

Titanium substituted $\text{LiCoTi}_x\text{Mn}_{1-x}\text{O}_4$ ($0.04 \leq x \leq 0.16$): High-Voltage cathode materials for Li-Ion Batteries

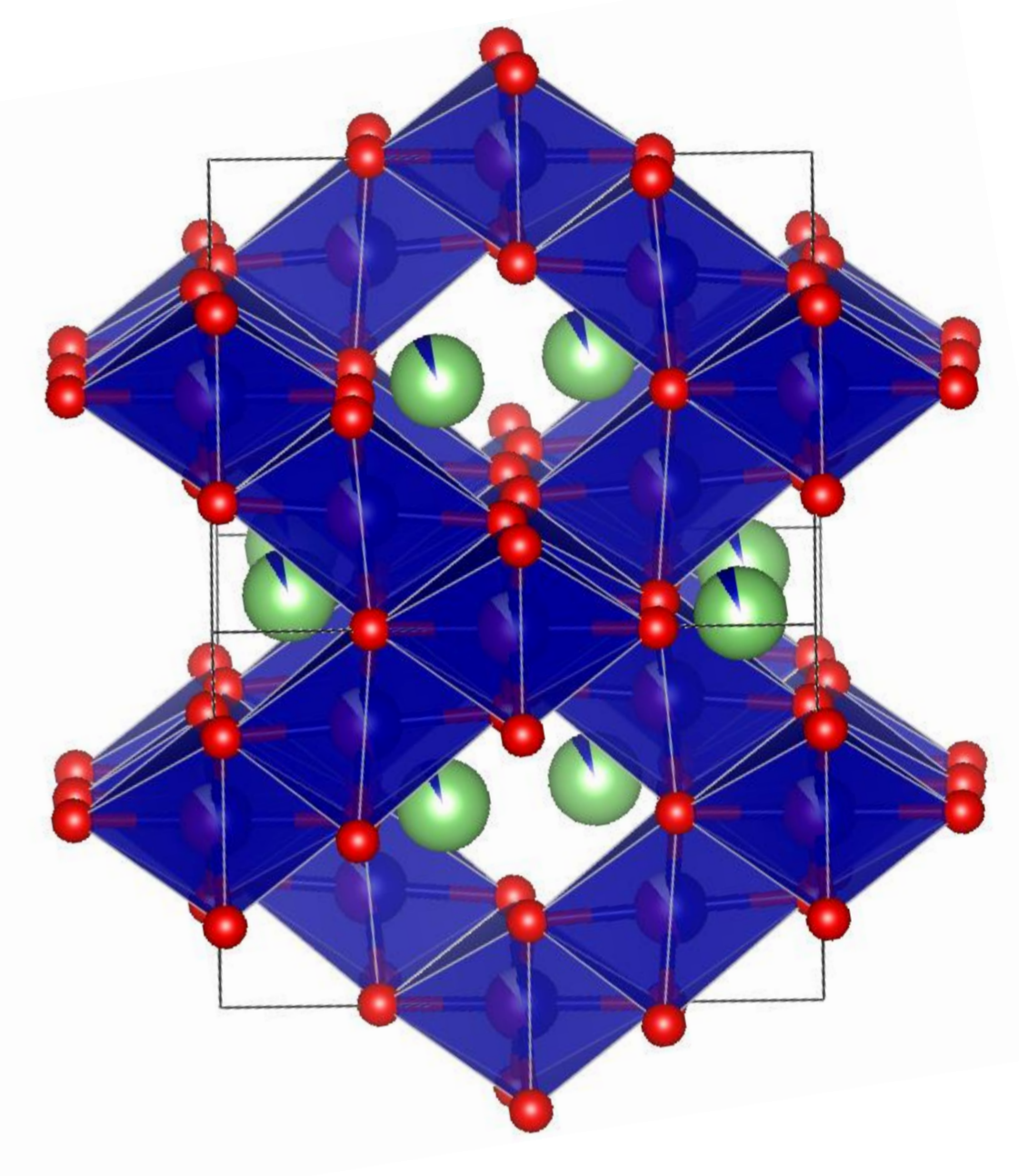
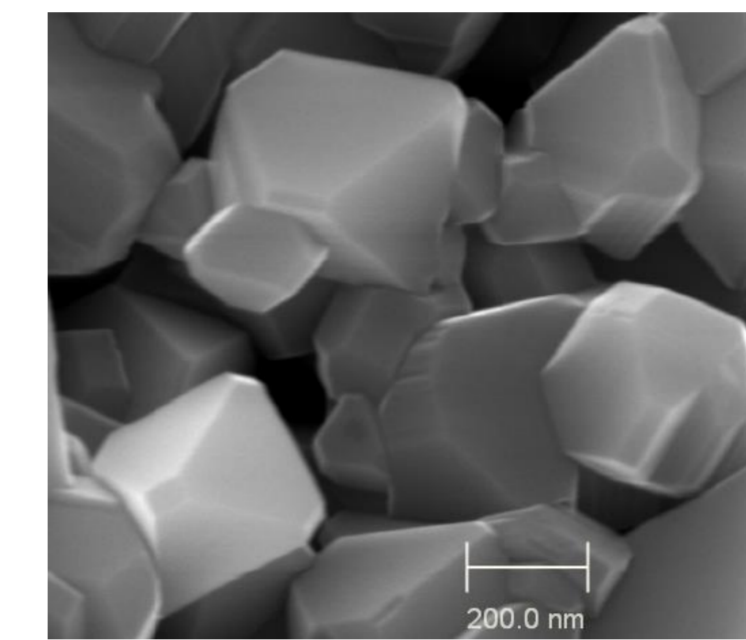
