Regulating Dynamic Electrochemical Interface of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Spinel Cathode for Realizing Simultaneous Mn and Ni Redox in Rechargeable Lithium Batteries

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The exploding electric-vehicle market requires cost-effective high-energy materials for rechargeable lithium batteries. The manganese-rich spinel oxide LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) can store a capacity greater than 200 mAh g$^{-1}$ based on the multi-cation (Ni$^{2+}$/Ni$^{4+}$ and Mn$^{3+}$/Mn$^{4+}$) redox centers. However, its practical capacity is limited to Ni$^{2+}$/Ni$^{4+}$ redox (135 mAh g$^{-1}$) due to the poor reversibility of Mn$^{3+}$/Mn$^{4+}$ redox. This instability is generally attributed to the Jahn–Teller distortion of Mn$^{3+}$ and its disproportionation, which leads to severe Mn dissolution. Herein, for the first time, the excellent reversibility of Mn$^{3+}$/Mn$^{4+}$ redox within 2.3–4.3 V is demonstrated, requiring revisiting the previous theory. LNMO loses capacity only within a wide voltage range of 2.3–4.9 V. It is revealed that a dynamic evolution of the electrochemical interface, for example, potential-driven rocksalt phase formation and decomposition, repeatedly occurs during cycling. The interfacial evolution induces electrolyte degradation and surface passivation, impeding the charge-transfer reactions. It is further demonstrated that stabilizing the interface by electrolyte modification extends the cycle life of LNMO while using the multi-cation redox, enabling 71.5% capacity retention of LNMO after 500 cycles. The unveiled dynamic oxide interface will propose a new guideline for developing Mn-rich cathodes by realizing the reversible Mn redox.

1. Introduction

The worldwide growth of the electric-vehicle (EV) market requires better rechargeable lithium batteries (RLBs), including Li-ion and Li-metal systems, with higher energy density and lower price. For a decade, substituting cobalt with nickel in cathodes has been an effective strategy to reduce the materials cost for RLB production while increasing the energy density.[1–4] However, the rapid growth of EVs has led to the consumption of a tremendous amount of metal resources, eventually triggering a price surge of nickel and lithium.[5,6] The year-by-year price change of the most commonly used metal elements in cathode materials (Figure 1a) indicates that the rate of increase of the cost of lithium, nickel, and cobalt has significantly accelerated in recent years. In contrast, the price of manganese has remained incomparably low. Specifically, the lithium, nickel, cobalt, and manganese prices in the first quarter of 2022 were 75 400, 33 200, 70 200, and 1600 USD ton$^{-1}$, corresponding to 1257%, 241%, 217%, and 133% of those in 2020 (see Table S1, Supporting Information). Consequently, the increases in the metal cost per kilogram of LiCoO$_2$ (LCO), LiNi$_{0.8}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622), LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (NMC811), and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) over the past 2 years has been 27.7, 16.6, 16.7, and 5.9 USD kg$^{-1}$, respectively (Figure 1b and Table S2, Supporting Information). The materials cost of LNMO was only 34.5%
and 18.7% of that of NMC811 and LCO, and the price fluctuation of LNMO was less than 36% for NMC622 and NMC811. Thus, the use of Mn-rich chemistry has attracted attention from researchers as a promising option to realize cathode materials with high economic sustainability, price competitiveness, and reasonable energy density.[7–12]

Among the Mn-rich cathode materials, spinel-type LNMO is an attractive alternative to the Ni-rich layered oxides. LNMO is renowned for the high potential of the Ni$^{2+}$/Ni$^{4+}$ redox couple, 4.7 V (vs Li), offering a theoretical energy density of 690 Wh kg$^{-1}$, within a conventional voltage range of 3.5–4.9 V.[13,14] A more exciting feature of LNMO is its capability to store more energy using an additional Mn$^{3+}$/Mn$^{4+}$ redox reaction at 2.7 V (Figure 1c,d).[15–17] Thus, the simultaneous use of Ni and Mn multi-cation redox reactions in LNMO enables a high energy density exceeding 860 Wh kg$^{-1}$. Combining the high energy density with low materials cost, LNMO exhibits a high energy-to-cost ratio of 89.7 Wh USD$^{-1}$, corresponding to 547% and 279% of that of LCO and NMC811, respectively, when cycled over a wide voltage range (WVR), as illustrated in the spider maps in Figure 1e (see more details in Table S3, Supporting Information).[18–21]

