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# Paddle Wheel Mechanism in Lithium Sulfates: Arguments in Defense and Evidence Against

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The "paddle wheel" mechanism proposed by Lundén *et al.* to account for fast cation conductivity in "rotator" phase $Li_2SO_4$-based compositions involves $SO_4$ rotation/reorientation where $SO_4$ propels passage of the cation. Existing literature results are collated and interpreted to show that these results cannot be reconciled to the paddle wheel mechanism. A number of factors are cited herein that can contribute to facilitating intersite mobility of cations in the enhancement of ionic conductivity. The experimental results support ionic transport in $Li_2SO_4$-based compositions, and other sulfate-based compositions (viz., $Na_2SO_4$, $Ag_2SO_4$) by a "percolation-type" mechanism where "free volume" in the lattice framework plays a predominant role. The rotating sulfate anions in $Li_2SO_4$-based compositions may contribute to the conductivity, not by direct coupling with the $Li^+$ cation but indirectly by increasing the probability of a successful translational jump when favorable instantaneous orientations of the $SO_4$ oxygens occur at the transport "bottleneck", i.e., acting as a gate. That is, the gate action of the percolation-type mechanism assigns a passive role for $SO_4$ rotation/reorientation in simply allowing passage of the cation with no transfer of momentum. The facility of $Li^+$ passage through a large bottleneck size of the highly supple lattice of $Li_2SO_4$ is also considered a contributing factor.

## Introduction

The "paddle wheel" mechanism as the primary basis for enhanced $Li^+$ ion conductivity in $Li_2SO_4$-based compositions, as promoted by Lundén and his associates, is understood to involve the anion-rotation-assisted movement of the cation strongly coupled to the rotational motion of the translationally static $SO_4^{2-}$ ions. In this model, the strong coupling of the cation migration to the $SO_4$ rotation implies that $SO_4$ propels and thereby assists passage of the cation.

A number of studies on alkali sulfate-based compositions, including $Li_2SO_4$, carried out in our laboratory have shown that the presence of larger ionic radius isovalent or aliovalent guest ions on their respective sublattices has enhanced cation conductivity (*1–12*). The experiments incorporating $WO_4^{2-}$ and $SiO_4^{4-}$ on the $SO_4^{2-}$ sublattice were especially critical. The presence of the larger $WO_4^{2-}$, with 1.5 times the moment of inertia of $SO_4^{2-}$ (where the rotation/reorientation frequency $\nu_{(rot)}$ of $XO_4$ group is inversely proportional to its moment of inertia, $I$), and the aliovalent $SiO_4^{4-}$, accommodated either by excess cations on interstitial sites or by vacancies on the $SO_4^{2-}$ sublattice to maintain electrical neutrality, would lead to lower conductivity if the paddle wheel mechanism were operative. Con-

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trary to expectation, in each case enhanced $Na^+$ and $Li^+$ ion conductivities by factors up to 10 were observed.

Recently, Lundén and Dissanayake (*13*) presented arguments in defense of the paddle wheel mechanism from two main aspects. First they question our experimental conductivity measurement technique and the nature of the sample. Second they appear to offer, as Lundén has in previous publications, arguments to support their position without adequate consideration of all the experimental evidence. Their paper fails to provide new experimental results that clearly demonstrate or validate the paddle wheel mechanism. This communication therefore is an effort to clarify a number of interpretations and arguments used in defense of the paddle wheel concept and to put into proper perspective experimental evidence that cannot be reconciled to the paddle wheel model, which these authors did not consider. Finally, the existing experimental results are interpreted in terms of a percolation-type or hopping mechanism of ion transport, where the rotational motion of the $SO_4$ anion could act as an ancillary passive gate for ion passage.

## Electrical Conductivity Measurements

Our ac conductivity measurements were carried out on both compressed ground-particle samples prepared under a pressure of ~15 MPa (~20 tons $cm^{-2}$) and on uncompressed solidified fused mass samples, 1 cm in diam. and 1–2 mm thickness. Both surfaces of the sample were touched with graphite (Dag No. 154 Acheson) to ensure proper contact. Each sample was placed between two polished Pt discs that acted as blocking electrodes. The sample plus Pt discs was installed and maintained by a spring-loaded support between two disc-shaped stainless-steel electrodes, 1.0 cm in diam., with stainless-steel leads. The conductivity was measured by two methods, after allowing the sample to remain in the cell ~15 hr at ~150°C under reduced pressure ~$10^{-3}$ Torr, at 1 kHz and 10 kHz as a function of temperature with a heating rate of 1°C $min^{-1}$. The first method was the null method using a GR 1608-A Impedance Bridge with manual recording, and the second method was continuous automatic recording with a GenRad 1688 LC Digibridge interfaced to an Apple IIe microcomputer and Epson PX-85 printer. The conductivity values for both sample types using both measurement methods vary by less than 10% and are independent of frequency within limits of experimental error. Our conductivity technique has been confirmed on samples of $Ag/RbSO_4$ compositions with $\sigma$ values in the same conductivity range as those of $Li_2SO_4$ in an argon atmosphere over the frequency 0.10 Hz–10.0 kHz in 10-Hz intervals, by a more sophisticated setup in an independent laboratory (*14*). Furthermore, the same technique was used by Saito *et al.* (*15*), Imanaka *et al.* (*16*), Dissanayake *et al.* (*17*), and Touboul *et al.* (*18*) on $Li_2SO_4$ compositions, and Mellander *et al.* (*19*) on single crystals of $LiNaSO_4$. All conductivity measurements in these independent laboratories agree with our measurements within experimental limits for the same temperature regions. What is especially important is the good agreement between our conductivity values on compressed discs and on fused mass samples of $LiNaSO_4$, and the recently measured value on a $LiNaSO_4$ single crystal by Mellander *et al.* (*19*).

