PROPERTIES OF LiI - ALUMINA COMPOSITE ELECTROLYTES

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LiI and 14 different LiI - high surface area Al_2O_3 composite electrolyte materials have been examined by the ac-admittance method. The presented data span the temperature range from 25°C to 300°C, and the composition range from 20 to 70 mole % Al_2O_3 , respectively. Maxima are observed in the isothermal conductivity versus composition plots at 40-50 mole % Al_2O_3 . At 25°C the best material has a specific conductivity equal to $3.75 \cdot 10^{-5}$ S/cm, or a factor 100 to 1000 higher than for LiI at the same temperature. The enhanced conductivity results from an increase in the preexponential factors and a minimum in the overall activation energy for conduction occurring between 40 and 50 mole % alumina. The compositional dependence of the conductivity is discussed on basis of a pore-model. Preliminary analysis of Hebb-Wagner polarization data for the cell Li/LiI/C indicates that electronic leakage currents in LiI are carried by electrons.

1. INTRODUCTION

Significant increases in the ionic conductivity of LiI (1,2), CuCl (3), and AgI (4) have been observed, when these salts are mixed with a high surface area material, typically submicron or activated alumina. Since the invention in 1973 (1) of these so called composite solid electrolytes, several models have been proposed in order to account for the enhanced conductivity. All models assume that highly conducting paths are created along the interface between the ionic salt and the filler material (2,3,5). Especially LiI - alumina composite materials show promise as electrolytes in high temperature rechargeable batteries (6,7). However, some difficulties in reproducing the high conductivities claimed (6) have been experienced by other researchers (8). We are in the process of investigating a long range of LiI based composites by structural-, electrochemical-, calorimetric-, and surface sensitive methods (9). Some of the results obtained so far are presented in this paper. It is shown that high conductivities can be obtained independently of the source of the starting materials and modifications in the fabrication route. Density measurements on composites give useful information on the phase distribution.

2. EXPERIMENTAL SECTION

2.1 Chemicals

Two sources of anhydrous LiI were used: anhydrous LiI (Ventron) without further drying, and dehydrated $\text{LiI} \cdot 2\text{H}_2\text{O}$ (Merck) treated as described earlier (10). Two brands of activated alumina, H151 (Alcoa) and 09-H026-00-050 (Edwards) were dried 12 hours in vacuum at 600°C. All handling of the chemicals was carried out in an Ar-filled glovebox system including furnace, balance, and hydraulic press. The box was operated at a partial pressure of water lower than 2 vpm.

2.2 Composite fabrication

Method 1: Weighed amounts of LiI (Merck) and H151 spheres (2-3 mm ϕ) were heated together under vacuum at 550-650°C for 1 hour. The impregnated spheres were cooled down and ground. Method 2: LiI (Ventron) and the two types of alumina were ground separately, weighed amounts were mixed thoroughly, heat treated under Ar as above, and finally ground again.

2.3 Electrode mounting

13 mm ϕ electrolyte discs (0.8-1.2 mm thickness) with 0.015 mm thick Al-foil electrodes were pressed in a KBr-die at 7 or 10 tons/cm². Samples for Hebb-Wagner experiments were pressed with an aquadag carbon coated electrode on one side. A 0.5 mm thick Li-foil electrode was subsequently mounted on the opposite face of the disc. The discs were clamped between Pt-foil current collectors in an evacuable quartz/steel sample holder.

2.4 Ac-measurements

More than 200 ac-admittance spectra were recorded on equilibrated samples by means of a Solartron 1174 Frequency Response Analyser supplied with a preamplifier unit (11). The FRA and the Newtronic DSP-temperature controller of the furnace were controlled by a PDP 11/23 computer. The admittance was determined at 30-50 frequencies in the range 1 Hz to 999.9 kHz. The temperature was kept constant to within 0.3°C during measurements.

2.5 Hebb-Wagner measurements

The sample was polarized with an Oltronix power supply (C40-08D) equipped with a voltage divider.

Steady state currents were recorded with a Micrograph BD5 (Kipp). A Keithly 616 digital electrometer was used to monitor the voltage across the cell.