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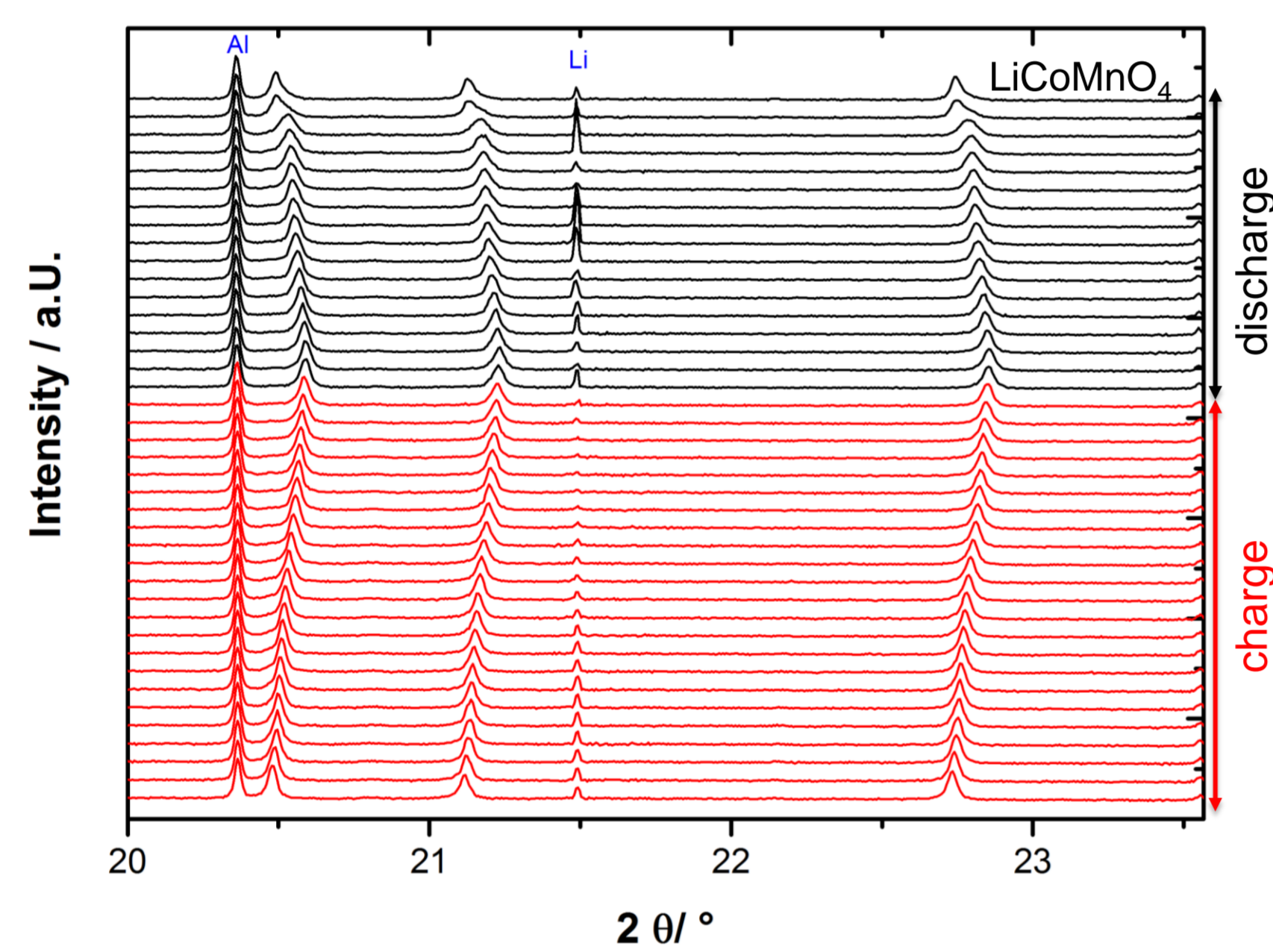
Motivation

- Batteries are essential for stationary as well as mobile energy storage applications.
