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Submitted on 1 Jan 1994

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Some properties of AgI-Ag₂O-MoO₃ electrolyte doped with Al₂O₃

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(Received 13 October 1993, revised 23 February 1994, accepted 24 February 1994)

Abstract. — Stoichiometric ratios of AgI, Ag₂O and MoO₃ were weighed into different crucibles. Different amounts of Al₂O₃ were added to all but one crucible so as to form the undoped ternary glassy 66.67 AgI-14.29 Ag₂O-19.04 MoO₃ system and the 66.67 AgI-14.29 Ag₂O-19.04 MoO₃ doped with 0.1, 0.3, 0.5, 0.7 weight % (w/o) of Al₂O₃ when the melts of these constituent chemicals were rapidly quenched in liquid nitrogen. The phases were characterized by XRD, electrical conductivity and transference number. The electrical conductivity at 300 K of the undoped glass is 0.003 S/cm and the doped sample with 0.5 w/o Al₂O₃ has the highest electrical conductivity at 300 K of 0.007 S/cm. These phases are solid electrolytes that were used to fabricate solid state electrochemical cells. The cell with the undoped electrolyte has an internal resistance of 150 Ω and the cell with the doped electrolyte (0.5 w/o Al₂O₃) has an internal resistance of 100 Ω. The differences observed in the characteristics of the doped and undoped phases and the differences in the battery performance are attributed to the chemical reaction between Al₂O₃ and the glass which resulted in a change of the glassy phase in the doped material.

1. Introduction.

Solid electrolytes characterized by exceptionally high ionic conductivity and relatively small electronic conductivity have attracted a great deal of attention because of their unique transport properties and potential applications in solid state electrochemical cells, sensors etc. Extensive researches have produced a number of good solid electrolyte materials. Efforts are still being carried out to find newer materials and methods of increasing the level of ionic conduction. These include the addition of aliovalent impurities, the stabilization of unique open-channel [1] structures and disordered glassy phases [2]. A number of investigations have reported significant enhancement [3, 4] and slight increments [5] in ionic conductivity by the dispersion of Al₂O₃ particles. These so-called dispersed solid electrolyte systems (DSES) have become increasingly important to both experimentalists and theorists [6-7]. In this paper, we report some properties of the ternary AgI-Ag₂O-MoO₃ system containing different amounts of
Al₂O₃ and the performance of the solid state electrochemical cells with the Al₂O₃ doped silver iodo molybdate electrolyte.

2. Experimental.

2.1 Material Preparation. — Stoichiometric ratios of AgI, Ag₂O (both 99 % purity) and MoO₃ (obtained by heating ammonium molybdate overnight at 400 °C) to form 66.67 AgI-14.29 Ag₂O-19.04 MoO₃ glass were mixed with different weight ratios of Al₂O₃ (Aldrich) in different silica crucibles. The compositions were melted at 600 °C in a carbolite furnace and the melt was quenched in liquid nitrogen.

2.2 Material Characterization.

2.2.1 XRD. — The doped and undoped samples were subjected to powder X-ray analysis using a Shimadzu XD5 diffractometer that uses Cu-Kα radiation of wavelength 1.542 Å. The X-ray tube was operated at 800 W.

2.2.2 Electrical conductivity. — The electrical conductivity of the samples was measured using the Solartron Schlumberger HF 1255 Frequency Response Analyser at 300 K in the frequency range of 1 kHz to 10 MHz. The solid phases were powdered and pelletized at 140 bar [8] and coated with silver dag on both circular faces before being mounted onto a conductivity mount with silver leads for connection to the Solartron equipment.

2.2.3 Microanalysis. — Microstructure and microanalysis were carried out using the Philips SEM 515 and EDAX 9800 equipments. The micrographs were taken at an accelerating voltage of 20 kV and the EDAX for 100 s.

