

ELECTRICAL CONDUCTIVITY OF THE $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ SYSTEM

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Summary

With a view to improving the electrical conductivity of Li_2SO_4 at the lowest possible temperature, Li_2CO_3 was added in the ratios of 10 - 90 mol% and its conductivity was measured. The system $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ has its eutectic at a composition of 60:40 mol%: this composition has the maximum conductivity of the series, $2.43 \times 10^{-3} \text{ (ohm cm)}^{-1}$ at 723 K. The high conductivity may be due to the quasiliquid state of the mobile species within the sublattice. Further, the addition of 5 mol% of LiCl to the eutectic gave rise to an increase in the conductivity, $1.13 \times 10^{-3} \text{ (ohm cm)}^{-1}$ at 553 K. This may be suitable as an electrolyte for application to power sources.

Introduction

The current interest in solid electrolytes is, to a great extent, due to their possible application to power sources or other electrochemical devices.

The sulphate-based solid electrolytes differ in some respects from other solid electrolyte materials. A special advantage is that, many mono and divalent cations are especially mobile in f.c.c. and b.c.c. sulphate phases. This means that a number of metals can be used as the power source anode [1]. The conductivity phases develop through the first order phase transition with exceptionally high enthalpies of transformation, making the materials interesting for heat storage.

The electrical conductivity of Li_2SO_4 has been measured over the temperature range 848 - 1243 K [2]. The f.c.c. phase of Li_2SO_4 has been studied in great detail [3]. A disadvantage for many practical applications is that this phase is stable only above 848 K. There is therefore reason to investigate whether the conductivity below this temperature can be increased sufficiently by some treatment to allow the salt to be applied in power sources. Kvist *et al.* [4 - 7] have studied the conductivity of binary systems of Li_2SO_4 over the temperature range 773 - 1305 K. The electrical conductivity of the monoclinic phase of pure Li_2SO_4 has been studied over the range 550 - 848 K [8].

A low melting point is one of the important criteria indicating high ionic conductivity in solid electrolytes [9]. Previous workers have observed

premelting effects in the f.c.c. phase of silver chloride and silver bromide [10]. Friauf [11] has recently shown that all the observations involving conductivity and diffusion in the region just below the melting point may be explained as being due to an anomalous rise in the defect concentration caused by a general softening of the lattice.

Taking all the above facts into account, the present investigation is aimed at the production of a lithium sulphate-based material with a high ionic conductivity at the lowest possible temperature. With this in view, the electrical conductivity of the $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ system has been studied over the range 10 - 90 mol% Li_2CO_3 . All the measurements were carried out at 1 kHz, but the frequency dependence of the conductivity is probably small; for high conductivity sulphate systems it has been found to be only 0.1% in the range 1 - 25 kHz [12].

Experimental

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, A.R. (99% pure), as supplied by SISCO (INDIA) was dried at 573 K for 6 h. This was then subjected to a repetitive weighing and heating cycle to confirm that it was completely dry. 90:10; 70:30; 60:40; 50:50; 30:70 and 10:90 mol% mixtures of the well dried Li_2SO_4 and Li_2CO_3 (99% pure, Moscow, USSR) were weighed with an accuracy of 0.0001 g. Each mixture was ground thoroughly before heating and then maintained at 40 K above its melting point for 4 h to homogenize the melt. The melt was then quenched in an aluminium mould at room temperature. A pure Li_2CO_3 sample was similarly prepared.

The samples thus obtained were ground flat and polished. To obtain a good electrical contact, thin aluminium foils were used before loading the sample in the sample holder, described elsewhere [8]. The use of silver paint was discontinued due to its diffusion into the sample, which had been confirmed by X-ray examination. Neither could platinum paste be used as its firing temperature (above 1073 K) is much higher than the melting point of the system.

5 mol% of LiCl (99% pure obtained from Germany) was added to the eutectic composition of $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ and the samples were prepared in the manner described above.

The a.c. electrical conductivity was measured with a Universal impedance bridge, TF 2700 AIMIL (India), at 1 kHz with an accuracy of $\pm 2\%$ in the temperature range 510 - 788 K. The conductivity measurements were recorded during the cooling cycle.

Results and discussion

Figure 1 shows the plots of $\log(\sigma T)$ versus $10^3/T$ for different compositions of $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$ together with that for pure Li_2SO_4 and pure Li_2CO_3 .

