

IONIC TRANSPORT STUDIES OF THE $\text{Li}_2\text{SO}_4\text{:Li}_2\text{CO}_3\text{:LiCl}$ SYSTEM*

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Summary

Two samples of $\text{Li}_2\text{SO}_4 \cdot \text{Li}_2\text{CO}_3 \cdot \text{LiCl}$, in the molar ratio of 57:38.5 have been prepared under different experimental conditions. One sample contained a dispersed second phase of Li_2CO_3 , the other Li_2O . These phases cause an enhancement in the conductivity compared with $\beta\text{-Li}_2\text{SO}_4$. The characteristics of cells with different electrode materials and $\text{Li}_2\text{SO}_4 \cdot \text{Li}_2\text{CO}_3 \cdot \text{LiCl}$ as the electrolyte have been examined.

Introduction

It is known that lithium sulphate crystallizes in a non-conducting monoclinic phase (β -phase) at room temperature, and in a highly conducting cubic phase beyond 575°C (α -phase) [1]. The existence of the latter phase in a stable form has stimulated interest in the application of lithium sulphate to power sources. In attempts [2 - 5] to improve the conductivity of monoclinic Li_2SO_4 , Li_2CO_3 was added in mol% ratios of 10 - 90 and the conductivity was measured at 1 kHz. An $\text{Li}_2\text{SO}_4 \cdot \text{Li}_2\text{CO}_3$ system with a composition of 60:40 mol% was found to exhibit the maximum conductivity, namely, $2.43 \times 10^{-3} (\Omega \text{ cm})^{-1}$ at 450°C . Further, the addition of 5 mol% LiCl to the eutectic increased the conductivity (σ) to $1.13 \times 10^{-3} (\Omega \text{ cm})^{-1}$ at 280°C . Such enhancement in the conductivity of monoclinic Li_2SO_4 has given rise to the possibility of using the material in power sources operating near ambient temperature. While the Arrhenius plot ($\log(\sigma T)$ versus $1000/T$) for undoped Li_2SO_4 was linear in the temperature range $250 - 550^\circ\text{C}$, an almost constant conductivity plateau was observed for the $\text{Li}_2\text{SO}_4 \cdot \text{Li}_2\text{CO}_3$ system between 300 and 400°C . The Arrhenius plot for the latter system could be separated into several regions of different activation energies. Such an observation is a typical characteristic of a divalent, ion-doped, ionically conducting, crystalline materials.

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In order to understand the origin of this behaviour of $\text{Li}_2\text{SO}_4 \cdot \text{Li}_2\text{CO}_3$, we have re-investigated this system by conducting impedance and modulus spectroscopic studies on samples prepared under different experimental conditions. It should be noted that earlier measurements on the system were limited to 1 kHz, and such a procedure is inadequate for separating interfacial and bulk conductivities.

Experimental

Powders of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (B.D.H., U.K.), Li_2CO_3 (E. Merck, F.R.G.) and LiCl (E. Merck, F.R.G.) were annealed at 300°C for 12 h, ground to a fine powder, and then mixed thoroughly in the mol% ratio 57.38.5. Two samples (I and II) with the same composition were prepared under different experimental conditions and studied at different temperatures.

Sample I was obtained by melting the above mixture of powders in a platinum crucible in open atmosphere, and then quenching to room temperature on a stainless-steel plate. The quenched material was annealed at 300°C in a vacuum furnace for 12 h and then pressed into a pellet. Sample II was prepared by melting the powder mixture under vacuum and then cooling to room temperature. Raman scattering studies revealed the presence of characteristic lines attributable to CO_3 in the spectra of sample I, but not sample II. Although no direct evidence for the presence of Li_2O in sample II could be obtained from Raman studies, the melting of Li_2CO_3 under vacuum is known to give rise to Li_2O [6].