Despite this benefit, a long-established hypothesis has restricted the use of multi-cation redox reactions in LNMO: The reduction of Mn$^{4+}$ to Mn$^{3+}$ inevitably results in poor capacity retention.[15,22–26] The Jahn–Teller distortion of the Mn$^{3+}$ octahedral sites causes the phase transition from cubic (Fm$ar{3}$m) to tetragonal (I4 1/amd) phases, inducing an extra anisotropic lattice strain. Furthermore, trivalent Mn is considered labile to the disproportionation into Mn$^{4+}$ and Mn$^{2+}$. The formation of Mn$^{2+}$, which has a high solubility in organic electrolytes, would lead to a rapid capacity loss. The reversible use of the Mn redox reaction, however, has been successfully demonstrated in many other cathode materials, such as Li-rich Mn-rich layered oxides,[27–31] disordered Li-rich rocksalt oxides,[32–35] and substituted spinel lithium manganese oxides.[36,37] The extended cycle life of Mn-based cathodes in many reports,[27,30,38] confirms that the formation of divalent and trivalent manganese cations does not necessarily result in deterioration of the battery performance. Instead, the results suggest that appropriate materials engineering based on the precise understanding of the degradation mechanism can facilitate the stable use of Mn-rich redox chemistry in batteries. Recently, some studies have demonstrated substantially improved reversibility of consecutive Ni
and Mn redox reactions in LNMO cathodes, realized by tuning the nickel–manganese ordering through additional annealing\cite{39} and adapting the secondary particle morphology.\cite{40,41} Despite the improvements, a comprehensive explanation of the inconsistent cycling performance and origin of the deterioration of LNMO upon wide-voltage cycling remain elusive.

Herein, we revisit the failure mechanism of LNMO cathodes when employing the multi-cation redox reaction of nickel and manganese using surface-sensitive structural and chemical probes. We demonstrate the unprecedentedly high reversibility of the Mn$^{3+}$/Mn$^{4+}$ redox reaction, offering 96.2% capacity retention during 100 cycles without any modification of the electrolyte or electrode, thereby disproving the conventional theory of LNMO degradation. The rapid capacity fade occurs only when the LNMO cathode simultaneously employs Mn$^{3+}$/Mn$^{4+}$ and Ni$^{2+}$/Ni$^{4+}$ redox reactions. We attribute the deterioration to a dynamic evolution of the electrochemical interface induced by the potential change, for example, the repeated formation and decomposition of the surface rocksalt phase at low and high voltages, respectively. The interfacial evolution accelerates the electrolyte decomposition and CEI formation, thereby increasing the cell impedance. Finally, we demonstrate that a simple electrolyte modification (e.g., EC exclusion) enables LNMO to possess a capacity retention of 91.0% after 100 cycles, an energy density of 715 Wh kg$^{-1}$, and a power density of 588 W kg$^{-1}$ within the voltage range of 2.3–4.9 V. We believe that this study will rejuvenate interest in Mn-rich spinel oxides with multi-cation redox capability as economically sustainable high-energy cathode materials.

2. Results and Discussion

2.1. Voltage-Range-Dependent Cyclability of LiNi$_{0.5}$Mn$_{1.5}$O$_4$

To examine the feasibility of simultaneously using manganese and nickel redox couples, we tested the cycle performances of the LNMO half cells at 0.2 C in three different voltage ranges: 2.3–4.3 V (low voltage range, LVR), 3.5–4.9 V (upper voltage range, UVR), and 2.3–4.9 V (WVR), as shown in Figure 2a. For the test, we used commercial LNMO particles with an average size of 3.5 µm (Figure S1, Supporting Information). Unexpectedly, the LNMO cell retained 96.2% of the initial capacity after 100 cycles in LVR, where the Mn$^{3+}$/Mn$^{4+}$ redox reaction is responsible for the voltage plateaus at 2.7 and 4.1 V (Figure 2b). During the prolonged cycling, the overpotential barely increased, as observed in the differential capacity versus voltage (dQ/dV) curves (Figure S2a, Supporting Information), and the coulombic efficiency (CE) remained higher than 99.2%. This result contradicts the conventional claim of the detrimental effect of trivalent manganese on the battery cycle life due to the Jahn–Teller distortion followed by a disproportionation.\cite{25,42,43} In fact, this result confirms the viability of exploiting the Mn$^{3+}$/Mn$^{4+}$ redox reaction reversibly in high-voltage spinel to achieve a high energy density exceeding 850 Wh kg$^{-1}$. In UVR using Ni$^{2+}$/Ni$^{4+}$ redox, i.e., the conventional voltage range, the LNMO cell retained 95.3% of the initial capacity after 100 cycles (Figure 2c). This capacity retention is consistent with the values in previous reports.\cite{44,45} However, when using the Ni$^{2+}$/Ni$^{4+}$ and Mn$^{3+}$/Mn$^{4+}$ redox couples together in WVR,
The LNMO cell rapidly lost its capacity, preserving only 56.1% after 100 cycles (Figure 2d). The dQ/dV profiles indicate the significant increases in the overpotential (Figure S2c,d, Supporting Information), reflecting the growing cell impedance during the cycling in WVR. The same phenomenon, that is, the voltage-range dependence of the cyclability, was observed under a higher current density of 1 C (Figure S3, Supporting Information). The LNMO cells lost 53.8% of the initial capacity after 300 cycles in WVR, whereas the losses were only 8.1% and 8.5%, respectively, in UVR and LVR. Despite the lower reversible capacity used at 1 C in WVR, rapid degradation of the LNMO cathodes could not be avoided.

