Supporting information for

Halide-stabilized $LiBH_4$, a room-temperature lithium fast-ion conductor

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SYNTHESIS

Starting materials: $LiBH_4$ (Aldrich, 90%), LiCl (Aldrich, 99.999%), LiBr (Aldrich, 99.999%), and LiI (Aldrich, 99.999%), were used as received. After grinding the appropriate amounts of the powders in an Argon-filled glove box, the powders were pressed into pellets and placed in a Pyrex glass with a plastic screw valve and calcined below 300^{o}C under vacuum for several hours. After the preheating, samples were heated at desired temperatures under either hydrogen or argon atmosphere for 4~12 hrs.

CHARACTERIZATION

X-ray diffraction measurement (Cu K_α) for the composite sample was performed by polyimide film cell to avoid hydration from humidity. Temperature dependence of the conductivity was observed from the complex ac impedance spectrum by use of either Solartron 1260 or an HP4192A impedance meter with a homemade conductivity cell. ^{1}H and ^{7}Li NMR spectra were obtained by a Chemagnetics CMX-300 spectrometer operated at 300 and 121 MHz under a field of 7 T, equipped with a high-temperature probe. Samples were packed into 5 mmϕ sealed glass tubes. Peak separation and integration of the NMR spectra were performed by the Dmfit program.[1]

