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Borohydride - Oxide Isomorphism in Design of Energy Storage Materials

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An increasing number of novel single, double and triple cation borohydrides has been structurally characterized in the last few years as hydrogen storage materials and solid state electrolytes for battery applications [1,2]. It is interesting to note that the majority of these novel metal borohydrides resemble structures of various metal oxides. This is not altogether surprising considering the fact that $[\text{BH}_4]^-$ and O^{2-} anions are isoelectronic. The particularity of the borohydride-oxide analogy is the double negative charge of O^{2-} vs. the simply charged borohydride $[\text{BH}_4]^-$, this providing a superior structural flexibility in oxides with respect to mixed valence compounds. Though somewhat handicapped by its lower charge regarding this issue, the borohydride anion obtains its versatility as a building block due to being a non-spherical anion with a tetrahedral shape as opposed to the oxide, which is approximately spherical. This commonly results in a lower symmetry of the borohydride when compared to the related oxide, the prototype very often showing a close packing of a readily polarisable soft oxide anion. We will show by means of in-situ synchrotron X-ray powder diffraction and ab initio calculations in the solid state that structural distortions in metal borohydrides compared to oxide prototypes have their origin in close hydridic di-hydrogen contacts of repulsive nature. These contacts may be suggested as a tool to tailor the crystal symmetry in complex metal hydrides in the future. Nearly twice as big as the oxide, the borohydride anion allows for connectivities of the coordination polyhedra rarely observed among the oxides such as tetrahedral edge sharing. We will show how the borohydride-oxide isomorphism, and cationic heterovalent substitution allow the prediction and design of novel borohydrides with high hydrogen content or high cation mobility.

[1] W.I.F. David, *Faraday Discuss.* 2011, 151, 399-414, [2] R. Černý, P. Schouwink, Y. Sadikin, et al., *Inorg. Chem.*, 2013, 52, 9941-9947

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