The stark contrast between the cycle life of LNMO in LVR and WVR suggests that the mere use of the Mn$^{3+}$/Mn$^{4+}$ redox reaction does not necessarily lead to capacity loss and resistance increase. Hence, deciphering the different degradation mechanisms of LNMO in LVR and WVR is crucial to realizing the complete use of multi-cation redox reactions in Mn-rich cathode materials. We first investigated the bulk characteristics of LNMO after 100 cycles in each of the three voltage ranges using X-ray diffraction (XRD) and synchrotron-based X-ray absorption spectroscopy. All the samples were discharged to 3.5 V before the measurement to match the Li stoichiometry. The full-pattern fitting results reveal that the lattice parameters were 8.17 Å (space group: Fd$ar{3}$m) for all the cycled LNMOs, identical to that of the pristine LNMO (Figure S4 and Table S4, Supporting Information). The full-width-half-maxima values of the (111) peak remained similar, with a standard deviation of less than 5% (Figure S5, Supporting Information), indicating little bulk structural evolution during cycling. The LNMO cathodes cycled in LVR and WVR undergo the reversible phase transformation between cubic (Fd$ar{3}$m) and tetragonal (I4$_1$/amd) phases (Figure S6, Supporting Information) and experience the Jahn–Teller distortion of Mn$^{3+}$. However, their bulk structures at 3.5 V after the prolonged cycling barely differ from that of LNMO cycled in UVR, in which Mn redox hardly occurs. The Mn K-edge X-ray absorption near-edge spectra (XANES) in Figure 2f captured only minor differences in the Mn oxidation states (+4) between the LNMOs discharged to 3.5 V after 100 cycles. The Ni K-edge XANES also showed negligible contrasts in the Ni oxidation states (Figure S7, Supporting Information). The overall results confirm negligible bulk degradation regardless of the amount of capacity loss.

In contrast, electrochemical impedance spectroscopy (EIS) analysis revealed significant differences in the cell resistances among the varying voltage ranges. Because of the ambiguous features of the semicircles in the Nyquist plot at 3.5 V (Figure S8, Supporting Information), we compared the EIS spectra of the cells cycled in WVR and UVR at 4.9 V and those in WVR and LVR at 2.3 V, respectively. As shown in Figure 2g–i, during 50 cycles in WVR, the charge-transfer resistance ($R_c$) increased consistently and significantly, whereas the $R_R$ values of the cells cycled in UVR and LVR remained stable. The increase of $R_c$, which predominantly contributed to the overpotential growth in WVR (Figure S2c,d, Supporting Information), is attributable to the parasitic reactions at the CEI, impeding the charge-transfer reactions. We note that within WVR, the $R_c$ value of the 50th cycle corresponds to 14- and 3-times-higher values compared with the 5th cycle at 4.9 and 2.3 V, respectively. The discrepancy observed at different potentials implies the possibility of CEI evolution in specific voltage regions.

### 2.2. Low-Voltage-Driven Spinel-to-Rocksalt Phase Transformation at LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Surface

