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THE EFFECT OF DIFFERENT INTERNAL SURFACES IN COMPOSITE LITHIUM ELECTROLYTES

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Summary

A linear increase in the conductivity of LiI–alumina composite electrolytes with increasing specific surface area (2.4 - 260 $m^2\,g^{-1}$) of the alumina is demonstrated. Part of the enhanced conductivity is probably due to normal doping of the LiI by the alumina. Replacing 25% of the LiI by LiBr does not change the conductivity. Replacing part of the LiI by Li_3N has a detrimental effect.

Introduction

LiI–alumina composite electrolytes were introduced in 1973 by Liang [1]. However, it is still uncertain whether these materials can compete with other solid lithium electrolytes in high-drain lithium batteries. All proposed models [2, 3] predict a maximum in the conductivity at intermediate alumina concentrations, based on the assumption that the conductive paths will be blocked at high alumina contents. As pointed out earlier [4] it is not possible to pack real oxide particles/aggregates to 100% theoretical density (as the cube-shaped volume segments are in the models). This leads to the practical problem that composite electrolytes with a high secondary phase content can never be 100% dense (which, in turn, hinders mathematical description as well as practical use). Accordingly, the decrease in the conductivity at high alumina contents is mainly due to this imperfection of the samples.

Several co-existing phenomena have been associated with the enhanced conductivity: space charge phenomena [5, 6], chemical surface interactions [6], formation of new phases, presence of water, etc. However, a recent model calculation of the space charge layer contribution by Dudney [7] indicates a much lower contribution to the overall conductivity from this type of mechanism than has previously been considered. Part of the conductivity enhancement could be due to an increase in doping level. This has therefore been investigated in the present study, along with the influence of other salts (LiBr and Li_3N), on the properties of LiI–alumina composites. A recent review on composite electrolytes is given in ref. 8.

Experimental

Electrolyte fabrication

Anhydrous LiI (Ventron) and LiBr (Merck) were dried overnight under vacuum at 300 °C. Li$_3$N was kindly supplied by Dr S. Skaarup, Technical University of Denmark. Activated alumina from Alcoa (H151) and Edwards were received as 2 - 6 mm dia. hard spheres. The latter were milled down to an average grain size of 10 μm. After heat treatment of the aluminas [9] for periods between 0.5 and 4 h at constant temperature (600 or 1000 °C in air), the specific surface area of 1 gram samples was determined by nitrogen adsorption (BET method). Composites were made by mixing the appropriate materials in an argon-filled glove box (less than 2 ppm water); the mixture was compacted at 5 ton cm^{-2} and then heated to 50 - 100 °C above the melting point of the given salts for 1 h in argon. The impregnated material was pulverized again, and then discs (13 mm dia., 0.5 - 1 mm thick) were pressed from the composite powder at 10 ton cm^{-2}. Thin aluminum-foil electrodes were pressed onto the circular faces during this process.

Conductivity measurements

The electrolyte discs were placed between platinum electrodes in an evacuable sample holder. The cell was purged with pure argon (N48) during the measurements. The admittance was determined with a Solartron 1174 Frequency Response Analyser equipped with a pre-amplifier unit. These devices, as well as the temperature controller of the furnace, were controlled by a PDP 11/23 computer. Admittance spectra were recorded in the frequency range from 0.1 Hz to 999.9 kHz with 50 mV across the sample and a variable reference resistor in series (10 Ω - 1 MΩ). The present paper is based on analyses of 251 such admittance spectra.

Results and discussion

General features of admittance data

The admittance spectra from the composite discs with aluminum electrodes can be interpreted on the basis of the scheme for a symmetrical cell with blocking electrodes. At temperatures below 200 °C, an equivalent circuit consisting of one resistor in series with a CPA element (modelling a non-ideal double layer capacity) in parallel with a geometrical capacitor provides a very good fit of the experimental data. At temperatures higher than 200 °C, the depressed semi-circle shows a tendency to split into two strongly overlapping semi-circles. All equivalent circuits that have been tested to date in order to model the high temperature admittance plots, give component values with too high a degree of correlation. The conductivity data quoted in this study are therefore the overall conductivities which normally are found at the minimum in the imaginary part of the admittance in the range 1 kHz - 100 kHz. At temperatures higher than 300 °C, where

TABLE 1

Specific conductivity and fitted constants in Arrhenius expression for LiI–alumina composites (60/40 mole ratio) as a function of specific surface area of the alumina. Pre-exponential and activation energy are shown with standard deviations

A $(m^2 g^{-1})$	σ_{25} $(S\ cm^{-1} \times 10^{-6})$	σ_{300} $(S\ cm^{-1} \times 10^{-2})$	σ_0 $(S\ cm^{-1})$	ΔE (eV)
154	9.77	1.87	67.7 ± 5.1	0.405 ± 0.003
133	6.70	1.30	47.6 ± 5.1	0.405 ± 0.004
74	5.97	1.13	40.4 ± 3.4	0.404 ± 0.003
62	2.01	0.680	45.6 ± 2.2	0.435 ± 0.002
2.4	0.370	0.110	6.32 ± 0.73	0.428 ± 0.004

the sample resistances are lower than $10\ \Omega$, corrections for the admittance of the current collectors and the leads were made (approx. $1\ \Omega$ and 4×10^{-7} H).

