

LITHIUM IODIDE-BASED SOLID ELECTROLYTES

ALAN HOOPER

Materials Development Division, A.E.R.E., Harwell, Oxon. (U.K.)

Summary

Mixtures of anhydrous lithium iodide and lithium hydroxide monohydrate exhibit conductivity transitions in the region of 170 °C and 100 °C. At the lower temperature transition, increases of two to three orders of magnitude are observed in mixtures containing as little as 1/80 by weight of LiOH·H₂O. Stable conductivities of about 10⁻¹ ohm⁻¹ cm⁻¹ are attained at 250 °C and both transitions are, with some hysteresis, reversible. With alumina additions, however, cooling specimens from just above the lower transition leads to Arrhenius-type behaviour with activation energies in the range 0.4 - 0.5 eV. Stable room temperature conductivities in the region of 5 × 10⁻⁵ ohm⁻¹ cm⁻¹ have been achieved. These results are discussed in terms of a super-cooled liquid phase.

Introduction

The work described in this paper was carried out as part of an Anglo-Danish programme of research on materials for advanced batteries. Begun in 1978, its ultimate aim is the development and characterisation of materials for an all-solid-state, rechargeable, alkali (Li, Na) battery operating below 200 °C for vehicular transport and stationary energy storage applications, and the identification of the most promising materials and cell types for further development. Partially funded by the European Community Research and Development Programme on Energy Conservation, the programme is coordinated by the Atomic Energy Research Establishment, Harwell, and involves workers at three sites in Denmark (Odense University; Risø Laboratory, and the Danish Technical University, Lyngby) and four sites in England (Imperial College, Wolfson Institute for Solid State Ionics; University of Oxford, Inorganic Chemistry Department; University of Leeds, Ceramics and Physics Department, as well as AERE, Harwell, Materials Development Division).

A prerequisite for an all-solid-state cell is clearly a solid electrolyte and one phase of the project was concerned with the fabrication and study of materials, already described in the literature, which showed promise for this application but whose properties were not fully characterized or understood. For lithium based devices, one such material was the composite comprising lithium iodide and alumina.

By addition of high surface area alumina [1, 2], enhancements of up to three orders of magnitude in the ionic conductivity of anhydrous lithium iodide over the temperature range 25 - 300 °C, have been reported. Other workers, using equally dry conditions, however, produced much smaller enhancements [3]. By contrast, high conductivities were obtained by the addition of moisture or of lithium iodide hydrates to the anhydrous material [4 - 8]. Additionally, some reported cell electrolytes contained significant amounts of lithium hydroxide as well as LiI and Al₂O₃ [9]. Such mixtures do not appear to offer any advantage from a conductivity point of view and therefore one can conjecture that the presence of the hydroxide plays some other, more subtle, role within the electrolyte.

This paper describes some interesting results obtained from studies of the LiI/LiOH·H₂O/Al₂O₃ system.

Experimental

The materials used in this study were primarily anhydrous lithium iodide (Alfa Chemicals), lithium hydroxide monohydrate (Koch-Light) and γ -alumina (Alcoa, H151). Electrical measurements were made in the range 25 - 250 °C, either directly on unpressed powders in ceramic crucibles using stainless steel rod electrodes or on pressed discs. All specimen preparation, handling, and measurement were carried out in a flowing argon dry box. A Solartron 1191 Frequency Response Measurement System was used to carry out a.c. conductivity measurements.

Differential thermal analysis (DTA) experiments were carried out in air. In order to protect the samples they were loaded into the platinum crucibles inside the dry box with a covering of dry α -alumina powder. Transfer to the DTA rig was rapid and heating was commenced immediately. A Stanton Redcroft DTA 673-4 was employed.

Results

The ionic conductivities of LiI/LiOH·H₂O mixtures in the range 4 - 40 mol.% LiOH·H₂O as a function of temperature are characterized by two reversible transitions (Fig. 1). One, at approximately 170 °C, corresponds to a visually observable solid-liquid transformation and is seen as a sharp DTA peak. Stable conductivities of $2 \times 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 240 °C are found for 2:1 mole ratio samples. The second transition at around 100 °C is larger and sharper in terms of conductivity but has a corresponding DTA peak which is relatively weak. No physical change in the material is observed through this transition where conductivity changes of up to two orders of magnitude give rise to values of $\sim 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$, in the range 100 - 130 °C.

