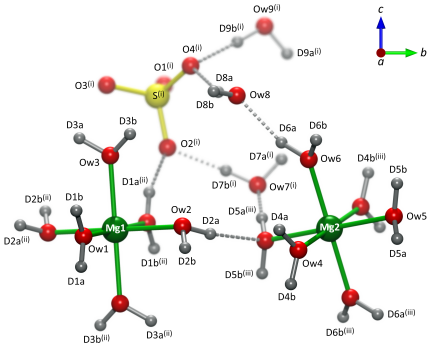

Figure 1. Asymmetric unit of $MgSO_4 \cdot 9D_2O$ as determined by neutron powder diffraction.

Keywords: neutron diffraction, cryohydrate, MgSO4.9H2O, meridianiite, Mars, icy satellites

MS19 Solid state oxygen fuel cell, hydrogen storage & battery materials

Chairs: Bernhard Frick, Kristina Edstroem

MS19-P1 Advanced transmission electron microscopy for Li-ion battery cathodes

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Advanced transmission electron microscopy (TEM) is by far the most suitable and direct tool to view materials down to atomic scale. Recent progress in the electron diffraction methods, related to implication of electron diffraction tomography, and in the aberration-corrected scanning TEM imaging will be illustrated here with the examples of atomic structure investigation on cathode materials for Li-ion batteries. Precession electron diffraction and electron diffraction tomography provide quantitative diffraction data with substantially suppressed dynamical effects, enabling reliable structure solution and refinement. The electron diffraction experiments require very small quantity of material, typically less than 1 μm^3, making this method applicable to virtually all samples extracted from electrochemical cells. Electron diffraction patterns can be taken at a very low electron dose, enabling investigation of the materials sensitive to the electron beam damage, such as polyanion Li-ion battery cathodes, particularly in their charged state. The capabilities of quantitative electron diffraction will be demonstrated using the Li_2CoPO_4F, Li_2FePO_4F and $LiMn_{0.5}Fe_{0.5}PO_4$ cathode materials. Aberration-corrected scanning TEM (STEM) techniques deliver the information on the local structural state with sub-angstrom resolution. High angle annular dark field STEM (HAADF-STEM) imaging provides clear visualization of the cation positions, whereas annular bright field STEM (ABF-STEM) shows the location of the "light" elements, such as O and Li. HAADF-STEM method has been applied to investigate the capacity and voltage fading in the layered rock-salt type oxides, which are determined to large degree by the cumulative local structure changes upon continuous electrochemical cycling. A comparative HAADF-STEM study of the layered oxides in the Li-Ru-Ti-O and Li-Ru-Sn-O systems at different stages (pristine, fully charged, discharged and cycled over different number of times) allowed establishing the cation migration pathways and identifying the cation traps responsible for the degradation of the electrochemical performance. ABF-STEM visualizes changes in the oxygen sublattice upon Li extraction and provides direct observation of O-O peroxo dimers in $Li_{0.5}IrO_3$ and O vacancy formation in $Li_xFe_{0.56}TeO_6$ helping us to establish the fundamental

relation between the anionic redox process and the evolution of the O-O bonding in layered oxides.

Keywords: Li-ion battery, cathode, crystal structure, transmission electron microscopy

MS19-P2 Heterometallic single precursor of oxides for Na-ion battery cathode materials

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After decades of improvements of and investments in the Li-ion battery technology, attention has been shifted toward Na-ion battery, mainly because of sodium's low cost. A lot of different materials are investigated as potential cathode for Na-ion batteries, especially the layered oxides of transition metals, NaT_MO_2 (with T_M = Ti, V, Cr, Mn, Fe, Co, Ni…), which are traditionally synthesized via solid state techniques.

These solid state techniques involve high energy ball-milling of several precursors (usually sodium carbonate and transition metal oxide) followed by calcination at high temperature (800-1000°C) for long reaction times, (8-12 hours) [2]. This long and energy consuming process was required in order to obtain a homogeneous mixing of the precursors. Recently, it was reported that synthesizing heterometallic single precursor can reduce the duration and the calcination temperature due to the pre-organized precursor design [3]. The high temperature phase of lithium cobalt oxide (HT-$LiCoO_2$) was obtained using heterometallic Li-Co alkoxides/aryloxide complexes as precursors [3] at as low temperatures as 350-450°C instead of 600-900°C required for the solid state synthesis [4].

The crystal structure of Na_xCoO_2 (x<1) has octahedral CoO_2 layers and prismatic coordinated sodium ions (Figure 1)[1]. The content of sodium influences the crystal structure and the lattice parameters of the unit cell. In the end, the amount of sodium in the structure also determines the specific capacity of sodium ion batteries.

We synthesized the Na_xCoO_2 starting from heterometallic complexes of sodium and cobalt. The method of heterometallic complexes is also applied to other transitions metals: nickel, iron and manganese. The obtained oxides will be characterized and tested as sodium ion battery cathode materials. We will present our first efforts, results of syntheses and characterizations.

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