

EVALUATION OF SOLID ELECTROLYTES FOR HIGH TEMPERATURE LITHIUM BATTERIES: A PRELIMINARY STUDY*

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(Received October 26, 1977)

Summary

The lithium ionic conductivity of materials prepared by reaction of lithium iodide with anhydrous and hydrated aluminum sulfate has been investigated by a.c. conductivity and n.m.r. techniques. The a.c. measurements indicated thermally activated diffusion with an activation energy of 8.3 kcal/mol. From ^7Li n.m.r., the characteristic time of motion, τ_c , was determined from the observed line width at a given temperature. The plot of $\log \tau_c$ as a function of $1/T$ is linear and gives an activation energy of 6.3 kcal/mol.

Introduction

The use of high energy density, high power density battery systems in energy storage and electromotive applications is at present the subject of much research activity [1]. The key to success in such applications is high current capacity which places specific demands on the components of any such electrochemical system. Several alternative strategies, based on alkali metal anodes, aprotic organic electrolyte solutions, molten salt and solid electrolyte systems, are currently under development. Depending on the electrolyte, each of these alternative approaches has its own particular advantages and disadvantages [2].

Organic electrolyte systems have the advantage of ambient temperature operation. However, problems due to dendritic deposition of lithium, low ionic conductivity of the media, problems of solvent transport, and solubility of cathode active materials, often exist. Molten salt and solid electrolyte systems are capable of higher current densities than organic electrolytes, by virtue of their operation at elevated temperature. Molten salt systems suffer from corrosion problems, including that of the separator. Solid electrolytes, on the other hand, act as natural separators, eliminating

*Paper presented at The International Symposium on Molten Electrolytes and High Temperature Batteries organized by the Electrochemistry Group of the Chemical Society, Brighton, Gt. Britain, September 22 - 23, 1977.

the separator problem encountered in molten salts. Although the solid electrolytes offer greater design freedom, among the disadvantages are the problems of interfacial resistance and the incompatible thermal expansion coefficient [3].

In the field of solid electrolyte systems, the subject of the present paper, certain ceramic materials, notably sodium β -alumina, exhibit the required ionic conductivity at high temperature, *i.e.*, 300 °C, and Na/S battery systems have been successfully fabricated. The present technical problem appears to be the economical fabrication of thin ceramic tubes and/or discs of sodium β -alumina that would allow high current densities, and yet have sufficient integrity to maintain effective separation of the components [4].

The ionic conductivity of most non-ceramic solid electrolytes is too low for high current density operation of the cell at ambient temperatures. A comparison of the ionic conductivities for a range of solid electrolytes is shown in Fig. 1 [5]. Silver ion conductors, such as AgI and RbAg_4I_5 , are one exception, and recently it has been shown that a combination of CuBr with

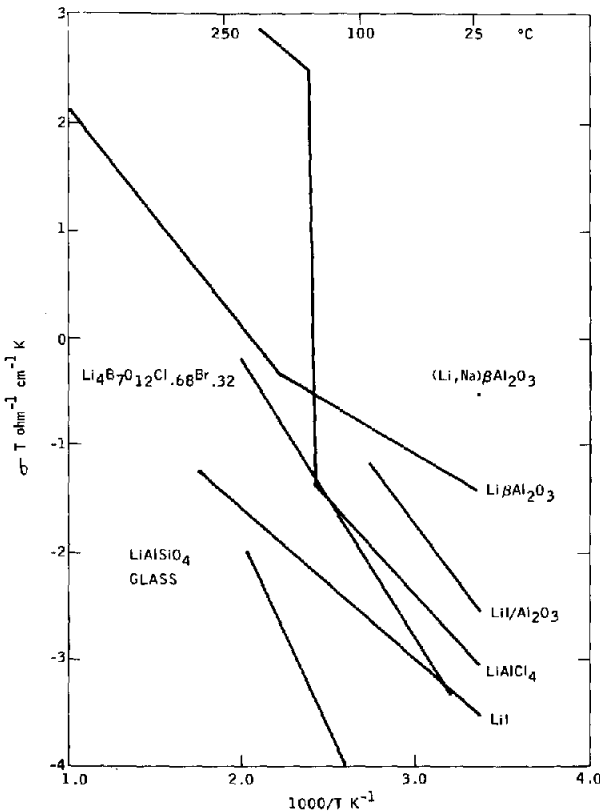


Fig. 1. Comparison of conductivities for some lithium solid electrolytes (see, for example, [5], $(\text{Li}, \text{Na})\beta\text{-Al}_2\text{O}_3$, [13] and $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}_{0.68}\text{Br}_{0.32}$, [9]).

