Karlsruhe Institute of Technology

IAM Institute for Applied Materials
Energy Storage Systems (ESS)

DESY

USER MEETING
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Investigation of transition metal doping effect on $LiNi_{0.5-x}Mn_{1.5}O_4$ spinel cathode by in-situ XRD studies during electrochemical cycling

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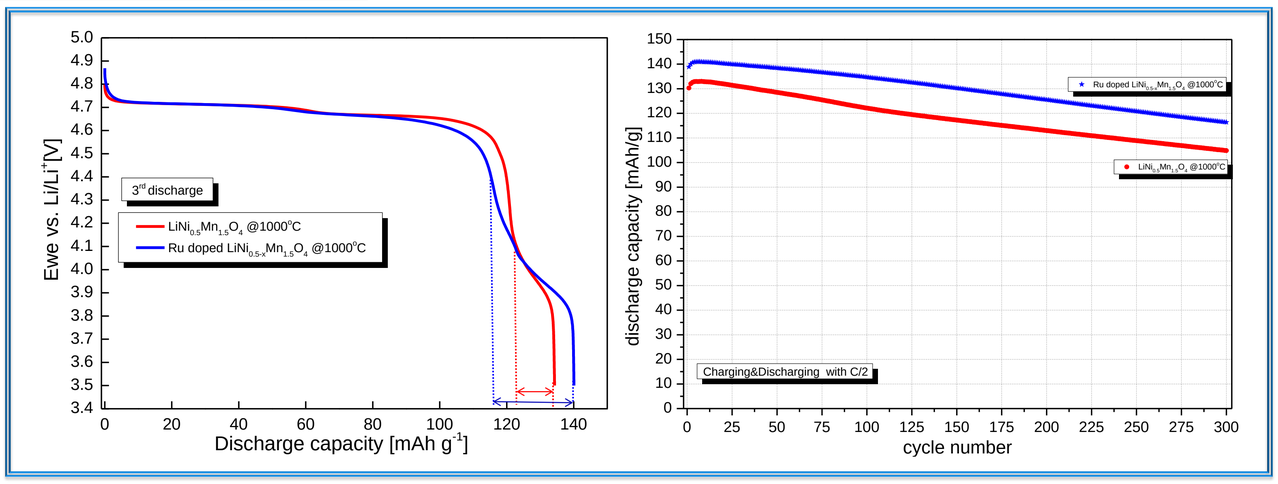
INTRODUCTION

The spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode shows impressive electrochemical performance like large reversible capacity at a high operating voltage around 4.7 V which makes it a promising and suitable cathode material for high energy battery applications [1]. But $LiNi_{0.5}Mn_{1.5}O_4$ cathode and its derivatives are suffering from some problems like self-discharging phenomena. Because of this reason, *ex situ* XRD experiments are not suitable to study the structural changes of these materials at different voltages. Therefore, it is essential to do in situ studies under real operation conditions to fully understand the structural changes at different voltage ranges. The in-situ cell consists of a stack of cathode, anode, separator, current collectors, electrolyte, and glass windows (total thickness is a few mm). Therefore, this set up requires a high energy x-ray beam to be able to penetrate the whole system and also an x-ray source with high brilliance as well as high angular and energy resolution in order to reliably perform Rietveld refinement or Pair Distribution Function (PDF) analysis on the data (especially to resolve the complex diffraction patterns due to e.g. overlapping reflections from different crystallographic phases, possible superstructure reflections and low symmetry materials). Synchrotron radiation offers these preconditions for good data analysis. Moreover, the XRD experiment is performed during electrochemical reaction (*in-situ*), therefore a reasonably fast acquisition time is necessary to observe e.g. phase evolution. Using a synchrotron source, the acquisition time to measure a reliable diffraction pattern is less than 10 minutes compared to 6 – 10 hours using a laboratory diffractometer.