2.3 Battery Fabrication. — The undoped glass and the composite material with 0.5 w/o Al₂O₃ were used to fabricate two electrochemical cells, the anode containing 1:1 weight ratio [9] of silver powder and electrolyte and the cathode containing iodine, electrolyte and carbon in the ratio 5:5:1. The anode-electrolyte-cathode were pelletized at a pressure of 140 bar and clamped between two copper current collectors with leads for external connections. The OCV and internal resistance of the cells were measured and the cells were finally discharged at a constant load current of 0.03 mA. The method of cell fabrication, internal resistance measurement and cell discharge has been described elsewhere [10-11]. The transference number was measured via the emf method [12]. The quantities of cathodic and anodic materials present in the two cells are as follows:

\[
\begin{align*}
C_1 & = (1 \text{ g Ag} + 1 \text{ g SM}^*/4 \text{ g SM}^*/(1 \text{ g I}_2 + 1 \text{ g SM}^* + 0.2 \text{ g C}) \\
C_2 & = (1 \text{ g Ag} + 1 \text{ g SM})/4 \text{ g SM}/(1 \text{ g I}_2 + 1 \text{ g SM} + 0.2 \text{ g C})
\end{align*}
\]

Here SM is the 66.67 AgI-14.29 Ag₂O-19.04 MoO₃ glass and SM* is the 66.67 AgI-14.29 Ag₂O-19.04 MoO₃ glass doped with 0.5 w/o Al₂O₃.

3. Results.

3.1 XRD. — Figures 1a-d show the X-ray diffractograms for the chemical components in the glass and that of the silver iodo molybdate glass. Figures 2a-d represent the X-ray diffraction pattern of the composite material containing 0.1, 0.3, 0.5 and 0.7 w/o of Al₂O₃, compared to the XRD pattern of the Al₂O₃ used, figure 2e. The coherent length of the samples doped with different amounts of Al₂O₃, taken at 2θ = 46° is 2.87, 2.51, 2.23 and 2.47 respectively.
3.2 ELECTRICAL CONDUCTIVITY. — The electrical conductivity at 300 K as a function of dopant concentration is shown in figure 3. The sample with 0.5 w/o Al₂O₃ has the highest electrical conductivity of $7 \times 10^{-3}$ S cm⁻¹ and is twice the electrical conductivity of the undoped glass. The negative imaginary impedance, $-Z_1$ versus real impedance, $Z_R$ plot is shown in figure 4.

3.3 MICROANALYSIS. — Figures 5a to 5e shown the SEM micrographs of the doped glasses in increasing order of Al₂O₃ content up to 0.5 w/o. Table I lists the percentage composition of the various elements (atoms, ions, etc.) in the sample.

3.4 BATTERY PERFORMANCE AND CHARACTERISTICS. — The internal resistance of the undoped cell is 150 Ω and that of the doped cell is 100 Ω. The OCV of both batteries is 0.680 V.
Fig. 2. — X-ray diffractograms of silver iodomolybdate glass mixed with (a) 0.1 w/o, (b) 0.3 w/o, (c) 0.5 w/o and (d) 0.7 w/o $\text{Al}_2\text{O}_3$ content. (e) shows the diffractogram for the $\text{Al}_2\text{O}_3$ used as the dopant.
Fig. 3. — Electrical conductivity variation with Al$_2$O$_3$ content.

Fig. 4. — $Z_I$ (imaginary impedance) versus $Z_R$ (real impedance) for silver iodomolybdate glass doped with 0.5 w/o Al$_2$O$_3$, indicating that the transference number of the material is > 0.9. The discharge characteristics of the cells at a load current of 30 $\mu$A is shown in figure 6. Table II below summarizes some of the characteristics of the primary cells.
Fig. 5. — SEM micrographs for silver iodomolybdate glass doped with (a) 0.1 w/o Al$_2$O$_3$, showing many crystalline structures with high Ag and low Al content, (b) 0.3 w/o Al$_2$O$_3$ with high Al content at the centre. Ag content is high outside the circular area where Al is high but is also found in the circular area where Al is found in abundance, (c) a distinction between the smooth glassy phase and a crystalline phase. Al is in abundance in the crystalline region. This micrograph is that of another portion of the surface of the glass doped with 0.3 w/o Al$_2$O$_3$. (d) SEM micrograph of silver iodomolybdate glass doped with 0.5 w/o Al$_2$O$_3$. The circular area in this microregion contains only Al and no Ag. The rod-like crystalline structures which is believed to be joined crystalline structures as observed in (a) is thought to be $\gamma$-AgI but mapping for Ag in some of the regions containing these rod-like structures as in (e) which is another portion of the same glass doped with 0.5 w/o Al$_2$O$_3$ shows no Ag at all, thus discarding the belief that these rod-like structures are $\gamma$-AgI.