3. RESULTS AND DISCUSSION

3.1 Survey of ac-conductivity results

Three series of LiI - alumina composites were made using two methods and a total of four different chemicals, see Table I. Complex plane plotting of the admittance data obtained at lower temperatures showed one depressed semicircle (depression $\sim 20^\circ$) and a high frequency geometrical branch. The semicircle gradually becomes more and more flat with increasing temperature above $\sim 200^\circ\text{C}$. The sample conductivity was determined by extrapolating the geometrical branch to zero phase shift. An equivalent circuit description of this new type of polyphase solid electrolytes is under development in our group. The Arrhenius plot of the LiI-alumina (Edw.) series in Fig.1, and the conductivity versus alumina content plot in Fig.2 are representative of the three series of composites. Conductivities were reproducible and independent of the thermal history of the samples.

3.2 Influence of chemicals and fabrication route

The uncontrolled impurity content of the starting materials and the contact time with different crucible materials (alumina, silica, aluminium) during the heat treatment of the three series of composites did not seem to influence the general trends in the final conductivities of the composites. This strongly supports the idea that the conductivity increase is due to LiI-alumina interfacial phenomena, and not due to an increase in the defect concentration in LiI due to contamination.

Hotpressing at $250\text{--}300^\circ\text{C}$ does not improve the conductivity nor the density significantly compared with coldpressing at 10 tons/cm². Series 1 composites compressed at 7 tons/cm² had slightly lower conductivities compared with the two other series. However, even compression at the high pressure only yields pellets with 80-90 % of the theoretical density (see section 3.5). The effect

Series no.	Mole % Al_2O_3	LiI	Al_2O_3	Meth.no.
1	10,20,30,40	Merck	H151	1
2	25,35,45,50,70	Ventron	H151	2
3	20,30,40,50,60	Ventron	Edw.	2

TABLE I. Investigated LiI - alumina composites. Meth.no. refers to section 2.2 .

of consecutive firings and grindings on the grain size distribution should be investigated.

Figure 1. Arrhenius plot of specific conductivity of LiI (0) and three LiI-alumina (Edw.) composites. Numbers refer to content of Al_2O_3 in mole % in the composites.

Figure 2. Specific conductivity isotherms for the LiI-alumina(Edwards) composite system.

3.3 Dependence on alumina content

A conductivity enhancement effect (the composite effect) is confirmed in the present study of the effect of mixing LiI with two different aluminas, cf. Figs.1 and 2. Depending on the purity of the LiI used for comparison, the conductivity enhancements are of the order 100 to 1000. The LiI data shown in Fig.1 was obtained on pellets made from dehydrated $\text{LiI} \cdot 2\text{H}_2\text{O}$ (Merck) as in ref.(10). The highest conductivities are observed for mixtures with 40–50 mole % alumina, irrespectively the source of alumina and LiI used. Liang (1) found a conductivity maximum at 45 mole % alumina using Alcoa F1 alumina. The three sorts of alumina have similar specific areas and porosities according to the manufacturers. When the content of alumina has increased beyond 50 mole % a decrease in the conductivity occurs, cf. Fig.2. This partly results from the decreasing LiI-content per volume, partly from a blocking effect from that fraction of the porous alumina which is not in contact with any LiI.

3.4 Temperature dependence of conductivity

The ionic conductivity of pure LiI typically shifts from an extrinsic, impurity controlled region into intrinsic behaviour (10) with increasing temperature as seen in Fig.1. In contrast, all the composites investigated only show one regime. Both the $\log \sigma$ vs $1/T$ and the $\log(\sigma T)$ vs $1/T$ relationships were tested by least squares fitting. The $\log(\sigma T)$ vs $1/T$ relation gave for all samples an only slightly better fit compared to the simple fit. However, the difference between the two types of fit is not statistically significant. In order not to impose any theoretically based expectations on our data we prefer to present the derived constants from the simple fit. Table II lists the preexponential factors and the overall energy of activation for conduction for selected compositions. From Table II it is seen that the maximum in the observed conductivities coincides with a minimum in the activation energy. Still, the main reason for the conductivity enhancements resides in the increased preexponential factors compared to bulk LiI. According to the proposed model (3) the main Li-ion transport should take place in a thin layer along the LiI-alumina interfaces. As observed, one would expect a lower energy of activation for this type of surface conduction compared to transport through bulk LiI. The jump distances and attempt frequencies for the interface transport may differ from the values in bulk LiI, which means that the increased prefactors cannot necessarily be interpreted as due to an increased concentration of charge carriers.