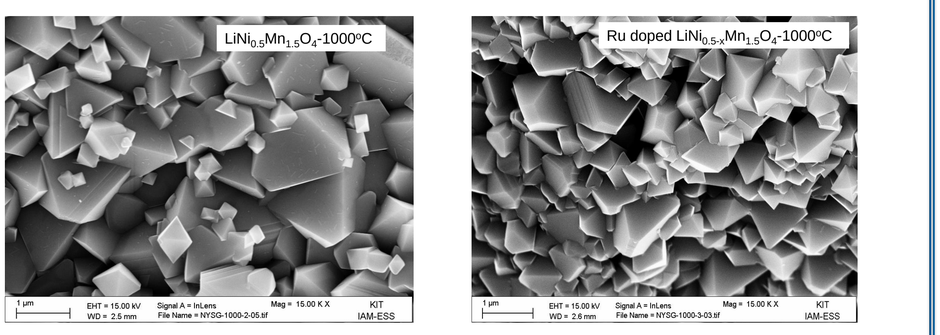
RESULTS

Electrochemical Performances



→ ***Even though Ru doped $LiNi_{0.5-x}Mn_{1.5}O_4$ @1000°C (blue curve) has larger 4V electrochemical activity than $LiNi_{0.5}Mn_{1.5}O_4$ @ 1000°C (red curve) which corresponds to the Mn^{3+}/Mn^{4+}electrochemical reaction, it has better capacity and cycling stability.***

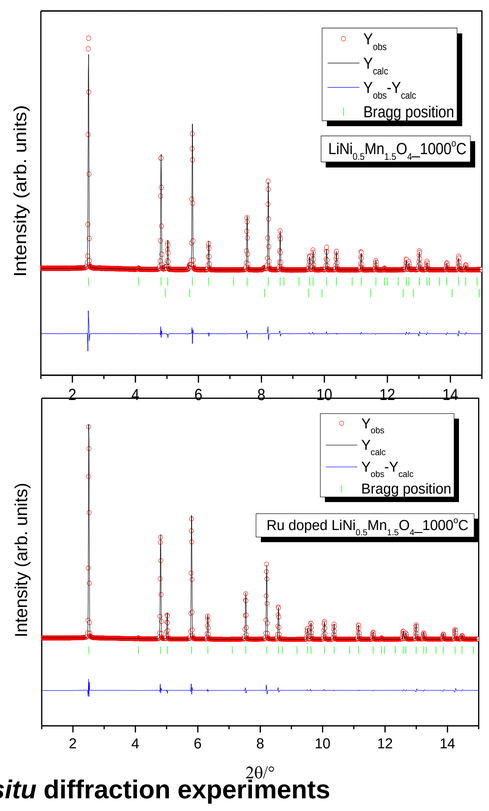
SEM images



→ ***The particles are well shaped and they have high crystallinity for both materials ($LiNi_{0.5}Mn_{1.5}O_4$ and Ru doped $LiNi_{0.5-x}Mn_{1.5}O_4$) synthesized at 1000°C***

***X-Ray Diffraction* :** *Ex situ* and *in situ* X-ray diffraction experiments were carried out at the High Resolution Powder Diffraction beamline (P02.1) at PETRA-III, DESY, using synchrotron radiation with an energy of 60 keV (λ=0.207260 Å)

Rietveld Refinement

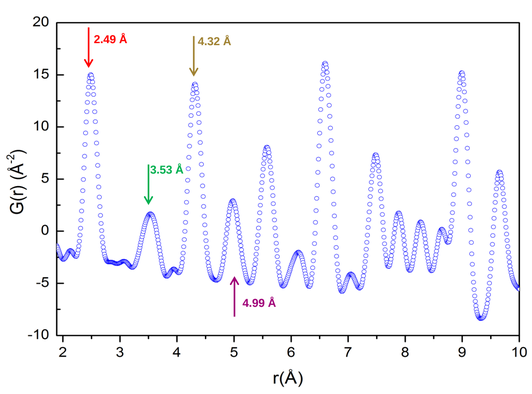


a = 8.1789(1)Å
~5% $Li_xNi_{1-x}O$

→ ***The impurity phase ($Li_xNi_{1-x}O$) vanishes after Ru-doping on $LiNi_{0.5-x}Mn_{1.5}O_4$***

