SEARCH FOR NEW SOLID STATE LITHIUM-ION CONDUCTORS

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Abstract: We have experimentally searched new solid state lithium-ion conductors for thin film lithium-ion batteries using ac complex impedance measurements, and found superior lithium-ion conductivity in two materials $LiBH_4$ and Li_3AlH_6. The conductivities of $LiBH_4$ and Li_3AlH_6 at room temperature (RT) were 4.1×10^{-8} S/cm and 1.4×10^{-7} S/cm, respectively. $LiBH_4$ exhibited lithium fast-ionic conductivity of higher than 1.0×10^{-3} S/cm accompanied by a structural transition. We also demonstrated the enhancement of the conductivity of these materials by addition of lithium iodide LiI. By adding 0.33 molar ratio of LiI into $LiBH_4$ and Li_3AlH_6, the conductivity at RT increased about 1000 times for the former and about 35 times for the latter.

Keywords: MEMS, micro power supply, thin film lithium-ion battery, complex hydride, solid state electrolyte

INTRODUCTION

Thin film lithium-ion batteries [1-4] enabling batteries' integration with other micro devices onto a single chip may be an appropriate choice for micro power supplies of microelectromechanical systems (MEMS). One good example may be micro sensor nodes, where thin film lithium-ion batteries, micro sensors, and micro energy harvesters [5-8] are integrated. This kind of sensor nodes do not ask us to replace batteries periodically because micro sensors will consume energy stored in thin film lithium-ion batteries which are replenished by micro energy harvesters obtaining energy from the environment in the form of vibration et al. Such micro sensor nodes with less maintenance are essential to establish sensor communication society [9], where a large number of micro sensor nodes are distributed from place to place.

In order to establish reliable thin film lithium-ion batteries, one of the keys is to develop solid state electrolytes with high lithium-ion conductivity along with electrical and chemical stability. Thus, so far, many researchers have been working on the search for solid state electrolytes, and developed various classes of materials such as oxides [10, 11], sulfides [12, 13], nitrides [14], and halides [15, 16]. However, there is no material satisfying all requirements at once. Thus further materials' search is necessary in another class of materials whose lithium-ion conductivity have not been investigated. For this purpose, we searched $LiBH_4$ and Li_3AlH_6, those are complex hydrides with ionic bonding between Li^+ cation and $(BH_4)^-$ or $(AlH_6)^{3-}$ complex anions.

$LiBH_4$ and Li_3AlH_6 are electrical insulators with a wide bandgap [17-19]. The crystal structures at RT are different between these complex hydrides, that is, orthorhombic phase for $LiBH_4$ [20] and trigonal phase for Li_3AlH_6 [21]. In addition, $LiBH_4$ shows structural phase transition between law temperature (LT, orthorhombic) phase and high temperature (HT, hexagonal) phase at around 390 K (Fig. 1). The coordination number of Li^+ cation [21, 22], ionic radius [23] and valence of anions of these hydrides (listed in Table I) are also different between these complex hydrides.

In this paper, we report on the investigation of lithium-ion conductivity in $LiBH_4$ and Li_3AlH_6. We also discuss the enhancement of the conductivity of these complex hydrides by addition of lithium iodide LiI.

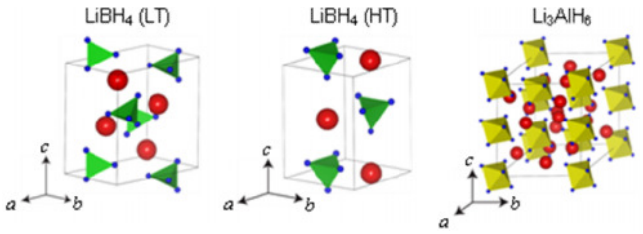

FIG. 1. The schematic crystal structure of LT phase and HT phase of $LiBH_4$, and Li_3AlH_6. Large and small circles correspond to Li and H atoms, respectively. B atoms are embedded in $(BH_4)^-$ tetrahedra. Al atoms are embedded in $(AlH_6)^{3-}$ octahedra.

