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**Suppression of Voltage-Decay in Li₂MnO₃ Cathode via
Re-construction of Layered-Spinel Coexist Phases**

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ABSTRACT

Voltage decay, i.e., voltage decrease during electrochemical cycling is a decade-long challenge for lithium-ion battery. This issue not only leads to a substantial loss of the energy density, but also raises challenge for the battery management system, hindering the commercial application of high capacity lithium-rich oxide. Here, we show that through a combined electrochemical conditioning and thermal treatment, Li_2MnO_3 , the parent compound of lithium-rich oxide that typically displays severe voltage and capacity decay, could be converted into a new phase that essentially suppresses the voltage decay with improved capacity retention and rate performance. By combining atomic-sensitive nuclear magnetic resonance, differential electrochemical mass spectrometry and synchrotron-based resonant inelastic X-ray scattering, we disclose that treatment triggers the formation of three-coexisting phases, i.e., lithium-rich layered, spinel and defect spinel phase, which enables improved reversibility of the oxygen redox activity and enhanced manganese redox reactions in the initial cycle. Our findings suggest the key role of local structure on the voltage decay problem and provide insights for material optimizations towards lithium- and manganese-rich cathodes without voltage decay.

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Through a combined electrochemical-thermal treatment, Li_2MnO_3 could be converted into new layered-spinel phases that essentially suppress the voltage decay.

INTRODUCTION

Lithium ion battery, which can convert chemical energy into electric energy, has been widely used in the portable device, such as the laptop and mobile phone. However, the pressing demand of high capacity and stability has yet to be solved, especially the cathode that has been the bottleneck of the battery capacity. The Li-rich layered oxide, has gained much attention due to the extremely high capacity of over 280 mAh g⁻¹.¹⁻³ Recent research reveals the extra capacity in Li-rich oxide comes from the participation of oxygen redox.^{4,5, 6} The complex chemical and structural evolution of Li-rich cathode has attracted extensive efforts, however, the critical problem of voltage decay remains unsolved with its mechanism elusive.^{7,8}

In the past two decades, tremendous efforts have been devoted to understanding the origin of voltage decay. Several mechanisms have been proposed to explain this phenomena, e.g., structural defects and transition metal (TM) migration during electrochemical cycling, which may induce structural evolution from layered to spinel-like phase;^{7,9,10} on the other hand, the increased low-voltage redox couples, surface side reaction and oxygen release are proposed to be related with voltage decay.^{11,12} The voltage decay issue has been partially mitigated by several groups, nevertheless, a completely removal has not been reached yet.^{13,14,15,16} For example, Y. S. Meng et. al minimized the voltage degradation of Li-rich layered Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ with micrometer-sized particles, leading to decreased surface area and increased structural mechanical stability.¹⁴ Recently, C.S. Wang et. al enabled slight voltage fade on constructed O2-structured Li-rich cathode with fluorinated electrolyte.¹³ However, the fundamental clarification and the efficient solution for the voltage decay with a sustained high energy density has yet to be found.^{7,8, 15,17} The debates and arguments on the fundamental mechanism of the voltage decay problem stem from the complicated Li-rich material involving complicated stoichiometry and chemistry. Therefore, new comprehensive and comparative studies of both the structural and chemical evolutions of a relatively simple model system become valuable. Li₂MnO₃ (LMO), the parent compound of the Li-rich material with O3 structure, thus becomes an ideal candidate for such a purpose.

Here, we perform a comparative study of the electrochemistry, structure and chemistry of

