

Halide-Stabilized LiBH_4 , a Room-Temperature Lithium Fast-Ion Conductor

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Solid state lithium ion electrolytes with conductivity exceeding 10^{-3} Scm^{-1} and good chemical stability in contact with both cathode and anode electrodes are actively investigated for their application to solid-state batteries and supercapacitors of high energy density. Liquid-free batteries show various advantages over currently commercialized ones. These include safety issues caused by flammable organic electrolytes and irreversible capacity loss during the discharge cycles originated by the solid electrolyte interface. To date, a wide variety of materials have been found to have high lithium ion conductivity.¹ These include oxides,² sulfide based crystals and glasses,³ multimetal halides,^{1,3} and composite-type electrolytes.⁴ Such systems have been demonstrated as electrolytes of all-solid-state batteries.⁵ However, the oxide ceramic system frequently involves the problem of seriously high grain boundary resistance. Also, the reactivity of the sulfide-based electrolytes with cathode materials leads to difficulty in battery design. Thus, efforts in search of a novel electrolyte system have been continued.

Recently, we have discovered a novel lithium ion conductor, LiBH_4 ,⁶ which has been known as a reducing reagent, and has attracted attention as a candidate hydrogen storage material.⁷ This was one of the first lithium ion conductors of metal hydride system to be discovered. The conductivity of pure LiBH_4 shows a jump at 115 °C, accompanied with a crystal structure transition from orthorhombic to hexagonal,⁸ reaching 10^{-2} Scm^{-1} above 170 °C. No obvious polarization at the lithium metal- LiBH_4 interface was observed under a high current density exceeding 40 mA/cm². This suggests high electrochemical reaction rates at the LiBH_4 -lithium metal interface, which is one of the most favorable properties for solid lithium battery applications.

However, from an application point of view, room-temperature stabilization of the HT phase is highly desired. We have found that incorporation of lithium halides (LiX), including LiCl , LiBr , and LiI , to LiBH_4 can stabilize the HT phase at low temperature. Figure 1 shows the electrical conductivities of the LiBH_4 - LiX composites together with those for pure LiI and LiBH_4 . All the samples containing LiX showed a substantial decrease in transition temperature (T_{tr}), with the most significant decrease being found in LiI -doped samples. The $3\text{LiBH}_4 \cdot \text{LiI}$ sample showed no apparent transition to below room temperature. These results suggest that T_{tr} can be controlled by a new scheme of chemical modification by LiX . The conductivity of HT form followed an Arrhenius temperature dependence. The activation energy for the LiI -doped sample was lower than those for the LiCl - and LiBr -doped samples.

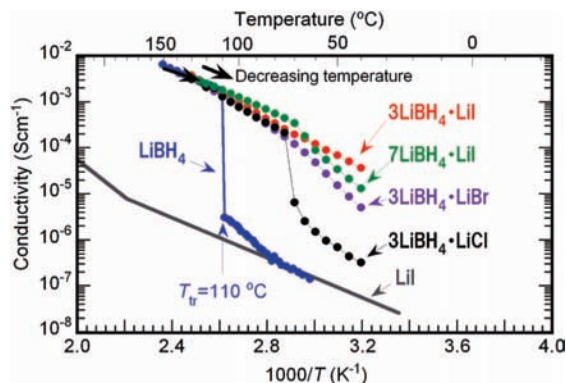


Figure 1. Dc electrical conductivities of LiBH_4 ,⁶ LiI ,⁴ and LiBH_4 - LiX composites ($X = \text{Cl}, \text{Br}, \text{and I}$) obtained by ac impedance measurements with 100 mV of applied voltage from their decreasing temperature.

$7\text{LiBH}_4 \cdot \text{LiI}$ showed even lower activation energy than LiBH_4 , suggesting that doping can improve the lithium ion mobility.

As shown in Figure 2, the $\text{LiBH}_4 \cdot \text{LiI}$ sample showed sharp XRD peaks from LiBH_4 ⁸ and LiI .⁹ As all peaks can be indexed by an HT LiBH_4 phase and LiI , room-temperature stabilization of the HT

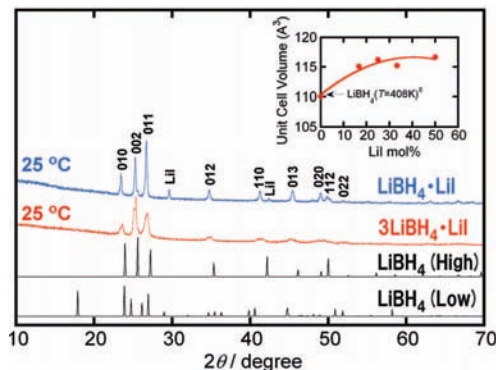


Figure 2. $\text{Cu K}\alpha$ XRD pattern of LiBH_4 - LiI at 25 °C. Calculated XRD patterns for low- and high-temperature forms of LiBH_4 ⁸ are also shown. Peak indices for LiBH_4 - LiI are from the high-temperature hexagonal phase. (Inset) Estimated unit cell volume for LiBH_4 - LiI binary at room temperature.

phase by LiI doping was confirmed. Peaks for $3\text{LiBH}_4 \cdot \text{LiI}$ somehow became broader than those for $\text{LiBH}_4 \cdot \text{LiI}$. However, LiI peaks disappeared, and the peaks can be indexed as those of a single LiBH_4 HT phase. The inset of Figure 2 shows an estimated unit cell volume for LiBH_4 - LiI . Expansion of the lattice volume with

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LiI addition from LiBH_4 ($Z = 2$, $V = 110 \text{ \AA}^3$)⁸ and LiI ($Z = 4$, $V = 218.79 \text{ \AA}^3$)⁹ was observed, suggesting formation of a $\text{LiBH}_4\text{-LiI}$ solid solution. The expansion of the lattice can be explained by a difference in ionic radius for I^- (2.11 Å) > BH_4^- (2.05 Å).¹⁰ The unit cell volume did not follow a simple Vegard's law. This may suggest the existence of line compounds having rather narrow solid solution compositional ranges. A major geometrical change in the coordination of Li ions due to an electronic structure change by substitution of BH_4^- with a high-polarity anion (I^-) may also be related to this deviation from Vegard's law.

