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# Microstructural Investigation on Degradation Mechanism of Layered $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ Cathode Materials by Analytical TEM/STEM

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Electrochemical performance of lithium ion batteries is associated with structural and chemical stability of electrode materials. Lithium transition-metal oxides has been considered as promising cathode materials for Li ion batteries.[1] $LiNi_xCo_yMn_zO_2$ (NCM) is one candidate for next outstanding cathode materials due to its high capacity and cost effectiveness compared with $LiCoO_2$. However, as the fraction of nickel rises to enhance the charge/discharge capacity, especially $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, cation mixing, which results from the migration of transition metal ions into vacant lithium sites, is accelerated owing to similar ionic radii between nickel and lithium.[2] It leads to lattice distortion and collapse of layered structure and results in capacity fading and poor cycleability and has a difficulty in commercialization despite of its high capacity. However, the inevitable lattice distortions and chemical evolution have not been investigated intensely.

Herein, we report the structural evolution localized at the surface regions through electron diffraction and high resolution imaging analyses with aberration-corrected transmission electron microscopy and scanning transmission electron microscopy.[3] Fig. 1 presents that repetition of volumetric change generates cracks and voids associated with deterioration of electrochemical performance. Structural change is related with (003) intensity in electron diffraction and it can be presented by dark field TEM imaging at a glance. Drastic structural degradation during early cycling is analyzed through high resolution TEM/STEM imaging as shown in Fig. 2. Statistically investigated degree of degradation is related with the electrochemical performance such as rapid capacity and voltage fading. Electron energy loss spectroscopy elucidates that the structural evolution caused by the migration of Ni ions accompanies chemical modification of Mn ions and creation of hole states at the O2p level. This study provides an insight into correlating structural and chemical evolution with degradation mechanism on the battery performances of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode materials [4].

References:

[1] W. Liu *et al.*, Angewandte Chemie **54**, (2015), p.4440-4457.
[2] S.-K. Jung *et al.*, Advanced Energy Materials **4**, (2014), p.1300787.
[3] N. Y. Kim *et al.*, Journal of Power Sources **307**, (2016), p.641-648.
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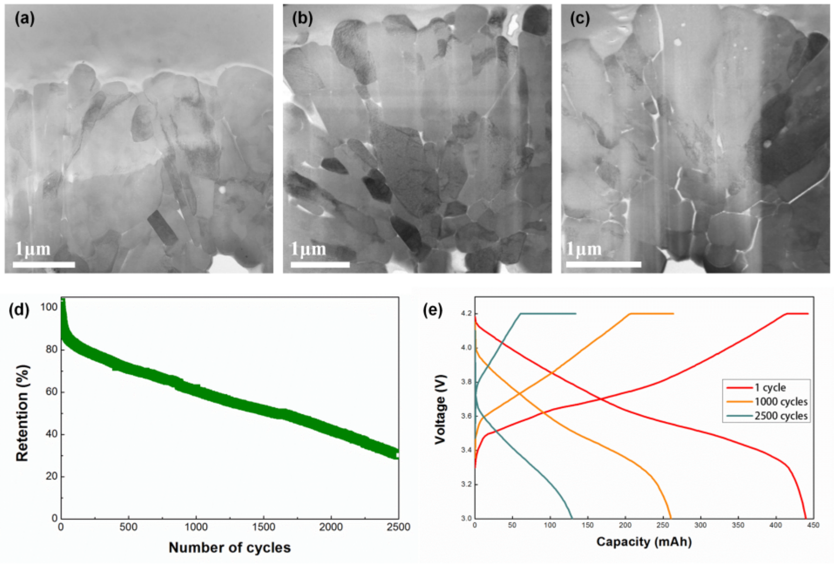
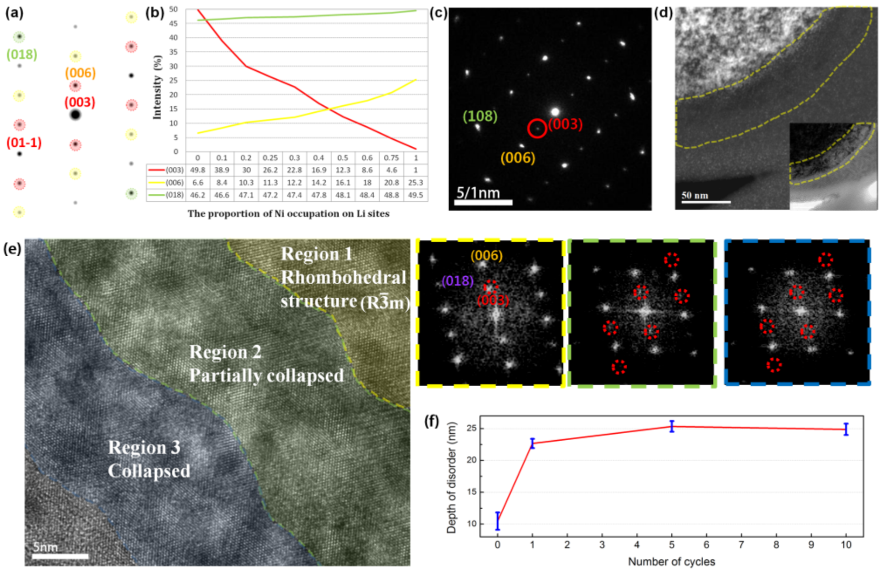


**Figure 1.** (a)-(c) Propagation of cracks and voids between primary particles. (d) and (e) Degradation of electrochemical performance as increase in cycling from pristine to 10 and to 2500 cycles.



| | 0 | 0.1 | 0.2 | 0.25 | 0.3 | 0.4 | 0.5 | 0.6 | 0.75 | 1 |
|---|---|---|---|---|---|---|---|---|---|---|
| (003) | 49.8 | 38.9 | 30 | 26.2 | 22.8 | 16.9 | 12.3 | 8.6 | 4.6 | 1 |
| (006) | 6.6 | 8.4 | 10.3 | 11.3 | 12.2 | 14.2 | 16.1 | 18 | 20.8 | 25.3 |
| (018) | 46.2 | 46.6 | 47.1 | 47.2 | 47.4 | 47.8 | 48.1 | 48.4 | 48.8 | 49.5 |

The proportion of Ni occupation on Li sites

**Figure 2.** (a) and (b) Electron diffraction pattern of layered cathode $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ materials and their intensities variations in accordance with the degree of cation mixing. (c) and (d) Experimental results of electron diffraction and dark field TEM imaging at a (003) reflection. (e) High resolution TEM image and corresponding digital diffractograms present gradual collapse of layered structure toward vicinity of the interface. (e) Graph represents the gradual disordering as increase of cycles.