an electrochemically conditioned then thermal treated Li_2MnO_3 (T-LMO) system, in comparison with standard LMO. The standard LMO has been proved with no reversible oxygen redox, the undesired gas release and associated severe voltage degradation directly hinder its electrochemical application.^{18,19} Our work shows that the electrochemical-thermal treatment leads to optimized layered-spinel phases, which suppress the voltage decay and enhance the reversible chemical reactions for improved capacity retention and rate performance. Although the electrochemical-thermal treatment has been applied to investigate the voltage decay in $\text{Li}_{1.2}\text{Ni}_x\text{Mn}_y\text{Co}_z\text{O}_2$ compound before, the specific TM contribution stays unclear and the voltage decay issue in the followed cycling process needs further addressed.^{20,21,22} We choose LMO with the hope of eliminating the influence from the complex TM elements in typical Li-rich compounds. A set of characterizations were combined to provide complementary insights in both structure and chemistry. *In-situ* variable temperature X-ray diffraction (XRD), Raman and solid-state nuclear magnetic resonance (ssNMR) spectroscopy revealed the local structural before/after electrochemical-thermal treatment. The chemical states of oxygen and Mn were probed by the *operando* differential electrochemical mass spectrometry (DEMS) and resonant inelastic X-ray scattering (RIXS) spectroscopy. The results confirm that the treated material exhibits enhanced reversibility of oxygen and Mn redox activity in the initial cycle, with mitigated gas release. The study on the parent LMO compound and the in-depth characterizations on structural, chemical and electrochemical properties upon the electrochemical-thermal treatment offer profound insights into the voltage decay mechanism and its solution in Li-rich system.

RESULTS

Electrochemical performance

The pristine LMO material with space group of $C2/m$ was synthesized via conventional solid-state method. The composition was confirmed by inductively coupled plasma/atomic emission spectrometer (ICP-AES). All samples were operated in coin-type cell using Li as counter electrode and tested with current density of 20 mA g^{-1} at room temperature. The pristine LMO went through electrochemical charge-discharge for two cycles and then thermal treated at 280°C in the air, the final material was named as T-LMO. The process is detailed

in the 'Methods' section.

The comparison on electrochemical behavior between the pristine and treated LMO is presented in **Figure 1**. The pristine LMO shows the typical and severe voltage/capacity decay upon cycling (**Figure 1a, 1b**).^{23,24} **Figure S1a** shows the average voltage during discharge is obtained via dividing the total energy density by the total discharge capacity measured in the working voltage range between 2.0 V and 4.8 V. For pristine LMO, an average voltage of 3.1 V is delivered for the initial discharge process and decreases to 2.8 V after 35 cycles. The voltage decay has been ascribed to the structural degradation, low-voltage redox couples and so on.^{7,9,10,11} In contrast, the treated T-LMO sample presents improved cycle performance in both the voltage and the capacity (**Figure 1c, 1d**). The T-LMO delivers an averaged discharge voltage of 3.2 V in the initial cycle, and the average voltage value is nearly sustained at the thirty-fifth cycle. As revealed in the differential capacity vs. voltage (dQ/dV) plots (**Figure S1b, S1c**), for discharge process, the peak at 2.2 V and 3.0 V for LMO exhibits a continuous shift to lower voltage upon cycling, while T-LMO delivers a very stable voltage peak position. Additionally, the capacity in T-LMO is not larger, whereas the capacity retention is improved compared with that in pristine LMO. The capacity retention after 35 cycles increases from the 39% for the pristine LMO to 75% for the treated T-LMO. Therefore, the treatment of the T-LMO material essentially eliminates the voltage decay and enhances energy density compared with that of the pristine LMO.

Moreover, the treated T-LMO sample also delivers enhanced rate capability (**Figure S1d**). When cycled at 3C (1C = 200 mA g⁻¹), the discharge capacity for T-LMO is twice of that of the pristine LMO. Based on the EIS data (**Figure S2**), T-LMO shows decreased slope of fitting line, indicating that the treated LMO cathode exhibits enhanced Li ion diffusion coefficient (around five times higher) than that of the pristine LMO.^{25,26}

To further analyze the electrochemical difference between pristine and treated LMO, the initial cycle curves for the two samples are plotted together in **Figure 2a**. For pristine LMO, the plateau above 4.5 V appears as the typical behavior of Li-rich cathode, which corresponds to the delithiation, charge compensation and oxygen release process.^{27,28,29,19} Upon discharge, S-shaped curve is presented with discharge capacity of around 200 mAh g⁻¹. It is interesting

that the characteristic charge plateau (above 4.5 V) is shortened in T-LMO sample. Simultaneously, the plateaus appear at around 4.1 V charged state and 4.0 V/2.8 V discharged state, which can be seen clearer in the dQ/dV plots (**Figure 2b**), indicating that spinel phase may exist in T-LMO.³⁰

