Electromigration in fcc Li$_2$SO$_4$(K) and in hcp Li$_{0.4}$Na$_{1.6}$SO$_4$

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Electromigration of impurity (0.1 to 1.3%) K ions in fcc Li$_2$SO$_4$ has been studied at about 650 °C. It is found that the mobility of the impurity K ion is either slightly larger or approximately equal to that of the abundant Li ion. On the other hand, the diffusivity of the K-ion is known to be some 40% less than that of the Li-ion. Possible explanations of this apparent discrepancy are discussed. For hcp Li$_{0.4}$Na$_{1.6}$SO$_4$ at 560 °C the mobility is found to be some 55% higher for the Li ions than for the Na ions.

At present much interest is focused on solid electrolytes, i. e. compounds where at least one ionic species is extremely mobile. In our laboratory we are carrying out an extensive study of sulfates with this property. Above 572 °C Li$_2$SO$_4$ has a phase where the sulfate ions form a fcc lattice. This phase can accomodate a small amount of impurity cations with a large radius such as K$^+$ (l. c. [1]). The effect of such additions is very pronounced on mechanical properties while it is small on e. g. the electrical conductivity [2,3]. From geometrical considerations one would expect impurity K-ions to be far less mobile than the Li-ions, while according to a study of the diffusion of impurity cations in Li$_2$SO$_4$, the ratio between the diffusion coefficients for K and Li, D$_K$/D$_{Li}$, is about 0.68 at 600 °C and 0.43 at 850° (l. c. [4]).

We decided to measure the mobility of potassium as an impurity with the technique we had used previously to study the isotope effect in pure lithium sulfate [5]. (The interpretation of an earlier attempt to study electromigration in such mixtures [6] is not straightforward, since it is likely that the chosen composition, about 10% K$_2$SO$_4$, falls into a two-phase region.) Li$_{0.4}$Na$_{1.6}$SO$_4$ has been included in our studies.

Experimental

A melt of the desired composition was allowed to solidify in a U-shaped cell [5], see Figure 1. A platinum net served as the anode and molten lead as the cathode. After quenching, the salt was divided into samples for which the Li and K contents were determined by means of atomic absorption spectrophotometry. We made 6 electromigration experiments
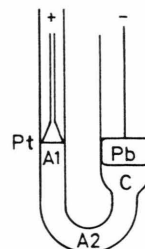
Fig. 1. Electromigration cell (Vycor) with platinum anode and lead cathode. The division of the samples in three groups (A1, A2, C) is indicated.

with fcc Li$_2$SO$_4$ containing small amounts of K$_2$SO$_4$ and one with Li$_{0.4}$Na$_{1.6}$SO$_4$· in the hexagonal phase. Data for these experiments are quoted in Table 1. The fact that the mechanical properties of Li$_2$SO$_4$ are affected strongly by the addition of K$_2$SO$_4$ can cause some trouble at the anode, which is supposed to slide down at the same rate as the salt is consumed. If the salt becomes too soft, the anode tends to penetrate into the salt column, while if the salt is too stiff the contact can become bad between salt and anode, and either local overheating or mechanical strain might break the platinum net with the result that the remaining part of the anode (a gold tube that held the net) penetrates down into the salt. (This latter occurred in the present experiments no 15, 16, 19, 21.)

Calculation of Mobility Differences

The evaluation of the experiments is based on considering transport across an arbitrarily chosen cross-section, situated at a position where the composition remains unchanged during the whole experiment [6,7]. For the volume between this cross-section and the anode, the analysis carried out after the electromigration gives the amount N_i of component i. One also needs to know the amount present initially, N_i^0, in order to calculate the change

$\Delta N_i = N_i - N_i^0$. There can be some uncertainty concerning N_i^0, if the liquid salt has not been quenched rapidly enough to avoid segregation during solidification. If one thus actually starts with an inhomogeneous distribution, diffusion tends to smear out the inhomogeneities, while electromigration has two effects: in the regions near the electrodes it tends to enrich some component, and in the main part of the cell it will shift the position of existing inhomogeneities. When we decided to use the present method of filling the cell (An alternative would be to press slabs, check the composition of each one, and then stack them. This procedure would be tedious, and it has other disadvantages too.), we assumed that we would get an approximately homogeneous composition over large parts of the cell, and we did get this for a blind run. The "practical range of enrichment" [7] is $(\pi D t)^{\frac{1}{2}}$ where D is the diffusion coefficient and t the duration of the experiment. Accordingly, for our experiments we needed to consider composition changes only within a couple of cm from the anode. By determining after the run the composition not only in this part but also in the rest of the cell, we attempted to estimate how much stratification there was initially present within the cell.

