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Titanium substituted $LiCoTi_xMn_{1-x}O_4$ ($0.04 \leq x \leq 0.16$):

High-Voltage cathode materials for Li-Ion Batteries

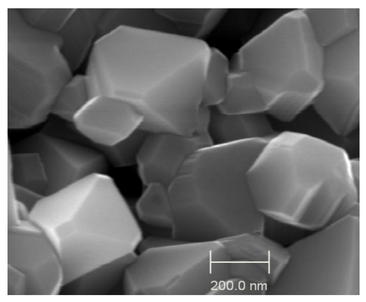
Christoph Dräger[1], Sylvio Indris[1], Aiswarya Bhaskar[1], Helmut Ehrenberg[1]

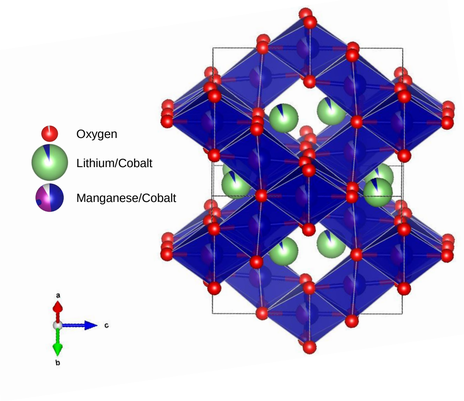
[1]Karlsruher Institut für Technologie (KIT), Institut für Angewandte Materialien (IAM-ESS), 76344 Eggenstein-Leopoldshafen, Germany

Motivation

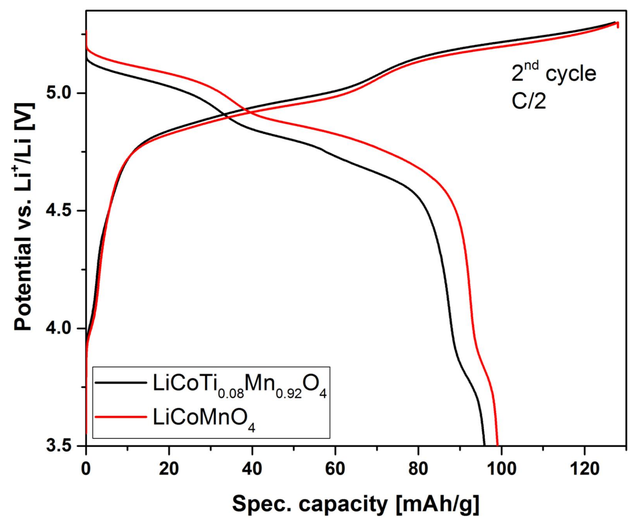
- The specific capacity and operating potential of commonly used high-rate $LiMn_2O_4$ spinel cathode material is low which leads to an inferior energy density when combined in a LIB.
- The operating potential and specific capacity of a Mn-based spinel can be raised by substituting Mn^{3+} with Co^{3+}.
- Substituting Mn^{4+} with Ti^{4+} could reduce the formation of Mn^{3+} and therefore could reduce the oxygen loss during cycling, which improves the structural stability of the active material.

