INTERFACIAL CONDUCTION IN LITHIUM IODIDE CONTAINING INERT OXIDES

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Summary

Temperature-dependent conductivities are reported for a lithium iodide sample sandwiched between two fused silica plates and for an LiI film deposited on a silica plate. The existence of an $LiI-SiO_2$ interfacial conduction path possessing a conductivity of about 5 ohm^{-1} cm^{-1} at 25 °C is confirmed. In addition, an infiltration technique for the preparation of LiI–ceramic particle composites is discussed.

Introduction

Liang [1] first reported that the addition of fine alumina particles to lithium iodide increased the room-temperature ionic conductivity by more than a factor of one hundred. An earlier phase of the present investigation [2] identified grain boundaries and LiI–ceramic interfaces as regions of extremely rapid ion transport. This study focuses on ionic transport along the LiI–silica interface and attributes the enhanced conductivity observed for LiI–ceramic particle composites to enhanced ionic mobility along their interfaces.

Experimental

Planar LiI–SiO₂ interface

The charge transport characteristics of a planar LiI–silica interface were studied by "sandwiching" molten LiI between two fused silica plates spaced 0.2 mm apart. Gold wire electrodes were attached to the silica plates so that the a.c. impedance (10 Hz - 500 kHz) could be measured parallel and perpendicular to the $LiI-SiO_2$ interface. Figure 1 is a schematic representation of the $LiI-SiO_2$ sandwich employed.

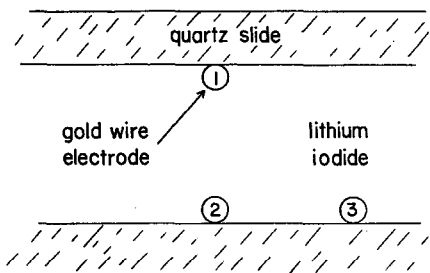*Present affiliation: Medtronic, Inc., Brooklyn Center, Minnesota 55430, U.S.A.

Fig. 1. Schematic illustration of lithium iodide sandwiched between two fused silica plates with gold wire electrodes.
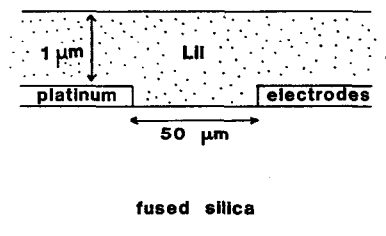
Fig. 2. Schematic illustration of lithium iodide which has been vapor-deposited on a fused silica plate with sputtered platinum electrodes.

The temperature-dependent conductivity of an LiI film approximately one micron in thickness was determined by depositing LiI onto a silica plate containing two sputtered platinum electrodes separated by a 50 μm gap (see Fig. 2). The film was deposited by the evaporation of LiI in an argon gas atmosphere.

The physical geometry of the LiI–SiO$_2$ sandwich shown in Fig. 1 suggests that the total ion flux between electrodes 2 and 3 resulted from the sum of the ion transport along the core of the interface and through the bulk. Accordingly, the conductivity measured between electrodes 2 and 3 can be expressed as

$$\sigma_{\parallel} = f_b \sigma_b + f_i \sigma_i \tag{1}$$

where f_b and f_i are the fractions of sites which comprise the bulk and interfacial regions, respectively, and σ_b and σ_i are the corresponding bulk and interfacial conductivities. The conductivity measured perpendicular to the interface between electrodes 1 and 2 is the bulk conductivity; that is,

$$\sigma_{\perp} = \sigma_b \tag{2}$$

For the case where $f_b \gg f_i$, the interfacial conductivity can be isolated by subtracting eqn. (2) from eqn. (1), yielding

$$\sigma_{\parallel} - \sigma_{\perp} = f_i \sigma_i \tag{3}$$

The interfacial conductivity can be written in the form

$$\sigma_i = (\sigma_i^o / T) \exp(-h_i / kT) \tag{4}$$

where σ_i^o is the pre-exponential factor and h_i is the enthalpy of migration along the core of the interface. Substitution of eqn. (4) into eqn. (3) yields