To assess the voltage range-interface correlation, we thoroughly investigated the crystallographic and chemical structures of the cycled LNMO surface using high-resolution transmission electron microscopy (HR-TEM) coupled with spatially resolved electron energy loss spectroscopy (EELS) and soft X-ray absorption spectroscopy. For the analyses, all the electrodes were discharged to 3.5 V after 100 cycles at 1 C. Although all the selected area diffraction patterns of LNMOs within the three different voltage ranges indicated a spinel phase, identical to the pristine state (Figure S9, Supporting Information), the HR-TEM images unambiguously revealed distinctive surface structures of the LNMOs (Figure 3a–c). After cycling in LVR, the LNMO surface transformed into a rocksalt phase with a thickness of 7–10 nm, as probed by the fast Fourier transformation (FFT) patterns of 10 x 10 nm$^2$ area (Figure 3a). Inside the rocksalt layer, the original spinel phase remained intact. The parallel orientation of the lattice fringes in the HR-TEM image and the FFT patterns indicate that the rocksalt phase is coherent with the spinel phase, sharing the oxygen framework. The coherency is the evidence of cation densification caused by oxygen release. The Mn L-edge EELS spectra collected with 4-nm-gaps from the surface to the bulk reveal the divalent manganese cations up to 8-nm away from the surface. After cycling in UVR, in contrast, the LNMO surface maintained the spinel structure, as confirmed by the FFT patterns and Mn$^{3+}$-dominant EELS spectra (Figure 3b). This result indicates that the rocksalt phase formation is unfavorable in the high-voltage range. Only thin CEI (<1 nm) was observed due to the electrochemical oxidation of the electrolyte at such a high voltage (Figure S10, Supporting information). When cycled in WVR, the surface evolved to become more complex. The LNMO surface consisted of a 1.5-nm-thick rocksalt phase and a 4-nm-thick outer CEI layer of low crystallinity (Figure 3c). Because WVR includes LVR, one can imagine the rocksalt phase forming in WVR such as in LVR. However, the rocksalt phase was thinner in WVR (∼1.5 nm) than in LVR (∼7 nm), and the rocksalt phase hardly formed in UVR. These differences suggest the spontaneous formation of the rocksalt phase at low voltage and its instability at high voltage. We hypothesized that the rocksalt phase formed in LVR could be decomposed when charged to a high voltage such as 4.9 V. The dissociation of the rocksalt phase into TM and O could trigger the electrolyte decomposition, which results in the CEI formation.

The near-edge X-ray absorption fine structure (NEXAFS) spectroscopy offers more detailed information about the chemical states of the surface regimes. The Mn L-edge NEXAFS spectra obtained in total electron yield mode (TEY, probing depth = 5–10 nm) allow comparison of the Mn oxidation states in the pristine LNMO, cycled LNMOs, and Mn$_3$O$_4$.
The NEXAFS spectrum of LNMO cycled in LVR unambiguously confirms that the Mn$^{2+}$ dominates the surface due to the rocksalt phase. Consistent with the HR-TEM and EELS analyses, the amount of the reduced Mn from the rocksalt phase was in the order of LVR $>$ WVR $>$ UVR = uncycled LNMO. The Ni L-edge NEXAFS spectra show no difference between the samples (Figure S11, Supporting Information) because both the spinel and rocksalt phases contain Ni$^{2+}$ at 3.5 V. The O K-edge NEXAFS spectra consistently probed the reduced Mn$^{2+}$ cations\[46,47\] in the pre-edge region, confirming the surface rocksalt phases in LVR and WVR (Figure S12a, Supporting Information). However, the O K-edge fluorescence yield (FY) NEXAFS spectra (probing depth $= 150–200$ nm) revealed negligible differences between the cycled samples and the pristine LNMO, indicating the well-preserved bulk spinel phase in all the samples (Figure S12b, Supporting Information).

The C K-edge NEXAFS spectra offer information on organic species originating from the electrolyte decomposition. As shown in Figure 3e, the C K-edge NEXAFS spectrum of the LNMO cycled in LVR differed negligibly from that of the uncycled electrode. This result is attributed to the high stability of the electrolyte in the voltage range of 2.3–4.3 V. In contrast, the spectrum of the LNMO cycled in WVR contains intense peaks at 288.3 and 290.1 eV, corresponding to C–O, –CH$_2$ and CO$_3^{2−}$, RO species, respectively. At the same time, the intensity of the C $\pi^*$ peak at 285.5 eV decreased in WVR because the CEI layer covered the conductive carbon. Given the weaker CEI features in UVR and LVR than in WVR, we concluded that cycling over a WVR provokes rigorous electrolyte decomposition and CEI formation, whereas cycling either in high- or low-voltage ranges does not.