- Li-Ion Batteries offer high energy and power densities as well as good cycling stability.
- The specific capacity and operating potential of commonly used high-rate LiMn_2O_4 spinel material is low which leads to an inferior energy density when combined in a LIB.
- The operating potential of a Mn-based spinel can be raised by substituting Mn^{3+} with Co^{3+} , which leads to a high energy density when combined in a Li-Ion Battery.

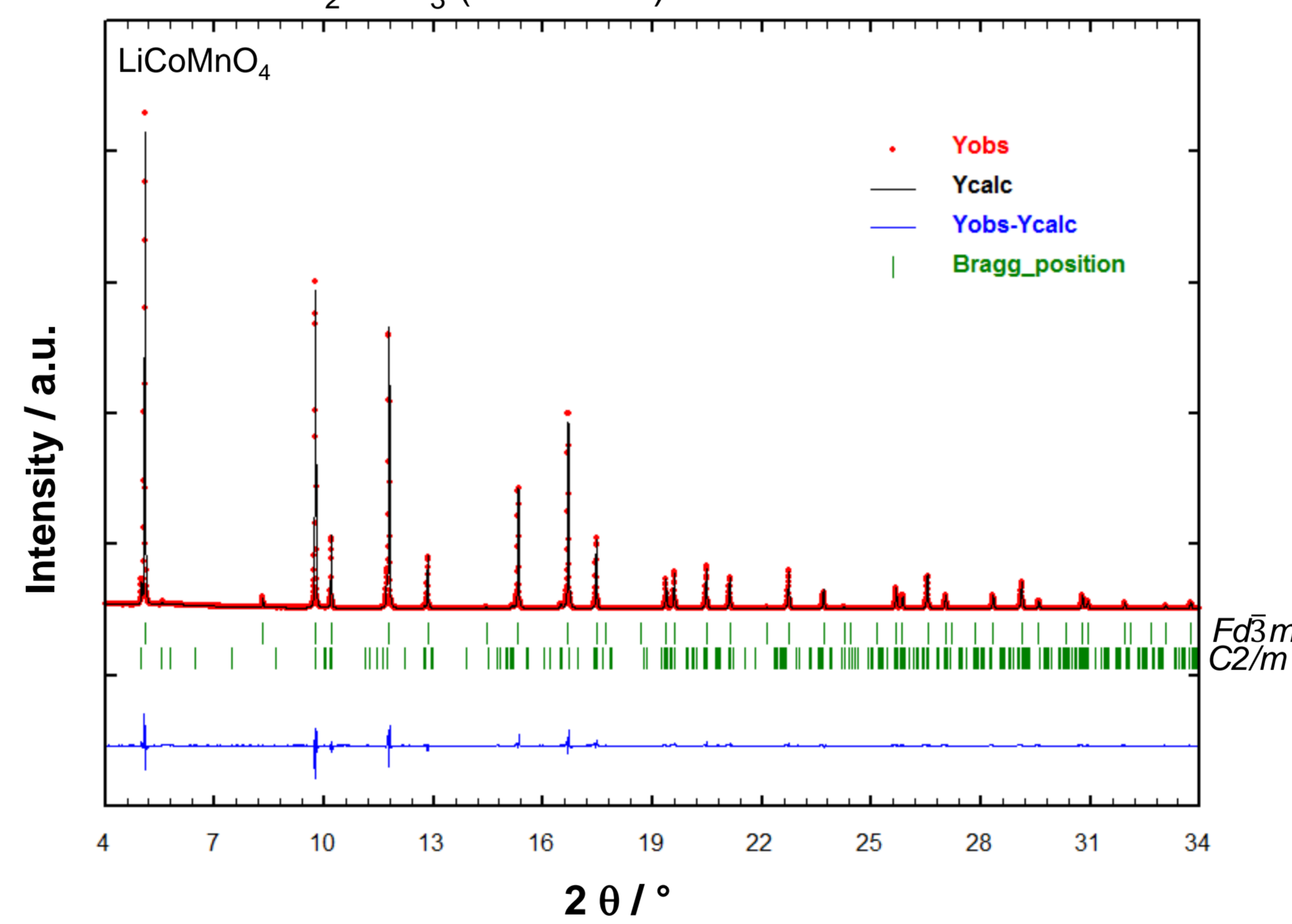
