

Comparison of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5-2x}\text{Ru}_x\text{Mn}_{1.5}\text{O}_4$ Spinel Materials as High Voltage Cathodes for Lithium-ion Batteries

Nilüfer Kızıltaş Yavuz^[a], Aiswarya Bhaskar^[a], Murat Yavuz^[a, b], Kristian Nikolowski^[a, b], Peter Jakes^[c],
Rüdiger-A. Eichel^[c], 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

^[c]Forschungszentrum Jülich, Institute of Energy and Climate Research, Fundamental Electrochemistry (IEK-9)
Wilhelm-Johnen Straße, D-52425 Jülich, 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]. Moreover, in this material all the Mn ions are expected to be in its tetravalent form. Nevertheless, electrochemical performance at high rates still needs to be improved to meet the required power density [1-2]. In the ideal $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel, no Mn ions exist in its trivalent state, which is well-known as Jahn-Teller ion causing structural instability. However, usually a small amount of Mn^{3+} remains in the compound as a result of oxygen deficiency after the high temperature synthesis process [3]. It has been reported that the 4d orbitals with a larger radius of the second row transition metal ions (e.g. Ru^{4+}) overlapping with the 2p orbitals of oxygen favors wider conduction bands leading to better electrical conductivity [4]. Also the ionic radii of Ru^{4+} (0.62 Å) and Ni^{2+} (0.69 Å) are similar which allows the Ru^{4+} cation to substitute Ni^{2+} . It has been reported that the doping of Ru improves the rate capability and also the high-rate cycling stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [2, 5]. In the present work, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Ru-doped $\text{LiNi}_{0.5-2x}\text{Ru}_x\text{Mn}_{1.5}\text{O}_4$ ($x=0.05$), synthesized via Pechini method using metal acetate precursors have been investigated.

Experimental Details

Synthesis:

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.4}\text{Ru}_{0.05}\text{Mn}_{1.5}\text{O}_4$ materials were synthesized by citric acid-assisted sol-gel method. Metal acetate 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 400°C for 5 h to remove the carbon. The precursor is then preannealed at 600°C for 24h and post annealed at 800°C and 1000°C to get the final products.

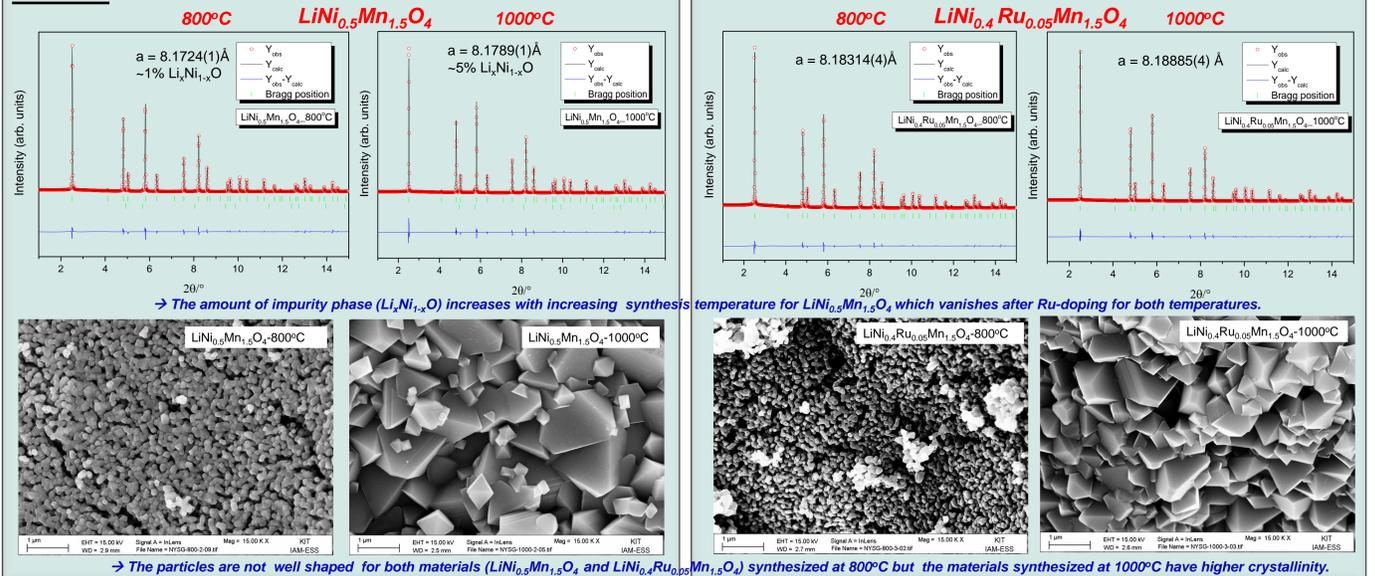
Characterization:

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 ($\lambda=0.207260$ Å). The morphology of the particles was studied with Zeiss Supra 55 SEM (Scanning Electron Microscope) with primary energy of 15 keV and in-lens detector.

