

Supporting Information

Structural origin of overcharge-induced thermal instability of Ni-containing layered-cathodes for high-energy-density lithium batteries

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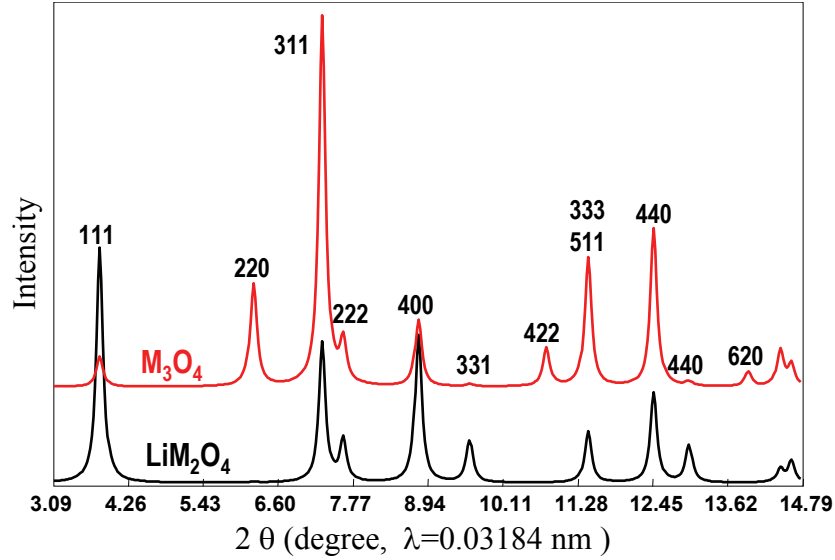


Figure S1. Calculated X-ray diffraction (XRD) patterns of the LiM_2O_4 -type ($\text{M}=\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$, black line) and M_3O_4 -type spinel structure (red line). The space group of the spinel structure is $\text{Fd}\bar{3}\text{m}$. The 16d site is occupied by Ni, Co and Mn atoms. The 8a site is occupied by Li for LiM_2O_4 -type structure, while by Li, Ni, Co and Mn atoms for M_3O_4 -type structure. Note, the XRD patterns of the LiM_2O_4 -type and M_3O_4 -type structure are quite different, e.g. the intensities of 220 and 422 peaks are strong for the M_3O_4 -type structure but close to zero for the LiM_2O_4 -type structure.

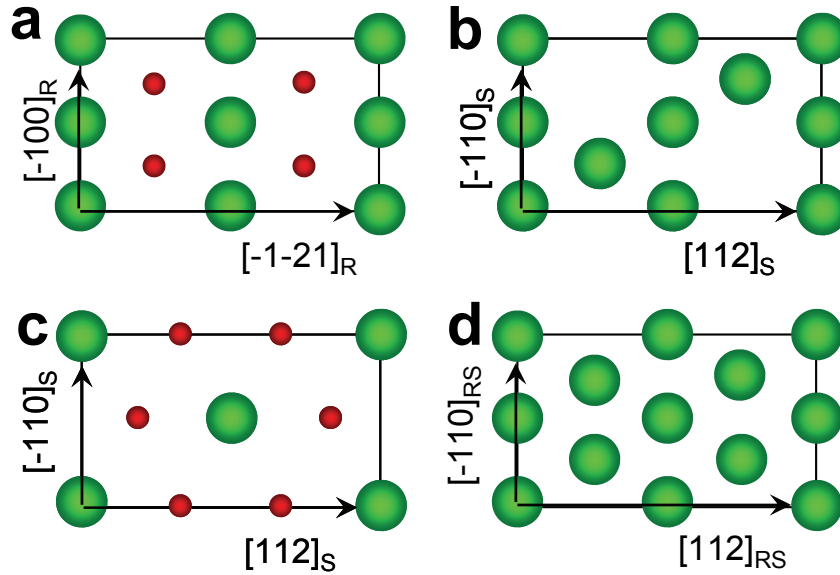


Figure S2. Cation planes of rhombohedral, spinel and rock-salt structure. (a) $(012)_{\text{R}}$ cation plane of the rhombohedral structure. The red and green balls represent Li and Ni (Co, Al), respectively. (b-c) $(11\bar{1})_{\text{S}}$ cation plane of the spinel structure at (b) A and (c) B position (see Figure 2III for A and B position). (d) $(11\bar{1})_{\text{RS}}$ cation plane of the rock-salt structure. The rhombohedral $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ phase consists of a $(012)_{\text{R}}$ O plane, and cation plane along the $[8\ 16\ 1]_{\text{R}}$ direction (equivalently to the

reciprocal $[012]_R^*$ direction). After charge, Li atoms are removed from the $(012)_R$ cation plane, e.g., the A plane in Figure 2-I-g. Two Ni (Co, Al) atoms from the neighboring $(012)_R$ cation plane (the B plane in Figure 2-I-g) move into the A plane, thus inducing phase transformation from the rhombohedral phase to the spinel phase. Since the atomic arrangements of the rhombohedral phase in the A and B $(012)_R$ planes are the same, the spinel phase has the same probability to nucleate on its A $(11-1)_S$ cation plane, either on the A $(012)_R$, or the B $(012)_R$ plane of the rhombohedral phase, resulting in the formation of antiphase domains (Figure S3). At the surface, with the loss of Li and O, the spinel structure transforms to the rock-salt structure.

