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On the Ionic Conductivity and Phase Transitions in the Li_2SO_4–Li_2WO_4 System and Their Relation to Ion Transport Mechanism

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Secco *et al.* have performed several measurements of ionic conductivity, which they have considered as "convincing evidence" that the "paddle-wheel" mechanism does not contribute significantly to ion conductivity in Li_2SO_4-based compositions. However, a comparison of their results in the high-conductivity range with those of other investigators suggests that their data are artifacts. The cause of this is that the resistance of their sulfate-rich samples is about 0.1 ohm at high temperatures. Thus, their results are reliable only for "normal," i.e., low, conductivities. It is briefly summarized why the "paddle-wheel" mechanism for ion transport is superior to a percolation-type mechanism for a few high-conducting phases.

Introduction

It is characteristic of ionic compounds that the electrical conductivity is many orders of magnitude smaller in the solid state than for a melt or an aqueous solution. However, some solid phases have ionic conductivities similar to what is characteristic of a liquid phase. This appears to be the only property that all solid electrolytes (superionic conductors, fast ion conductors) have in common, while other properties can vary very much; e.g., while it is characteristic for other solid electrolytes that ions with "the right" radius are much more mobile than smaller or larger ones, a series of diffusion studies in the late 1960s revealed for a couple of cubic sulfate phases that the ionic radii had little influence on the mobilities of mono- and divalent cations. After considering also the structure of the cubic phases and all other studies that had been made of different properties, it was concluded that the cation mobility is enhanced by the coupled rotation of the translationally immobile sulfate ions (*1–4*). However, Secco *et al.* have objected vigorously to this interpretation (*5–10*).

Secco *et al.* put much emphasis on their own conductivity studies for mixtures of sulfates with either tungstate or silicate. It has been pointed out several times that some of their results are in pronounced disagreement with those of all other relevant conduc-

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tivity studies (*11, 12*), but Secco has made no attempts to explain these disagreements (*8–10*). The purpose of the present paper is to solve the controversy, taking into account not only the evidence discussed previously but also three more studies. Two of these appeared at about the same time as the paper by Campbell, MacDonald, and Secco (CMS) (*10*). One concerns the phase diagram of the Li_2SO_4–Li_2WO_4 system (*13*); the other is an additional conductivity study of some pure lithium salts (*14*). The third paper is on the conductivity and phase diagram of the systems Li_2SO_4–Li_3PO_4 (*15*).

Transition Enthalpies and Phase Diagrams

For pure Li_2SO_4 CMS report a latent heat for the monoclinic–cubic transition, which is in good agreement with what was obtained in another recent investigation (*16*). CMS find that the transition occurs at 572°C, while the results of several other investigations fall in the range 575 to 578°C.

The liquidus curve of the system Li_2SO_4–Li_2WO_4 was determined earlier by Kislova, Posypaiko, and Bergman (KPB) (*17*), but the phase diagram by Gunawardane, Dissanayake, and Glasser (GDG) (*13*) is new (see Fig. 1). The results of CMS disagree in some important points with those of KPB and GDG. Thus, while both KPB and GDG report a eutectic (KPB at 68 mole% Li_2SO_4 and 596°C; GDG at 66 mole% and 581°C), CMS state "there was no discernible evidence of melting up to 650°C." However, CMS report a DSC endotherm at 595°C for which the transition enthalpy has a maximum at 67–68 mole% Li_2SO_4, i.e., at the composition where the two other groups find the eutectic.

For pure Li_2WO_4 the melting point is 738°C according to KPB, GDG, and others (*18*). KPB report a polymorph transition at about 660°C, but this was not observed by GDG, who find that the transition between the rhombohedral phase I and the tetragonal phase II occurs at 410°C for pure Li_2WO_4 but at 520°C when about 35 mole% Li_2SO_4 is dissolved. While there thus is a large solid solubility for the sulfate in both tungstate phases according to GDG (Fig. 1), CMS report that both endotherms observed by them, at 595 and 572°C, respectively, extend beyond 95 mole% Li_2SO_4 (*8–10*) and that the latter actually starts at the pure sulfate. The usual interpretation of such widely extended endotherms is that the solid solubility is very small for the high-temperature phases of both sulfate and tungstate.