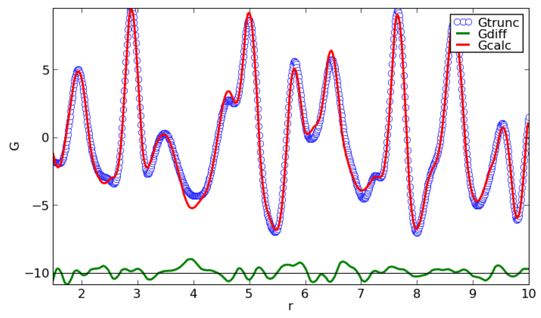
a = 8.18885(4) Å

Pair Distribution Function Analysis (PDF)



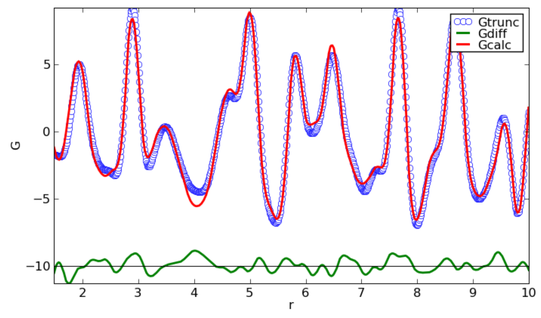
***Pair Distribution Function (PDF)* gives the probability of finding any two atoms separated by a distance r.**

→PDF peak position gives bond lengths directly
→Intensities of PDF peaks yield coordination numbers
→The PDF peak width gives information about atomic vibrations and disorder



$LiNi_{0.5}Mn_{1.5}O_4$ main phase : %91.5
$Li_{1-x}Ni_xO$ impurity : %8.5
Rwp: %8.9

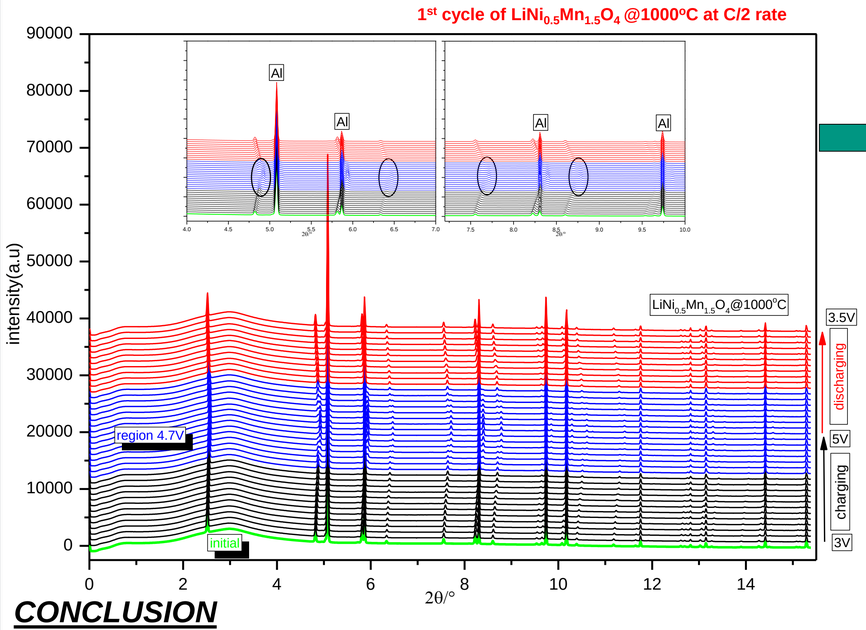
	$LiNi_{0.5}Mn_{1.5}O_4$		*Ru-doped $LiNi_{0.5-x}Mn_{1.5}O_4$*	
	PDF	**Rietveld**	**PDF**	**Rietveld**
a (Å)	8.172	8.179	8.196	8.189
Metal-O (Å)	1.943	1.943	1.961	1.945