The validity of the higher conductivity observed for our 10-mole% $Li_2WO_4$ in $Li_2SO_4$ compositions (*7, 11*) has been questioned on the basis that several phases may be present, including a "liquid" phase, in accordance with the published phase diagram (20). A more mobile liquid phase is expected to increase the conductivity to a maximum value at the supposed eutectic composition, viz., 67–68 mole% $Li_2SO_4$. Such is not the case, since the maximum conductivity occurs at 90 mole% $Li_2SO_4$ which, to our view, appears within the single-phase region of the originally reported phase diagram (*20*). It is further stated that "non-homogeneities" or heterogeneities, grain boundaries, two solid phases, etc., are responsible for the higher conductivity. In the recent study by Touboul *et al.* (*18*), cited by Lundén and Dissanayake (*13*), a decrease in conductivity is reported for the mixture of two solid phases in $Li_2SO_4$–$Li_3PO_4$. To attribute high conductivity in the $Li_2SO_4$–$Li_2WO_4$ to the presence of "two solid" phases without more adequate evidence is speculative. Furthermore, this can be a self-defeating argument if the presence of two solid is envisaged to disrupt the continuity and effectiveness of the supposed cation–anion coupled motion. Also, it should be pointed out that 80 mole% $Li_2WO_4$ in $Li_2SO_4$ composition at 575°C, i.e., on the $Li_2WO_4$-rich side of the phase diagram identified as a single solid phase I, gives rise to the same conductivity value as pure $Li_2SO_4$. This common feature is not surprising, in view of the higher conductivity by a factor 100 for the same 80 mole% $Li_2WO_4$ composition at 500°C reported by Dissanayake *et al.* (*17*). The most significant experimental fact is that $Li_2WO_4$ in its high temperature phase is reported to have the same conductivity value and same activation energy (*21*), within experimental error, as do the cubic rotator phase of $Li_2SO_4$ and $Li_3Na(SO_4)_2$, even though $Li_2WO_4$ is not known as a rotator phase.

Lundén further questions the variation in the experimentally measured conductivity values for $Li_2WO_4$ at 578°C (factor of 2) and for monoclinic $Li_2SO_4$ at 496 C (factor of 10) between our group and other research groups. He also contrasts our conductivity values with those values obtained in thesis studies at Göthenburg (factor of 70). The results of Touboul *et al.* (*18*) are lower than the Göthenburg values (factor 5), they differ from ours (factor 14), and show differences with the earlier values of Kimura and Greenblatt (*22*) on the same $Li_2SO_4$–$Li_3PO_4$ system. It is not uncommon to encounter considerable variations in ionic conductivity values for the same single crystal compound; e.g., $\sigma$ values for Na $\beta$-alumina range from 0.088 to 0.227 S cm$^{-1}$, using the ac technique (*23–25*). The variation and differences in solid state measured ionic conductivity values can originate with a number of factors, viz., component purity, nature of sample and method of preparation, cell and electrode material reactivity at high temperature (quartz versus noble metal), experimental technique, sample–electrode contact, capacitive and resistive anomalies, etc. It would appear therefore inappropriate to place undue emphasis on a single measurement of 2 mole% $Li_2WO_4$ with a 10% variation, considering the limits of experimental error in such conductivity values, and to use this measurement to refute one proposed mechanism and to defend another.

In concluding this topic, it should be clearly stated that we do not claim that our measured conductivity values are absolute values. We do, however, make a strong claim for internal consistency in all our measurements. [Our values have been checked independently by four different workers.] A similar claim of internal consistency was also made recently by Touboul *et al.* (*18*). The same consistent relative increases were observed in Lundén's laboratory as recorded by Ljungmark (*26*), using the U-cell method favored by Lundén, for 5 and 10 mole% $Li_2WO_4$ in $Li_2SO_4$, and for 5 and 10 mole% $Li_2MoO_4$ in $Li_2SO_4$ compositions, as presented in Fig. 1. It is to be noted that the activation energy for all four plots in the rotator phase region is 0.45 ± 0.04 eV. One might have expected that two phase presence with an active role by grain boundaries or mobile liquid in enhancing the conductivity as speculated (*13*) would be accompanied by a lower activation energy for the anion-substituted $Li_2SO_4$. Therefore, these very important experimental facts, viz., (i) the same $Li^+$ conductivity and same activation energy in the nonrotator $Li_2WO_4$; (ii) the increase in $Li^+$ conductivity with the same activation energy for $Li_2SO_4$–$Li_2WO_4$ and $Li_2SO_4$–$Li_2MoO_4$ compositions relative to pure $Li_2SO_4$; (iii) the higher $Li^+$ conductivity in the single phase $Li_2WO_4$-rich region of the $Li_2SO_4$–$Li_2WO_4$ system; and (iv) the higher $Li^+$ conductivity in $LiNaSO_4$ with 3.5 mole% $SiO_4^{4-}$ relative to pure $LiNaSO_4$, in both compressed disc and uncompressed solidified fused mass samples, cannot be reconciled to the paddle wheel mechanism of cation transport.