Conductivity measurements were made over the temperature range $25 - 450^\circ\text{C}$ in a cell that was first evacuated and then continuously flushed with argon gas. Complex impedance investigations were conducted in the frequency (F) range 5 Hz - 10 MHz by analysing the amplitude and phase with a Hewlett-Packard model 3575A gain phase meter.

Open-circuit voltage measurements and battery characterization were carried out using a Keithley 614 electrometer. The cells were housed in a Teflon tube closed by two stainless-steel discs of 10 mm dia. and 5 mm thickness. Each cell consisted of $\text{Li}/\text{solid electrolyte}/\text{electrode}$, assembly was carried out in an argon-filled dry box to ensure the stability of lithium metal.

Results and discussion

Complex impedance data were obtained for both samples I and II at different temperatures, typical results for sample II are shown in Fig. 1. As the temperature is increased, it can be seen that all the depressed semicircles both shift to higher frequencies and decrease in size, resulting in a smaller intercept with the real axis. All the semicircles are followed by an

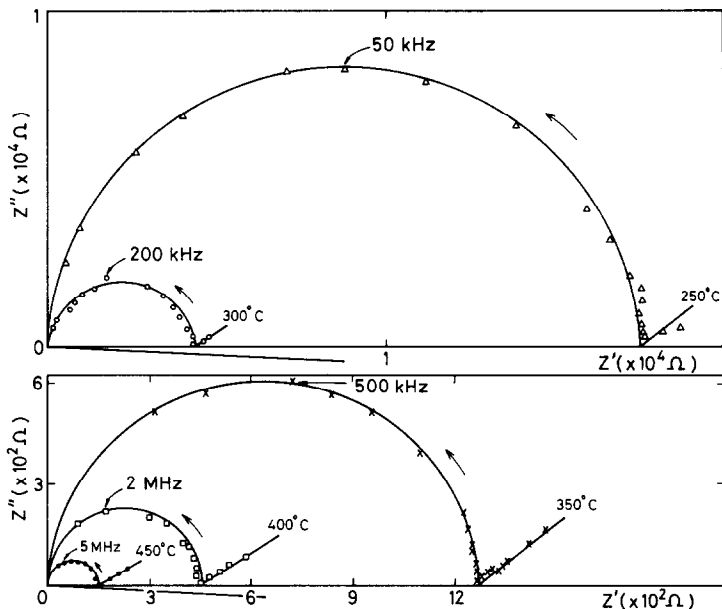


Fig 1 Impedance plots of Li_2SO_4 Li_2CO_3 LiCl system (sample II)

inclined straight line at lower frequencies. A similar trend was observed in the data for sample I.

The high-frequency and low-frequency arcs arise from bulk relaxation and interfacial effects, respectively. The high-frequency data are due to ionic migration through the bulk of the solid electrolyte and the intercept gives the true bulk resistance, excluding the electrode polarization. Conductivity data for samples I and II as a function of temperature are given in Fig. 2. Both samples I and II exhibit Arrhenius behaviour. Both the difference in conductivity between the two samples and the enhancement of the individual values compared with that for $\beta\text{-Li}_2\text{SO}_4$ (also shown in Fig. 2) can be attributed to the presence of Li_2CO_3 and Li_2O in samples I and II, respectively, as indicated by Raman studies. Sample I has a conductivity at 250°C of $1.73 \times 10^{-4} (\Omega \text{ cm})^{-1}$ with an activation energy of 0.9 eV , these values are comparable with those reported earlier [2]. By comparison, the conductivity of sample II at 450°C is $1.3 \times 10^{-3} (\Omega \text{ cm})^{-1}$.

