

Short Communication

Electrical Conductivity of a System of Ag_2SO_4 : AgI Eutectic Added to $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$

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Summary

The electrical conductivity of rapidly quenched specimens of $48\text{Ag}_2\text{SO}_4$: 52AgI eutectic added to $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ has been measured as a function of frequency and temperature. The results show a significant enhancement in the conductivity of the $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ system with a maximum value at 12.5 mol% eutectic. This phenomenon is explained in terms of the dispersive nature of the fine eutectic crystallites in the crystalline matrix of the Li_2SO_4 : Ag_2SO_4 system.

Introduction

The electrical conductivity of solid electrolytes is an important parameter that influences the range and type of the applications of such materials. Various techniques have been employed to enhance the ionic conductivity, σ , namely:

- (i) the addition of aliovalent impurities [1, 2];
- (ii) the stabilization of unique, open-channel structures [3 - 5];
- (iii) the dispersion of a second insoluble phase into a different matrix [6 - 8];
- (iv) partial trapping of the high temperature, high conducting phase at room temperature [9, 10].

For example, an investigation of the electrical conductivity of Li_2SO_4 : Ag_2SO_4 solid electrolytes prepared by twin-roller quenching revealed a maximum at a composition of $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ [10].

There are numerous published examples of composite electrolytes in which the dispersion of fine particles of a conducting or insulating phase into the crystalline matrix is found to enhance the conductivity. This can be explained as being due to an increased interfacial conduction [12]. According to Takahashi *et al.* [11], the Ag_2SO_4 : AgI system forms a eutectic

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at 48 mol% Ag_2SO_4 with a melting point as low as 158 °C. Also, the solubility of Ag_2SO_4 in $\alpha\text{-AgI}$ is reported to be 25 mol% at 151 °C. Further, the compound $\text{Ag}_4\text{I}_2\text{SO}_4$ is stable between 119 °C and 148 °C. These data clearly merited a study into whether the addition of Ag_2SO_4 : AgI eutectic (with fine crystallite size and low melting point) to the base system $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ would cause an enhancement in the conductivity.

Experimental

Material preparation

The starting materials, Ag_2SO_4 (E. Merck, India), Li_2SO_4 and AgI (Fluka A.G., Switzerland), were of AR quality. The Ag_2SO_4 : AgI (48:52) eutectic and the Ag_2SO_4 - Li_2SO_4 electrolyte were prepared by the twin-roller quenching technique [10]. The resulting materials were characterized by X-ray diffraction (Philips, Model PW 1710) and scanning electron microscopy (Cambridge Stereoscan, Model 250 MK3) at room temperature.

Electrical measurements

The above materials were obtained in the form of thin flakes and could not withstand the pressure of the sample holder. Accordingly, the flakes were crushed into fine particles and then pelletized at 10 tons cm^{-2} . To ensure good electrical contact, silver discs were pressed against both sides of the sample surfaces using a specially designed holder [13]. The a.c. electrical conductivity was measured as a function of frequency (10 Hz - 13 MHz), at various temperatures during cooling from 130 °C to 40 °C, by the two-probe method, with a Hewlett-Packard 4192A LF impedance analyzer at 5 mV OSC level. The temperature was controlled to ± 1 °C with a Eurotherm temperature controller.

Results and discussion

Figure 1 gives the X-ray diffraction pattern of a quenched sample of Li_2SO_4 : Ag_2SO_4 : eutectic (26.25:61.25:12.5) at room temperature. The data show the presence of Li_2SO_4 , Ag_2SO_4 and AgI , together with partial traces of the highly conducting phase $\alpha\text{-AgI}$. The formation of the latter may be due to the fast quenching rate of the twin-roller method, as this technique has also been used for the partial trapping of the high-temperature phases in the Li_2SO_4 - Ag_2SO_4 binary system [10].

From impedance studies, it is concluded that the conductivity of the above material is the sum of contributions from both the intergranular and granular regions, excluding electrode effects. Similar results have been obtained for AgI added to the $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ system [14].

