

Gulino et al. - Combined effect of halogenation and SiO₂ nanoparticles addition on the Li-ion conductivity of LiBH₄

Combined Effect of Halogenation and SiO₂ Addition on the Li-Ion Conductivity of LiBH₄

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Supporting Information

Figure S1: IR–ATR spectrum of $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ SSs and pure LiBH₄

Figure S2: Density of $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ SSs as a function of halide concentration

Figure S3: PXD patterns of $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ SSs with different v/v % of SiO₂

Figure S4: IR–ATR spectrum of $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ SSs with different v/v % of SiO₂

IR-ATR spectrum of $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ SSs and pure LiBH₄

The infrared spectra were collected in Attenuated Total Reflection mode with a Bruker Alpha-P spectrometer, equipped with a diamond crystal. The instrument was placed inside a nitrogen filled glovebox. All the spectra were recorded in the 5000–400 cm⁻¹ range with a resolution of 2 cm⁻¹, average of 50 scans.

Results obtained for $h\text{-Li}(\text{BH}_4)_{1-\alpha}(\text{X})_\alpha$ (X = I, Br) solid solutions are reported in **Figure S1a** and **Figure S1b**, together with the spectrum for pure orthorhombic LiBH₄. The IR-ATR spectrum of LiBH₄ shows two main sets of absorption bands. The bands in the 2400–2000 cm⁻¹ region are due to stretching of the B-H bonds, while the bands in the 1600–800 cm⁻¹ region are related to the B-H bending vibration modes.^{10,40,42} The stabilization of the hexagonal phase of the LiBH₄ through the incorporation of either I- or Br- leads to a change in the spectra.^{10,12} Furthermore, the IR spectra in the low frequency region (1500–600 cm⁻¹) become more complex, reflecting a change in the symmetry of the BH₄ anions. In the low frequency region, **Figure S1a** shows the presence of new peaks at ~1170 cm⁻¹, 1020 cm⁻¹ and 960 cm⁻¹, in agreement with results described by Rude et al.⁴². In **Figure S1b**, only the peak at ~1170 cm⁻¹ can be clearly observed in all spectra.

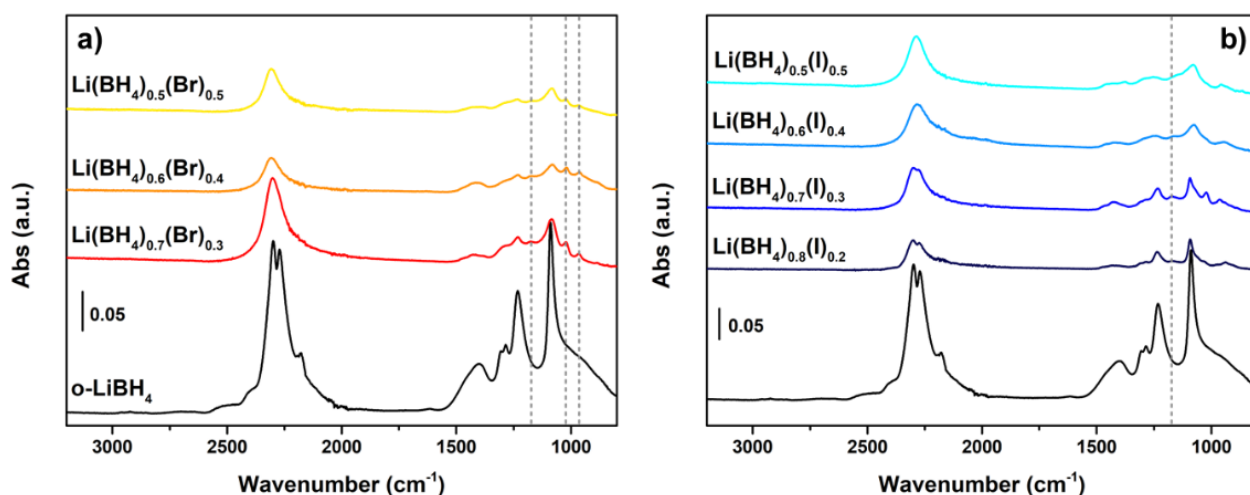


Figure S1. IR-ATR spectrum of pure orthorhombic LiBH₄ (bottom) and of a) **Br0.3, Br0.4, Br0.5** samples and b) **I0.2, I0.3, I0.4, I0.5** samples. Grey lines highlight the presence of new absorption bands in the SS samples with respect the orthorhombic LiBH₄

