PDF Experiments and In-situ Investigations of Li-ion Battery Electrode Materials

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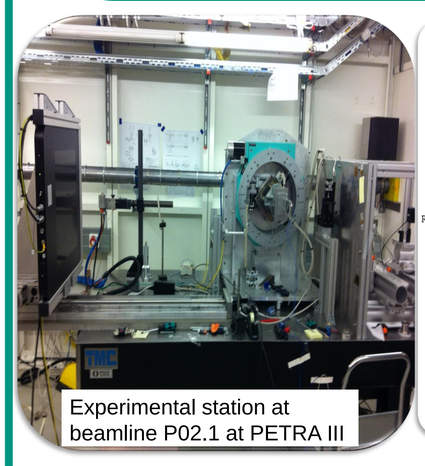
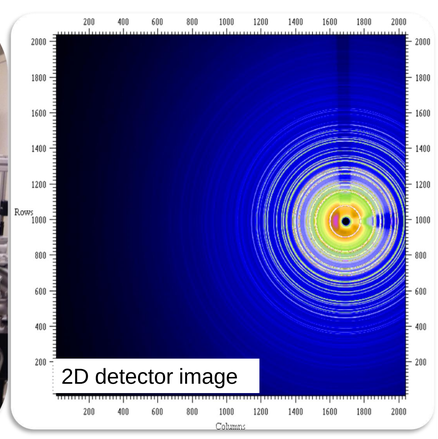
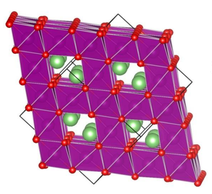
Introduction

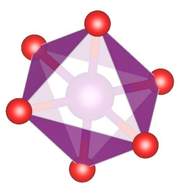
The knowledge about the local arrangement of the atoms in Li-ion battery materials is of central importance since it is correlated to parameters like capacity, rate capability, reversibility and life time. For this purpose the Pair Distribution Function (PDF)/ Total scattering method is used to obtain information about the structural arrangement in *as prepared* materials (*ex situ*) and about the disorder or local ordering that occurs due to (de)intercalation of lithium, which is correlated to degradation and fatigue in Li-ion battery materials. The PDF analysis/Total scattering technique, gives information about the local atomic arrangement in materials as well as the long range (average) structure. It mainly gives the probability of finding any two atoms at given distance "r" and it can be considered as a bond length distribution.

$LiMn_2O_4$ is, in principle, an excellent candidate as cathode material in Li-ion batteries. The theoretical capacity of $LiMn_2O_4$ is 148 mAh/g, corresponding to one Li+ extracted from $LiMn_2O_4$. However, there are some challenges with the material like; Oxygen loss in the structure occurred during synthesis, Mn dissolution in electrolyte etc. There are some possible solutions to overcome some of these problems like partial substitution of anions e.g. oxygen by fluorine. Fluorine substitution can reduce the manganese oxidation state but improve the chemical stability of the spinel. To study the behaviour of these and certainly also of other materials during lithium insertion and extraction, high resolution in situ diffraction is a very powerful tool. Information on the phase behaviour, the reversibility of possibly occurring phase transitions, on changes in the microstructure as well as on the condition of the electrodes at high cycle numbers, can be obtained during cycling with an optimized setup.