The dependence of the electrical conductivity, σ , on temperature, T , for different amounts of Ag_2SO_4 : AgI (48:52) eutectic added to $30\text{Li}_2\text{SO}_4$: $70\text{Ag}_2\text{SO}_4$ is shown in Fig. 2. The corresponding $\log \sigma T$ versus mol% of eutectic plots for five different temperatures are given in Fig. 3. It can be seen that whereas the conductivity increases at all temperatures, a decrease

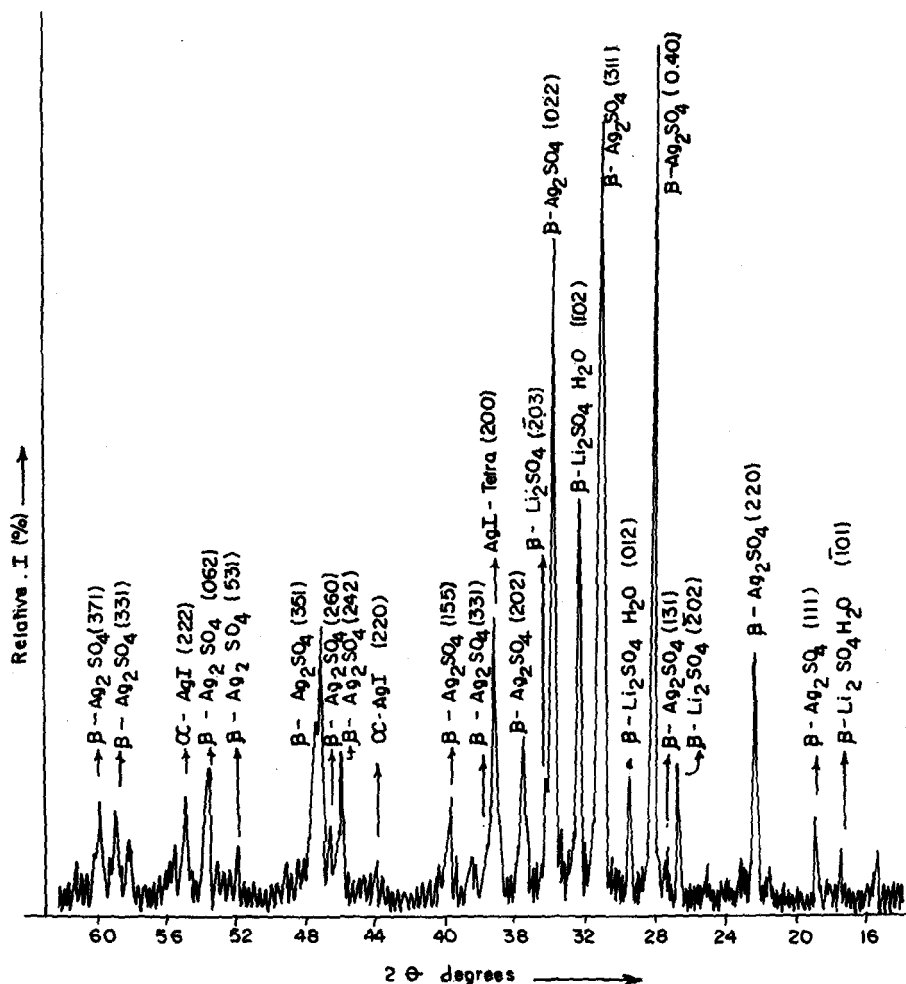


Fig. 1. X-ray diffraction pattern for a sample of Li_2SO_4 : Ag_2SO_4 :eutectic (26.25:61.25:12.5) at 25 °C.

is observed for the addition of eutectic beyond 12.5 mol%. These results can be explained in terms of the principles of dispersed-phase theory of composite electrolytes. Such materials (composite electrolytes) form a special class of heterogeneous solid systems with conductivities that are greater than those of the individual phases. Within the framework of the theory, it is widely accepted that the overall effect is a result of an enhanced conductivity along the interface between the matrix phase and the dispersoid particles, possibly through the formation of space-charge layers [7, 15, 16]. As mentioned above, the samples under study here are multiphase mixtures in which one of the phases possesses a high ionic conductivity. In order to