Each cell was divided into about 20 samples. The result of the cation analysis is summarized in Table 1, where we compare the part close to the anode (A1), the main part of the narrow tube (A2) and the wide tube (C), cf Figure 1. For each part

we quote only the highest and the lowest content of solute (K for no. 15 – 20, Li for no. 21). In the wide tube (C) large differences could be found between adjacent samples. It is possible that the rather complicated cathode reactions [8] caused some changes in composition during the electrolysis. Also, a segregation of the obtained order can be expected from the steep slopes of the phase diagram [2]. Concerning the main part of the narrow tube we find not only that the variation in composition is less than in tube C, cf Table 1, but also that for most runs the composition showed long range trends over a number of samples. These observations lead to the conclusion that, as expected, segregation effects during solidification were much less severe in this part of the cell than in the wide part, and that in the narrow tube there existed regions where composition changes during the electromigration period can be neglected. After thus finding that the basic assumption for evaluating the experiments is fulfilled, our interest is concentrated on region A1. In all experiments but one the lowest solute concentration was found in the sample just below the anode, while in the remaining one (no. 19) the minimum was instead found inside the hollow anode. (The anode penetrated into the salt column for runs no. 15, 16 and 19.) For two runs (15 and 16) samples located inside the anode showed a higher solute concentration than the average one. Since the salt trapped inside the anode had been affected by electromigration only during part of the experiment,

Table 1. Electromigration in fcc Li_2SO_4 with K_2SO_4 as impurity (no 15—20) and in hcp $Li_{0.4}Na_{1.6}SO_4$ (no 21). The relative difference in mobility, $\Delta b/b$, is calculated for two different assumptions regarding the initial composition in the region near the anode, namely that the solute concentration was the same as (I), or larger than (II) the average for the whole cell.

Exp.	Phase	Solute[a] equiv. %	Temp. °C	Duration hours	Transp. charge mFaraday	Current density A/cm²	Composition of samples solute equiv. %			$\Delta b/b$ for assumptions	
							Sect. A1	Sect. A2	Sect. C	I	II
15 [b]	fcc	0.13	690	8.0	125.7	1.2	0.10— 0.16 [c]	0.13— 0.14	0.09— 0.17	−0.008	−0.027
16	fcc	0.44	610	8.0	126.3	1.2	0.28— 0.97 [c]	0.41— 0.74	0.12— 0.66	−0.013	−0.094
17	fcc	0.46	690	7.0	108.7	1.1	0.39— 0.47	0.44— 0.49	0.38— 0.55	−0.009	−0.048
18	fcc	0.79	660	10.0	155.7	1.1	0.43— 1.40	1.44— 1.48	0.25— 1.27	−0.016	−0.048
19	fcc	0.86	630	4.5	58.4	1.0	0.18— 1.01	0.92— 1.10	0.68— 1.06	−0.18	−0.24
20	fcc	1.31	665	6.3	96.2	1.1	1.26— 1.76	1.48— 1.85	0.80— 1.85	−0.003	−0.12
21	hcp	20	560	6.5	98.6	1.1	2.3 —18.5	20.2 —32.5	19.6 —51.5	0.50	
							Exp. 15—18 average			−0.012	−0.05
							Exp. 15—18 standard deviation			0.004	0.03

[a] K_2SO_4 for no 15—20; Si_2SO_4 for no 21.   [b] numbered in sequence with previous experiments [6].
[c] highest content in top sample found inside the anode tube.

these samples should give a clue to the initial concentration at the very top of the salt column. If this salt solidified last, we would expect an above-average concentration of solute at the top. From these observations one concludes that the initial solute concentration in part A1 was either close to the average one or somewhat higher, and that the low concentrations found afterwards at the anode are a strong indication that the solute cations migrated faster than the abundant ones. The mobility difference $\Delta b/b$ was estimated for two different assumptions; that is the initial composition of the samples near the anode was supposed to be

I the average composition in the whole cell (except for run 15, where a part of tube A was taken as the reference),

II the highest concentration of K found in any sample.

The results, see Table 1, can be summarized in the following way. In the range 0.1 to 0.8 equiv. % K (exp. 15 – 18) the mobilities of Li and K are nearly equal, with an indication that b_K might be slightly larger than b_{Li}. The results for no. 19 are a little more uncertain, which partly is due to the fact that the transported charge was lower for that experiment. For a mixture with somewhat more than 1% K^+ it seems as if b_K can be up to about 10% higher than b_{Li} (exp. 20). (This might be fortuitus but it points in the same direction as the large mobility differences observed at about 7% K^+, exp. 13 and 14, l. c. [6]).

