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Kathodenmaterialien für Hochleistungsbatterien der nächsten Generation: Einfluss von Nicht-Stöchiometrie und aliovalenter Dotierung

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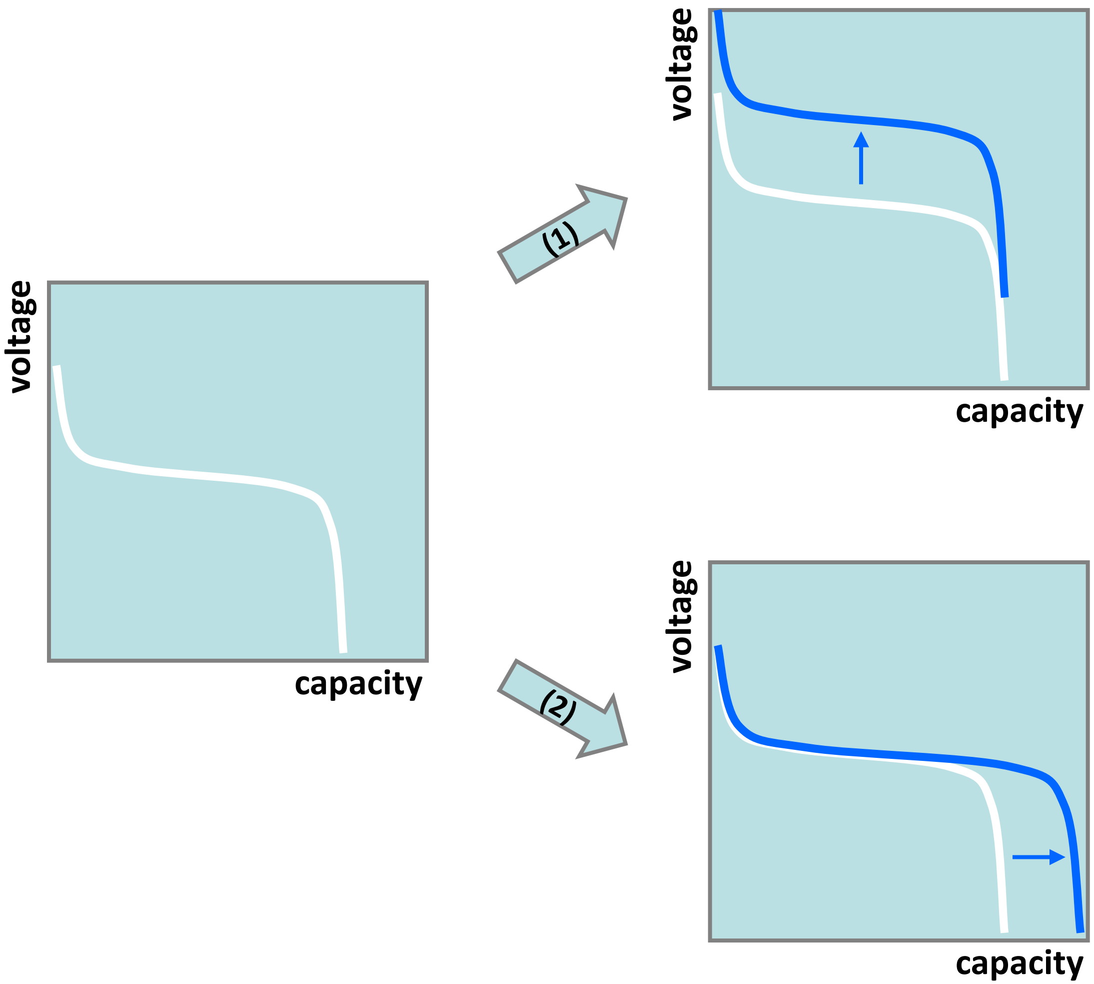
Cathode materials for next generation high energy batteries: influence of non-stoichiometry and aliovalent doping

strategies for next-generation lithium-ion batteries



high-voltage cathode materials:

- $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ (3D framework structure)
- voltage: **5 V**
- capacity: 140 mAg^{-1}

high-capacity cathode materials:

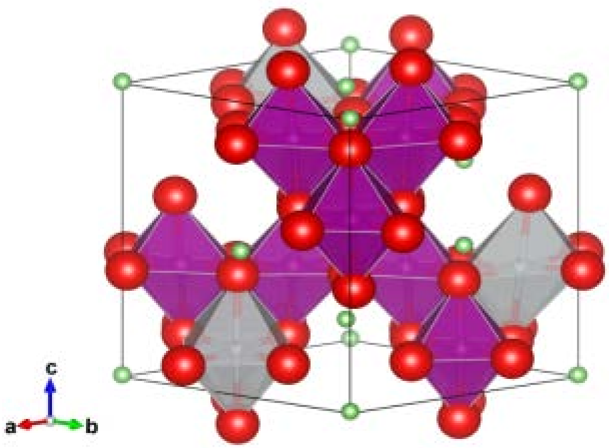
- $Li_2MnO_3 - Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (2D layered structure)
- voltage: 4 V
- capacity: **250 $mAhg^{-1}$**

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

possible structures

ordered spinel

***P*$4_3$32**

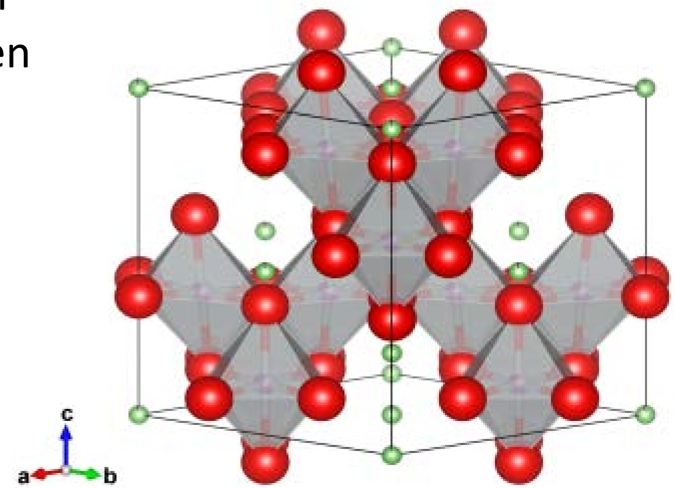


Mn^{4+} and Ni^{2+}
ordered on octahedral sites

thermally induced
order → disorder
transition between
700 and 730 °C

disordered spinel

***F*d-3m**



Mn^{4+} and Ni^{2+}
randomly distributed on octahedral sites
oxygen deficiency above 712 °C; occurrence of Mn^{3+}