*N,N*¹-dimethyl triethylene diamine dibromide also shows high conductivity, $2 \times 10^{-2} (\Omega \text{ cm})^{-1}$ at 25 °C, with low activation energy (4.1 kcal/mol) [6].

In this report we discuss results obtained for one class of solid, non-ceramic, lithium ion conductors which we have examined as potential components in the lithium/titanium disulfide cell. Combinations of lithium iodide with anhydrous and hydrated aluminum sulfate have been prepared and the electrical, structural and microscopic properties of the products examined by conductivity, X-ray diffraction, and nuclear magnetic resonance measurements. Lithium sulfate based electrolytes have previously been investigated by Heed *et al.* [7]. Li_2SO_4 itself exhibits high Li^+ conductivity at temperatures above 573 K, where the structure transforms to an *fcc* phase of Li_2SO_4 , or forms other phases with broad composition ranges which give good conductors. Heed *et al.* also reported that a *bcc* phase could be prepared by partial substitution of iodide for sulfate in the system $(\text{Li, Ag})_2(\text{SO}_4\text{I}_2)$ with a conductivity of $10^{-3} (\Omega \text{ cm})^{-1}$ at ambient temperature. High conductivities for mixed phases were also found in this system with values dependent on the composition and pretreatment of the sample.

The aims of our study were to investigate the chemistry of the reaction between LiI and $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, to correlate the structure, chemistry, and mobility of the resulting materials and to determine the relationship between the macroscopic mobility of lithium as determined by conductivity measurements and the mobility from the n.m.r. determination of the lithium ion hopping rate. Ideally, a direct correlation is possible between these two classes of observations, but the complex nature of the solid state systems, and their effect on the resulting diffusion mechanism, often obscures this relationship [8, 9]. In the present case, we find good agreement between these two probes of ionic motion.

Experimental and results

The materials examined were prepared by heating LiI with anhydrous or hydrated aluminum sulfate. The LiI was obtained from the Foote Mineral Company. Chemical analysis indicated less than 0.1% impurities, most probably mainly lithium oxide. The X-ray powder pattern recorded under Mylar to exclude moisture was completely indexed as a face centered cubic cell with a lattice parameter in agreement with the literature value. N.m.r. observations show no evidence for protons. The sample was handled in a dry nitrogen atmosphere, since exposure to moisture results in rapid hydration. The LiI reflections in the X-ray pattern decay in minutes to be replaced by lines which may be indexed as hydrates. A conspicuous proton signal is observed in the wideline n.m.r. of such products.

Anhydrous aluminum sulfate was prepared by crystallization from aqueous solution at temperatures above 80 °C. The X-ray pattern of this material was completely indexed on the rhombohedral unit cell reported in the literature with lattice parameters $a = 8.09$, $c = 21.88 \text{ \AA}$. Dehydration of

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 250°C gives a product with 5 - 6 remaining water molecules depending on the heating time. The powder X-ray pattern of this material is poorly defined with broad lines and not readily indexed, nor was it possible to assign the lines to any reported hydrate or oxyhydrate. The material was not sensitive to atmospheric moisture and the integrated proton wide-line n.m.r. signal is consistent with 5 - 6 remaining water molecules.

Reaction of LiI with anhydrous $\text{Al}_2(\text{SO}_4)_3$ in 1:1 mol ratio at 250°C gives a brown solid which contains (8 - 10 W%) free iodine. The powder X-ray pattern is very similar to that of pure anhydrous $\text{Al}_2(\text{SO}_4)_3$; only one broad weak reflection is observed with $d = 3.99 \text{ \AA}$, which cannot be indexed on the rhombohedral cell. No lines corresponding to LiI, $\text{LiI} \cdot \text{H}_2\text{O}$ or $\text{LiI} \cdot 3\text{H}_2\text{O}$ are observed. The product is relatively (to LiI) stable in air.