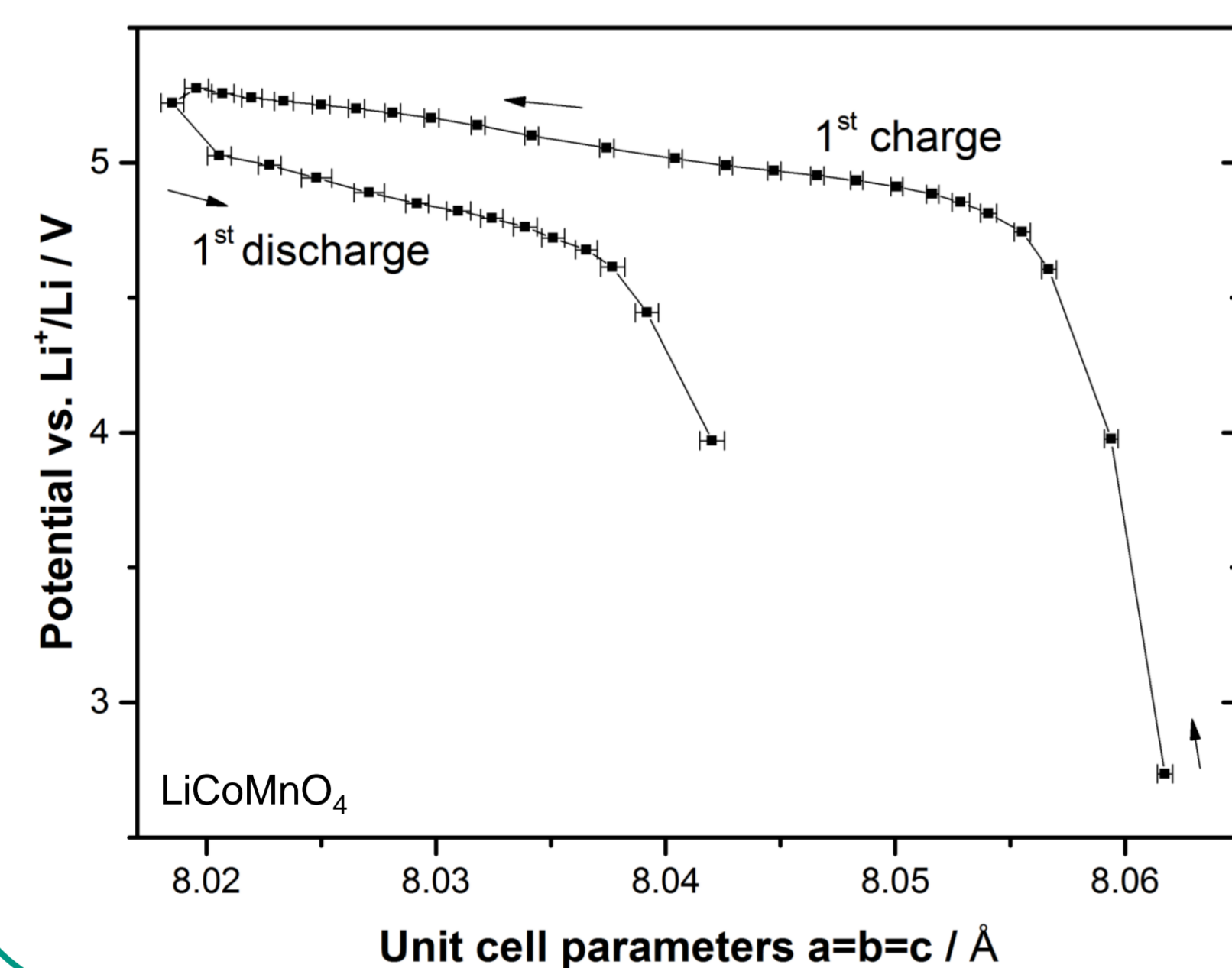
Morphology



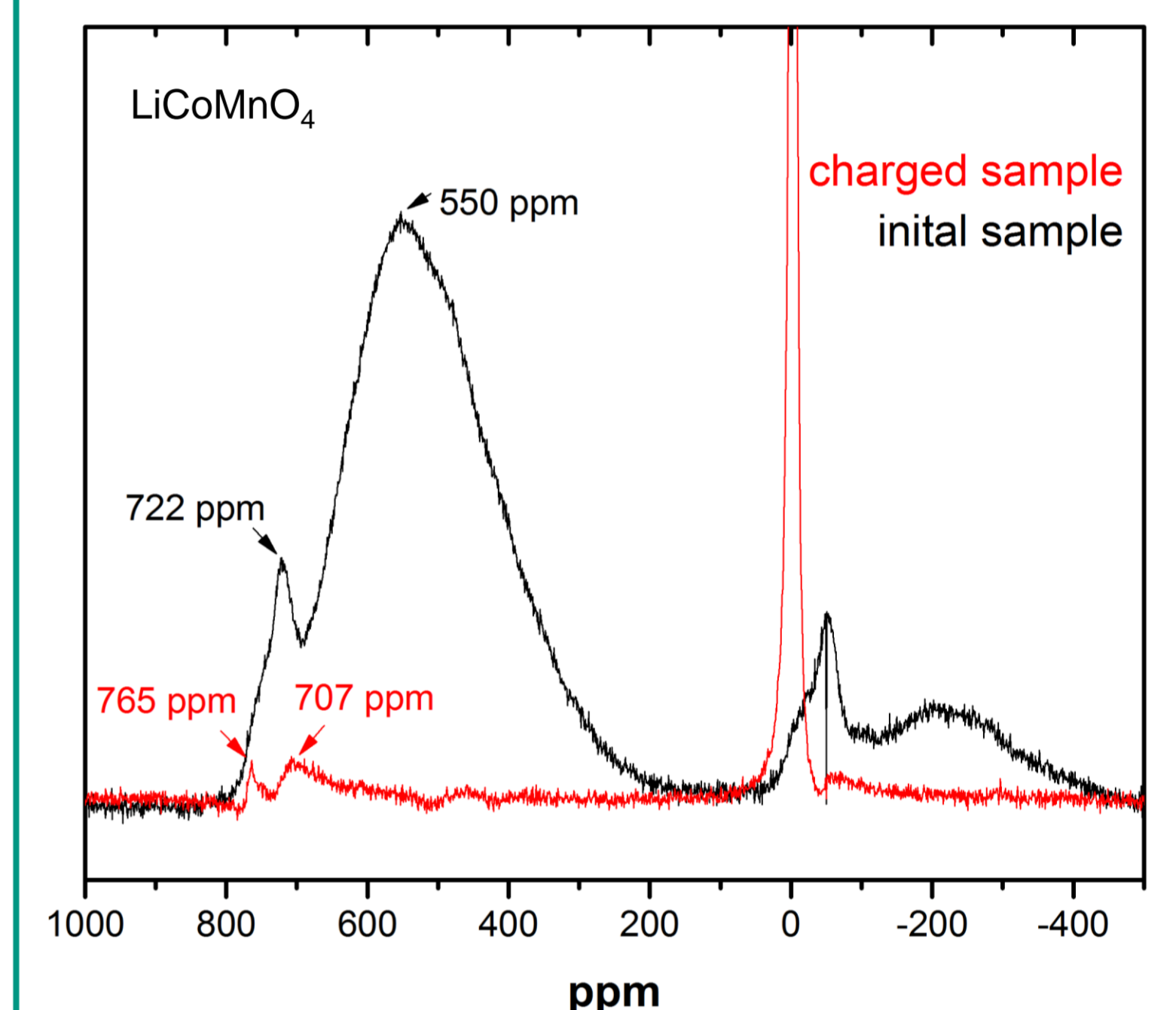
Structural evolution during 1st cycle: *In situ* synchrotron powder diffraction



- 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: $C2/m$).