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

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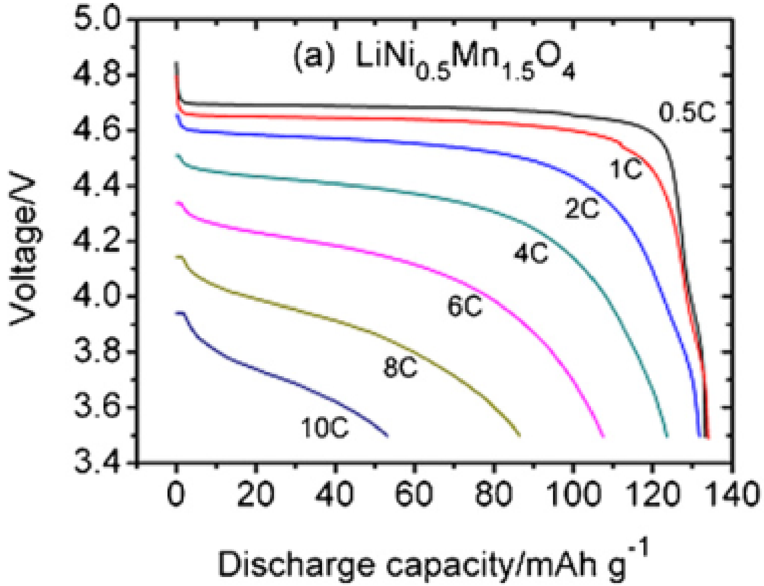
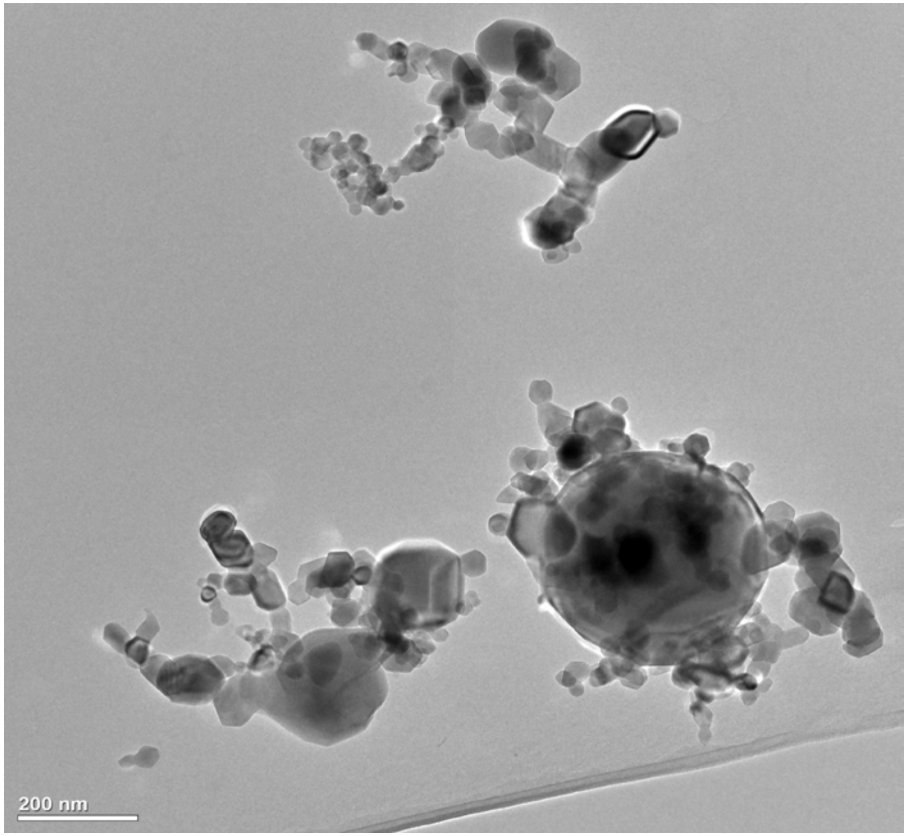
ordered $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$





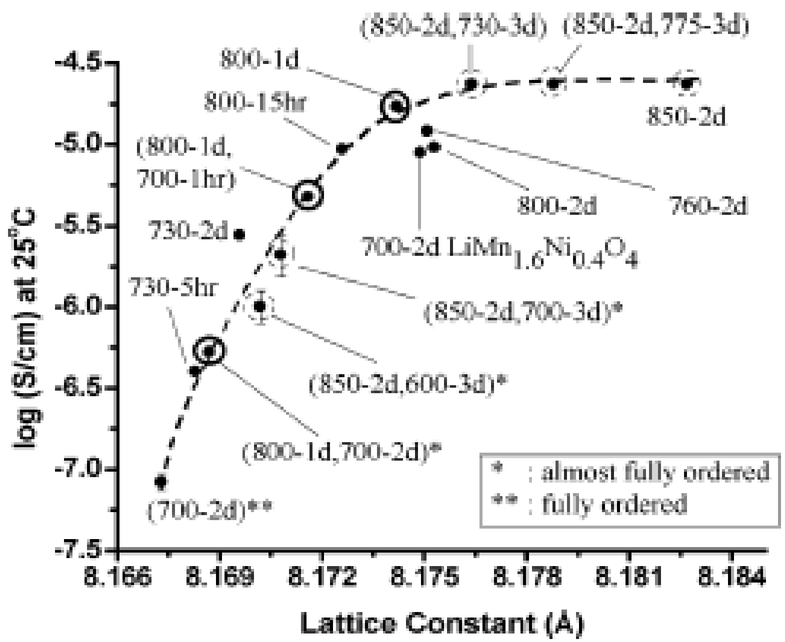
TEM of ordered $LiNi_{0.5}Mn_{1.5}O_4$

→ The poor ionic conductivity leads to loss of capacity at high discharge currents (Zhong, G. B., et al. (2011))

→ Small particle size compensates the poor ionic conductivity of the ordered $LiNi_{0.5}Mn_{1.5}O_4$ because of the shorter diffusion ways

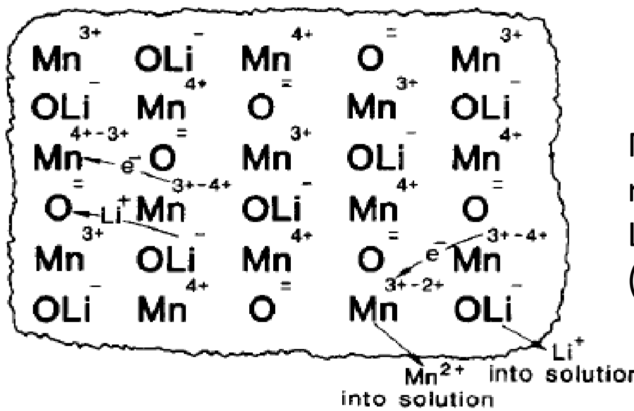
$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