Layered-spinel coexist phases

The elimination of the voltage decay in T-LMO and its improved capacity/rate performance trigger an intriguing question on what has been fundamentally changed in the T-LMO material. The XRD and refinement results are presented in **Figure S3** and **Table S2**. The diffraction patterns of pristine LMO fits well with that of Li_2MnO_3 , which has a two-dimension layered phase with both Li/Mn atoms distributed in the octahedral site (**Figure S3a**).³¹ For T-LMO, the main peaks match well with that of the pristine LMO (**Figure S3d**). However, a new peak at around 36° and a shoulder at around 44° appear in the XRD result for T-LMO, which are aligned with the peaks of LiMn_2O_4 and $\text{Li}_2\text{Mn}_4\text{O}_9$ references.

Compared with the crystallinity-sensitive XRD technique, the Raman spectroscopy provides information on the short-range order of material.³²⁻³⁴ In **Figure 2c**, the pristine LMO exhibits broad peaks at 483 and 605 cm^{-1} , representing the bending E_g and stretching A_{1g} modes in Li_2MnO_3 , respectively.^{32, 35} The weak peaks at around 400 cm^{-1} come from the monoclinic Li_2MnO_3 component.³² Compared with pristine LMO, these two kinds of features become weaken in T-LMO. A new shoulder appears at around 633 cm^{-1} , which fits well with the peak of LiMn_2O_4 and $\text{Li}_2\text{Mn}_4\text{O}_9$ species. Therefore, the Raman spectroscopy results indicate layered-spinel coexist phases exist in T-LMO, which is consistent with the XRD result. However, it is worth noting that it is not easy for Raman and XRD techniques to resolve spinel species, such as $\text{Li}_2\text{Mn}_4\text{O}_9$ and LiMn_2O_4 with subtle difference in cationic site occupancy.

^7Li magic-angle spinning (MAS) ssNMR was further performed to trace the local environment of Li. **Figure 2d** and **Figure S4a** shows the ^7Li projection magic-angle turning and phase-adjusted sideband separation (pjMATPASS) spectra for the pristine, two cycled and treated LMO.³⁶ The pristine LMO shows two isotropic peaks resulting from Li in

octahedral site (LiO_6). The main peak with a shoulder at around 748 ppm comes from Li in the Li layer and the one at around 1500 ppm can be referred to Li in the TM layer.^{37,28} For pristine LMO, the small peak at around 0 ppm comes from residual Li_2CO_3 .³⁸ The main peaks at around 748 ppm and 1500 ppm remain in two cycled LMO sample (**Figure S4a**). The sharp signal with enhanced intensity at around 0 ppm mainly corresponds to the solid electrolyte interphase (SEI) components, such as Li_2CO_3 and LiF .^{28,39} For treated T-LMO sample, it exhibits some Li ions still left in the TM layer as that for LMO and two cycled LMO. The remained sidebands at around ± 250 ppm in T-LMO come from peak at around 0 ppm. Besides the similar peaks in LMO, a new peak appears at around 529 ppm in T-LMO, which can be ascribed to Li in tetrahedral site as that in LiMn_2O_4 .⁴⁰ Meanwhile, a broad peak at around 660 ppm fits well with that of $\text{Li}_2\text{Mn}_4\text{O}_9$ reference with Li in tetrahedral site (**Figure S4b**).⁴⁰ Although a small amount of disordered shell may exist in T-LMO sample, but their intensity is too low to be detected here which might be overlapped by the strong NMR signal associated with Li contained in the crystalline core of the particles.²⁹ The T-LMO curve is deconvoluted by standard reference spectrum (black curve), which shows that T-LMO is consist of 35.5% LMO, 16.9% LiMn_2O_4 and 47.6% $\text{Li}_2\text{Mn}_4\text{O}_9$. The NMR spectra result provides the direct evidence that new spinel phases appear in T-LMO, which may due to cation rearrangement.

