

Increasing societal demand for mobile devices and electric mobility brought rapid development of lithium based secondary batteries. At present the state-of-the-art lithium-ion batteries still use a flammable liquid electrolytes constituting operational safety hazards potentially affecting home solar energy leveling. A shortage of metals used for production of Li-ion batteries creates additional security issues.

These are only some reasons that brought a rapid increase of new ideas for better Li-ion technology like all solid state batteries, or search for so called post-lithium alternatives. The post-lithium batteries must be based on abundant metals, elements, compete with the present technology in energy density, pose no safety issues. Sodium is the first candidate to replace lithium due to physicochemical similarity of the elements. Variety of new developments were already done, new hydroborate solid state electrolytes were discovered, some of them with participation of the author. The all solid state battery incorporates such electrolytes and it is believed to overcome safety issues additionally increasing energy density.

The next leap in the rechargeable battery development is believed to usage of multivalent working cations, like magnesium, calcium or aluminum. A large Earth abundance of these elements and high theoretical volumetric energy densities are appealing. Unfortunately, larger charge densities related to multivalent cations does not allow for simple transfer of knowledge obtained for monovalent ones. One of the major limitation in rapid development of multivalent batteries is lack of the ultimate electrolytes. Liquid carbonate electrolytes form blocking layers at the electrodes, halide based ones are corrosive for electrodes. Again a variety of new concepts emerges, with this related to solid state ionic conductors being particularly appealing. Once such conductor is invented the safety and stability problems of multivalent secondary batteries shall be solved. Such goal still requires basic understanding of the processes beyond multivalent ion transport in solids. This is focus of the present project.

Surprisingly Mg ionic conductors based on hydroborates combined with other molecules like ammonia, ethylenediamine or similar are superior to the oxide or thiospinel based ones. There are some attempts to rationalize Mg conduction mechanism in these materials, however no systematic understanding is known. Without a hint of such understanding the trial and error method remains only one viable instead of rational design. In order to change such situation in this project we propose:

(i) theoretical analysis, with quantum mechanical methods, of the spatial and temporal correlations and relation between local structural properties and the activation energies – all related to Mg mobility in $\text{Mg}(\text{BH}_4)_2$ with glymes, ethylenediamine, amionboranes, ammonia and novel molecules in solid state electrolytes. This will allow finding of common aspects related to Mg^{2+} cation mobility ultimately giving a simple descriptor that may guide experimental research or bring a novel understanding of cation diffusion or improved ionic conductor.

(ii) calculations of the thermodynamic, electrochemical and mechanical stability regimes for such ionic conductors. Each solid state ionic conductor must be stable in contacts with anode and cathode, must withstand mechanical stresses related to plating, volume changes of the electrodes or temperature fluctuations. Once a fair understanding of Mg based electrolyte is achieved our research will be extended to calcium, possibly aluminum cations. The pioneering understanding obtained within this project shall contribute to development of new working secondary battery concepts.

The calculations will be performed at the Department of Structural Research IFJ – PAN with our own computer resources supplemented with remote access to supercomputers. We will use density functional methods due to unknown charge transfer and polarization or other processes accompanying diffusion of multivalent ions in the lattice.