Dielectric properties of the above samples have also been studied. A typical plot of $\log F$ versus $\log \epsilon'$ for sample II is given in Fig. 3. It can be seen that the dielectric constant (ϵ') has a small value at low temperatures where space-charge effects are absent. At low frequencies and high temperatures, ionic migration takes place and results in an increase in ϵ' by creation of space-charge layers at the electrodes. The value of ϵ' has been found to decrease with increase in frequency and become saturated at higher frequencies for both samples I and II. It is interesting to note that the ϵ' value becomes constant at relatively higher frequencies when the tempera-

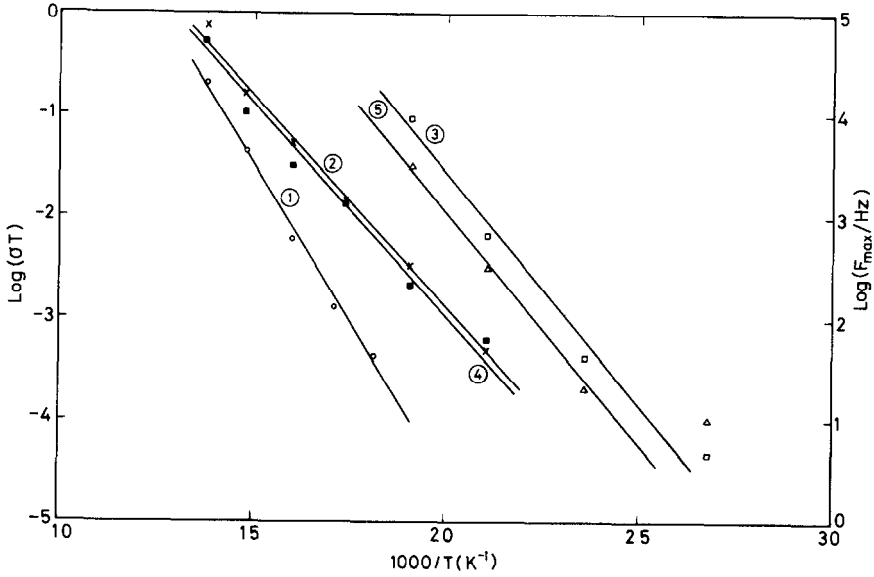


Fig 2 Arrhenius plots of Li_2SO_4 Li_2CO_3 LiCl system 1, β - Li_2SO_4 , 2, sample II, 3, sample I, 4, $\log F_{\text{max}}$ vs $1000/T$ (sample II), 5, $\log F_{\text{max}}$ vs $1000/T$ (sample I)

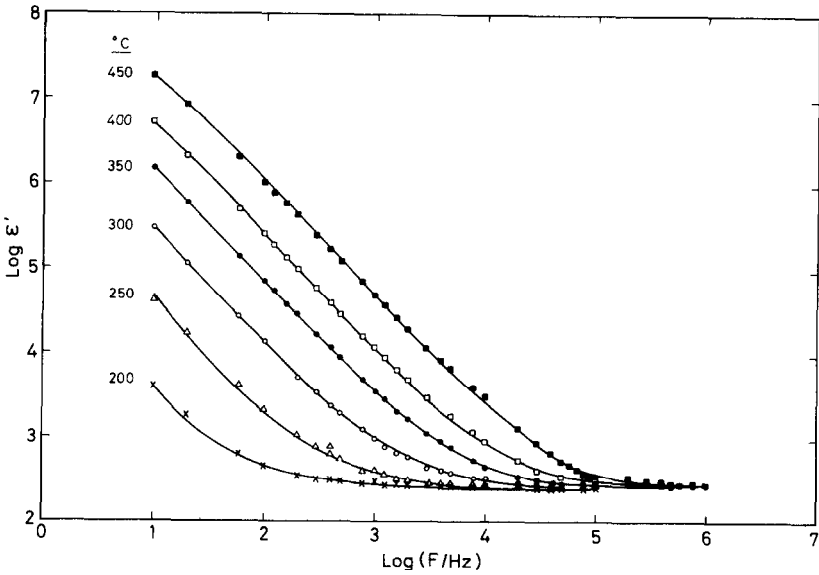


Fig 3 Plots of $\log \epsilon'$ vs $\log F$ for Li_2SO_4 Li_2CO_3 LiCl system (sample II) at different temperatures

ture is raised This may be due to the fact that, at high temperatures, the jump frequency of the mobile ion is large and resonates with the frequency of the applied electric field