Tuned oxygen and manganese oxidation

After structural comparison, the activity of oxygen and manganese was further probed to reveal the charge compensation in electrochemistry. *Operando* DEMS was performed to monitor the released anionic species during charging process.^{4,19} The *operando* DEMS data was collected with active material loading of around 8 mg (**Figure 3**). In the initial charge process for typical LMO, carbon dioxide gas evolves at the beginning, accompanying with large amount of oxygen gas release at the maximum of carbon dioxide evolution. The total gas evolution is summed to be 59.3 mmol CO_2 per mol of active material and 70.2 mmol O_2 per mol of active material. The CO_2 gas may result from the electrolyte decomposition, the reaction between electrolyte and O_2 , and impurity Li_2CO_3 decomposition.^{29,41} In contrast, the T-LMO electrode delivers a minimal amount of carbon dioxide and oxygen gas release. The

1 cumulative CO₂ and O₂ detected from T-LMO during the initial charge process is 10.5 mmol
2 and 9.1 mmol per mol of active material, respectively. The reduced gas release in treated
3 sample indicates the improved electrochemical stability for T-LMO material when operating
4 at high voltage in the battery. In addition, the different outgassing behaviors between LMO
5 and T-LMO under identical cycling conditions imply the two materials have different oxygen
6 activity.

7 Therefore, the lattice (non-released) oxygen redox states were further investigated
8 through O-K RIXS, which has been established as the technique for detecting oxidized
9 oxygen states in battery cathodes.⁴²⁻⁴⁴ It is known that a RIXS feature at 523.7 eV emission
10 energy and 531.0 eV excitation energy is characteristic to the oxidized oxygen in the lattice
11 of most Li-rich compounds.^{4, 42, 45, 46} **Figure 4a** presents the O-K RIXS data measured with
12 excitation energy at 531.0 eV. When charged to 4.8 V, the T-LMO sample shows much
13 enhanced peak intensity at the characteristic emission energy of 523.7 eV. In contrast, the
14 negligible change observed for the standard LMO electrodes upon cycling indicates that
15 majority of the oxygen oxidation reactions during the charging of LMO take place in the
16 form of gas release and surface reactions that are consistent with the DEMS results above.¹⁹
17 More importantly, the oxidized oxygen feature at the 523.7 eV (gray area) decreases in the
18 followed discharged state, suggesting a reversible lattice oxygen redox reaction in treated
19 LMO.

20 The Mn redox mechanism was further probed through Mn-L RIXS. It has been
21 demonstrated previously that, inverse partial fluorescence yield (iPFY) signals of Mn-L could
22 be extracted from a full map of RIXS (mRIXS) with no spectral lineshape distortion for
23 quantitative analysis of the Mn states.^{42,43} The mRIXS results collected from all the
24 representative samples are shown in **Figure S5**, with the extracted mRIXS-iPFY spectra and
25 quantitative fittings (dotted lines) plotted in **Figure 4b, 4d**. **Figure 4c** and **Table S2** provides
26 directly the quantitative results of the Mn oxidation states in all the samples at different
27 electrochemical states. The pristine LMO is dominated by Mn⁴⁺, as expected. However, the
28 T-LMO shows around 25% of Mn³⁺ and 75% of Mn⁴⁺. The mean valence state of manganese
29 for T-LMO is significantly reduced from that of LMO, which is consistent with the structural

characterization from XRD and Raman data ($\text{Mn}^{3.5+}$ for LiMn_2O_4 phase, Mn^{4+} for $\text{Li}_2\text{Mn}_2\text{O}_5$ phase). For T-LMO, the low-voltage plateau (below 4.5 V) during the initial charge process mainly comes from the Mn oxidation with valence state increases from 3.75 to 3.90, which is similar to that reported in LiMn_2O_4 .³⁰

The combined results and analysis of the *operando* DEMS, O-K RIXS, and Mn-L mRIXS-iPFY consistently show that the T-LMO has significantly amount of spinel phase mixed with the original layered structure. The system, although still displays a short high-voltage plateau, delivers enhanced lattice oxygen and Mn redox reactions with a suppressed oxygen release.

