In-situ TEM Investigation of Degradation Process in Ni-Rich Cathodes.

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Background incl. aims

Lithium-ion batteries have become integral for energy storage in various applications, including electric vehicles, and portable electronics [1]. Cathode materials such as $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC), $LiNi_xCo_yAl_{1-x-y}O_2$ (NCA), $LiCoO_2$ (LCO), and $LiMn_2O_4$ (LMO) are widely used [2]. However, challenges like fast capacity fade, high cost, and poor cycling performance persist. Layered $LiNiO_2$ (LNO) shows promise but suffers from structural changes and oxygen evolution during cycling [3]. During cycling we can identify three distinct stages where, the layered O3 stacking sequence is reduced from trigonal structure with rhombohedral symmetry $R\bar{3}m$ to monoclinic C2/m, then into a layered mixture of O3 and O1 (H2-H3) stacking and further to a rocksalt phase ($Fm\bar{3}m$) [4]. Among all phases, the H2 to H3 transformation results in poor structural stability especially while operating at high voltages [5]. This study aims to investigate the degradation mechanism of LNO cathodes, focusing on its initial O3 stacking sequence.

Methods

The degradation dynamics of LNO cathodes were investigated using in situ electron microscopy, electron energy loss spectroscopy (EELS), and four-dimensional scanning transmission electron microscopy (4D-STEM). This degradation has been monitored in real-time, which traces for the structural changes taking place for Li^+ diffusion and degradation taking place with the chemical composition. A constant potential of +4.3 V was applied and the first delithiation cycle was examined via in situ TEM. On the other hand, EELS contributed to valuable insights regarding the changes of chemical composition during cycling, while 4D-STEM aided in obtaining high-resolution images and analysis of diffraction in order to complete the characterization of structural transformations taking place within the material of the cathode.

Results

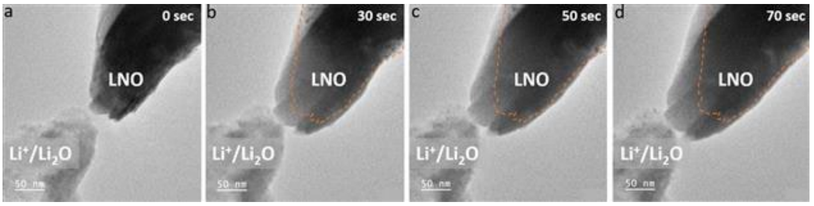
Observations revealed the layered structure of pristine LNO, with cation mixing layers rapidly forming new Ni-rich phases mixed with Li_2O phase near the reaction front and pure NiO species further away. During the first delithiation cycle, expansion occurred as the particle was charged versus a Li metal source as the anode, resulting in increased c lattice parameters and phase transitions from H1 to monoclinic, then to H2 and H3 (representing collapse of the layered structure).

Conclusion

The study sheds light on the degradation mechanism of LNO cathodes with the O3 stacking sequence, elucidating structural and compositional changes during cycling. Future work will focus on comparing simulated and experimental phase reconstruction mechanisms from layered to spinel phases and investigating oxygen loss in LNO cathodes during cycling.

Keywords
Lithium-ion batteries, Ni-rich cathodes, degradation mechanisms, in situ TEM.

Graphic:



Keywords:

Lithium-ion, Ni-rich, degradation, in-situ TEM.

Reference:

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