

Article

Enhanced Electrochemical Performance of Surface-Modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode at High Voltages

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Abstract

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) has emerged as a highly competitive cobalt-free cathode material for higher-energy-density lithium-ion batteries. However, its practical application is hindered by severe capacity degradation, particularly under high-voltage operation. To solve this problem, we put forward a surface modification strategy employing a $\text{Li}_{0.4}\text{La}_{0.54}\text{TiO}_3$ (LLTO) coating. The LLTO coating forms a protective cathode–electrolyte interphase that helps to inhibit interfacial side reactions, enabling enhanced electrochemical performance up to 5 V. As a result, the optimized 1 wt% LLTO-coated LNMO exhibits a remarkable capacity retention of 96.5% after 200 cycles at 0.1 C and delivers a high-rate capacity of 103.5 mAh g^{-1} at 2 C, significantly outperforming its pristine counterpart (86.8% and 89.6 mAh g^{-1} , respectively). This work provides a viable and efficient surface modification approach for achieving robust high-voltage LNMO cathode material, underscoring its great potential for next-generation energy storage systems.

Keywords: lithium-ion batteries; high voltage; $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; Surface modification; electrochemical performance

1. Introduction

Lithium-ion batteries serve as a very important part of contemporary energy storage, dominating the markets for consumer electronics, communications, and electric vehicles [1–3]. Although considerable advancements have been achieved, the cathode material continues to be a critical bottleneck restricting energy density and cost-effectiveness [2–8]. Among next-generation cathodes, cobalt-free spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is considered a highly potential candidate owing to its rapid three-dimensional Li^+ diffusion pathways, elevated working voltage ($\sim 4.7 \text{ V vs. Li}^+/\text{Li}$), and substantial theoretical energy density approaching 650 Wh kg^{-1} [9–13]. Nevertheless, the practical application of LNMO is hampered by severe interfacial side reactions at high voltages, including transition metal dissolution, phase transitions, and electrolyte decomposition, leading to poor cycling stability [14–21].

Extensive research efforts have focused on stabilizing the LNMO interface by applying various coating materials, including oxides (Al_2O_3 [22,23], TiO_2 [24], SiO_2 [25]), fluorides (AlF_3 [26], PrF_3 [27]), and phosphates (Li_3PO_4 [28], AlPO_4 [29]). These coatings act as



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physical barriers, isolating the cathode from the corrosive electrolyte and improving cyclability. For instance, an ultrathin composite $\text{Al}_2\text{O}_3/\text{LiAlO}_2$ coating layer can enhance the cycling stability of LNMO to 84.99% over 350 cycles at 1 C [22]. Similarly, phosphate-based coatings like Li_3PO_4 and AlPO_4 have been shown to mitigate HF attack and reduce surface Li^+ depletion [28,29]. However, many conventional coatings are inert or possess low ionic conductivity, which can increase interfacial impedance and seriously affect the rate capability as well as long-term cycling stability.

To overcome this trade-off, recent strategies have adopted active or ion-conductive coatings that simultaneously passivate the surface and facilitate Li^+ transport, showing promise in improving both stability and kinetics [30–32]. For example, Wang et al. demonstrated that a Li_2ZrO_3 coating reduces the charge transfer resistance of LNMO and improves its capacity retention at 5 C [33]. Chang et al. developed a $\text{Li}_2\text{O}-0.2\text{B}_2\text{O}_3-1.8\text{SiO}_2$ hybrid coating that increases the retained capacity from 69% to 83% after 100 cycles [34]. Additionally, Liu et al. reported a $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ coating that contributes to the suppression of transition metal dissolution while maintaining high ionic conductivity [35]. Despite these advances, it is crucial to develop an appropriate strategy for maintaining interfacial stability of LNMO under prolonged high-voltage cycling.