The ^7Li NMR spin–lattice relaxation time (T_1) of HT LiBH_4 was explained well by the BPP formula,¹¹ giving correlation times of the lithium ionic motion. The calculated conductivity obtained by the Nernst–Einstein equation agreed well with the measured conductivity within 15% difference, assuming the carrier concentration equals the overall lithium concentration and the jump distance is equal to the nearest Li–Li distance (4.26 Å).^{6,8} This confirmed the lithium ions are a unique charge carrier. As shown in Figure 3a, T_1 for $3\text{LiBH}_4\cdot\text{LiI}$ showed no discontinuity by the transition,

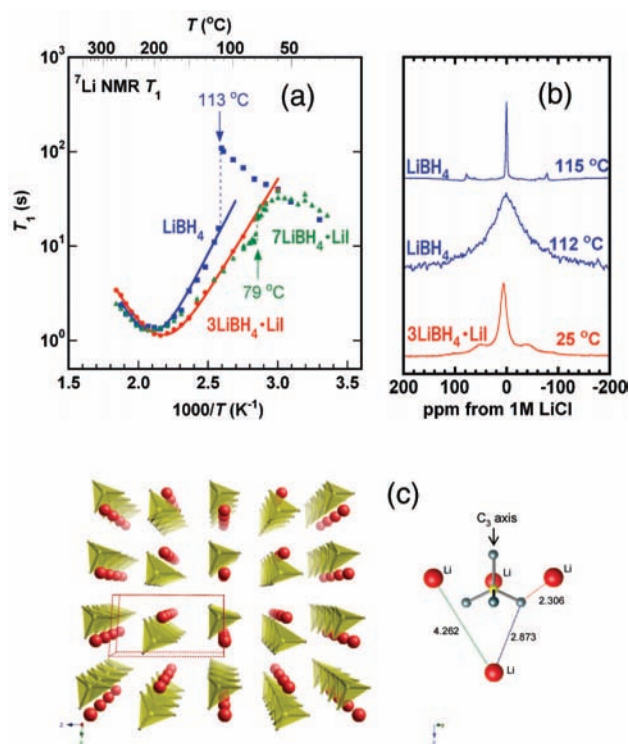


Figure 3. (a) Temperature dependence of ^7Li NMR spin–lattice relaxation times (T_1 's) for LiBH_4 , $7\text{LiBH}_4\cdot\text{LiI}$, and $3\text{LiBH}_4\cdot\text{LiI}$, respectively. Solid lines are fitting by BPP formula.^{6,11} (b) Temperature variation of ^7Li NMR spectra for LiBH_4 and $3\text{LiBH}_4\cdot\text{LiI}$. (c) Crystal structure of the high-temperature form of LiBH_4 .⁸ A cutoff image around BH_4^- unit is shown in the right side.

whereas $7\text{LiBH}_4\cdot\text{LiI}$ showed a small jump in T_1 at 79 °C, showing good consistency with the conductivity results. Low activation energies for LiI-doped sample were also observed in T_1 and suggested an increase in lithium ion mobility by the doping.

Figure 3b shows the ^7Li NMR spectrum of LiBH_4 . A motional narrowing by a fast lithium ionic motion above T_{tr} was observed. The subpeaks observed at both sides of the main peak can be interpreted as a first-order nuclear–quadrupolar interaction with its coupling constant $\nu_Q = 37.0$ kHz. This represents residual anisotropy in ionic migration, implying that an ionic conduction path is

not fully three-dimensionally isotropic, which is expected from the crystal structure of the hexagonal LiBH_4 ,⁸ as shown in Figure 3c, where a two-dimensional diffusion via the ab plane is suggested.⁶ The ^7Li NMR line shape of $3\text{LiBH}_4\cdot\text{LiI}$ remains the same from 150 °C to room temperature, giving direct evidence of the superionic phase stabilization to room temperature. The ν_Q value was decreased to $\nu_Q = 31.6$ kHz ($3\text{LiBH}_4\cdot\text{LiI}$ at 150 °C). This may be explained by a change of the local coordination environment of lithium ions by an anion substitution of the solid solution, from BH_4^- to spherical I^- .

In conclusion, a new series of lithium superionic conductors based on LiBH_4 and metal halides was developed. We have succeeded in imparting room-temperature high lithium ion conductivity to a hydride system that had not been considered a lithium ion electrolyte. A preliminary study reveals versatile properties for application of this material to all-solid-state batteries. These include a lightweight, well characterized interface with metallic anodes, and thermal and electrochemical stability. We believe that the chemical modification technique for metal hydride described will be useful and can be extended to obtain new and valuable ionic and storage devices.

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Supporting Information Available: Experimental methods, XRD and ^7Li NMR results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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