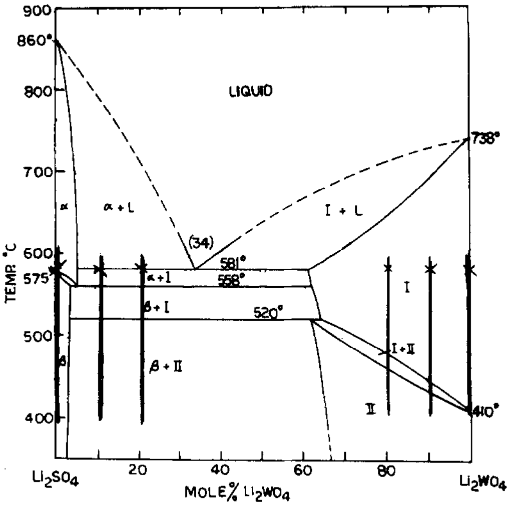

FIG. 1. Phase diagram according to Gunawardane, Dissanayake, and Glasser (*13*). The vertical lines for 0, 10, 20, 80, 90, and 100 mole% indicate approximately the temperature range that was covered in the electrical/conductivity studies of Secco *et al.* The crosses (×) mark the points of their conductivity isotherm (*10*).

On the sulfate-rich side of the phase diagram, GDG find that the solid solubility of tungstate is rather limited, about 5 mole% in the fcc phase, and somewhat less in the monoclinic phase. This is in agreement with our conclusion (*11, 12*) that the solubility is between 2 and 5 mole% in the fcc phase. It is found that the electrical conductivity of a mixture containing 2 mole% tungstate is lower than that of pure cubic lithium sulfate, while it is higher for a mixture with 5 mole%, see below.

Electrical Conductivity

It is well known for impedance measurements that an arrangement that is reliable in one conductivity range may have serious shortcomings in another range. In our own determinations of electrical conductivities of sulfate systems we sometimes use quartz capillary U-cells in the upper part of the temperature range and pressed pellets in the lower part (*16*), while Secco *et al.* always use the same pellet technique for their measurements.

It is of importance to remember a fundamental difference between solid salts depending on whether the conductivity is of the order of 1 S/cm or several magnitudes lower. In the latter case it is normal to find deviations of one order of magnitude, or even considerably higher, between two samples of a salt, depending on grain size, impurity level, etc. On the other hand, the importance of the latter parameters is much lower in cases with a high bulk conductivity. There can then hardly be any pronounced enhancement of the grain boundary conductivity relative to that of the bulk, and it is also of little importance whether soluble ions are homo- or aliovalent (*12*). Furthermore, at least when the salt is plastic as is the case with fcc Li_2SO_4, it is not likely that the grain boundary impedances are considerably larger than that of the bulk.

The conductivity of pure Li_2WO_4 at 578°C is 7.4×10^{-4} S/cm according to CMS (*10*). Lal *et al.* report 16×10^{-4} S/cm (*14*). An earlier investigation (*19*) did not use temperatures above 500°C, but an extrapolation to 578°C gives 12×10^{-4} S/cm.

The conductivity of monoclinic Li_2SO_4 has been studied in several laboratories: e.g., five studies conducted at 496°C found values of 0.87×10^{-4} S/cm (*16*), 1.1×10^{-4} S/cm (*14*), 2.0×10^{-4} S/cm (*20*), 8.2×10^{-4} S/cm (*7*), and 3.4×10^{-4} (*15*).

The quoted comparisons and others show that Secco *et al.* used a measuring technique that gives reliable results for salts with "normal" ion conductivities. However, the situation is different when they use this technique for fcc Li_2SO_4 or bcc $LiNaSO_4$. In both cases their results deviate very strongly from what has been reported from all other investigations. Surprisingly enough, Secco has never commented on any of these deviations, neither in the first report (*7*), nor on any later occasion (*8–10*). Some of these deviations are:

1. For pure Li_2SO_4 at 578°C, Gundusharma, MacLean, and Secco (GMS) report that the conductivity is 0.011 S/cm, and they obtained 0.017 S/cm for bcc $LiNaSO_4$ at 560°C (*7*), while in both cases the conductivity is about 1 S/cm according to most other investigations (*11, 12*). However, there is agreement between Secco *et al.* and other studies concerning the temperature dependence of the two "undoped" salts.

2. Ljungmark (*11, 21*) found that the conductivity is about 17% higher if 10 mole% Li_2WO_4 is added to Li_2SO_4, while according to GMS, such an addition gives conductivities that are 3.2 to 16 times that of the pure sulfate, depending on how the mixture was prepared and whether the frequency was 1 or 10 kHz.

3. There are deviations regarding the temperature dependence between GMS and the two earlier investigations of sulfate–tungstate mixtures (*21, 22*). GMS report that their "uncompressed solidified sample shows negligible activation energy for Li^+ ion mobility," which they make no attempt to explain. (According to their plot, the activation energy actually is negative at 1 kHz.)

4. GMS measured the conductivity at both 10 and 1 kHz for five samples. It was the same for three of them, but it was much higher at 10 kHz for the other two. GMS

present two alternative interpretations of the observed frequency dependence, but they have never tested their ideas by extending their measurements to other frequencies.

