

Figure 1. Coupled decomposition of electrolyte and O₂ gas release: excerpts from *in operando* Raman spectra of (a) LLO and (b) LLO@NFO2 electrodes.

expected, we confirmed that O₂ gas is the driving force behind the decomposition of DMC. In particular, a rapid decline of Raman band intensity for DMC was not observed (Figures 1b, S2b, and S3b). A pronounced DMC signal in the LLO@NFO2 electrode was observed, and the Raman band intensity was relatively steady, compared to a cliff-like drop around 4.4 V, followed by a low level in the LLO electrode (Figure S4). More precisely, the oxidation of O²⁻ at a high voltage plateau (~4.4 V) on charge becomes more reversible after the NFO-coating in LLO@NFO2. Consequently, it is more challenging to trigger the decomposition of DMC.

By comparing *in operando* Raman spectra, the overall structural evolution mechanism from TM cation and oxygen anion redox can be understood. According to Flores et al.,¹⁶ layered LiMO₂ oxides with *R*3*m* space groups can be characterized by two Raman activity modes. As shown in Figure 2a,d, in the low wavenumber region (400–680 cm⁻¹), the strong E_g band dominates the spectral characteristics. These bands centered around 517 cm⁻¹ show different behaviors. Specifically, the band gradually weakens in the delithiated state. It disappears in the pristine LLO, while in LLO@NFO2, the intensity of the band remains at a high level during the first cycle. Therefore, we believe that the oxygen environment in the two oxides is different. The M-O-N (M = Ni, Co, Mn from MO₆ octahedra; N = Ni, Fe from NO₆ octahedra) adjusts the local oxygen environment and enhances the redox reversibility of anions. A high level of Mn⁴⁺/Ni²⁺ fraction was observed on charge, suggesting higher M disorder and lattice oxygen activity in LLO@NFO2 (Figure S4).^{17,18} The twin peaks centered around 850–880 cm⁻¹ are attributed to O-O vibrations (Figure 2b,e).^{19,20} Upon charge, peroxy O-O signals disappear immediately (~4.4 V) in LLO, whereas these signals remain steady in LLO@NFO2. The rapid drop of peroxy O-O signals indicates that peroxides may be oxidized to O₂ gas in LLO. This

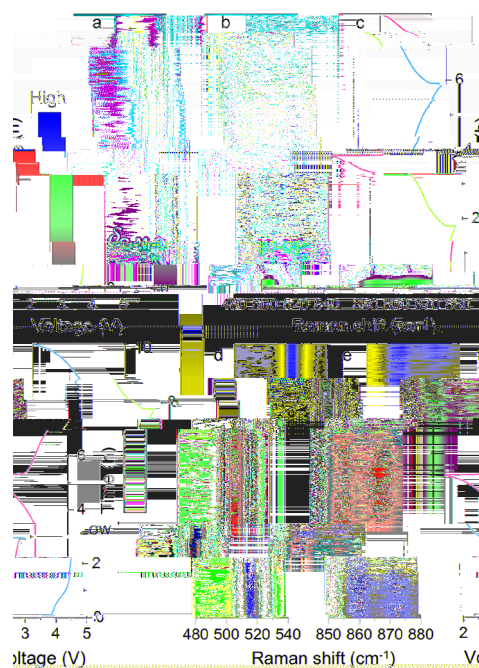


Figure 2. Evolution of the bending modes $\delta(\text{O-M-O})$ with E_g symmetry, peroxy O-O (O₂²⁻) bond stretching of the Raman spectra, and corresponding charge/discharge curves for (a–c) LLO and (d–f) LLO@NFO2 electrodes.

finding was further confirmed by *operando* differential electrochemical mass spectrometry (Figure S5).

Coupling between irreversible anion redox (oxygen release) and electrolyte decomposition (DMC component) in Li-rich layered oxides has been first visualized by *in operando* Raman spectroscopy. We successfully achieved oxygen-deficient NFO coating on the surface of LLO by a simple solvothermal method, and a strong M-O-N bond was formed at the interface of LLO and NFO coating. The NFO coating stabilizes the lattice oxygen at the interface, improves the reversibility of oxygen in the reaction, and inhibits oxygen precipitation. Our findings provide significant insight into the unsatisfactory electrochemical properties of Li-rich layered oxides at high voltage operating. Accordingly, further studies are needed to develop novel electrolytes for Li-rich layered oxides.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.2c02509>.

Experimental section, structural and morphology characterizations, electrochemical performance, and detailed analysis (PDF)

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Notes

The authors declare no competing financial interest.

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