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Density of h-Li(BH₄)_{1- α} (X) _{α} SSs as a function of halide concentration

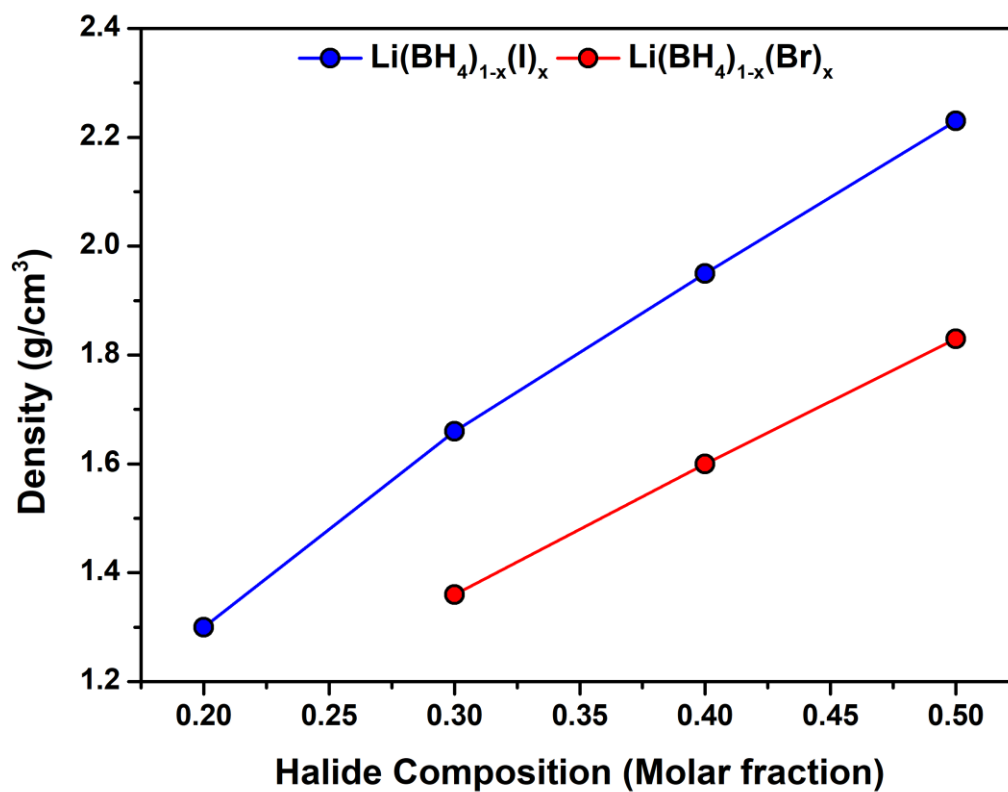


Figure S2. Density of h-Li(BH₄)_{1- α} (X) _{α} SSs as a function of halide composition (molar fraction), calculated from lattice constants of the unit cell, determined from the Rietveld refinement of PXD patterns. Red cycles for h-Li(BH₄)_{1- α} (Br) _{α} and blue cycles for h-Li(BH₄)_{1- α} (I) _{α} .

PXD patterns of $h\text{-Li}(\text{BH}_4)_{1-a}(\text{X})_a$ SSs with different v/v % of SiO₂