## Paddle Wheel Mechanism

### *A. Arguments in Defense*

An intensive literature search and personal communications with Lundén have uncovered no primary experimental evidence for the proposed paddle wheel mechanism, but only secondary arguments related to physical and structural properties. That is, the high conductivity observed in the high temperature of $Li_2SO_4$-based compositions is associated with a high degree of oxygen disorder, along with a high enthalpy of transition relative to the enthalpy of fusion. These facts suggested a premelting process with rapid rotational reordering of the tetrahedral $SO_4$ groups.

Neutron powder diffraction data for $Li_2SO_4$ at 908 K (*27, 28*) have been interpreted to show that $Li^+$ ions occupy a statistical distribution of sites instantaneously displaced in short-range correlation with the instantaneous orientations of the surrounding $SO_4^{2-}$ ions. It is concluded that the rotating $SO_4$ groups represent a superposition of a large number of different instantaneous $SO_4$ orientations, each coupled in a cooperative way to the motion of the $Li^+$ ions and of the $SO_4$ groups in its immediate vicinity. Brillouin scattering studies on fcc $Li_2SO_4$ yielded a low elastic wave velocity of the transverse mode in the ⟨110⟩ direction.

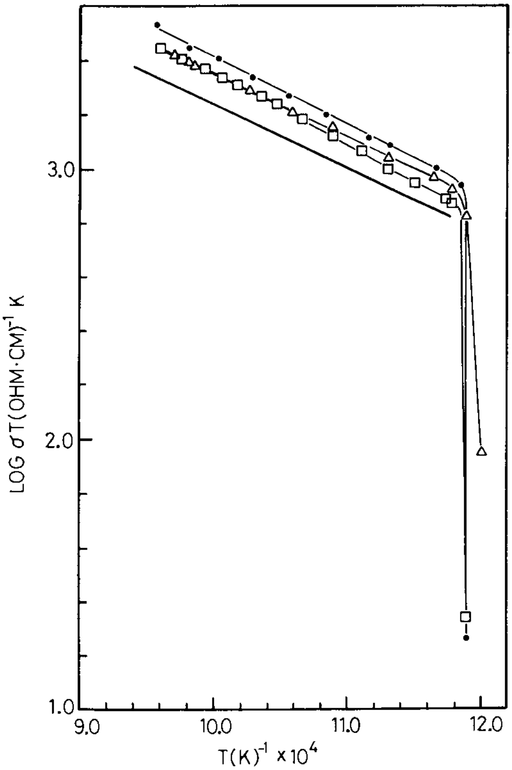

FIG. 1. Plots of log $\sigma T$ versus $T(K)^{-1}$ of ——, pure $Li_2SO_4$; △, 5 mole% $Li_2/WO_4$ in $Li_2SO_4$; ●, 10 mole% $Li_2WO_4$ in $Li_2SO_4$; □, 5 mole% $Li_2MoO_4$ in $Li_2SO_4$ (Ref. (*26*)).

This result was interpreted as indirect support for the rotation–translational coupling, i.e., an interaction between transverse mode oscillations and the reorientations of the $SO_4^{2-}$ ion (*29–31*).

Lundén and associates (*32–35*) have invoked and stressed the large difference between the transition enthalpy of rotator phase $Li_2SO_4$-based compounds and their respective enthalpy of fusion, in contrast to the nonrotator phase compounds, to support the paddle wheel mechanism. It was pointed out (*36*) and later recognized by Lundén and Thomas (*34*) that since the rotational motion of $SO_4$ groups gives rise to oxygen disorder, a more representative

