Increase in Cycling Stability of Doped $LiNi_{0.5}Mn_{1.5}O_4$-Spinels during Charging between 2.0 and 5.0 V

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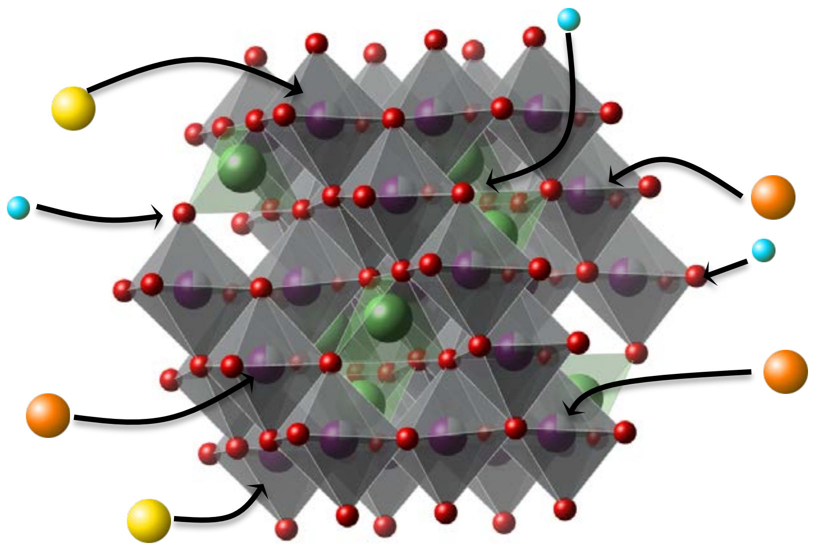
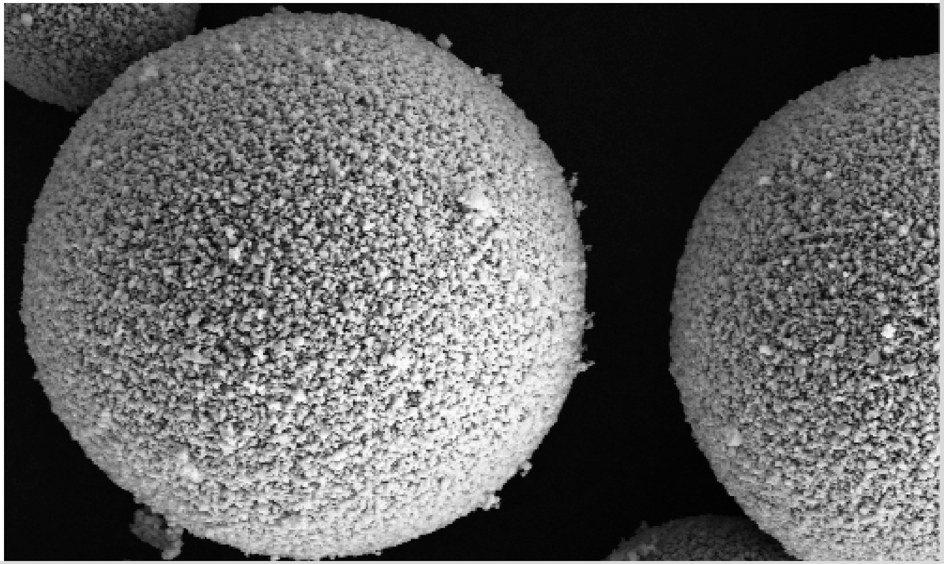
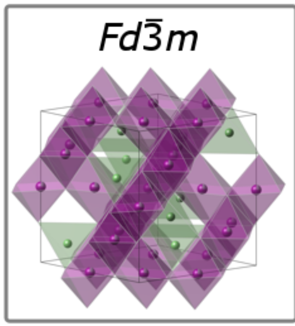
Projektträger Jülich Forschungszentrum Jülich

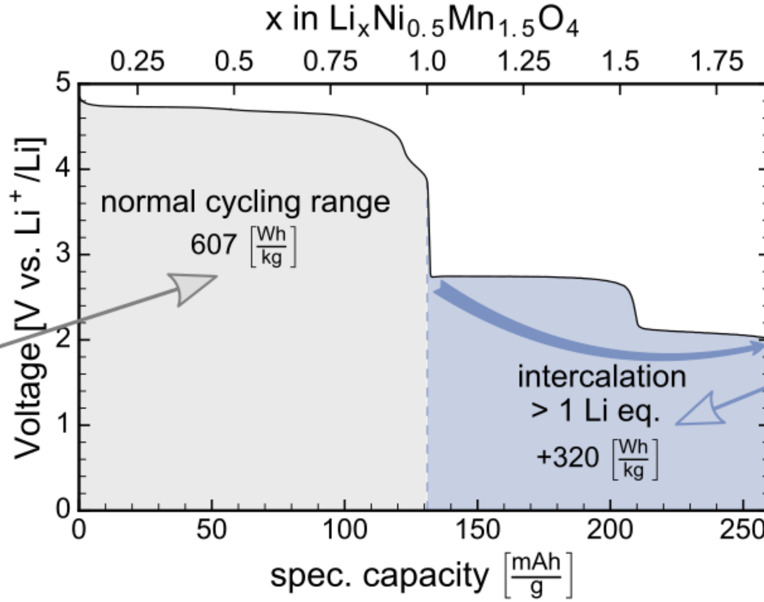




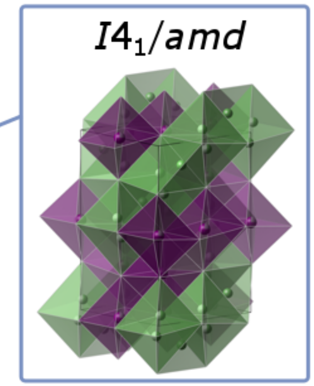
Motivation – Doping Elements



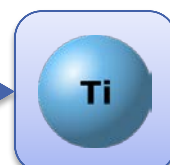
+ stable cycling
+ high voltage



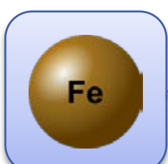
+ additional energy
− cycling unstable



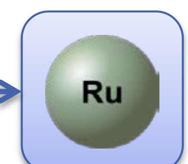
Doping can improve the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ high voltage spinel



