Total Scattering Experiments on Li-ion Battery Electrode Materials

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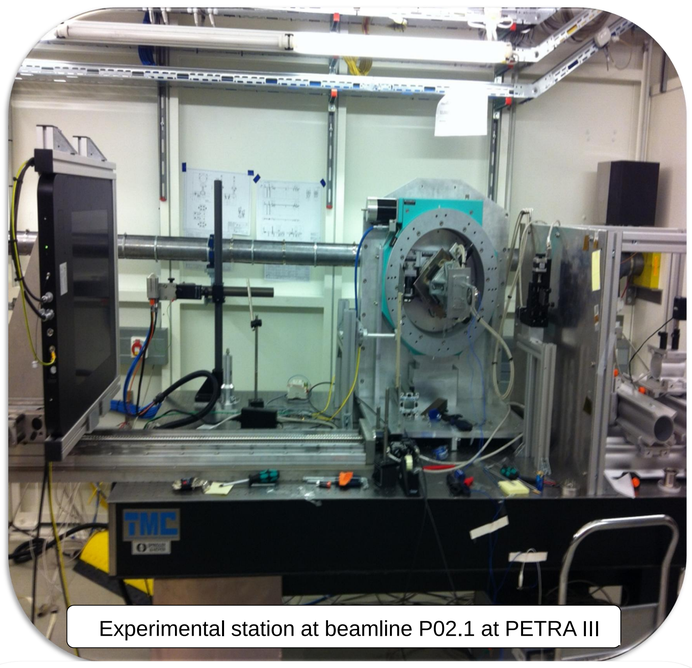
Introduction

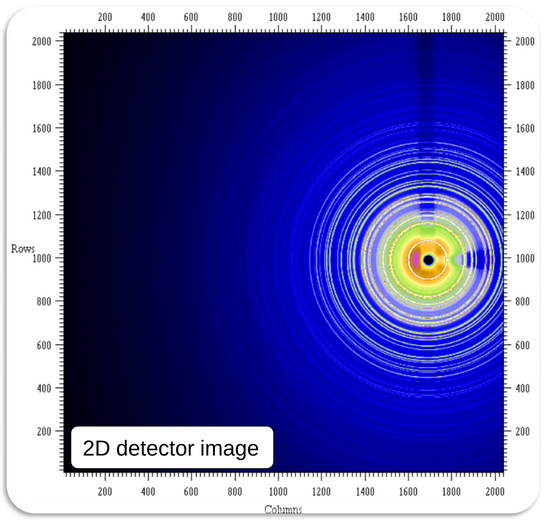
The knowledge about the local arrangement of the atoms in Li-ion battery materials is of central importance since it is correlated to parameters like capacity, rate capability, reversibility and life time. For this purpose the Pair Distribution Function (PDF)/ Total scattering method is used to obtain 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.



Experimental station at beamline P02.1 at PETRA III

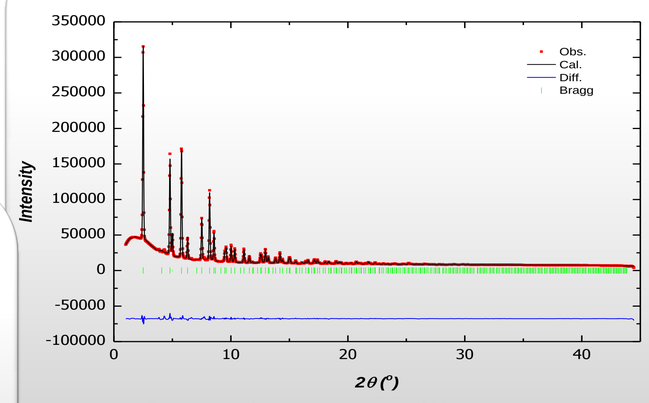
Experimental Details

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 $Å^{-1}$.

