

IN SITU XAFS ANALYSIS OF ELECTROCHEMICAL REACTIONS IN RECHARGEABLE LITHIUM BATTERIES

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The electrochemical reaction in a lithium rechargeable battery includes intercalation (charge process) and deintercalation (discharge process) of the lithium ion accompanied by the redox reaction of the transition metals in a cathode material, which often undergoes complex structural transformation. X-ray Absorption Fine Structure (XAFS) is suitable for the analysis of the electrochemical reactions because it affords local structural information of an absorber atom in a powder material of unknown structure. Chemical states and structural changes accompanying the electrochemical Li deintercalation of $\text{Li}_{1-x}(\text{Mn},\text{M})_2\text{O}_4$ (M=Ni,Cr,Co) were revealed by the in situ XAFS technique utilizing an in situ cell composed of a thin film cathode, a liquid electrolyte and a lithium foil anode. XAFS measurements were carried out at BL-10B and 12C, PF, Tsukuba in a transmission mode at various stages of the charge process. XANES analyses of Mn and M as a function of x showed that the origin of the high voltage (ca.5 V) in the rechargeable battery is due to the oxidation of M^{2+} to M^{4+} (in the case of M=Ni) and M^{3+} to M^{4+} (M=Cr,Co), while the origin of the low voltage (3.9-4.3 V) can be ascribed to the oxidation of Mn^{3+} to Mn^{4+} . The EXAFS analysis of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ revealed that Ni^{2+} is oxidized to Ni^{4+} via the Ni^{3+} state with a Jahn-Teller distorted Ni^{3+} -O octahedron. We also report our recent studies on in situ XAFS-XRD analyses of $\text{Li}(\text{Li},\text{Cr},\text{Mn})\text{O}_2$ and Nb_2O_5 cathodes of the lithium batteries.

Keywords: IN SITU ANALYSIS, XAFS, LITHIUM BATTERY

EXTENDED CO-OPERATIVITY IN LI-ION INSERTION/EXTRACTION PROCESSES

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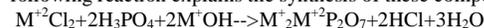
Much effort has been made in our research in Uppsala to understand through single-crystal XRD methods lithium insertion-extraction mechanisms in a number of different cathode materials used in secondary lithium-ion (polymer) batteries. An electrochemical method is used to vary the lithium content of our samples in a reversible manner. Diffraction studies on series of compounds with varying lithium content reveal lithiation induced structural changes. In favorable cases it is also possible to follow the charge redistribution in the materials with deformation electron density studies. A general feature is beginning to emerge; namely, the formation of superlattices during these processes. These can be described as a combination of displacive and compositional modulations of the parent structures. There are examples of both commensurate and incommensurate modulations. Further, the resulting sequences of structural changes and corresponding rearrangements in electron density combine to suggest a high degree of co-operativity in the processes. These ideas will be illustrated for V_6O_{13} and LiMn_2O_4 - and some general conclusions drawn relating to the more precise nature of this co-operativity.

Keywords: Li-BATTERY, SUPERSTRUCTURE, ELECTRON DENSITY

SOFT HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $\text{M}'_2\text{M}''_2\text{P}_2\text{O}_7$ COMPOUNDS

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Studies on the synthesis and structure of NASICON and related compounds were made extensively for obtaining an insight into the relationship of the structure and mechanism of ionic mobility. Here we report a new group of condensed phosphates and discuss their structures, which seem to be good fast ionic conductors. $\text{M}'_2\text{M}''_2\text{P}_2\text{O}_7$ (where $\text{M}'=\text{Na}$ and K ; $\text{M}''=\text{Co}$, Mn and Cu) crystals were synthesized by hydrothermal techniques at 200-250°C and 50-100 bars under the molar ratio. $\text{M}'_2\text{O}:\text{M}''_2\text{O}:\text{P}_2\text{O}_5::3-5:1.5-2.5:10-12$. The following reaction explains the synthesis of these compounds.



Crystallization was initiated by spontaneous nucleation and the rate of nucleation was controlled by gradual rise of temperature. These crystals exhibit vitreous to subvitreous luster having a size of 0.5-3 mm with less twinning.

Structural Characterization: Single crystal X-ray diffraction structural data were collected. The unit cell parameters were obtained using the method of short vectors followed by least squares refinement of 22-28 reflections are as follows: $\text{Na}_2\text{COP}_2\text{O}_7$ a=6.536, b=6.657, c=6.6078 Å, $\alpha=112.61$, $\beta=112.31$, $\gamma=90^\circ$ Triclinic. $\text{Na}_2\text{MnP}_2\text{O}_7$ a=6.714, b=6.5037, c=6.518 Å, $\alpha=92.10$, $\beta=92.14$, $\gamma=83.84^\circ$ Triclinic. $\text{Na}_2\text{CuP}_2\text{O}_7$ a=17.617, c=13.276 Å, $\alpha=\beta=\gamma=90^\circ$, Tetragonal. It can be visualized from the 3-dimensional structures of these compounds that they are ideal for ionic mobility. The ionic conductivity measurements were carried out which confirmed that they exhibit ionic conductivity with values ranging from 10^{-5} to 10^{-3} Ohm cm^2 at 593°K with $E_a=0.63$ to 1.2eV.

Keywords: HYDR THERMAL STRUCTURE IONIC CONDUCTIVITY

TEM INVESTIGATIONS ON MICROCRYSTALLINE SiO_2

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Microcrystalline quartz as agates and flint show a complex microstructure. Heaney and Post [1] revealed, most fine-grained quartz contains a certain amount of moganite, a SiO_2 -modification with a special structure type containing 4-rings of tetrahedra [2]. The investigations focuses on the quartz-moganite system in the microcrystalline fabric varieties chalcedony and quartzine: In contrast to quartzine in chalcedony the transition from quartz to moganite shows disordered zones [3]. The so-called Defocused Dark-Field method (DDF) - is used to get more information about the microstructure of chalcedony. The method offers the possibility to visualize orientational relations in the fabric. A pair of images taken in over- and under-focus, respectively, and viewed as a stereo pair shows the orientation as the third spatial dimension. The application of this method shows that a kind of "fractal" character [4] (self similarity in dimensions 1cm - 0,1 mm - 1000 nm) of some features in the fabric of micro-crystalline quartz is extended to smaller dimensions: in chalcedony crystallites with dimension of 1000 nm are built up of mosaic blocks with 10 nm size. Often twisted crystallites are visible.

References

- [1] P.J. Heaney, J.E. Post, Science 255 (1992) 441-443.
- [2] G. Miehe, H. Graetsch, Eur. J. Minral. 4 (1992) 693-706.
- [3] C. Wahl, G. Miehe, H.Fuess, Contr. Min. (2002) in press.
- [4] P.J. Heaney, A.M. Davis, Science 269 (1995) 1562-1565.

Keywords: MICROCRYSTALLINE QUARTZ, MOGANITE, TEM