In the case of the LiI–alumina composites (Table 1) a simple $\log \sigma$ versus $1/T$ gave the best fit, whereas a $\log \sigma T$ versus $1/T$ fit gave a slightly better representation of the LiBr/I–, LiBr– and LiI/Li$_3$N composite data, cf. Table 2.

Influence of alumina surface area

Systematic investigations of the dependence of the ionic conductivity of the alumina surface area are available only for CuCl–alumina composites [10]. In 1985, we started [9] a similar study on LiI–alumina composites. Composite electrolytes were made with identical composition, 40/60 mole ratio alumina/LiI, and the samples were heat treated in parallel to ensure that the impurity level (degree of doping) was constant in all samples. Electron micrographs (up to $\times 30\,000$ magnification) of the $62 \cdot 260\ m^2 g^{-1}$ aluminas show aggregates composed of spherical "cloudy" sub-aggregates. The $74 \cdot 260\ m^2 g^{-1}$ aluminas were shown by XRD to be the gamma form of Al$_2$O$_3$ (JCPDS no. 10-425), whereas the $2.4\ m^2 g^{-1}$ alumina is corundum and consists of aggregates of thin plates. The $62\ m^2 g^{-1}$ alumina is a mixture of the two forms. As seen from Table 1 and Fig. 1, an increase in conductivity is observed with increase in the surface area of the alumina. This suggests that the Li-salt/alumina interfaces are highly conductive: to such an extent that the blocking effect of the 40 vol% bulk alumina phase is more than compensated.

A high degree of scatter of the 6 composite conductivities around (any) smooth function in surface area is obvious, even from the semi-logarithmic plot of Fig. 1. Three sources of error must be considered before fitting a function to the data, namely, errors in (i) specific area determination (10 - 20%), (ii) specific conductivity measurement (2 - 5%), and (iii) the degree of perfection of the sample (% of theoretical density, size and spatial distribution of microcracks, etc.). Assuming that a proper interpretation of the

TABLE 2

Specific conductivity and fitted constants in Arrhenius expression for various new composite electrolytes

	LiBr/I 30% alu	LiBr/I 35% alu	LiBr 30% alu	LiI/Li$_3$N 28% alu	LiI[a] 40% alu	Unit
A	260	260	260	260	390	m^2 g^{-1}
σ_{25}	1.02	1.48	0.0633	0.0554	3.71	10^{-5} S cm^{-1}
σ_{100}	2.67	3.59	0.225	0.245	5.09	10^{-4} S cm^{-1}
σ_{300}	2.19	2.67	0.284	0.417	1.71	10^{-2} S cm^{-1}
σ_o[b]	10.3 ± 0.5	10.6 ± 0.5	3.01 ± 0.51	7.75 ± 3.67	1.54 ± 0.32	S K cm^{-1}
ΔE[b]	0.445 ± 0.003	0.437 ± 0.002	0.485 ± 0.006	0.517 ± 0.017	0.364 ± 0.004	eV
d	3.24	3.12	2.96	2.98	3.13	g cm^{-3}

(a) From ref. 4; (b) least-squares fit to $\sigma = \sigma_o/T \exp(-\Delta E/RT)$; alu = high surface-area alumina; d = density of composite; LiBr/I: LiBr/LiI = 25/75 ratio; LiI/Li$_3$N = 70/30 ratio.
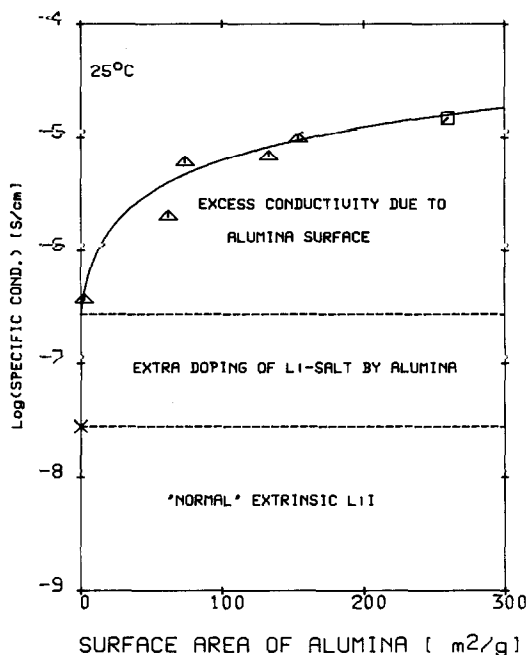
Fig. 1. Specific conductivity at 25 °C for: △, LiI–alumina 60/40 ratio; □, (0.75 LiI + 0.25 LiBr)–alumina 65/35 ratio as a function of the specific surface area of alumina. Polycrystalline LiI is shown for reference (×). Two contributions to the total conductivity are indicated.

