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Lithium ion conducting solids for ambient applications

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A number of pure substances and mixtures have been investigated as possible lithium ion conductors. Of the pure substances investigated $LiI \cdot H_2O$ shows promise. However, better characteristics were found for $LiI/LiOH \cdot H_2O/Al_2O_3$.

1. Introduction

In this paper two types of material have been investigated as possible lithium ion conducting solid electrolytes. The first group consists of pure lithium salts (mainly halides) and their hydrates. The second group consists of electrolytes prepared using a mixture of several components. These are based on reports of other workers namely Owens and Hanson [1], Liang [2] and Hooper [3].

Owens and Hanson [1] have claimed that the conductivities of the pure lithium halides could be enhanced by adding a high surface area material such as silica or alumina, and a controlled amount of water. We prepared similar mixtures using lithium fluoride, alumina and water, and lithium iodide, silica and water.

Liang [2] claimed that a conductivity of $1.0 \times 10^{-4} (\Omega\,cm)^{-1}$ could be obtained from a mixture of lithium iodide and alumina in which the alumina was pretreated with the organometallic compound *n*-butyl lithium which donated lithium to the surface of the alumina; this being the key feature of the preparation which was reputedly responsible for the high conductivity.

Hooper [3] claimed a room temperature conductivity of $5.0 \times 10^{-5} (\Omega\,cm)^{-1}$ for a three-component mixture of lithium iodide, lithium hydroxide monohydrate and alumina which was temperature cycled to around 130° C. Accordingly, we investigated the effect of temperature cycling on similar mixtures using lithium iodide with lithium hydroxide, iodide and sulphate monohydrates, with and without alumina. The conductivities of the materials were determined using a.c. impedance, and where a genuine conductivity of greater than $10^{-6} (\Omega\,cm)^{-1}$ was found, the stability of the material against lithium metal was measured together with the sustainable lithium ion current.

The results are given in table form together with a note as to the suitability of the material for use as a solid electrolyte.

2. Experimental procedure

Commercially available materials were used except for some of the hydrates of lithium halides which were prepared by allowing the lower hydrate (or pure halide) to take up sufficient moisture to form the required hydrate. The source of the materials is given in Table 1.

Table 1. Origin of materials used

LiF	BDH extra pure 98%)
LiCl	(BDH 99%)
$LiCl \cdot H_2O$	(Prepared by deliquescence from the above)
LiBr	(BDH 99%)
$LiBr \cdot H_2O$	(Ultra-pure, ex-Lancaster synthesis)
LiI	(MERCK 99% pure)
$LiI \cdot H_2O$	(BDH 96%)
$LiI \cdot 2H_2O$	(Prepared by deliquescence from the above)
$LiI \cdot 3H_2O$	(Ventron 99%)
$LiOH \cdot H_2O$	(BDH 99%)
$Li_2SO_4 \cdot H_2O$	(BDH 99%)
Al_2O_3	(Alcoa H151)
SiO_2	(Cab-O-Sil EHS, Deggussa)
n-butyl lithium	(Aldrich, in 1.5 mol dm^{-3} hexane)

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Table 2. The room temperature conductivities of lithium halides and hydrates

Material	*Conductivity* $(\Omega\ \text{cm})^{-1}$	*Steady lithium ion current,* $i\,(\mu\text{A})$	*Suitability as a solid electrolyte*
LiF	10^{-9}	–	Negligible conductivity
LiF/H_2O	10^{-4}	Rapid fall off with time	No hydrate formed: conductivity due to free water, ∴ unstable to lithium metal
LiCl	2.9×10^{-9}	–	Low conductivity
LiCl·H_2O	6.0×10^{-4}	Fall off with time	Seems to be unstable to lithium
LiBr	4.7×10^{-9}	–	Low conductivity
LiBr·H_2O	3.7×10^{-8}	Fall off with time	Seems unstable to lithium metal
LiI	6.5×10^{-8}	–	Low conductivity
LiI·H_2O	1.3×10^{-6}	15	Possible low drain applications
LiI·$2H_2O$	1.0×10^{-7}	–	Low conductivity
LiI·$3H_2O$	5.5×10^{-6}	Rapid fall off with time	Conductivity due to free water present, ∴ unstable to lithium metal
LiOH·H_2O	10^{-8}	–	Low conductivity
Li_2SO_4·H_2O	10^{-6}	None possible	Possible proton conductor

