Lithium Diffusion Pathways in Modern Solid State Electrolytes

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Rapid development of portable energy storage media permanently requires materials, which are cheaper, safer, more stable\robust and have better electrochemical performance compared to the existing analogues. On the other hand the concept of all solid ceramic Li ion batteries is now actively explored as potentially safer, more stable and capable to operate at higher potentials alternative to conventional Li-ion batteries based on liquid electrolytes.

To large extent the electrochemical energy storage and energy conversion are diffusion-based/limited processes, where the knowledge about underlying diffusion pathways and mechanisms is essential. However, the experimental information about preferable diffusion pathways of polycrystalline (non-cubic) materials can hardly be obtained *per see* by bulk (e.g. resistivity, impedance spectroscopy, quasielastic neutron scattering *etc*) measurements. The majority of theoretical methods typically utilized for prediction of diffusion pathways are often based on molecular dynamics simulations (either force-field or *ab initio*) and create certain challenges for the modelling of diffusion properties of new materials.

The diffusion process in a material is determined by its crystal structure and in many cases the crystal structure is a key for its understanding. At the moment there are several methods available and capable to predict the preferred ion diffusion pathways with high reliability on the basis of the underlying crystal structure, *e.g.* analysis of topology based on Voronoi-Dirichlet partitioning, Hirschfeld approach, differential bond valence method *etc*. However most of them requires accurate structural input, which, along with the fact, that modern "green energy" production and storage is based on light atoms, where conventional X-ray methods have certain limitations, makes neutron-based scattering techniques highly relevant. Neutron powder diffraction is a powerful experimental tool, well suited for the localization of Li under the presence of heavier elements, delivering accurate fractional coordinates, lattice dimensions, Debye-Waller factors etc. Probe of nuclear density distribution in lithium conducting materials by the analyses of probability density function from anharmonic refinements of powder diffraction data and/or the reconstruction of electron/nuclear densities by maximum entropy method [1] opens ample opportunities for the development of new generation solid state lithium conductors.

In the current contribution the application of differential bond valence method for the prediction and neutron diffraction-based techniques for the experimental evaluation of ion diffusion pathways in model materials [1], modern solid state lithium electrolytes [2-4] and promising materials for electrochemical energy conversion and storage [5,6] will be presented and discussed in brief.

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