doi:10.1017/S1431927621011818
Microsc. Microanal. 27 (Suppl 1), 2021

Unveiling the roles of Co and Mn in structural stability for Ni-rich Cathodes

Lei Yu[1] and Jianguo Wen[2]

[1]Argonne National Laboratory, United States, [2]Argonne National Laboratory, Lemont, Illinois, United States

Ternary Ni-rich layered oxides (LiNixMnyCozO2 Ni-rich NMC; $x \geq 0.5$) have been regarded as one of most promising cathode candidates for next-generation Lithium-ion battery. They combine the advantages of multiple elements. Among them, it is well known that the main Ni contributes to high capacity, Co improves conductivity and reduces Li/Ni disorder, and Mn enhances thermal stability. However, the effects of Co and Mn components on stabilizing the layered structure remain unclear. Especially, meeting with commercialization, the cost of raw materials also must be considered. It is very important to understand their individual roles and design reasonable component ratios for advanced electrode materials [1].

In this study, the structural evolution of binary LiNi0.6Co0.4O2 (NC64) and LiNi0.6Mn0.4O2 (NM64) were investigated by aberration-corrected high-resolution TEM (HRTEM) and electron energy loss spectroscopy (EELS), respectively. As shown in Figure 1, both of NC64 and NM64 presented a complete rock-salt phase on the surface after prolonged cycles, which suggests that surface phase transformation was independent of the Co and Mn content. The formation of rock-salt phase inevitably results form a reduction reaction of surface Ni4+ ions with the electrolyte. Then, a clear difference was observed in the subsurface area. The subsurface structure of NC64 completely transited to a spinel-like structure. Such an irreversible phase transition is related to oxygen release, which triggers transition metal (TM) migration to Li slab. By comparison, the structure stability of NM64 was superior and it remained a typical layered structure on the bulk after 100 cycles.

EELS is utilized to analyze the redox reversibility and valance evolution of transition metal elements. As shown in Figure 2, the O K-edge prepeak only decreases near the surface of NM64, and the L edges of Ni and Mn consistently show leftward shifts near the surface. These results suggest that severe structural deterioration only occurs on surface areas of the NM64 particles. In contrast, for NC64, the decrease of O K-edge prepeak not only occurs on the surface, but also extends into the bulk. Furthermore, its energy position of whole Ni-L edge also shows leftward shifts compared with the bulk of NM64. These results further demonstrate the lower valence state of Ni and irreversible phase transition occurred in the bulk of NC64.

In summary, for Ni-rich cathodes, although high Ni contents were previously recognized as the origin of capacity degradation, it is found that Co also promotes the irreversible structural transformation, while Mn inhibits irreversible phase transitions during cycling. [2]