TABLE I

A COMPARISON OF RELEVANT THERMODYNAMIC AND KINETIC PROPERTIES FOR FAST ION CONDUCTING COMPOUNDS

| Salt | $T_t$(K) | $\Delta H_t$ (kJ mole$^{-1}$) | $\Delta S_t$ (J mole$^{-1}$ · K$^{-1}$) | $\sigma$(S · cm$^{-1}$) at 823K | $Q(\sigma T)$ (eV) | $Q(D)$ (eV) | $Q(\Delta\nu)$ (eV) | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Li_2SO_4$[a] | 850 | 24.8 | 29.1 | 0.86 | 0.43 | 0.34 | 0.40 | (*30, 33, 39*) |
| $LiNaSO_4$[a] | 791 | 24.7 | 31.2 | 0.93 | 0.44 | 0.63 | 0.86 | (*30, 33, 34, 55*) |
| $LiAgSO_4$[a] | 728 | 34.3 | 47.1 | 1.17 | 0.40 | 0.52 | 0.72 | (*30, 39*) |
| $Li_{1.33}Zn_{0.33}SO_4$[a] | 755 | 25.2 | 33.4 | 1.00 | 0.36 | 0.19 | | (*30, 33*) |
| $Na_2SO_4$[b] | 520 | 11.6 | 22.5 | 0.0007 | 0.47 | | | (*2, 3, 49, 50*) |
| $Ag_2SO_4$[b] | 693 | 17.0 | 24.5 | 0.02 | 0.49 | | | (*3*) |
| AgI[b] | 420 | 6.2 | 14.7 | 2.62 | 0.11 | | | (*33*) |
| $Li_2CdCl_4$[b] | 620 | | | 1.6[c] | 0.37 | | | (*51, 52*) |
| $Li_2MnClb_4$[b] | 630 | | | 1.1[c] | 0.45 | | | (*51*) |
| $Li_2MgCl_4$[b] | 630 | | | 1.0[c] | 0.46 | | | (*51*) |
| $Li_3N$[b] | | | | 1.0[c]<br>0.8[c] | 0.30<br>0.49 | | | (*52, 53*) |

*Note*. $T_t$ transition temperature, $\Delta H_t$ transition enthalpy, $\Delta S_t$ transition entropy, $\sigma$ ionic conductivity, $Q(\sigma T)$ activation energy from conductivity data, $Q(D)$ activation energy fromLi$^+$ diffusion data, $Q(\Delta\nu)$ activation energy from rotational bandwidth data.

[a] Rotator phases.

[b] Nonrotator phases.

[c] Extrapolated values from 773 K.

property for comparison is the entropy of transition for rotator and nonrotator phases. Table I provides the relevant thermodynamic and kinetic data for fast conducting sulfates, $Li_2MCl_4$ spinels, $Li_3N$ and AgI. It is evident that there is no correlation between $\Delta S_t$ values and $\sigma$ values, and that the activation energies Q($\sigma$T) for all sulfates both rotator and nonrotator phases, except $Li_{1.33}Zn_{0.33}SO_4$, are effectively constant within limits, i.e., 0.44 ± 0.04 eV. It is to be noted also that the nonrotators, $Na_2SO_4$ and $Ag_2SO_4$, have $\Delta S_t$ values comparable to that of the prototype rotator $Li_2SO_4$. Furthermore, some nonrotators have conductivity $\sigma$ values equal to or greater than those for $Li_2SO_4$-based compositions. The evident correlation between the increase in conductivity with the larger ionic radius of the guest ion, i.e., $r_{Na^+} = 116$ pm, $r_{Ag^+} = 129$ pm (CN = 6), is consistent with lattice expansion and increase in free volumes.

Recently, Lundén (*37*) invoked the higher cation diffusion for $Li_2SO_4$-based compounds linking high cation mobility with high conductivity in support of the paddle-wheel model. The cation diffusion coefficients *D*, determined by tracer techniques, for a number of fast conducting $Li^+$- and $Ag^+$-bearing compounds are given in Table II. We note the tabulated *D* values do not show any clear distinctive feature for $Li_2SO_4$ rotator phases relative to nonrotator phase compounds. Furthermore, we note the *D* values for $Li_2SO_4$-based compounds are inversely related to their respective conduc-

TABLE II

DIFFUSION COEFFICIENTS FOR $Li^+$ AND $Ag^+$ in Some Fast Ion Conductors

| Salt | Temp (°C) | $D$(cm$^2$s$^{-1}$) × 10$^5$ | Ref. |
|---|---|---|---|
| $Li_2SO_4$ | 550 | 1.59 | (*30, 54*) |
| $LiNaSO_4$ | 550 | $Li^+$ 1.00<br>$Na^+$ 0.93 | (*30, 54*) |
| $LiAgSO_4$ | 550 | $Li^+$ 1.03<br>$Ag^+$ 1.00 | (*30, 54*) |
| $Li_{1.33}Zn_{0.33}SO_4$ | 550 | $Li^+$ 1.30<br>$Zn^{2+}$ 0.14 | (*30*) |
| $\alpha$-AgI | 200 | 1.76 | (*52*) |
| $\alpha$-$RbAg_4I_5$ | 25 | 1.75 | (*52*) |

tivity $\sigma$ values in Table I, and the nonrotator $Ag^+$ compounds show comparable and higher diffusion coefficients than the $Li_2SO_4$-based compounds.

In summary, the structural studies show only that $SO_4$ rotational motion occurs in $Li_2SO_4$. These studies do not provide clear-cut evidence that $Li^+$ translational motion is strongly coupled to the rotational motion, i.e., to the paddle wheel mechanism of ion transport. Furthermore, the so-called rotator phase $Li_2SO_4$-based compositions do not exhibit distinctive correlations either with respect to $\Delta S_t$ or with $\sigma$ and $D$ values, when compared to nonrotator phases.