(dis)ordered $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$



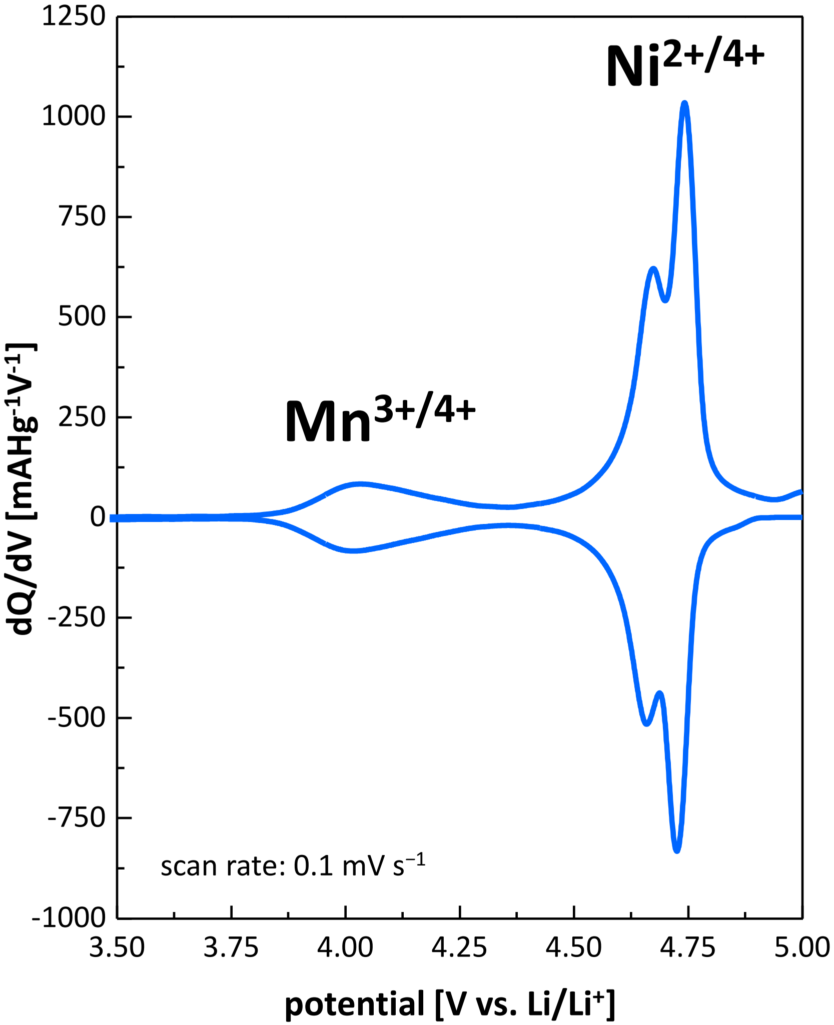
Conductivities of $LiNi_{0.5}Mn_{1.5}O_4$ pellets vs. their conductivities. (Samples named after their post-treatment (temp-time)) (Kunduraci et al. 2006)

- → Post-treatment temperatures above 730 °C lead to disordered spinel and bigger lattice constant
- → Bigger lattice constant is related to better conductivity
- → Disordered spinel has an oxygen deficiency which leads to Mn^{3+} in the lattice
- → The electron-hopping mechanism proposed by Hunter (1981) for $LiMn_2O_4$ leads to increased electron conductivity



Mechanism for Mn reduction at the surface of $LiMn_2O_4$
(Hunter, J. C. (1981))

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials



electrochemistry (discharge reaction):

- 4.7 V region can be attributed to a *two-electron process* involving the $Ni^{2+/4+}$-redox couple

  $$Li_{1-2x}Ni_{0.5-x}Ni_xMn_{1.5}O_4 + 2xLi^+ + 2xe^- \rightarrow LiNi_{0.5}Mn_{1.5}O_4$$

- capacity released around 4.0 V is owing to a *one-electron process* involving the $Mn^{3+/4+}$-redox couple

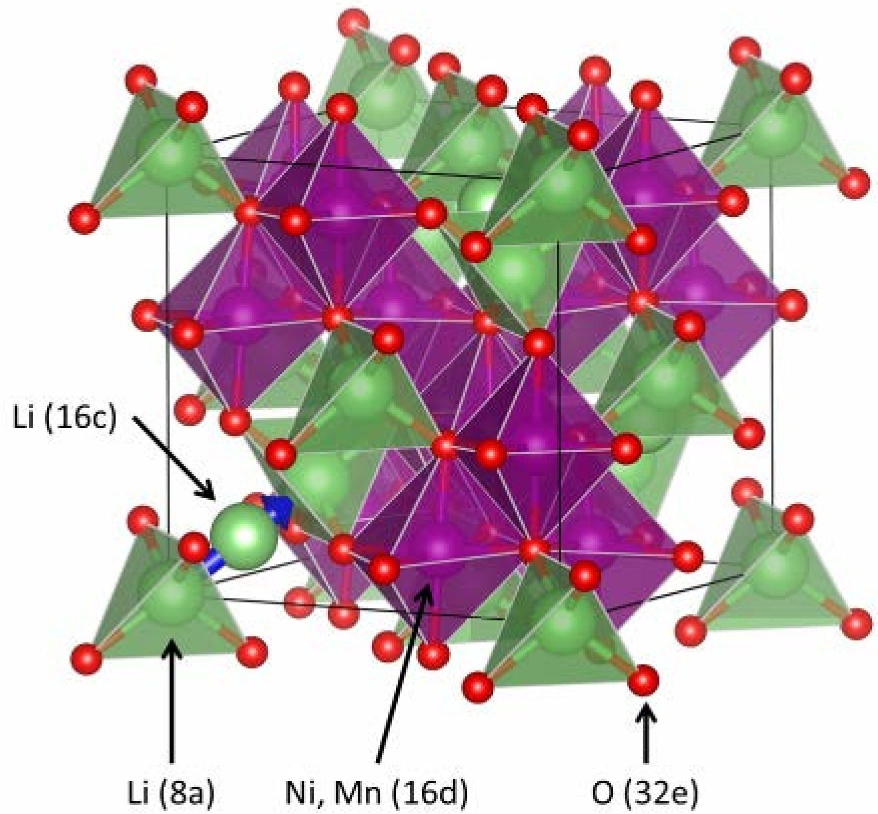
  $$Li_{1-y}Ni_{0.5}Mn_{1.5-y}Mn_yO_4 + yLi^+ + ye^- \rightarrow LiNi_{0.5}Mn_{1.5}O_4$$

processing:

- critical impact of calcination temperature on defect structure [A. Bhaskar et al., J. Electrochem. Soc. **157** (2010) A689]
  - formation of oxygen vacancies, charge-compensated by Mn^{3+}
  - Jahn-Teller ion Mn^{3+} causes severe structural instability
  - disproportionation $2Mn^{3+} \leftrightarrow Mn^{4+} + Mn^{2+}$, where Mn^{2+} leaches into the electrolyte, leading to a *capacity fading* mechanism through structural degradation of the parent spinel

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

disordered spinel-type structure (cubic spacegroup *Fd*-3*m*):



- random distribution of transition metal ions on the 16*d*-sites
- diffusion pathway for lithium ions along tetrahedral 8a- and octahedral 16*c*-sites