- Lattice constant increases
- Stability improves
- Higher capacity

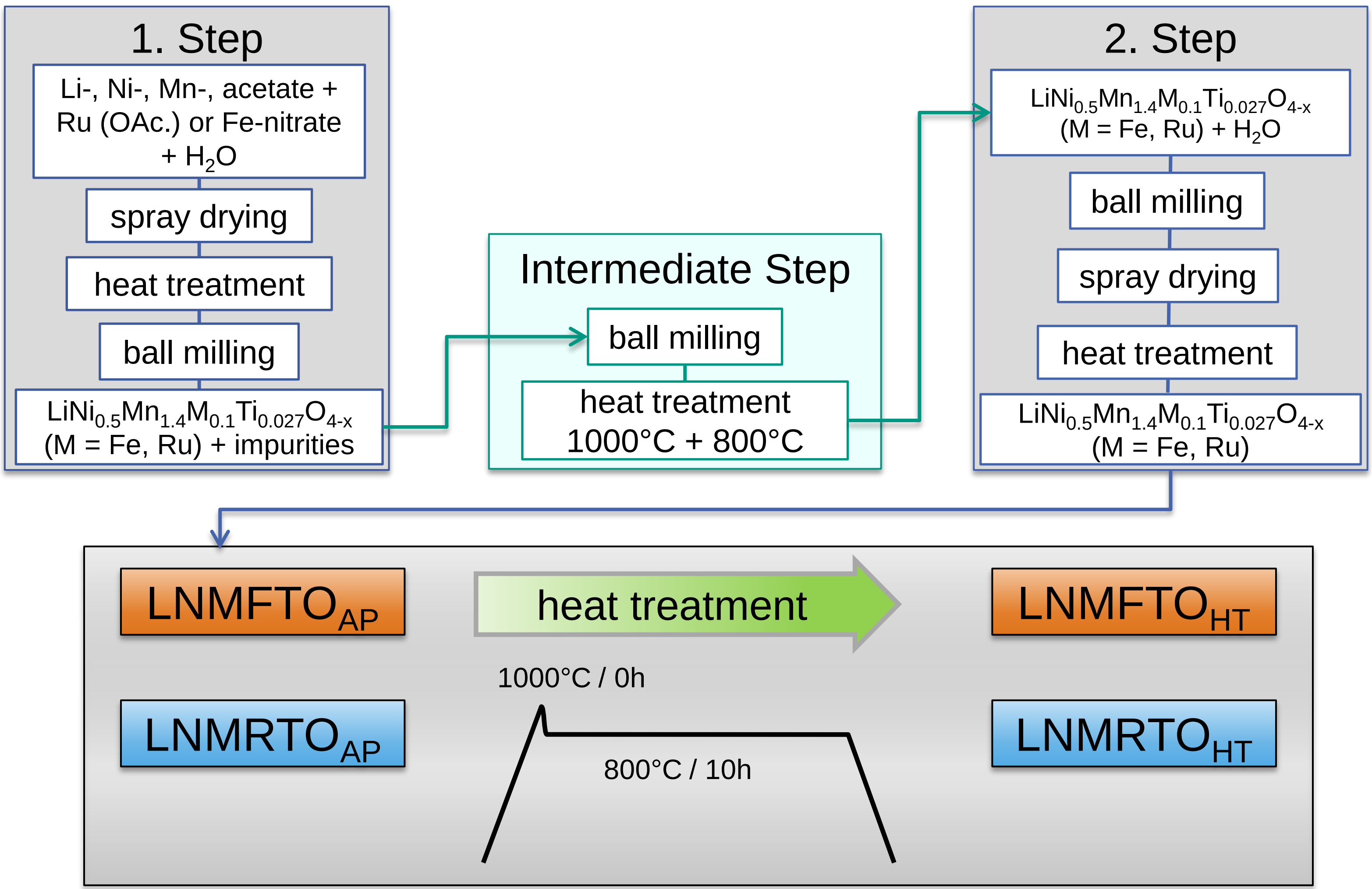


- Increases electronic conductivity
- Decreases impurity phase

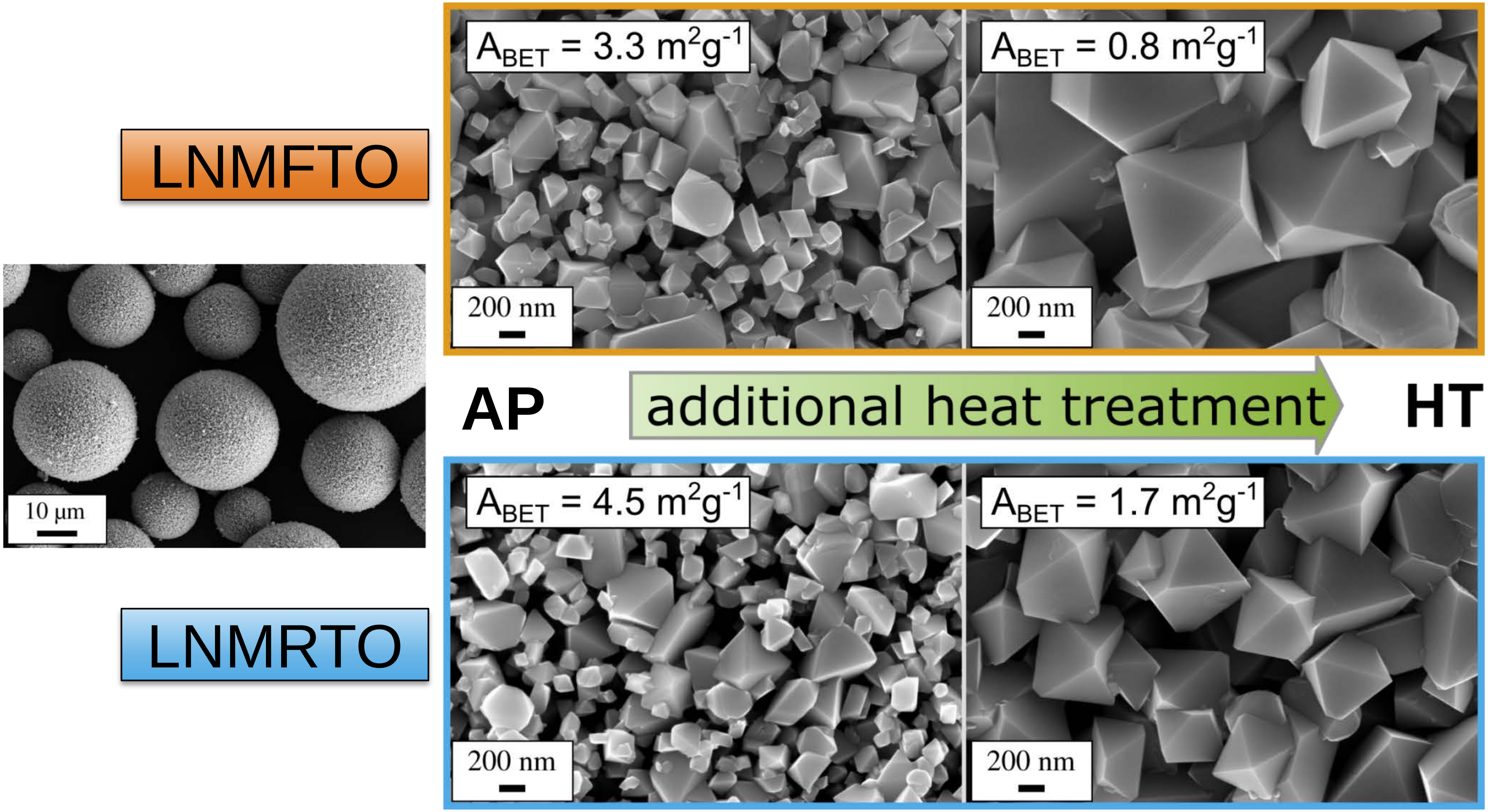


- Increases useable capacity
- Increases rate capability

Ru-Ti Doping – Synthesis



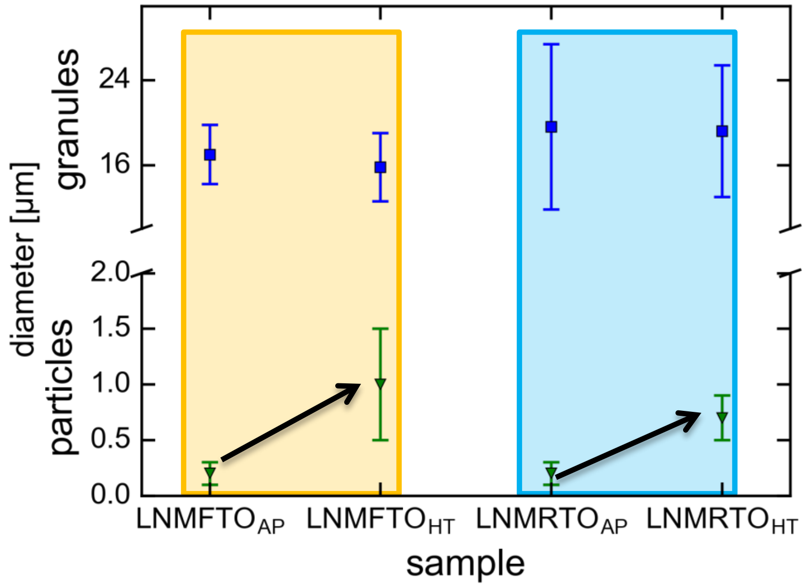
Ru-Ti vs. Fe-Ti Doping – Morphology

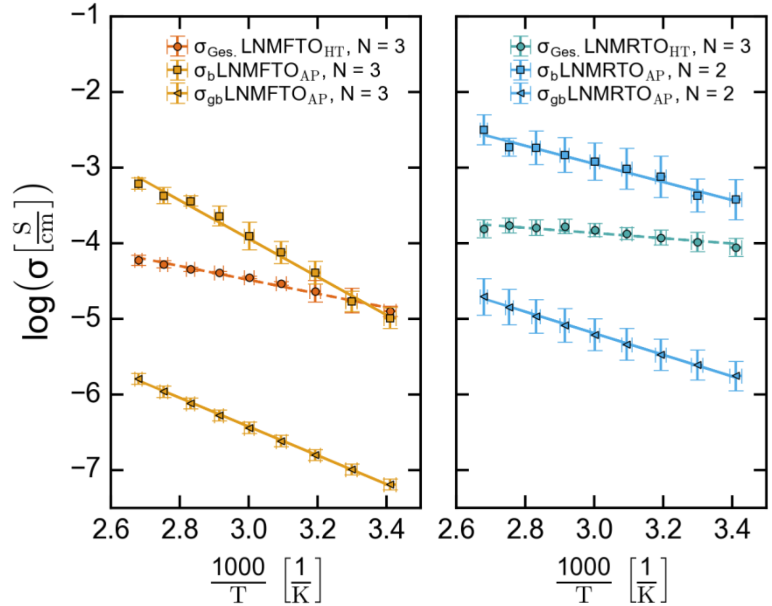


[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Ru-Ti vs. Fe-Ti Doping – Properties