4. Discussion.
The X-ray diffraction pattern of the undoped sample shows the amorphous hump characteristic of the heavy element compounds used in this study. The X-ray diffractogram of the doped samples also distinguishingly show the continuous spectra typical of amorphous materials and peaks indicating the presence of a crystalline phase. It was thought that these peaks were due to
Fig. 5 (continued).
Table I. — Elemental starting composition compared with EDAX data.

<table>
<thead>
<tr>
<th>Starting composition, %</th>
<th>EDAX data, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
</tr>
<tr>
<td>0.1 w/o Al</td>
<td>52.53</td>
</tr>
<tr>
<td>0.3 w/o Al</td>
<td>52.28</td>
</tr>
<tr>
<td>0.5 w/o Al</td>
<td>52.03</td>
</tr>
<tr>
<td>0.7 w/o Al</td>
<td>51.79</td>
</tr>
</tbody>
</table>

Fig. 6. — Discharge characteristics of the cells at 30 μA load current.

Table II. — Characteristics of silver iodo molybdate cells, doped ($C_1$) and undoped ($C_2$).

<table>
<thead>
<tr>
<th></th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density, $J$ (A cm$^{-2}$)</td>
<td>$2.3 \times 10^{-5}$</td>
<td>$2.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Discharge capacity, $Q$(C)</td>
<td>39.6</td>
<td>32.4</td>
</tr>
<tr>
<td>Energy density, $E$ (J/g)</td>
<td>2.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Diameter, $d$ (mm)</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Weight (g)</td>
<td>9.1</td>
<td>9.1</td>
</tr>
</tbody>
</table>
\( \gamma \text{-AgI} \) but upon SEM examination we did not observe crystalline structures attributable to \( \gamma \text{-AgI} \) as in our earlier work on 70 AgI-20 Ag2O-3 CeO2-7 V2O5 [10]. Glasses with high AgI content solidifies with \( \gamma \text{-AgI} \) protruding the surface from the bulk [13]. Thus the peaks observed must be due to crystalline structures observed in the SEM micrographs which form as a result of the chemical reaction that took place between the dopant and glass during preparation.

The \( \text{Al}_2\text{O}_3 \) doping of the silver iodo molybdate glass in this work has little influence on the electrical conductivity. This is to be expected since the amount of dopant used is small. It has been reported [4] that a maximum conductivity of \( 6 \times 10^{-4} \text{ S cm}^{-1} \) at room temperature was obtained for AgI containing 30 mole\% (m/o) or \( \approx 16 \text{ w/o undoped } \text{Al}_2\text{O}_3 \) (0.06 \( \mu \) particle size). Lithium iodide containing 33-45 m/o aluminium oxide exhibit conductivities of the order of \( 10^{-5} \text{ S cm}^{-1} \) at 25 °C which is 2 orders of magnitude higher than the undoped LiI [3]. Little influence on the electrical conductivity with small amount of doping has also been reported in [5] where a maximum in the electrical conductivity was observed when 0.4 AgI 0.6 AgPO3 glass was doped with 1 w/o of \( \text{Al}_2\text{O}_3 \). The maximum electrical conductivity reported was \( \approx 10^{-3} \text{ S cm}^{-1} \) and is about a factor higher than the electrical conductivity of the undoped glass. Using the results in [5] as our guide, we have chosen doping concentrations of less than 1 w/o \( \text{Al}_2\text{O}_3 \) to see if a maximum exist in the electrical conductivity for this range. In the present work, the maximum electrical conductivity observed is \( 7 \times 10^{-3} \text{ S cm}^{-1} \) at 0.5 w/o \( \text{Al}_2\text{O}_3 \) content and is more that twice the electrical conductivity of the undoped glass.

