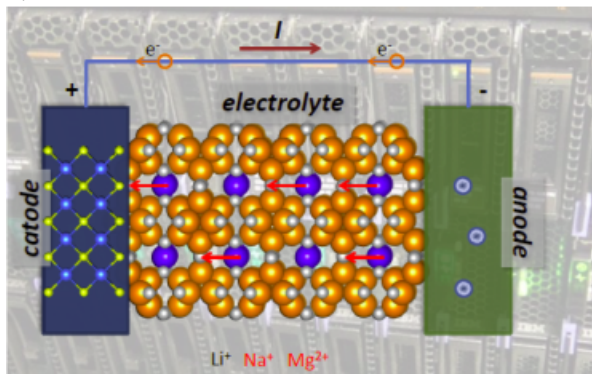


The societal discussions and research focus tackles more often so called renewable energy sources. Renewable source mean that the rate of their creation is comparable to the rate of their exploitation. There are few renewable energy sources, like wind, solar, tidal, biomass and geothermal energy. However most of the are inherently intermittent. Some of them are also dispersed. Implementation of such energy sources will require strategies to alleviate the intermittent characteristics. Such strategy would require proper energy storage methods. One of the possibilities is related to electrochemical energy storage in batteries. The schematic view of the modern rechargeable battery is presented in Figure 1.



**Figure 1.** Schematic view of the rechargeable battery. The solid state electrolyte facilitates ion (blue spheres) transport between anode and cathode. Moving ions could be lithium but also sodium or magnesium.

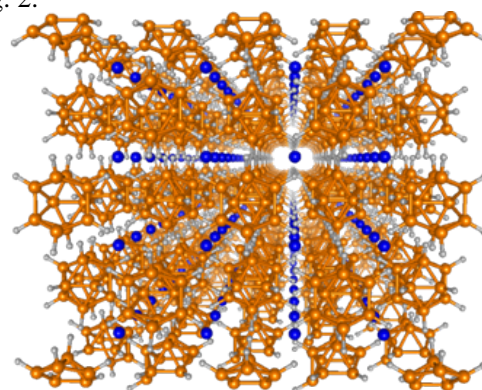
The operational principle is related to the transport of ion between electrodes. During the discharge process ions move from anode to cathode providing electricity. Most of the portable electronics is equipped with such lithium batteries – because lithium ions are the active metal that is transported between electrodes. While the development of electrode materials allows steady progress and improvement of the cell capacity, the development of better electrolytes is crucial for large scale applications due to safety issues. Examples of safety problems can be found everywhere – like grounding of the Dreamliner airplanes due to fire of the liquid electrolyte in Li-ion batteries. On the large scale such problems can be catastrophic. Development of the solid state electrolytes will minimize safety issues, however finding of the material appropriate for the electrolyte is a formidable task. It requires the synergy of numerous research disciplines such as materials science, physics, chemistry, biology and others. This complexity is related to the fact

that properties of solids are usually different from these of liquids. Ionic conductivity is one of the few exceptions and there are known examples of solids (AgI) with ionic conductivity comparable to liquid electrolytes. Since, in the rechargeable battery the type of the active ion is unique the solid electrolyte must be conductive for such particular element (usually lithium, but also sodium or magnesium in the future). This is a serious constraint to the material and the origin of difficulties.

Solution of these problems requires, among other, extensive basic research. Such research is the objective of the present project. It is focused on understanding of the mechanism of the ionic conductivity in recently discovered superionic conductors closo dodecaborates. These exotic materials like  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  exhibits ionic conductivity comparable to the best known sodium conductor based on alumina, conductivity that is favorable to be considered in the application in future rechargeable batteries. The property evaluation will be performed by extensive calculations based on quantum mechanics. An extraordinary progress in development of computational power, advancement of computer implementations of cutting-edge computational methods for solid state materials have shaped the possibility of computer-based materials design or accurate property calculations without reference to the experiment. A property of selected material is calculated by solution of the Schrödinger (or Dirac) equations for many electron systems. Further calculations of atomic motion in finite temperatures is done by solution of appropriate equations of atomic motion in the potential calculated within quantum methods. While this is still challenging task it can be done for such compounds that are not well characterized experimentally. In this project such calculations will done.

In dodecaborates the ion conductivity mechanism is related to the coupling of rotational and translational degrees of freedom, however atomic-scale details of cation transport are unknown. Within this project we will address scientific questions related to this new class of ionic conductors like thermodynamic or electrochemical stability; the origin and the mechanism of the ionic conductivity and possibility of modifying cation diffusivity by ionic substitution. Dodecaborates have complex crystal lattice due to the complexity of  $\text{B}_{12}\text{H}_{12}$  anion, see Fig. 2.

The calculations will be performed within density functional theory and methods of statistical mechanics. For selected dodecaborates (with such cations as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) research shall provide description of the properties such as electronic structure: ionic conductors must be electric insulator for electrons; stability – these materials must not decompose under finite electric bias, elevated temperature or moderate mechanical stress. Moreover the calculations shall provide information about the ion transport on the atomic scale. The diffusion of ions, blue spheres in Fig. 2, through the crystal lattice is complex phenomena and it took almost 100 years to understand it for simple conductors like  $\text{Ag}_2\text{S}$  or  $\text{PbF}_2$ . We expect that the first understanding of this process in  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  will be obtained within this project. The spectroscopic properties, like Raman, infrared vibrations, NMR chemical shifts, directly comparable with the experimental data will be provided. The large size of the anion requires models consisting of several hundred of electrons. The influence of ion substitution on the diffusivity in these materials will studied with molecular dynamics methods. At each stage of the project the calculated properties will be critically confronted with available experimental data.



**Figure 2.** View of the atomic structure of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  superionic conductor. Na cations are blue, boron is orange and hydrogen gray.