

Investigation of transition metal doping effect on $\text{LiNi}_{0.5-x}\text{Mn}_{1.5}\text{O}_4$ spinel cathode by in-situ XRD studies during electrochemical cycling

Nilüfer Kızıltaş-Yavuz^[a], Aiswarya Bhaskar^[a], Murat Yavuz^[a, b], Michael Knapp^[a, b], Helmut Ehrenberg^[a, b]

^[a]Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)-Energy Storage Systems (ESS)

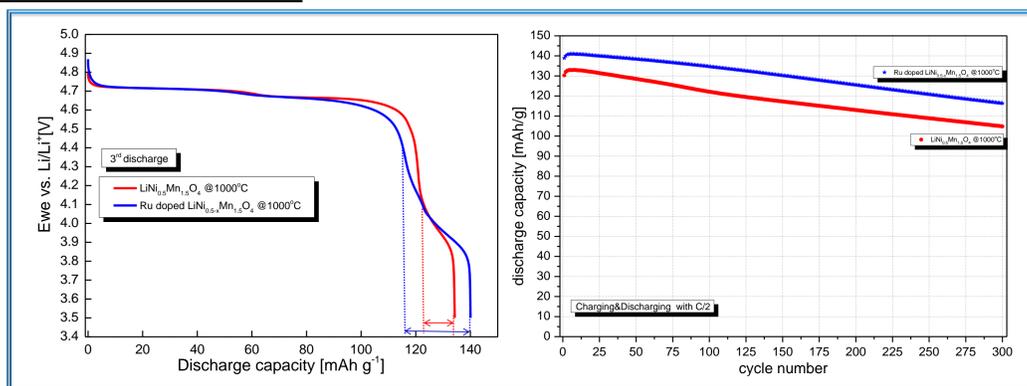
^[b]Helmholtz Institute of Ulm (HIU) Electrochemical Energy Storage, Karlsruhe Institute of Technology (KIT),
Herman-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

INTRODUCTION

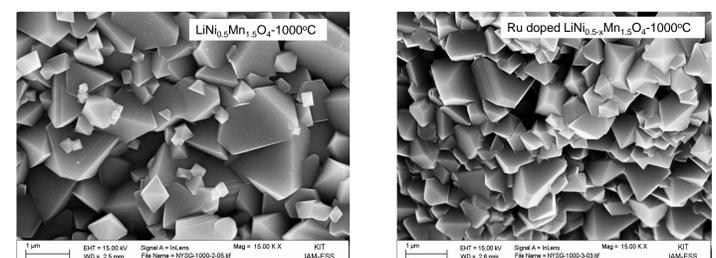
The spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode shows impressive electrochemical performance like large reversible capacity at a high operating voltage around 4.7 V which makes it a promising and suitable cathode material for high energy battery applications [1]. But $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 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



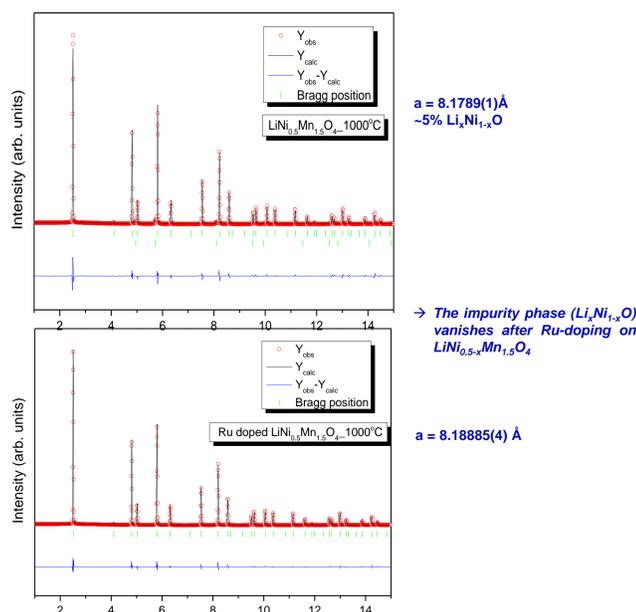
SEM images



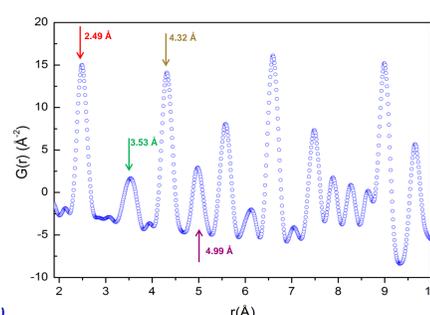
→ The particles are well shaped and they have high crystallinity for both materials ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Ru doped $\text{LiNi}_{0.5-x}\text{Mn}_{1.5}\text{O}_4$) synthesized at 1000°C