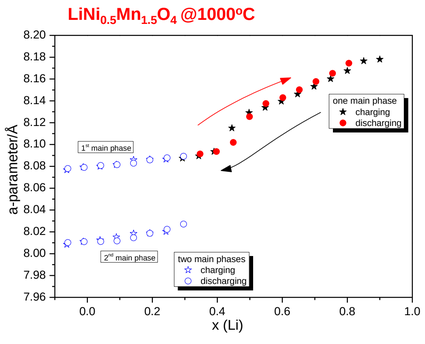
Ru-doped $LiNi_{0.5-x}Mn_{1.5}O_4$ main phase
Rwp: %10.9

In situ diffraction experiments

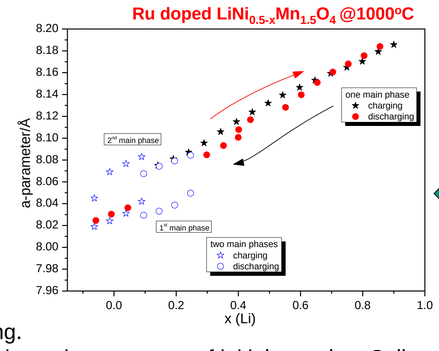
1st cycle of $LiNi_{0.5}Mn_{1.5}O_4$ @1000°C at C/2 rate



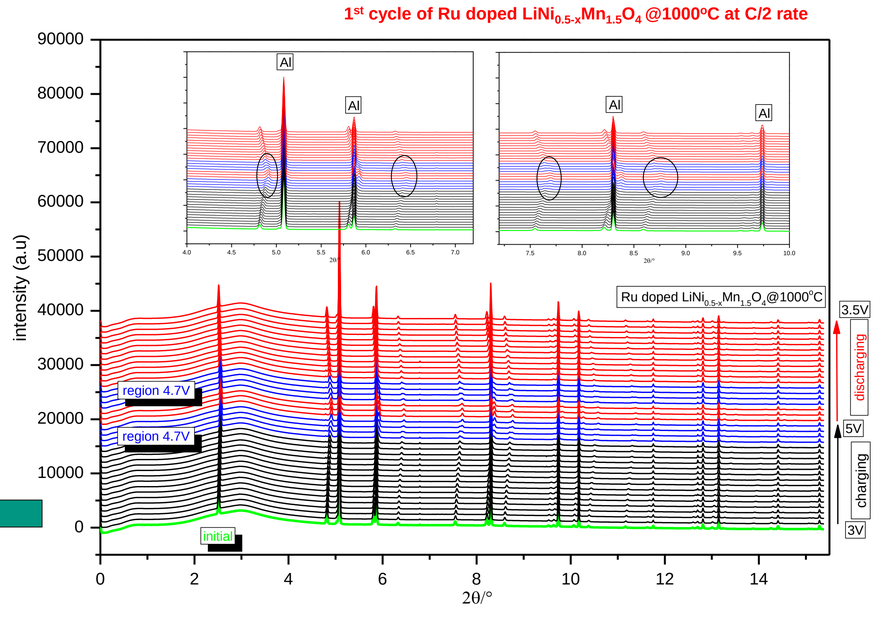
$LiNi_{0.5}Mn_{1.5}O_4$ @1000°C



Ru doped $LiNi_{0.5-x}Mn_{1.5}O_4$ @1000°C



1st cycle of Ru doped $LiNi_{0.5-x}Mn_{1.5}O_4$ @1000°C at C/2 rate



CONCLUSION

- $LiNi_{0.5}Mn_{1.5}O_4$ contains small amounts of $Li_xNi_{1-x}O_4$ impurity which has been vanished after Ru-doping.
- Rietveld refinement (average) and Pair Distribution Function (local) technique were applied to investigate the structures of initial samples. Cell parameters and metal-oxygen distances increased with Ru^{+4} (0.62 Å) doping because of the higher amount of Mn^{+3} (0.645 Å).
- An intermediate phase (2nd main phase ($Fd\bar{3}m$)) appears at ~4.7 V for both materials, on both charging & discharging processes where Ni^{2+}/ Ni^{4+} electrochemical reaction takes place [1].

References

[1] A. Bhaskar, N. N. Bramnik, A. Senyshyn, H. Fuess, H. Ehrenberg, *J. Electrochem. Soc.*, 157 (6), A689-A695, 2010