admittance data is given, conductivity data will always be on the conservative side of the true conductivity value of a perfect sample of the same material. A linear least-squares fit was therefore performed using the conductivity as the independent variable. The fit ($r = 0.974$) gives the following relation between specific conductivity (S cm^{-1}) and specific area of alumina (m^2 g^{-1}) for the 5 LiI–alumina (60/40 mole ratio) and the 65/35 mole ratio LiBr/i–alumina composites at 25 °C:

$$\sigma = 6.02 \times 10^{-8}A + 2.74 \times 10^{-7} \tag{1}$$

Equation (1) gives the full curve in Fig. 1 when shown in a semilogarithmic plot. Assuming that the linear relation holds, two interesting cases arise.

(i) Extrapolation to high alumina surface area values. The highest specific conductivity reported for LiI–alumina composites, apart from that of Liang et al. [11], was obtained in our laboratories, namely, 3.71×10^{-5} S cm^{-1} for a 60/40 ratio with a specific surface area of alumina equal to 390 m^2 g^{-1}. The estimated value from eqn. (1) for 390 m^2 g^{-1} is 2.3×10^{-5} S cm^{-1}, which is in fair agreement with the observed value. On the
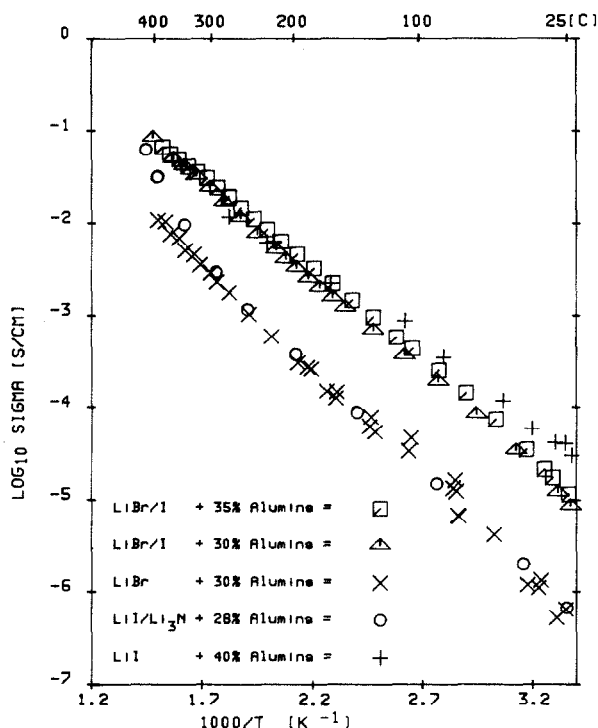
Fig. 2. Arrhenius plot of specific conductivity for 5 different composite electrolytes: LiI–alumina with 390 $m^2 g^{-1}$ alumina, and four others with 260 $m^2 g^{-1}$ alumina. Mole ratios as in Table 2.

other hand, the conductivity reported by Liang et al. [11] of 10^{-4} S cm^{-1} at 25 °C would, according to eqn. (1), correspond to a specific surface area of ~1665 m^2 g^{-1}, which is unrealistically high.

   (ii) Extrapolation to zero surface area of alumina. This corresponds to a hypothetical situation where the only effect of the alumina should be to reduce the conductivity of the LiI in proportion to the alumina volume fraction. However, the extrapolated conductivity is 2.74×10^{-7} S cm^{-1}, which is higher than any reported value for LiI. The value is roughly 10 times higher than our own value for a polycrystalline LiI pellet made from the same source as the composites. This is taken to indicate that part of the enhanced conductivity of LiI–alumina composites is due to an increased doping level of the LiI phase arising from the alumina (Li-vacancy concentration approximately 10 times higher than in the starting material). The nature of the aliovalent ion(s) deriving from the alumina is unknown at present. The data of Fig. 1 suggest two contributions to the conductivity enhancement according to this doping model.

