Highvoltage-Spinels for Lithium-Ion Batteries: Effects of Synthesis and Composition on the Cycling Stability

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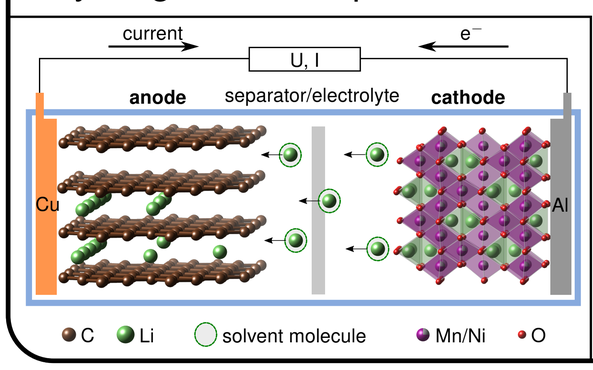
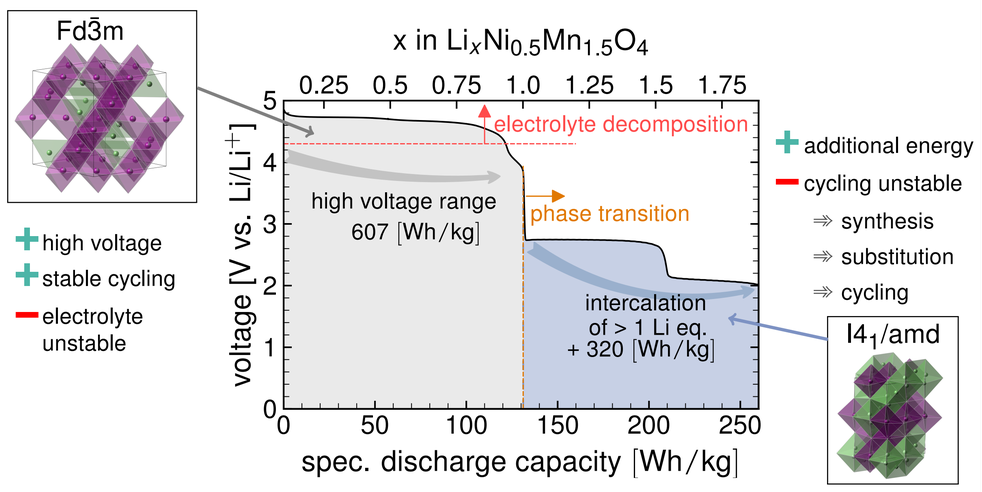
Motivation

The lattice of the $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel offers the ability to host up to 2 Li eq., which leads to a favorable capacity. If a metallic lithium anode is used a theoretical capacity of 282 mAh g^{-1} is reached.

Cycling of 2 Li eq. in the voltage range of 2.0 to 5.0 V is accompanied by a phase transition. This and a dissolution of manganese into the electrolyte is leading to a severe capacity fade. Here Mn in LNMO is partially substituted by Ru-Ti as well as Fe-Ti. The materials are compared regarding their capacity retention at different cycling conditions.



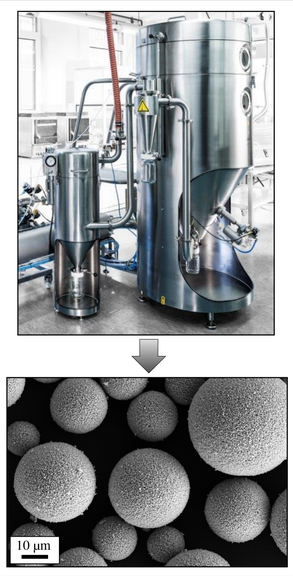


Synthesis

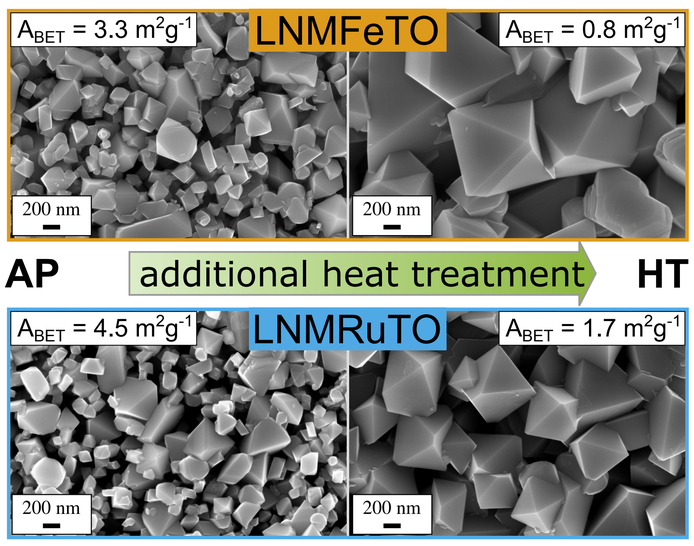
- reactants
  - Li, Ni, Mn-acetate
  - substituent (M: Fe/Ru + Ti)
- spray-drying and heat treatment
- **product:**

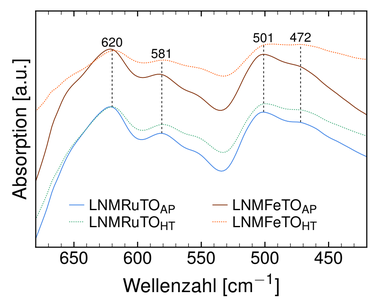
$LiNi_{0.5}Mn_{1.4}M_{0.1}Ti_{0.03}O_{4-\delta}$

