

Capturing Oxygen-Driven Electrolyte Oxidation during High-Voltage Cycling in Li-Rich Layered Oxide Cathodes

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Cite This: *ACS Energy Lett.* 2023, 8, 417–419



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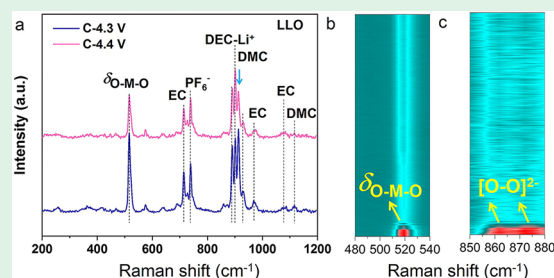


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ABSTRACT: We use *in operando* Raman spectroscopy to investigate the structural evolution mechanism of transition metal cation and oxygen anion redox in Li-rich layered oxide cathodes. We directly capture the release of oxygen-driven electrolyte oxidation (especially the dimethyl carbonate component) at high-voltage operation (4.4 V).



Exploring cathode materials with an elevated cutoff voltage is an effective method to access high discharge capacity and energy density.¹ Li-ion batteries (LIBs) powered by Li-rich layered oxides ($\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$; TM (transition metal) = Ni, Co, Mn, etc.) have the highest promise regarding energy density (500 Wh kg^{-1}).^{2–5} However, oxidation of O^{2-} anions when charged to a high voltage (usually $\sim 4.4 \text{ V}$ vs Li^+/Li) drives oxygen to escape from the lattice (O-loss).⁶ Molecular O_2 has been detected during the first charge/discharge process by mass spectrometry and gas chromatography.^{7,8} This type of irreversible anion redox is highly correlated with voltage fade, transition metal migration, and electrolyte consumption, resulting in persistent loss of energy density.^{9,10}

The persistent consumption of carbonate-based electrolytes in LIBs operated at high cutoff voltages remains a problem to be addressed. One solution is to replace the carbonate solvent. An alternative is to modify the commercial carbonate electrolyte, such as adding additives in the electrolyte in small amounts.^{11–13} However, questions remain on the origin of electrolyte decomposition, and when such a degradation starts has not been exhaustively studied yet. More importantly, cathode materials may significantly affect electrolyte decomposition, but this point has often been overlooked in battery chemistry.

Here, we report the oxygen-driven electrolyte oxidation mechanism in a typical Li-rich layered oxide, $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.62}\text{O}_2$ (LLO), as deduced by *in operando* Raman spectroscopy (Figure S1). To explore the evolution of superoxo species and solvent on charge, we used Raman spectroscopy with a higher resolution than in previous studies.^{5,8,14} The ability of

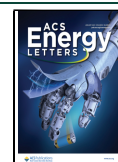
Raman spectroscopy to provide unique structural information allowed us to directly capture species changes, such as the oxygen reaction intermediate and decomposition of dimethyl carbonate (DMC). We provide direct evidence that oxygen gas, which originates from irreversible oxygen redox of surface lattice oxygen in LLO, drives DMC oxidation during high-voltage cycling ($\sim 4.4 \text{ V}$). In particular, DMC signals of LLO ($\sim 916 \text{ cm}^{-1}$) decrease almost immediately upon charge (Figures S2a and S3a). The evident weakness of DMC signals is attributed to the partial decomposition of DMC. To find out when the decomposition starts, we carefully evaluated the data.