Experimental station at beamline P02.1 at PETRA III




Structure of spinel $LiMn_2O_4$

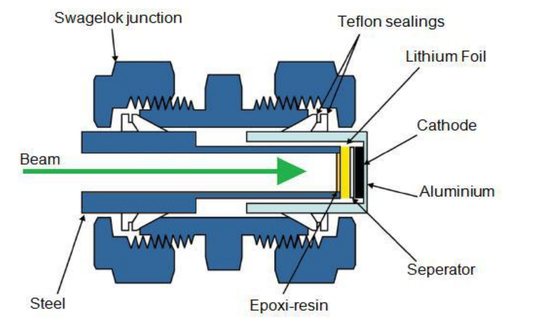


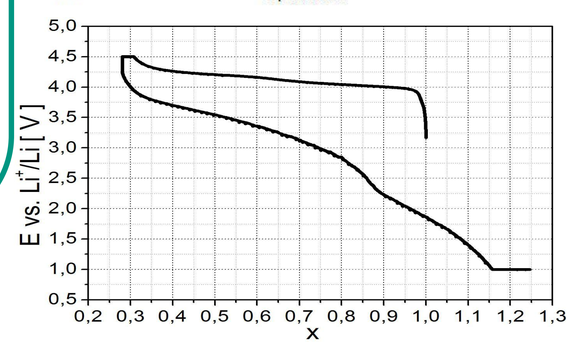
3D network of MnO_6 octahedra

Experimental Details

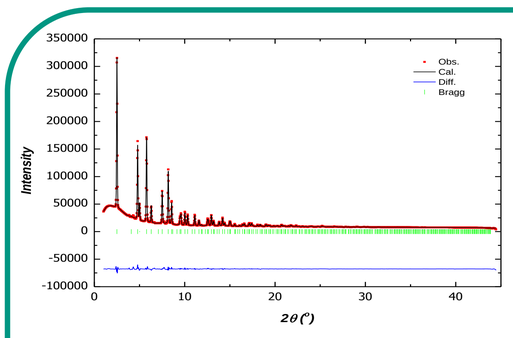
PETRA III
X-ray diffraction experiments were carried out at the High Resolution Powder Diffraction beamline (P02.1) at PETRA-III, DESY, using X-rays with an energy of 60 keV (λ=0.2079 Å). The extended region of the reciprocal space is very important for the PDF analysis. Because of this reason high energy X-rays were used. The 2D diffraction pattern of $LiMn_2O_4$ in a capillary was recorded on the "XRD 1621" flat panel detector (Perkin Elmer) and the sample-detector distance was approximetaly 440mm. The max. Q-value was about 22 $Å^{-1}$.

B2
The diffraction experiments were carried out at beamline B2 at HASYLAB, DESY,using a dedicated sample holder. A wavelength of = 0.6881 A ° (18 keV) was selected by a doublecrystal Si(111) monochromator. With the on-site readable image plate detector (OBI).The cell was cycled in galvanostatic mode with a constant current of I = 0.38 mA. This corresponds to a rate of C/20.

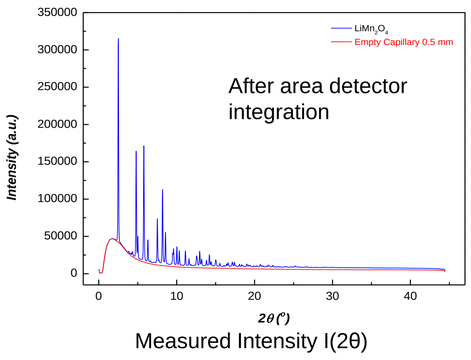




Results



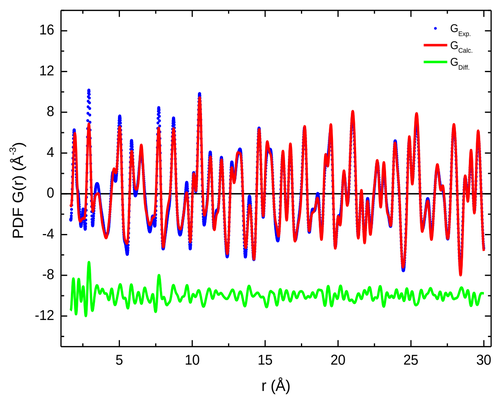
Rietveld refinement results of X-ray diffraction pattern of $LiMn_2O_4$



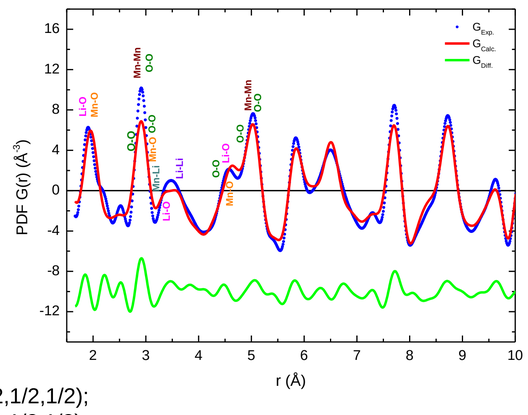
Measured Intensity I(2θ)

Parameter	Rietveld	PDF
a, Å	8.242(2)	8.242(4)
x(O)[a]	0.262	0.262(4)
B(Mn), Å²	0.52635	0.0081(1)
B(Li), Å²	0.39025	0.032
B(O), Å²	1.03836	0.03581
	6.90	16.9(2)

