1
Cathode	graphite + iodine + electrolyte (5:5:1)
Open-circuit potential (OCP) (V)	2.27
Discharge time from OCP to 1.5 V (h)	142
Discharge time from OCP to 1.0 V (h)	176
Short-circuit current (maximum) (mA)	2.19
Initial current density (μA cm^{-2})	19.1
Final current density (μA cm^{-2})	16.3
Discharge capacity (mAh)	1.99
Specific energy (Wh kg^{-1})	5.2

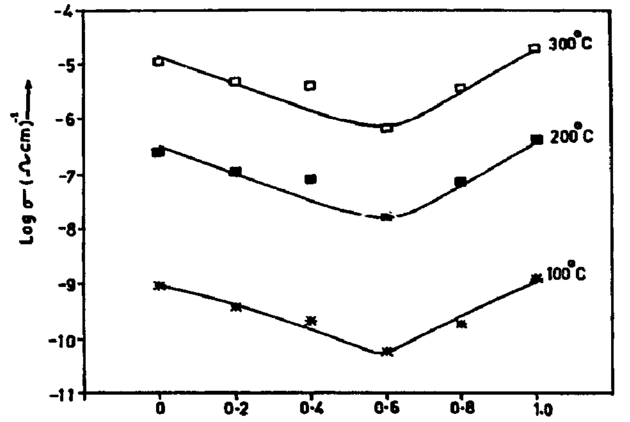

Fig. 2. Electrical conductivity as a function of compositional variable *R* at different temperatures.

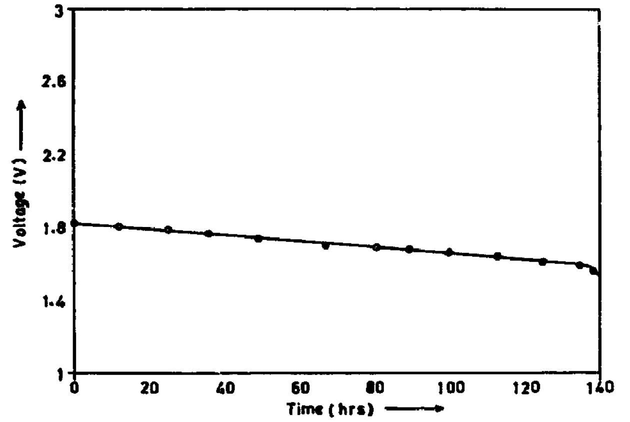

Fig. 3. Discharge characteristics of ($30Na_2O$–$60B_2O_3$–$10Tl_2O$) electrochemical cell at room temperature.

Transport number measurements were performed in the electrolyte (G1) using Wagner's polarization technique [12]. The values of transference numbers (t_{ion} and t_{ele}) thus obtained are 0.92 and 0.08, respectively. This suggests that the charge transport in the glass electrolyte is predominantly ionic.

3.1. Electrochemical cell

High ionic conductivity values of the glasses coupled with negligible electronic contribution [13] has encouraged the construction and characterization of laboratory-type electrochemical cell. This was assembled with sodium as the negative electrode and graphite + iodine + electrolyte (5:5:1) as the positive electrode. The cell gave an open-circuit potential in the 2.15–2.27 V range which remained constant for several days. The value is in good agreement with the theoretically calculated potential [14]. This suggests that there is no self-discharge process; the latter might have occurred if there was any electronic conduction in the electrolyte or any reaction between the electrolyte and the current-collector.

The discharge characteristics were studied at room temperature using a cell with configuration: Na/glass(G1)/(graphite + iodine + electrolyte). In order to improve the ionic transport in the positive electrode, a small quantity of electrolyte was incorporated in graphite.

The discharge capacity of the cell is about 2 mAh and the specific energy is 5.2 Wh kg^{-1}. The discharge characteristics of the cell with graphite + iodine + electrolyte (5:5:1) as a positive electrode under a constant load of 100 kΩ is given in Fig. 3. Both the voltage and the current were measured during discharge as a function of time. As the load is decreased, the current increases and the cell discharges quite rapidly during the first few days. The cell performance parameters are given in Table 2.

4. Conclusions

Using $30Na_2O$–$60B_2O_3$–$10Tl_2O$ glass electrolyte, an electrochemical cell has been fabricated for which the open-circuit potential and the maximum short-circuit current are be 2.27 V and 2.19 mA, respectively. The transference number data indicates that ionic conduction is predominant in this glass system.

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