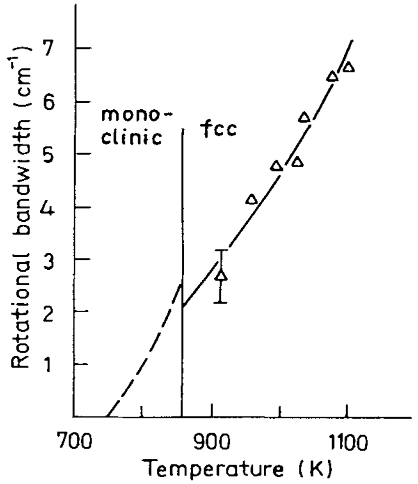

FIG. 2. Reorientation broadening versus temperature in the monoclinic phase and the fcc rotator phase of $Li_2SO_4$ (Ref. (*39*)).

### *B. Evidence Against or Failure to Support the Mechanism*

Frech and Cazzanelli (*38*) studied the band-width of the 92 $cm^{-1}$ librational mode of the $SO_4$ group in $Li_2SO_4$ using a discriminating Raman spectroscopic analytical technique. Plots of the logarithmic bandwidth of the 92 $cm^{-1}$ mode versus $1/T$, and of log conductivity $\sigma$ for the $Li^+$ ion versus $1/T$ reported earlier (*26*), failed to show any meaningful correlation with regard to the jump in conductivity and the bandwidth break, their respective transition temperatures, or their activation energies over the critical temperature region. Börjesson and Torell (*39*) extended the temperature range of this study in an attempt to separate the component of $SO_4$ reorientation from the symmetric $A_1$ sulfate internal mode, by comparison of polarized and depolarized spectral bandwidths. The plot of the rotational bandwidth versus temperature, Fig. 2, shows that the excess broadening in the low temperature monoclinic phase joins monotonically to that of the high temperature cubic phase. Figure 2 shows once again the failure to observe any parallel discontinuity in the bandwidth–temperature behavior to correlate with the observed discontinuity in the conductivity–temperature at 575°C. That is, the transition of $Li_2SO_4$ from the monoclinic to the cubic plastic phase occurs as a sharp first order transition at 575°C, with a concomitant sharp jump in $Li^+$ ion conductivity, but the reorientational motion in the $SO_4$ ion sublattice becomes significant in the monoclinic phase at 450°C and continues monotonically up to 800°C. One would have expected a sharp discontinuity in the bandwidth–temperature behavior to occur near the phase transition temperature. This correlation of conductivity–temperature jump with bandwidth–temperature discontinuity was observed for other superionic conductors (*40*).

The pronounced difference observed by Börjesson and Torell regarding $SO_4$ rotations between fcc $Li_2SO_4$ and hexagonal $Na_2SO_4$ is not relevant to the paddle wheel mechanism, which involves strong rotation–transport coupling between $SO_4^{2-}$ and $Li^+$. The crucial fact is that Raman studies did not provide evidence for such coupling. Börjesson and Torell also report a significant dispartiy between the activation energies for $SO_4^{2-}$ rotation/reorientation in fcc $Li_2SO_4$ and bcc $LiAgSO_4$ (0.40 and 0.72 eV, respectively) and the activation energies for cation diffusion (0.34 and 0.52 eV, respectively), shown in Table I. If there were coupling between the reorientations of the $SO_4^{2-}$ ions and the diffusing cations, one would have expected the activation energies to be very similar.

A recent study by Mellander and Lazarus (*41*) on the dependence of $Li^+$ ion conductivity in the plastic phase of $Li_2SO_4$ at 650°C as a function of pressure showed a meaningful decrease in conductivity for pressures up to 0.6 GPa. From their data they calculated the jump frequency to be $2 \times 10^{11}$ $sec^{-1}$ at 700°C, whereas the librational mode for $SO_4^{2-}$ corresponds to $27.6 \times 10^{11}$ $sec^{-1}$ this leads to a jump to rotation ratio of $7 \times 10^{-2}$.

A theoretical analysis using a rigid ion model to test for $Li^+$ ion–sulfate ion coupling in plastic phase $Li_2SO_4$ was carried out by means of constant pressure molecular dynamics (*42*). This analysis revealed that, in a given simulation, only one unequivocal example of a "knock-on" in a 1000 occurred, i.e., a ratio of $1 \times 10^{-3}$ prevails.

In summary, independent structural and dynamical studies have failed to provide primary experimental support for the paddle wheel model of ion transport in $Li_2SO_4$.

## Percolation-type Mechanism

To postulate a mechanism for ion transport in a solid, one must consider the various factors that can affect intersite mobility, viz., crystal structure and lattice disorder, number of activated mobile ions, ion–ion interactions, vibration amplitudes of nonparticipating ions, lattice free volume, number of occupancy sites, accessibility of empty sites to mobile ions, intersite bottleneck size, lattice compressibility or resiliency, etc.

TABLE III

CONDUCTIVITY VALUES FOR SOME $Li_2SO_4$–$Na_2SO_4$ COMPOSITIONS[a]

| Composition | log $\sigma T$($T$ = 470°C) | log $\sigma T$($T$ = 395°C) |
|---|---|---|
| $Na_2SO_4$ | −1.00 | −1.40 |
| 0.90 $Na_2SO_4$ : 0.10 $Li_2SO_4$ | −0.40 | −0.83 |
| 0.80 $Na_2SO_4$ : 0.20 $Li_2SO_4$ | −0.34 | −0.84 |

*Note.* $T$ = 470°C, *one-phase* region; $T$ = 395°C, *two-phase* region.