Physical





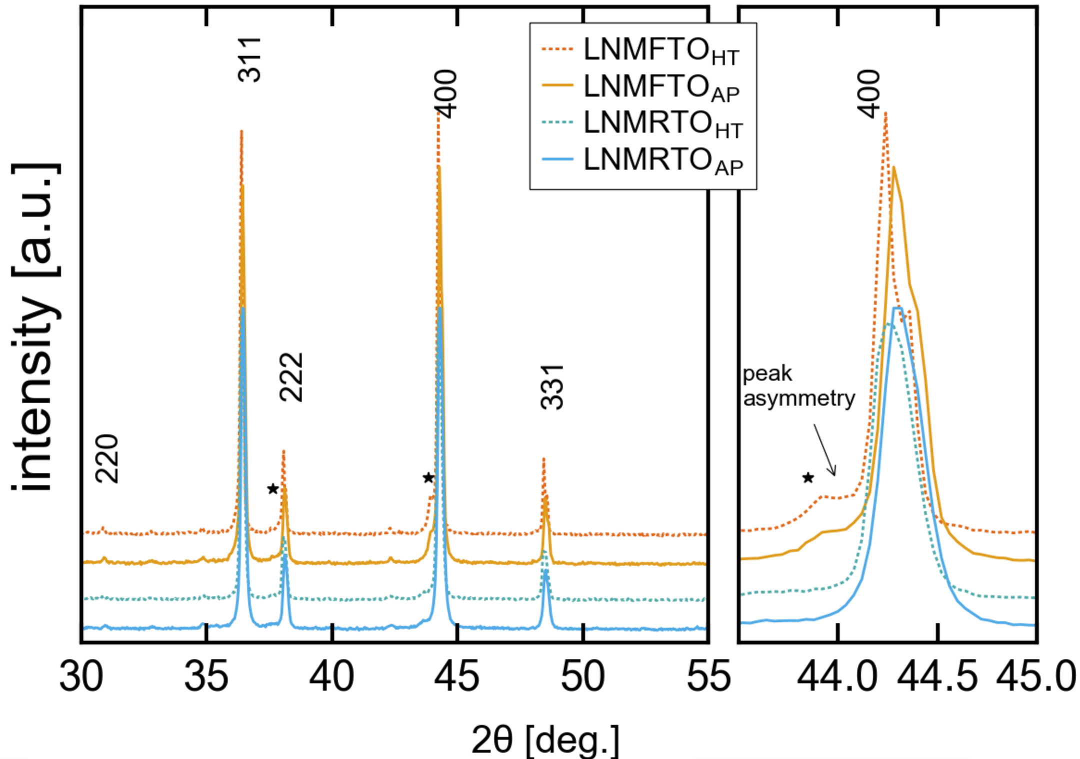
Chemical

Material	Li[1]	Ni[1]	Mn[1]	Fe[1]	Ru[1]	Ti[1]
LNMRTO$_{AP}$	1.0	0.51	1.41	-	0.09	0.03
LNMRTO$_{HT}$	1.0	0.51	1.40	-	0.09	0.03
LNMFTO$_{AP}$	1.0	0.49	1.39	0.10	-	0.03
LNMFTO$_{HT}$	1.0	0.49	1.39	0.10	-	0.03

[1] data in mol

- Strong increase of particle size
- No change in granule size
- LNMRTO exhibits higher conductivity
- Bulk conductivity of HT higher than AP
- Chemical composition as targeted