Table I. Coordination number of Li^+ cation, and complex anion's ionic radius and valence of LT phase of $LiBH_4$, HT phases of $LiBH_4$, and Li_3AlH_6.

	Coordination number of Li^+ cation	Complex anion	
		Ionic radius (nm)	Valence [formula]
LT phase of $LiBH_4$	9[b]	0.205[d]	1 [$(BH_4)^-$]
HT phase of $LiBH_4$	13[b]		
Li_3AlH_6	6[c]	0.256[d]	3 [$(AlH_6)^{3-}$]

[b]Reference 20
[c]Reference 21
[d]Reference 23

EXPERIMENTAL

$LiBH_4$ was purchased from Aldrich Co. Ltd. Li_3AlH_6 was synthesized by mechanical milling of appropriate amounts of LiH and $LiAlH_4$ (LiH and $LiAlH_4$ were purchased from Alfa Aesar and Aldrich Co. Ltd., respectively) for 5 h under a He atmosphere and subsequent heat treatment at 383 K for 20 h. LiI (purchased from Aldrich Co. Ltd.) with nominal compositions of $LiBH_4$+xLiI (x = 0, 0.07, 0.14, 0.20, 0.33, and 1.00) and Li_3AlH_6+xLiI (x = 0 and 0.33) were mechanically milled. The samples were examined by powder x-ray diffraction (XRD) (Cu $K\alpha$ radiation, RT). The electrical conductivity was determined by ac complex impedance measurements between RT and 393 K or 433 K in heating and cooling runs. A pair of Li or Au foils was used as the electrodes. The samples were always handled in a glove box filled with purified Ar/He.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the electrical conductivity of $LiBH_4$+xLiI (x = 0, 0.33). In heating process, the conductivity of $LiBH_4$ increased with increasing temperature. A discontinuous jump was observed at around 390 K, which corresponds to the structural transition temperature from the LT phase to the HT phase. The conductivity in the HT phase was as high as 10^{-3} S/cm, which is comparable to those of high lithium-ion conductors [11, 24-27] at room temperature. Below and above 390 K, the temperature dependences of the conductivity showed Arrhenius behaviors. The activation energies E_a for the conduction were evaluated using the equation

$$\sigma T = \sigma_0 exp(-E_a/k_B T)$$

where σ is the conductivity, σ_0 is the preexponential parameter, and k_B is the Boltzmann constant. We obtained E_a of 0.69 and 0.53 eV for the LT phase and the HT phase, respectively.

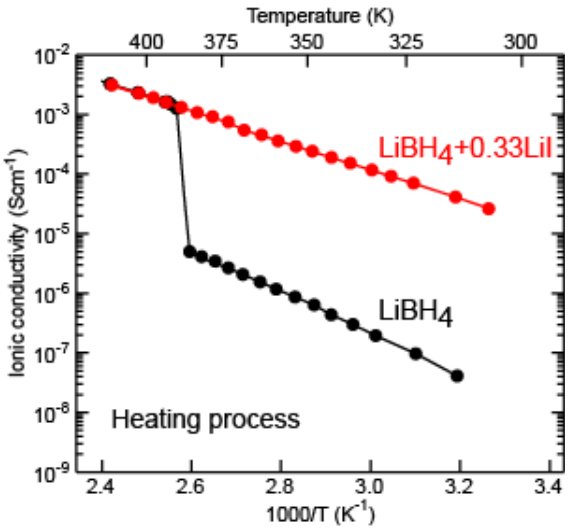

Figure 2. Temperature dependence of the conductivity of $LiBH_4$ (black) and $LiBH_4$+0.33LiI (red).

The effect of addition of LiI on the conductivity of $LiBH_4$ was evaluated by comparing the conductivity of $LiBH_4$+0.33LiI with the conductivity of $LiBH_4$ (see Fig. 2). In contrast to $LiBH_4$, $LiBH_4$+0.33LiI showed no apparent transition within the temperature range of this measurement. As a result, the conductivity at RT became approximately 1000 times higher for $LiBH_4$+0.33LiI than that for $LiBH_4$.