The frequency dependence of the dielectric loss (ϵ'') or $\tan \delta$ for both the samples has been studied. Typical data for sample II are presented in Fig 4 The value of $\tan \delta$ increases with increase in frequency to yield a peak value. The position of this peak shifts to higher frequencies with increase in temperature Similar behaviour is exhibited by sample I However, a large uncertainty exists in determining the peak value of the $\tan \delta$ owing to the broad nature of the $\tan \delta$ versus $\log F$ curves. In materials with high ionic conductivity, the a.c dielectric loss is defined by

$$\epsilon''(\omega) = \frac{\sigma(\omega) - \sigma_{d.c.}}{\omega\epsilon_0} \text{ and } \tan \delta = \frac{\epsilon''}{\epsilon'}$$

where $\sigma(\omega)$ is the measured a.c. conductivity at a given frequency (ω); and $\sigma_{d.c.}$ is the d.c conductivity. Due to the proximity of $\sigma(\omega)$ and $\sigma_{d.c.}$, a large uncertainty exists in determining the position of the $\tan \delta$ peak. Hence, complex electric modulus ($M^* = M + jM''$) formalism, which has a definite advantage over complex permittivity ($\epsilon^* = (M^*)^{-1} = \epsilon' - j\epsilon''$) formalism, has been undertaken A plot of the complex modulus spectrum (M'' versus $\log F$) will suppress the grain boundary effects and will mainly reflect the bulk properties of the electrolyte

The complex modulus spectrum for samples I and II were obtained at different temperatures, the data for sample II are given in Fig 5 As expected, the $M''(\omega)$ peak is unambiguously defined The shapes of the peaks at different temperatures remain constant and the frequency (F_{\max}) corresponding to the maximum value of M'' (M_{\max}) shifts to a higher value A plot of $\log F_{\max}$ versus $1000/T$ (Fig 2) exhibits Arrhenius behaviour for

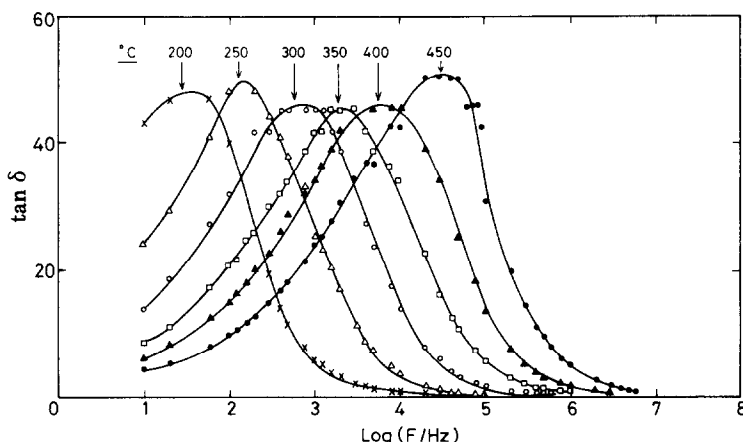


Fig 4 Plots of $\tan \delta$ vs $\log F$ for Li_2SO_4 Li_2CO_3 LiCl system (sample II) at different temperatures