Ru-Ti vs. Fe-Ti Doping– Composition



LNMFTO

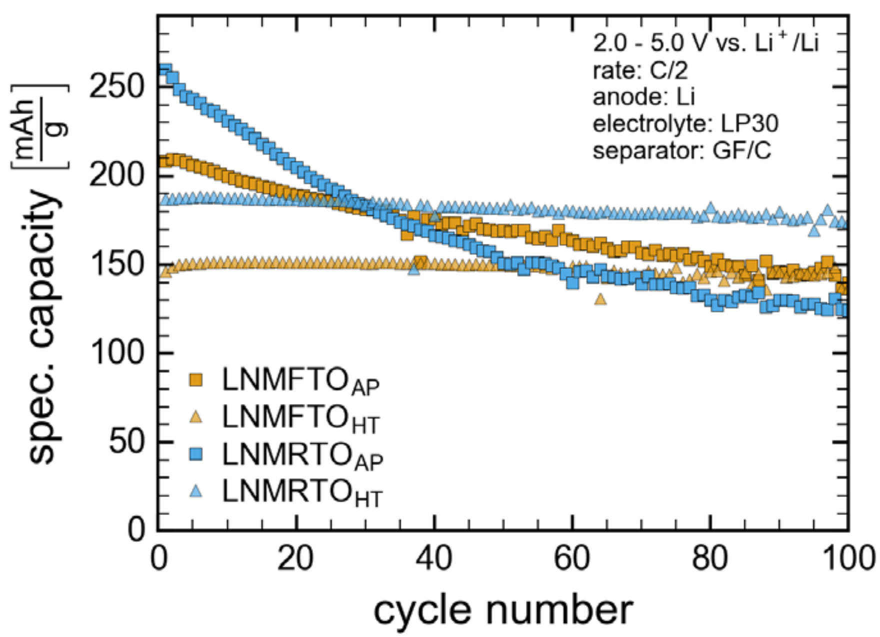
- rock salt impurity (ca. 3 wt%)
- two spinel phases
  $LNMO_1$: ca. 85 wt.%; $LNMO_2$: ca. 13 wt%
- Temperature treatment:
  - Lattice parameter increases
    8.181 Å → 8.188 Å

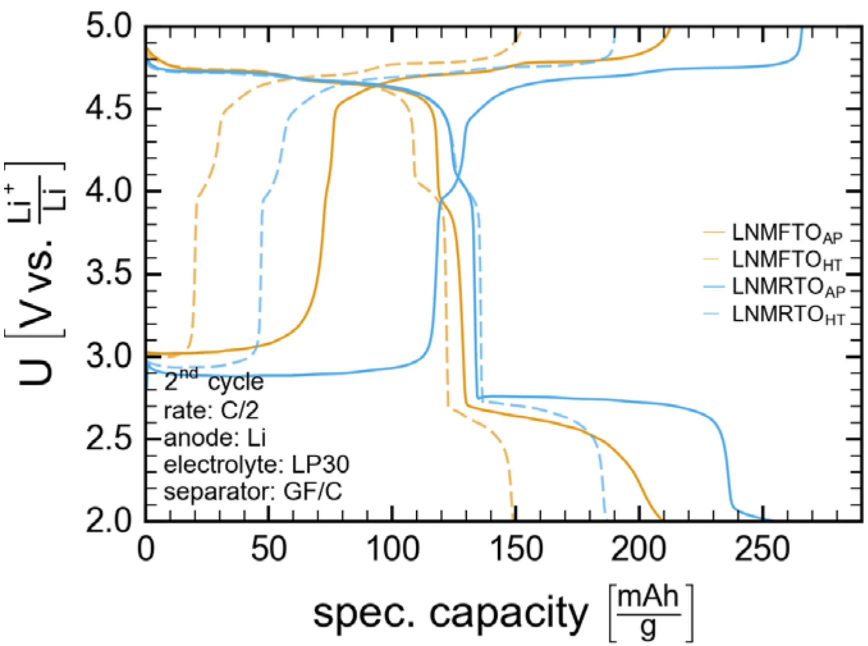
LNMRTO

- higher phase purity
- one spinel phase
- temperature treatment:
  - Lattice parameter increases
    8.187 Å → 8.190 Å

[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Ru-Ti vs. Fe-Ti Doping – Electrochemistry





LNMFTO

mod
- capacity low compared to RuTi

HT
- high stability but low capacity

LNMRTO

mod
- nearly theoretical capacity
- severe capacity fade

HT
- very good stability at a lower capacity

[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Ru-Ti vs. Fe-Ti Doping – Electrochemistry

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capacity loss

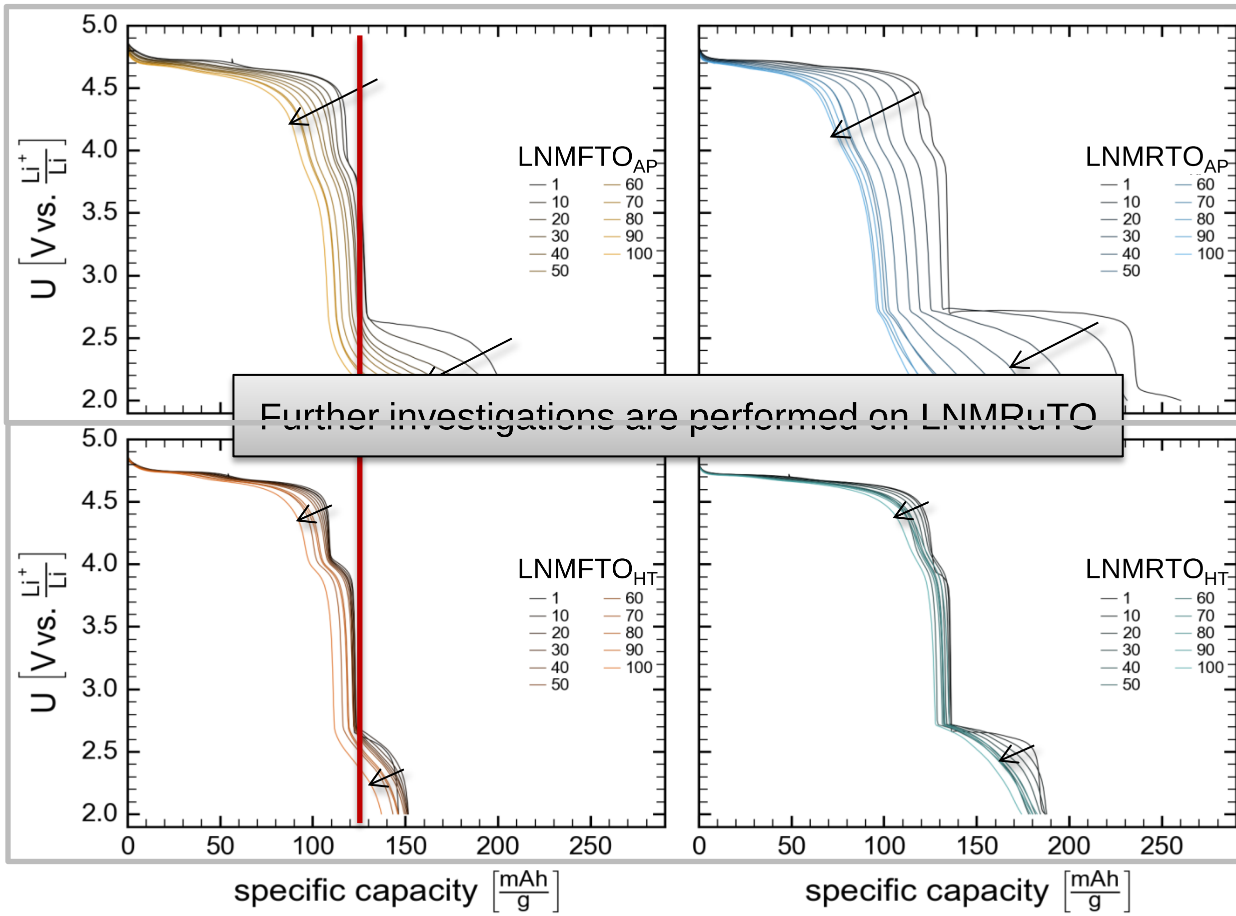
- starts in low voltage region
- high voltage capacity is decreased with increasing cycle number
- loss is more severe for AP samples
- Higher stability of HT samples likely due to lower degree of Li^+-ion intercalation