Samples similar to those reported by Owens and Hanson [1] were made up using 56 mol% lithium halide, 34 mol% alumina or silica and sufficient water (triple distilled) to form the monohydrate of the halide. The preparation of the lithiated alumina electrolyte was carried out exactly as described by Liang [2]. The two and three-component mixtures similar to those described by Hooper [3] were made up using 2 : 1 mole ratios of lithium iodide : lithium salt monohydrate, and 2 : 1 : 1 mole ratio for samples containing alumina. The temperature cycled samples were prepared by placing in an evacuable vessel, heating to 135° C, then allowing to cool as soon as this temperature was attained. All materials were handled in a dry air glove box (< 15 ppm water content), except the preparation involving *n*-butyl lithium which was performed under dry argon. The conductivity of the materials was determined using a.c. impedance. Discs of the materials were formed (0.3 mm thick) between stainless steel electrodes (2.0 cm^2 area) at 1000 kg cm^{-2} pressure in a perspex cell and the a.c. impedance spectrum recorded over the range 1 MHz → 1 Hz using 10 points per decade. Where a conductivity of $10^{-6}(\Omega\ \text{cm})^{-1}$ or higher was found, d.c. measurements were performed using lithium electrodes (placed between the sample disc and the stainless steel electrodes), and the lithium ion current noted when a potential of 0.2 V was applied across the cell.

3. Results

The results are given in table form. Table 2 shows the pure lithium salts and hydrates investigated, and Tables 3 and 4 the mixed systems based on the reports of Owens and Hanson, Liang and Hooper.

Table 3. The room temperature conductivities of the mixed electrolytes based on those reported by Owens, Hanson and Liang

Material	*Conductivity* $(\Omega\ \text{cm})^{-1}$	*Steady lithium ion current,* $i\,(\mu\text{A})$	*Suitability as a solid electrolyte*
LiF/Al_2O_3/H_2O	6.0×10^{-4}	Rapid fall off with time	No hydrate formed; conductivity due to free water, ∴ unstable to lithium
LiI/SiO_2/H_2O	5.0×10^{-7}	3.0	Conductivity too low
LiI/Al_2O_3(C_4H_9Li)	2.0×10^{-6}	11.0	Pellets fragile and prone to degradation

Table 4. The room temperature conductivities of the mixed electrolytes before and after temperature cycling based on those reported by Hooper

Material	*Conductivity* $(\Omega\ \mathrm{cm})^{-1}$	*Steady lithium ion current,* $i\ (\mu A)$	*Suitability as a solid electrolyte*
Before temperature cycling			
$LiI/LiOH \cdot H_2O$	1.0×10^{-7}	–	Conductivity too low
$LiI/LiI \cdot H_2O$	5.0×10^{-7}	–	Conductivity too low
$LiI/Li_2SO_4H_2O$	4.5×10^{-7}	–	Conductivity too low
$LiI/LiOH \cdot H_2O/Al_2O_3$	3.0×10^{-5}	60	Should be investigated further
$LiI/LiI \cdot H_2O/Al_2O_3$	2.5×10^{-6}	–	Not investigated
$LiI/Li_2SO_4 \cdot H_2O/Al_2O_3$	1.0×10^{-7}	–	Conductivity too low
After temperature cycling			
$LiI/LiOH \cdot H_2O$	6.0×10^{-7}	–	Conductivity too low
$LiI/LiI \cdot H_2O$	1.8×10^{-6}	–	Conductivity too low
$LiI/Li_2SO_4H_2O$	5.0×10^{-7}	–	Conductivity too low
$LiI/LiOH \cdot H_2O/Al_2O_3$	4.0×10^{-6}	–	Not investigated
$LiI/LiI \cdot H_2O/Al_2O_3$	2.8×10^{-6}	–	Not investigated
$LiI/Li_2SO_4 \cdot H_2O/Al_2O_3$	–	–	Results inconclusive

4. Conclusions

It must be concluded that of the pure solids reported here, only lithium iodide monohydrate may find an application in low drain devices. However, when the mixtures were considered the $LiI/LiOH \cdot H_2O/Al_2O_3$ system sustained a much higher current than any of the pure solids and looks suitable for applications in low drain devices.

References

[1] B. B. Owens and H. J. Hanson, US Patent No. 4007122 (1977).
[2] C. C. Liang, US Patent no, 4150203.
[3] A. Hooper, *Proc. Int. Conf. of Fast Ionic Transport in Solids*, Gatlinburg, Tennessee, USA, May 18–22 (1981) (edited by J. B. Bates and G. C. Farrington) p. 339.