In situ PDF Experiments during Electrochemical Cycling of Cathode Materials for Li-ion Batteries

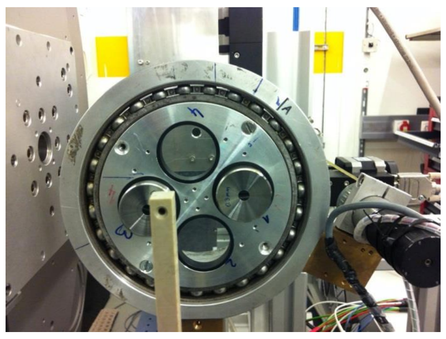
M. Yavuz*[1,2], N. K. Yavuz[2], M. Knapp[1,2], A. Bhaskar[2], K. Nikolowski[1,2], H. Ehrenberg[1,2]
[1]Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage,
[2]Institute for Applied Materials-Energy Storage Systems (IAM-ESS),
Karlsruhe Institute of Technology (KIT), Herman-von-Helmholtz Platz 1,
76344 Eggenstein-Leopoldshafen, Germany

Introduction

The Pair Distribution Function (PDF)/ Total scattering method is used to obtain information about the structural arrangement 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.

In situ investigations are of crucial importance to elucidate the processes during charging and discharging, because ex-situ studies can give unsatisfying or even misleading information due to relaxation phenomena [1,2]. The aim of this research is to show the applicability of *in situ* PDF measurements on a standard $LiMn_2O_4$ spinel, which is an excellent candidate as cathode material in Li-ion batteries, during electrochemical cycling.

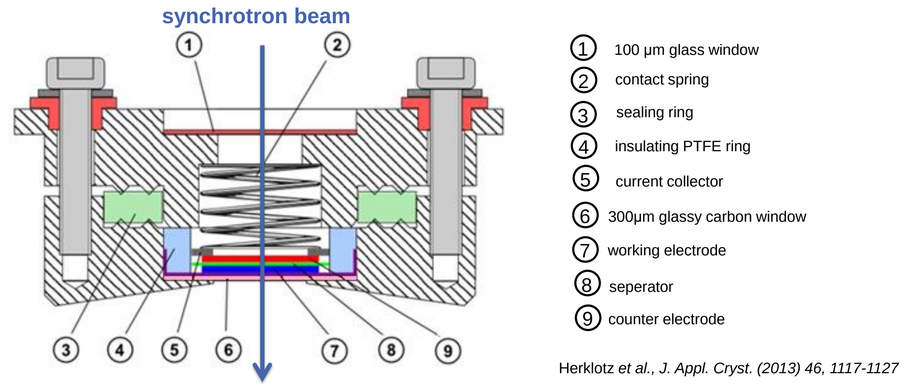
Experimental Details



***In situ* cell holder**

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=0.20726 Å). The 2D diffraction patterns of $LiMn_2O_4$ sample in an *in situ* cell are recorded on a flat panel detector (Perkin Elmer). The sample-detector distance was approximately 400mm. The max. Q-value was about 24 $Å^{-1}$.