### 2.3. Decomposition of Rocksalt Phase at High Voltage Triggering Rigorous CEI Formation

To verify the evolution of the surface rocksalt phase of LNMO in WVR, we monitored the surface rocksalt phase of LNMO, which was grown during 99 cycles in LVR, after being charged to 3.5, 4.3, and 4.9 V, respectively. Figure 4a presents the voltage profile of the 99th cycle and the following charge process for the sample preparation. The Mn L-edge EELS spectra (Figure 4b) reveal that the rocksalt phase containing Mn$^{2+}$ remains at 3.5 and 4.3 V. However, charging LNMO to 4.9 V eliminates the Mn$^{2+}$ cations from the surface. As a result, Mn$^{3+}$ cations dominate the LNMO surface. The HR-TEM image and FFT patterns (Figure 4c) further confirm the high-voltage-driven rocksalt decomposition, resulting in the reduced thickness of the rocksalt phase to 2 nm. The Mn L-edge EELS depth profiles (gap = 2 nm) also reveal the superficial existence of Mn$^{3+}$. At the same time, we observed that the C–O (or –CH$_2$) and CO$_3^{2−}$ (or RO$^-$) peaks intensified in the C K-edge NEXAFS spectra after the 4.9 V charging process (Figure 4d), implying the coupling between the rocksalt phase dissociation and CEI formation. All the experimental evidence validates the destabilization of the MO-type rocksalt phase in a high-voltage regime. It is worth highlighting that the finding is consistent with our previous study reporting the high-voltage-driven decomposition of surface rocksalt and disordered spinel phases in the Ni-rich...
layered cathode, which occurs when the charge voltage exceeds 4.6 V.\textsuperscript{[48]}

To establish the correlation between the rocksalt decomposition and electrolyte degradation, we tested the electrochemical stability of rocksalt-type metal monoxides, NiO and MnO, and spinel-type manganese oxide, Mn$_3$O$_4$, under a constant current condition. In addition, we conducted gas chromatography-flame ionization detection (GC-FID) for quantitative analysis of the gas collected inside the pouch cells during the charging process to attain a comprehensive understanding of the complex decomposition reactions. Lithium titanium oxide (Li$_4$Ti$_5$O$_{12}$, LTO) electrodes were applied as anodes instead of Li metal to minimize the side reactions.\textsuperscript{[49]} For comparison, an LNMO||LTO cell was charged with the same current density for the same duration. A long voltage plateau appeared at 4.4 V versus Li (2.8 V vs LTO) for the NiO cell, indicating rocksalt phase oxidation (Figure 4e). Notably, the potential was lower than the Ni$^{2+}$/Ni$^{4+}$ redox potential of LNMO. Figure S13, Supporting Information, shows that the oxidation was irreversible, resulting in a negligible capacity for the following discharge to 2.3 V (vs Li). MnO and Mn$_3$O$_4$, which possibly exist on the surface of LNMO cycled within LVR, were also labile.
to oxidation over 4.3 V (vs Li) (Figure S14, Supporting Information). These results prove that the LNMO cathodes experience repeated rocksalt formation and decomposition during cycling in WVRs utilizing multi-cation redox reactions. More importantly, the GC-FID quantification results indicate that the rocksalt decomposition triggers significant electrolyte decomposition (Figure 4f). Despite the lower oxidation potential, the total amount of gaseous byproducts was incomparably higher in the NiO pouch cell than in the LNMO pouch cell. The major components were CO₂ and CO, accounting for 94.6% and 3.9%, respectively, of the released gas from the NiO cell. In contrast, the LNMO cell released less than 1% of CO₂ gas compared with the NiO cell and no CO gas during the charging process, indicating that the topotactic delithiation reaction efficiently utilized most electrons without significant parasitic reactions. The rigorous gas evolution behavior of NiO results in the swelling of the pouch cell, whereas the LNMO cell maintains its original shape (Figure S15, Supporting Information). A viable cause of the stimulated electrolyte decomposition in the rocksalt cell is reactive oxygen species (ROS) released from the lattice of transition metal oxides at high potential [49-51]. The ROS, for example, singlet oxygen, spontaneously attacks the electrolyte solvents such as ethylene carbonate and initiates the ring-opening reactions, generating various gases such as CH₄, CO, and CO₂, together with soluble byproducts such as glycolic acid and oxalic acid [49, 51-53]. The byproducts can be electrochemically and chemically reactive to form CEI layers, further stimulating the electrolyte. We confirmed that the LNMO cathodes released 192, 2200, and 10 times more CO, CH₄, and CO₂ when cycled in WVR than in UVR (Figure S16, Supporting Information).

In summary, in WVR, the LNMO cathodes experience the repeated formation and decomposition of the surface rocksalt phase at low and high voltages, which induce the ROS evolution, resulting in continuous deterioration of the electrolyte and electrochemical interface (Figure 4g). The accumulation of the complex side reactions results in a steady increase in the charge-transfer resistance and rapid capacity decrease. Note that LNMO is known to unlikely release ROS from its lattice below 5 V [30, 52], Therefore, no chemical reaction between ROS and the carbonate electrolyte is expected in LNMO cells merely cycled in UVR under conventional conditions and we confirmed only trace amounts of gas evolution in UVR (Figure S16, Supporting Information).

