

Electrical conductivity and activation volume for α -Li₂SO₄

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The electrical conductivity of the solid electrolyte α -Li₂SO₄ is investigated for the temperature range 580–800 °C and for pressures up to 0.6 GPa. The migration enthalpy at normal pressure is 0.45 ± 0.05 eV, a somewhat larger value than that for most solid electrolytes. The migration volume is 0.5 – 0.6 cm³mole⁻¹. The small size of the lithium ion and the rotational freedom of the sulfate groups may be of importance for the ionic conductivity in α -Li₂SO₄.

The solid electrolyte (superionic conductor) α -Li₂SO₄, which is stable for temperatures between a first-order phase transition at 575 °C and the melting temperature 860 °C, has a very high ionic conductivity, up to $3 \Omega^{-1}\text{cm}^{-1}$ close to the melting temperature.¹ The structure of α -Li₂SO₄ is face-centered cubic (space lattice *Fm 3m*) with the sulfate ions situated at the origin and the oxygen ions rotationally disordered about the sulfur atom. The charge carriers are the highly mobile lithium ions which occupy the $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions in the lattice; it has also been suggested that the rotational freedom of the sulfate groups helps to facilitate the cation motion.^{2,3}

The migration enthalpy ΔH_m for a solid electrolyte can be determined from measurements of the temperature dependence of the ionic conductivity σ by the Arrhenius relation

$$\sigma T = (\sigma T)_0 \exp(-\Delta H_m/k_B T), \quad (1)$$

where T is the absolute temperature and k_B the Boltzmann constant. The activation volume ΔV can, in a similar way, be calculated from the pressure dependence of the ionic conductivity by

$$\Delta V = \Delta V_m = k_B T \left[\left(\frac{\partial \ln R}{\partial p} \right)_T + \kappa \gamma \right], \quad (2)$$

where ΔV_m is the migration volume, R is the sample resistance, p is the pressure, κ is the isothermal compressibility, and γ is the Grüneisen parameter. Both the temperature and the pressure dependences of the ionic conductivity have been found to be small for solid electrolytes.^{4–8} This leads to small values of ΔH_m and ΔV_m ; even negative values of ΔV_m have been found for some systems.⁶

The migration volume is most commonly associated with the lattice dilation caused by the migrating ion, although other interpretations of ΔV_m have been suggested.⁹ For β alumina it has been shown that the size of the mobile ion is related to the pressure dependence of the ionic conductivity. It was suggested that ions that are too small to fit into the voids that constitute the diffusion path will be attracted towards the sides of the passages.⁴ This leads to an increase of the conductivity with increasing pressure which, in turn, leads to a negative activation volume, provided that the $\kappa \gamma$ term in Eq. (2) is not too large.

In the present work the temperature and pressure dependences of the electrical conductivity of α -Li₂SO₄ were studied in the pressure range up to 0.6 GPa. The temperature of the α - β transition increases with increasing pressure,^{10,11}

but all measurements were well within the stability region of the superionic α phase. The α -Li₂SO₄ phase is of special interest because the small size of the lithium ion and the rotational freedom of the sulfate groups may influence the ionic conductivity.

The high-pressure system utilized purified argon gas as the pressure fluid. It, as well as the temperature measurement system, have been described earlier.¹² The lithium sulfate powder (stated to be 99.2% pure, C. T. Baker Chemicals, Deventer, Holland) was dried in air at 180 °C for 72 h before use. Two types of samples were used. The first type was cast in a cylindrical quartz mold, and two platinum-platinum 10% rhodium thermocouples inside the samples served both for the temperature measurement and as potential and current leads for four-wire impedance measurements. The resistance for this kind of sample was only a few ohms. The size of the sample had to be kept small since the temperature gradients inside an internally heated pressure cell can be considerable. In order to get a higher resistance, a second type of sample was used which consisted of a thin alumina tube which had been filled with molten Li₂SO₄. Two platinum wires, inserted from each end of the tube, served as electrodes. For this type of sample a platinum-platinum 10% rhodium thermocouple was attached to the middle of the alumina tube. This type of sample had a resistance of about 300 Ω . No difference could be found in the results using samples of the first or the second type. This ensures that samples enclosed in the alumina tubes were also exposed to the pressure in the high-pressure cell.