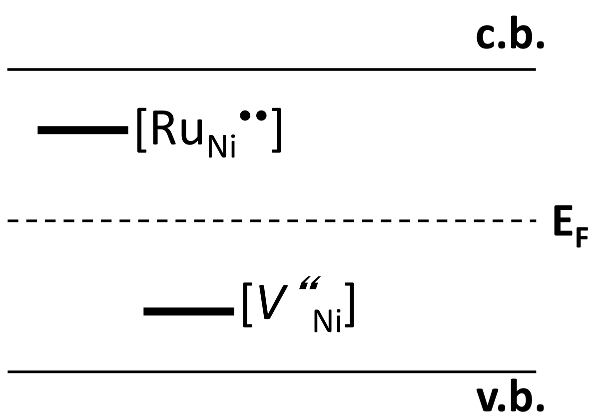
electrochemistry:

- $LiNi_{0.5}Mn_{1.5}O_4$ is a promising candidate cathode material
- high capacity of ~140 $mAhg^{-1}$
- high-voltage plateau in the 5-V range
- improved cyclic performance at modest current rates

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials – improved electronic and ionic conductivity

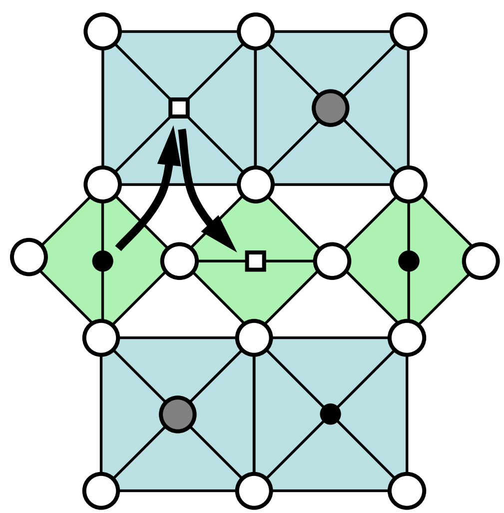
improving the **electronic** conductivity:

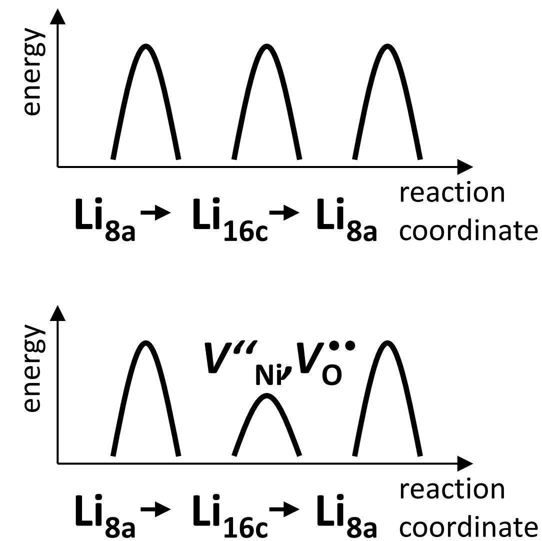
- donor doping increases number of conduction electrons



improving the **ionic** conductivity:

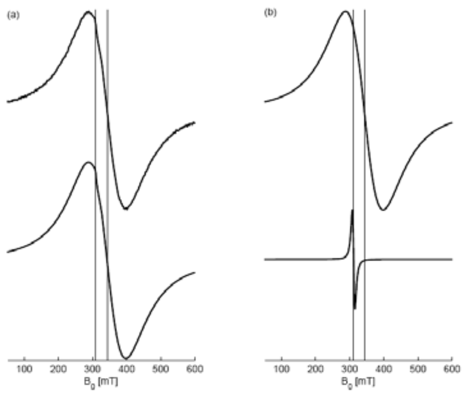
- donor doping additionally impacts concentration of lattice vacancies along the Li-pathway by two mechanisms:
  (1) oxygen vacancies: reduced activation barrier for Li-hopping process
  (2) nickel-vacancies: statistically increased Li-hopping rate



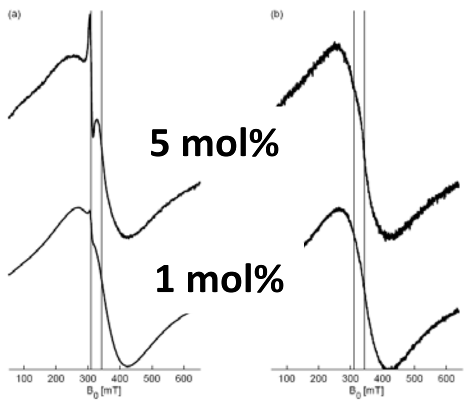


$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials
– defect chemistry: enhanced mixed electronic-ionic conductivity

undoped $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$



RuO_2-doped $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$

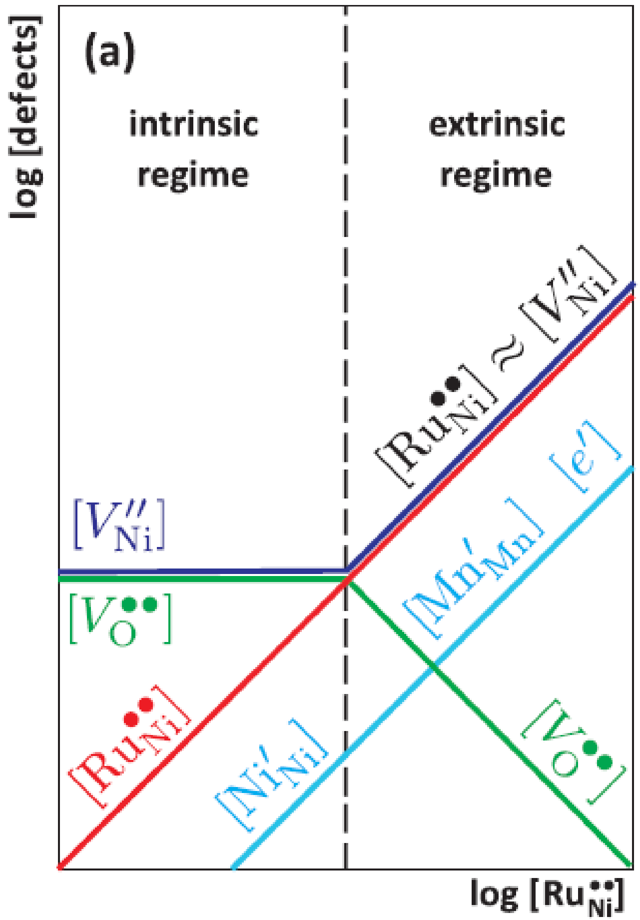


- **undoped $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$**:
  - exchange-coupled Mn-O-Ni-chains
  - small amount of $[Ni'_{Ni}]$
- **RuO_2-doped $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$**:
  - aliovalent Ru^{4+}-doping on Ni^{2+}-sites, acting as donor
  - isovalent substitution for Mn^{4+} suppressed by non-stoichiometry
  - charge compensation by acceptor-type $[V''_{Ni}]$, $[Ni'_{Ni}]$, $[Mn'_{Mn}]$ and $[e']$
- **defect chemistry**:

$$2[\mathrm{Ru}^{\bullet\bullet}_{\mathrm{Ni}}] \approx 2[V''_{\mathrm{Ni}}] + [\mathrm{Ni}'_{\mathrm{Ni}}] + [\mathrm{Mn}'_{\mathrm{Mn}}] + [e']$$

