

Lithium-excess Cathode Ceramics: EC-Performance and Nanostructure

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Project B4

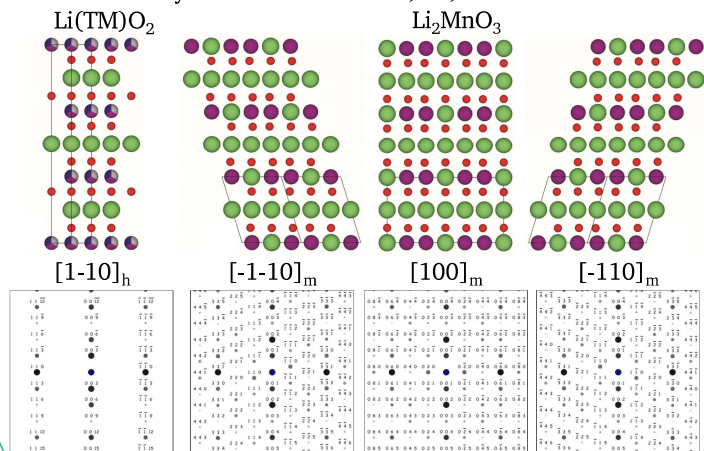
Motivation

Rechargeable Lithium Ion Batteries (LIB) are nowadays the most important energy source for mobile electronic devices. The established LIB technology based on LiCoO_2 cathode active material has reached its physical capacity limit and new materials need to be developed for the next generation of LIBs. Much research is dedicated to the integrated structures of Li_2MnO_3 and Li(TM)O_2 ($\text{TM} = \text{Ni, Co, Mn}$) because of its potential to house reversible capacities $> 250 \text{ mAhg}^{-1}$ [1]. The nanostructure of these blends is very complex and highly depends on the synthesis conditions [2]. For this study, two integrated structures with the same nominal composition of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ were synthesized. Transmission electron microscopy (TEM) was used to analyze the nanostructure of two pristine powders and coin cells have been fabricated to measure the electrochemical (EC-) performance. The discrepancies in the EC-performance can be interpreted as a result of the nanostructural constitution.

The integrated structures

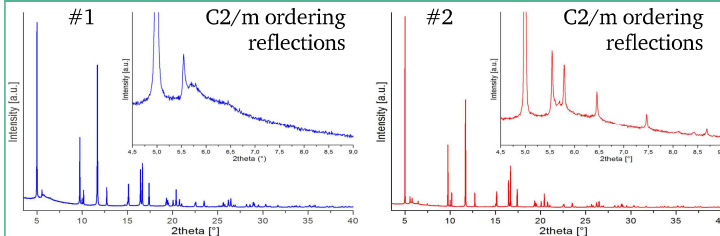
The Li(TM)O_2 crystallizes in the R-3m spacegroup and the Li_2MnO_3 in the C2/m symmetry. The phases are integrated in a cubic close packed oxygen lattice and differ in the cation ordering on the octahedral sites. Rotational stacking faults of the Li_2MnO_3 phase are common in this system.

● Ni, Co, Mn ● Mn ● Li ● O



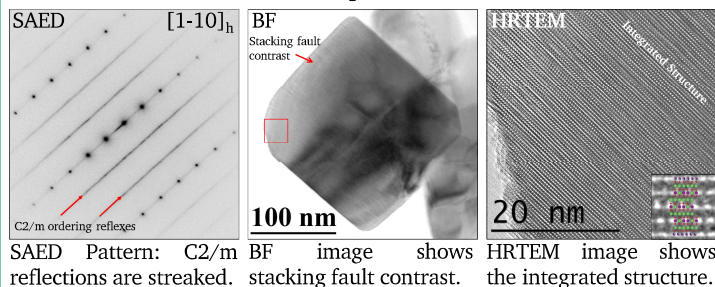
The corresponding simulated selected area electron diffraction pattern (SAED) are displayed under the structure model.

Results: XRD and TEM Analysis



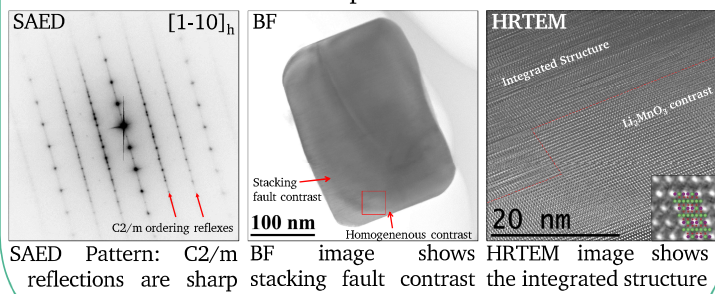
Synchrotron XRD-pattern of sample #1 and #2: both pattern show a Warren-shaped reflexes of the C2/m ordering reflections caused poor translational symmetry in c-direction. Sample #2 exhibits additional sharp reflections indicating parts with higher crystallinity [3,4].

Sample #1



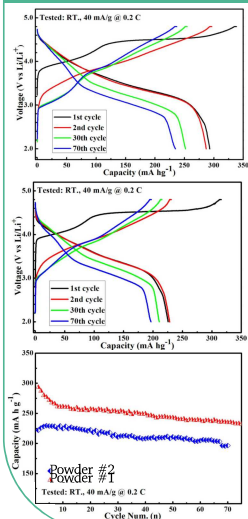
SAED Pattern: C2/m reflections are streaked. BF image shows stacking fault contrast. HRTEM image shows the integrated structure.

Sample #2



SAED Pattern: C2/m reflections are sharp and streaked. BF image shows stacking fault contrast with parts of homogeneous contrast. HRTEM image shows the integrated structure and pure Li_2MnO_3 like regions.

Results: EC-Measurements



Voltage profile of powder #1:

- Characteristic first cycle profile with plateau at 4.5 V
- Reversible capacity $> 250 \text{ mAhg}^{-1}$ for the first 30 cycles
- Voltage and capacity fade accompanied with change to strong spinel-like characteristic in voltage profile

Voltage profile of powder #2:

- Characteristic first cycle profile with plateau at 4.5 V
- Reversible capacity $< 250 \text{ mAhg}^{-1}$
- Voltage and capacity fade accompanied with change to minor spinel-like characteristic in voltage profile

Capacity retention plot of powder #1 and #2:

- Capacity $> 250 \text{ mAhg}^{-1}$ for powder #1 decreases fast in first ten cycles and fades slower upon extended cycling
- Small increase of capacity for powder #2 then continuous capacity fade upon extended cycling

Conclusion

The two active materials were characterized by their EC-performance and by their nanostructure. Sample #1 has good EC-characteristics and the two phases are finely integrated on the nanometer scale. Sample #2 is composed of phase integrated and monoclinic parts. The monoclinic structure is believed to be EC-inactive explaining the low first cycle capacity [5]. Because of the phase segregation, the EC-active integrated structure has a higher Li(TM)O_2 content making it less susceptible to spinel formation [6].

Literature

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- [2] Boulineau, a., Croguennec, L., Delmas, C. & Weill, F. *Solid State Ionics* **180**, 1652–1659 (2010).
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- [5] Yu, D. Y. W., Yanagida, K., Kato, Y. & Nakamura, H. *J. Electrochem. Soc.* **156**, A417 (2009).
- [6] Johnson, C. C. S., Li, N., Lefief, C., Vaughey, J. T. & Thackeray, M. M. *Chem.* **2**, 6095–6106 (2008).