

# LONG BATTERY CYCLABILITY ACHIEVED COMBINING HALOGENATION AND INTERFACE ENGINEERING USING COMPLEX HYDRIDE SOLID-STATE ELECTROLYTE

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Different approaches to achieve the RT Li<sup>+</sup> conductivity required for batteries applications in LiBH<sub>4</sub> are reported, such as halide substitution and the addition of oxide to form composites. We investigated the effect of halogenation on the structural and electrochemical properties in the LiBH<sub>4</sub>-LiI, LiBH<sub>4</sub>-LiBr and LiBH<sub>4</sub>-LiBr-LiCl systems.<sup>1,2</sup> In all these systems, the presence of the anions (I<sup>-</sup>, Br<sup>-</sup> and Br<sup>-</sup>+Cl<sup>-</sup>) leads to a stabilization of the high temperature polymorph of the LiBH<sub>4</sub>, greatly enhancing the Li-ion conductivity at RT. Secondly, the effect of SiO<sub>2</sub> addition to LiBH<sub>4</sub> by ball-milling on the Li-ion conductivity was analysed. The Li-ion conductivity was enhanced for all the composite conductors by the creation of an interface layer where the conductivity is drastically enhanced.<sup>3</sup> Finally, the possibility to have a synergetic effect between these two approaches has been studied.

In this work, the effect of nanocomposite formation *via* ball milling on the electrochemical properties of halogenated *h*-Li(BH<sub>4</sub>)<sub>0.8</sub>(I)<sub>0.2</sub> has been explored extensively. The resulting *h*-Li(BH<sub>4</sub>)<sub>0.8</sub>(I)<sub>0.2</sub>-SiO<sub>2</sub> demonstrated a higher conductivity with respect to pristine LiBH<sub>4</sub> an even with respect to the pure solid solution. The electrochemical stability window is equal to that of the LiBH<sub>4</sub>, but the stability against Li-metal is drastically improved by the addition of oxide nanoparticles. This effect is likely caused by an enhancement of the mechanical strength of the samples. Importantly, we have assembled an all-solid state battery cell (Li|*h*-Li(BH<sub>4</sub>)<sub>0.8</sub>(I)<sub>0.2</sub>-SiO<sub>2</sub> |TiS<sub>2</sub>) that has shown a high and long-term cyclability, i.e. over 200 cycles, even at high C-rate, demonstrating that the addition of oxide nanoparticles significantly improves the stability of the electrolyte

## References

- (1) Gulino, V. et al. *Chem. Mater.* **2019**, *31* (14), 5133–5144.
- (2) Gulino, V. et al. *ACS Appl. Energy Mater.* **2021**, *4* (7), 7327–7337.
- (3) Gulino, V. et al. *ACS Appl. Energy Mater.* **2020**, *3* (5), 4941–4948.



During the past 4 years, I focused on many aspects of solid-state electrolytes research, especially on complex hydrides. I obtain my PhD title in October 2020 (University of Turin, supervised by Marcello Baricco) and, the same month, I joined the MCC (Utrecht University, Netherlands) group of Petra de Jongh as postdoctoral researcher. During this path, I joined both the Radovan Černý group and joined Prof. Petra de Jongh group for a period of 3 months. As a postdoctoral fellow I am working on the practical design of the battery cells and on the synthesis and characterization of novel SSE and sulfur cathodes. In addition, I am part of the RELEASE consortium, working on CO<sub>2</sub> electroreduction.