

## ***In-Situ* TEM Study of Chemo-Mechanical Degradation Pathways of LiNiO<sub>2</sub>-Derived Layered Oxide Cathodes for Lithium-Ion Batteries**

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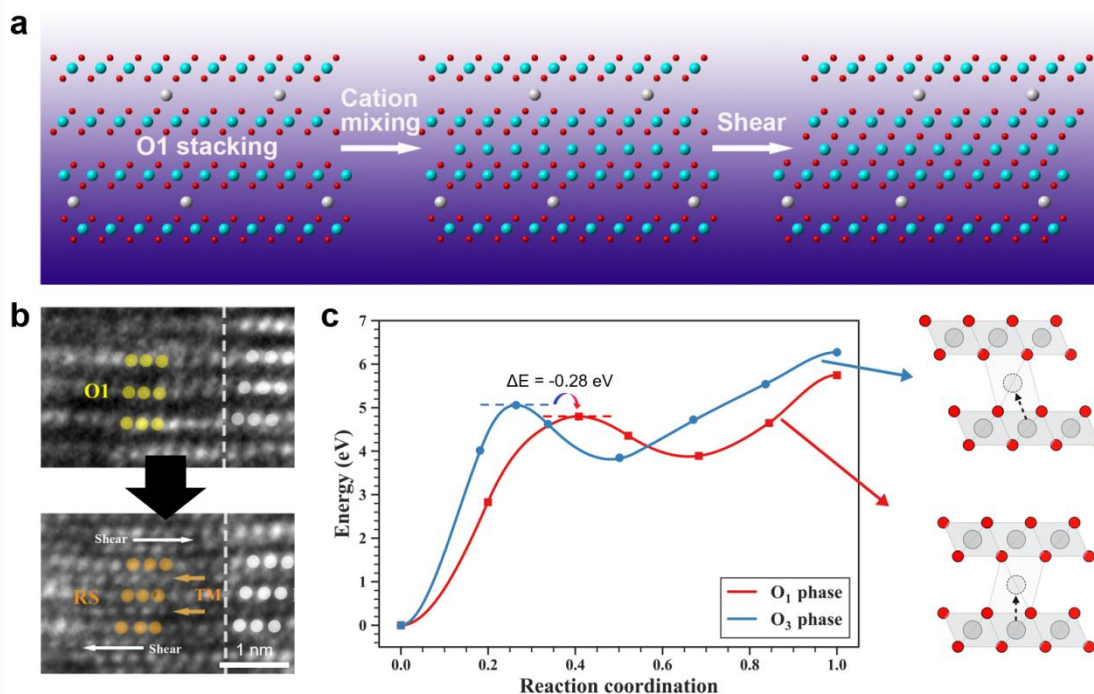
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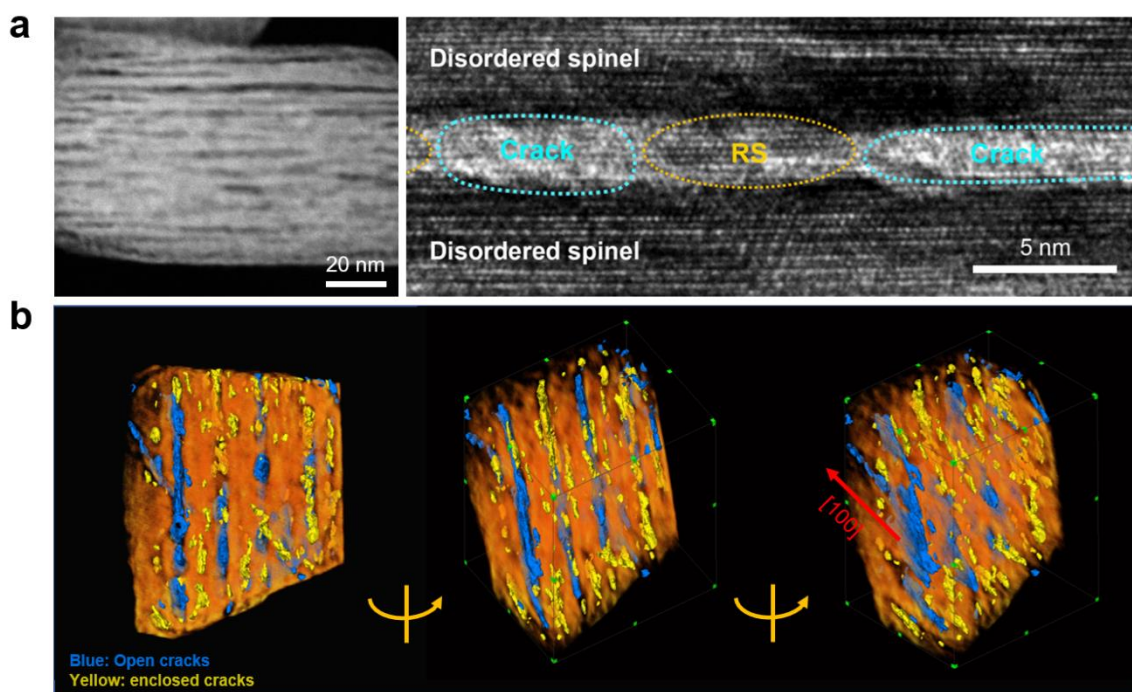
The urgent demand for low-cost and high-capacity lithium-ion batteries and the soaring price of cobalt make low-cobalt/cobalt-free high-nickel cathode materials become the focus of research in the battery field [1, 2]. An in-depth understanding of the atomic-scale failure mechanism of cobalt-free high-nickel oxide cathode materials will provide important guidance for the design of cathode materials for the next-generation high-energy-density lithium-ion batteries.