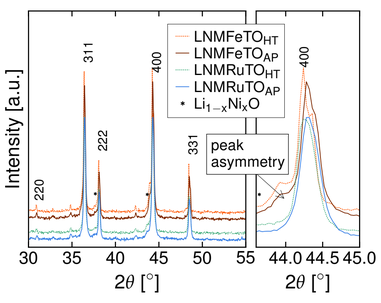
M = Fe: LNMFeTO
M = Ru: LNMRuTO



Structure and Morphology



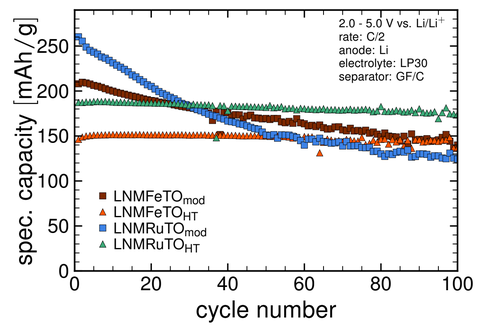


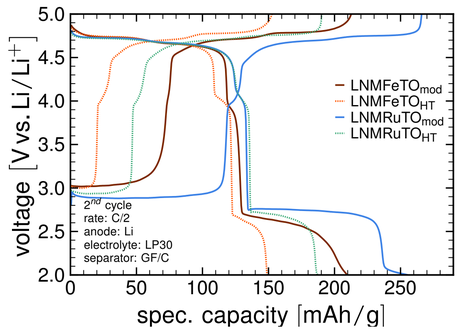


- before heat treatment
  - truncated octahedral particles
  - inhomogeneous particle size distribution
- after heat treatment
  - strong decrease of surface area
  - good faceted octahedral particles
  - degree of Ni and Mn ordering decreases
- phase purity: LNMRuTO 97 %, LNMFeTO 84 %

Electrochemistry

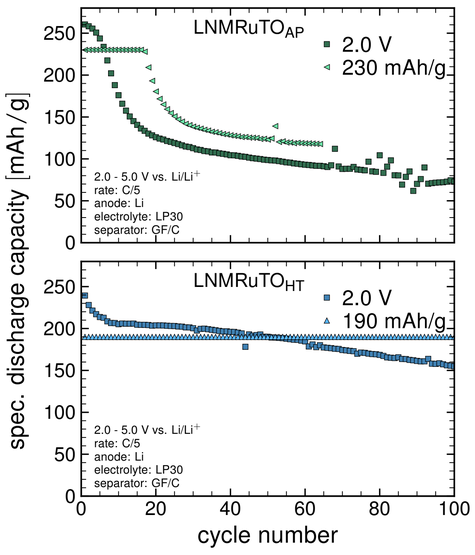
Fe-Ti vs. Ru-Ti substituted spinels

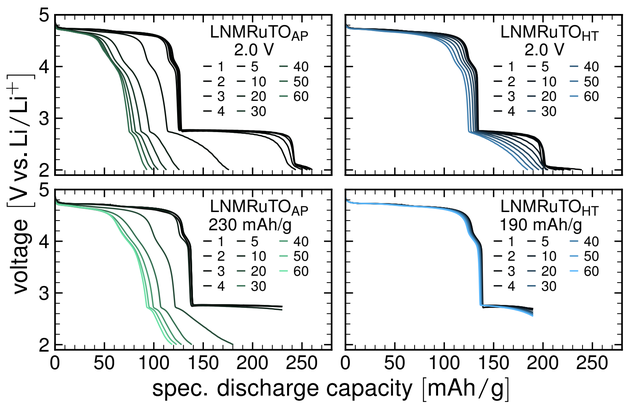




- Fe- and Ti-substituted spinels exhibit lower capacities (ca. 50 mAh g^{-1})
  - high-voltage capacities show small differences
  - large differences in low-voltage capacities
  - ⇛ lower phase purity (ca. 84 %) of Fe-Ti samples results in low capacities
- HT samples display lower initial capacities but excellent capacity retention

Cutoff criteria





- AP samples exhibit extreme loss of low and high voltage capacities
- cutoff criteria influences capacity retention
- > 100 cycles of stable cycling can be achieved

Conclusion

Mn in LNMO spinels has been substituted by Fe-Ti or Ru-Ti. The Ru-Ti-substituted spinels exhibit superior capacities. High temperature annealing lead to decreased surface areas, good defined octahedral crystal shapes and excellent capacity retention at the expense of high initial capacities. However capacities as high as 190 mAh g^{-1} could be cycled for 100 cycles with a loss of 10 mAh g^{-1} at a rate of C/2. Using a cutoff criteria defined by a specific capacity lead to further improvement of the capacity retention.

References & Acknowledgements

A. Höweling, A. Stoll, D.O. Schmidt, H. Geßwein, U. Simon, J.R. Binder, "Influence of synthesis, dopants and cycling conditions on the cycling stability of doped $LiNi_{0.5}Mn_{1.5}O_4$ spinels", *Journal of The Electrochemical Society*, vol. 164, pp. A6349-A6358, 2017.

GEFÖRDERT VOM

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