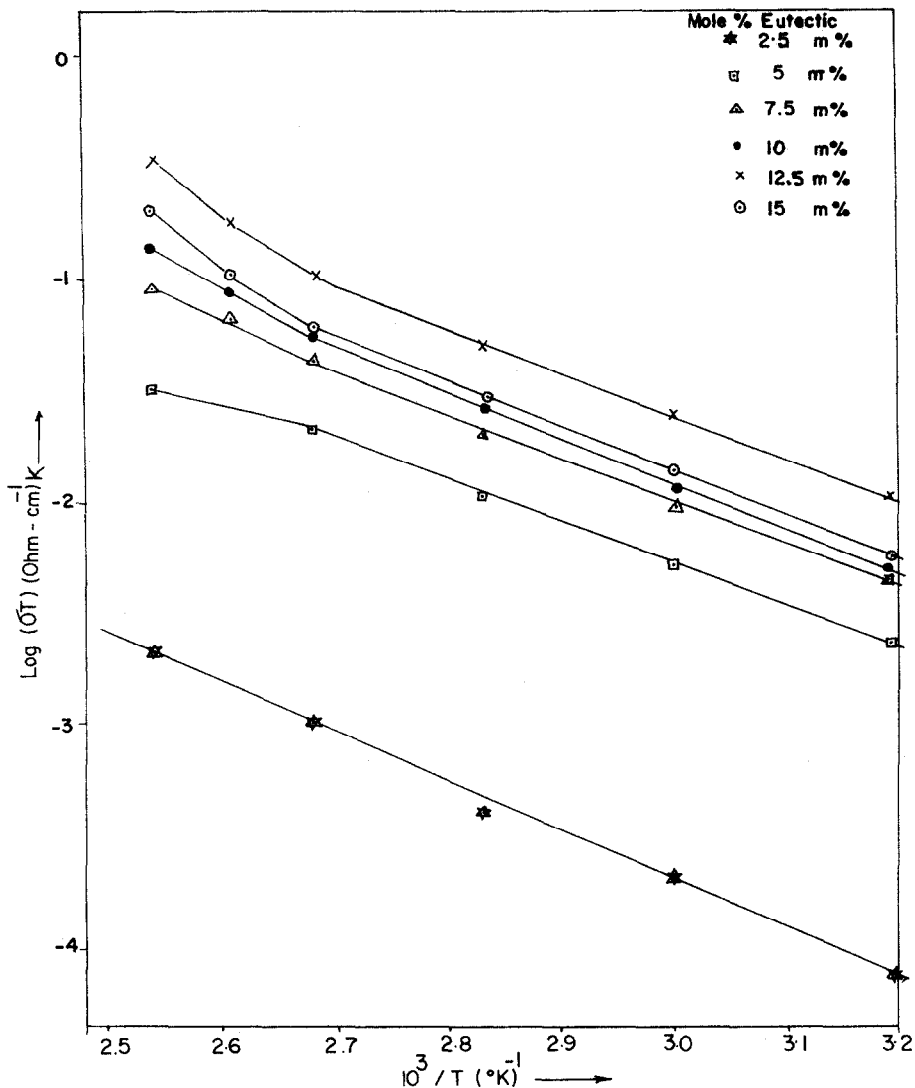


Fig. 2. Temperature dependence of conductivity for $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ with differing amounts of eutectic.

understand the nature of grain boundaries and their effect on the total conductivity, the samples were characterized by scanning electron microscopy.

Figure 4(a) and (b) shows the microstructure of the quenched $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ sample and the eutectic $\text{Ag}_2\text{SO}_4:\text{AgI}$ (48:52), respectively. It can be clearly seen that the eutectic mixture has a very fine crystallite size. Scanning electron microscopic analysis of the individual Li_2SO_4 and Ag_2SO_4 solids revealed that the grains of Li_2SO_4 were larger than those of Ag_2SO_4 . The $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ system is principally a heterogeneous mixture of inert phases of $\beta\text{-Li}_2\text{SO}_4$ and $\beta\text{-Ag}_2\text{SO}_4$, together