$LiMn_2O_4$

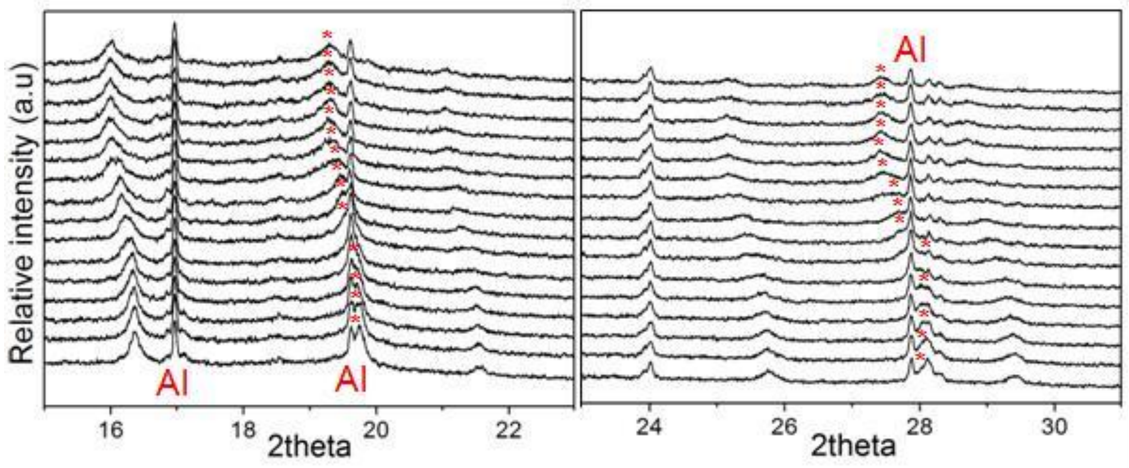


Experimental and the calculated results of PDF Analysis

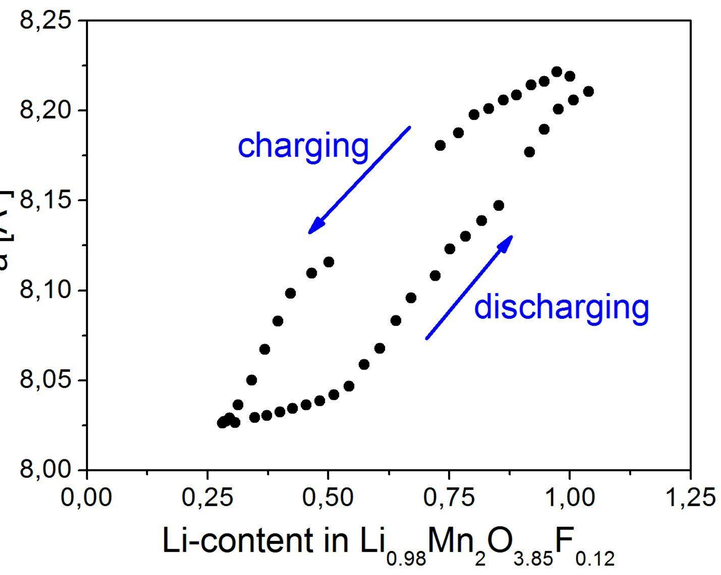


Mn 16d (1/2,1/2,1/2);
Li 8a (1/8,1/8,1/8);
O 32e (x,x,x).
Atomic positions are refined in the space group $Fd\bar{3}m$

$Li_{0.98}Mn_2O_{3.85}F_{0.12}$



In-situ synchrotron diffraction pattern during discharging from 4.5V to 1.7 V.



Conclusion

Rietveld analysis and the Pair Distribution Function technique were applied successfully to investigate the structure of the spinel $LiMn_2O_4$, and the structural parameters determined using both methods are in good agreement. Additionally, using the PDF method the distribution of the bond length was obtained for the $LiMn_2O_4$ material.

All in-situ synchrotron diffraction patterns in the present work could be explained by a reversible single-phase Li extraction/insertion mechanism for $Li_{0.98}Mn_2O_{3.85}F_{0.12}$. This reversibility is concluded from changes of the lattice parameter during Li extraction/insertion. The lattice parameter is practically the same after electrochemical cycling.

References

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