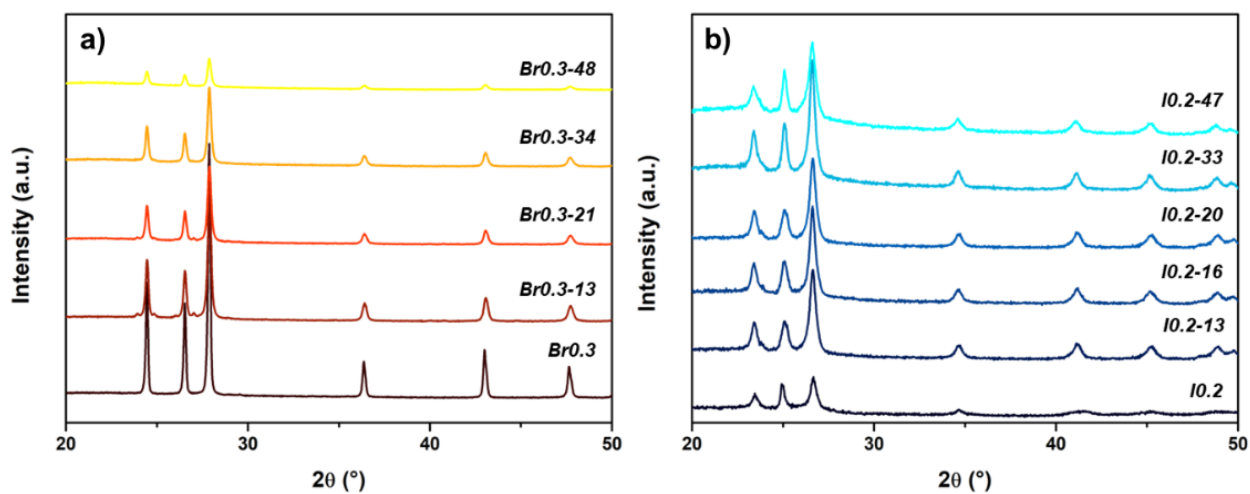


Figure S3. PXD patterns of a) $h\text{-Li}(\text{BH}_4)_{0.7}(\text{Br})_{0.3}$ b) $h\text{-Li}(\text{BH}_4)_{0.8}(\text{I})_{0.2}$, with different v/v % of SiO₂ (see Table 1 in the main text).

IR–ATR spectrum of h-Li(BH₄)_{1- α} (X) _{α} SSs with different v/v % of SiO₂

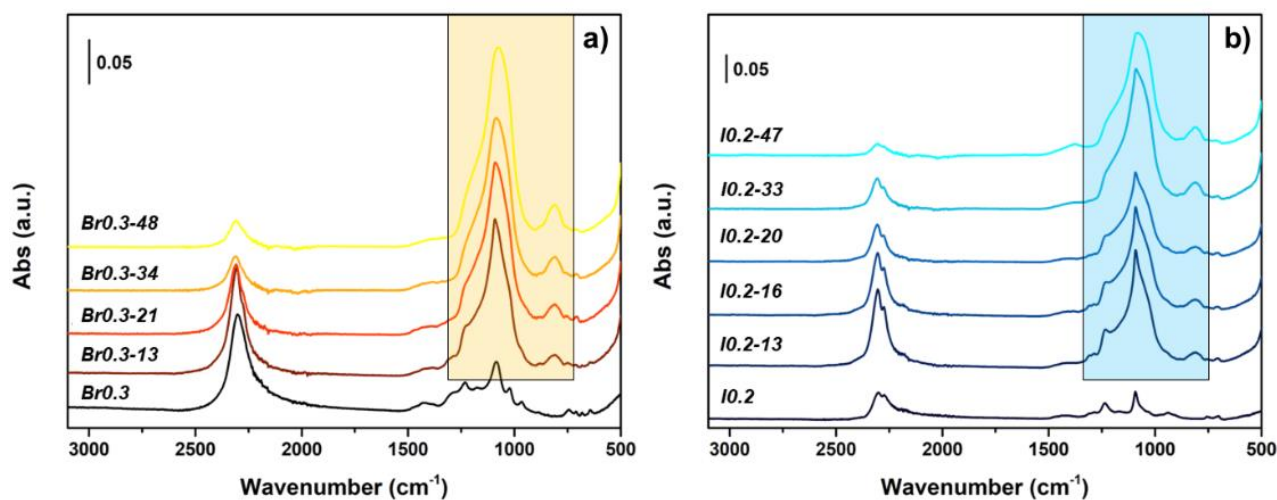


Figure S4. IR–ATR spectra of a) *h*-Li(BH₄)_{0.7}(Br)_{0.3} and b) *h*-Li(BH₄)_{0.8}(I)_{0.2} samples, with different v/v % of SiO₂. The spectrum of sample **Br0.3** and **I0.2** are also reported (bottom).

The presence of the SiO₂ is clearly highlighted by the intense and broad absorption band in the region 1300–750 cm⁻¹.