Concerning the experiment with $Li_{0.4}Na_{1.6}SO_4$, it seems obvious that b_{Li} is significantly higher (about 55%) than b_{Na}.

Discussion

A comparison of relative cation mobilities in hcp $Li_{0.4}Na_{1.6}O_4$ and in fcc Li_2SO_4 (K) gives an indication that the mobility of impurity ions is enhanced in solid sulfate systems, since in both systems the diluted ion (Li in hcp $Li_{0.4}Na_{1.6}SO_4$ and K in fcc Li_2SO_4) has a higher mobility than the abundant one. This would suggest that the situation in solid electrolytes could be opposite to that in melts, where the mobility of an ion is reduced when it becomes diluted. After this comment on the experiment with hcp $Li_{0.4}Na_{1.6}SO_4$, we shall devote the rest of the discussion to fcc Li_2SO_4 (K).

In ordinary solids the concentration of available lattice vacancies is small, but in fcc Li_2SO_4 there is a large excess of possible cation positions. To each sulfate ion there correspond two tetrahedral and one octahedral position [9]. The latter positions are larger than the former, and in fact there seems to be adequate space for two lithium ions in the same octahedral position [3]. It has previously been suggested [3, 9] that a very large fraction of the lithium ions is in tetrahedral positions, leaving nearly all the octahedral ones vacant. From studies of diffusion in Li_2SO_4 doped with $MgSO_4$, however, it seems more likely that most of the lithium ions are in octahedral positions [10, 11], and some additional support of this model has been obtained by computer calculations of potential energies for a simple model [10]. It has also been estimated, that at 600 °C something like 20% of the lithium ions are in activated states [10]. Let us consider a model with two types of sites, of which most of the α-sites are occupied by cations and most of the β-sites are vacant, without specifying whether α stands for tetrahedral or octahedral sites. From geometrical considerations it seems evident that a transition between two sites of the same kind can take place only via a site of the opposite type, which thus serves as an intermediate position. In the case of fcc Li_2SO_4 there seems to be space for potassium ions only in octahedral positions (which, however, hardly have room for both a K^+ and a Li^+ ion)[†] and from such geometrical considerations one might expect the potassium ion to be fairly immobile. On the other hand, the experiments show that it is very mobile. This apparent contradiction can, at least in part, be removed by remembering that strong rotational oscillations must be expected for the sulfate groups, as already pointed out by Førland and Krogh-Moe [9]. In their discussion of the rather high diffusivity of monovalent anions (halides) in fcc Li_2SO_4 Kvist and Bengtzelius consider the sulfate ions to act like cogwheels [13].

[†] With increasing temperature a larger fraction of the β-sites becomes occupied by Li-ions, i. e. an unsymmetrical distribution of cations becomes more common. Since we expect the presence of K-ions always to be correlated with an unsymmetrical distribution, we might here have an explanation why thermomigration tends to enrich impurity K^+ at the hot side [12]. It should perhaps be mentioned that the duration of the present experiments was too short to allow much of a contribution from thermomigration to the obtained separation. The thus neglected contribution from thermomigration would be in the opposite direction of the observed electromigration in tube A.

The relation between the mobility b^+ and the diffusion coefficient D^+ of the monovalent cations of a pure salt with zero anion mobility can be expressed by means of the Nernst-Einstein factor [††]

$$\alpha^+ = (R\,T/F)\,(b^+/D^+) \qquad (1)$$

where $b^+ = \Lambda/F$, Λ is the equivalent conductivity, T the absolute temperature, R the gas constant and F the Faraday constant.

If there are several monovalent cationic species (i) present, one can, in analogy with Eq. (1), introduce the factors

$$\alpha_i = (R\,T/F)\,(b_i/D_i) \qquad (2)$$

where $$\Sigma\, x_i\, b_i = \Lambda/F \qquad (3)$$

and x_i the molar fractions.

By combining self-diffusion and conductivity measurements in pure lithium sulfate [14] one obtains that the Nernst-Einstein factor α^+ of Eq. (1), here called α_{Li}, increases from 1.1 to 1.4 in the temperature range $600-800\,°C$. The present experiments show that b_K is approximately equal to b_{Li}, at least for $0.001 < x_K < 0.008$, see Table 1, and in this concentration range the conductivity is only slightly lower than for pure Li_2SO_4 (l. c. [2, 3]). From Eq. (3) it follows that for these mixtures b_{Li} is approximately equal to Λ/F, and we thus obtain a value for b_K that can be inserted in Eq. (2) together with the diffusion coefficients [4]. The result is that $\alpha_K = 1.9$ at $650\,°C$ if $b_K = b_{Li}$ and $\alpha_K = 2.0$ if $\Delta b/b = -0.05$. While α_{Li} (1.2 at $650\,°C$) should give information on the transport mechanism, (It is found that the vacancy mechanism is dominant, but that there is also some contribution from a ring mechanism [11].) ,we cannot interpret α_K in the same conventional way.