P. Jakes, H. Wang, Y. Feng, L. Li, K. Nikolowski, H. Ehrenberg, R.-A. Eichel, submitted

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials
– defect chemistry: enhanced mixed electronic-ionic conductivity



defect chemistry:

$$2[\mathrm{Ru}_{\mathrm{Ni}}^{\bullet\bullet}] \approx 2[V''_{\mathrm{Ni}}] + [\mathrm{Ni}'_{\mathrm{Ni}}] + [\mathrm{Mn}'_{\mathrm{Mn}}] + [e']$$

→ **improved ionic conduction by increased Li-jump rate**

→ **improved electronic conduction by increased number of conduction electrons (and polarons)**

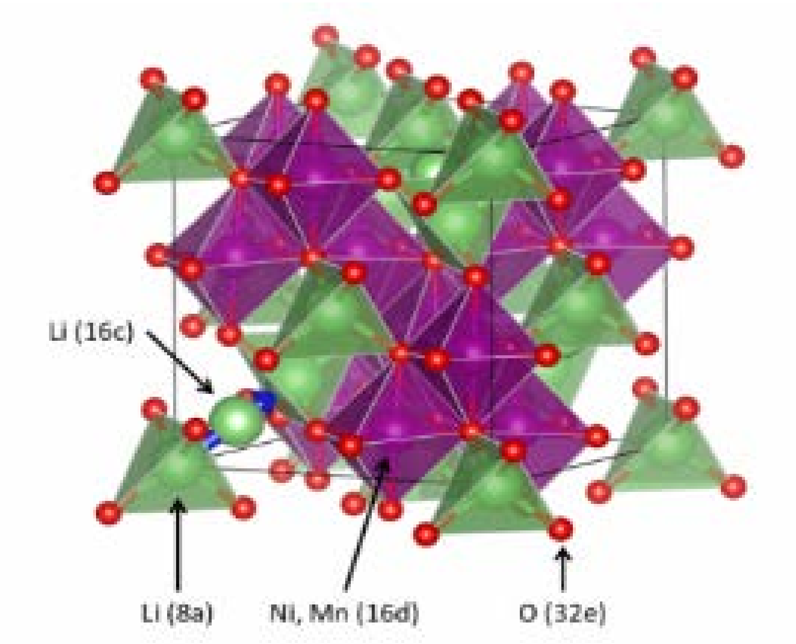
→ **vanishing impact of increased activation barrier for Li-hopping process**

P. Jakes, H. Wang, Y. Feng, L. Li, K. Nikolowski, H. Ehrenberg, R.-A. Eichel, submitted

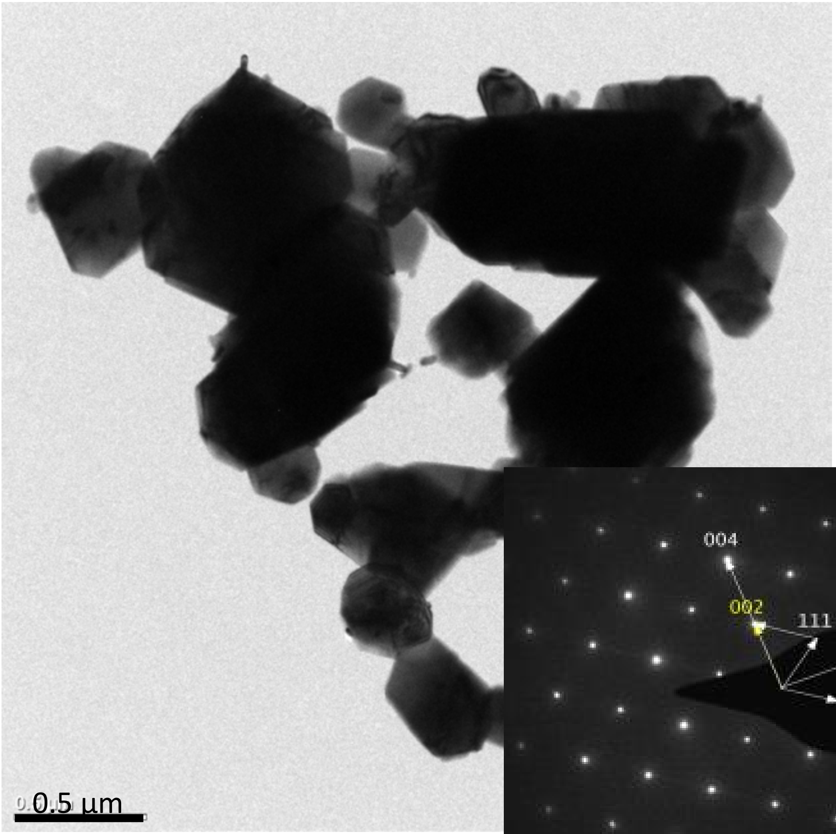
$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

Ru-doped $LiNi_{0.5}Mn_{1.5}O_4$

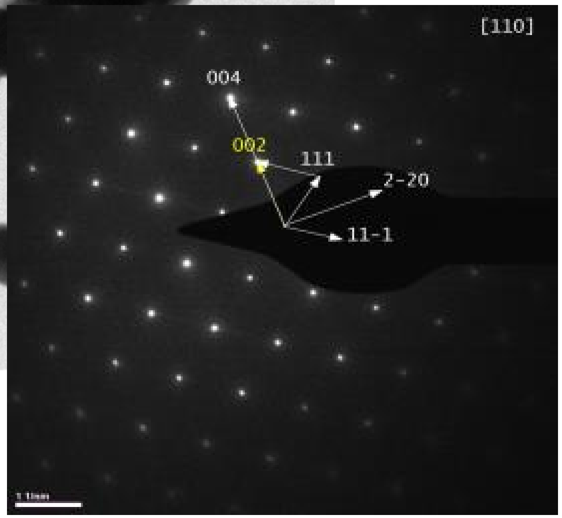
Ru-doping leads to the disordered spinel structure with a random distribution of transition metal ions on the 16*d*-sites



Structure of Ru-doped $LiNi_{0.5}Mn_{1.5}O_4$ (*Fd*-3m)



