

Lithium Diffusion and Diffraction

A. Senyshyn,¹ M. Monchak,^{1,2} O. Dolotko,¹ H. Ehrenberg^{3,4}

¹Maier-Leibnitz Zentrum, Technische Universität München, Lichtenbergstrasse 1,
D-85748 Garching b. München, Germany

²Strukturforschung, Darmstadt University of Technology, Petersenstrasse 23,
D-64287 Darmstadt, Germany

³Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT),
Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

⁴Helmholtz-Institute Ulm for Electrochemical Energy Storage (HIU),
P.O. Box 3640, D-76021 Karlsruhe, Germany

Corresponding author: A. Senyshyn, E-Mail: anatoliy.senyshyn@frm2.tum.de

The rapid development of energy storage media permanently requires new electrode and electrolyte materials, which are cheaper, more stable/robust and have better electrochemical performance. To a large extent the electrochemical energy storage and energy conversion are diffusion-based processes, where the knowledge about underlying diffusion pathways and mechanisms becomes crucial. Unfortunately the information about preferable diffusion pathways of polycrystalline (non-cubic) materials can not be directly obtained by bulk (e.g. resistivity, impedance spectroscopy, quasielastic neutron scattering *etc*) measurements.

Theoretical methods for prediction of diffusion pathways are often based on molecular dynamics simulations (either force-field or *ab initio*), which creates sufficient challenges for the modeling of diffusion properties of new materials. Compared to molecular dynamics the bond valence modeling is a simple tool, which may give necessary first approximation for the mechanisms of ion diffusion in materials with primarily ionic type of bonding. It is assumed that the ion transport from one equilibrium site to the other one might follow a pathway, along which, the valences mismatch $\Delta V = |V - V_{nom}|$ between bond V and V_{nom} nominal valences remains as small as possible [1]. The total bond valence sum V of cation A can be expressed as $V = \sum_X S_{A-X}$, where individual bond valences S_{A-X} are calculated using R_{A-X} bonds to adjacent anions X and tabulated R and b parameter sets as $S_{A-X} = e^{\frac{R-R_{A-X}}{b}}$. The model is characterised by the high predictive capabilities and can be easily adapted to different kinds of anionic and cationic diffusion species.

On the other hand the diffusion processes in a material are determined by its crystal structure, and there are several methods to predict the preferred ion diffusion pathways with high reliability on the basis of the underlying crystal structure, *i.e.* the analyses of probability density function from anharmonic refinements of powder diffraction data and the reconstruction of electron/nuclear densities by maximum entropy method [2].

In the current contribution the application of bond valence method for the prediction (and diffraction-based techniques for the evaluation) of ion diffusion pathways in different materials for electrochemical energy conversion and storage will be presented and discussed.

References

- [1] J. D. Garrett, J. E. Greedan, S. Faggiani, S. Carbotte, I. D. Brown, *J. Sol. State Chem.* **42** (1982) 183.
[2] A. Senyshyn, H. Boysen, R. Niewa, J. Banys, M. Kinka, Y. Burak, V. Adamiv, F. Izumi, I. Chumak, H. Fuess, *J. Phys. D: Appl. Phys.* **45** (2012) 175305.

