

Short Communication

Transport properties of AgI–Ag₂O–P₂O₅–MoO₃ amorphous solid electrolyte

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Abstract

The transport properties of a new solid glassy electrolyte AgI–Ag₂O–P₂O₅–MoO₃ are investigated. The addition of AgI to the host Ag₂O:P₂O₅:MoO₃ system enhances the conductivity by almost three orders of magnitude. The density and glass transition temperature vary linearly with AgI content. Studies with electrochemical cells have demonstrated the utility of this material for technological applications.

Keywords: Glass; Silver conductors; Batteries

1. Introduction

The search for new glassy solid electrolytes has gained considerable momentum, because such glasses have the advantages of homogeneity, absence of grain boundaries, ease of preparation of films with large flat surfaces, and the diversity of composition and transparency compared with polycrystalline electrolytes. Accordingly, a number of glasses which support high ionic conductivity [1] have been examined and progress has been made towards understanding the complex phenomenology of transport in highly-disordered systems [2]. Among all the solid electrolyte materials studied to date, Ag⁺ conductors are the most abundant and well-investigated class. Since the discovery of fast ion conduction in the cubic phase of AgI, many crystalline and non-crystalline solid electrolytes have been identified [3]. In recent years, many AgI-doped oxide glasses have been shown to have excellent cation-conducting properties [1].

The AgI–Ag₂O–B₂O₃ system has been explored over the whole glass-forming region and investigations have also been performed on systems in which the AgI is replaced by (or mixed with) AgCl and AgBr. From an application point of view, much effort has been directed towards improving the ionic conductivity of Ag-based glasses. In this respect, work has concentrated on making glasses by mixing two glass formers and then adding a dopant salt. It is observed that conductivity usually increases upon such addition. Electrical conductivity, short-range orders and glass transitions in AgI–Ag₂O–B₂O₃ vitreous electrolytes have been studied in great

detail [4–6]. Substantial knowledge has been gained on the properties of boron [4–6], phosphorous [7–10] and borophosphate glasses [11–15]. On the other hand, very few papers [16–19] have dealt with solid electrolyte based on phosphomolybdate glass and, to our knowledge, no studies have been reported on AgI addition to the system.

In previous work [19], we have investigated the glass-forming region, density, conductivity and transport number of the ternary Ag₂O–P₂O₅–MoO₃ system, for $n=0.66, 1, 2,$ and 3 and $y=0.2-1$ where $n=P_2O_5+MoO_3/Ag_2O$ and $y=P_2O_5/P_2O_5+MoO_3$. In that study, the preparation of glasses using a binary mixture of AgPO₃ and AgMoO₄ gave the homogeneous glass, whereas, three components exhibited silver dispersion in the matrix. The maximum conductivity was observed in the $n=0.66$ series. A system with $n=1,$ $y=0.5$ was prepared by using three (Ag₂O, P₂O₅, MoO₃) and two (AgPO₃:AgMoO₄) components. The work reported here involves the preparation, density, glass-transition temperature, scanning electron microscopic (SEM) analysis, electrical conductivity, transport number and electrochemical application of AgI–Ag₂O–P₂O₅–MoO₃ glass systems.

2. Experimental

The samples were synthesized by preheating weighed amounts of AgNO₃ (Johnson Matthey), NH₄H₂PO₄, (NH₄)₂MoO₇·4H₂O and AgI (Fluka, p.a.) at 400 °C for 2 h. After evolution of the decomposition products, the tem-

perature was raised to 600 °C and maintained for 30 min in order to yield a homogeneous melt. The melts were poured into stainless-steel molds that were kept at room temperature.

The undoped samples were made by using two different methods: (i) from $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5:\text{MoO}_3$, by thermal decomposition of the above-mentioned starting ingredients, and (ii) from $\text{AgPO}_3:\text{AgMoO}_4$ salts. All samples were transparent and varied from orange to brown in colour. After preparation, the samples were kept in a desiccator to prevent moisture contamination and photochemical decomposition.