Thickness of interface layer

If the Li-salt phase is in total contact with a second phase of very high surface area, then a large fraction of the lithium ions will be "surface" atoms. Already at $150 \ m^2 \ g^{-1}$, the fraction is high. The composites studied here have densities in the range 3.0 - 3.3 g cm^{-3}, from which it follows that a 1 cm^3 composite contains about 1 g of alumina. In a model calculation, the alumina can be assumed to be distributed as parallel plates ($d = 1$), rods ($d = 2$) or cubes ($d = 3$) evenly positioned in a 1 cm cube. The average Li-salt thickness (distance between alumina slabs, rods, etc.) will then, to a first approximation, be given by:

$$t = 2dv/A \qquad\qquad (2)$$

where v is the volume fraction of the Li salt. Setting $d = 3$ and $A = 150$ m^2 g^{-1}, the average Li-salt layer thickness is around 240 Å. If the Li-salt phase is, in fact, distributed in such thin layers between the alumina particles, then there is no longer a basis for a distinction between space charge layer and bulk Li salt. This value is also so low that the approximations used in the various model calculations are not valid. Commercial aluminas are available up to 400 m^2 g^{-1}, but it should be possible to produce aluminas with specific areas (but, unavoidably, also with large concentrations of hydroxyl groups) in the range up to 800 m^2 g^{-1}. From this point of view, it should still be possible to improve the conductivity of composites to a technologically acceptable level.

Temperature dependence of conductivity

The Li-salt/alumina composites described here and in the literature all show only one regime in the Arrhenius plots, in contrast to many of the silver halide– and copper halide–alumina composites [5, 6, 10]. In this regime, the apparent activation energy for conduction increases with increase in temperature. A form of compensation law is evident for Li halide/alumina composites, namely, the higher the conductivity, the lower the overall activation energy for ionic conduction. If it is assumed that the doping concentration c_2 in the LiI is at least 10 times higher in the composites than in the "pure" LiI (see above), then the transition temperature (T_{knee}) to the intrinsic activation energy for LiI, *e.g.*, 0.81 eV [12], should be shifted to a higher temperature according to:

$$\ln(c_1/c_2) = (E_{intr}/R)(1/T_2 - 1/T_1) \qquad\qquad (3)$$

where c_i is the doping concentration corresponding to transition temperature T_i. With $T_1 = 180$ °C, it can be seen that the transition should be shifted at least to 240 °C, which partly explains why the onset of intrinsic conduction has not been observed. For LiBr–alumina (*cf.* Table 2), the activation energy of 0.485 eV is identical to the value for LiBr *i.e.*, 0.47 eV obtained by Mercier *et al.* [13].

Effect of conductive salt–salt grain boundaries

In order to obtain composites with high conductivities, it would seem reasonable to try to incorporate a lithium conductor with a conductivity as high as possible in the composite.

Mercier *et al.* [13] have observed positive deviations in the conductivity of the LiI–LiBr system. The maximum in the conductivity occurred at 25 mol% LiBr. At this composition, the material consists of a mixture of two solid solutions (both cubic) with 85 and 7 mol% I, respectively. It was argued that the maximum in conductivity, 5×10^{-7} S cm^{-1} at 25 °C, was due to a maximum concentration of conductive grain boundaries occurring at 25 mol% LiBr. The 30 and 35 mol% alumina composites made with this two phase Li-conducting mixture have higher conductivities than the LiI/LiBr mixture itself. The conductivity is higher for the composite containing more alumina, indicating that the salt/alumina interfaces are more conductive than the salt/salt interfaces. Based upon the pore model for optimizing the conductivity of composites [4], 35 mol% alumina was calculated to be the composition where the salt volume just matches the free volume in the close-packed alumina aggregates. Apparently, it matters very little that 25% of the LiI has been replaced by LiBr. There is a slight difference in activation energy, but the conductivity obtained is what would have been expected from a 100% LiI/alumina composite, *cf.*, Fig. 1. On the other hand, the conductivity of the LiBr/alumina composite is between 10 and 20 times lower than that for the mixed and 100% LiI samples. This fact leads to the conclusion that proton conduction, if any, is not important in properly made/handled composites. (The high surface-area aluminas exhibit a small weight loss (0.1 to 0.5%) on prolonged firing, which means that some alkalies and/or hydroxyl groups are present in the aluminas.) The proton content, if any, should be the same in all the composites where aluminas with identical surface areas have been used.

The conductivity of LiBr/alumina and LiI–Li$_3$N/alumina is quite low in comparison with the other composites. The reason for the detrimental effect of adding Li$_3$N is unknown. The present investigation thus emphasizes the "unique" properties of LiI in composites with alumina.

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