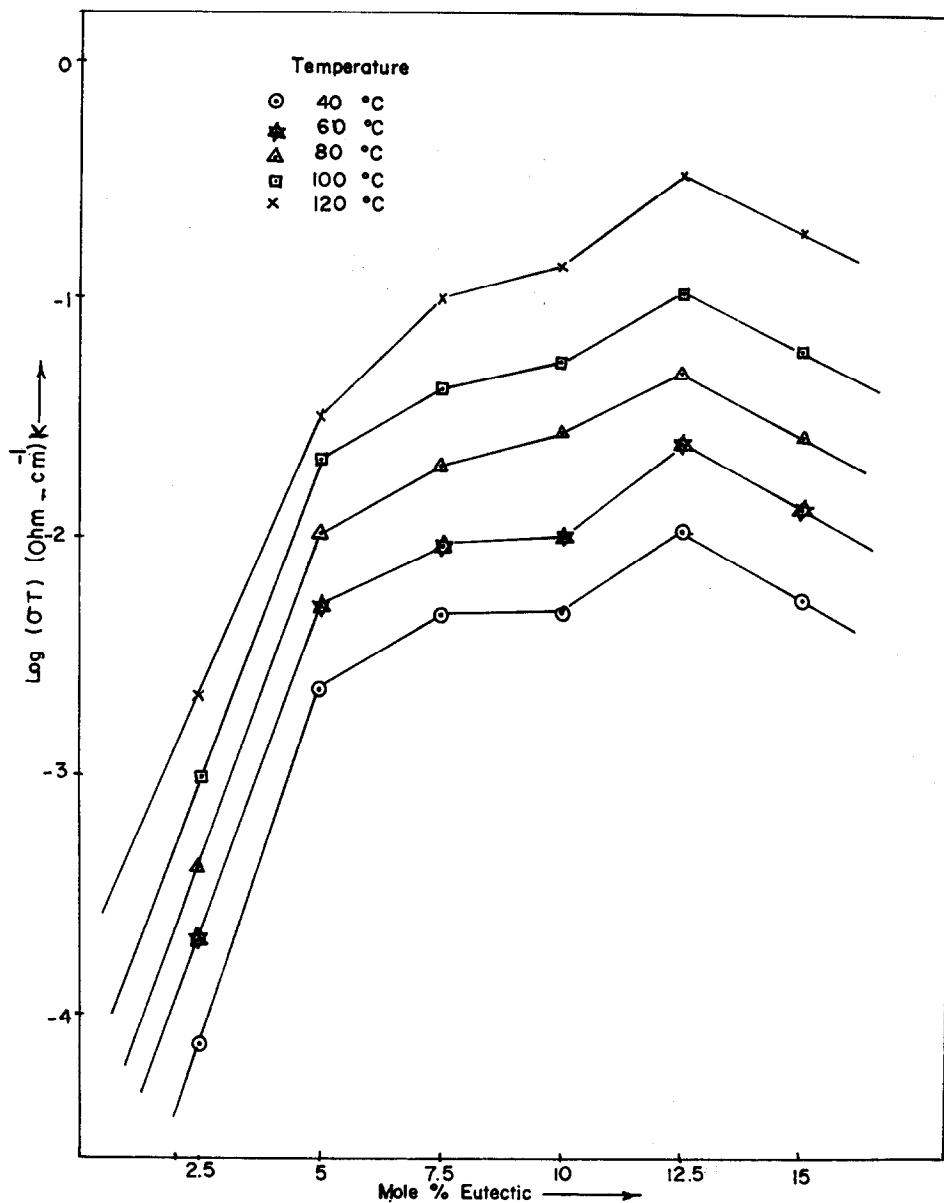


Fig. 3. Variation of conductivity with eutectic content at different temperatures.

with partially-trapped high temperature phases (bcc LiAgSO_4 and $\alpha\text{-Ag}_2\text{SO}_4$), as confirmed by X-ray diffraction [10]. The geometry of the Li_2SO_4 grains is elongated rather than spherical (Fig. 4(a)). This morphology is expected to provide a larger surface area of contact and thus to facilitate the contribution of grain boundaries towards the increase in conductivity. The mechanism of conductivity enhancement in the case of $\text{Ag}_2\text{SO}_4\text{:AgI}$ eutectic

