

## Complex hydrides as electrolytes for Na solid-state batteries: From boosted characterizations techniques towards better performance

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Complex hydrides were deeply investigated for solid-state hydrogen storage, and since few years also as solid-electrolytes [1]. Elevated ionic motion occurs only after a structural phase transition, which generally occurs beyond room temperature (rt). The transition temperature depends on the charge, size and shape of the hydride's polyanion. Frustrating the anion sublattice, either by anion replacing or anion mixing, is an effective strategy to stabilize down to rt the conductive phase. Following this approach, we studied a group of fast Na<sup>+</sup> conductors, obtained by mechanical mixing of different closo-hydroborates and carboranates. Among them, Na<sub>4</sub>(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub>(B<sub>12</sub>H<sub>12</sub>) features a superior ionic conductivity of 2 mS cm<sup>-1</sup> at rt, with a low activation energy of 314 meV [2]. Electrochemical stability of 4.1 V vs. Na<sup>+</sup>/Na is compatible with high-voltage operating positive electrodes [3, 4]. It is limited by the electrochemical stability of less stable anion, confirming that [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> is the more robust anion of the pool [5]. Such evidence has motivated the search for alternative strategies to frustrate the anion landscape in NaCB<sub>11</sub>H<sub>12</sub>. High-energy mechanical milling stabilized a new conductive phase at rt ( $\sigma = 3.4 \text{ mS cm}^{-1}$ ), featuring a bcc anion sublattice, different from the fcc packing in the high-temperature polymorph. IR, XPS and MS analysis have been carried out, to get further insights. The critical current density will be discussed, underlying the crucial role of stacking pressure for targeting enhanced electrochemical performance.

[1] Matsuo et al Adv. Energy Mater. 2011, 1 161.

[2] Brighi et al J Power Sources 2018 404 7.

[3] Murgia et al Electrochem Commun 2019 106 106534.

[4] Asakura et al Energy Environ Sci 2020.

[5] Brighi et al Cell Press Phys Sci 2020 1 100217.