Structural evolution during thermal treatment

In order to further reveal the origin of structural difference between pristine and treated LMO, the evolution process during thermal treatment was further analyzed via *in-situ* variable temperature XRD. Indeed, the *in-situ* variable temperature XRD reveals the structural evolution during thermal treating process (**Figure 5a**). The structural transformation starts at around 200 °C in the relithiated LMO sample. Several diffraction peaks decrease intensities and broaden, such as the (020) diffraction peak, where the reduced (020) may result from a phase transformation from Li/Mn order to disorder in TM layer, or increased stacking fault.⁴⁷ Close inspection of the diffraction peak at 37 ° reveals that a shoulder peak appears and grows at a lower diffraction angle when the temperature increases from 210 °C to 350 °C, and finally the diffraction peak settles at the lower angle of 36 °. A similar trend is also observed for the peak at around 44 °. Simultaneously, the peak ratio between (-133) and (-331) enhanced with the increased temperature. These features indicate structural evolution from LMO layered phase to layered-spinel coexist phases. After cooling down to 25 °C, the final structure at 350 °C is well kept, suggesting the treated material is a thermodynamically stabilized system.

The Raman data (**Figure 5b**) is consistent with the structural evolution observed by *in-situ* variable temperature XRD. The features below 500 cm^{-1} become weaken when temperature increases from 210 to 350 °C. A new shoulder appears at around 633 cm^{-1} at 210 °C treated sample and grows as a peak when temperature increases to 350 °C. Therefore, the

in-situ variable temperature XRD and Raman data consistently suggest that the material evolves from layered structure to layered-spinel coexisting phase during thermal treatment process.

In the electrochemical performance (**Figure 5c**), the above 4.5 V plateau length is shortened upon the increased treated temperature. The spinel-related plateaus at around 4.1 V charge and 4.0 V/2.8 V discharge become more obvious with increased temperature.⁴⁸ The evolution of layered and spinel-like features under increased temperatures, indicating the layered-spinel coexist phases are thermal-driven in the cycled LMO system, and more importantly, **Figure 5** shows that the amount of the phase transformation could be controlled through the heating temperature.

It is worth noting that the effect of initial electrochemical two cycles treatment need to be further explored. The XRD and NMR data show the two cycled LMO material remains mainly in layer phase (**Figure 5a, S4a**). Besides, in electrochemistry (**Figure S6**), the cycled sample without thermal treatment presents severe voltage degradation. Combined with previous reports, the initial two cycle electrochemical process may produce some defects or disordered phase^{29,28}, which is an important step for the followed formation of unique layered-spinel phases.

DISCUSSION

The commercialization of Li-rich layered oxides has been hindered by its electrochemical performance, especially the voltage decay during cycling. Extensive efforts have been made to reveal the relationship between the voltage decay and other chemical/structural changes. However, its fundamental understanding remains elusive and the practical solution has not been found. Therefore, understanding and eliminating the voltage fade in a relatively simple model compound, LMO, becomes particularly important to clarify the debates on the mechanism and to provide insights for optimizations.

In previous works, the electrochemical cycling performance of Li-rich cathodes has been efficiently improved through surface treatment, such as spinel phase coating.^{49,50} However, the effect of surface coating usually works on the stabilization toward cyclic capacity, but not the average working voltage^{49,50}, indicating the average voltage decay may evolves from the

changes of bulk structure of the materials. Here, the voltage decay is essentially suppressed via the quantified partial phase transformation from layered to spinel in the Li-rich parent compound. Through the electrochemical-thermal treatment, the spinel LiMn_2O_4 and $\text{Li}_2\text{Mn}_4\text{O}_9$ phase emerge with Li ions partially sit in the tetrahedral site and Mn ions partially sit in the octahedral site in Li plane. Such layered-spinel coexist phases lead to stabilized average voltage during cycling. The enhanced lattice oxygen redox reversibility (**Figure 4**, RIXS) and the reduced oxygen release (**Figure 3**, DEMS) confirm the positive effect of the emerged layered-spinel coexist phases.