$$\ln(\sigma_{dif} T) = \ln(f_i \sigma_i^o) - h_i / kT \tag{5}$$

where $\sigma_{dif} = \sigma_{\parallel} - \sigma_{\perp}$. If the conductivity measured along the LiI–SiO$_2$ interface can be expressed as the weighted sum of the interfacial and bulk conductivity given in eqn. (1), then the slope of a plot of $\ln(\sigma_{dif} T)$ vs. $1/T$ should
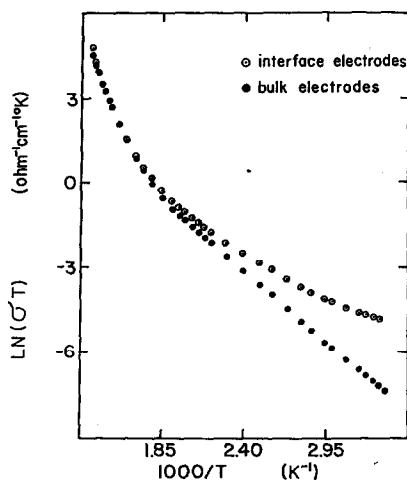
Fig. 3. Arrhenius plot of the conductivity measured between the bulk electrodes (electrodes 1 and 2 of Fig. 1) and the interfacial electrodes (2 and 3).
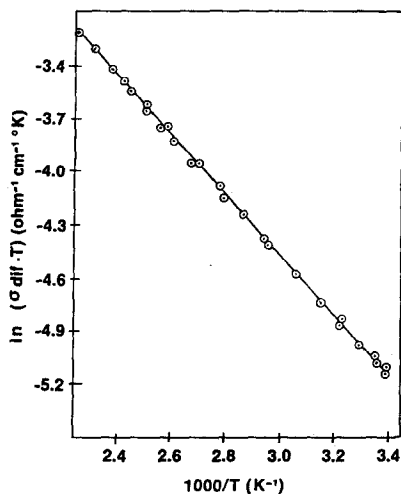
Fig. 4. A plot of $\ln(\sigma_{dif}T)$ as a function of inverse temperature for LiI sandwiched between silica plates.

TABLE 1

The bulk and interfacial enthalpies of migration, pre-exponential factors, and conductivities at 25 °C

Region	Pre-exponential (ohm^{-1} cm^{-1} K)	Enthalpy of migration (eV)	Conductivity at 25 °C (ohm^{-1} cm^{-1})
Bulk	600	0.39	5×10^{-7}
Interface	2×10^5	0.15	2

be $(-h_i/k)$ and the intercept should be $\ln(f_i\sigma_i^0)$. Figure 4 is such a plot of the data represented in Fig. 3.

Table 1 lists the interfacial enthalpy of migration and pre-exponential factor calculated from the slope and intercept of Fig. 4 and the single crystal LiI values determined in a previous study [2]. As predicted, the enthalpy of migration along the core of the interface is less than the bulk value and the interfacial conductivity is much larger than the bulk conductivity.

The interfacial pre-exponential factor cannot be directly calculated from the intercept value of Fig. 4 since the quantity f_i is lumped together with σ_i^0. An estimate of the value of f_i is given by the expression

$$f_i = A_v n_a / n_v \qquad (6)$$

where A_v is the interfacial area per unit volume, n_a the number of cation sites per unit interfacial area, and n_v the number of cation sites per unit

volume LiI. For the LiI–SiO$_2$ sandwich employed in this study, the value of f_i was about 10^{-6}.

Lithium iodide thin film

The study of the LiI–SiO$_2$ interface by the sandwich technique was limited by the inherently large bulk component of the conductivity measured along the interface. To reduce the number of bulk sites which contributes to the conductivity, a thin film of LiI was deposited on a fused silica plate containing two platinum electrodes. The increased interfacial character of the LiI thin-film resulted in a large room-temperature conductivity, as shown in Fig. 5. The enhanced conductivity of the thin film can again be attributed to rapid ion transport along the LiI–SiO$_2$ interface.

The conductivity measured along the interface for the thin film can be approximated by the expression

$$\sigma_\parallel = f_i \sigma_i \tag{7}$$

which is derived from eqn. (1) for the case where $f_i \sigma_i \gg f_b \sigma_b$. The value of f_i for the thin film was estimated to be 3×10^{-4} and the value of $\sigma_\parallel$ at room temperature was 3×10^{-3} ohm^{-1} cm^{-1}; hence, the value of σ_i at 25 °C was about 10 ohm^{-1} cm^{-1}. This value is in good agreement with the value determined for the planar LiI–SiO$_2$ interface created by sandwiching LiI between two silica plates.

Infiltrated LiI–SiO$_2$ composites

Lithium iodide–silica particle composites were produced by a novel infiltration technique. Cylindrical compacts consisting of fused silica (200 m^2/g) were isostatically pressed at 55 kpsi (380 MPa). The pressed pellets had densities which were about 35% of the theoretical density. LiI–SiO$_2$ composites were formed by immersing the silica pellets in a crucible of molten LiI for about one hour under an argon atmosphere. The molten LiI infiltrated into the porous silica compacts to form composites with the same external dimensions as the original silica compacts.

