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Structural Evolution of Overcharged $LiNiO_2$-Based Cathode Materials During Thermal Decomposition Studied by in-situ TEM

Lijun Wu, Yongning Zhou, Xiaojian Wang, Xiao-Qing Yang and Yimei Zhu

Brookhaven National Laboratory, Upton, NY 11973

Layer-structured oxides with transition metals such as Ni, and Mn have been considered as good cathode materials to replace $LiCoO_2$ for lithium batteries due to their lower cost and higher capacities. The thermal instability in charged, especially over charged, states at elevated temperatures, however, is still a major concern on this class of materials. Recent studies on Co, Al, Mn doped $LiNiO_2$-based materials using time-resolved X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) with or without the presence of electrolyte show a series of phase transformations during heating [1]. Due to the averaging nature of X-ray techniques, detailed knowledge about how the structural transformation initiated and propagated through new phase nucleation and growth at microscopic level is very limited. Therefore, further studies using local probes with high spatial resolution are needed. Here, we present our in-situ transmission electron microscopy (TEM) studies on the structural modification of overcharged $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode materials during a heating process.

High resolution transmission electron microscopy (HRTEM) and electron diffraction were carried out using JEM-3000F equipped with an ultra high resolution objective-lens pole-piece and a Gatan double-tilt heating stage capable of altering temperature in sample area from room temperature to 1000 ºC. The $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particle samples harvested from overcharged cell were first examined at room temperature. Fig. 1(a) and (b) show a typical low-magnification bright field TEM image and the corresponding selected area electron diffraction pattern (SAEDP). The SAEDP confirms that the main phase is the rhombohedral $Li(NCA)O_2$ (NCA = $Ni_{0.8}Co_{0.15}Al_{0.05}$). The HRTEM image taken from the edge of the particle (Fig. 1c), however, reveals that the particle actually has a core-shell structure with the rhombohedral structure in the core, the spinel structure in the shell and the rock-salt structure at the surface (marked as R, S and RS in Fig. 1(c), respectively). To evaluate the structure evolution of the overcharged $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles with temperature, we heated the samples to an elevated temperature for half hour in the microscope, and then cooled it down to room temperature for imaging. Fig. 2 shows the HRTEM images after heating at 100, 200 and 300 ºC, respectively. The area is the same as that shown in Fig. 1(c). After heating at 100 ºC (Fig. 2(a)), the area which has rhombohedral structure at room temperature transforms to the spinel structure. Meanwhile, the rock-salt phase grows from the surface to the shell of the particle. Further heating the sample to 200 ºC and 300 ºC, the phase with the spinel structure grows more and more into the core of the particles, while the rock-salt phase propagates from the surface to the interior of the particles. After heating the sample to 400 ºC, the majority phase becomes rock-salt.

For over charged $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ sample, it has similar core-shell makeup but with the CdI_2-type structure $(NiCoMn)O_2$, rather than rock-salt structure at the surface. By heating the sample, the rhombohedral structure in the core transforms to the spinel structure, which then transforms to the Co_3O_4 type spinel structure at higher temperature, thus push the formation of the rock-salt phase to much higher temperature.

