

Electron microscopy investigations on the fatigued cathode composite of commercial 18650-Li-ion cells

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SEM Characterisation

Uncycled Cathode Composite

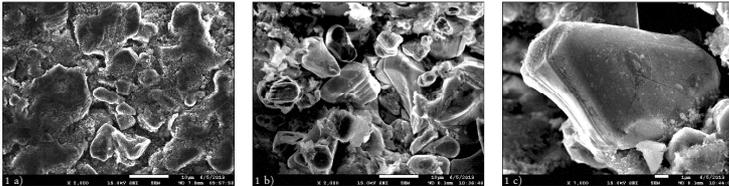


Fig 1: a) Top view of the cathode composite of the uncycled LIB. Adhesion of binder to LiCoO_2 is good.

b) Cross sectional view of the cathode composite. Less binder material in the bulk than on the surface.

c) Close-up of a LiCoO_2 grain. The layer structure and the absence of major cracks is visible.

Cycled Cathode Composite

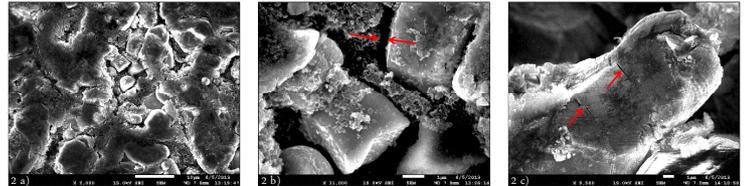


Fig 2: a) Top view of the cathode composite of the cycled LIB.

b) Detail of the binder adhesion. A gap between the binder and the LiCoO_2 ceramics is marked with red arrows.

c) Close-up of a LiCoO_2 grain. The particle is heavily fractured.

Introduction: For this study, commercially available 18650-Li-ion batteries (LIB) were analyzed with electron microscopy. The aim of this work is to identify effects in the cathode composite responsible for the capacity fade during cycling. The active cathode material is layered LiCoO_2 . From previously published literature, it is known that Co ions migrate from the transition metal layer to the Li-ion layer which finalizes in the formation of a spinel phase [1][2]. Another detrimental effect is the formation of microcracks and the introduction of a turbostratic disorder in the layered structure [1][2]. These effects were found in lab fabricated LIBs with industrial or self-synthesized material. Here, commercial LIBs were used to verify these effects in real life devices.

Experimental: A fresh ($z = 0$ cycles) and a cycled ($z = 600$ cycles) 18650-LIB were opened under Ar-atmosphere and the cathode composite rinsed with DMC. For the scanning electron microscopy (SEM) analysis, the cathode composite was cut with a scissor and glued to a carbon pad. For the transition electron microscopy (TEM) studies, different sample preparation approaches were conducted. Powder samples were prepared by dissolving the PVDF in NMP to extract the LiCoO_2 . For ion milling, a TEM-Cu-ring was glued to the cathode composite and gently detached from the Al current collector. For the ultramicrotomy samples, the cathode composite was embedded into epoxy-resin. With a diamond knife, slices of 100 nm thickness were cut.

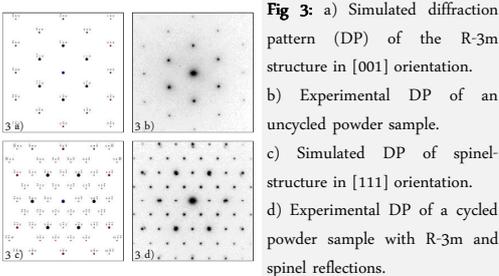


Fig 3: a) Simulated diffraction pattern (DP) of the R-3m structure in [001] orientation.

b) Experimental DP of an uncycled powder sample.

c) Simulated DP of spinel-structure in [111] orientation.

d) Experimental DP of a cycled powder sample with R-3m and spinel reflections.

- Literature:**
- [1] Wang, H. et al., TEM Study of Electrochemical Cycling-Induced Damage and Disorder in LiCoO_2 Cathodes for Rechargeable Lithium Batteries. *Journal of The Electrochemical Society* **146**, 473–480 (1999).
 - [2] Gabrisch, H et al., Hexagonal to Cubic Spinel Transformation in Lithiated Cobalt Oxide. *Journal of The Electrochemical Society* **151**, A891 (2004).
 - [3] Vetter, J. et al., Ageing mechanisms in lithium-ion batteries. *Journal of Power Sources* **147**, 269–281 (2005).

