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NMR DETECTION OF A HIGHLY CONDUCTIVE PHASE IN A COMPOSITE SOLID ELECTROLYTE $LiBr \cdot H_2O-Al_2O_3$

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Occurrence of a highly conductive phase was confirmed by a ^7Li NMR study in a composite solid electrolyte $LiBr \cdot H_2O-Al_2O_3$. Thickness of an interfacial layer on a dispersed alumina particle was estimated to be 0.2 μm for $3LiBr \cdot H_2O-2Al_2O_3$. Changes of the relative intensity in an X-ray diffraction pattern were pointed out.

Since Liang[1)] found that dispersion of Al_2O_3 to LiI enhanced the ionic conductivity of the system by an order of magnitude, similar effects have been noticed in several other systems of a composite solid electrolyte.[2-5)] This enhancement is explained in terms of a thin interfacial layer on an Al_2O_3 particle with much higher ionic conductivity than the matrix conductor has.[3,6)] This model reproduces fairly well the observed dependence of enhancement upon the composition.[6)] Occurrence of this layer, however, has not yet been detected by any experimental technique, and remains a hypothesis. For deeper understanding of the enhancement effect, it seems essential to make clear the nature of such a phase. The present study was performed to obtain some experimental evidence for such a highly conductive phase in a composite solid electrolyte $LiBr \cdot H_2O-Al_2O_3$, in which the maximum enhancement of about 6 was obtained at 40 mol% Al_2O_3 content.[2)]

The composite electrolyte with 40 and 70 mol% Al_2O_3 was obtained after Nakamura and Goodenough.[2)] One of starting materials, LiBr, was obtained by dehydrating $LiBr \cdot xH_2O$ (Merk, Suprapur) in vacuum at 150 °C. Active alumina was a neutral γ-alumina for column chromatography (Woelm, active grade 1). About 0.7 cm^3 of the product was taken in an NMR sample tube, which was sealed off after a higher hydrate or anhydrate was eliminated from the sample by controlling the water

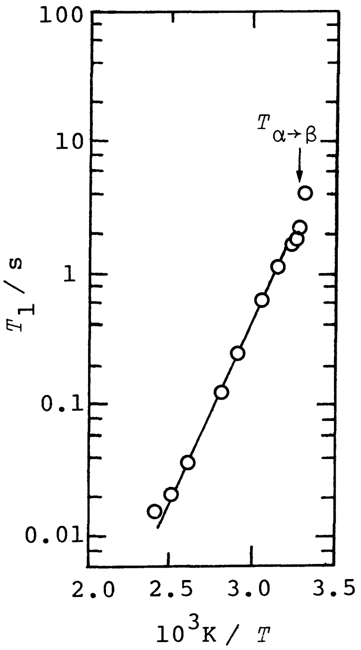

Fig. 1. (left) T_1 *vs.* $1/T$ of $LiBr\cdot H_2O$.

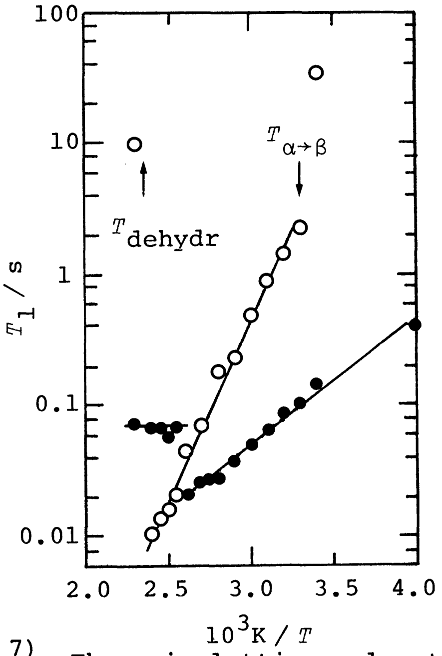

Fig. 2. (right) T_1 *vs.* $1/T$ of the composite electrolyte $3LiBr\cdot H_2O-2Al_2O_3$.

vapour pressure over the sample.[7] The spin-lattice relaxation time T_1 of ^7Li nucleus was measured from 250 to 435 K at 23.32 MHz by using a pulsed NMR spectrometer Bruker 322s. The 180°-τ-90° pulse sequence was mainly employed. Sometimes the $90°_{comb}-\tau-90°$ sequence was also used, and the two methods gave the same T_1 values within the experimental error. Results were shown in Figs. 1 and 2.

Lithium bromide monohydrate exhibits a phase transition at 33.0 °C. The high-temperature phase, α-$LiBr\cdot H_2O$, is stable up to 156 °C, at which the dehydration occurs.[8] The crystal structure of this α-phase belongs to the space group O_h^1-Pm3m with $a = 4.296$ Å and contains one formula unit.[9] The Li atom is statistically distributed on three face-centered positions of the unit cell, and all the Li atoms are equivalent crystallographycally.