Reaction of LiI with $\text{Al}_2(\text{SO}_4)_3 \cdot 5 - 6\text{H}_2\text{O}$ at 250°C also gives a brown product containing (8 - 10 W%) free iodine. The X-ray powder pattern of this material is significantly sharper than the hydrated aluminum sulfate, but there is little resemblance between the two diffraction patterns. There is again no evidence for the presence of LiI, $\text{LiI} \cdot \text{H}_2\text{O}$ or $\text{LiI} \cdot 3\text{H}_2\text{O}$. The detailed nature of this product is not at present known.

Thermogravimetric analyses of the various materials were obtained in air. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ begins to dehydrate at around 100°C . Considerably more rigorous conditions, $\sim 250^\circ\text{C}$, are required to dehydrate $\text{Al}_2(\text{SO}_4)_3 \cdot 5.5\text{H}_2\text{O}$. In contrast, in mixtures of LiI and hydrated aluminum sulphates, weight loss occurs at lower temperatures and is accompanied by the evolution of iodine. $\text{Al}_2(\text{SO}_4)_3$ at high temperatures decomposes with the evolution of SO_2 and SO_3 [10] which suggests that SO_3 is the effective oxidizing agent for the reaction $2\text{I} \rightarrow \text{I}_2$, Li_2O , or LiOH , being formed simultaneously. However, as determined from the free iodine produced, only approximately 30% of the LiI is converted in this way. The disappearance of all LiI lines from the diffraction pattern indicates reaction of the remaining LiI and perhaps also the LiOH with $\text{Al}_2(\text{SO}_4)_3$ to give the highly conducting phase. Reaction of LiOH or Li_2O under the same conditions gives materials with much lower conductivities.

The ionic conductivity of Li^+ was studied by both a.c. conductivity and n.m.r. techniques. The a.c. conductivity was measured at a frequency of 1 kHz with a 0.5 in diameter electrolyte pellet 0.05 - 0.15 cm thick sandwiched between two layers of lithium foil. Variation of the conductivity with temperature for the hydrated sample is shown in Fig. 2. For simple thermally-activated diffusion, $\log \sigma T$ should vary linearly with $1/T$, as found here. From the slope of the plot, the activation energy is found to be 8.3 kcal/mol.

N.m.r. techniques are applied to the examination of this system in several ways. The proton (^1H) n.m.r. signal is monitored to check for possible hydration of products, and its integrated intensity provides a measure of the extent of hydration, as mentioned in the preceding discussion. Chemical and structural changes of the $\text{Al}_2(\text{SO}_4)_3$ matrix can be traced by studying variations in the resonance shift and quadrupole coupling constants of the ^{27}Al nuclei. Finally, motional averaging of the ^7Li interactions results in a tem-

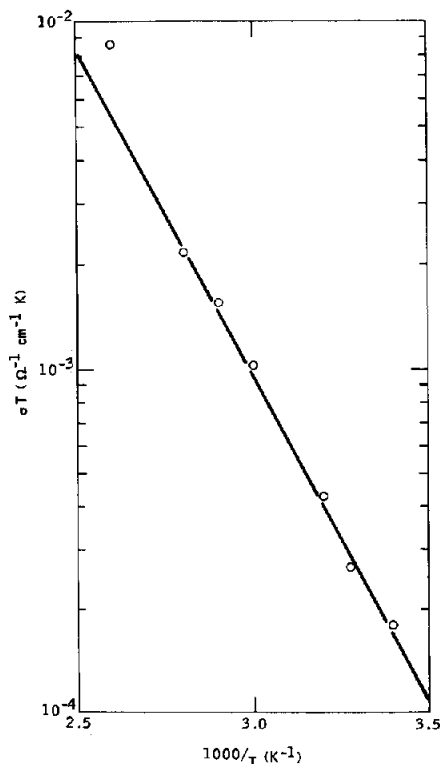


Fig. 2. Temperature variation of the conductivity of $\text{LiI}:\text{Al}_2(\text{SO}_4)_3 \cdot 5.5\text{H}_2\text{O}$.

perature dependence of the ^7Li n.m.r. line width, which, as shown below, can be related to the rate of Li ion motion.