The glassy and semi-crystalline states at room temperature were checked by means of X-ray powder diffraction (Philips, PW 1710 diffractometer, $\text{Cu K}\alpha$ radiation, operated at 40 kV and 20 mA) and SEM (Cambridge Stereoscan 200 Model). The densities were measured at room temperature by the Archimedes method using toluene as the immersion fluid. Differential thermal analysis (DTA) (Dupont 2000 Model) was used to study the glass-transition temperature, T_g . The latter was identified by a shift of the base line in an endothermic direction while heating at 10 °C/min. The DTA patterns of partially crystalline samples were characterized by sharp endothermic peaks due to the phase transition or the melting process. Measurements of a.c. conductivity were carried out in the 20–400 °C temperature range using a cell with electrodes obtained by gold deposition on both sides of the sample. The functional dependence of a.c. conductivity at each temperature was recorded in the frequency range 10^{-2} to 10^6 Hz using a frequency response analyser (Solartron 1255 Model) equipped with an in-house impedance adapter ($10^{12} \Omega$, 3 pF). The electronic transport numbers of a few representative glasses ($n=1/y=0.5$, $n=0.66/y=0.66$ and $n=0.66/y=0.66/x=0.6$) were determined at room temperature by the Tubandt method and using the following cell configuration: $\text{Ag}(+)/\text{silver-glass composite}/\text{glass}/\text{silver-glass composite}/\text{Ag}(-)$, termed cell No. 1. A low current ($1\text{--}10 \mu\text{A cm}^{-2}$) was used in order to prevent dendrite formation.

In order to test the practicality of these electrolytes, a few electrochemical cells with the following configuration were fabricated: $\text{Ag}(+)/\text{silver-glass composite}/\text{glass}/\text{glass-I}_2\text{-graphite}$, termed cell No. 2. The discharge characteristics were studied systematically under different loads (1.5 and 10 k Ω) and current conditions. Prior to this, different compositions of both electrodes were employed in order to reduce the negative polarization phenomenon. The optimum compositions were 60:40 silver:glass composite and a 50:45:5 glass: I_2 :graphite weight ratio.

3. Results and discussion

When undoped glasses were prepared with method (i), deposition of metallic silver was observed at high Ag_2O contents. The amount of deposited silver was determined by the temperature and the age of the melt. Therefore, samples of composition $n=1$, $y=0.5$ were prepared by method (ii),

using AgPO_3 and Ag_2MoO_4 . For three components SEM examination revealed that the resulting glass is not homogeneous and the silver dispersion phase is well separated. The size of the silver particles is less than 1 μm . On the other hand, the binary mixture provides good mixing that results in a glass with good homogeneity. These results indicate that for the preparation of glasses with $n=1$, it is more convenient to start from pure thermodynamically stable salts such as AgPO_3 and AgMoO_4 . Further, when AgI is added to glass with $n=0.66$, $y=0.66$, up to $x=0.6$, a homogeneous glass is obtained; beyond this concentration, the glass becomes crystallized.

The density of the glasses increases linearly with AgI content, as shown in Fig. 1. This is due to the increased silver ion content which, in turn, reduces the specific volume. These results are in good agreement with the findings of Minami et al. [20].

The dependence of T_g on AgI concentration is displayed in Fig. 2. The values of T_g are lower for the series $n=1$, compared with those for the series $n=0.66$. This is due to weakening of the glass structure by the increased number of

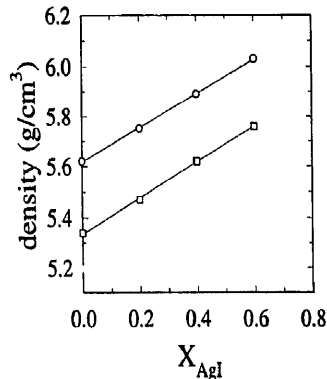


Fig. 1. Density vs. AgI content for (O) $n=0.66$, $y=0.66$, and (□) $n=1$, $y=0.5$ glasses.

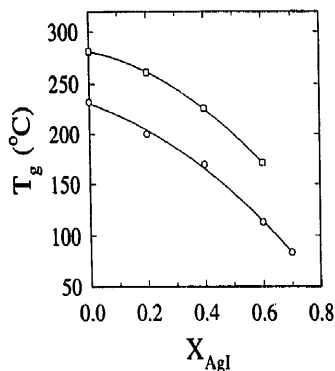


Fig. 2. T_g vs. AgI content for (O) $n=0.66$, $y=0.66$, and (□) $n=1$, $y=0.5$ glasses.

Table 1
Density, T_g and conductivity data for glasses

Composition (x)	Density (g cm^{-3})	T_g ($^{\circ}\text{C}$)	σ_n (S cm^{-1})	$(\sigma T)_0$ (SK cm^{-1})	E_a (eV)	σT_g (S cm^{-1})
a) $n=0.66, y=0.66$						
0.0	5.62	232	1.4×10^{-5}	3.0×10^5	0.458	1.6×10^{-2}
0.2	5.75	200	5.8×10^{-5}	9.8×10^4	0.393	1.3×10^{-2}
0.4	5.89	169	2.9×10^{-4}	9.8×10^4	0.353	2.1×10^{-2}
0.6	6.03	113	1.2×10^{-3}	4.5×10^4	0.298	1.5×10^{-2}
0.7	7.96	84	5.6×10^{-4}	1.0×10^6	0.396	7.3×10^{-3}
b) $n=1, y=0.5$						
0.0	5.34	281	6.7×10^{-6}	6.4×10^4	0.437	1.2×10^{-2}
0.2	5.47	261	3.7×10^{-5}	4.2×10^4	0.384	1.9×10^{-2}
0.4	5.62	226	3.0×10^{-4}	3.0×10^4	0.322	3.4×10^{-2}
0.6	5.76	171	2.8×10^{-3}	6.4×10^3	0.227	3.8×10^{-2}