In this work, a perovskite-type $\text{Li}_{0.4}\text{La}_{0.54}\text{TiO}_3$ (LLTO) was employed as a protective layer for LNMO via a facile hydrothermal method. While the bulk stability and ionic conductivity of LLTO can be influenced by the voltage and its grain boundaries [36,37], the ultrathin coating architecture used here is designed primarily to engineer the electrode-electrolyte interface. The LLTO layer plays a role as a physical barrier to isolate the cathode material from the electrolyte. The impact of coating content on the crystal structural, morphological, and electrochemical characteristics of LNMO was systematically studied. The optimized 1 wt% LLTO-coated LNMO delivers improved capacity retention of 96.5% after 200 cycles at 0.1 C up to 5 V, as well as a high-rate capacity of 103.5 mAh g^{-1} at 2 C. These results demonstrate that an optimized LLTO coating significantly enhances cycling stability, rate capability, and interfacial charge transfer, offering an effective and scalable approach to realizing durable high-voltage LNMO cathodes for emerging lithium-ion batteries.

2. Experimental

2.1. Synthesis of $\text{Li}_{0.4}\text{La}_{0.54}\text{TiO}_3@\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode

A pristine LNMO sample was prepared via a sol-gel process. Stoichiometric ratios of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$, and $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ were dispersed in deionized water, and subsequently citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$) was added as a chelating agent. The mixture was stirred at 50 °C with the pH adjusted to 7.0 to produce a uniform sol. The resulting sol was dried at 120 °C for 24 h to gain the precursor. The dried gel was subsequently calcined in a muffle oven at 800 °C for 18 h in air, followed by cooling to 600 °C and holding for 2 h, using a ramp rate of 5°C min^{-1} .

The $\text{Li}_{0.4}\text{La}_{0.54}\text{TiO}_3@\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LLTO@LNMO) materials were obtained using a hydrothermal process. Specifically, LiOH , $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, and $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ were mixed with deionized water and stirred for 6 h to yield a clear precursor solution. The as-synthesized LNMO powder was then dispersed into the aforementioned solution with constant stirring for 2 h. The mixture was treated via a hydrothermal reaction at 120 °C for 18 h. After centrifugation and washing, the product was dried at 80 °C for 12 h and subsequently annealed at 500 °C for 4 h in air to obtain the LLTO@LNMO. The mass ratios of the LLTO coating in the composites were controlled to be 1, 2, and 3 wt%, and the corresponding samples are denoted as 1-LLTO@LNMO, 2-LLTO@LNMO, and 3-LLTO@LNMO, respectively. The schematic diagram of the preparation process of LNMO and LLTO@LNMO cathodes is shown in Figure 1.

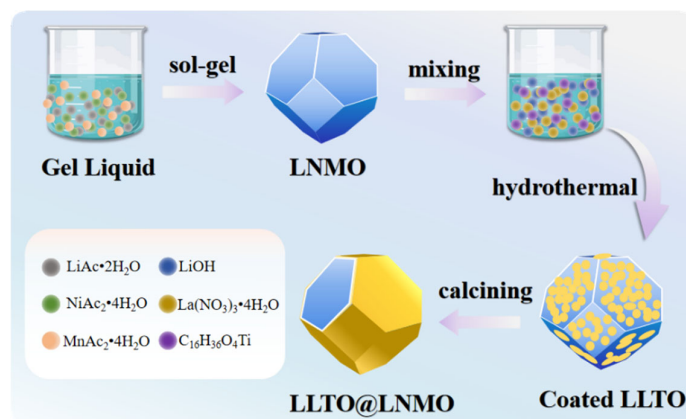


Figure 1. Schematic illustration of the preparation of LNMO and LLTO@LNMO cathode materials.

2.2. Materials Characterization

The crystalline structure was characterized by powder X-ray diffraction (XRD, D8 Advance, Bruker, Berlin, Germany) with Cu K α radiation over a 2θ range from 10° to 90° . Rietveld refinement was conducted employing the General Structure Analysis System (GSASII, Version 5455) software. Morphological and microstructural features were examined by field-emission scanning electron microscopy (FESEM, ZEISS SIGMA 300, ZEISS, Jena, Germany) and transmission electron microscopy (TEM, FEI Tecnai G2 F20, FEI, Hillsboro, OR, America). The surface elemental composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5000 VP4, ULVAC-PHI, Chigasaki, Japan) with an Al K α source.