Interestingly, we found that the decreased DMC signal started around 4.4 V (Figure 1a). It is well-established that O_2 gas is released in Li-rich layered cathodes at $\sim 4.4 \text{ V}$, which is ascribed to the irreversible oxygen redox.^{7,10,15} Now, the DMC decomposition and O_2 release processes can be connected. Therefore, minimizing O_2 release would provide definite proof for the inhibited decomposition of DMC. We introduced an oxygen-deficient NiFe_2O_4 (NFO) coating on the LLO to stabilize the surface lattice oxygen. The phase-compatible NFO coating was previously applied to $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ and showed remarkable ability in suppressing O_2 gas release.⁸ As

Received: November 6, 2022

Accepted: December 1, 2022

Published: December 7, 2022



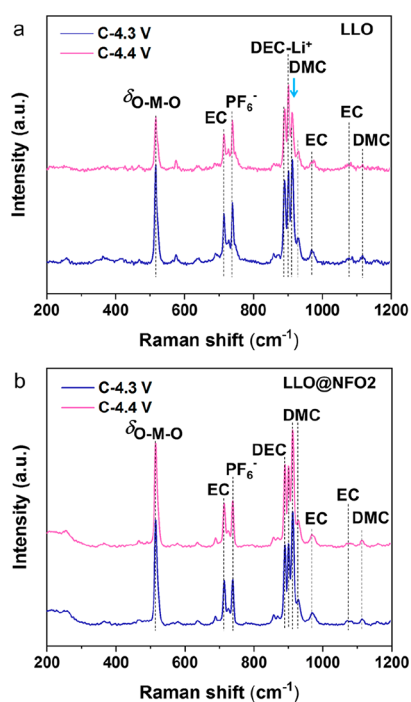


Figure 1. Coupled decomposition of electrolyte and O_2 gas release: excerpts from *in operando* Raman spectra of (a) LLO and (b) LLO@NFO2 electrodes.

expected, we confirmed that O_2 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 O^{2-} 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 LiMO_2 oxides with $R\bar{3}m$ space groups can be characterized by two Raman activity modes. As shown in Figure 2a,d, in the low wavenumber region ($400\text{--}680\text{ cm}^{-1}$), 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 MO_6 octahedra; N = Ni, Fe from NO_6 octahedra) adjusts the local oxygen environment and enhances the redox reversibility of anions. A high level of $\text{Mn}^{4+}/\text{Ni}^{2+}$ 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 $850\text{--}880\text{ cm}^{-1}$ 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 O_2 gas in LLO. This

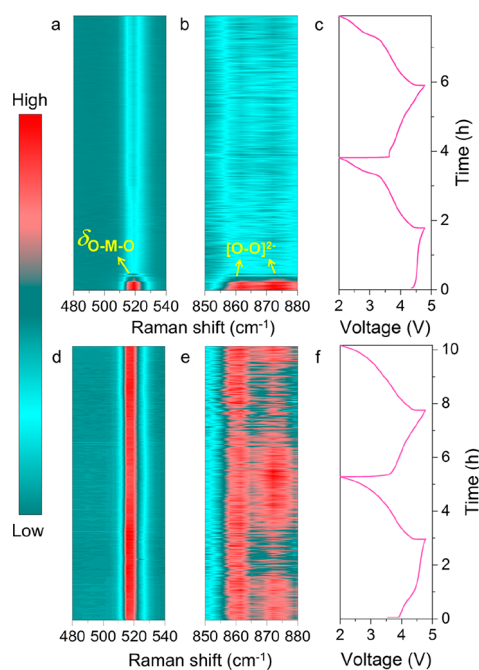


Figure 2. Evolution of the bending modes $\delta(\text{O-M-O})$ with E_g symmetry, peroxy O-O (O_2^{2-}) bond stretching of the Raman spectra, and corresponding charge/discharge curves for (a–c) LLO and (d–f) LLO@NFO2 electrodes.

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.

ACKNOWLEDGMENTS

We acknowledge support from Guangxi Natural Science Foundation (grant no. 2021GXNSFDA075012), Guangxi Technology Base and Talent Subject (GUIKE AD20297086), National Natural Science Foundation of China (grant nos. 22169004, U20A20249), Special Fund for Guangxi Distinguished Expert, and Innovation Project of Guangxi Graduate Education (JGY2022031).

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