The impedance measurements were performed using a General Radio GR1608A impedance bridge and a Hewlett-Packard HP302A wave analyzer as a zero detection unit, a HP4262A inductance-capacitance-resistivity (LCR) meter and, for some measurements, a HP4275A LCR meter. The first instrument could be used only for two-wire measurements, while the last two were used with a four-wire technique. The sample resistance was determined from complex impedance plots.¹³ Since the cells had blocking electrodes, the complex impedance plots are expected to show a semi-circle and a straight line. Because of the limited frequency range used, only the straight line was detected in the present measurements (see Fig. 1), and the sample resistance was obtained from the intersection of the straight line and the real axis. The temperature dependence of the electrical conductivity was studied in the temperature range 580–800 °C at normal pressure; an example is shown in Fig. 2. Since the samples used did not allow an accurate deter-

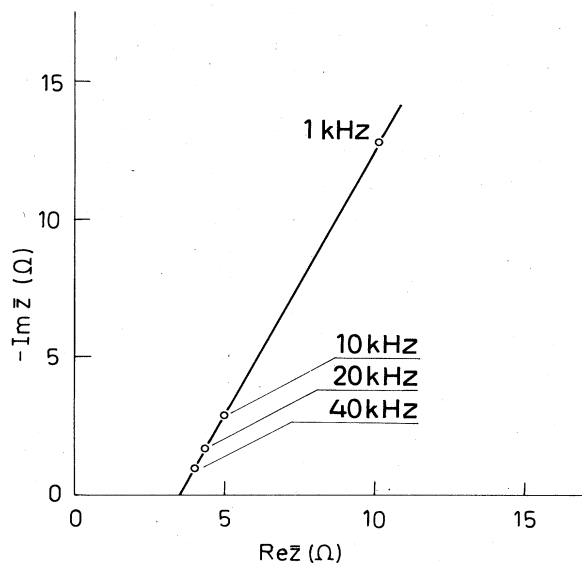


FIG. 1. Complex impedance plot of a Li_2SO_4 sample at 650°C and 0.60 GPa .

mination of the cell constant, $\ln(T/R)$ vs $1/T$, where R is the sample resistance, was plotted instead of $\ln(\sigma T)$ vs $1/T$. The average value of the migration enthalpy ΔH_m was found to be $0.45 \pm 0.05\text{ eV}$, in excellent agreement with the value $0.44 \pm 0.03\text{ eV}$ given by Kvist and Trolle.¹⁴ Those values are larger than the migration enthalpy determined from diffusion measurements, reported to be $0.34 \pm 0.04\text{ eV}$.¹⁴

The migration volume was calculated from Eq. (2) using the isothermal compressibility $\kappa = 5.82 \times 10^{-11}\text{ m}^3\text{N}^{-1}$ and the Grüneisen parameter $\gamma = 0.63$.^{15,16} An example of a $\ln(1/R)$ versus pressure plot is shown in Fig. 3. In the cal-

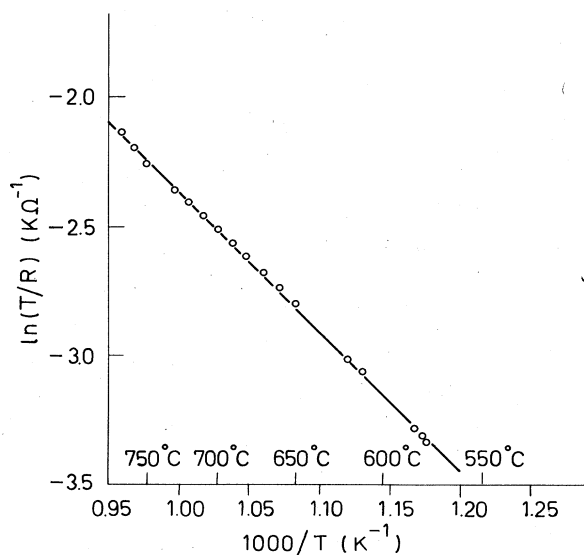


FIG. 2. Temperature dependence of $\ln(T/R)$ for $\alpha\text{-Li}_2\text{SO}_4$ at normal pressure.

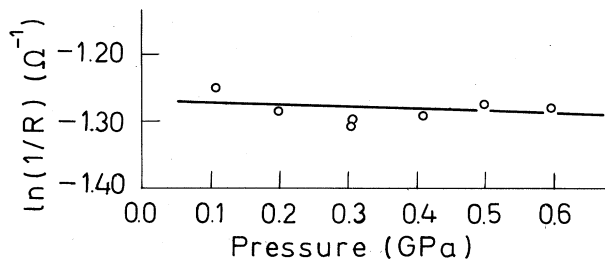


FIG. 3. Pressure dependence of $\ln(1/R)$ for $\alpha\text{-Li}_2\text{SO}_4$ at 650°C .

ulation of the migration volume the results for pressures below 0.15 GPa have been ignored because of the difficulties in maintaining a constant temperature in that pressure range. The estimated accuracy of the migration volume measurement is $\pm 0.4\text{ cm}^3\text{ mole}^{-1}$, and the calculated values are shown in Table I.

