Investigating the formation of surface reconstruction layers in Ni-rich cathode materials using STEM

Lara Ahrens[1,2], Kilian Vettori[3], Dr. Shibabrata Basak[4], Prof. Dr. Rüdiger-A. Eichel[4], Prof. Dr. Joachim Mayer[1,2]
[1]Central Facility for Electron Microscopy (GFE), RWTH Aachen University, Aachen, Germany, [2]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, Jülich, Germany, [3]Physical-Chemical Institute, Justus-Liebig-University, Gießen, Germany, [4]Institute of Energy and Climate Research (IEK-9), Forschungszentrum Jülich , Jülich, Germany

Background incl. aims

Lithium-ion batteries (LIB) are a key technology towards an emission-reduced transportation sector, in particular for electrical vehicles (EVs). One of the most promising cathode materials for LIBs are Ni-rich NMC cathode materials (LixNiyMnzCo1-y-zO2, with $x > 0$, $y > 0.6$). The main benefits of Ni-rich cathodes are an increased capacity, a high energy density and lower cost compared to conventional LIBs, which are needed to push the mileage limit and to make EVs more affordable. Although the advantages are great, Ni-rich NMC suffers from thermal and structural instabilities leading to a shorter life time and server capacity fading. The main degradation mechanisms occurring in NMC are: formation of surface reconstruction layer, formation of cathode-electrolyte interface (CEI), degradation of electrolyte and cracking of particles. [1,2]

This study focuses on the formation of surface reconstruction layer, specifically on the phase transition from layered structure (space group R-3m) to rocksalt phase (space group Fm-3m). [3] In the rocksalt phase the transition metals occupy the Li-positions and thus block the Li-diffusion paths. [4] A core-shell model describes the growth of this surface reconstruction layer, in which the degradation starts at the top of the surfaces and propagates into the bulk. [4] The aim of this study is to observe the phase change from layer structure to rocksalt structure and provide an answer to the questions: Does the rocksalt layer grow over time while the cell is kept under the harsh conditions of 4.5V and if so, is a trend in thickness growth of the rocksalt layer measurable?

Methods

A set of coin-half-cells against lithium was kept at high voltage of 4.5V for over 30 days. Every 2 days an electrochemical impedance spectroscopy (EIS) measurement was conducted. Afterwards, the cells were dissembled and the cathode sheets were rinsed with solvent. Using FIB-SEM allowed to cut very thin lamellas out of the cycled cathode sheets. However, preparing the sample for analysis presents several challenges. Firstly, the organic binder that surrounds the NMC particles melts faster under the ion-beam, leading to instabilities. Secondly, powder samples tend to redepositing and curtaining due to the pores in between. Finally, NMC is sensitive to the ion-beam, requiring lower voltages to be applied to reduce the amorphous layer on top. STEM was used to image the surface area of the particles down to atomic scale. Since the electron beam affects the NMC material and can lead to a phase transition from layered to rocksalt structure, it is very important to control the dose of the electron beam. [5] In addition, EEL spectra were acquired to provide a better understanding of the degradation process by monitoring the valance states of the transition metals. Moreover, further analytical methods such X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) were applied to investigate e.g. CEI formation.

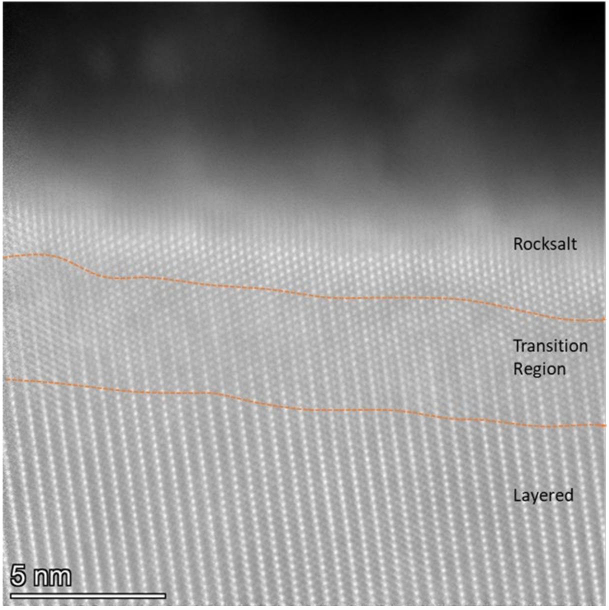
Results

The EIS measurements showed an exponentially growing charge transfer resistance (Rct) which is an easily accessible indicator for degradation. Looking at the particles at atomic scale, the formation of rocksalt was present as depicted in Figure 1. The transition from layered to rocksalt appeared gradually and a typical transition region was visible. Interestingly, the variation of the thickness of rocksalt layer varied significantly within a lamella and even within one particle. It could be observed that the surrounding of the surface influenced the tendency to form rocksalt. A comparable, continuous trend in the growth of the surface reconstruction layer, as the Rct suggested, was not evident globally. However, the maximum thickness of degraded surface increased over time.

Conclusion

HRSTEM coupled with EELS provided a great insight into the rocksalt formation. The study indicates that while the core-shell model is generally a valid approximation for describing surface reconstruction in Ni-rich NMC, the real world is more complex. Therefore, it is crucial to comprehend the conditions under which a rocksalt structure is formed. Furthermore, understanding the time-correlation of different degradation mechanisms is crucial to improve battery materials.

Graphic:



Keywords:

Li-ion batteries, degradation, high voltage

Reference:

[1] Dose et al., ACS Energy Lett. 10, 3524–3530 (2022).
[2] Jiang et al., Adv. Energy Mater. 48, 2103005 (2021).
[3] Bak et al., ACS Appl. Mater. Interfaces 6, 24, 22594–22601 (2014).
[4] Jung et al., Adv. Energy Mater. 4, 1300787 (2014).
[5] Lin et al., Sci Rep 4, 5694 (2014).