TEM of disordered Ru-doped $LiNi_{0.5}Mn_{1.5}O_4$

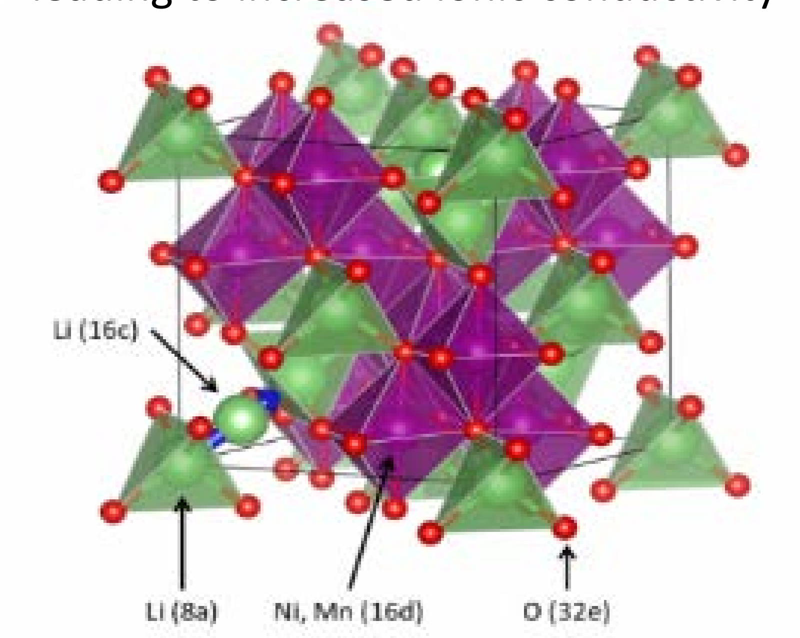


TEM diffraction pattern of Ru-doped $LiNi_{0.5}Mn_{1.5}O_4$ (*Fd*-3m)

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

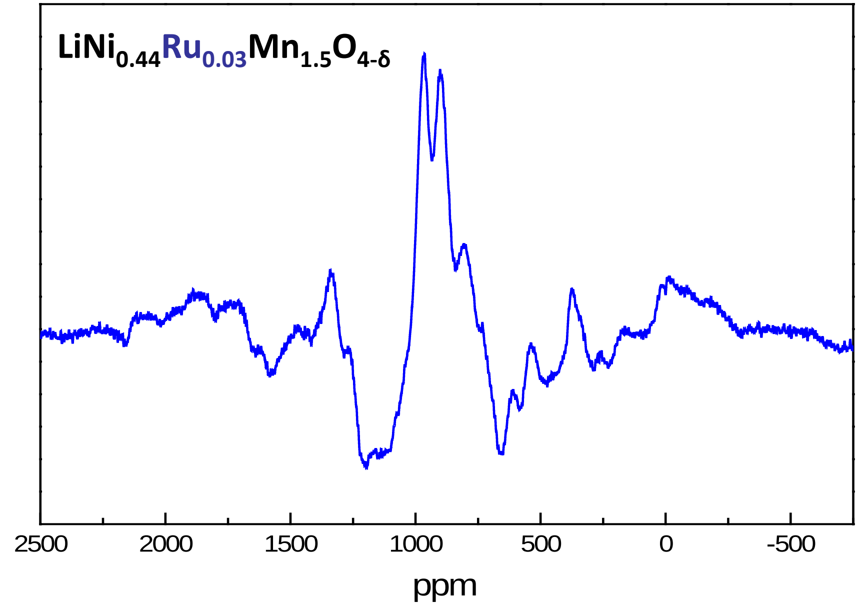
Li-mobility in RuO_2-doped LNMO – MAS-NMR

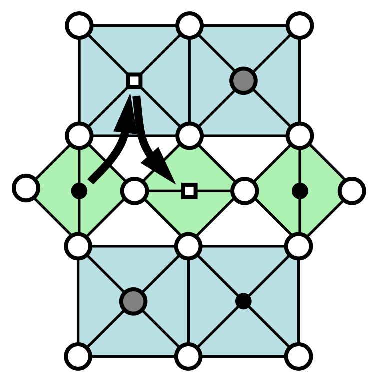
NMR for Ru-doped $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$
Li-distribution on different lattice sites
→ additional Li pathways over 16c position leading to increased ionic conductivity

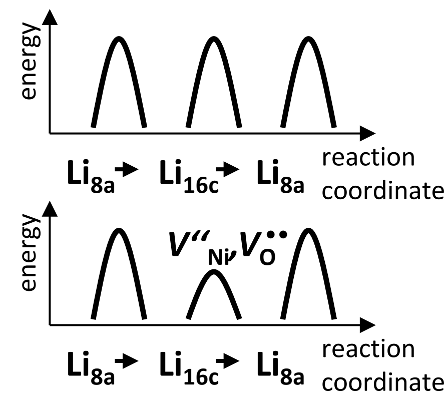


Structure of Ru-doped $LiNi_{0.5}Mn_{1.5}O_4$ (Fd-3m)

(⁷Li-NMR @ 400 MHz, 67 kHz MAS)