Although the practical application of the Li- and Mn-rich material, especially the long-term cycling performance still needs further efforts, the results here provide some new insights for guidelines to eliminate voltage decay. It has been confirmed that Li-rich oxides evolve from layered phase to spinel-like phase during electrochemical cycling^{28,25}, however, it is worth noting that the spinel-like phase for cycled layered phase is not the same as the layered-spinel phases of T-LMO shown in this work. This is evidenced in three sets of data. First, the operating voltage is the intrinsic property for battery material. However, the average voltage value for treated T-LMO is obviously different with that of the cycled LMO (**Figure S2a**), which means the treated and the simply cycled LMO material are of different phases. This also indicates the layered-spinel phases shown in this work is not the root cause of the voltage decay. Second, the electrochemical curve feature is another characteristic behavior of material. The spinel-like feature shown in electrochemical curve for T-LMO is not the same as that of the cycled LMO (**Figure S1, S6**). Third, our temperature dependent *in-situ* XRD results show directly that the two cycled LMO is close to the standard layered structure, but the T-LMO displays strong spinel signatures with different electrochemical profile, that could even be tuned by the heating temperature (**Figure 5**).

On the other hand, the *in-situ* formation of the spinel $\text{LiMn}_2\text{O}_4/\text{Li}_2\text{Mn}_4\text{O}_9$ phase through electrochemical-thermal treatment is different from mechanically adding spinel phase into layered LMO. The interwoven layered-spinel phases deliver enhanced capacity behavior toward capacity and stability than that of $\text{LiMn}_2\text{O}_4/\text{Li}_2\text{Mn}_4\text{O}_9$ phase alone,⁵¹ especially in the wide charge-discharge voltage window used here. Although the specific local structure of the

coexist phases needs further exploration, the present result discloses that the layered-spinel coexist phases are optimal method for stabilizing the voltage evolution in Li- and Mn-rich cathode.

CONCLUSION

We present a voltage-decay free LMO through a combined electrochemical conditioning and thermal treatment. Experimental results reveal *in-situ* formation of the spinel phases, which are combined with the original layered structure, providing much improved electrochemical performance of voltage stability, capacity retention, and rate performance. As explicated in **Figure 6**, the electrochemical-thermal driven layered-spinel phases are observed via XRD, Raman and ssNMR method. In treated material, the cationic redistribution induces electronic configuration evolution for manganese. Combined with *operando* DEMS and RIXS spectroscopy, we discover that the oxygen activity in LMO is tuned through such phase transformation, indicated by the reversible oxygen and manganese redox reaction found in T-LMO. Such layered-spinel coexist phases with electronic configuration evolution are suggested to stabilize voltage evolution during cycling. We hope these findings will provide guidelines to design the local structure of Li-ion battery cathode material with stabilized electrochemical performance.

METHODS

Synthesis of pristine LMO and reference LiMn_2O_4 , $\text{Li}_2\text{Mn}_4\text{O}_9$ sample. The LMO and reference samples were prepared by conventional solid-state reaction. Stoichiometric amount of Li_2CO_3 (Sinopharm Chemical Reagent Co., Ltd., AR) and MnCO_3 (Alfa Aesar, 99.9%) were mixed via ball milling in acetone for 4 h and dried in air. To compensate for Li loss at high temperature, 1wt% extra amount of Li_2CO_3 was used in the starting material. The precursor was then pelletized and calcined at oven. The LMO sample was sintered at 750 °C for 12 h in air. The reference sample LiMn_2O_4 was calcined at 600 °C for 12 h and 850 °C for 24 h in air. The reference sample $\text{Li}_2\text{Mn}_4\text{O}_9$ was calcined at 400 °C for 32 h in air.