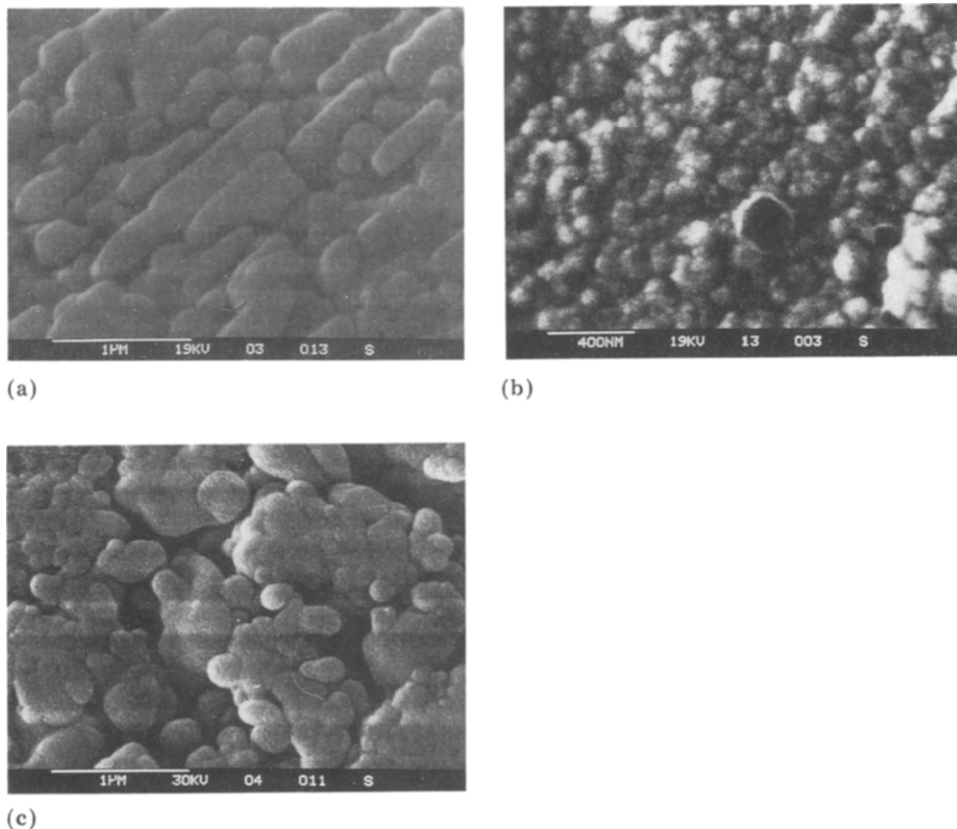


Fig. 4. Scanning electron micrographs of: (a) $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$; (b) $48\text{Ag}_2\text{SO}_4:52\text{AgI}$ eutectic; (c) $\text{Li}_2\text{SO}_4:\text{Ag}_2\text{SO}_4$: eutectic (61.25:26.25:12.5).

added to the $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ system appears to be similar to that reported for composite electrolytes of the type: $\text{AgI}:\text{AgBr}$ [17, 18] and $\text{Li}_2\text{SO}_4:\text{Li}_2\text{CO}_3$ [19]. More recently, Lunden *et al.* [20] have reported a similar type of conductivity behaviour in the $\text{Li}_2\text{SO}_4:\text{Ag}_2\text{SO}_4:\text{AgI}$ system.

In the above solid-electrolyte systems, the conductivity enhancement has been attributed to increased interfacial conduction in the region between the finely dispersed grains. In the case of $\text{Li}_2\text{SO}_4:\text{Ag}_2\text{SO}_4$:eutectic (61.25:26.25:12.5), the optimum dispersion (Fig. 4(c)) of very fine crystallites in the conducting matrix of $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ leads to a maximum in the conductivity (Fig. 3); the value is $2.2 \times 10^{-4} (\text{ohm cm})^{-1}$ at 100°C . The material possesses a fair stability on account of its low AgI content, and could possibly be used in novel types of technological devices.

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