In agreement with XRD, SEM observations show that doped samples consist of a glassy phase and precipitates of a foreign crystalline phase. There are two types of glassy phase, one the silver iodo molybdate glass and the other contains a lot of Al from the mappings carried out. Figure 5a shows crystalline structures of quite a definite shape on the glass doped with 0.1 w/o \( \text{Al}_2\text{O}_3 \). The mapping done in this microregion does not indicate an abundance of Al. The distribution of Ag however is quite homogeneous which led us to imply in the beginning that these crystalline structures could be \( \gamma \text{-AgI} \). Figure 5b shows the surface of the glass doped with 0.3 w/o \( \text{Al}_2\text{O}_3 \). The almost circular phase at the centre of this micrograph contain a lot of Al. Ag is more concentrated outside the phase containing a lot of Al. The areas outside the phase containing a lot of Al is crystalline and similar to that in figure 5a. Figure 5c is another portion of the glass doped with 0.3 w/o \( \text{Al}_2\text{O}_3 \). A crystalline-in-glass (smooth) phase is observed, but the Al mapping in the crystalline phase showed quite a lot of Al, though not as abundant in the glassy phase containing a lot of Al in figure 5b. Figure 5d shows the surface of the glass doped with 0.5 w/o \( \text{Al}_2\text{O}_3 \). Again mapping shows that Al is concentrated in the almost circular smooth (glassy) phases. Some rod-like crystallites are observed, possibly due to smaller crystallites joining together. If these rod-like crystallites are \( \gamma \text{-AgI} \), then upon mapping Ag in these areas, one would expect an abundance of Ag, but this was not observed. This evidence support our view that the crystalline peaks in the X-ray diffractogram cannot be attributed to \( \gamma \text{-AgI} \) even though the areas outside the smooth circular glassy phase containing a lot of Al in figure 5e does contain a lot of Ag. In short, from these evidence and observations made in [10], we suggest that the crystalline phase to which the peaks in the XRD pattern can be attributed to is the product of a chemical reaction between the dopant and the glass that took place during the preparation of the sample. Such reaction probably involves a change of chemical composition of the glassy phase in the doped material that led to the observed values of the electrical conductivity.

The cell reaction is \( \text{Ag} + (1/2) \text{I}_2 \rightarrow \text{AgI} \), and the theoretical electromotive force is given by \( E = -\Delta G/ZF \), where \( E \) is the theoretical electromotive force, \( \Delta G \) is the change in Gibb’s free energy of AgI formation which is equal to 66 kJ mol\(^{-1} \), \( Z \) is the valency of the conducting ion and has the value of unity and \( F \) is Faraday’s number. Hence the theoretical electromotive force is 0.687 V. The measured open circuit voltage for both cells \( C_1 \) and \( C_2 \) is 0.680 V. Thus
the ionic transference number is 0.99. This implies that the doped glass is still an ionic conductor.

The internal resistance of the cell is reduced to 67 % of the internal resistance of the undoped cell when the electrolyte contains 0.5 w/o Al2O3. The decrease in internal resistance of the doped cell is expected since the doped electrolyte has a higher electrical conductivity. Correspondingly, the time taken for the cell with the doped electrolyte to discharge to \( V = 0.650 \) V is about 50 h longer than the time taken for the cell with the undoped electrolyte to discharge to the same voltage. Since the anodic and cathodic quantities are the same in both cells, the longer cell life for cell C2 is attributed to the higher conductivity of its electrolyte. During the internal resistance measurement, when a current of 30 \( \mu \)A was drawn out of the battery, the cell potential dropped to 0.674 V. This is consistent with the voltage of the cell at the beginning of discharge under a constant load current of 30 \( \mu \)A. The fast drop in cell potential after reaching \( V = 0.650 \) V is attributable to the slow diffusion of iodine into the electrolyte, forming the low conducting AgI at room temperature on reaction with the silver ions and electrons. The low conducting AgI increases the internal resistance of the cell and leads to the sudden large voltage drop. Iodine diffusion also takes place out of the cathode. The effect of iodine diffusion can be observed on the sides of the cell and also on the copper current collector.

5. Conclusions.

The crystalline peaks in the XRD pattern of the doped glass is attributable to the crystalline phase that is a product of a chemical reaction between the dopant and glass. Such reaction probably involves a change of chemical composition of the glassy phase in the doped material in comparison with the initial glass. We suppose that the observed electrical conductivity and cell performance are the consequences of this decomposition.

Acknowledgments.

The authors would like to thank the Director of the Centre for Foundation Studies in Science, University of Malaya for the votes PJP 155/91 and PJP 71/92 and the Head of the Nuclear Science Department, National University of Malaysia for allowing this collaborative work. A. K. Arof thanks the Nippon Sheet Glass Foundation for the grant given which supported some of this work.

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