non-bridging oxygens that result from the high content of the modifier. Also, the co-ordination number of Mo reduces from 6 to 4 with increase in the modifier (Ag_2O) concentration [21]. Further weakening of the glass structure caused by the addition of AgI produces a continuous drop in T_g (Fig. 3). The maximum decrease in T_g with respect to intake of AgI is equal to 84 and 170 $^{\circ}\text{C}$ for $n=0.66$ and 1, respectively.

Over the entire temperature range of investigation, the conductivity of all glasses obeyed the Arrhenius law, namely:

$$(\sigma T) = (\sigma T)_0 \exp(-E_a/kT) \quad (1)$$

The values of room temperature conductivity, pre-exponential factor, activation enthalpy of ion migration, along with the density and glass-transition temperature, are presented in Table 1. The variation in the conductivity as a function of AgI content at room temperature and T_g are given in Fig. 3(a) and (b), respectively. At room temperature, the conductivity rises with increase in AgI content; this is consistent with earlier studies [22]. On the other hand, the room-

temperature dependence of conductivity (Fig. 3(a)) is almost linear and exhibits little change with variation of n . Thus, with x_{AgI} the concentration of mobile Ag^+ carriers attains a saturation level, independent of the Ag_2O content. These results indicate that the high polarizability of I^- plays an important role in promoting Ag^+ transport. For $x=0.7$, partial crystallization of the sample causes a decrease in conductivity. It is very interesting to observe almost a constant conductivity at the glass-transition temperature (Fig. 3(b)). In this case, thermally activated charge carriers have equal probability with that of disorder produced as a result of a modified glass network in the system which gives enhanced conductivity. As expected, the maximum in conductivity coincides with the minimum activation enthalpy of ion migration (Table 1).

Transport number determination (cell No. 1) in the doped systems by the Tubandt method demonstrated ionic conductivity without any dendritic formation. It is well known that the addition of AgI provides an increase in solubility of the silver dispersoid. This result is further confirmed by the e.m.f. value of 687 mV for the Ag/glass/I cell which is the same as the thermodynamic value for AgI formation.

The discharge characteristics for the optimum composition of electrodes (cell No. 2) at $n=0.66, y=0.66$ and $x=0.6$ under different load conditions are presented in Fig. 4. The cell discharge parameters are displayed in Table 2. These

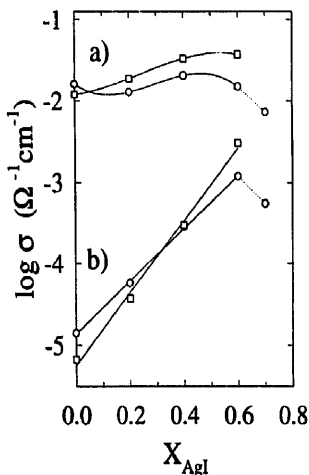


Fig. 3. Conductivity at (a) T_g and (b) room temperature vs. AgI content for (O) $n=0.66, y=0.66$, and (□) $n=1, y=0.5$ glasses.

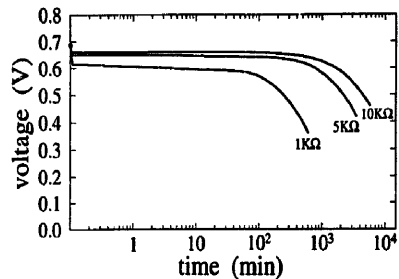


Fig. 4. Typical discharge curves under different load conditions for cell No. 2.

Table 2
Characteristics and performance of cell No. 2

Parameters	Load (k Ω)		
	10	5	1
Open-circuit voltage (V)	0.683	0.683	0.683
Operating voltage (V)	0.645	0.635	0.600
Operating time (h)	118	59	8
Discharge capacity (mAh)	7.66	7.49	4.8
Energy density (Wh g ⁻¹)	4.94	1.83	1.10

results demonstrate the stability of the electrolyte and the small polarization, compared with the work reported in the literature. Thus, it is concluded that the present material is useful for technological applications.

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