Instead of calculating α_{Li} and α_K one could compare the $\Delta b/b$ of Table 1 with an estimated relative difference in diffusion coefficients

$$\Delta D/D \cong (D_{Li} - D_K)/D_{Li} = 0.41$$

at the average temperature of the electromigration experiments. To our knowledge, the only cases for which both electromigration mobilities and diffusion coefficients for the two cations have been measured over the whole concentration range are for the two molten systems $LiNO_3 - KNO_3$ (l. c. [15]) and $NaNO_3 - KNO_3$ (l. c. [16]). After recalculating

the reported external mobilities (measured relative to the strip that contained the melt) to internal ones, one obtains that the ratio $(b_1/b_2)/(D_1/D_2)$ where subscript 1 stands for the light cation and 2 for the heavy one, depends on both the composition of the mixture and the temperature. The numerical values of this ratio for these two molten systems fall between 0.47 and 0.97, while for our solid Li_2SO_4 $(b_1/b_2)/(D_1/D_2) = 0.59$. This similarity might be fortuitous, since there is much evidence that the transport mechanism in a melt is quite different from that in a solid, and it is only in the solid that it seems safe to talk of fairly well defined cation positions. At least for a solid, one would expect that relative electromigration mobilities of different cation species can be predicted from a comparison of their diffusion coefficients, but this assumption seems to be violated by the present experiments. There is, however, a certain possibility that this is only apparent, and that b_K is strongly dependent on the concentration in the range below 0.1%. In fact, the samples analysed in the diffusion experiment contained between 0.006 and 0.1 mole % K. Experiments with solutions of Na_2SO_4 or Ag_2SO_4 in K_2SO_4 (l. c. [17, 18]) indicate in both cases that the solute ions occur in pairs. (In the latter case the pairs were, however, dissociated for Ag^+ concentrations less than one per cent.) It is possible that some kind of inhomogeneous distribution of solute ions occurs also in the present case, where the solute ion is larger than the abundant cation. Before looking for an explanation for any concentration dependence of b_K, its existence should be confirmed by measuring D_K and $\Delta b/b$ over the same concentration range.

It is normally not expected that an external electrical field of the strength used in electromigration experiments has any influence on the atomic transport mechanism [§], i. e. that such a field could enhance the mobility of the solute K^+ ions. Let us, however, follow the practice of the Wirtz model for

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[††] While some authors define the Nernst-Einstein factor as we have done here, others prefer to consider $1/\alpha$, which often is called the Haven ratio.

[§] Dicave and Emery [19] claim that the presence of a temperature gradient increases the diffusion coefficient in liquid systems. Since this would violate the basic assumptions of the current interpretation of transport phenomena, we have chosen to make a check in a system where convection cannot be present, namely a solid salt, bcc AgI. We found no evidence in support of their statement [20]. Furthermore, Korsching (priv. com.) has recently found for a liquid mixture (n-heptan—n-hexadecan) that thermomigration experiments give the same diffusion coefficient as isothermal determinations do.

thermomigration and divide the activation energy of the jump process in three parts, corresponding to the initial site (H_0), the intermediate position (H_i) and final site (H_f). It seems more likely that an external field can affect the situation at the intermediate position (which in our case might involve a tetrahedral position as well as the saddlepoints that separate this position from the initial and final octahedral positions; the cogwheel model, which as yet is only qualitative, might change this picture of the "intermediate position" somewhat) than that it has any influence on either H_0 or H_f. If the activation energy actually is influenced by an external field this could possibly be checked by studying if $\Delta b/b$ is influenced by the current density or by comparing the temperature dependence of $\Delta b/b$ with that of D_K and D_{Li}. If the external field changes the activation energy only for the solute, there would not be any detectable deviations from Ohm's law for these dilute systems. It might be profitable to study electromigration of other impurities, such as Na^+ or Mg^{2+} which have a high solubility in Li_2SO_4.

In summary, we have not yet found any convincing explanation why $\Delta b/b$ differs from what one might expect from diffusion studies. This problem is of some practical importance for technical applications of solid electrolytes.

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