LNMFTO

- poor electrochemical properties
- No distinct 2.7 V plateau
- Low capacity:

ca. 125 mAh g^{-1} (3.5 – 5.0 V)

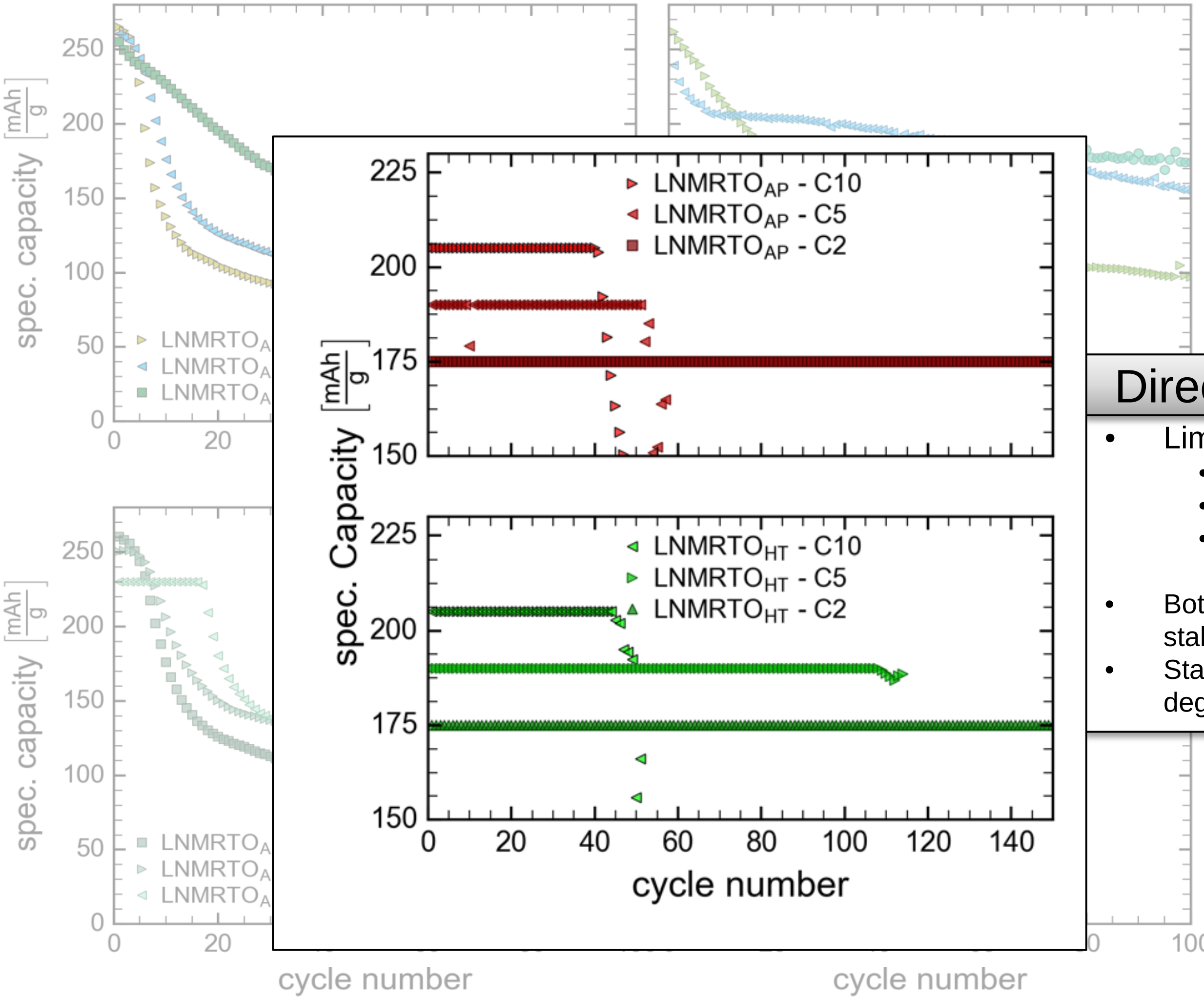
$$85\ wt\%\ LNMO_1 \cdot 146\ \frac{mAh}{g} = 124\ \frac{mAh}{g}$$



Further investigations are performed on LNMRuTO

[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Ru-Ti vs. Fe-Ti Doping – Electrochemistry



C-rate

- Initial capacities increase at lower rates
  - Low voltage capacity
- At C/10 similar initial capacity

Direct comparison

- Limits:
  - C/2: 175 mAh/g
  - C/5: 190 mAh/g
  - C/10: 205 mAh/g
- Both materials exhibits equal stabilities at same capacity limit
- Stability mainly depends on degree of Li intercalation

…gligible
…ncreased

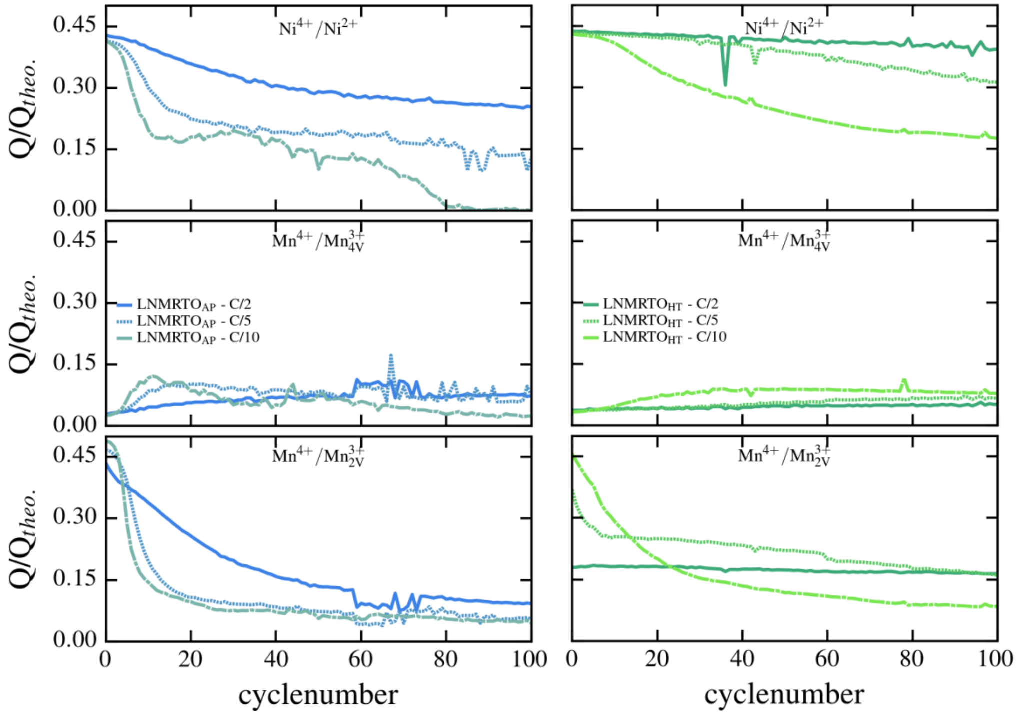
- AP: severe capacity fade after 20 cycles
- HT: Stable cycling possible for 100 cycles