We note that the spinel-to-rocksalt surface reconstruction is confined in the 7–9 nm from the particle surface in LVR and does not further progress into the particle center (Figure 3a). Therefore, we can expect that the frequency of transition between LVR and UVR may affect the lifespan of the LNMO. To evaluate the effect of the voltage range alteration frequency on the cycle life of LNMO, we cycled LNMO alternating LVR and UVR every 5 cycles and 50 cycles (Figure S17, Supporting Information). In the end, the LNMO experienced 100 LVR and 100 UVR cycles in both conditions. As shown in Figure S17b, Supporting Information, the capacity loss of LNMO was more severe under alternating voltage ranges every five cycles. At the same time, the LNMO suffered a significant and continuous overpotential increase during the long-term cycling (Figure S17c,d, Supporting Information). In contrast, the overpotential barely increased for the 50-cycle-alteration condition.

The EIS spectra of the LNMO cathodes after 200 cycles (100 LVR + 100 UVR cycles) reveal that the overpotential increase during the more frequent voltage transition is due to the degradation at the cathode-electrolyte interface (Figure S18, Supporting Information). The degradation impedes the charge transfer reactions fast during the 5-cycle-alteration, resulting in 3.3-times-higher $R_c$ compared to the 50-cycle-alteration. We conducted an X-ray photoelectron spectroscopy (XPS) analysis of the corresponding cathodes to trace the CEI components at the cathode surface. In O 1s XPS spectra, the peak area ratios of the CEI components (sum of C–O, C=O, CO₃, and LiPF₆O₂) to the TM-O were 1.1, 0.8, and 0.6 for the pristine, 50-cycle-altered, and 5-cycle-altered electrodes, respectively (Figure S19a-c, Supporting Information). Consistent with the O 1s XPS spectra, the C 1s spectra show the most dominant CEI components for the 5-cycle-altered electrode (Figure S19d-f, Supporting Information).

The results led us to conclude that frequently alternating the voltage ranges induces electrolyte degradation at the CEI, impeding the charge transfer reactions. The WVR cycling indeed corresponds to the voltage alteration between LVR and UVR every single cycle. Accordingly, rigorous degradation occurs in WVR by repeating the rocksalt formation at the low voltage and decomposition at the high voltage, which repeatedly causes ROS evolution and electrolyte decomposition.

2.4. Improved Performances of LiNi₀.₅Mn₁.₅O₄ by Modulating Cathode–Electrolyte Interaction

The proposed degradation mechanism implies that tuning the stability of the cathode–electrolyte interaction is the key to realizing long-term cycling of the LNMO cathodes in WVR. In modulating the interfacial stability, we found that a simple modification of the electrolyte formulation can effectively improve the reversibility of the multi-cation redox in LNMO. Figure 5a shows the lifespan of LNMO in WVR by with various electrolytes; 1 M LiPF₆ in EC/DEC (1:1 v/v) (LP40), 1 M LiPF₆ in EC/DMC (1:1 v/v) (LP30), 2 M LiPF₆ in EC/DEC (1:1 v/v) (2 M LP40), 1 M LiPF₆ in DMC (1 M EC-free), and 2 M LiPF₆ in DMC (2 M EC-free). The poor reduction stability of pure DEC solvent in contact with Li metal limited the use of DEC as a sole solvent in electrolyte (Figure S20b, Supporting Information). The LNMO in LP30 showed poor capacity retention of 50.9% for 100 cycles similar to the LP40 case losing 32.3% capacity. The result indicates that the kinds of linear carbonate solvents (DMC or DEC) don’t significantly affect the cycle life of LNMO when EC is mixed. In 2 M LP40, the LNMO showed 16.9% less capacity than in 1 M LP40, indicating the sluggish kinetics of the 2 M LP40 electrolyte. From the fact that the ionic conductivity of 2 M LP40 was 81.2% of that of 1 M LP40 (Figure S21 and Table S5, Supporting Information), we attribute the sluggish kinetics to the slow interfacial charge transfer reaction or desolvation. Despite the low capacity, the 2 M LP40 offered improved capacity retention of 91.0%. The improvement can be attributable to the altered solvation structure with increased contact ion pairs [30], which likely affects the CEI composition and stability.