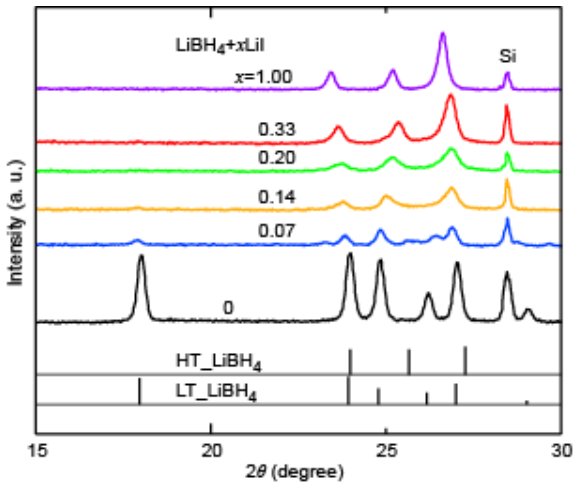

Figure 3. XRD patterns of $LiBH_4$+xLiI (x = 0, 0.07, 0.14, 0.20, 0.33, and 1.00). Positions of the diffraction peaks are calibrated by Si internal standard.

Table II. Lattice constants, a and c, of the HT phase of $LiBH_4$+xLiI for x = 0, 0.33, and 1.00. Lattice constants for x = 0.07, 0.14, and 0.20 are left blank as none of them are indexed by orthorhombic and hexagonal unit cells. Lattice constants of (hexagonal-)LiI are also added for reference.

x in $LiBH_4$ + xLiI	a (Å)	c (Å)
0	4.24±0.02[a]	6.87±0.03[a]
0.07	-	-
0.14	-	-
0.20	-	-
0.33	4.354±0.002	7.035±0.005
1.00	4.389±0.001	7.073±0.003
LiI	4.514±0.001[b]	7.311±0.002[b]

[a]Reference 28
[b]Reference 29

The origin responsible for the higher conductivity of $LiBH_4$ due to addition of LiI was examined by powder XRD at RT. Figure 3 shows the powder XRD patterns of $LiBH_4$+xLiI (x = 0, 0.07, 0.14, 0.20, 0.33, and 1.00). The diffraction peak intensities of the LT phase of $LiBH_4$ (x = 0) drastically decrease with x = 0.07. Only the peaks corresponding to the HT phase

can be detected with x = 0.33 and 1.00. This indicated that the higher conductivity of $LiBH_4$ is attributed to the stabilization of the HT phase of $LiBH_4$ at RT by addition of LiI. The $LiBH_4 + xLiI$ pseudobinary system probably forms $Li(BH_4$-I) solid-solutions, similar to Li(Br-I) in the LiBr + xLiI system [30]. The lattice constants of the HT phase (x =0, 0.33 and 1.00) summarized in Table II are found to increase with increasing x; as is well comparable with the previous estimation of the unit-cell volumes [31].

The conductivities of Li_3AlH_6+xLiI (x = 0, 0.33) were then investigated, and the results are shown in Fig. 4. Temperature dependences of the conductivity of Li_3AlH_6 showed Arrhenius behaviors between RT and 393 K; the conductivity increased almost linearly from 1.4×10^{-7} to 1.6×10^{-5} S/cm for Li_3AlH_6. In addition, E_a of Li_3AlH_6 was 0.61 eV. This value is comparable with E_a of the LT phase of $LiBH_4$. In contrast to $LiBH_4$, Li_3AlH_6 did not show conductivity jump.

The effect of addition of LiI on the conductivity of Li_3AlH_6 was evaluated by comparing the conductivity of Li_3AlH_6+0.33LiI with the conductivity of Li_3AlH_6 (see Fig. 4). At RT, the conductivity became about 35 times higher for Li_3AlH_6+0.33LiI than that for Li_3AlH_6. The addition of LiI also decreased E_a to 0.48 eV, which is a value smaller than that of the HT phase of $LiBH_4$ (0.53 eV).

