

ADF-STEM Analysis of Surface Structures in Partially Delithiated Li_xCoO_2 Particles

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Lithium Ion Battery (LIB) is a rechargeable storage device, which has been widely used in many technological applications due to its high energy density. As the application field of LIB expands very rapidly, fundamental understanding of a lithium ion diffusion mechanism becomes crucial to design more efficient and safer electrode materials. LiCoO_2 is a primary cathode material which has layered rock salt structure. Lithium ions can be intercalated or deintercalated through topotactic redox reactions. Previous studies have shown that several phase transitions or structural changes would occur during electrochemical reactions [1-3]. Although charge/discharge properties of Li_xCoO_2 should be largely affected by these phase transitions, the actual lithium ion diffusion mechanism has not been clarified so far. In this study, we analyzed the structural changes of partially delithiated Li_xCoO_2 particles by a combination of XRD, XPS and atomic resolution STEM observations.

Pristine LiCoO_2 powder was chemically delithiated to extract lithium ions uniformly using NO_2BF_4 oxidant (5.1 V vs. Li^+/Li) in acetonitrile solvent. During chemical reactions, the solution was stirred in an argon filled glove box, where the target Li content was set to $x=0.85$. Subsequently, the bulk and surface structures of reaction products were characterized by powder XRD and XPS measurements. For STEM observations, the powders were embedded in epoxy resin and thermally cured at 60 °C. The fixed product was then mechanically ground and finally thinned by cryogenic Ar ion milling. STEM observations were carried out by JEM-ARM 200F (Cold FEG, JEOL Ltd.) at 200kV.

Although the redox potential of NO_2BF_4 is much higher than that of Li_xCoO_2 (3.4 ~ 4.3 V vs. Li^+/Li), XRD patterns showed little difference before and after the chemical reaction. On the other hand, XPS analysis, which is very sensitive to surface structures, clearly showed that Co valence state was changed. These results suggest that the crystal structure was altered only at the particle surface region under the oxidation. Fig. 1 shows high-angle annular dark-field (HAADF) STEM images taken along the [210] direction near the particle surface. Although basic layered structures are almost maintained, bright contrasts can be seen at Li columns. It seems that Li sites are partially occupied by Co atoms after the delithiation. Since lithium ion diffusion is in two-dimensional manner in this material, these anti-site defects could easily block lithium migration paths and hinder further delithiation from inner part of the particle. Moreover, simultaneous low-angle annular dark-field (LAADF) STEM images represent diffuse bright contrasts at the surface region (Fig. 2). Because LAADF images are more sensitive to local lattice distortions, these features indicate that the surface

region is highly structurally distorted. Considering that the phase stability of Li_xCoO_2 would gradually decrease as Li concentration x is reduced, above results suggest that a steep concentration gradient was immediately formed near the surface after the reaction due to the higher redox potential of the oxidant. Because the surface region with low x content is extremely unstable, the structure was transformed into cation-rich thin distorted layers with large strains as observed by LAADF STEM imaging. The observed surface structural changes by chemical delithiation may be regarded as a structure degradation of the cathode by high-rate charging, important to be considered for boosting charge in LIB systems.

References

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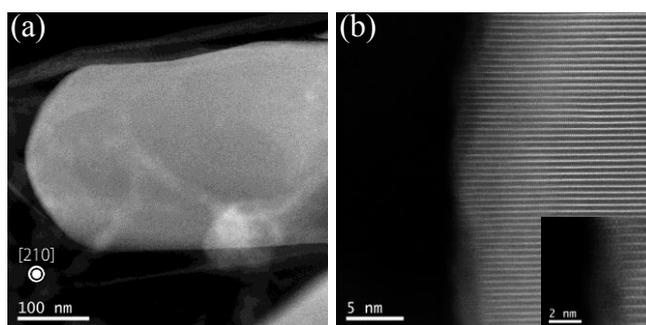


Fig. 1. HAADF-STEM images of a chemically reacted particle, (a) a low-magnification image of the particle, and (b) a magnified image of the surface region of the same particle. The inset shows the anti-site defects at Li columns.

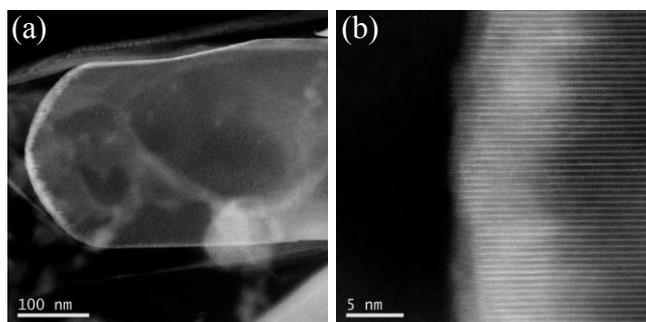


Fig. 2. LAADF-STEM images of a chemically reacted particle, (a) a low-magnification image of the particle, and (b) a magnified image of the surface region of the same particle.