The central ^{27}Al n.m.r. absorption line is sharp in anhydrous $\text{Al}_2(\text{SO}_4)_3$ and in the product $\text{LiAl}_2(\text{SO}_4)_3$, being well articulated and 3G wide in each case. Satellite lines corresponding to $(\pm 3/2 \leftrightarrow \pm 1/2)$ transitions are also observed, and their splitting, ~ 82 G, indicates a quadrupole interaction strength of ~ 620 kHz. A diamagnetic chemical shift of ~ 100 ppm is observed in both samples. The similarity of the chemical shifts and quadrupole coupling strengths suggests that only minor changes in the aluminum environment occur with the inclusion of the LiI, in agreement with the minor structural changes observed in the X-ray analysis. By contrast, the ^{27}Al n.m.r. signals are much broader in $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and the reaction product with LiI. In principle, such broadening could result from the protons in the waters of hydration or from structural disorder. To check, we have examined the fully hydrated crystalline material $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and again find a sharp line (~ 5 G in width), comparable chemical shifts (~ 150 ppm) and quadrupole coupling constants (~ 600 kHz). We therefore attribute the broadening to structural disorder, again consistent with the conclusions of the X-ray studies.

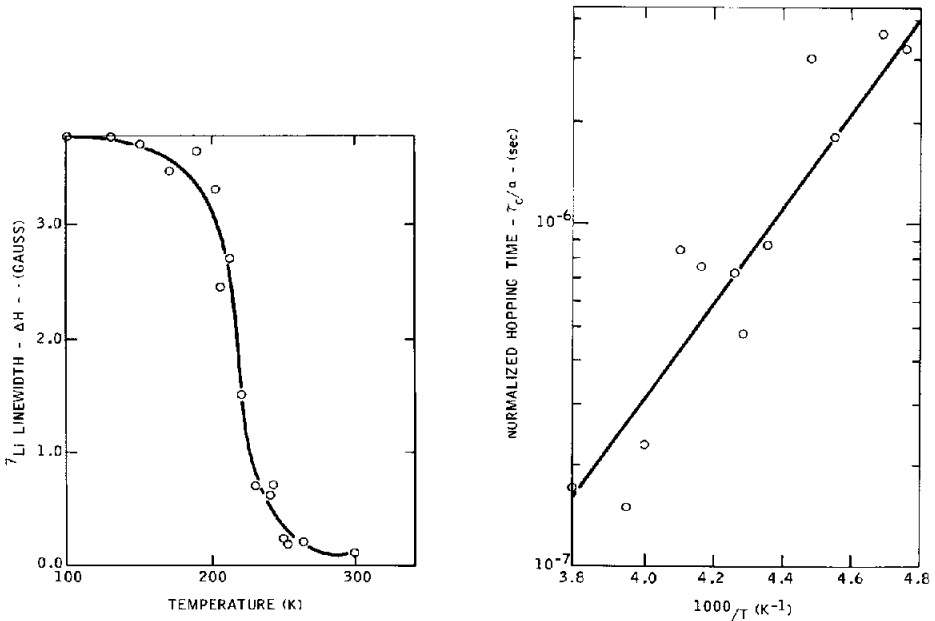


Fig. 3. Temperature dependence of ${}^7\text{Li}$ linewidth in $\text{LiI}:\text{Al}_2(\text{SO}_4)_3 \cdot 5.5\text{H}_2\text{O}$.

Fig. 4. Temperature dependence of hopping time deduced from ${}^7\text{Li}$ linewidth data.

