

# SYNTHESIS OF LI-TETRAALKYLAMMONIUM BOROHYDRIDES AS SOLID-STATE ELECTROLYTES FOR LI-ION BATTERIES

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Nowadays rechargeable batteries are applied in small, portable devices, in mobile phones or watches, as well as in large-scale electricity storage units in smart grids.<sup>1,2</sup> Most commonly used Li-ion batteries with liquid electrolyte have a good performance. Recently, there has been a movement towards all-solid-state lithium batteries, which, along with improved operational safety, provide high power and high energy density.<sup>3</sup> Here we show that combination of lithium borohydride LiBH<sub>4</sub>, with tetraalkylammonium [R<sub>4</sub>N][BH<sub>4</sub>] (R = Me, Et, <sup>n</sup>Pr, <sup>n</sup>Bu) borohydrides allows to obtain double cation salts with significantly higher ionic conductivity at ambient temperature in comparison to LiBH<sub>4</sub>. The rotational and conformational freedom of the BH<sub>4</sub><sup>-</sup> anions and R<sub>4</sub>N<sup>+</sup> cations favours ion mobility thanks to the paddle-and-wheel mechanism. Furthermore, the organic cation lowers the melting temperature of the double salts, making them suitable for the melt infiltration onto the micro-batteries. We obtained a number of new phases by ball-milling [R<sub>4</sub>N][BH<sub>4</sub>] (R = Me, Et, <sup>n</sup>Pr, <sup>n</sup>Bu) with LiBH<sub>4</sub> in different ratios. Two distinct stoichiometric phases form in each system, showing 1:1 and 1:2 R<sub>4</sub>N/Li ratios. The four crystal structures for R = Me and Et were determined from X-ray powder diffraction data, establishing interesting structural relations in this potentially large series. Study of the pure phases of [R<sub>4</sub>N]<sub>n</sub>[Li(BH<sub>4</sub>)<sub>(n+1)</sub>] (n = 1,2) by electrochemical impedance spectroscopy (EIS) showed a high ionic conductivity (ca 10<sup>-5</sup>–10<sup>-3</sup> S/cm at 40–90°C). These phases show melting temperatures from 60–200°C, that facilitates their impregnation into the assembly of 3D electrodes. Currently, the thermal properties of the phases are being investigated by TGA/DSC and by *in situ* powder diffraction to determine if these compounds indeed behave as plastic crystals. Furthermore, we are doing DFT optimization and molecular dynamics study of conductivity mechanisms coupled to the experimental determination of the activation barriers for Li ion diffusion.

## References

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