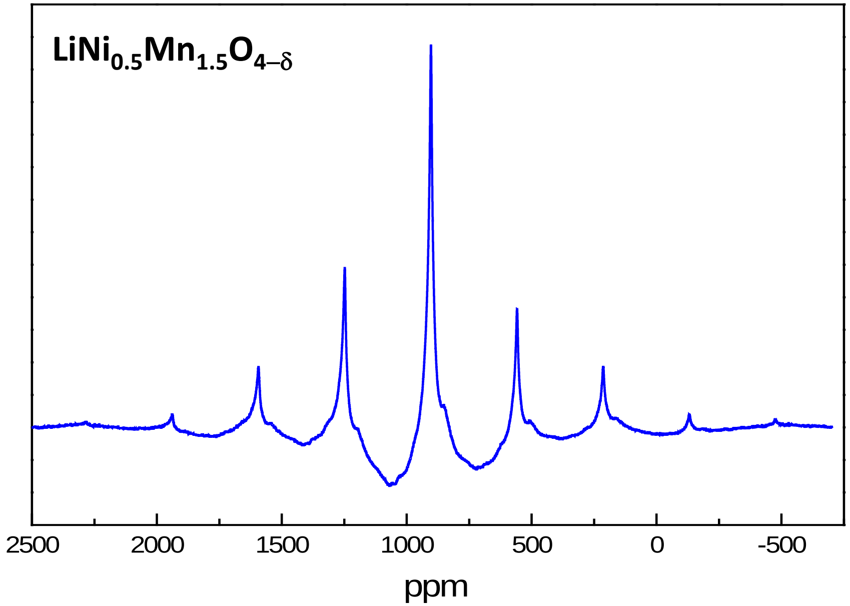


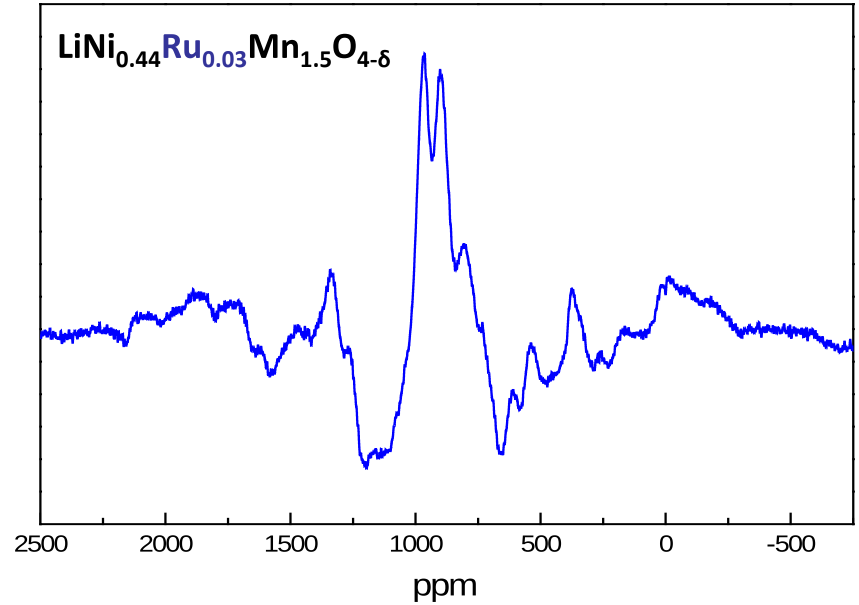


$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials

Li-mobility in RuO_2-doped LNMO – MAS-NMR

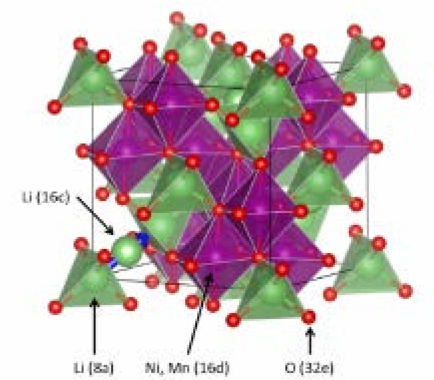
(^{7}Li-NMR @ 400 MHz, 67 kHz MAS)





as function of defect structure:

- modified Li-distribution on lattice sites
- increased Li-mobility



$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials: rate capability

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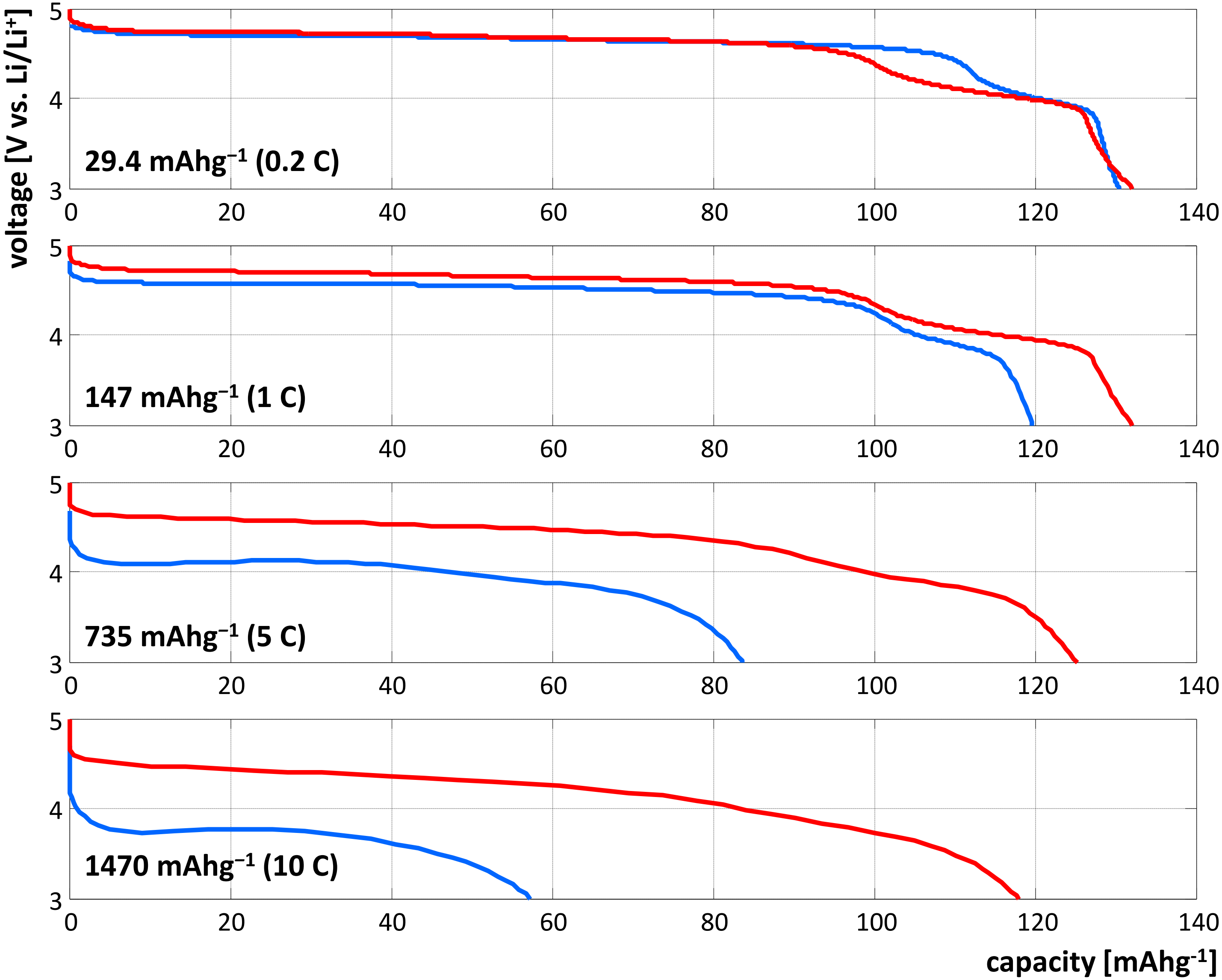
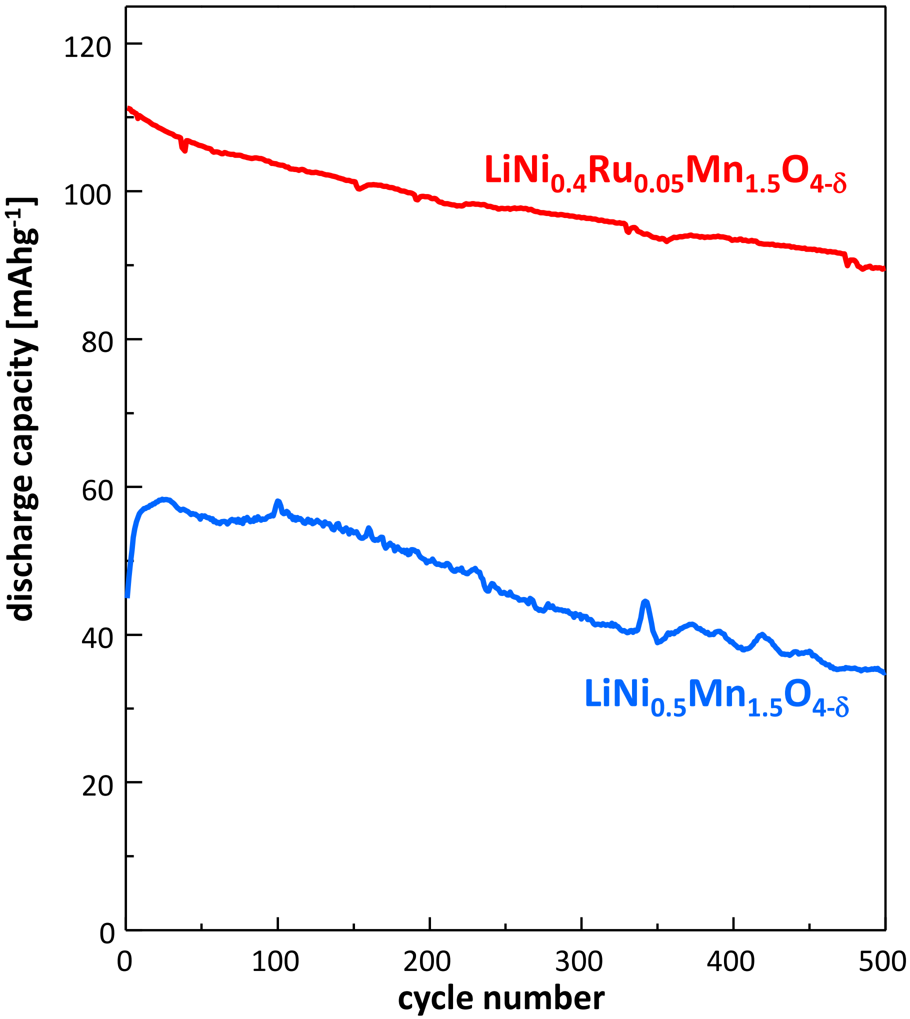