The relationship among the rhombohedral, spinel, the O1 and rock-salt structures:

The orientation relationship among the rhombohedral, spinel, and rock-salt structures is determined based on the high resolution images (see Figure 2) as follows:

$$\begin{aligned}(012)_R &\parallel (11-1)_S \parallel (11-1)_{RS} \\ (-210)_R &\parallel (-110)_S \parallel (-110)_{RS} \\ [-1-21]_R &\parallel [112]_S \parallel [112]_S\end{aligned}\tag{1}$$

The lattice relation among three structures can be further deduced:

$$\begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix}_R \approx \begin{pmatrix} 0.25 & -0.25 & 0 \\ 0 & 0.25 & -0.25 \\ 1 & 1 & 1 \end{pmatrix} \times \begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix}_S \approx \begin{pmatrix} 0.5 & -0.5 & 0 \\ 0 & 0.5 & -0.5 \\ 2 & 2 & 2 \end{pmatrix} \times \begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix}_{RS}\tag{2}$$

The orientation relationship among the rhombohedral, the O1, and the spinel structures is determined based on the SAEDP and high resolution images (see Figure 4) as follows:

$$\begin{aligned}(100)_R &\parallel (100)_{O1} \parallel (2-1-1)_S \\ (010)_R &\parallel (010)_{O1} \parallel (11-2)_S \\ [001]_R &\parallel [001]_{O1} \parallel [111]_S\end{aligned}\tag{3}$$

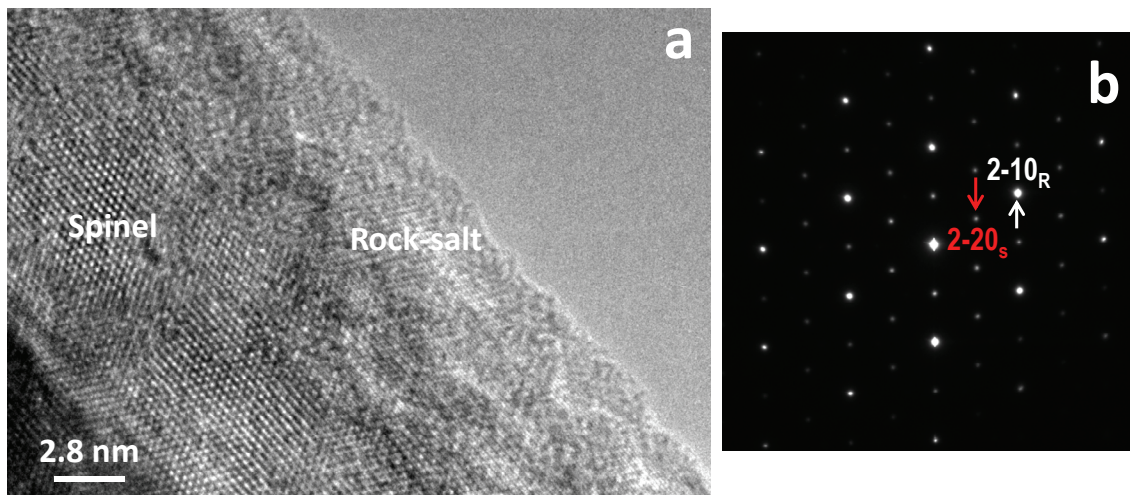


Figure S3. HRTEM image (a) and SAEDP (b) of an overcharged $\text{Li}_x(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ particle viewed along [001] direction, showing the rock-salt structure at the surface and the spinel structure in the shell.

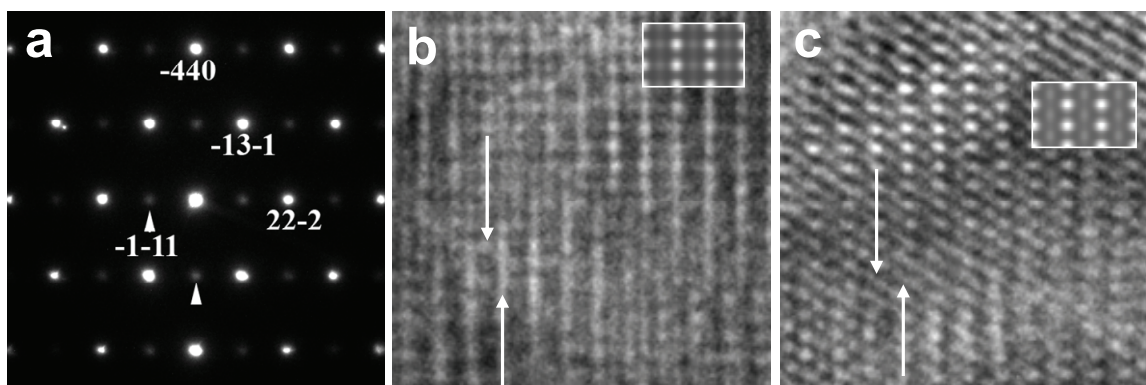


Figure S4. SAEDP and high resolution images of the spinel structure. (a) SAEDP from the thin area of an overcharged particle. The SAEDP can be indexed as [112] zone pattern of the spinel structure. (b-c) HRTEM images from the thin area of the same particle of (a). The insets in (b) and (c) are the calculated images with thickness=20nm and defocus=4nm, and thickness=16nm and defocus=2.5nm, respectively. The antiphase domains are observed in both images as indicated by the arrows.