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 ($\lambda = 0.207260 \text{ \AA}$)

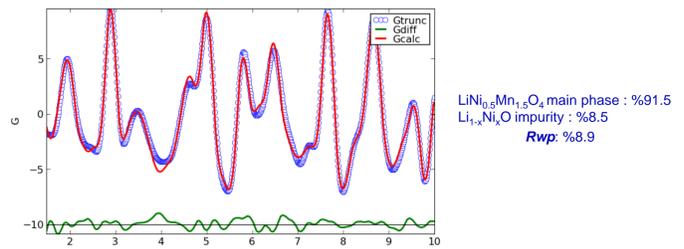
Rietveld Refinement



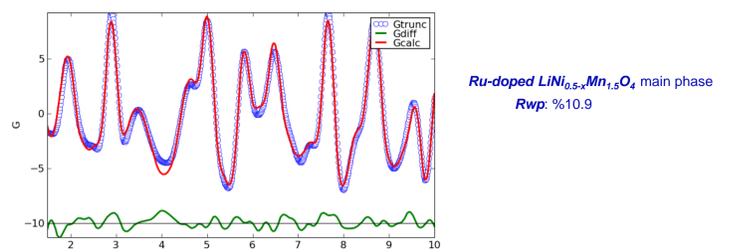
Pair Distribution Function Analysis (PDF)



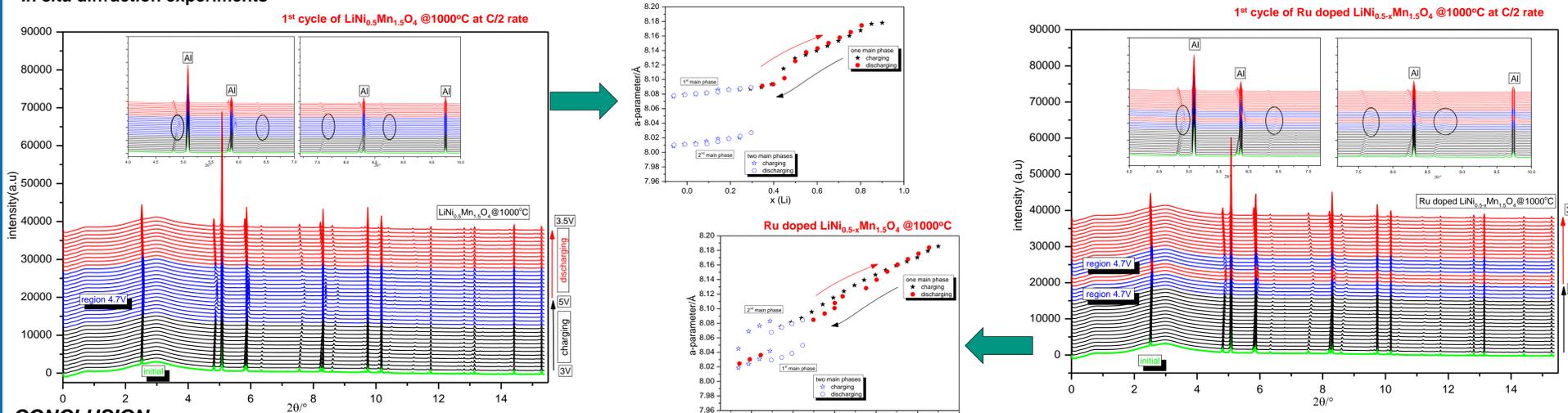
→ PDF peak position gives bond lengths directly
→ Intensities of PDF peaks yield coordination numbers
→ The PDF peak width gives information about atomic vibrations and disorder



| | $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ | | Ru-doped $\text{LiNi}_{0.5-x}\text{Mn}_{1.5}\text{O}_4$ | |
|-------------|--|----------|---|----------|
| | 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 |



In situ diffraction experiments



CONCLUSION

- LiNi_{0.5}Mn_{1.5}O₄ contains small amounts of Li_xNi_{1-x}O₄ 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 Ru⁴⁺ (0.62 Å) doping because of the higher amount of Mn³⁺ (0.645 Å).
- An intermediate phase (2nd main phase (*Fd3m*)) appears at ~4.7 V for both materials, on both charging & discharging processes where Ni²⁺/Ni⁴⁺ 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