3.5 Pore-model for LiI - alumina composites

Previous models (3,5) have visualized a two component composite material as a continuous salt phase in which a large volume fraction of very small oxide particles has been dispersed. One

Mole % Al_2O_3	N	σ^0 (S/cm)	ΔE (eV)
25	20	28.64	0.382±0.004
35	15	10.44	0.336±0.006
45	14	45.88	0.369±0.006
50	16	25.69	0.370±0.009
70	22	27.86	0.448±0.009
0	9	0.481	0.43 ±0.04
20	10	6.17	0.349±0.009
30	13	7.95	0.327±0.003
40	11	14.22	0.330±0.007
50	10	11.00	0.331±0.006
60	12	14.48	0.372±0.005

TABLE II. LiI-alumina composite data. Constants in $\sigma = \sigma^0 \cdot \exp(-\Delta E/RT)$ determined by least squares fitting. N is number of data points used in fit. Upper half of Table: Series 2; lower half: Series 3. Values for pure LiI (0%) are for extrinsic region.

out of several problems in testing such models is related to the fact that the state of aggregation and specific surface area of the oxide filler are difficult to control. We suggest an almost opposite picture of the phase distribution in the composite materials. Commercially available activated aluminas are received as stable aggregates, often 2–10 mm^2 spheres, with high specific areas (200–400 m^2/g) and high porosities (60–70%). Grinding the materials down to 10–100 μ powder is not likely to affect these parameters much since the pores responsible for the large surface and porosity are of dimensions lower than 1000 Å. The pore system of the alumina thus beforehand provides an interconnected network of surfaces. When such a system is filled with a salt via the melt impregnation method used in this and most other studies three limiting situations may arise: i) At low concentrations of alumina the aggregates are filled with salt, and these aggregates are embedded in the excess salt matrix; ii) at a certain composition the porosity of the aggregates and the volume of added salt exactly match, i.e. ideally no excess salt or empty pores are present; and iii) at high volume fractions of alumina only part of the pore system is filled with salt. The density as function of alumina content was calculated on basis of this model using for LiI $d=4.06 \text{ g/cm}^3$, and for alumina $d=1.38 \text{ g/cm}^3$ and 69% porosity. The full curve in Fig.3 is the result of this model calculation. An anomaly in the slope of the curve is predicted at the composition (43%) where the shift from completely filled to only partly filled pores occurs. The experimental densities, apart from Series 1 pressed at only 7 t/cm², are seen to follow the predicted trend. For cold pressing one would not expect to reach 100% TD. We conclude that the pore-model therefore gives a satisfactory explanation of the observed conductivity maxima and density data.

Figure 3. Densities of LiI-alumina composites. Key: Series 1 ($\blacktriangledown$), Series 2 ($\triangle$), and Series 3 ($\circ$). Full curve shows the theoretical density (see section 3.5).

Figure 4. Steady state currents in Hebb-Wagner experiments on pure LiI at 51°C. Configuration and polarity of cell are indicated in the figure.

3.6 Electronic leakage current in LiI

Liang et al. (6) found a small electron hole conduction in a 50-60 mole % alumina-LiI composite equilibrated with Li-metal. To our knowledge no study of the electronic conduction in pure LiI has been reported. We have started a Hebb-Wagner study of LiI and LiI-composites equilibrated with various electrode materials. Data have been analysed for the cell $(-)\text{Li}/\text{LiI}/\text{C}(+)$. As in (6) it was necessary to use potentials close to the decomposition voltage (appr. 2.8V) in order to measure the electronic background currents. Contrary to (6) we observe a plateau in the steady state current before reaching the decomposition region, see Fig.4. Our preliminary conclusion is that electron conduction is present in Li-equilibrated LiI (for appropriate formulas, see 3,4,6). At 2.5 V and 54°C we find $\sigma = 2.25 \cdot 10^{-8}$ S/cm. From a leakage current vs $1/T$ plot at 2.76 V an approximate enthalpy of activation for electron conduction of 0.58 eV was determined. The shift in carrier type going from LiI to LiI-alumina is parallel to what has been found for β -AgI-alumina composites (4) and pure β -AgI (12). The composite has hole conduction, whereas pure AgI has electron conduction according to a recent study (12).

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