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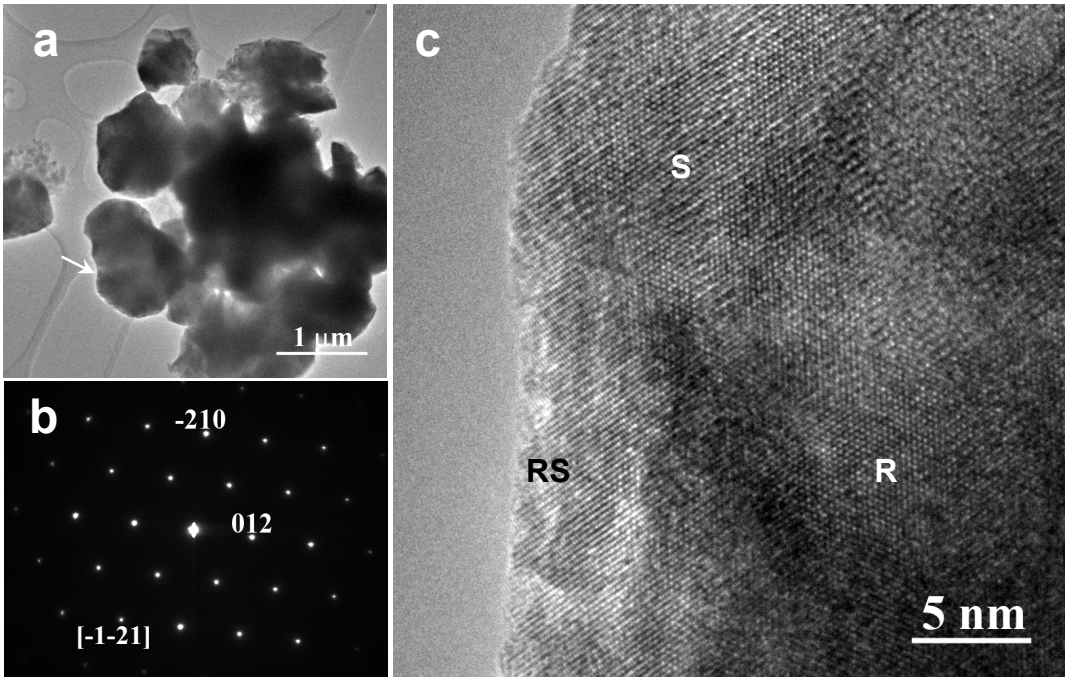

FIG. 1. (a) Bright-field image and (b) SAEDP from overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material. The SAEDP can be indexed as the rhombohedral [-1-21] pattern. (c) High resolution image from the edge of the particle indicated by the arrow in (a). There are three phases in the image area. The rhombohedral phase (R) shows a pseudo-hexagonal pattern, the spinel phase (S) has alternate strong and weak contrast and the rock-salt phase (RS) exhibits fine fringes.

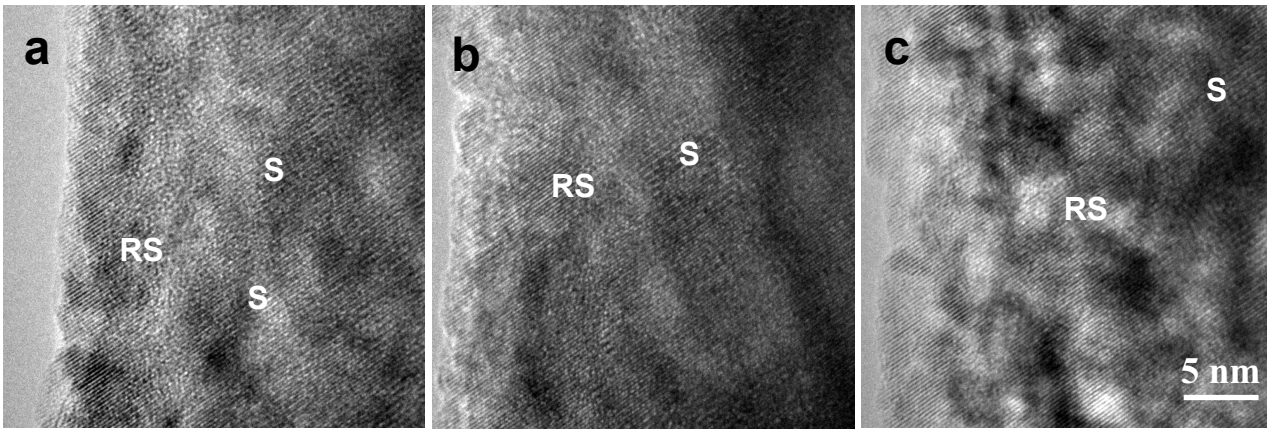

FIG. 2. High resolution images taken from the same area shown in FIG. 1(c) after heating at (a) 100 ºC, (b) 200 ºC and (c) 300 ºC.

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