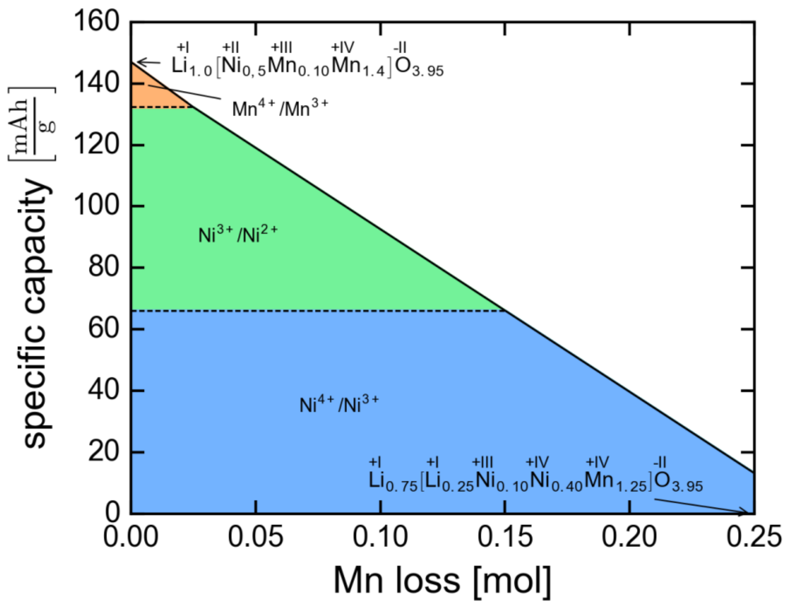
[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Mechanisms for capacity loss

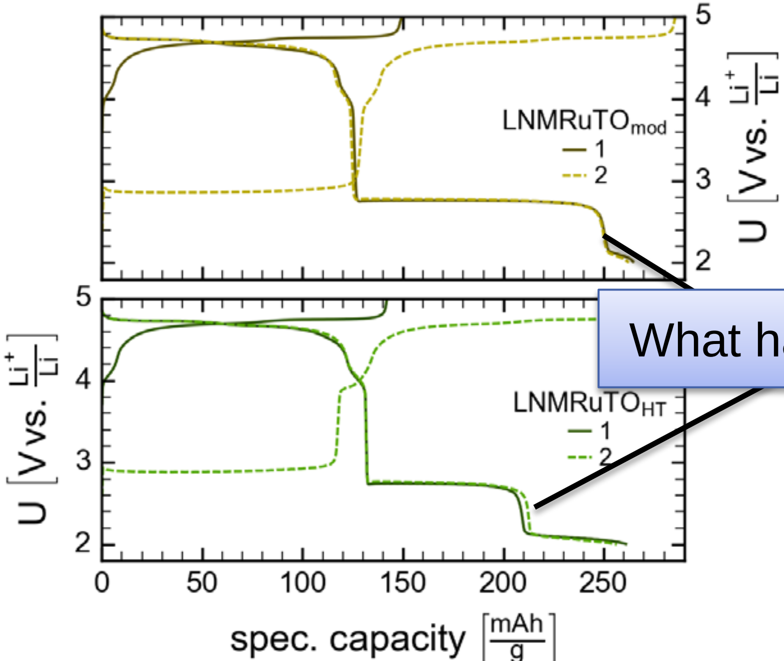
- Loss of contact
- Irreversible reactions
  - Both should lead to a simultaneous decrease of all capacity plateaus

- Loss of active Material
  - Strong increase of Mn^{3+} in low voltage region → Mn disproportionation & dissolution
  - Reduces capacity very effectively

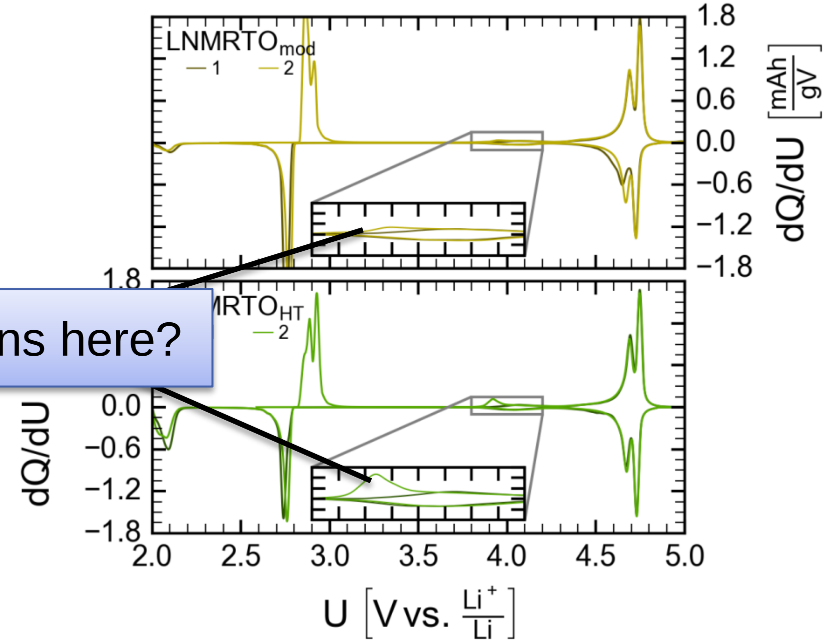




Ru-Ti doping – voltage profile (C/10)



What happens here?



general

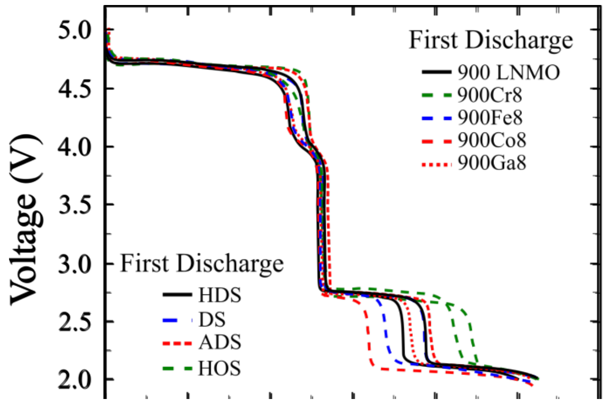
- discharge capacity equal for HT and mod sample
- CE is better for HT sample