Summarizing, there are so many results that can be questioned for one reason or another that it is difficult to avoid the conclusion that Secco *et al.* are using a technique that gives erroneous results when the resistance of the sample is of the order of 0.1 ohm. Most of their samples were about 1 mm thick and had a surface area of 100 mm^2 (*9*). Under such circumstances one must carefully consider resistive and capacitive contributions from the electrodes and the interface between the electrodes and the sample.

In their recent study of the electrical conductivity of the sulfate–vanadate system, Touboul, Sephar, and Quarton (*15*) used the pellet technique over a much wider range than Secco *et al.* ever have used, but in their interpretation they are well aware of the fact that their technique is inaccurate when the resistance of the pellet becomes very low.

Cation Mobility Mechanisms in Some Sulfate Phases

It is evident from the preceding section that the actual figures reported by Secco *et al.* for the high-conductivity regions should be considered as artifacts. Still, comparisons of the relative values might give some information on the effect of varying the composition of a solid phase. For more than 20 years Secco and his co-workers have studied the electrical conductivity of a number of systems of oxyacid salts. The information in the literature concerning the phase diagrams of such systems is limited. Thus it is quite natural that Secco *et al.* have not made much distinction between one- and two-phase regions, when they interpret their conductivity data.

It is obvious that GMS and CMS are convinced that the samples containing 10 and 20 mole% Li_2WO_4, respectively, can be compared directly with the undoped sulfate. However, a comparison with the phase diagram of GDG (Fig. 1) shows that phase boundaries are intersected at 520, 558, and 581°C (*13*) and that we are dealing with two-phase regions in the entire temperature range studied (β + II, β + I, α + I, and α + liquid). The mixtures of the monoclinic sulfate with the tungstate phases are to be considered composite electrolytes for which it often is found that the conductivity is enhanced (*16*, *23*, *24*). This was also observed in a recent study of the electrical conductivity of the Li_2SO_4–Li_2WO_4 system at temperatures below 500°C (*25*); work is in progress on conductivity studies above this temperature.

In a few papers Secco (*7*, *9*, *10*) declares that if the anion-rotation "cog-wheel" mechanism were operative, the presence of the lower frequency WO_4^{-2} would lead to lower conductivity. This is exactly what was found when Kvist studied a sample containing 2 mole% Li_2WO_4 (*11*, *12*, *22*). Due to an oversight (*26*), Secco has never commented on this result, and a straight line was drawn between 0 and 10 mole% in Fig. 2 of CMS, neglecting the results for 2 as well as for 5 mole%, obtained by Kvist and Ljungmark, respectively.

Secco argues that the same ion transport mechanism should work in Li_2SO_4, $LiNaSO_4$, Na_2SO_4, and Ag_2SO_4 (*9*) despite the fact that there are large differences concerning several physical properties between the two cubic phases and the two hexagonal ones (*3*, *4*). Thus, numerous investigations have shown that the conductivity is very much enhanced if aliovalent cations are added to sodium or silver sulfate. One of the most recent findings is that the conductivity at 650°C is about 70 times higher for $Na_{1.8}Mg_{0.1}SO_4$ than for Na_2SO_4 (*27*). On the other hand, at this temperature the conductivity of $Li_{1.8}Mg_{0.1}SO_4$ is 88% of that of Li_2SO_4 (*21*).

Secco has recently reinterpreted some experiments by other authors as evidence against the paddle-wheel model (*8*). The "words of caution" that Secco has found in a review paper (*28*) actually refer to *all* models that were known around 1977, which we find quite reasonable. The molecular dynamic studies (*29*) neither prove nor disprove the paddle-wheel model. Secco also refers to bandwidth studies by Frech and Cazzanelli (*30*). However, that study is limited to the monoclinic phase, since it was impossible to keep the single crystal intact when it passed through the transition to the cubic phase. The bandwidth break at 450°C commented on by Secco (*8*) is interpreted by Frech *et al.* (*30*). It might be added in this connection that a neutron powder diffraction study of monoclinic Li_2SO_4 at 550°C (*31*) has shown strong torsional vibrations of the sulfate group. It is by no means clear how Secco (*8*) can find that the pressure dependence of the electrical conductivity (*32*) favors his model over ours. It is not easy to follow his interpretation of some conductivity data in his Figs. 2 and 3 (*8*). Far more important in our opinion is the report by Touboul *et al.* (*15*) that the conductivity of cubic Li_2SO_4 decreases slightly when Li_3PO_4 is added, which is found to be "according to a 'paddle-wheel' mechanism and not to a 'percolation' mechanism."

In conclusion, Secco has not yet presented evidence in favor of any ion transport mechanism that is in better agreement with *all* kinds of investigations than the paddle-wheel mechanism is.

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