[a] Taken from B.Sc. thesis of R. Samson (1987).

The qualitative resemblance of the log conductivity $\sigma$ versus $T^{-1}$ plot with its sharp jump at the phase transition for $Li_2SO_4$, $Na_2SO_4$, $Ag_2SO_4$, $K_2SO_4$, AgI, to the site percolation probability function, i.e., to the $P(p)$ plot (*43*), provides evidence for the relevance of the percolation model for ion transport in these compounds. The jump in conductivity at the transition is accompanied by a molar volume expansion, i.e., $\Delta V/V$ of 3 to 4.5% for $Li_2SO_4$, $Na_2SO_4$, and $Ag_2SO_4$, which immediately suggests, *ceteris paribus*, a primary role for structural free volume in this behavior. Experimental correlations between enhanced ion conductivity data and ionic radius of isovalent guest ions, as well as the percentage of volume increase, have appeared in an earlier report (*9*). Recently, Dissanayake *et al.* (*17*) interpreted their higher conductivity values for $Li_2SO_4$–$Li_2WO_4$ compositions in terms of the larger $WO_4^{2-}$ giving rise to more interstitial space for $Li^+$ ion migration. Similarly, the higher conductivity values for $Li_2SO_4$–$Na_2SO_4$ compositions in the $Na_2SO_4$-rich single phase region of phase diagram (*44*), given in Table III, are consistent with more interstitial space free volume for facility of movement provided to the smaller radius $Li^+$ ion by the fixed $SO_4$ sublattice of the hexagonal structure $Na_2SO_4$. The same $\Delta\log(\sigma T)$–$\Delta V\%$ dependence is observed with glass and crystal phases of $Na_4UO_2(SO_4)_3$, where the glass molar volume is larger by ~7% (*12*). Angell has shown the corollary of this conductivity–volume expansion relationship by computer simulation studies on glass electrolytes, where a reduction in free volume and space available for ionic mobility leads to lower conductivity (*45*). The decrease in conductivity with increased pressure at constant temperature, i.e., decrease in free volume as reported by Mellander and Lazarus (*41*) for fcc $Li_2SO_4$ parallels the computer simulation result for glass electrolytes.

Touboul *et al.* (*18*) interpreted their lower conductivity values for the $Li_2SO_4$–$Li_3PO_4$ system as "strong proof" of the paddle wheel mechanism. Taking P–O and S–O bond distances as 152 pm and 149 pm in their respective tetrahedra, one calculates the moment of inertia ratio $I_{(PO_4)}/I_{(SO_4)}$ to be 1.04—an insignificant effect on the rotation frequency, where $\nu_{(rot)}$ = constant × $I^{-1}$. However, the incorporation of $PO_4^{3-}$ on the $SO_4^{2-}$ sublattice with interstitial $Li^+$, which was suggested to maintain electroneutrality in the absence of $SO_4^{2-}$ vacancies, is equivalent to an increase in lattice density or a decrease in free volume resulting in the observed drop in conductivity, as expected (*41, 45*).

The results and discussion herein favor ion transport by a percolation-type mechanism where ion mobility is enhanced by a more open structural framework or larger free volume. The analogy of the percolation model still leaves unanswered the question of whether other factors contribute to ion passage through the bottleneck separating two available sites. In the case of the cubic $Li_2SO_4$-based rotator compositions, the rotational motion of the $SO_4$ group and the compressibility of the lattice appear prominent. $SO_4^{2-}$ rotation can facilitate passage of $Li^+$ ion through the bottleneck by providing an energetically favorable orientation, as suggested by Cava (*46*), which recently received qualified support with model calculations by Frech (*47*). That is, $SO_4^{2-}$ would act as a gate for $Li^+$ passage—open in favorable orientation, but closed in unfavorable orientation. [The "gate" function bears no similarity to the paddle wheel action proposed by Lundén]. The efficiency of the "open" orientation will be highest, i.e., maximum contribution to $Li^+$, when the jump frequency of $Li^+$ is matched or synchronized with the $SO_4^{2-}$ rotation frequency. The ratio of rotation frequency to $Li^+$ jump frequency drops from ~14 to ~9 when $SO_4^{2-}$ is replaced by $WO_4^{2-}$ or $MoO_4^{2-}$ in $Li_2SO_4$, thereby increasing the $Li^+$ conductivity as observed (*7, 26*). The gate concept is also consistent with the unusually high conductivity and very low activation energy observed when $SiO_4^{4-}$ is incorporated in $LiNaSO_4$ with accompanying $SO_4^{2-}$ vacancies on its sublattice. These vacancies represent a permanent "open" gate condition.

A comparison of the reported isothermal compressibilities of $Li_2SO_4$ (*41*) and NASICON (*48*) shows that $\kappa_T(Li_2SO_4)/\kappa_T$ (NASICON) = 25; i.e., $Li_2SO_4$ is more compressible or deformable by a factor of 25 relative to NASICON. Another salient property relating to ion dynamics is activation volume $\Delta V^*$, which is a measure of the volume change or lattice expansion as the mobile ion passes through the transport bottleneck. The $Li_2SO_4$ to NASICON activation volume ratio is 0.2, i.e., $\Delta V^*$ ($Li_2SO_4$)/ $\Delta V^*$ (NASICON) (*41, 48*). That is, a low $\Delta V^*$ implies a large bottleneck size with easy transport of $Li^+$ ion resulting in a high conductivity $\sigma$. These properties are compatible with the high conductivity of $Li_2SO_4$ relative to other compounds without invoking paddle wheel action.