Electrochemical measurements. The cathodes were prepared by mixing 80 wt% active

materials, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) binder together with N-methyl-2-pyrrolidone (NMP) as the solvent. The mixture was coated on aluminum foil, pressed at 20 MPa and dried at 120 °C in air for 2 h. The 2025 coin-type cells consisting of the as-prepared cathode, Li metal as anode, and Celgard 2325 as separator were assembled in argon-filled glove box. The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (volume ratio 3:7). All cells were cycled between 2.0 and 4.8 V (versus Li/Li⁺) at current density of 20 mA g⁻¹ at room temperature on Land CT 2001A battery testers, except otherwise defined. The electrochemical impedance spectroscopy (EIS) measurements were performed from 100 kHz to 10 mHz with an amplitude of 10 mV using a multichannel potentiostat (PARSTAT MC).

Electrochemical-thermal treatment. The two cycled coin-type cells were disassembled in the argon-filled glove box. The cathode electrodes were carefully extracted from the cells and then rinsed in dimethyl carbonate (DMC) solvent immediately to remove electrolyte residues and dried under vacuum overnight. The obtained electrodes were then transferred from the glove box into an oven and treated with different temperatures (210 °C, 280 °C, 350 °C) in the air for four hours. The weight loss during high temperature treatment was below 3% of that of electrode, which primarily results from the decomposition of carbon and binder.^{21,22} For comparison, one of the obtained electrodes was kept in the argon-filled glove box in room temperature. After thermal treatment/kept in glove box, the electrodes were reassembled to coin-type cells with a fresh Li metal as the counter electrode.

Materials characterizations. The XRD data was collected on a Rigaku Ultima IV powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) source at a scanning rate of 10° min⁻¹. Rietveld refinement was performed using General Structure Analysis System (GSAS) software with EXPGUI interface⁵². Schematic diagrams were drawn by VESTA software⁵³. Raman spectroscopy (Horiba LabRaman HR evolution) was collected with a wavelength of 632.8 nm and power of 7 mW. The chemical compositions of the sample was determined using ICP-AES (IRIS Intrepid II XSP, Thermo Electron).

***In-situ* variable temperature XRD.** The electrode for *in-situ* variable temperature XRD was carried out with carbon current collector to minimize the signal overlap between material and collector. The representative cells were cycled to representative state, transferred into argon-filled glove box and disassembled. The obtained electrode was then rinsed in DMC solvent immediately and dried in vacuum overnight. To track the structural evolution during thermal treatment process, the prepared electrode was heated from room temperature to 350 °C in air condition (heating rate = 3 °C min⁻¹). The temperature was kept for four minutes at every desired point and followed with the XRD record. The XRD was performed on Bruker D8 Discover diffractometer equipped with a Cu K α radiation.

***Operando* DEMS.** The *Operando* DEMS experiment was carried out at room temperature through a Swagelok-type electrochemical cell and quadrupole mass spectrometer (Hiden Analytical). The cell was electrochemical controlled by Land CT 2001A battery testers in room temperature. During the measurement, high-purity argon gas flowed through the main chamber of the cell as the carrier gas, the flow rate was controlled at 0.5 mL min⁻¹ using a digital mass flow meter (Bronkhost). The positive electrodes were prepared with mass of around 8 mg.

ssNMR. The ⁷Li Magic Angle Spinning (MAS) NMR experiments were performed on a Bruker-AVANCE-400M NMR spectrometer (9.4 T) with the ⁷Li Larmor frequency of 155.6 MHz using a 1.3 mm double-resonance MAS probe. The samples were packed into 1.3 mm MAS rotors in argon-filled glove box and the sample spinning rate of 40 kHz was used during the measurements. The pjMATPASS experiment was used to eliminate the sidebands with a $\pi/2$ pulse width of 1.74 μ s and a recycle delay of 0.1 s. 1M LiCl with the chemical shift at 0 ppm was employed as the reference.

