Influence of the synthesis route of $Li(Ni,Mn)_2O_4$ on the structure measured by XRD

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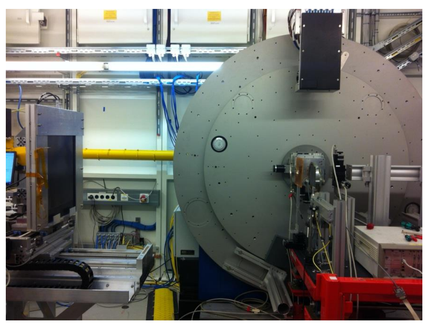
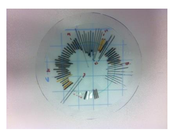
Introduction

The spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode shows impressive electrochemical performance like large reversible capacity at high operating voltage around 4.7 V which makes it a promising and suitable cathode material for high power battery applications [1]. These good properties require the knowledge about the local arrangement of the atoms in the spinel which is correlated to parameters like capacity, rate capability, reversibility and life time. Using nitrates as precursors, the spinel $LiNi_{0.5}Mn_{1.5}O_4$ has been synthesized with sol-gel technique at different annealing temperatures. The effect of temperature on the structure of the material has been studied with pair distribution function (PDF) analysis.

Experimental Details



Experimental Setup at Petra III (P02.1)



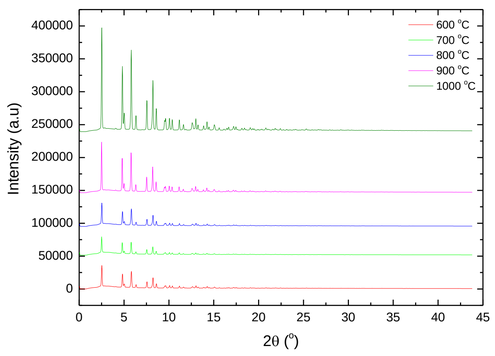
Capillary holder

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=0.2079 Å). The 2D diffraction patterns of $LiNi_{0.5}Mn_{1.5}O_4$ samples in a kapton capillary (0.0403") were recorded on the "XRD 1621" flat panel detector (Perkin Elmer) and the sample-detector distance was approximately 400mm. The max. Q-value was about 23 $Å^{-1}$.

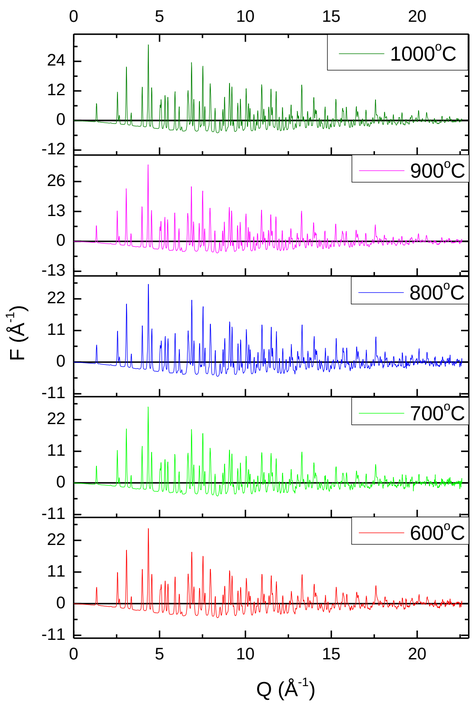
Sample Preparation

The $LiNi_{0.5}Mn_{1.5}O_4$ samples were synthesized by a citric acid-assisted sol-gel method. Metal nitrate precursors were dissolved in a citric acid and Ethylene glycol (1:4) mixture by heating at 90°C. Later the solution was heated up to 180°C to evaporate the excess ethylene glycol from the mixture. The obtained gel was precalcined at 450°C for 12 h to remove the carbon. The precursor is then annealed at different temperatures for 12 h to get the final sample.

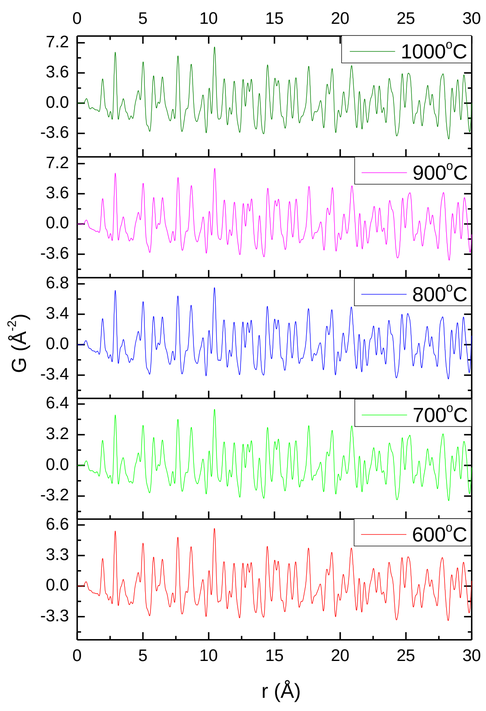
Results



The X-ray diffraction patterns of $LiNi_{0.5}Mn_{1.5}O_2$ at different reannealed temperatures

