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Litium Fast-Ion Conduction in Complex Hydrides

Complex hydrides can be a potential candidate for solid electrolytes for lithium ion batteries. In this study, we investigated the electrical conductivities of complex hydrides Li_2BNH_6 and $Li_4BN_3H_{10}$ consisting of $[BH_4]^-$ and $[NH_2]^-$ anions, focusing on their low melting temperatures. We also studied the localized rotational diffusion of the $[BH_4]^-$ anions in $LiBH_4$-LiI system.

We have reported that complex hydrides Li_2BNH_6 and $Li_4BN_3H_{10}$ consisting of $[BH_4]^-$ and $[NH_2]^-$ complex anions, shown in Figure 1, exhibit lithium fast-ion conductions [1]. The relatively low melting temperatures (around 360 K and 460 K for Li_2BNH_6 and $Li_4BN_3H_{10}$, respectively) suggest the possible enhancement of total ion conductivity in these temperature ranges. As shown in Figure 2, Li_2BNH_6 exhibits fast-ionic conductivity of 1×10^{-4} S/cm even at room temperature, which is four and five orders of magnitude higher than those of the host hydrides $LiBH_4$ and $LiNH_2$, respectively. Moreover, the conductivity increases monotonically upon heating. The activation energy for conduction decreases significantly at around 368 K from 0.66 eV (303–348 K) to 0.24 eV (above 368 K) as a result of the melting of Li_2BNH_6. The total ionic conductivity reaches 6×10^{-2} S/cm after melting at the highest temperature measured, 378 K. $Li_4BN_3H_{10}$ also shows high conductivity of 2×10^{-4} S/cm at room temperature, and the value reaches 2×10^{-1} S/cm at 513 K after melting. Raman spectroscopy confirmed both the $[BH_4]^-$ and $[NH_2]^-$ complex anions remain intact within Li_2BNH_6 and $Li_4BN_3H_{10}$ even after melting. These results suggest that Li_2BNH_6 and $Li_4BN_3H_{10}$ could be used as a new type of ***"ionic liquid"*** as well as a solid-state fast-ionic conductor [2].

We also investigated the localized rotational diffusion of the $[BH_4]^-$ complex anions in $Li(BH_4)_{1-x}I_x$, which shows lithium fast-ion conductivity of the order of 10^{-5} S/cm at room temperature, by means of quasielastic and inelastic neutron scattering and Raman spectroscopy to clarify the mechanism of the increased ion conductivity [3, 4]. The motions of $[BH_4]^-$ are thermally activated and characterized by activation energies in the order of 40 meV. The motion is dominated by 90 reorientations around the 4-fold symmetry axis of the tetrahedraly shaped $[BH_4]^-$ ions. As compared to the pure $LiBH_4$, the presence of I^- markedly reduces activation energies and increases the rotational frequencies by more than a factor of 100. The result suggests that the rotational motion of the translationally static $[BH_4]^-$ anions may enhance the mobility of Li^+ ions (paddle wheel mechanism).

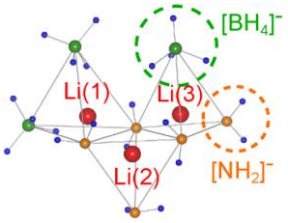

Fig. 1 Local atomistic structure of the complex hydride $Li_4BN_3H_{10}$. $Li_4(BH_4)(NH_2)_3$ have plural occupation sites for Li^+ ions with different tetrahedral coordination consisting of $[BH_4]^-$ and $[NH_2]^-$ anions

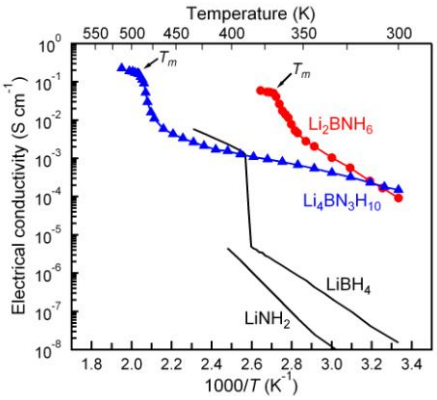

Fig. 2 Electrical conductivities of Li_2BNH_6 and $Li_4BN_3H_{10}$. The melting temperatures are indicated as T_m. For reference, the data of the host hydrides $LiBH_4$ and $LiNH_2$ are also shown.

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Key Words

complex hydride, fast-ion conduction, ionic liquid

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