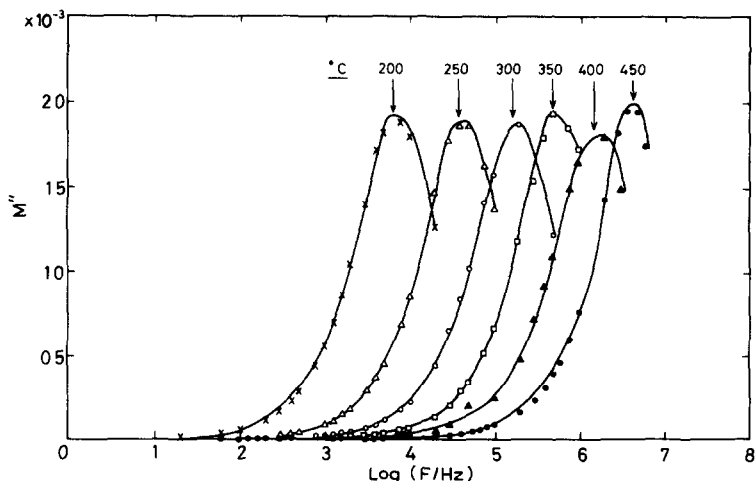


Fig 5 Plots of M'' vs $\log F$ for Li_2SO_4 Li_2CO_3 LiCl system (sample II) at different temperatures

both samples I and II. The activation energies calculated from the $\log F_{\max}$ versus $1000/T$ and $\log(\sigma T)$ versus $1000/T$ plots are comparable within experimental error. Comparison of both the peak maxima and the shape of $\log F$ versus M'' and $\log F$ versus Z'' curves reveals no substantial differences. This finding implies that the investigated samples are more akin to Debye-type solids which are usually described by a single parallel RC combination [7].

In order to study the suitability of Li_2SO_4 Li_2CO_3 LiCl as a solid electrolyte for battery purposes, the open-circuit voltages (OCVs) of four cells using the highly conducting mixture (*ie*, sample I) as solid electrolyte with different cathodes were measured at 20°C . The results are given in Table 1.

It is found that the experimentally measured OCVs are higher than the corresponding theoretical values [8] for cells 1 - 3. Since these experimental values are comparable with the theoretical voltage of lithium metal with

TABLE 1

Theoretical and measured open-circuit voltages for given cells (electrolyte Li_2SO_4 Li_2CO_3 LiCl)

Cell no	Configuration	Open-circuit voltage (V)	
		Theoretical	Measured
1	$\text{Li}/\text{electrolyte}/\text{AgI}, \text{Ag}$	2.089	2.9
2	$\text{Li}/\text{electrolyte}/\text{PbI}, \text{Pb}$	1.88	2.85
3	$\text{Li}/\text{electrolyte}/\text{CuI}, \text{Cu}$	2.06	2.8
4	$\text{Li}/\text{electrolyte}/\text{CuCl} + \text{Cu} + \text{LiCl}$	2.75	2.75

reference to iodine (I_2), which is about 2.9 V, it is probable that I_2 is formed at the cathode. While the OCVs of cells 1 - 3 do not remain stable for long periods, the OCV of cell 4 (Li/electrolyte/CuCl + Cu + LiCl) has been found to be stable at 2.75 V for several months. From a comparison of the measured and theoretical OCV of cell 4, it can be concluded that the electronic conductivity is negligible and that the ionic transport number is close to unity. Similar studies have been carried out using CuCl + Cu + LiCl as cathode and Li_2SO_4 Li_2CO_3 as electrolyte instead of Li_2SO_4 Li_2CO_3 - LiCl. The OCV was 2.75 V and remained stable for quite a long time.

The discharge characteristics of a cell comprising Li/electrolyte sample I/V_2O_5 has been studied at 100 °C. Current was drawn from the cell by connecting to a resistive load of 1 M Ω . The OCV was 3.52 V. After a discharge of about 8.5 min, the OCV fell to 2.8 V and then declined to 1 V in about 25 h.

Conclusion

The greater conductivity of samples I and II compared with undoped Li_2SO_4 has been attributed to the presence and effect of a second, dispersed phase of Li_2CO_3 or Li_2O . The frequency dependence of the dielectric constant has been explained on the basis of interfacial polarization of Li ions. The dielectric loss behaviour suggests the relaxation mechanism is of the Debye type. The activation energies calculated from impedance and modulus data are comparable. A study of the characteristics of cells using different cathode materials indicates that a CuCl + Cu + LiCl cathode is the most stable.

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