In 1 M LiPF₆ in DMC, the LNMO stably retained its capacity for the initial 30 cycles and then started to lose it, exhibiting...
73.2% capacity retention after 100 cycles. Nevertheless, the achievable capacity at the 100th cycle in the 1 m EC-free electrolyte was still higher than the EC-contained electrolytes (LP30, LP40, and 2 m LP40) but lower than that in the 2 m EC-free electrolyte (91.0%). The inferior cyclability of the LNMO half cells with the 1 m EC-free electrolyte compared to the 2 m EC-free electrolyte is attributable to the worse reversibility of the Li metal cycling in the 1 m EC-free electrolyte, showing 84% higher overpotential in the 100th cycle than that of the 2 m case (Figure S22a, Supporting Information). We found that the rate of overpotential increase of Li||Li symmetric cells was much faster in the 1 m EC-free electrolyte than in the 2 m EC-free electrolyte, resulting in a more rapid capacity fading in the half-cell test condition. The 2 m EC-free DMC electrolyte showed better reduction stability than an EC-free EMC-based electrolyte (Figures S20, S22, and S23, Supporting information), while previous studies used EMC-based electrolytes to improve the high-voltage performances of LIBs.[55–57] In summary, the simple modification of electrolyte formulation, including solvent composition and salt concentration, substantially affects the stability of the LNMO cathodes when cycled within a WVR. We believe that search for better electrolytes to achieve practically viable cycle life will be an essential topic for further studies.

The modified electrolyte without EC can avoid the ring-opening reaction that triggers the serial electrolyte
decomposition processes. Thus, we attribute the ROS evolution in the conventional electrolyte to the catalytic effect of EC on extracting oxygen from the TM oxides.\[^{[9]}\] In addition to the ROS, the dynamic interfacial evolution and the rocksalt phase decomposition can accelerate the TM dissolution into the electrolyte. The ICP-OES analysis of the electrolytes from the cycled cells confirms that the TM dissolution occurs more rigorously in LP40 than in the EC-free electrolyte (Figure S24, Supporting information). The dissolved Mn\(^{2+}\) prefers the solvation with EC, inducing the degradation of the bulk electrolyte and solid-electrolyte interphase of anodes.\[^{[58]}\] During the 100 cycles, the overpotential remained small in the EC-free electrolyte while it rapidly increased in LP40 and LP30 (Figure Sb, Figures S25 and S26, Supporting Information). The overpotential increase and capacity loss of the LNMO with LP40 were more accelerated when the active-material loading was higher (≈5.6 mg cm\(^{-2}\)) (Figure S27, Supporting information).

The explicit degradation of the LNMO in the commercial electrolyte was also observed by long-term cyclic voltammetry (Figure S28, Supporting Information). The increased overpotential in LP40 induces the decreased use of Mn\(^{3+}/Mn^{4+}\) redox capacity. As shown in the XRD patterns of the LNMO cathodes discharged to 2.3 V after 100 CV cycles (Figure S29, Supporting Information), the tetragonal phase is more pronounced in the EC-free electrolyte than in LP40. Considering the significantly better capacity retention in the EC-free electrolyte (Figure 5a), the result invalidates the direct correlation between the degree of phase transition and the capacity fade. Contrarily, the results show that the degradation at the interface can retard the bulk phase transformation, which is analogous to the Grey group’s report on the bulk fatigue due to the increased overpotential.

We attribute the extended cycle life of LNMO in the EC-free electrolyte to the suppressed increase of \(R_{ct}\), as shown in the EIS spectra (Figure 5c). In LP40, the \(R_{ct}\) increased by 263% during the 40 cycles after the 10th cycle. In contrast, only a 76% increase in \(R_{ct}\) was observed in the EC-free electrolyte (see Table S6, Supporting Information, for details). The results indicate a more stable electrochemical interface in the EC-free electrolyte than in LP40, enabling more prolonged cycling with higher capacity.

The Mn L-edge TEY-NEXAFS spectra clarify the consequence of the electrolyte modification (Figure 5d). Surprisingly, divalent manganese cations were barely present at 3.5 V (vs Li) at the LNMO surface after cycling in the EC-free electrolyte in all the voltage ranges, indicating the diminished surface reconstruction into the rocksalt phase. In addition, the C K-edge TEY-NEXAFS spectra reveal only minor increases of the C–O, –CH\(_2\), and CO\(_2\)\(^{+}\) peaks at 288.3 and 290.1 eV, respectively, indicating the mitigated electrolyte decomposition (Figure 5e). The results suggest that EC is the primary electrolyte component that triggers severe degradation of the electrochemical interface for the cathodes requiring cycling over wider voltage ranges than the conventional ranges. In addition, the results reconcile the strong coupling between the rocksalt formation/decomposition, electrolyte decomposition, and CEI formation in the cathodes (Figure S30, Supporting Information). Detailed studies on the mechanisms of the rocksalt phase formation in specific electrolytes and the speciation of ROS evolved from the rocksalt phase decomposition will be interesting topics for further research for the development of high-capacity cathode materials over WVRs, such as LNMO and Li-/Mn-rich layered oxides.