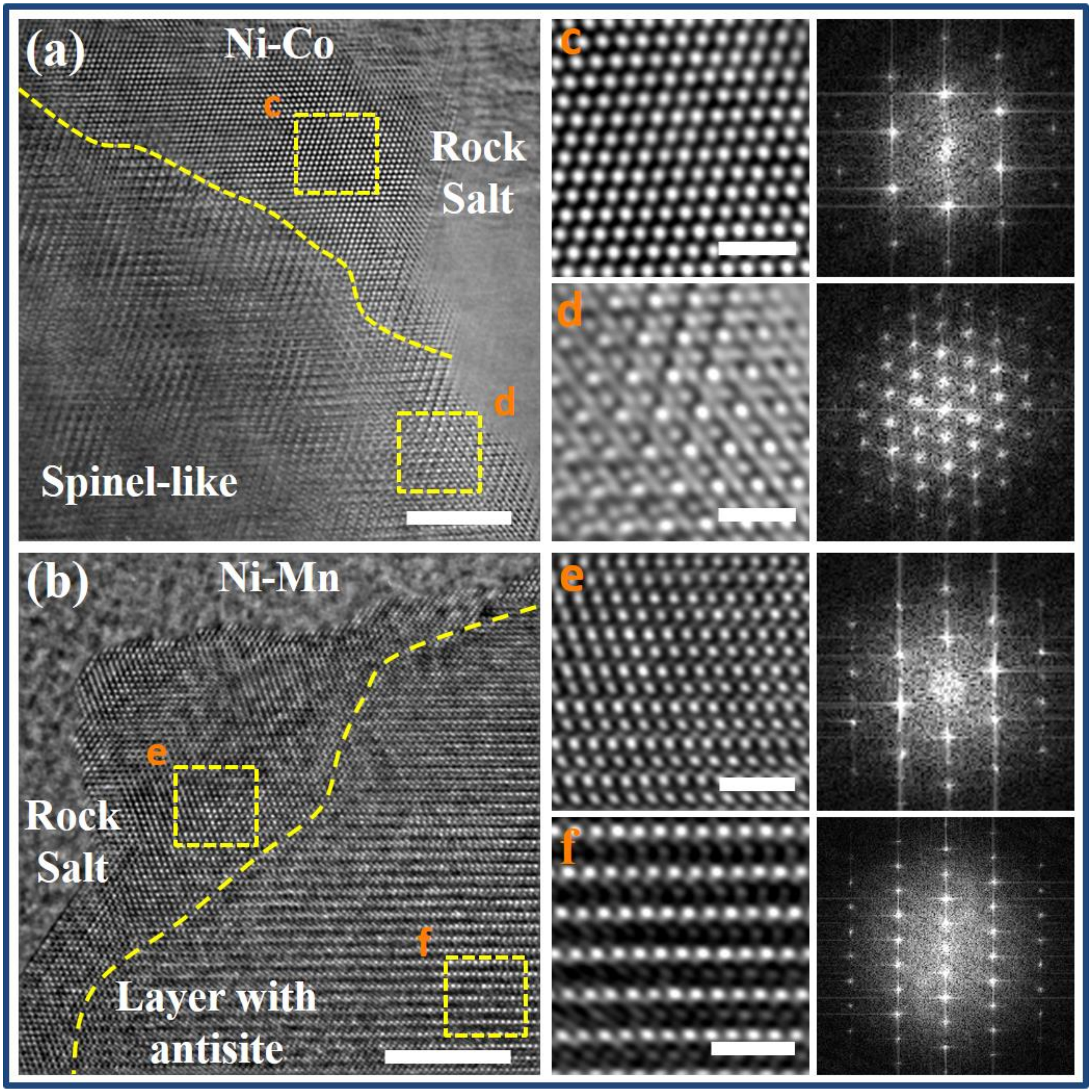

Figure 1. Figure 1. HRTEM images showing the atomic structures of NC64 (a) and NM64 (b) after 100 cycles, respectively. The figures in the middle and right columns are enlarged images and corresponding fast Fourier transform (FFT) images. Scale bars, 5 nm (a, b), 1 nm (c, d, e, f).

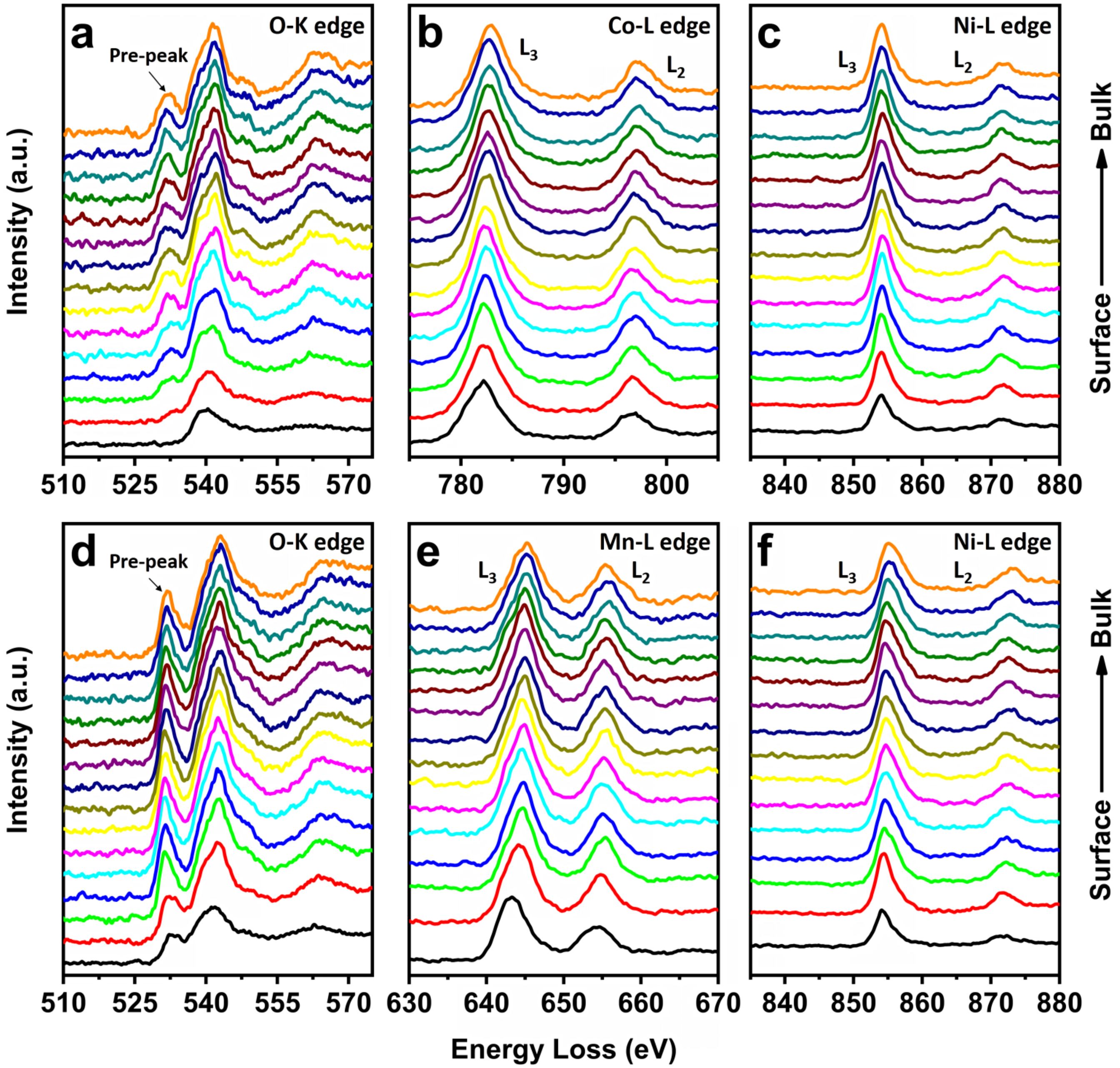

Figure 2. Figure 2. EELS line profiles of O-K, Co-L, and Ni-L edges for NC64 (upper row). EELS line profiles of O-K, Mn-L, and Ni-L edges for NM64 (lower row).

References

[1] T. Liu, L. Yu, J. Liu, J. Lu, X. Bi, A. Dai, M. Li, M. Li, Z. Hu, L. Ma, D. Luo, J. Zheng, T. Wu, Y. Ren, J. Wen, F. Pan and K. Amine, Nat. Energy, 2021, DOI: 10.1038/s41560-021-00776-y.

[2] This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.