O-K and Mn-L RIXS. The RIXS was measured in iRIXS endstation at Beamline 8.0.1 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL).⁵⁴ The

desired electrodes were electrochemically cycled to the state of charge, disassembled in the argon-filled glove box, soaked in DMC solvent immediately to lock the state of charge and dried in vacuum overnight. The electrodes were cut in desired size and mounted into the copper holder and then transferred into the main chamber with suitcase to avoid any air exposure. The O-*K* and Mn-*L* RIXS data were collected via the ultra-high-efficiency modular spectrometer and ultra-high-through modular spectrometer, respectively.⁵⁵ All data were collected from the side of the electrodes facing the current collector. During the O-*K* RIXS experiment, the samples were kept moving to minimize the effect of radiation on oxygen signals and enlarge the test area. The spectra were normalized to the beam flux measured via the gold mesh. The final data were achieved via multi-step data processing including normalization to collecting time, energy calibration and background correction, which has been detailed in previous work.⁵⁶

Mn-*L* iPFY. The Mn-*L* iPFY spectra were achieved by the formula $iPFY = m/PFY_{O-K}$, where *m* was a normalization coefficient and PFY_{O-K} was achieved by integrating the intensity across emission energy range from 506 eV to 530 eV in the Mn-*L* RIXS. Principles of iPFY have been explained in previous work.^{54,57} Quantitative fittings of Mn-*L* iPFY follows the linear combination method with three standard experimental spectra on Mn^{2+/3+/4+}.⁵⁸

CONFLICTS OF INTEREST

There are no conflicts to declare.

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1 FIGURES

Figure 1. Cycling performance of the pristine and treated LMO. (a) Charge-discharge profiles, and **(b)** normalized charge-discharge profiles of pristine LMO material. **(c)** Charge-discharge profiles, and **(d)** normalized charge-discharge profiles of treated LMO material. Cells were cycled between 2.0 V and 4.8 V with current density of 20 mA g^{-1} .

Figure 2. The electrochemical and structural comparison for the pristine and treated LMO. (a) The charge-discharge curves and (b) dQ/dV plots for the pristine and treated LMO in the initial cycle. (c) Raman spectra for the pristine and treated LMO. (d) ⁷Li pJMATPASS NMR spectra for the pristine, treated LMO and fitting result for T-LMO. The asterisk indicates sidebands. Pure LiMn₂O₄ and Li₂Mn₄O₉ were measured as reference.

Figure 3. Different oxygen activity in the initial charge process. Gas evolution for (a) the pristine and (b) treated LMO cathode via *operando* DEMS measurement. Cells were cycled between 2.0 V and 4.8 V with current density of 20 mA g⁻¹.

Figure 4. Charge compensation for pristine and treated LMO. (a) The O-K RIXS spectra with excitation energy of 531.0 eV. The treated T-LMO delivers enhanced intensity at 523.7

1 eV emission energy and 531.0 eV emission energy, indicating the enhanced lattice oxygen
2 activity. **(b)** The Mn-*L* iPFY spectra for bulk probe of manganese valence state. Standard
3 experimental spectra of Mn²⁺, Mn³⁺ and Mn⁴⁺ are shown at the bottom. **(c)** The content of
4 bulk manganese valence state through quantitative fitting of Mn-*L* iPFY spectra in **(b)**. **(d)**
5 The average valence state of manganese from Mn-*L* iPFY spectra. **(e)** Typical Mn-*L* mRIXS
6 for LMO sample at pristine state.

Figure 5. The evolution of cationic distribution. (a) *in-situ* variable temperature XRD patterns for relithiated LMO during thermal treatment process. The asterisk in (a) comes from the instrumental background. (b) Raman spectra for samples after treated with elevated temperatures at 210 °C, 280 °C and 350 °C, respectively. (c) The initial charge-discharge curves for the pristine and treated LMO series.

Figure 6. Schematic for electrochemical-thermal treated Li-rich oxides with voltage-decay free. The gray, red and blue ball represents Li, O and Mn, respectively. Pristine LMO with cation atoms in octahedral sites delivers severe gas release and voltage decay. For treated T-LMO, the *in-situ* formed layered-spinel coexist phases deliver stabilized voltage evolution in electrochemical cycling. Besides, the spinel component in coexist phase is supposed to accommodate the oxygen release in the initial charge process, which likely helps to stabilize the average voltage in followed cycling.