Recovery of ^7Li magnetization after a 180°-pulse for pure $LiBr\cdot H_2O$ was described with a single time constant (T_1). It is consistent with the crystal structure if the e^2qQ/h value at a Li nucleus is small. In the α-phase region, T_1 increases linearly with increase of $1/T$ with an activation energy of 52 kJ mol^{-1}. This value is in good agreement with the value (57 kJ mol^{-1}) obtained from the ionic conductivity.[2] This agreement means that these T_1 values are governed by the Li diffusion in the crystal. Below the phase transition temperature, T_1 shows an anomalous increase.

In the composite electrolyte, two T_1 values were obtained. One component, which is shown by an open circle in Fig. 2, coincides well with T_1 of pure hydrate, and shows an anomaly and a discontinuous increase at the phase transition and the dehydration temperatures, respectively, of $LiBr \cdot H_2O$. This component was attributed to Li in the $LiBr \cdot H_2O$ matrix.

The second component, which is shown by a solid circle in Fig. 2, gave a very low activation energy of 18 kJ mol^{-1} between 250 and about 390 K, suggesting a very fast diffusion of Li. This component is continuous at the phase transition and the dehydration temperatures of $LiBr \cdot H_2O$, while it shows a discontinuous increase at about 390 K. The latter was not observed in pure $LiBr \cdot H_2O$.

If formation of the composite electrolyte introduced a large e^2qQ/h at a Li site in the $LiBr \cdot H_2O$ lattice, the second component might be either of W_1 or W_2 of a Li nucleus in the matrix $LiBr \cdot H_2O$. This possibility, however, is excluded by two observations: one is the different temperature dependence of T_1 as described above. Second, a magnetization ratio of the two components was about 1 in the whole temperature region. If the second component were either of W_1 or W_2, it would be theoretically 1:4.$^{10)}$ It is therefore clear that two distinct compounds of Li exist in this composite electrolyte. Occurrence of a highly conductive phase in such a system was thus proved for the first time.

Using the magnetization ratio mentioned above, the thickness of an interfacial layer between an alumina particle and the conductor matrix was estimated. Alumina particles were assumed to have the same radius r ($\simeq$0.5 μm) and to be coated with the layer of thickness t. Differences in molar volume and Li content between the two Li compounds were neglected as a first approximation. Then the volume fraction of the thin layer to the total volume of the Li compounds f is given by

$$f = 3\left(\frac{t}{r}\right) \frac{v_{Al_2O_3}}{v_{LiBr \cdot H_2O}} \frac{x_{Al_2O_3}}{x_{LiBr \cdot H_2O}}$$

where v is a molar volume and x a mole fraction in the starting mixture. In the frame of the above approximation, f corresponds to the magnetization ratio, and the thickness was estimated to be 0.2 μm. Stoneham *et al.*$^{6)}$ estimates it to be several hundred Å.

The powder X-ray diffraction pattern showed presence of only $LiBr \cdot H_2O$ and γ-Al_2O_3. Reflections assigned to $LiBr \cdot H_2O$ were sharp, but some changes in the relative intensity were recognized as shown in Fig. 3. Changes in 110 and 200 reflections are significant. (In Fig. 3, the ordinate is so scaled that the remaining reflections of the two samples have a similar intensity.) They suggest that the highly conductive phase has a cubic unit cell the dimension of which is

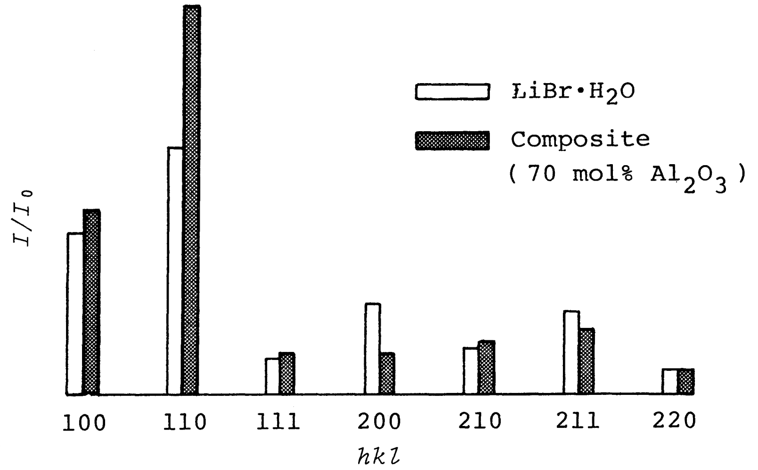

Fig. 3. Relative intensity of the powder X-ray diffraction (arbitrary scale).

very close to that of LiBr•H_2O. Because a contribution of Li to these intensities are very small (<0.6%), this change cannot be explained simply by formation of many Li defects in the LiBr•H_2O lattice, or rather distribution of Br and/or H_2O molecule in this cell should be considerably modified.

The present NMR and X-ray measurements indicate that the highly conductive layer in the LiBr•H_2O-Al_2O_3 composite electrolyte is a distinct compound rather than a modified LiBr•H_2O lattice formed by, for example, a double layer at the interface.

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