2.3. Electrochemical Measurements

The coating slurry was formulated by mixing the active material, conductive carbon (Super P), and polyvinylidene fluoride (PVDF) binder in a mass ratio of 80:10:10, using N-methyl-2-pyrrolidone (NMP) as the solvent. The homogeneous slurry was coated onto an aluminum foil and dried in a vacuum at 120°C for 12 h. CR2032-type coin cells were assembled in an argon-filled glove box (H_2O , $\text{O}_2 < 0.1$ ppm) using lithium metal as the counter/reference electrode, a polypropylene (PP) membrane as the separator, and 1 M LiPF_6 in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (1:1:1 by volume) as the electrolyte.

Galvanostatic charge–discharge tests were conducted on a LAND battery test system operating a voltage window of 3.0–5.0 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an IVIUM electrochemical workstation. The CV scans were recorded at $0.1\text{--}2.0\text{ mV s}^{-1}$ within 3.0–5.0 V. For the EIS measurements, a sinusoidal signal with an AC amplitude of 5 mV was applied across a frequency spectrum between 100 kHz and 0.01 Hz.

3. Results and Discussion

3.1. Structural and Morphological Characterization

The crystal structures of LNMO and coated samples with different LLTO contents (1-LLTO@LNMO, 2-LLTO@LNMO, and 3-LLTO@LNMO) were characterized by XRD. As shown in Figure 2a, all synthesized samples display sharp diffraction peaks corresponding to the spinel structure with the Fd-3m space group (JCPDS No. 80-2162) [38]. No peaks consistent with the LLTO coating material are detected, suggesting that the LNMO crystalline structure is not influenced by the coating. In addition, Rietveld refinement was conducted to obtain more detailed structural information (Figures 2b,c and S1). The refined patterns exhibit excellent agreement with the experimental data. By analyzing the refined

lattice parameters (Table S1), it is observed that the lattice parameters of the coated samples are slightly larger than those of pristine LNMO. It is reported that ion exchange arises between LNMO and LLTO within the temperature range of 500 to 800 °C [39]. An annealing temperature of 500 °C was adopted in our experiments to mitigate ion doping into the LNMO lattice. Therefore, the slight increase in the refined lattice parameters for coated samples likely results from the oxidation of the LNMO surface induced by the hydrothermal treatment [40], rather than a homogeneous change in the bulk crystal structure.

