

Our society relies on electrical storage devices, from smartphones and laptops to vehicles and to wider industrial applications. The development of energy storage systems is a vital goal of material science, as this is a key to the technology enabling the shift from fossil to renewable energies. With increased production of sustainable energy from renewable sources (solar, wind), the need for efficient energy storage systems has stimulated intense research interest in the area of batteries and super-capacitors. The very important factor to consider is the safety of the batteries. With this respect solid state batteries using inorganic solid electrolytes (so called all-solid-state batteries) instead of flammable organic liquid electrolytes present a very promising technological development. Solid state electrolytes offers several advantages over current battery technologies including stability, efficiency and safety.

Unfortunately, majority of super – ionic inorganic materials exhibits ionic diffusion on the level of typical solids. Only a few of thousands of superionic inorganic materials exhibit ionic diffusion that makes them candidates for potential electrolytes - examples of such compounds are:  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ,  $\text{Li}_7\text{P}_3\text{S}_{11}$ ,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{11}$ ,  $\text{Li}_3\text{PS}_4$  or  $\text{LiBH}_4$ . The intriguing point is that these few materials exhibit extraordinary fast diffusion and high conductivity – higher by several order of magnitude compared to standard solids and comparable with the ionic diffusion in liquid electrolytes. The reason of this effect is not understood. The lack of understanding of the diffusion mechanisms is a consequence of the rather unfortunate situation in the electrolyte science - majority of the studies is just devoted to synthesis of new compounds for electrolytes and electrodes and to their electrochemical characterization. There is, however, a growing awareness that further progress in the electrolyte systems heavily relies on a thoroughgoing understanding of the mechanisms of ionic diffusion on molecular (ionic) level.

The awareness manifests itself in extensive attempt to model diffusion mechanisms in solids by means of computational methods. Generally, ionic diffusion in solids is considered as a sequence of hopping of individual ions between available lattice sites. The crystal structure determines the diffusion channels and the energy landscape along the diffusion pathway. The maximum of the energy landscape creates a bottleneck for the ionic movement. Molecular Dynamics calculations indicate that the key to the fast diffusion lies in stimulating correlation in the ionic motion – *i.e.* creating a situation when multiple ions simultaneously (in a time range of ps) hop to the nearest available lattice sites. Although this explanation is highly original and interesting, it is so far based only on the predictions of calculations. It has also been suggested that reduced dimensionality of the diffusion pathways (like for instance a snake-like diffusion path) is the reason of fast translation movement. One should be aware that for many materials there is not a single diffusion mechanism involved, but many processes run in parallel.

In order to reveal the mechanisms of ionic diffusion and visualise the process on the ionic level, unique experimental and theoretical tools are required. Motivated by the prospects of battery design with solid electrolytes we shall apply Nuclear Magnetic Resonance (NMR) relaxometry accompanied by other NMR methods and impedance spectroscopy to understand the conditions required for fast, long-range ionic diffusion and, hence, fast conductivity. Standard NMR relaxation experiments are performed at a single magnetic field (resonance frequency) versus temperature. Here the studies will be carried out in a remarkably broad range of magnetic fields encompassing five orders of magnitude: from about  $30\mu\text{T}$  to  $3\text{T}$  (this means from about  $1\text{ kHz}$  to  $120\text{ MHz}$ , referring to  $^1\text{H}$  resonance frequency) versus temperature and pressure. Frequency dependent relaxation studies possess the exceptional potential to reveal the underlying mechanisms of ionic motion (not only the time scale). As spin relaxation is a quantum-mechanical phenomenon, to fully profit from the remarkable experimental opportunities, a parallel development of spin relaxation models dedicated to solid electrolytes constitutes a part of the project. One could cite numerous examples of misleading conclusions drawn from NMR relaxation experiments interpreted in terms of incorrect theoretical models. The common disappointment stems from the lack of understanding that in classical relaxation experiments performed at a single, high frequency one is not able to probe long range translation motion, but only local, fast dynamics that is not related to the conductivity – fast local motion is not a promise of large conductivity.

As a part of the project we plan a unique experiment: we shall perform NMR relaxometry studies in the full frequency range changing not only temperature, but also pressure. Pressure causes changes in the structure in terms of inter-ionic distances. Correlated motion involving multiple ions requires large activation volume – this implies that correlation effects should be considerably suppressed under high pressure. In this way we will be able for the first time to directly verify the concept of correlated ionic dynamics leading to highly enhanced conductivity.

The project combines unique experimental methodology with advanced theoretical modelling. It attempts to give a deep insight into a very important subject of fundamental science – mechanisms of ionic motion in solids – being at the same time of utmost importance for the battery technology. Unravelling the physical reasons of extraordinary ionic transport is a very importance step for tailoring of novel solid state electrolytes.