Lithium nickelate, LiNiO<sub>2</sub>, is a cathode material that satisfies both the high-energy and the no-cobalt requirements. LiNiO<sub>2</sub> was extensively explored in the 1990s, but its electrochemical cycling and thermal instabilities have plagued its commercialization. It has only recently resurfaced [3] as one of the most promising high-energy cathode materials for LIBs due to the discovery of effective non-cobalt dopants that can inhibit oxygen loss in deep charged states [4, 5]. However, LiNiO<sub>2</sub>-derived materials have inherited many of the intrinsic structural and thermal instability of LiNiO<sub>2</sub> involving complex chemo-mechanical degradation behaviors involving multiscale cracking, cation mixing, oxygen loss, and O1 phase transformation [6]. Understanding the atomic pathways of the chemomechanical degradation is key to the continued improvement and engineering of LiNiO<sub>2</sub>-derived low-cobalt/cobalt-free materials.

In this contribution, we report the atomic-scale phase degradation and oxygen loss mechanism in LiNiO<sub>2</sub>-derived cathodes using *in-situ* electron diffraction and atomic-resolution TEM. Aided by the state-of-the-art *in-situ* atomic-scale transmission electron microscopy (TEM), electron tomography and first-principles calculations, we reveal the concurrent structural and mechanical degradation pathway of LiNiO<sub>2</sub>-derived layered cathode material. Through statistical *in-situ* TEM observations, the evolution path of O1 phase under thermal abuse conditions was captured at the atomic scale both in pure LiNiO<sub>2</sub> and a doped LiNiO<sub>2</sub> cathode [7]. Fig. 1 shows that different from the conventional evolution path from O3 phase to rocksalt, the transformation from O1 phase to rocksalt takes place via a two-step pathway involving cation mixing and shear along the (003) planes—a degradation mechanism that has never been observed before. First-principles calculations rationalize the new degradation pathway as the kinetic barriers of a Ni migration in O1 lattice is lower than that in the O3 lattice. These results imply that the lattice-shear induced O1 stacking fault or phase provides a highway for transition metal migration and phase transformation towards rocksalt upon oxygen loss. Aside from the structural degradation, mechanical failure also occurs with exacerbated oxygen loss in the cathode material. TEM nanotomography (Fig. 2) shows that planar cracks form in the cathode particle. Tomographic segmentation analysis shows that these cracks include both open cracks (connecting to the particle's surface) and closed cracks (embedded in the particle) and they all propagate along the [100] direction on (003) planes. Between the discontinuous planar cracks, discrete rocksalt patches were identified, indicating a concurrent structure and mechanical degradation.[7] Our work provides new insights into the chemo-mechanical degradation mechanism of LiNiO<sub>2</sub>-derived cathodes and offers useful guidance for the development of next-generation high-energy cathode materials [8].



**Figure 1.** Atomic-scale transformation pathway from O1 phase to rocksalt phase. (a) Schematic illustration of the two-step phase transformation pathway. (b) In-situ high-resolution transmission electron microscopy (HRTEM) images showing the phase transformation process from O1 to rocksalt. (c) Calculated energy barriers for Ni migration from TM layer to Li layer in O3 (blue) and O1 (red) lattice.



**Figure 2.** Chemo-mechanical degradation through concurrent planar cracking and rocksalt transformation. (a) Formation of planar cracks and discrete rocksalt domains on the (003) plane. (b) 3D

configuration of the cracks obtained by TEM nano-tomography. Open cracks and closed cracks are segmented and highlighted in blue and yellow, respectively.

#### References:

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