Results and discussion

Planar LiI–SiO$_2$ interface

Figure 3 is an Arrhenius plot of the conductivity measured between the bulk electrodes (electrodes 1 and 2 in Fig. 1) and the interfacial electrodes (2 and 3). The conductivity measured along the interface ($\sigma_\parallel$) was larger than that measured perpendicular to the interface ($\sigma_\perp$) at low temperatures. The "excess" conductivity observed along the LiI–SiO$_2$ interface can be attributed to rapid Li$^+$ ion transport along the core of the interface.

Rapid ion transport along microstructural imperfections, such as dislocations and grain boundaries, has been well-documented [3, 4]. The lattice strain energy associated with a jump from one lattice site to another has been
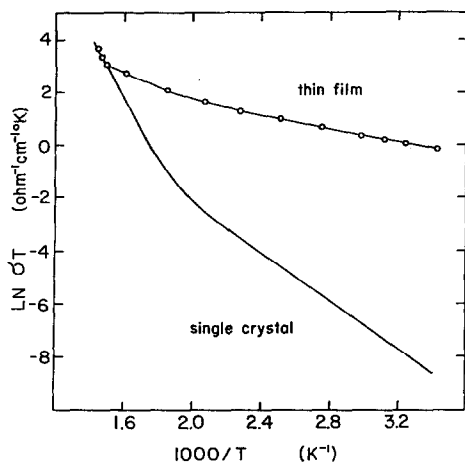
Fig. 5. Arrhenius plot for an LiI single crystal and thin film.

identified as the primary contribution to the energy of migration [5]. The lattice distortion which exists at the core of a microstructural imperfection reduces the strain energy associated with ionic transport; hence, the ionic mobility along the core is greater than the bulk mobility [6].

Infiltrated LiI–SiO₂ composite

The interfacial conductivity represents an upper limit for Li$^+$ ion conductivity in LiI–ceramic composites. The largest room-temperature conductivity reported for any LiI–ceramic composite has been 1×10^{-4} ohm^{-1} cm^{-1} [7], which is far below the theoretical upper limit of about 5 ohm^{-1} cm^{-1}. Unlike the planar LiI–SiO₂ interface characteristic of the sandwich or thin-film arrangements, the continuity of the interface formed when ceramic particles are added to LiI is poor. In addition, the sandwich and thin-film interfaces were oriented parallel to the applied field, which is not the case for the interfaces existing between dispersed particles and an LiI matrix. The discontinuity and misorientation of an LiI–particle interface may be sufficient to explain why the composite failed to reach the theoretical limit [8].

To insure maximum continuity of the LiI–ceramic particle interface, the ceramic particle density should be maximized so as to provide as much particle-to-particle contact as possible. One method which has been employed in this study to maximize particle-to-particle contact involves the impregnation of a pressed ceramic particle compact with molten LiI. The dipping of high surface-area silica (200 m²/g) compacts into molten LiI gave composite densities of greater than 90% of the theoretical density.

Infiltration of ceramic compacts is an easier method for the preparation of LiI–ceramic particle composites than the mechanical mixing and melting method employed by previous investigators (see, for example, refs. 1 and 7).

The results of the LiI–SiO₂ sandwich and thin-film experiments suggest that the conductivity increases as the interfacial-to-bulk site fraction increases.

The infiltration of pressed particle compacts with molten LiI insures that the interfacial-to-bulk site fraction is maximized because the amount of LiI absorbed by the pressed particle compact is limited to only that needed to fill the voids within the compact.

The conductivity of infiltrated LiI–SiO$_2$ composites was about 1×10^{-5} ohm^{-1} cm^{-1} at room temperature. This value is similar to that reported by Liang [1] for LiI–Al$_2$O$_3$ composites. It would appear that the use of ceramic particles inherently limits the continuity of the LiI–ceramic interface. As a point of speculation, the use of high surface area, ceramic needles, instead of particles, may increase the interfacial continuity and may result in significantly larger composite conductivities than those achieved to date. The optimum composite geometry, for a battery application, would consist of high surface area ceramic needles, of a length equal to the length of the composite electrolyte, aligned parallel to the field direction of that of the concentration gradient.

Conclusions

The enhanced conductivity observed when ceramic particles were added to LiI can be attributed to rapid ion transport along the core of the LiI–ceramic interface. Conductivity studies of LiI sandwiched between silica plates and thin-film LiI suggest that the interfacial conductivity was about 5 ohm^{-1} cm^{-1} at 25 °C. The enthalpy of migration along the LiI–SiO$_2$ interface was found to be 0.15 eV, as compared with 0.39 eV for bulk migration.

The continuity and orientation of the LiI–ceramic interface were identified as critical parameters determining the conductivity of the composites. The infiltration of ceramic compacts with molten LiI has several advantages which include ease of fabrication, maximization of particle-to-particle contact, and maximization of the interfacial to bulk site fraction.

Acknowledgement

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