In addition to the extended cycle life, the interface modulation offers higher rate-capability to LNMO for utilizing the multication redox. In the EC-free electrolyte, the LNMO cathodes delivered 226, 205, 192, 180, 166, 154, and 139 mAh g\(^{-1}\) at 0.05, 0.2, 0.5, 1, 2, 3, and 5 C, respectively (Figure 5f and Figure S31, Supporting Information). In LP40, the capacities were consistently smaller, and the difference became larger at higher C-rates. The voltage profiles (Figure S32, Supporting Information) show that the overpotential of both the Ni and Mn redox plateaus remained lower in the EC-free electrolyte than in LP40. Given the enhanced charge-transfer kinetics, the commercial LNMO could exhibit high energy densities of 866, 801, 758, 715, 665, 624, and 574 Wh kg\(^{-1}\) at 0.05, 0.2, 0.5, 1, 2, 3, and 5 C, respectively. These values are 1.1%, 3.1%, 5.2%, 8.1%, 14.7%, 21.3%, and 25.3% larger than those for LP40, respectively. The corresponding power densities were 17, 116, 292, 588, 1188, 1796, and 3034 W kg\(^{-1}\) for the EC-free electrolyte, respectively, as shown in the Ragone plot in Figure 5g. At a high C-rate of 3 C within WVR, the LNMO cathode showed capacity retention of 71.5% and 57.5% after 500 and 700 cycles in the 2 m EC-free electrolyte, while it retained 20.1% of capacity after 500 cycles in LP40 (Figure S33, Supporting Information). We note that the LNMO cathodes can be coupled with the prelithiated graphite anodes to form full cells using the EC-free electrolyte due to the high electrochemical stability and rate capability of the graphite anodes in the 2 m LiPF\(_6\) in DMC (Figures S34 and S35, Supporting Information). The LNMO[2 mL PF\(_6\)] in DMC|graphite full cell exhibited 119 mAh g\(^{-1}\) at 3 C, retaining 71.5% of capacity after 200 cycles (Figure S36, Supporting Information). To our best knowledge, LNMO of such excellent power density and lifespan has been unprecedented when using multi-cation redox reactions. Although extended cycle life has been achieved in a few studies by adapting secondary particle morphology\[^{[40,41]}\] and additional heat treatments,\[^{[39]}\] the enlarged particle size largely limited the rate performances due to the reduced active interfaces.

Compared with the Ni\(^{2+}/Ni^{4+}\) voltage plateau, the Mn\(^{3+}/Mn^{4+}\) voltage plateau shortens more significantly as the C-rate increases (Figure 5f and Figure S32, Supporting Information), consistent with previous studies.\[^{[39,60]}\] Note that the kinetics varies considerably with the electrolyte formulation, particle size, and surface area, unambiguously confirming that boosting the interfacial charge transfer is crucial to maximizing the energy and power densities of LNMO and realizing prolonged cycling. In addition to the electrolyte modification demonstrated in this study, we believe that surface engineering through the coating, doping, and facet-controlling will further improve the performance of LNMO for next-generation RLBs.

### 3. Conclusion

In summary, we unveiled the dynamic surface reconstruction in LNMO driven by a large (>2.5 V) potential change, reestablishing the failure mechanism of LNMO when simultaneously using Ni and Mn redox for high-energy storage. The LNMO surface transforms into a rocksalt structure at low voltage, followed by the dissociation of the rocksalt layer accompanied by...
electrolyte decomposition at high voltage. The repeated interfacial evolution results in a rapid surge of charge-transfer impedance, inducing capacity decay as cycling progresses. In contrast, we revealed the excellent reversibility of the Mn$^{3+}$/Mn$^{4+}$ redox reaction under the condition that the cathode potential remained below 4.3 V, suggesting the necessity to revisit the conventional degradation theory that overestimates the consequence of Jahn–Teller distortion. Finally, we demonstrate that electrolyte formulation is an effective strategy to enhance the interfacial stability of LNMO, suppressing the spinel-to-rocksalt transformation. The stable electrochemical interface offers LNMO excellent performance in terms of cyclability, reversible capacity, and power density, which are superior to those obtained in commercial electrolytes. Our discovery of the prominent role of interfaces on the cycling of LNMO proposes modulating the CEI stability density, which are superior to those obtained in commercial performance in terms of cyclability, reversible capacity, and power.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
cathode-electrolyte interfaces, EC-free electrolytes, Mn-rich cathodes, multi-cation redox, rechargeable Li batteries, spinel oxides, surface reconstruction

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