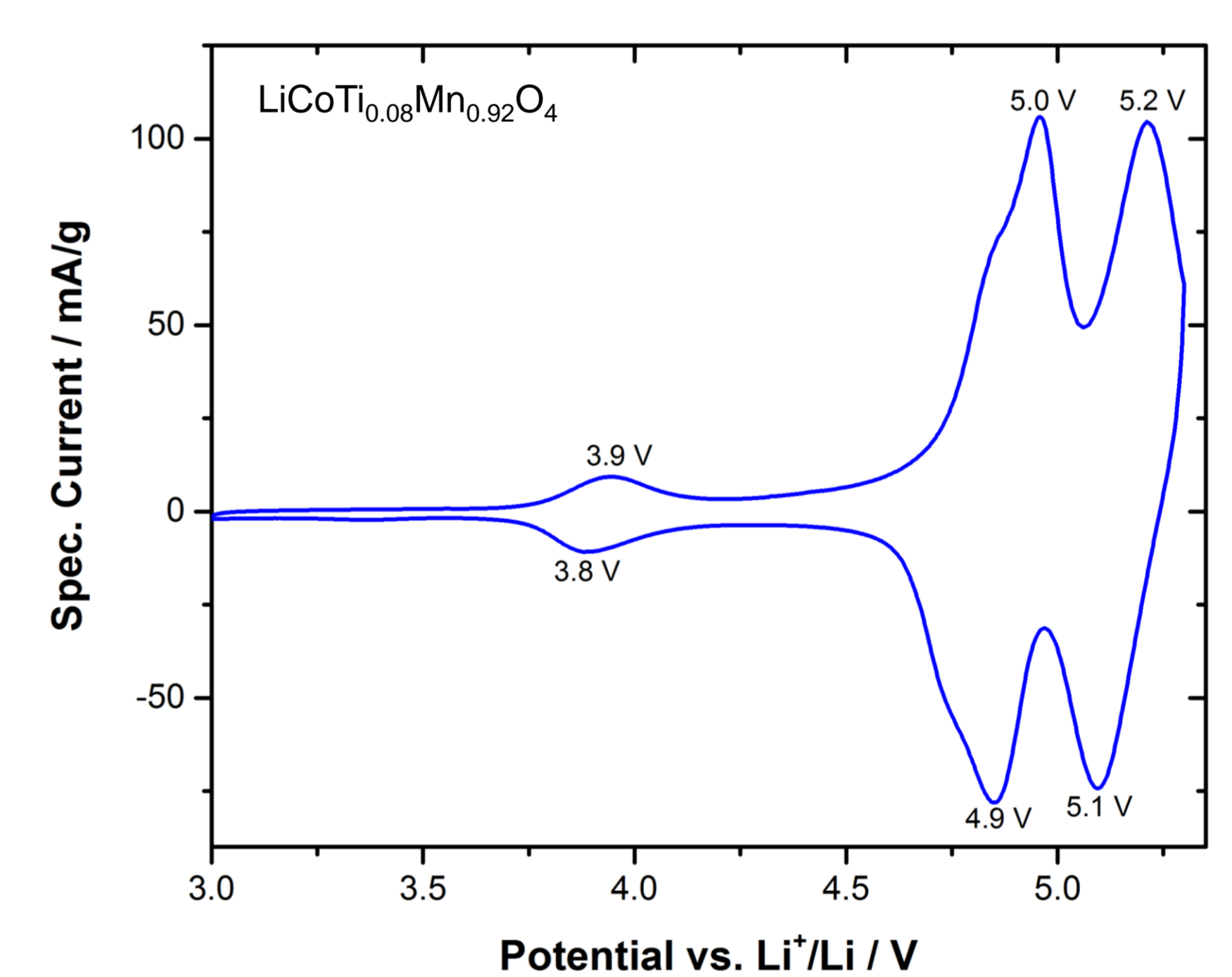
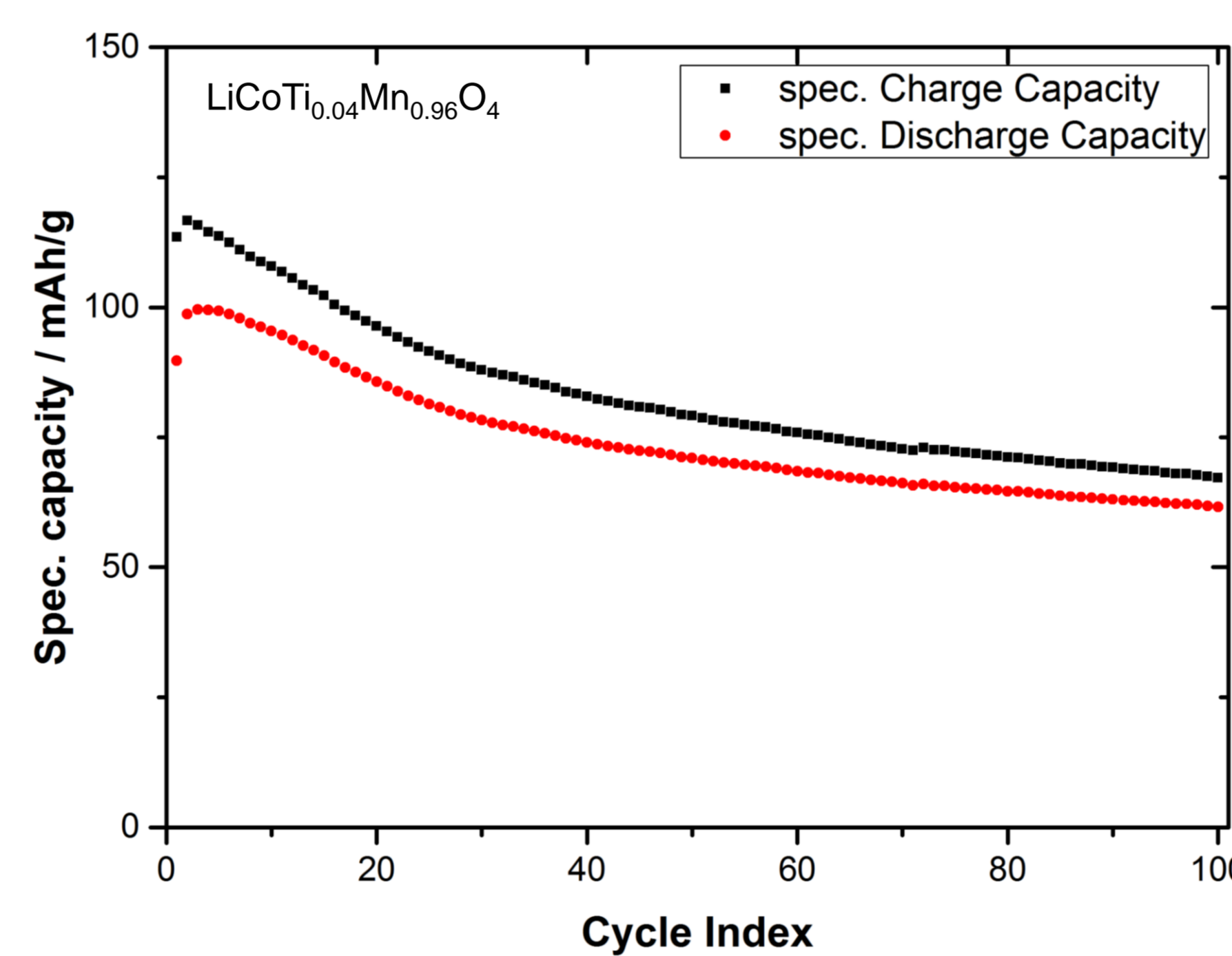
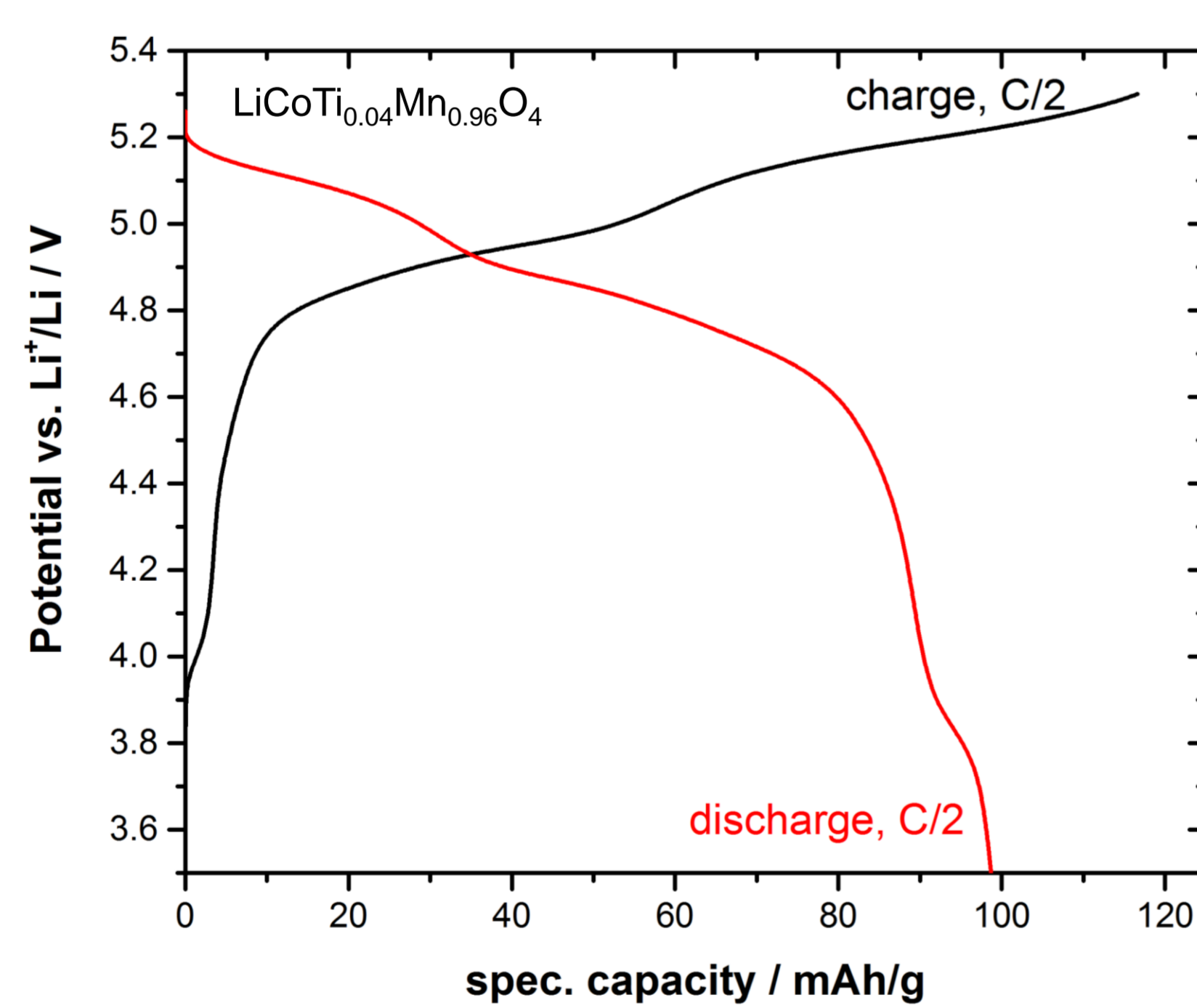


⁷Li-MAS NMR



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

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.

Summary and conclusions

- Ti^{4+} -substituted $\text{LiCoTi}_x\text{Mn}_{1-x}\text{O}_4$ ($0.04 \leq x \leq 0.16$) can be synthesized by a sol-gel method.
- Electrochemical cycling reveals a reversible capacity above 5.0 V.
- The $\text{LiCoTi}_x\text{Mn}_{1-x}\text{O}_4$ materials show a solid-solution mechanism of Li intercalation/deintercalation irrespective of the dopant amounts.

Acknowledgment

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