## Summary

Experimental work to date, based on structural and ion dynamics studies in attempts to provide explicit support for the paddle wheel model of ion transport, have been unsuccessful. On the other hand, ion conductivity–temperature measurements on pure sulfates and on analogous sulfates incorporating isovalent or aliovalent guest anions show a definite qualitative resemblance to the percolation model of ion transport with free volume shown to play a predominant role; i.e., higher volume enhances the conductivity. The energetically favorable orientation provided by the rotation of $SO_4^{2-}$ in rotator compositions, i.e., open gate configuration, and the ease of cation passage through a large bottleneck size of a highly supple lattice are presented as contributing or determining factors.

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*Note added in proof.* Lundén has provided me with a photocopy of galley proofs of a study by M. A. K. L. Dissanayake, M. A. Careem, P. W. S. K. Bandaranayake, and C. N. Wijayasekera [*Solid State Ionics* **47** (1991) (in press)] on the ionic conductivity of $\alpha$-$Li_2SO_4$ incorporating 2.5–4.0 mole% $Li_2WO_4$. They interpret their data as convincing evidence for the "paddle wheel" mechanism of ion transport. A cursory examination of their results shows a 5% drop in conductivity at 600°C and an 11% drop at 700°C for 1.0 mole% increase, viz 2.5–3.5, in $Li_2WO_4$ content while an increase in 0.5 mole% of $Li_2WO_4$, i.e., 3.5–4.0, affects a 25% increase in conductivity at 600 and 700°C. Furthermore, their data differ from the Göthenburg results for undoped $\alpha$-$Li_2SO_4$, 6% higher at 600°C and 5% lower at 700°C—an overall difference of 11%. It has been our experience, consistent with literature reports, that measured conductivity data with less than 10% experimental error are the exception rather than the rule. Dissanayake *et al.* further conclude without experimental evidence that the higher conductivity values observed with $Li_2WO_4$ compositions greater than 4 mole%, i.e., 4–10, are due to the "two solid" phase presence. Invoking the "two solid" phase effect is a self-defeating argument militating against this interpretation as described in the above text. Furthermore, it bears repeating that Touboul *et al.* (*18*) report a decrease in conductivity for the "two solid" phase presence.

Tables I and II include the compound $LiAgSO_4$ with relevant data taken from literature sources cited. It is to be noted that no such intermediate compound is evident in the phase diagram of the $Li_2SO_4$–$Ag_2SO_4$ bindary system [H. Øye, *Acta Chem. Scand.* **18,** 361 (1964)].

## References

1. M. Natarajan and E. A. Secco, *Can. J. Chem.* **53,** 1542 (1975).
2. R. MacL. Murray and E. A. Secco, *Can. J. Chem.* **56,** 2616 (1978).
3. M. S. Kumari and E. A. Secco, *Can. J. Chem.* **61,** 599, 2804 (1983).
4. M. S. Kumari and E. A. Secco, *Can. J. Chem.* **63,** 324 (1985).
5. E. A. Secco, *Phys. Status Solidi A* **88,** K75 (1985).
6. M. D. Leblanc, U. M. Gundusharma, and E. A. Secco, *Solid State Ionics* **20,** 61 (1986).
7. U. M. Gundusharma, C. MacLean, and E. A. Secco, *Solid State Commun.* **57,** 479 (1986).
8. U. M. Gundusharma and E. A. Secco, *Can. J. Chem.* **65,** 1205 (1987).
9. E. A. Secco, *Solid State Commun.* **66,** 921 (1988).
10. K. G. MacDonald, C. MacLean, and E. A. Secco, *Can. J. Chem.* **66,** 3132 (1988).
11. A. S. Campbell, K. G. MacDonald, and E. A. Secco, *J. Solid State Chem.* **81,** 65 (1989).
12. U. M. Gundusharma and E. A. Secco, *Appl. Phys.* **A51,** 7 (1990).
13. A. Lundén and M. A. K. L. Dissanayake, *J. Solid State Chem.* **90,** 179 (1991).
14. A. Ahmad, Canada Centre for mineral and energy technology, Ottawa, Ontario, Canada, personal communication.
15. Y. Saito, T. Maruyama, and K. Kobayashi, *Solid State Ionics* **14,** 265 (1984).
16. N. Imanaka, G-Y. Adachi, and J. Shiokawa, *Can. J. Chem.* **61,** 1557 (1983).
17. M. A. K. L. Dissanayake, M. A. Careem, P. W. S. K. Bandaranayake, R. P. Gunawardane, and C. N. Wijesekara, *Solid State Ionics* **40/41,** 23 (1990).
18. M. Touboul, N. Sephar, and M. Quarton, *Solid State Ionics* **38,** 225 (1990).
19. B-E. Mellander, B. Granéli, and J. Roos, *Solid State Ionics* **40/41,** 162 (1990).
20. R. P. Gunawardane, M. A. K. L. Dissanayake, and F. P. Glasser, *Br. Ceram. Trans. J.* **88,** 45 (1989).
21. J. Schoonman and P. H. Bottelberghs, *in* "Solid Electrolytes" (P. Hagenmuller and W. van Gool, Eds.), p. 340, Academic Press, New York (1978).
22. N. Kimura and M. Greenblatt, *Mater. Res. Bull.* **19,** 1653 (1984).
23. M. S. Whittingham and R. A. Huggins, *J. Chem. Phys.* **54,** 414 (1971).
24. R. D. Armstrong, T. Dickinson, and J. Turner, *J. Electrochem. Soc.* **118,** 1135 (1971).
25. P. Vashishta, J. N. Mundy, and G. K. Shenoy (Eds.), "Fast Ion Transport in Solids," p. 162, North-Holland, New York (1979).

