

MS38-O2 Layered and 2D materials: electronic properties and structural instabilities from first principles

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I will present recent work on the understanding of the electronic properties of layered materials and their 2D relatives by means of first principles electronic structure calculations. In particular, I will focus on the correlation between the crystal structure and the electronic properties, with special emphasis on the structural instabilities with an electronic origin. This will be done in connection to recent experimental studies that have been able to demonstrate the presence of charge density waves (CDW) in several 2D materials like NbSe₂ and TiSe₂. I will also discuss the correlation between the electronic structure and the experimental STM images and STS spectra on some of these systems, which provide crucial insight for the understanding of their CDW and superconducting instabilities.

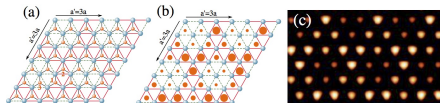


Figure 1. (a) 3x3 CDW structure of single-layer NbSe₂. Blue (orange) balls represent Nb (Se) atoms. (b) Schematic STM image predicted for the 3x3 CDW structure taking only into account the height of the different Se atoms. (c) STM image obtained from first principles.

Keywords: 2D materials, DFT, first principles, charge density waves, structural instabilities, electronic structures, low dimensional solids, surfaces.

MS38-O3 Preferred orientation of Li⁺ diffusion in nano-LiMnPO₄

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Transition metal containing olivine-structured materials, LiMPO₄ (M=Fe, Mn, Co, Ni), are considered to be useful as cathode material for lithium ion batteries. They show an excellent structural stability versus Li⁺ insertion/extraction due to the strong covalent P-O bond¹. Particularly, LiMnPO₄ is attractive because of its high cell voltage (4.1 V vs. Li^{+/}Li), providing 20 % higher energy density than the commercial LiFePO₄. LiMnPO₄ consists of slightly distorted LiO₆ and MnO₆ octahedra and PO₄ tetrahedra (Fig. 1)². LiO₆ octahedra are edge-shared with PO₄ tetrahedra. Since the Li⁺ diffusion occurs along the *b*-axis via edge-sharing LiO₆ octahedra and hence in one preferred orientation of the crystal structure, a morphology control is important to tune the length of the Li⁺ channels in a single particle³. We therefore synthesized various shapes and sizes of nano-LiMnPO₄ (Fig. 2) to examine the preferred direction of the Li⁺ diffusion in single LiMnPO₄ particles. The electron diffraction patterns were indexed using transmission electron microscopy to determine the (hkl)-planes and hence the orientation of the *b*-axis in the nanoparticles. Furthermore, the Li⁺ diffusion coefficients were determined using electrochemical techniques. According to our measurements for each different shape of nano-LiMnPO₄, the Li⁺ diffusion occurs always along the shortest facet dimension in a single nanoparticle. The resulting specific capacity was different depending on the shape of LiMnPO₄ particles although the total specific surface areas were the same. This study helps to design the desired shapes and sizes of LiMnPO₄ for obtaining high energy Li-ion batteries.

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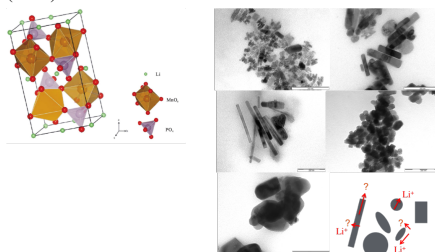


Figure 1. The crystal structure of LiMnPO₄ with Pnma space group. Fig. 2. TEM images show the various shapes and sizes of LiMnPO₄ nanoparticles. The scale bar is 200 nm.

Keywords: Nano-LiMnPO₄, Li⁺ diffusion, crystal structure, lithium ion battery

MS38-O4 X-ray studies on polymers and composites: the combination of 2D WAXS, SAXS and X-ray imaging techniques

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Polymers, elastomers, composites, foams and textiles find their applications in growing industrial markets such as aerospace, automotive, building products, electronics, energy and medicine. While some of these polymer materials are amorphous, a large proportion exhibit local order with regularly arranged chains (crystallite domains) leading to varying amounts of crystallinity and hence can be characterized by X-Ray diffraction techniques. Structural information beside phase identification and quantification can be obtained for the polymer crystallinity, the polymer orientation, the crystalline microstructure and the non-crystalline periodicity and size. Structural variations, such as those induced by e.g. inorganic phases as in composites can be monitored by dynamic studies through in-situ experiments at process conditions (temperature, humidity, mechanical load). Preferred orientation or texturing is a dominant effect in polymers, especially in processed parts. Orientation is also the dominant feature in controlling the mechanical and physical properties of polymers which is of major interest for researchers and manufacturers. For the study of those orientation behaviors, a combination of SAXS and WAXS transmission experiments are conducted using a BRUKER Nanostar and an IPDS-II X-ray machine; both containing a 2D detector.

Investigations have been made for different synthetic polymer fiber and composite systems[1,2]. The figure 1 shows 2D images obtained for a carbon fibre reinforced polymer system with a strong texturing. The evaluation of the WAXS 2 θ range reveals information about the crystal structure parameters and the crystalline domain size (a). In contrast, integrating the azimuth (360° in Φ at 2θ 12.02° for C(002)) gives the possibility to quantify polymer ordering through the determination of peak width (FWHM). SAXS enables the study of nano-particle and nano domain sizes in dependence of their orientation distributions (b). X-ray phase contrast imaging (XPCI) reveals materials voids and cracks (c).

[1] *Polymer*, **55**, 5695-5707 (2014).

[2] *Journal of Polymer Science, Part B: Polymer Physics*, **52**, 496–506 (2014).

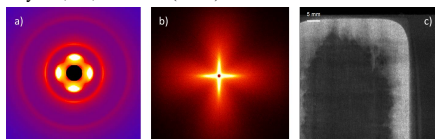


Figure 1. 2D images from WAXS (a), SAXS (b) and X-ray phase contrast imaging (c).

Keywords: SAXS, WAXS, X-ray phase contrast imaging, 2D detection techniques