Both conductivity transitions remain on initial heating for mixtures containing alumina dispersions. If such samples are cooled immediately after

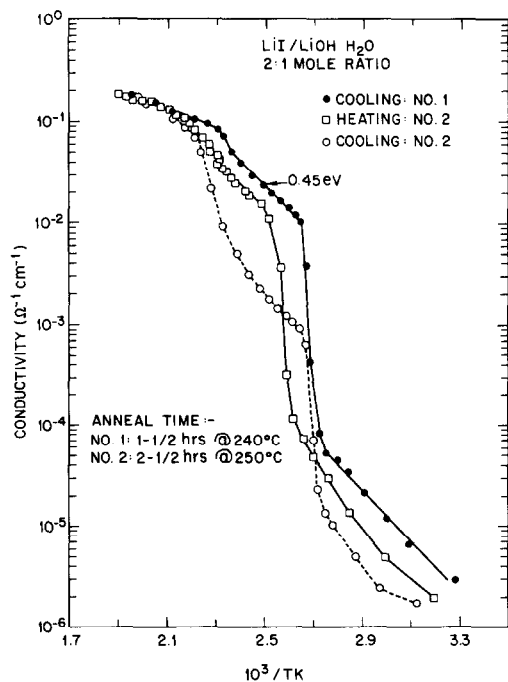


Fig. 1. Conductivity vs. reciprocal absolute temperature for two samples of LiI/LiOH·H₂O (2:1 mole ratio).

passing through the low temperature transition, however, the reverse transition is suppressed and their conductivities have an Arrhenius-type behaviour down to room temperature with an activation energy of 0.45 ± 0.01 eV (Fig. 2). This leads to stable, elevated low temperature conductivities; typically 7×10^{-5} $\text{ohm}^{-1} \text{cm}^{-1}$ at 25 °C, for a 2:1:1 mole ratio of LiI:LiOH·H₂O:Al₂O₃ (Alcoa H151). If the specimens are annealed at temperatures above the transition, however, their conductivity becomes time dependent, and subsequent cooling leads to correspondingly lower room temperature values, but with similar activation energies (Fig. 2). Crushing and re-pressing at this point restores, at least partially, the pre-annealed values.

Data were obtained for a series of samples in the mole ratio 16:1:*x* for *x* from 0 to 16. On immediate cooling from temperatures around 135 °C, it was shown that, above the transition point, the conductivity varies inversely with alumina content, but below about 100 °C the situation changes, and the level of conductivity is essentially determined by a balance between the higher temperature value and the degree to which the transition is subsequently retraced (Fig. 3). At 50 °C, the ionic conductivity is a maximum for an alumina content of around 30 mol.%, and a plot of conductivity *versus* alumina content has the same general shape as that previously described at room temperature for reportedly dry LiI-Al₂O₃ mixtures [1].

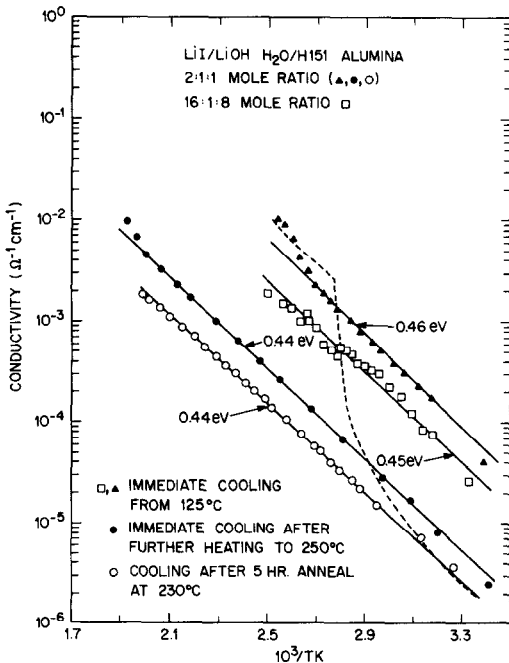


Fig. 2. Conductivity vs. reciprocal absolute temperature for pressed discs of LiI/LiOH·H₂O/Alcoa H151 alumina (2:1:1 and 16:1:8 mole ratio).

Experiments with a variety of aluminas indicate that the room temperature conductivity varies inversely with the second phase particle size. Measurements over a range of temperature show this to be due to the lesser ability of the larger particles to suppress the low temperature transition. In suitable form, MgO and SiO₂ are equally as effective as Al₂O₃ in enhancing conductivity.

