MS25-O3

Local structure and lithium diffusion pathways in nanostructured $Li_4Mn_2O_5$ rock-salt cathode probed

Maria Diaz-Lopez[1], Yves Joly[1], Claire V. Colin[1], Valerie Pralong[2], Pierre Bordet[1]

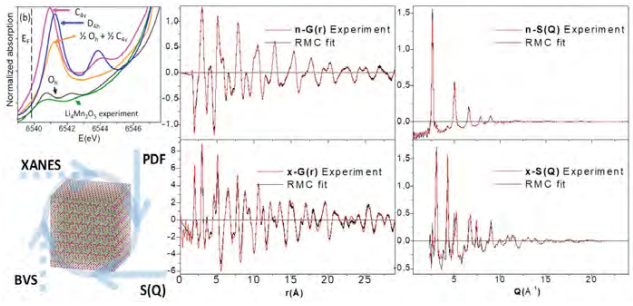
1. Institut Néel CNRS, Grenoble, France
2. Crismat Ensicaen, Caen, France

email: maria.diaz-lopez@neel.cnrs.fr

The full structural description of a complex nanostructured $Li_4Mn_2O_5$ high capacity cathode showing record reversible capacities superior to the state-of-the-art Li-Mn-O electrodes [1], was achieved for the first time by the combined study of Near-Edge X-ray Absorption Spectroscopy (XANES), Pair Distribution Function (PDF) analysis of neutron and X-ray total scattering data. An initial model was proposed based the knowledge of the average rock-salt structure and the octahedral coordination environment of manganese indicated by XANES performed at the Mn K-edge. A combined Reverse Monte Carlo (RMC) refinement of neutron and X-ray total scattering data shows that while the manganese framework remains cubic and well-ordered a high degree of disorder exists for both oxygen and lithium, which are displaced from their original rock-salt positions. The validity of the refined model was confirmed by the agreement between the XANES simulated spectra using FDMNES and the experiment. Additionally, we elucidated the unique and unusual 3D lithium diffusion pathway in nanocrystalline Li4 involving 5-coordinated lithium sites by bond valence energy landscape maps calculations.

The structural information revealed here [2] is essential for the understanding of nanostructured $Li_4Mn_2O_5$ performance as a cathode material and would have great implications on the design and development of future cathode materials based on $Li_4Mn_2O_5$.

Figure 1. Top left: XANES data at the Mn K-edge and simulations. Bottom left: schematic view of the RMC refinement approach performed in a box containing 21 000 atoms. The refinement constraints are given in dashed lines and the simultaneously modelled neutron and X-ray total scattering data in full lines. Right: refined data.



References:

[1] Freire et al. (2016). Nature Materials, 15, 173–177.
[2] Diaz-Lopez et al. (2018). Submitted.

Keywords: Reverse Monte Carlo modelling, XANES, total scattering

MS25-O4

Structure solution of organic crystals by a global fit to the pair distribution function

Martin U. Schmid[1], Dragica Prill[1], Carina Schlesinger[1],

1. Institut fuer Anorganische und Analytische Chemie, Goethe-Univ., Max-von-Laue-Str. 7, 60438 , Frankfurt am Main, Germany

email: m.schmidt@chemie.uni-frankfurt.de

Local structures in crystalline, nanocrystalline and amorphous organic compounds can be investigated using pair distribution functions (PDFs). For organic compounds, the experimental determination of the PDF curves is very similar to that of inorganic compounds. However, the fit of stuructural models to the PDF curve has rarely been done for organic compounds. In our previous research, the method developments for structure determination from PDF of organic compounds were successful with determination of molecular position and orientation starting from random values, and lattice parameters and space group given as an input.[1] For nanocrystalline compounds the space group and lattice parameters are typically unknown. Therefore, we developed a global procedure in which the lattice parameters, space group, molecular position and orientation are determined by a fit to PDF data[2]. The calculations are carried out with TOPAS6[3]. The optimisation initiates with a large set of random starting structures in various space groups. The space groups are chosen according to the space group frequency of the corresponding compound class, regarding the chemical class and the molecular symmetry. The optimisation of lattice parameters starts from random values within the sensible range. The ranges are automatically chosen depending on the size of the investigated molecule and space group in which the calculations are preformed. At the present stage of the development, the molecules are treated as rigid bodies (However, intramolecular degrees of freedom should not be a major problem, given the good functionalities provided by TOPAS). Barbituric Acid and other small organic molecules were chosen as an examples. Synchrotron powder patterns were recorded at the NSLS (Brookhaven, USA) with the wavelength of 0.18 Å. Results of the global fit to the PDF data will be shown.

References:

[1] D. Prill, P. Juhás, S. J. L. Billinge, M. U. Schmidt, Acta Cryst. A , 2015, 72, 62.
[2] D. Prill, C. Schlesinger, M. U. Schmidt, in preparation.
[3] A. A. Coelho, J. Appl. Cryst., 2018, 51, 210.

Keywords: organic compounds, pair distribution function, structure solution