

All solid-state batteries promise higher energy and power densities and higher operational safety than state-of-the-art lithium-ion batteries that use a flammable liquid electrolyte.

In the recent years, a variety of novel solid-state superionic conductors emerged; among them, the applicants developed a new class of solid-state electrolyte, namely hydroborates, to a point where they compete with state of the art oxide or sulfide based solid-state electrolytes. We realized a stable rechargeable 3 V all solid-state sodium battery based on a mixed anion hydroborate solid-state electrolyte, $\text{Na}_4(\text{B}_{12}\text{H}_{12})\text{O}(\text{B}_{10}\text{H}_{10})$. Unlike oxide or sulfide based electrolytes, the hydroborate is stable against sodium and a high capacity metallic sodium anode could be operated with a current density of $0.1 \text{ mA cm}^{-1}(\text{C}/5)$ at $60 \text{ }^\circ\text{C}$. Cycling at higher scan rates or lower temperatures leads to cell failure due to short-circuiting. Generally, the combination of high energy density (metallic anodes) and high power density (high rates) is a common challenge for solid-state batteries.

Our proposal addresses basic materials properties of this novel, yet under-explored class of solid electrolytes in view of potential battery application. Specifically the ones concerning the anode/electrolyte interface: (i) what is the microscopic origin and a role of solid electrolyte in battery short-circuiting (ii) what are the (electro-chemical) decomposition products of the hydroborate electrolyte and (iii) are stable interphases towards the electrodes formed as in the case of conventional Li-ion batteries?

To answer these questions, we identified the surface/interface stability to be essential. For hydroborates, detailed studies of their surface properties are missing and this project aims at filling this knowledge gap. In a combined experimental and theoretical approach, we will investigate the chemical and electrochemical compatibility between the electrolyte and the electrodes, including the identification of the reaction products at the border of stability limits and the effect of current density/temperature on long term cycling. Thereby, we will combine electrochemical characterization with scanning thermal techniques, microscopy, and operando X-ray diffraction. Theoretical calculations of the structure and the stability of surface and interfaces will complement the experiments.

The central aspects of this project are:

1. In depth experimental and theoretical study of a novel, yet under-explored class of solid electrolytes, that so far fulfills more criteria of a suitable electrolyte for solid-state batteries than any other solid electrolyte
2. The approach to understand the processes within the solid-state battery from the surface of the constituent elements and the resulting interfaces
3. Innovative experimental approaches to investigate the stability of the hydro-borate based electrolyte and its compatibility with the metallic anode, including spatially resolved in-situ x-ray diffraction.

The experimental work will be carried out in the lab Materials for Energy Conversion at Empa, where battery research is the core activity and by the Laboratory of Crystallography at the University of Geneva, headed by Prof. Radovan Černý who joints this proposal as a project partner. The Polish co-proposer, Prof. Zbigniew Łodziana, from the Department of Structural Research IFJ – PAN, Krakow, will provide theoretical expertise and research of thermodynamic, electrochemical and interfacial properties of hydroborates within density functional theory (DFT) methods.