Overview of insitu cell



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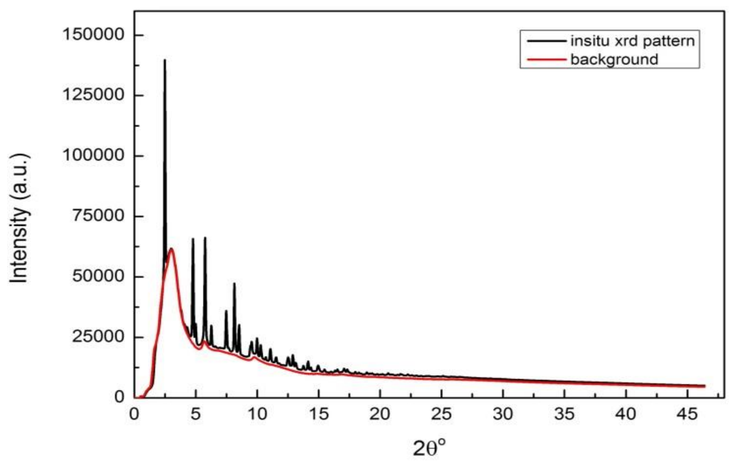
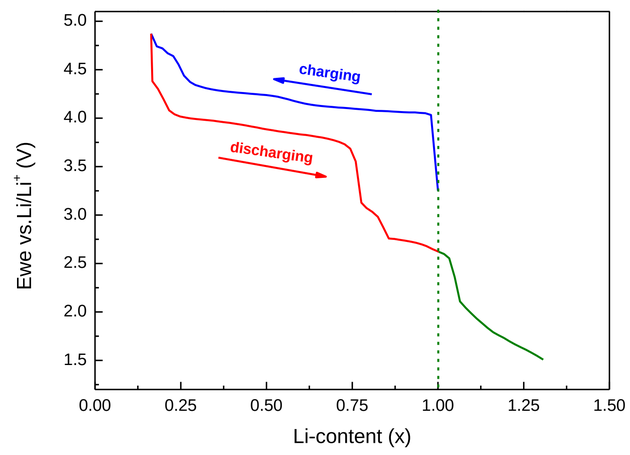
Results

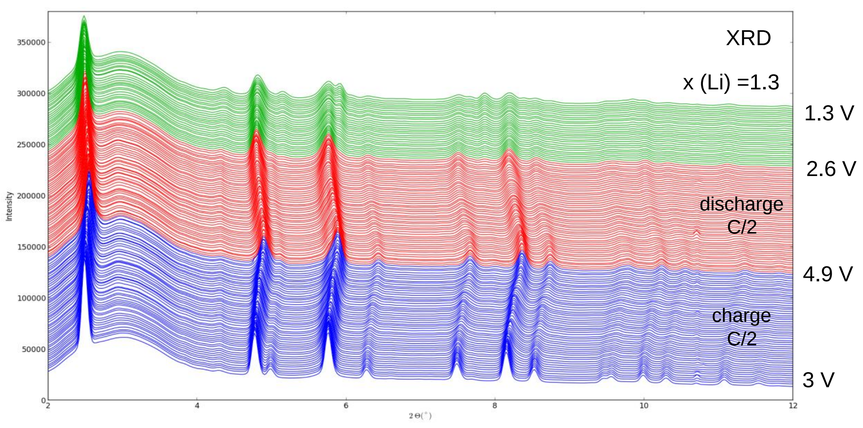


XRD pattern of *in situ* $LiMn_2O_4$ and background

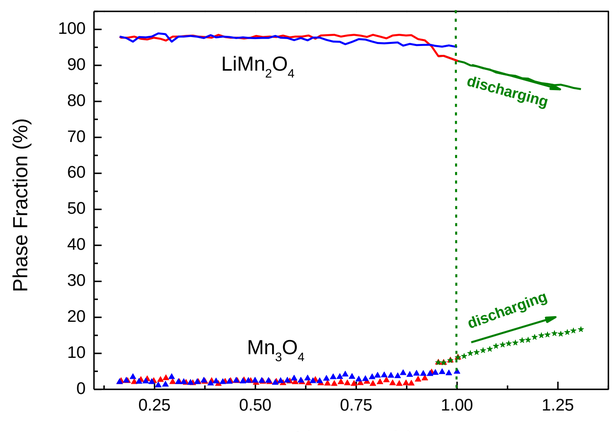
Background ;
-300µm glassy carbon window
-seperators (whatman glass microfibre)
-electrolyte (1M $LiPF_6$ in EC:DMC 1:1)
-lithium foil
-100 µm glass window