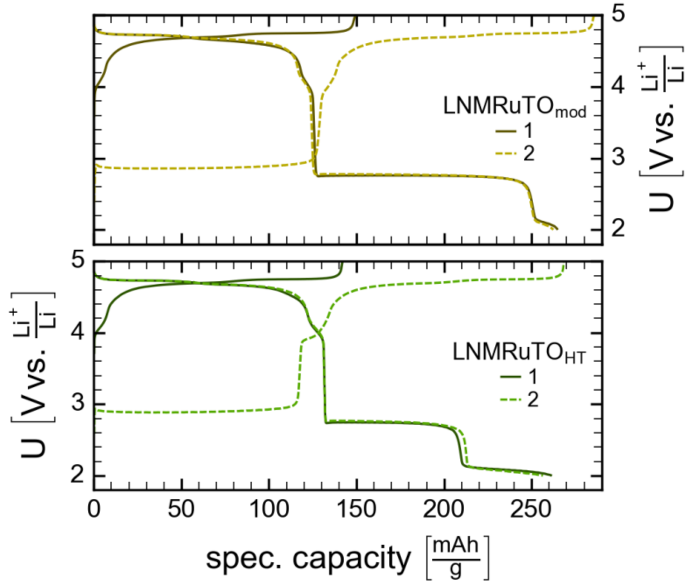
2.0 – 3.5 V

- discharge:
  - large capacity @ 2.7 V
  - small capacity @ ~2.1 V
- transition between voltage steps earlier for HT sample
- larger 2.1 V plateau is accompanied by ~3.9 V oxidation peak

[A. Höweling, et al., *J. Electrochem. Soc.*, **164**, A6349–A6358 (2017)]

Ru-Ti doping – 2 V capacities in literature





[illegible]

2.7 V plateau depends on

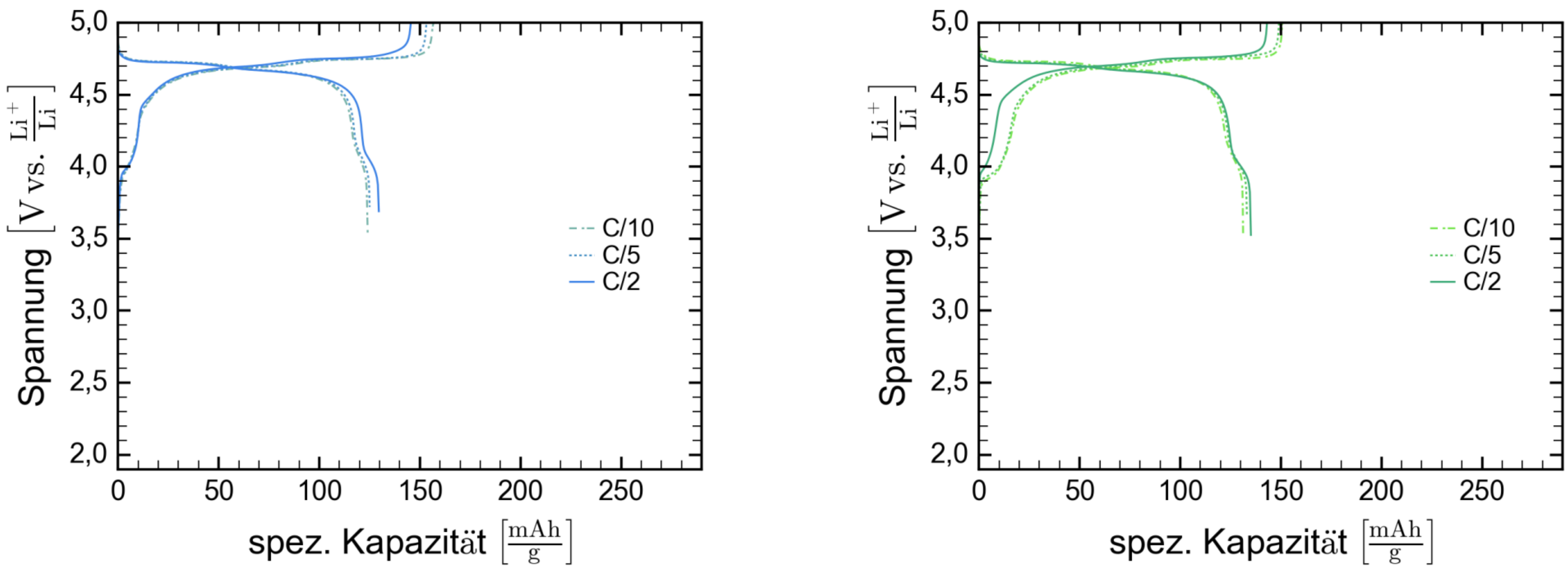
- ordering
- doping
- morphology
- annealing temperature

criteria	$LNMRuTO_{mod}$	$LNMRuTO_{HT}$
ordering	(+)	(-)
morphology	truncated	octahedral
temperature	800 °C	1000 °C
2.7 V capacity	larger	smaller

These are only observations!

Ru-Ti doping – voltage profile

LNMRTO$_{AP}$ | LNMRTO$_{HT}$



Above 3.5 V

- Both materials display only small changes of the voltage profile with the applied C-rate

Below 3.5 V

- Especially the HT-material shows an impact of the C-rate on the 2.7 V plateau

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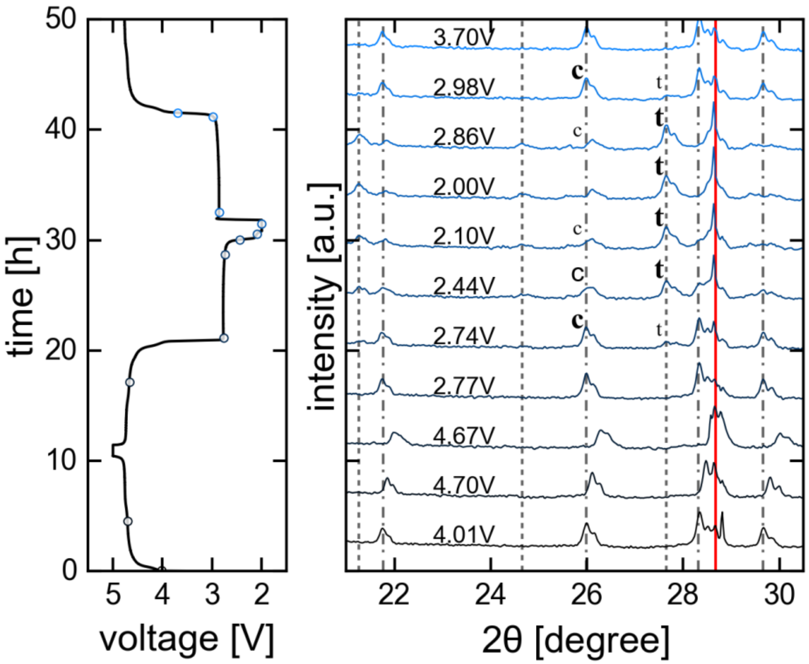
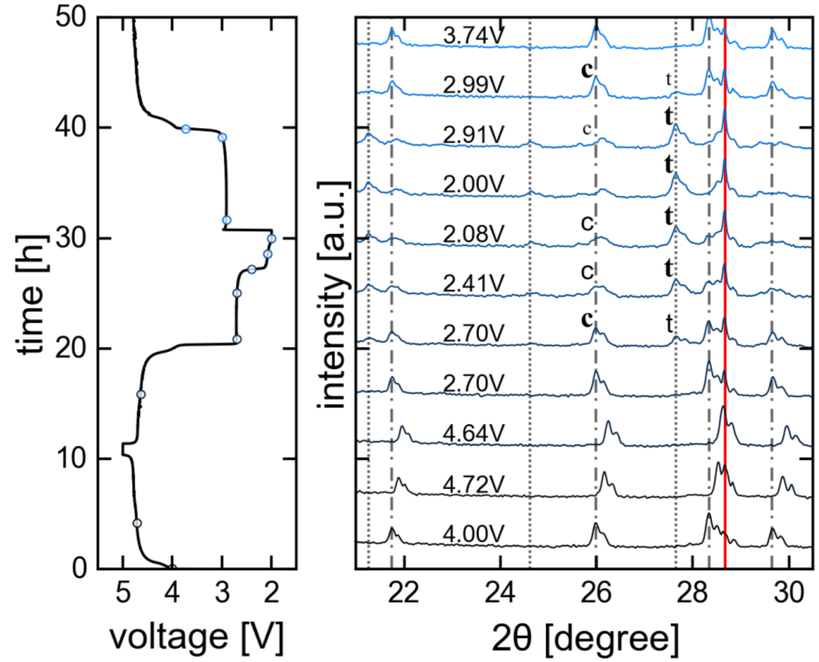
Ru-Ti doping – in-situ XRD