The low temperature conductivity transition has also been observed in other, LiOH free, hydrated systems, *e.g.*, LiI·H₂O/Al₂O₃. In this case, however, the transition is not completely quenched on cooling and a high activation energy leads to a relatively low conductivity at 25 °C. A nominally anhydrous LiI/Al₂O₃ sample exhibits only a small transition. Subsequent annealing at 250 °C produces data essentially the same as that seen for similarly treated samples containing LiOH.

Conclusions

(1) The high and stable conductivities found in mixtures of LiI and LiOH·H₂O above a sharp transition in the range 100 - 130 °C are probably related to the presence of small quantities of liquid phases. These might be associated with either LiI·*x*H₂O eutectic compositions or the hydrated LiI-LiOH system itself.

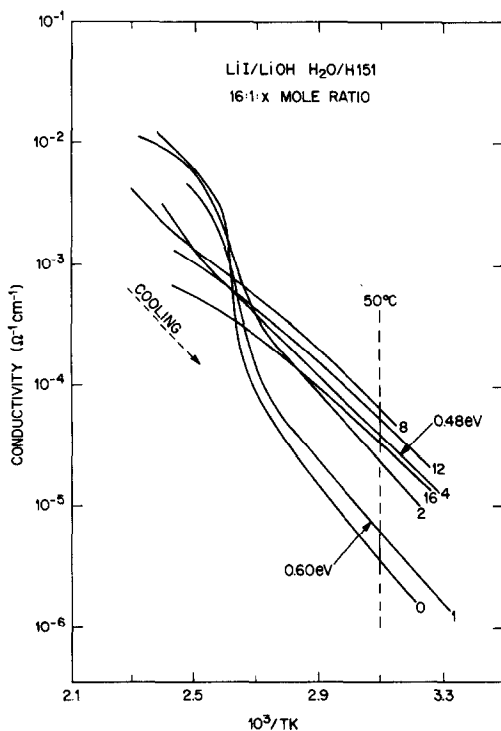


Fig. 3. Conductivity *vs.* reciprocal absolute temperature for a series of LiI/LiOH·H₂O/H151 discs (16:1:*x* mole ratios) on cooling from just above the "low temperature" transition point. (*x* values indicated by each curve.)

(2) The quenching of the conductivity transition on cooling by alumina additions might be explained in terms of a high conductivity "super-cooled" liquid phase present around each alumina particle.

(3) Higher and more stable room temperature conductivities are achieved in systems which contain LiOH·H₂O as opposed to other hydrates, *e.g.*, LiI·H₂O.

(4) A reliable low temperature route to an electrolyte with good room temperature properties has been identified. Also, by the use of very small additions of LiOH·H₂O it is possible to produce a material with both high, stable conductivity and mechanical strength around 130 °C, in the absence of any dispersed alumina.

(5) The results are in basic agreement with the basic premise that, in the LiI-Al₂O₃ system, the presence of a hydrated phase is advantageous to the production of high conductivities.

(6) Considerable insight has been gained into details of how previously observed [4] room temperature conductivities in similar systems were achieved, *via* annealing procedures typically in the range 100 - 150 °C.

Acknowledgements

The author is grateful to Mr R. J. Powell for considerable experimental assistance. The work was funded by the Department of Industry and the Commission of the European Communities: -316-78-1 EE UK.

References

- 1 C. C. Liang, *J. Electrochem. Soc.*, 120 (1973) 1289.
- 2 C. C. Liang, A. V. Joshi and N. E. Hamilton, *J. Appl. Electrochem.*, 8 (1978) 445.
- 3 U. Von-Alpen and M. F. Bell, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.) *Fast Ion Transport in Solids*, North Holland, Amsterdam, 1979, p. 463.
- 4 B. B. Owens and H. J. Hanson, *U.S. Pat. No. 4,007, 122* (1977).
- 5 S. Paek, B. B. Owens and J. B. Wagner, *J. Electrochem. Soc.*, 127 (1980) 2177.
- 6 J. B. Phipps and D. H. Whitmore, *Ext. Abstr.*, No. 371, Fall Meeting, Electrochemistry Soc., Hollywood, Florida, 1980.
- 7 P. M. Skarstad, D. B. Merritt and B. B. Owens, *Solid State Ionics*, 3/4 (1981) 277.
- 8 P. Hartwig and W. Weppner, *Solid State Ionics*, 3/4 (1981) 249.
- 9 For example, C. C. Liang, *U.S. Pats.* 3,730,775; 3,713,897.