"perfect" spinel (undoped, stoichiometric)

"defect spinel" (RuO_2: $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$)

P. Jakes, H. Wang, Y. Feng, L. Li, K. Nikolowski, H. Ehrenberg, R.-A. Eichel, submitted

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials: capacity retention @ 10 C



P. Jakes, H. Wang, Y. Feng, L. Li, K. Nikolowski, H. Ehrenberg, R.-A. Eichel, submitted

pros:

- increased amount of conduction electrons
  (i.e. electronic conductivity)
- increased amount of cation vacancies: enhanced Li^+-diffusion rates
  (i.e. ionic conductivity)

cons:

- oxygen non-stoichiometry, i.e. Mn^{3+}-oxydation states responsible for capacity fading
  ($\Rightarrow$ developing co-doping strategies)

$LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials: enhanced capacity retention with co-doped $Li[Ni_{0.5}Mn_{1.4}Fe_{0.1}][O_{3.8}F_{0.2}]$

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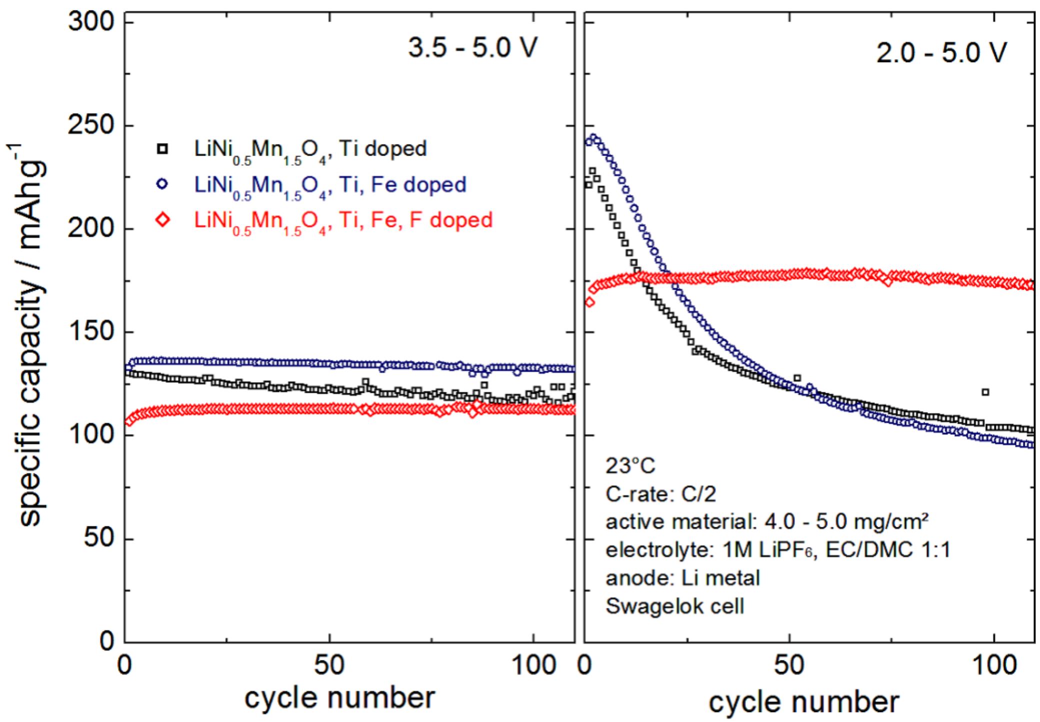
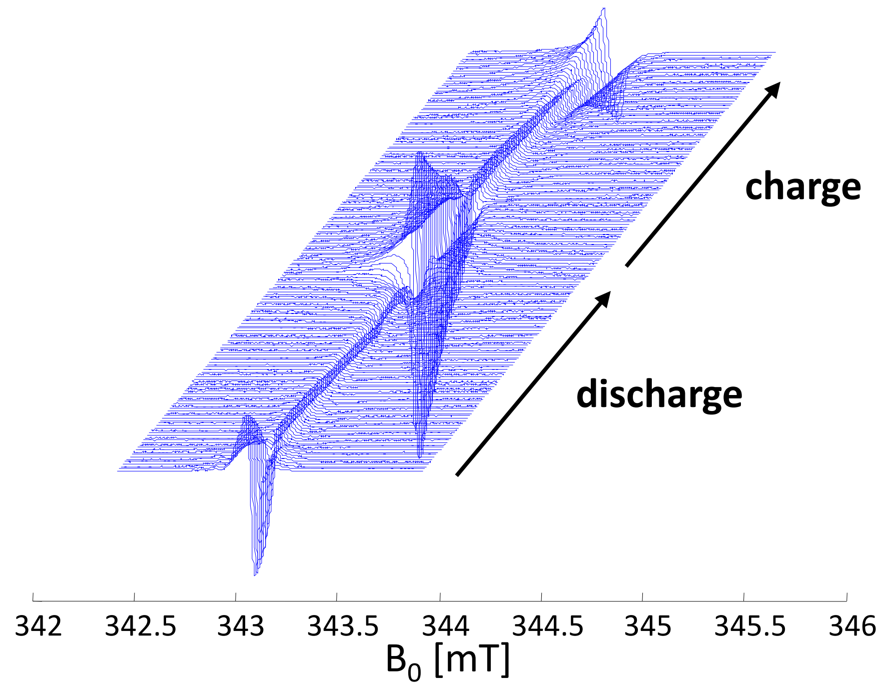
capacity retention



‚in-operando' EPR



P. Jakes, S. Glatthar, J. Binder, R.-A. Eichel, in preparation

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Prof. Dr. Yair Ein-Eli, Technion

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‚Nano-scale engineered electrolytes for high-energy density batteries‘

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Prof. Dr. Yair Ein-Eli, Technion

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*as of September 2013

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