LNMRTO$_{AP}$



LNMRTO$_{HT}$



general

- Both samples display cubic and tetragonal phase at 2.7 V
- Below 2.3 V cubic phase is still present
  - What is the reason for the voltage drop?

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Ru-Ti doping - Model

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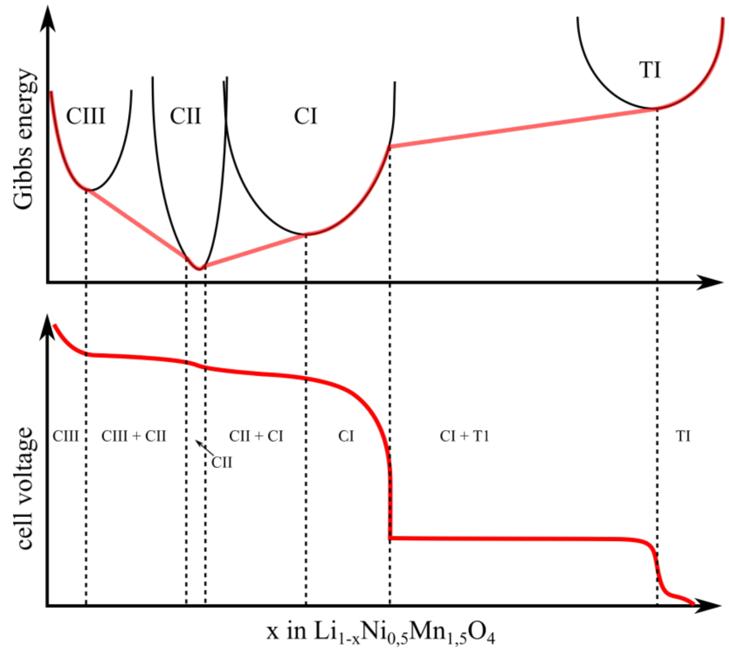
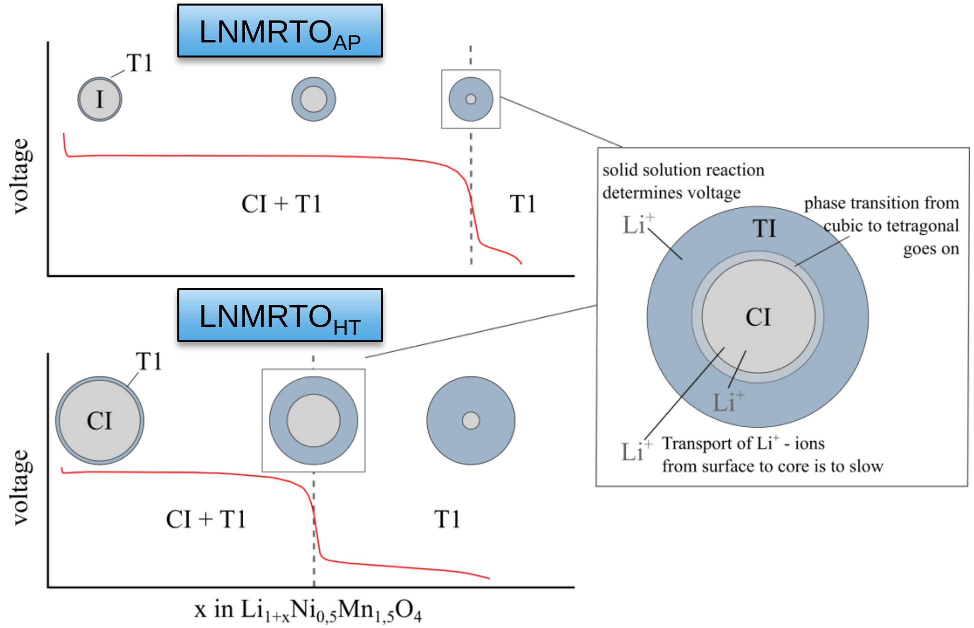
Theoretical phase diagram

- constant voltage
  - two phase reaction
- voltage drop:
  - solid solution reaction



[based on C. M. Julien and A. Mauger, *Ionics (Kiel).*, **19**, 951–988 (2013)]



Kinetic effect

- AP:
  - small particles→ Li transport is sufficient for complete phase transformation
- HT:
  - Larger particles→ Lit transport insufficient, voltage drops before cubic phase has been consumed

Conclusions

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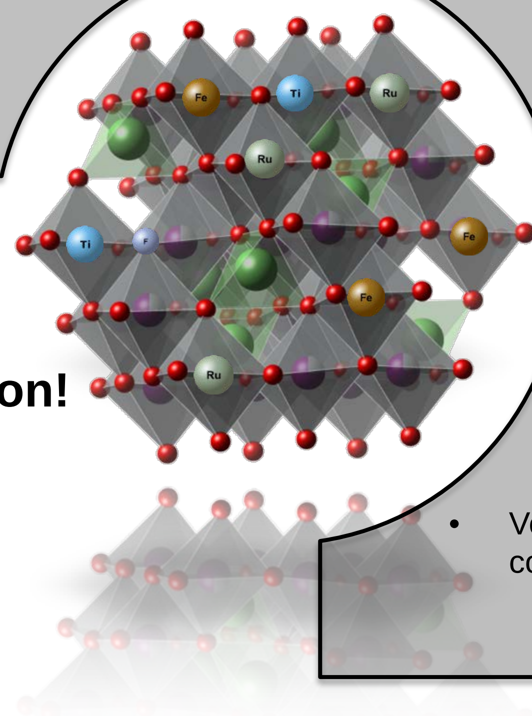
Fe-Ti vs. Ru-Ti

- Ru-Ti- and Fe-Ti-doped LNMO spinels were prepared
- Ru-Ti exhibits higher initial capacities
- Severe capacity fade of AP materials is reduced for HT samples
- Capacity of Fe-Ti-spinel limited due to impurity phase

Capacity retention

- A capacity of > 170 mAh g^{-1} can be cycled for 100 cycles
  - 2 – 3 V capacity influences capacity retention
    - Capacity fade is likely due to loss of active material



Kinetics model

- Voltage drop is determined by kinetics of lithium diffusion
- The Li-diffusion of HT-material is insufficient
- Voltage drops before cubic phase is consumed

Thank you for your attention!

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