

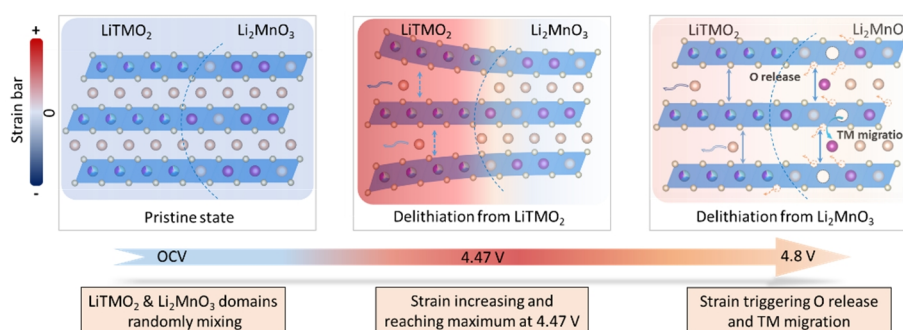
# Probing Structural Evolution of High-capacity Layered Oxide Cathode

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In transitional metal (TM) layered oxide cathode materials, the energy storage relies on Li-ion intercalation/de-intercalation in the Li layers. To achieve higher energy density, lithium- and manganese-rich (LMR) layered oxides are developed by enabling Li-storage in TM layers. Nevertheless, this process involves structural evolution (e.g., oxygen release) of cathode materials that

might eventually lead to performance degradation. Typically, LMR materials contain two structures (i.e.,  $\text{LiTMO}_2$  and  $\text{Li}_2\text{MnO}_3$ ) that exhibit different electrochemical behaviors during charging/discharging (Figure 1). Limited by characterization techniques, this process is difficult to observe, leaving the relevant mechanism study a challenge.



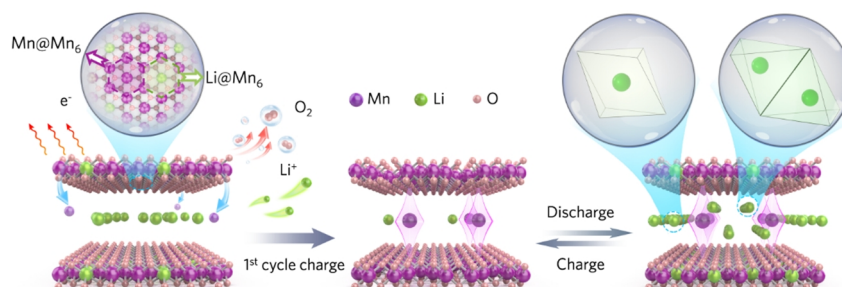
**Figure 1.** Schematic of the correlation of strain generation and O release as well as transition metal migration.

The  $\text{LiTMO}_2$  and  $\text{Li}_2\text{MnO}_3$  domains share a coherent lattice at the nanoscale but exhibit differentiated electrochemical activities due to different redox chemistries. The initial Li extraction predominately occurs in the  $\text{LiTMO}_2$  domains and results in local lattice expansion. The lattice expansion is partly confined by the inactive  $\text{Li}_2\text{MnO}_3$ , which results in tensile strain at the nanoscale. The accumulated tensile strain severely affects the structural stability of the composite LMR cathode, which may trigger the decomposition of  $\text{Li}_2\text{MnO}_3$  domains, oxygen release and transition metal (TM) migration. The activation of  $\text{Li}_2\text{MnO}_3$  and oxygen release in turn release the lattice strain at high voltages.

To overcome the difficulty in characterizing such materials, Pan and co-workers employed in situ Bragg coherent diffraction imaging to reveal the accumulating lattice strain within LMR particles.<sup>[1]</sup> It is revealed that the lattice strain causes the unstable structure

and oxygen release. Furthermore, the results of spinning-length X-ray diffraction show that the heterogeneous structural dynamics of LMR materials causes uneven Li-ion intercalation and de-intercalation, hence the lattice strain. Therefore, as a commonly observed phenomenon, accumulating lattice strain is undesirable in cathode materials as it may cause structural degradation.

Accordingly, to stabilize LMR materials for better electrochemical performance, some effective strategies have been proposed by Pan and co-workers. Through dispersing  $\text{Li@Mn}_6$  structural units in TM layers, lattice oxygen loss and irreversible phase transition could be effectively suppressed.<sup>[2]</sup> Accordingly, a layered oxide consisting of 0.48  $\text{Li@Mn}_6$  ordering and 0.52  $\text{Mn@Mn}_6$  structure was synthesized,<sup>[3]</sup> forming an elastic Mn layer after initial cycling (Figure 2). This elastic Mn layer not only enables extra  $\text{Li}^+$  storage in the tetrahedral sites of Li layer, achieving a reversible



**Figure 2.** Diagram of elastic lattice enabling reversible tetrahedral Li storage.

capacity as high as 600 mAh g<sup>-1</sup>, but also tolerates lattice strain during repeated cycling.

It is clarified that the Mn migration into the Li layer during the initial cycle stabilizes large number of tetrahedral sites for extra and reversible Li-ion storage in this layered compound.

By probing the origin of structural instability, it is suggested that the lattice strain observed not only affects the electrochemical performance of LMR, but also has implication in other layered cathode materials for Li-ion batteries. These findings will provide in-depth perspectives on designing and optimizing high-energy-density cathode materials.

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#### n COMPETING INTERESTS

The authors declare that they have no conflict of interest.

#### n ADDITIONAL INFORMATION

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