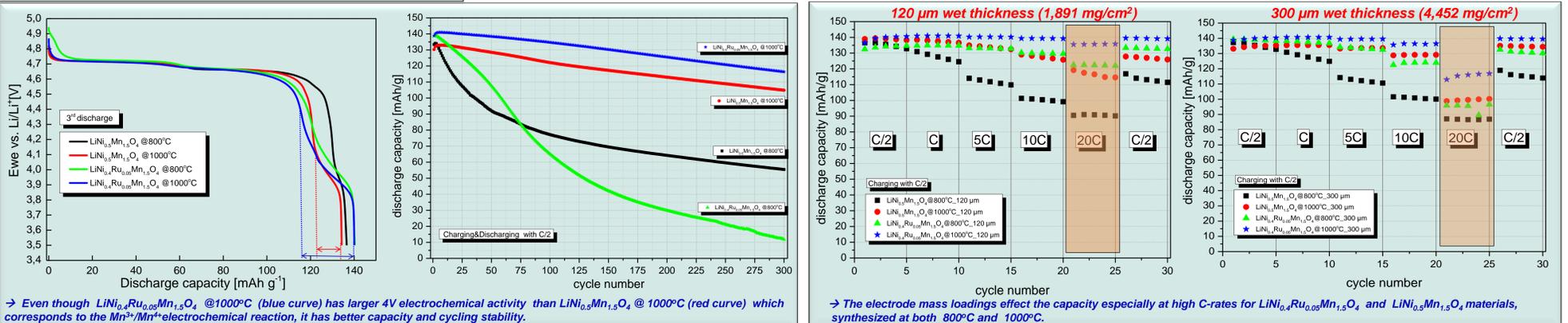
Electrochemical Experiments:

The cathode mixture was prepared by mixing 80% (w/w) of the active material with 10% (w/w) of Super C 65 carbon (TIMCAL) and 10% (w/w) of polyvinylidene fluoride (PVdF) binder. The mixture was coated on Aluminium foil, dried, punched out and pressed to obtain electrodes of 1.2 cm diameter. The obtained electrodes were electrochemically characterized with a VMP3 potentiostat.

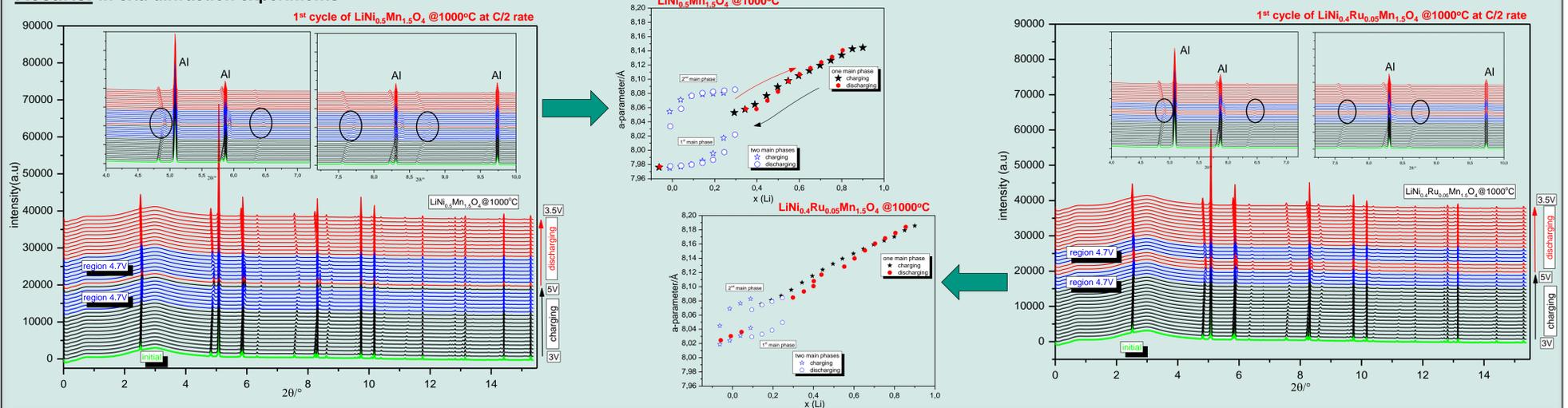
Results: Powder Characterization



Results: Electrochemical Investigations



Results: In situ diffraction experiments



Conclusion

- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ contains small amounts of $\text{Li}_2\text{Ni}_2\text{O}_7$ impurity which has been vanished after Ru-doping.
- The thickness (mass loading) of the cathode materials on Al-foil plays an important role especially at high C-rate.
- The amount of Mn^{3+} ions increases with the increase in annealing temperature because of the oxygen loss from the crystal lattice.
- The samples synthesized at 1000°C have better capacity retention than the ones synthesized at 800°C after 300 cycles ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has 79.5% and Ru-doped has 83%).
- Ru-doped sample synthesized at 1000°C exhibits a higher capacity than the undoped sample even though a larger 4 V electrochemical activity is observed which corresponds to the existence of Mn^{3+} .
- An intermediate phase (2^{nd} main phase ($Fd\bar{3}m$)) appears at ~4.7 V for both materials annealed at 1000°C, on both charging & discharging processes where $\text{Ni}^{2+}/\text{Ni}^{4+}$ 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
- [2] H. Wang, H. Xia, M. O. Lai, L. Lu, *Electrochem. Commun.*, 11, 1539-1542, 2009
- [3] Q. Zhong, A. Bonakdarpour, J.R. Dahn, *J. Electrochem. Soc.*, 144, 205, 1997
- [4] H. Matsumoto, D. Murakami, T. Shimura, S.I. Hashimoto, H. Iwahara, *J. Electrochem. Soc.*, 7, 107-111, 2001
- [5] H. Wang, T. A. Tan, P. Yang, M. O. Lai, L. Lu, *J. Phys. Chem. C*, 115, 6102-6110, 2011