TEM Characterisation

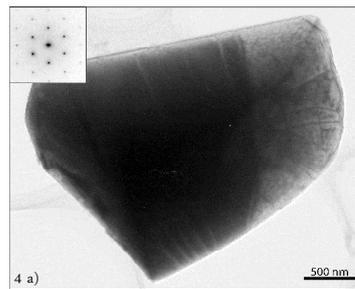
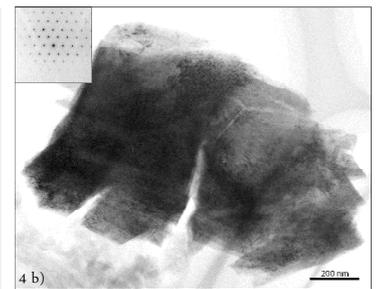


Fig 4: a) TEM micrograph of an uncycled LiCoO_2 particle.

No cracks and some dislocations are visible. The DP shows the R-3m phase.



b) TEM micrograph of the cycled LiCoO_2 . The particle is heavily fractured and the DP shows the existence of the spinel phase.

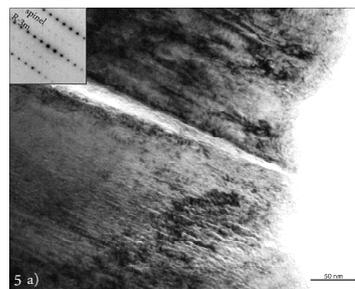


Fig 5: a) Bright field image of a cycled sample prepared by ion milling. The DP shows the R-3m [120] reflections and the spinel in [121] orientation.

b) Dark field image for a selected spinel reflex. The excited areas are the spinel phase.

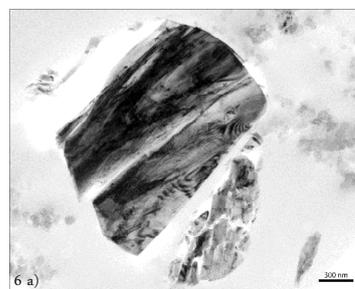
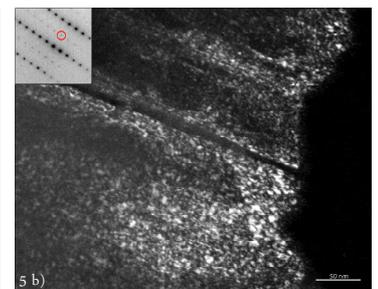
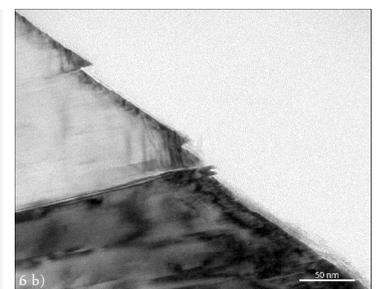


Fig 6: a) Ultramicrotomy slice of a LiCoO_2 grain with binder. Picture proves that ultramicrotomy is a suitable method to obtain cross sections of the cathode composite.

b) With ultramicrotomy it is possible to retain surface layers of the LiCoO_2 .



Conclusions: The electron microscopy analysis shows the detrimental effects of electrochemical cycling of the LIB to the cathode composite and the structure of the active ceramic LiCoO_2 . The effects which were previously found in lab fabricated cells, such as the cracking of the particles and a structural conversion from the R-3m structure to a spinel structure, can also be found in the cycled commercial 18650-LIBs. Additionally, problems with the electronic contact inside the cathode composite can be assumed due to the formation of voids between the active ceramic and the conductive carbon black/binder composite. This binder break-off has been stated by Vetter et al. [3] as a capacity fade mechanism, caused by the volume changes of the LiCoO_2 during Li deintercalation and intercalation or by binder corrosion. Furthermore we have shown that ultramicrotomy is a suitable method to prepare TEM cross-section samples of the cathode composite.