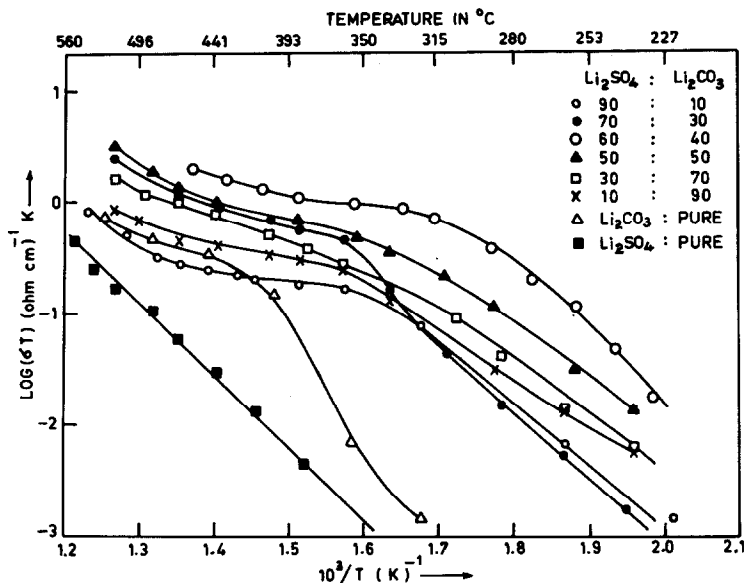


Fig. 1. Variation of the electrical conductivity of the Li_2SO_4 - Li_2CO_3 system with temperature.

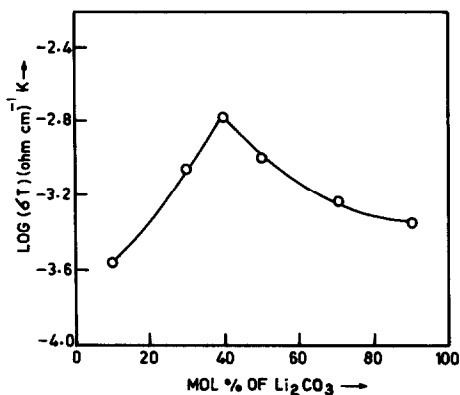


Fig. 2. Variation of electrical conductivity with mol% of Li_2CO_3 at 660 K.

In Fig. 2 the conductivity values at 660 K are plotted against Li_2CO_3 concentration. Both Figures indicate a maximum conductivity for the eutectic composition, the melting point of which is the minimum in the series [13].

The melting point of Li_2SO_4 is 1133 K and with the addition of Li_2CO_3 up to 40 mol%, *i.e.*, up to the eutectic composition, it decreases continuously. Beyond the eutectic composition, the melting point of the system increases continuously. The conductivity behaviour can be correlated with the melting points of the system; the lower the melting point the higher the conductivity, due to softening of the lattice. Similar behaviour has been reported in the case of the silver halides by Friauf [11].

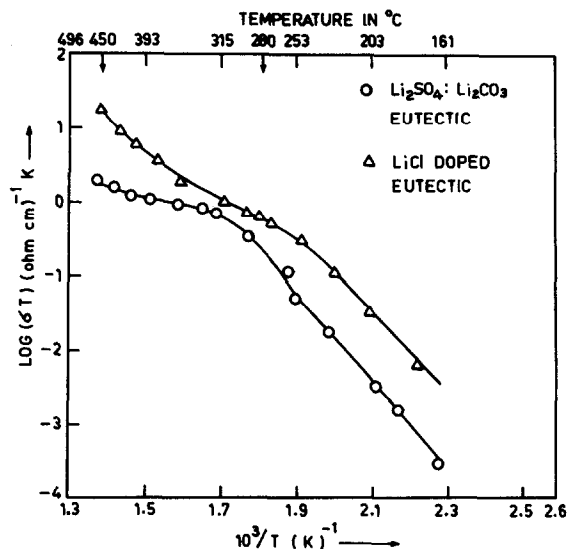


Fig. 3. Effect of LiCl addition on the electrical conductivity of the eutectic composition of Li_2SO_4 - Li_2CO_3 .

An almost constant conductivity plateau is observed in the Arrhenius plots of all the samples in Fig. 1. This is due to the presence of Li_2CO_3 which undergoes a phase transition at 683 K [14]. The presence of Li_2SO_4 may be the cause of a decrease in the phase transition temperature and, consequently, the change in curvature shifts to a lower temperature.

The anomalous behaviour of the Li_2SO_4 - Li_2CO_3 (70:30 mol%) sample below 593 K could be due to the presence of several phases, as these might not provide complete solid solubility in spite of the fact that both Li_2SO_4 and Li_2CO_3 are monoclinic.

Figure 3 shows the effect on the electrical conductivity of the addition of LiCl to the eutectic composition. When 5 mol% LiCl was added to the eutectic composition, the electrical conductivity was found to increase. The addition of the monovalent salt increases the number of cation vacancies which, in turn, enhances the conductivity. At 723 K the conductivity (2.52×10^{-2} (ohm cm)⁻¹) of the LiCl doped eutectic and that of Li_2SO_4 - Ag_2SO_4 (50:50 mol%), 6.1×10^{-2} (ohm cm)⁻¹, as reported by Kvist [15], are comparable.

Conclusion

The eutectic of Li_2SO_4 - Li_2CO_3 doped with 5 mol% LiCl has a high ionic conductivity (1.13×10^{-3} (ohm cm)⁻¹) at 553 K and may be suitable as an electrolyte material for an electrochemical power source.

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