The migration enthalpy of $\alpha\text{-Li}_2\text{SO}_4$ is larger than that for other solid electrolytes such as, e.g., $\alpha\text{-AgI}$ which has a ΔH_m value of 0.098 eV .⁸ The migration volume of $\alpha\text{-Li}_2\text{SO}_4$ is, however, low, even lower than that for $\alpha\text{-AgI}$. This may indicate a good fit of the Li ions to the diffusion path, but the rotational freedom of the sulfate ions might influence both the migration enthalpy and the migration volume. Both values, however, are probably small enough to exclude the possibility of contributions caused by defect formation. The defects present thus appear to be intrinsic to the lattice, as commonly found for other solid electrolytes.

Measurements of the electrical conductivity permit calculation of the jump frequency ω for the Li ions, provided that a jump diffusion model is appropriate. The frequency is then

$$\omega = \frac{k_B \sigma T}{nq^2 a^2 \alpha} \quad (3)$$

where k_B is the Boltzmann constant, n the number of Li ions per unit of volume, q the charge of the Li ions, a the jump distance, and α a geometrical factor. Using $n = 8/b^3$, where b is the lattice constant, and $\alpha = \frac{1}{6}$, the jump frequency can be calculated if the jump distance is known. The actual diffusion path of the mobile lithium ions is, however, not known. A lithium ion jump between tetrahedral sites $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ via the octahedral site $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the sulfate ion sublattice would give a total jump distance of 6.14 \AA , since the distance between the tetrahedral and the octahedral site is 3.07 \AA . The direct distance between two adjacent tetrahedral sites is 3.55 \AA . (All

TABLE I. The migration volume of $\alpha\text{-Li}_2\text{SO}_4$.

Temperature ($^\circ\text{C}$)	$kT \frac{\partial \ln R}{\partial p}$ ($\text{cm}^3\text{ mole}^{-1}$)	$k_B T \kappa \gamma$ ($\text{cm}^3\text{ mole}^{-1}$)	ΔV_m ($\text{cm}^3\text{ mole}^{-1}$)
650	0.23	0.28	0.51
700	0.24	0.30	0.54
750	0.32	0.31	0.63

distances are calculated using the cell constant at 700 °C.¹⁶)

For the F⁻-ion diffusion in the solid electrolyte β -PbF₂ it has been suggested that the diffusion path between two tetrahedral sites is bent toward, but does not pass directly through, the octahedral site.¹⁷ Since the structure of α -Li₂SO₄ can be considered to be an antiferroite structure, a similar diffusion path might be possible, because the small lithium ions may avoid the large octahedral positions. In fact, the results of neutron diffraction measurements show no detectable lithium ion occupancy of the octahedral site.² In a low-frequency Raman scattering study, a jump distance of about 3.7 Å was suggested.¹⁸

A recent molecular-dynamics simulation study, however, indicates lithium ion diffusion via the octahedral sites¹⁹ and, as was pointed out by Nilsson *et al.*,² a low occupancy of the octahedral site cannot be excluded. Furthermore, if only direct jumps between tetrahedral sites take place, the number of available sites for the lithium ions is equal to the number of lithium ions; i.e., defects would have to be created in order to facilitate ion migration. However, as was mentioned earlier, contributions from defect formation could not be detected in the present results.

Jumps via interstitial sites other than the octahedral site

or clusters of interstitials, vacancies, and relaxed ions, as have sometimes been suggested for the fluorite structure solid electrolytes,²⁰ might also explain the conductivity for α -Li₂SO₄. However, in the present system, the rotational freedom of the sulfate groups may be a more important factor for the lithium ion migration.

From the present results it cannot be unambiguously determined which diffusion mechanism is dominant. It should, however, be noted that if jump distances of 3.07 and 3.55 Å are inserted in Eq. (3) together with literature data^{1,16} we derive jump frequencies of 1.99×10^{11} and 1.93×10^{11} s⁻¹ at 700 °C, which are of the same order-of-magnitude as the frequency of reorientation of the sulfate ions calculated from neutron diffraction² and Raman scattering measurements.²¹

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