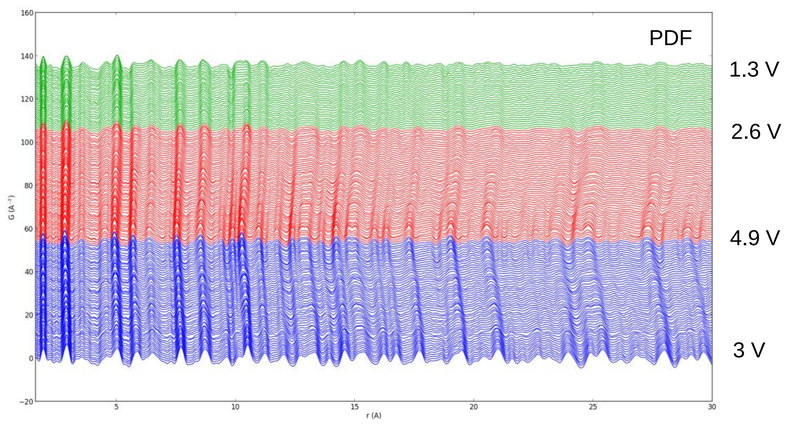
Voltage vs. Li-content of $LiMn_2O_4$



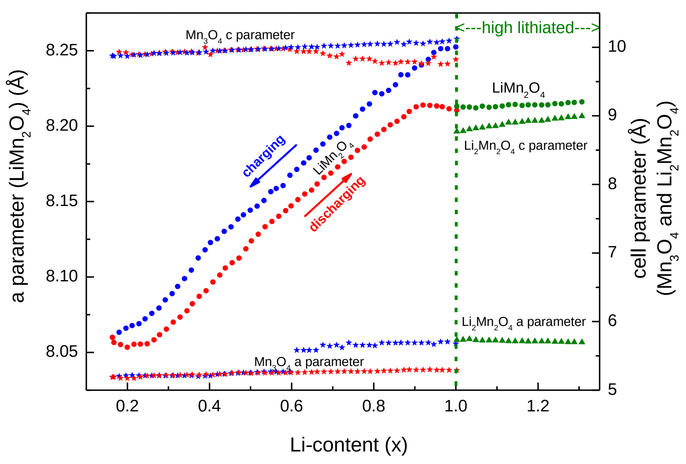
XRD patterns of *in situ* $LiMn_2O_4$ during electrochemical cycling



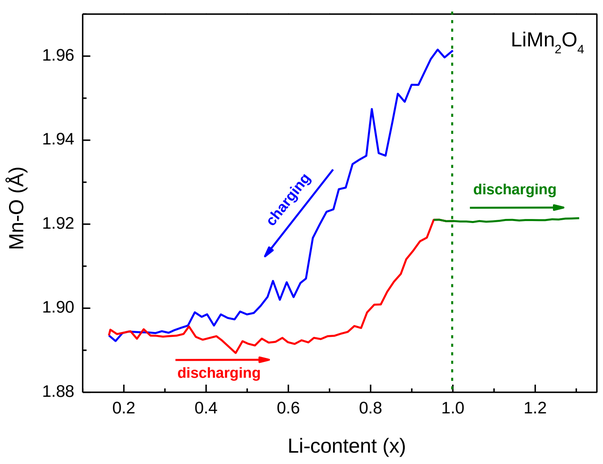
Phase Fraction vs. Li-content



PDFs of *in situ* $LiMn_2O_4$ during electrochemical cycling



Cell parameters vs. Li-content



Mn-O distances vs. Li-content

Conclusion

- It is possible to subtract the background/container from XRD pattern.
- For PDF refinements, Li-contents (x) were obtained from electrochemical measurements.
- In situ PDF analysis during electrochemcial cycling gives the details about structural and chemical transformations.
- All refinements were implemented with cubic main phase and tetragonal impurity phase.
- Refinement of selected parameters with symmetry constraints.

References

[1] C. Baehtz, Th. Buhrmester, N.N. Bramnik, K. Nikolowski, H. Ehrenberg, Solid State Ionics 176 (2005) 1647 – 1652.
[2] M. M. Thackeray, Prog. Solid State Chem. 25 (1997) 1-71.
*murat.yavuz@kit.edu