

MS19-P9 Crystal structure, microstructure and ionic conductivity of the cost-efficient sodium solid electrolyte $\text{Na}_3\text{YSi}_4\text{O}_{12}$

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There exist a number of solid-electrolyte materials for sodium battery technologies characterized by intermediate complexity of the corresponding crystal structures. Beside the well-known sodium solid-electrolytes, β^{++} -alumina and NASICON, $\text{Na}_3\text{YSi}_4\text{O}_{12}$ is another promising phase with a high ionic conductivity. Its main advantage over the two above-mentioned structures is a lower production complexity and thus associated costs. However, very little is known about the correlation between the complex crystal structure, with their one-dimensional ion migration pathways, the microstructure and the interplay with Na^+ ionic conductivity.

In this work, the phase content, the phase distribution, the migration pathways and the ionic conductivity of polycrystalline $\text{Na}_3\text{YSi}_4\text{O}_{12}$ -based materials, obtained by a glass-ceramic process, have been analyzed by means of X-ray powder diffraction, scanning electron microscopy, solid-state nuclear magnetic resonance and electrical impedance spectroscopy. These experimental results were discussed with respect to theoretical considerations of the crystal structure, based on the bond valence method and the Voronoi-Dirichlet approach, and other Na^+ conductors.

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Keywords: ionic conductivity, solid electrolyte, ceramic, bond valence, Structure conductivity correlation

MS19-P10 Experimental visualization of the Na diffusion paths in $\text{Na}_{0.7}\text{CoO}_2$, a prospective cathode material for Na-ion batteries

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The layered cobaltite Na CoO_2 ($0 < x < 1$) has been extensively studied during the last decade due to the unusual evolution of its electronic and magnetic properties with the Na content (and hence the $\text{Co}^{3+}/\text{Co}^{4+}$ ratio). Its phase diagram includes metallic and insulating phases, charge order, frustrated magnetism, and even a small region where superconductivity appears when H_2O molecules are intercalated between the CoO_2 layers. Interestingly, this material has also attracted the attention of applied sciences due to its structural similarity with Li_xCoO_2 , which is one of the most common electrode materials in Li-ion batteries. In view of the larger abundance of Na in the earth crust with respect to Li and the increasing interest on cheaper Na-ion batteries for grid storage, we have investigated the Na-ion diffusion in Na CoO_2 by means of NMR¹, μSR ², elastic³ and quasielastic⁴ neutron scattering in order to assess the use of this material as cathode for solid-state rechargeable batteries.

For this purpose we choose the material with $x=0.7$, where the tendency of Na ions to form ordered superstructures might reduce the ionic conductivity. By combining these techniques we could establish the existence two structural transitions at $T_1=290\text{K}$ and $T_2=400\text{K}$. Analyses of the anomalies in the Na-Na distances, the Debye-Waller factors and the scattering density in the paths connecting neighbouring Na sites unambiguously showed that both transitions are related to changes in the Na-ion mobility. Moreover, we found that ionic diffusion in this material occurs through the successive opening of first quasi-1D ($T_1 < T < T_2$) and then 2D ($T > T_2$) Na diffusion paths within the Na layers³. These findings provide new insight on the subtle mechanisms controlling the Na-ion diffusion in the Na CoO_2 series and indicate that even in the less favourable member of the family ion diffusion is already present at RT.

¹ Weller et al., PRL **102**, 056401 (2009)

² M. Månsson et al., Phys. Scr. **88** (2013) 068509

³ M. Medarde et al., PRL **110** (2013) 266401

⁴ F. Juranyi et al., EPJ Web Confs. **83** (2015) 02008

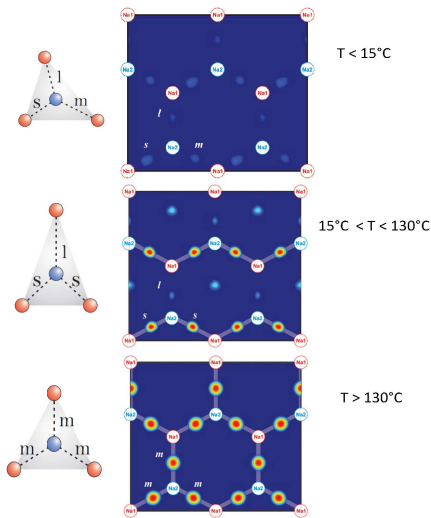


Figure 1. Na diffusion paths at different temperatures in one of the Na layers of $\text{Na}_{0.7}\text{CoO}_2$ with partially occupied NaI (red) and Na2 (blue) sites³.

Keywords: Na batteries, Na diffusion, neutron powder diffraction

MS19-P11 Advanced fuel cell component characterization by the development of *in-situ* SAXS flow cell

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The most commonly used technique for structural characterization at the nanoscale is transmission electron microscopy (TEM). However, there are several limitations to this technique: the information is only obtained on a very small part of the sample and the contrast between support and supported catalyst nanoparticles can be very weak for certain systems like Pt nanoparticles on a high-Z metal oxide support. This can make it difficult to distinguish the catalyst nanoparticles from individual support crystallites. Moreover, due to the very short electron absorption length in condensed matter, TEM investigations cannot be performed *in situ* during operation. These limitations of TEM can be overcome by small-angle X-ray scattering (SAXS): even for very small beam diameters of a couple of hundred micrometers, the scattering curve contains information of hundreds of millions of catalyst nanoparticles [1]. The support contribution to the scattering curve can be subtracted: in case of anomalous SAXS (ASAXS), several energies are used close to the Pt LIII absorption edge in an energy-tunable synchrotron radiation, while in laboratory SAXS diffractometer, incident X-Ray energy is fixed and measurements of both support and catalyst on support are required. The results of *in-situ* ASAXS experiments on Pt/IrTiO₃ will be presented. The conventional model of spherical catalyst particles to incorporate the particle-support interference effect will be explained. Moreover, an experimental setup to perform *in-situ* SAXS experiments in a laboratory machine will be shown on Pt / Vulcan carbon system. [1] Binniger T., Garganourakis M., Han J., Patru A., Fabbri E., Sereda O., Kötzer R., Menzel A., Schmidt T.J. *Phys. Rev. Applied*, 2015, 3, 024012

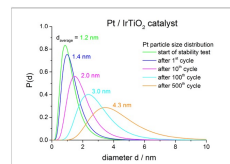


Figure 1. Evolution of the NPs size distribution

Keywords: small-angle X-ray scattering (SAXS), nanoscale characterisation