1. D. Massiot, et al., Modelling one- and two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.* **40** 70-76 (2002)

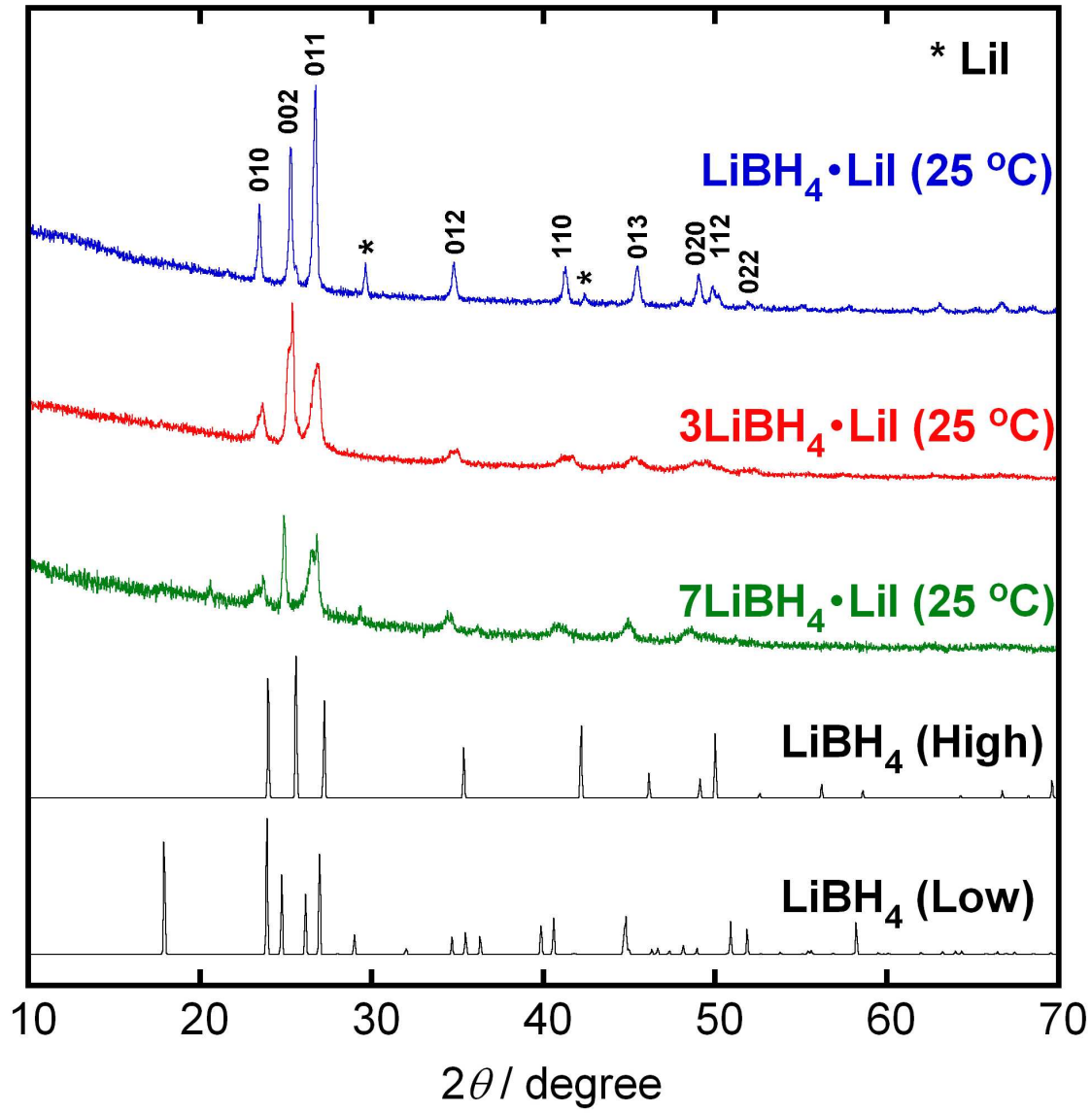

Figure 1. (a) Cu K_α XRD patterns of $LiBH_4$ and $LiBH_4$-LiI binary. Calculated patterns for low- and high-temperature forms of $LiBH_4$ and the measured patterns for $7LiBH_4$·LiI, $3LiBH_4$·LiI, and $LiBH_4$·LiI at 25°C are shown, respectively. Peak indices for $LiBH_4$·LiI are from the crystal data of high-temperature hexagonal phase of $LiBH_4$, $LiBH_4$(High).

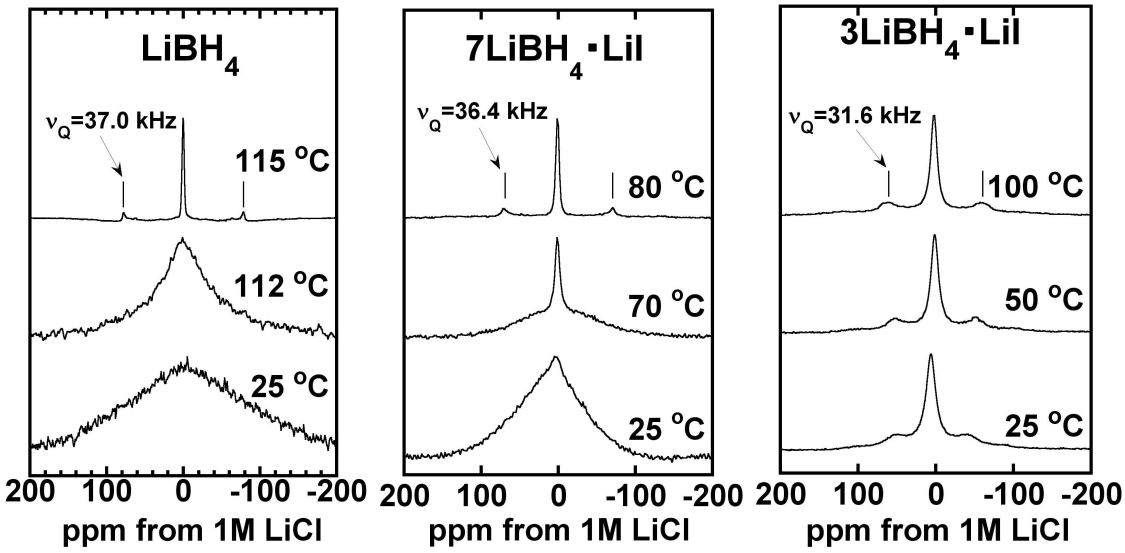

Figure 2. Temperature variation of ^{7}Li NMR spectra for $LiBH_4$, $7LiBH_4 \cdot LiI$, and $3LiBH_4 \cdot LiI$, respectively. A split by a first-order nuclear-quadrupole interaction is indexed in the figure. Simulation assuming 1st order quadrupole interaction yielded $\nu_Q = e^2qQ/h$=37.0 kHz (η=0), 36.4 kHz (η=0), and 31.6 kHz (η=0) for $LiBH_4$, $7LiBH_4 \cdot LiI$, and $3LiBH_4 \cdot LiI$, respectively.