26. H. Ljungmark, Ph.D. Thesis, pp. 72–73, Univ. of Göthenburg, Sweden, (1974).
27. L. Nilsson, Ph.D. Thesis, Univ. of Göthenburg, Sweden (1981).
28. L. Nilsson, J. O. Thomas, and B. C. Tofield, *J. Phys. C* **13,** 6441 (1980).
29. R. Aronsson, Ph.D. Thesis, Univ. of Göthenburg, Sweden (1983).
30. A. Lundén, A. Bengtzelius, R. Kaber, L. Nilsson, K. Schroeder, and R. Tärneberg, *Solid State Ionics* **9/10,** 89 (1983).
31. R. Aronsson, L. Börjesson, and L. Torell, *Solid State Ionics* **9/10,** 1383 (1983).
32. L. Börjesson and L. M. Torell, *Proc. Electrochem. Soc.* (*Molten Salts*), **86-1,** 21 (1986).
33. A. Lundén, *Solid State Commun.* **65,** 1237 (1988).
34. A. Lundén and J. O. Thomas, *in* "High Conductivity Solid Ionic Conductors-Recent Trends and Applications" (T. Takahashi, Ed.), p. 45, World Scientific, Singapore (1989).
35. A. Lundén, *Solid State Ionics* **28–30,** 163 (1988).
36. E. A. Secco, *in* "Proceedings, 6th International Conference Solid State Ionics, Garmisch-Partenkirchem, F.R.G., Sept 6–11, 1987" [oral discussion of papers in Ref. (*35*), pp. 163, 168].
37. A. Lundén, personal communication (1991).
38. R. Frech and E. Cazzanelli, *Solid State Ionics* **9/10,** 95 (1983).
39. L. Börjesson and L. M. Torell, *Phys. Rev. B* **32,** 2471 (1985).
40. A. K. Ivanov-shits and S. E. Sigarov, *Solid State Ionics* **40/41,** 76 (1990).
41. B-E. Mellander and D. Lazarus, *Phys. Rev. B* **31,** 6801 (1985).
42. R. W. Impey, M. L. Klein, and I. R. MacDonald, *J. Chem. Phys.* **82,** 4690 (1985).
43. J. M. Ziman, "Models of Disorder," Chap. 9, Cambridge Univ. Press, Cambridge (1979).
44. K. Schroeder and A. Kvist., *Z. Naturforsch.* **A23** (5), 774 (1968); *in* "Phase Diagrams for Ceramists" (E. M. Levin and H. F. McMurdie, Eds.), No. 4706, American Ceramic Soc., Washington, D.C. (1975).
45. C. A. Angell, *Solid State Ionics* **9/10,** 3 (1983); **18/19,** 72 (1986).
46. R. J. Cava, AT&T Bell Laboratories, Murray Hill, N.J., personal communication (1986).
47. R. Frech, *Mater. Res. Soc. Symp. Proc.* **135,** 219 (1989).
48. J. A. Kafalas and R. J. Cava, *in* "Fast Ion Transport in Solids" (P. Vashishta, J. N. Mundy, and G. K. Shenoy, Eds.), p. 419, North-Holland, New York (1979).
49. M. A. Careem and B-E. Mellander, *Solid State Ionics* **15,** 327 (1985).
50. J. E. Davies and W. F. Sanford, *J. Chem. Soc. Dalton Trans.*, 1912 (1975).
51. H. D. Lutz, W. Schmidt, and H. Haeusler, *Mater. Sci. Monogr.* **10,** 200 (1982); W. Schmidt and H. D. Lutz, *Ber. Bunsenges Phys. Chem.* **88,** 720 (1984); H. D. Lutz, P. Kuske, and K. Wussow, *Naturwissenschaften* **73,** 623 (1986).
52. S. Chandra, "Superionic Solids," Chap. 2, North-Holland, Amsterdam (1981).
53. A. Rabenau, *Solid State Ionics* **6,** 277 (1982).
54. A. Kvist and A. Bengtzelius, *Z. Naturforsch.* **A23,** 679 (1968).
55. L. Nilsson, N. H. Andersen, and A. Lundén, *Solid State Ionics* **34,** 111 (1989).