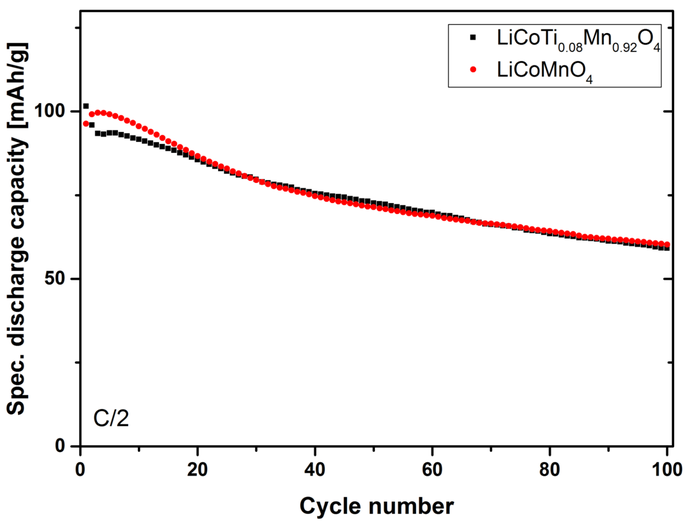
Morphology

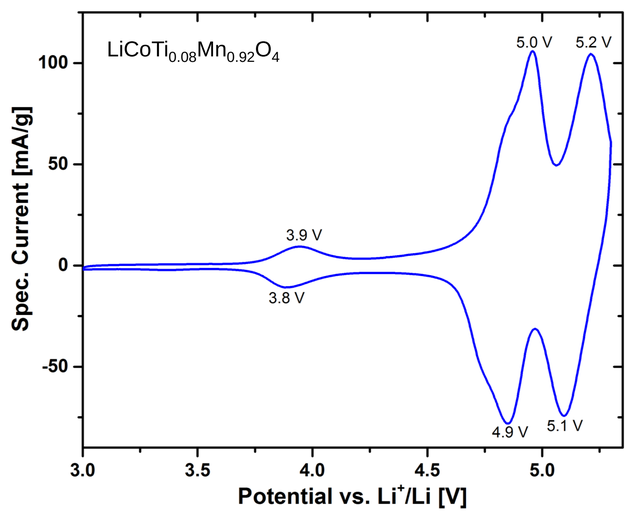




Electrochemical investigations

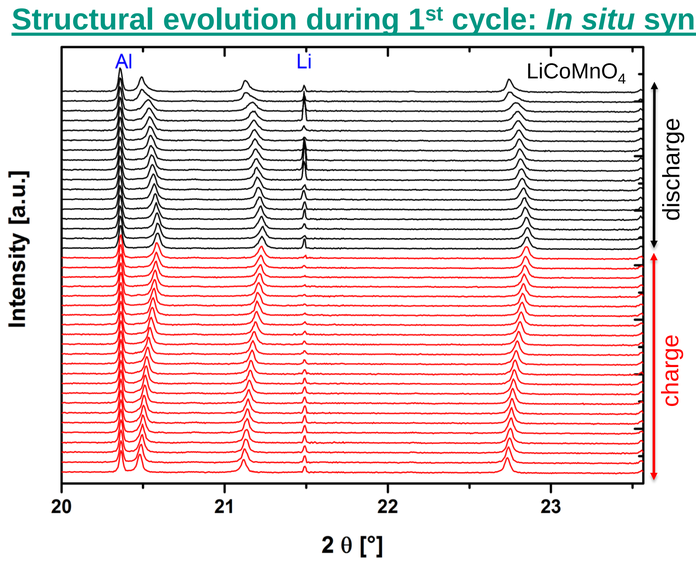


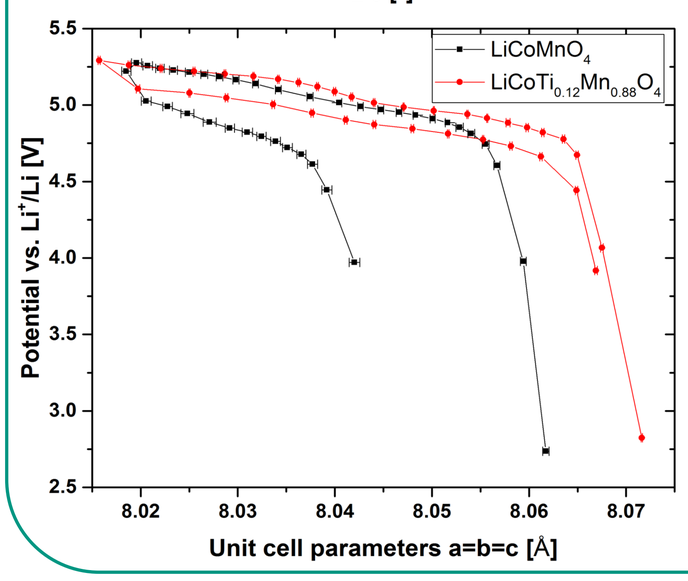




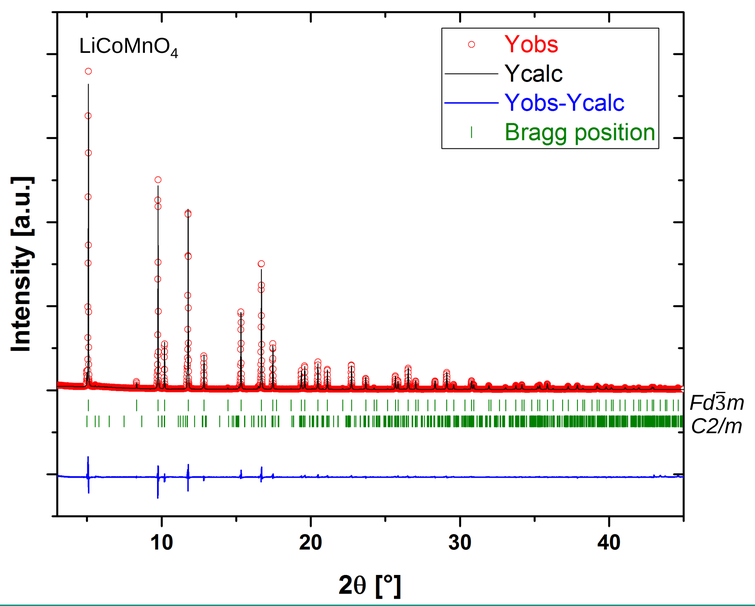
- Galvanostatic cycling against a Li-anode reveals a reversible discharge potential around 5.0 V with a spec. capacity of up to 100 mAh/g.
- CV measurements reveal a polarization of 0.1 V.

Structural evolution during 1st cycle: *In situ* synchrotron powder diffraction

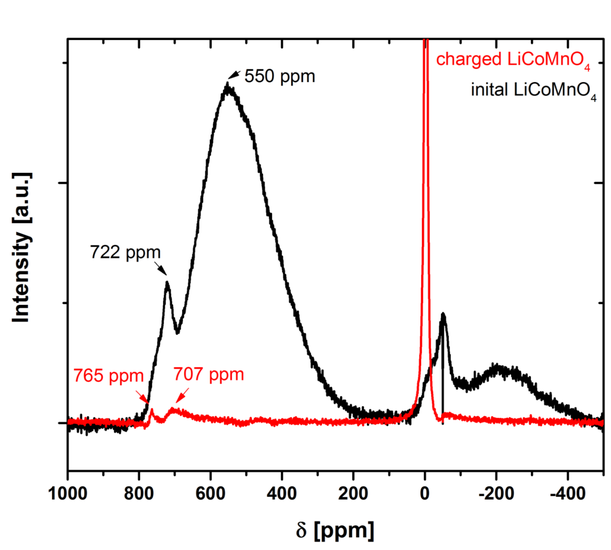




- $LiCoMnO_4$-based cathode materials were investigated via *in situ* synchrotron powder diffraction. All materials show the same solid-solution behavior during cycling.
- The lattice parameters do not return to their initial state after one full cycle and indicates irreversible changes in the spinel lattice which in turn leads to capacity losses.
- Rietveld refinement results of the initial materials confirm the spinel phase (SG $Fd\bar{3}m$) as the main phase. Small amounts of impurity can be identified as Li_2MnO_3 (SG: *C2/m*).



^{7}Li-MAS NMR



^{7}Li-MAS-NMR of $LiCoMnO_4$ shows 2 separated peaks. After the charge process (delithitiation), the intensity of NMR-signal is drastically reduced and the peaks are slightly shifted.

Acknowledgment

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Summary and conclusions

- Ti^{4+}-substituted $LiCoTi_xMn_{1-x}O_4$ ($0.04 \leq x \leq 0.16$) can be successfully synthesized by a sol-gel method.
- Electrochemical cycling reveals a reversible capacity above 5.0 V with and without Ti-substitution. No electrochemical activity regions corresponding to Ti are observed.
- The $LiCoTi_xMn_{1-x}O_4$ ($0.04 \leq x \leq 0.16$) materials show a solid-solution mechanism of Li intercalation/deintercalation irrespective of the dopant amounts.