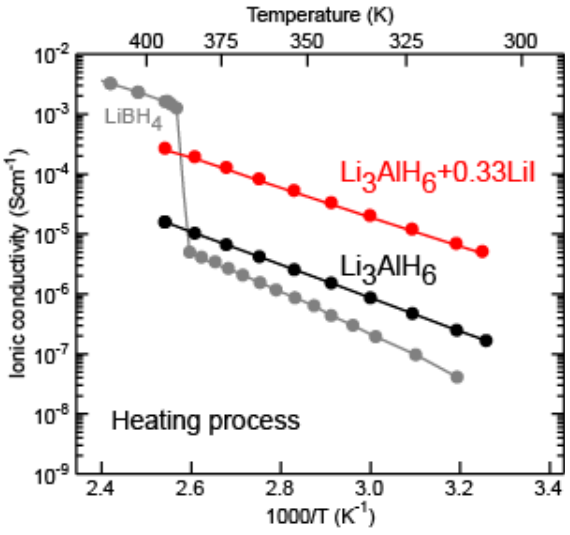

Figure 4. Temperature dependence of the conductivity of Li_3AlH_6 (black) and Li_3AlH_6+0.33LiI (red).

The origin responsible for the higher conductivity of Li_3AlH_6 due to addition of LiI may be the increase of carrier concentration caused by a dispersion of residual LiI [32], which is indicated by remaining XRD diffraction peaks of LiI (Fig. 5). Decomposition, hydration, and compounds formation were not likely to have been responsible for the enhancement of conductivity, because no XRD diffraction peaks other than those of Li_3AlH_6 and LiI were observed.

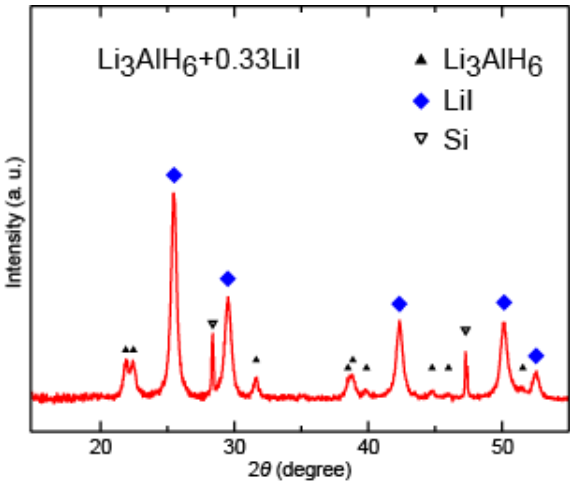

Figure 5. XRD patterns of Li_3AlH_6+0.33LiI. Positions of the diffraction peaks are calibrated by Si internal standard.

CONCLUSION

We have experimentally investigated the electrical conductivity in $LiBH_4$ and Li_3AlH_6 using ac complex impedance measurements in order to search new solid state lithium-ion conductors which are applicable as solid state electrolytes of thin film lithium-ion batteries. The conductivity of $LiBH_4$ and Li_3AlH_6 at RT were 4.1×10^{-8} S/cm and 1.4×10^{-7} S/cm, respectively. The conductivity of $LiBH_4$ jumped by three orders of magnitude due to structural transition at approximately 390 K. The HT phase of $LiBH_4$ exhibited a high conductivity of the order of 10^{-3} S/cm. By addition of LiI, the conductivities at RT were enhanced about 1000 times for $LiBH_4$ and about 35 times for Li_3AlH_6. We have succeeded in imparting room-temperature high lithium-ion conductivity to complex hydrides which had not been considered as lithium-ion electrolytes. We believe that discovery of lithium-ion conductivity in $LiBH_4$ and Li_3AlH_6 have broadened options of the solid state electrolytes of the thin film lithium-ion batteries, which will be integrated into micro devices as micro power sources.

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