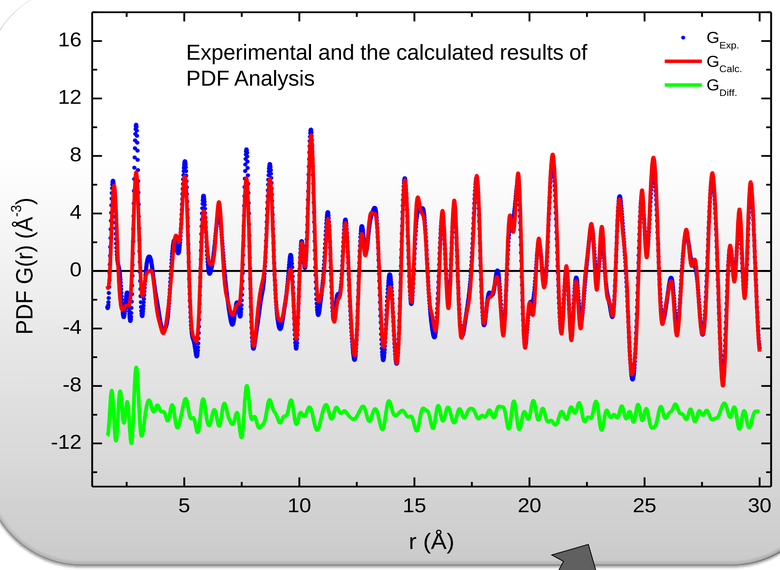


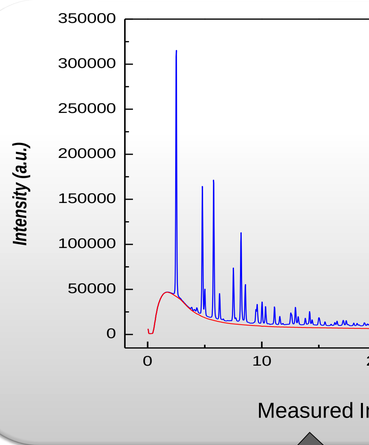
2D detector image

Results

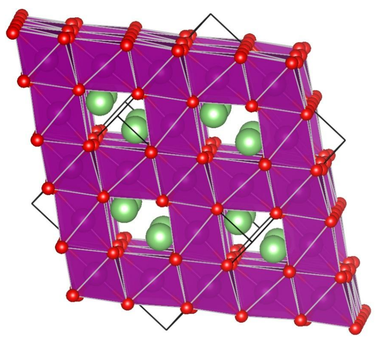


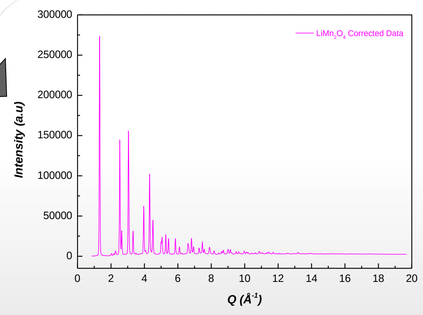
Rietveld refinement results of X-ray diffraction pattern of $LiMn_2O_4$





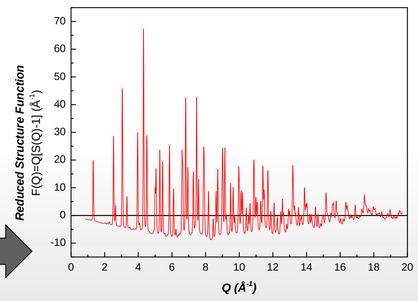
Measured Intensity I(2θ)


Structure of spinel $LiMn_2O_4$ with 3D network of MnO_6 octahedra.



After correction (background, Compton scattering and multiple scattering absorption)

$$Q = \frac{4\pi sin\theta}{\lambda}$$

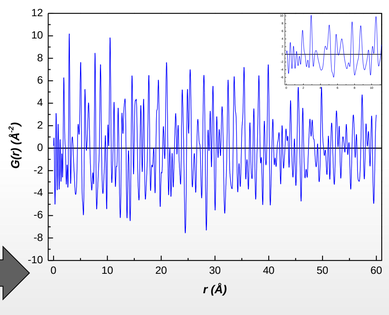


Reduced Structure Function F (Q)

After normalization

$$S(Q) = 1 + \frac{[I^{coh.}(Q) - \sum c_i |f_i(Q)|^2]}{|\sum c_i f_i(Q)|^2}$$

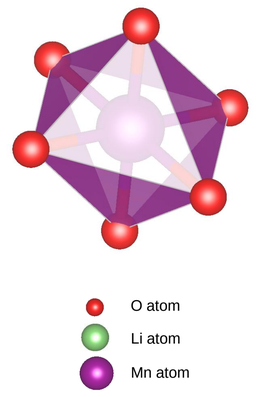
$$F(Q) = Q[S(Q) - 1]$$



Pair Distribution Function G(r)

After Fourier Transform

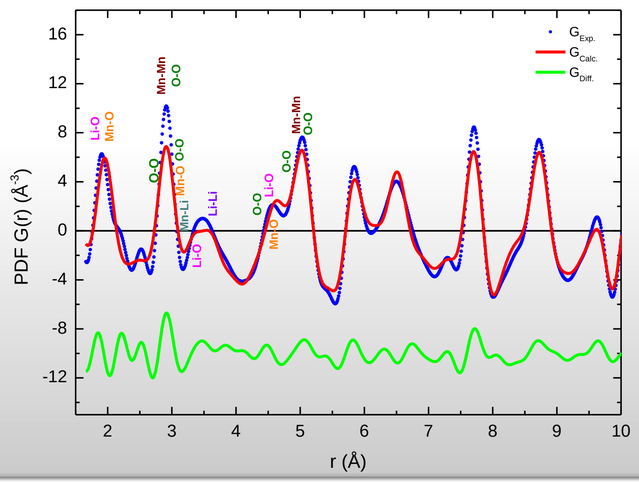
$$G(r) = \frac{2}{\pi}\int_{Qmin}^{Qmax} F(Q)\sin(Qr)dQ$$



3D network of MnO_6 octahedra

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.



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
$R_{wp}(R_G)$, %	6.90	16.9(2)

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 $Fd\bar{3}m$

References

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