The ${}^7\text{Li}$ n.m.r. line is approximately 0.1 G in width at room temperature in both hydrated and non-hydrated forms, reflecting an averaging of the Li nuclei interactions as a result of their motion in the solid. The integrated n.m.r. signal indicates that nearly all lithium atoms are mobile in both compounds. The resonance broadens in the vicinity of 225 K, reaching a width (separation between derivative maxima) of 3.7 G at low temperatures, as shown in Fig. 3. The characteristic time of motion can be determined from the observed line width at a given temperature $\Delta H(T)$ by use of the following phenomenological relation [11] :

$$\tau_c = \frac{1}{\alpha\gamma[\Delta H(T) - \Delta H_\infty]} \tan \left[\frac{\pi}{2} \left(\frac{\Delta H(T) - \Delta H_\infty}{\Delta H_0 - \Delta H_\infty} \right) \right]^2 \quad (1)$$

where ΔH_0 , ΔH_∞ are low and high temperature linewidths respectively, γ is the nuclear gyromagnetic factor, and α is a constant (approximately equal to 1), which is dependent on the detailed lineshape. A plot of $\log \tau_c$ as a function of $1/T$ gives a straight line, as in the conductivity case, with an activation energy of 6.3 ± 0.7 kcal/mol, as shown in Fig. 4. Analysis for the anhydrous case yields a similar activation energy.

Discussion

We have observed that the reaction of LiI with hydrated and anhydrous aluminum sulphates produces different products with different structures which do not contain unreacted LiI. Both materials, however, exhibit substantial ionic mobility. Previous conductivity studies have shown that defect induced mobility in LiI requires appreciably lower activation energies (10 kcal/mol) than the intrinsic lithium ion mobility in the pure solid where the activation energy is 20 kcal/mol. Several methods of increasing the lithium iodide conductivity by enhancement of the defect concentration have been described, notably by the addition of CaO and by co-mixture and treatment with finely divided Al_2O_3 . In every case so far reported the activation energy for conduction has been close to 10 kcal/mol [12]. The lower activation energy for the systems indicated in the present conductivity studies suggests that a different diffusion mechanism may apply.

It is well known that certain microscopic atomic motions may not contribute to the ionic diffusion in solids, and that n.m.r. measurements do not unambiguously indicate the presence of translational motion [7]. Thus, it is of interest to compare the conductivity as inferred from the n.m.r. data with the a.c. conductivity measurements. Such comparisons can be made in two ways: by comparison of the activation energies, as indicated in Figs. 2 and 4, and by a direct attempt to calculate the conductivity on the basis of inferred values for the microscopic hopping rate. The activation energies 8.3 ± 0.2 kcal/mol from the conductivity measurements and 6.3 ± 0.7 kcal/mol from the n.m.r. observations are in good agreement, especially considering the simple picture invoked for the diffusion mechanism and the phenomenological analysis of the n.m.r. data. Likewise, absolute values of the conductivity are in good agreement. Extrapolating the hop time data of Fig. 4 to 333 K, a value of $1/\tau_c \approx 2 \times 10^6 \text{ s}^{-1}$ is obtained. The conventional expression for conductivity resulting from N carrier hopping with a mean free path l is:

$$\sigma = \frac{Ne^2 l^2}{6kT} \left(\frac{1}{\tau_c} \right) \quad (2)$$

where e is the electron charge, k is Boltzmann's constant and T is the absolute temperature. In the absence of detailed structural information, we have assumed a mean-free path of $\sim 2 \text{ \AA}$. The calculated ionic density N is $2.5 \times 10^{21} \text{ cm}^{-3}$ and assuming that all the Li^+ ions are mobile, as indicated by the n.m.r. data, the conductivity calculated for n.m.r. data is $1.95 \times 10^{-6} (\Omega\text{-cm})^{-1}$. This value is in good agreement with the a.c. result of $3.2 \times 10^{-6} (\Omega\text{-cm})^{-1}$. In view of the simple diffusion model used and the assumptions which we have made, there is good agreement between the two results.

Presently, we are exploring fabrication of batteries employing multicell bipolar configurations of elements consisting of Li metal, the electrolyte and TiS_2 . Cell modules of open circuit voltages of 11.72 V and 55.7 V capable of $5 - 10 \mu\text{A/cm}^2$ current density at room temperature have been successfully fabricated.

Acknowledgements

The authors wish to thank Dr. J. A. Shropshire and Dr. M. S. Whittingham for helpful discussions.

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