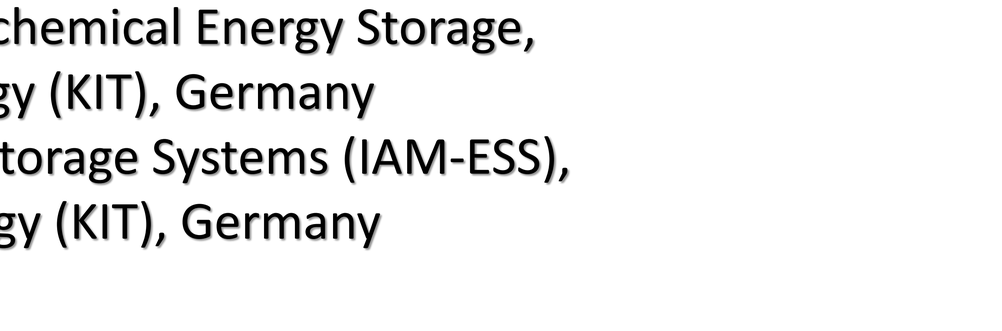


Reduced total scattering structure functions, F(Q), for $LiNi_{0.5}Mn_{1.5}O_4$ samples at different reannealed temperatures.

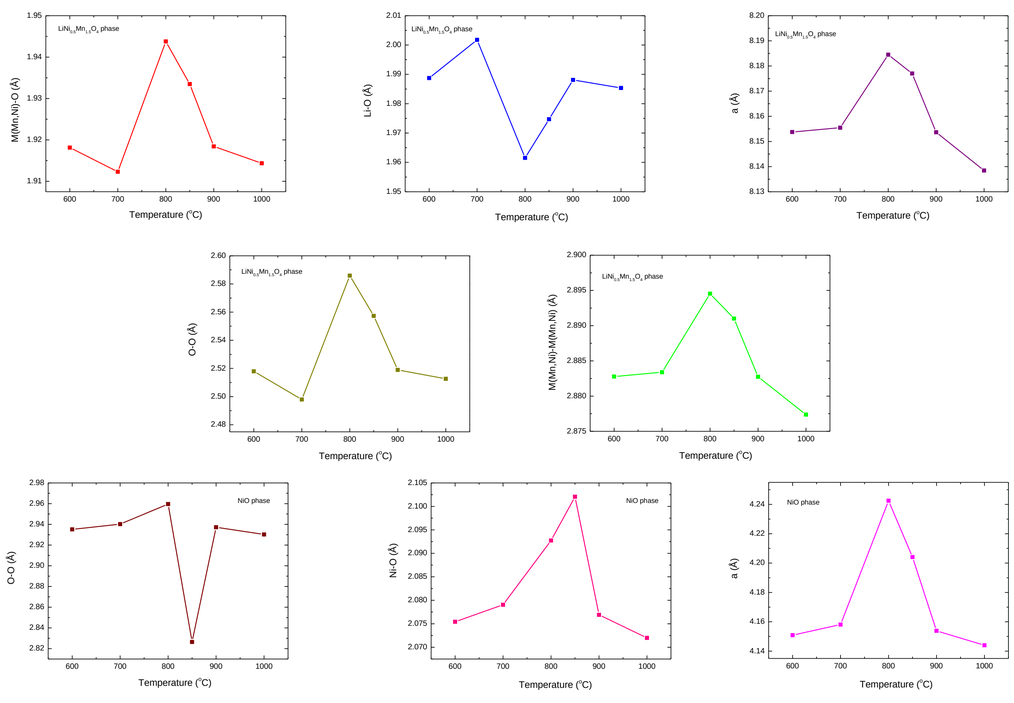


Experimental PDFs of $LiNi_{0.5}Mn_{1.5}O_4$ samples at different reannealed temperatures.

SEM images of $LiNi_{0.5}Mn_{1.5}O_4$ samples at different reannealed temperatures.



PDF refinements of $LiNi_{0.5}Mn_{1.5}O_4$ samples with two phases at different reannealed temperatures.



PDF refinement results of $LiNi_{0.5}Mn_{1.5}O_4$ ($Fd\bar{3}m$) and impurity phase NiO ($Fd\bar{3}m$)

Conclusion

The $LiNi_{0.5}Mn_{1.5}O_4$ samples have two phases, $Fd\bar{3}m$ (main phase) and $Fm\bar{3}m$ (NiO impurity phase). To achieve a high degree of crystallinity and high capacity, samples are reannealed at different temperature for 12 h. High temperature leads to oxygen deficiency in manganese-based spinels, which comes along with an increasing amount of Mn^{3+} and increasing cell parameter, because the ionic radius of Mn^{3+} is larger (0.645 Å in the high spin state) than Mn^{4+} (0.53 Å) and Li^+ (0.59 Å in tetrahedral coordination) [2]. The 800°C sample shows a step in the atomic distances according to PDF analysis, because of the increased amount of Mn^{3+}. We have changed the synthesis routes on the account of the increased Mn^{3+} because this leads to a decrease in the electrochemical capacity.

References

[1] Aiswarya Bhaskar, Natalia N. Bramnik, Anatoliy Senyshyn,Hartmut Fuess, Helmut Ehrenberg, Synthesis, Characterization, and Comparison of Electrochemical Properties of $LiM_{0.5}Mn_{1.5}O_4$ (M = Fe, Co, Ni) at Different Temperatures, Journal of The Electrochemical Society, 157 (6) , A689-A695, 2010
[2] A. A. Andriiko, A. Ye. Shpak, Y. O. Andriyko, J. R. Garcia, S. A. Khainakov, N. Y. Vlasenko, Formation of spinel structured compounds in the lithium permanganate thermal decomposition, J. Solid State Electrochem, 16:1993-1998, 2012.

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