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The Intermediate State of the Layered → Spinel Phase Transformation in $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ Cathode

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Layered $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) is a promising cathode material for lithium ion batteries (LIBs), which has a high rate capability, a long lifetime and theoretically a high specific capacity. The aluminum addition prevents the NCA layered structure from collapsing into an inactive rock-salt phase, but it also accelerates the spinel phase transformation. The spinel phase formed in the surface region increases the impedance of NCA, reduces the electrochemical activity and diminishes the overall capacity.

The layered → spinel phase transformation occurs via the migration and rearrangement of TM atoms within the same oxygen framework. 1/4 of the TM cations shift into the lithium layers, which results in the formation of a cubic spinel structure. The spinel phase is featured by the migration of TM cations from the 3a sites of the layered phase onto the 4d sites of the spinel phase, which takes 5 steps. The intermediate spinel phase is featured by incompletion of the 5 steps. Regardless what the specific layered dioxide is, the structure of the intermediate spinel has long been an unsettled problem. Density functional theory (DFT) calculation by Ceder etc. has shown that the occupation of tetrahedral sites in the lithium layer is an important feature of the intermediate spinel, but this mechanism has never been directly proved by experiment. Using High Resolution Electron Transmission Electron Microscopy (HRTEM), we are able to capture this intermediate status and propose a structure of the intermediate spinel phase.

Here, we present the diffractogram from the surface in the subsurface of a charged primary NCA particle (4.7 V, Figure 1). Figure 1a is a HRTEM view of a particle charged to 4.7 V. Three areas from the surface to the subsurface (A, B, C) are selected and their diffractograms are obtained (Figure 1b-d). In the surface region (Figure 1b), only the spinel spots are present, as marked by the yellow hexagons. There are no spots associated with the layered structure, i.e., the layered phase is completely transformed into the spinel phase in the surface region. In the diffractogram from the subsurface region (Figure 1c), an unknown diffraction (indicated by red lines) is present, which does not belong to either the spinel or the layered phase, so it can only be from the intermediate spinel. In the deeper subsurface (Figure 1d), a similar diffraction pattern with the intermediate spinel diffraction is present again. However, the spinel diffraction is more incomplete and the intermediate spinel diffraction is stronger.

Since the layered → spinel phase transformation is only caused by the migration of 4d cations in the layered phase, three possible structures of the intermediate spinel phase have been proposed only concerning the siting of 4d cations, as shown in Figure 2. Figure 2a is the [003] view of the complete spinel phase, where 4d cations in A-C layers are marked as red, blue and yellow, respectively. For the first proposed structure (Figure 2b), its simulated diffraction pattern matches the unknown diffraction in Figure 1b and c very well, but the structure is energetically and structural unfavorable, so it is only the average description of the intermediates spinel phase. To describe the short-term arrangement of the 4d cations, two other structures are proposed, as shown in Figure 2c and e. The third structure (Figure 2e and f) is more energetically and structurally favorable, but its [111] diffraction simulation presents some extra spots. Thisw proves that the third structure describes the short-term structure of the intermediates spinel while the first structure describes the average structure of the intermediate spinel.

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[3] This work was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012583.

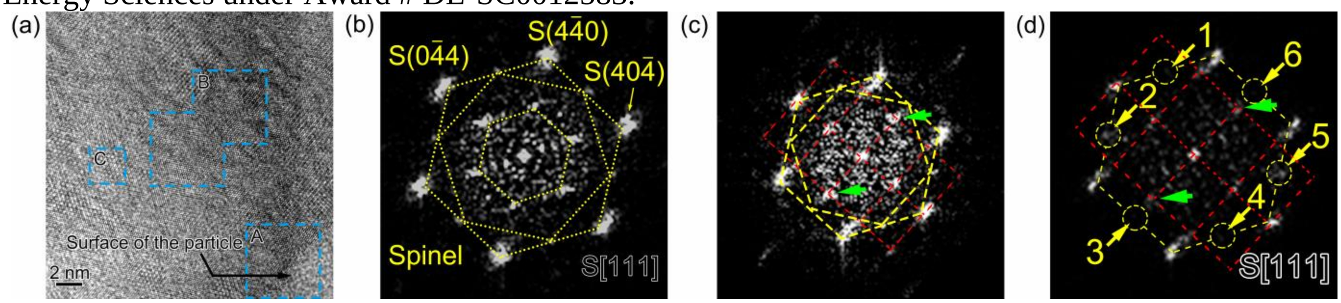

Figure 1. (a) HRTEM view of the particle charged to 4.7 V. Diffractograms are obtained from the three areas marked A-C. (b) Diffractogram from the surface (location A), indicating the complete spinel phase (marked by yellow hexagons). (c) Diffractogram from the subsurface region (location B). The spinel diffraction (yellow hexagons) is incomplete and an intermediate spinel diffraction is present (red lines). (d) Diffractogram from a deeper subsurface region (area C), which is similar to (c) but with more spinel diffraction missing.

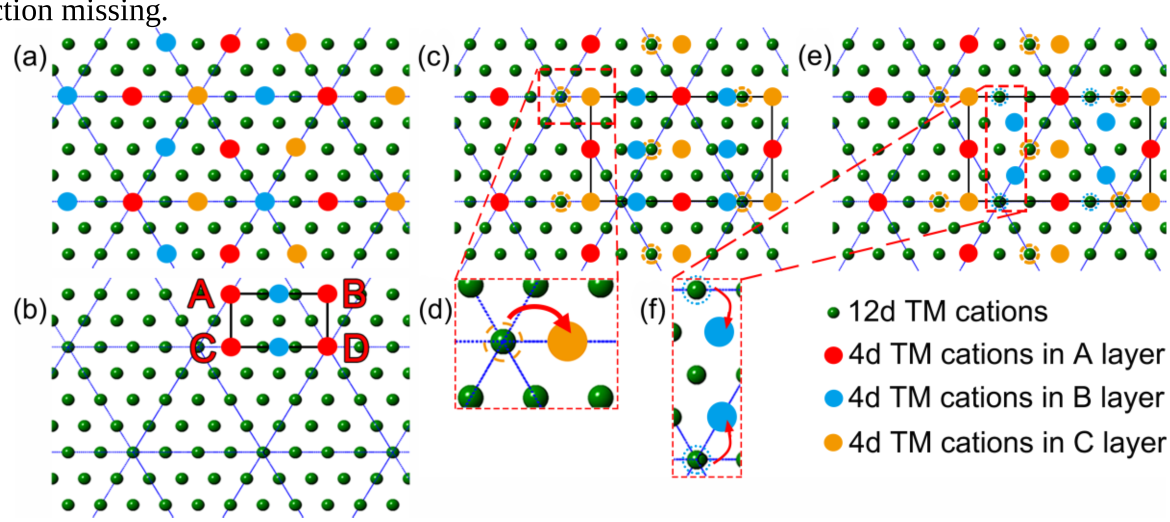

Figure 2. (a) The [003] projection view of the perfect spinel phase. (003) projection views of the (b) first, (c) the second and (e) the third intermediate spinel models. (d, f) Enlargements of the selected areas in (c, e), showing the featured migration of 4d TM cations.

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