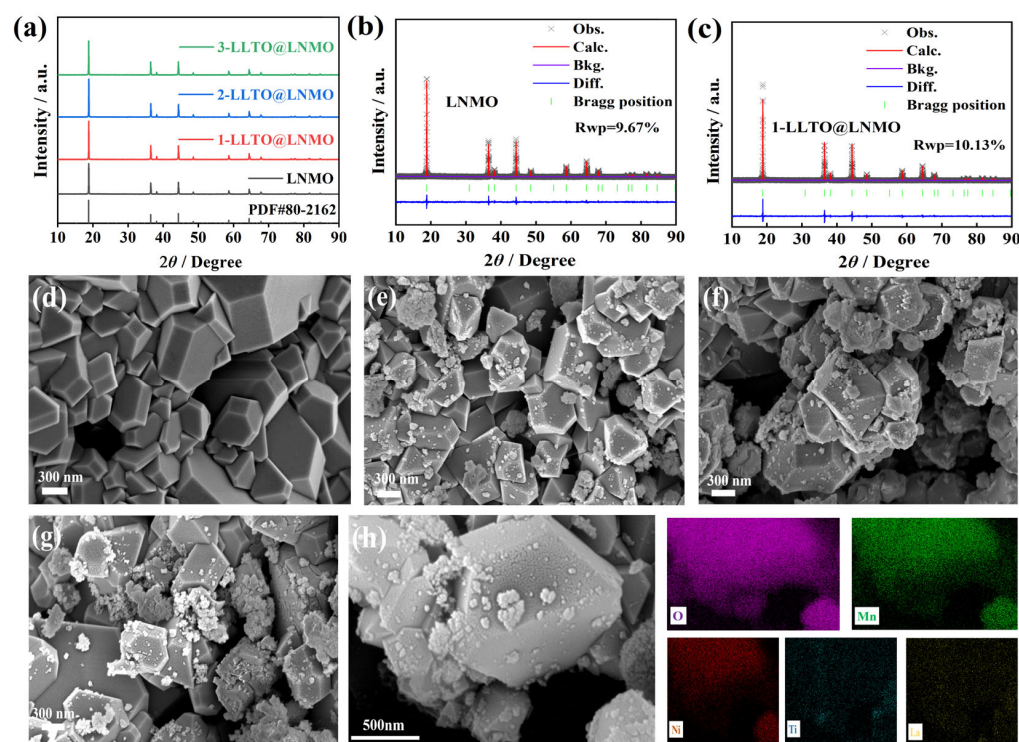


Figure 2. (a) XRD patterns showing the spinel structure of LNMO with varying LLTO coating contents. (b,c) Rietveld refinement profiles for pristine LNMO and 1-LLTO@LNMO, indicating good agreement with the experimental data. (d–g) FESEM images reveal the octahedral particle morphology and increased surface roughness for coated samples. (h) EDS elemental maps of 1-LLTO@LNMO confirming the presence and distribution of the coating elements (La, Ti) on the LNMO surface.

The morphology and elemental distribution of the samples were investigated by FESEM and EDS. As displayed in Figure 2d–g, all the coated samples retain a particle morphology similar to that of pristine LNMO, maintaining the typical feature of a regular octahedral spinel structure [41]. Therefore, it is evident that the LLTO coating on the surface does not affect the structure of LNMO. However, distinct differences are observed between the pristine LNMO and coated samples. In contrast to the smooth surface of pristine LNMO, the coated samples exhibit increased surface roughness with higher coating content, indicating the surface coating of the LLTO layer [42]. As the coating progressed, thicker coating layers were formed, accompanied by visible surface debris due to the coating material [43]. Subsequently, the distribution of each element was confirmed by EDS mapping (Figures 2h and S2), detecting Ni, Mn, and O in all samples, and La and Ti in coated LNMO samples. These results verify that the LLTO coating is applied onto the LNMO cathode, though with some inhomogeneity in thickness and coverage.

To further examine the internal lattice structure and the surface coating layer, HRTEM characterization was performed, and the details are shown in Figures 3 and S3. The particles maintain an octahedral shape, which matches the results from FESEM. At higher magnifi-

cation, clear lattice fringes and good crystallinity are visible. Additionally, the interplanar distance was calculated using the fast Fourier transform (FFT). The FFT patterns from the region marked by the yellow box in all samples display a lattice spacing of 0.482 nm, which is ascribed to the (111) crystal plane of spinel LNMO [44]. This indicates that the bulk phase of all samples retains a well-defined spinel structure of LNMO. Conversely, the FFT image from the region marked by the red box in Figure 3d shows a dot on the (110) plane with an interplanar distance of 0.271 nm [45], confirming the presence of a crystalline LLTO coating approximately 6–8 nm thick on the 1-LLTO@LNMO sample. As the coating content is added, the coating thickness increases in Figure S3a,c. And the coating is less uniform, with regions of agglomeration reaching ~15–50 nm in thickness. These results demonstrate that the LLTO lattice is coherently bonded to the LNMO surface, forming an atomically matched coherent interface. During the charging and discharging cycles, this bonding can enhance the structural integrity of LNMO and improve the stability of the interface [46].

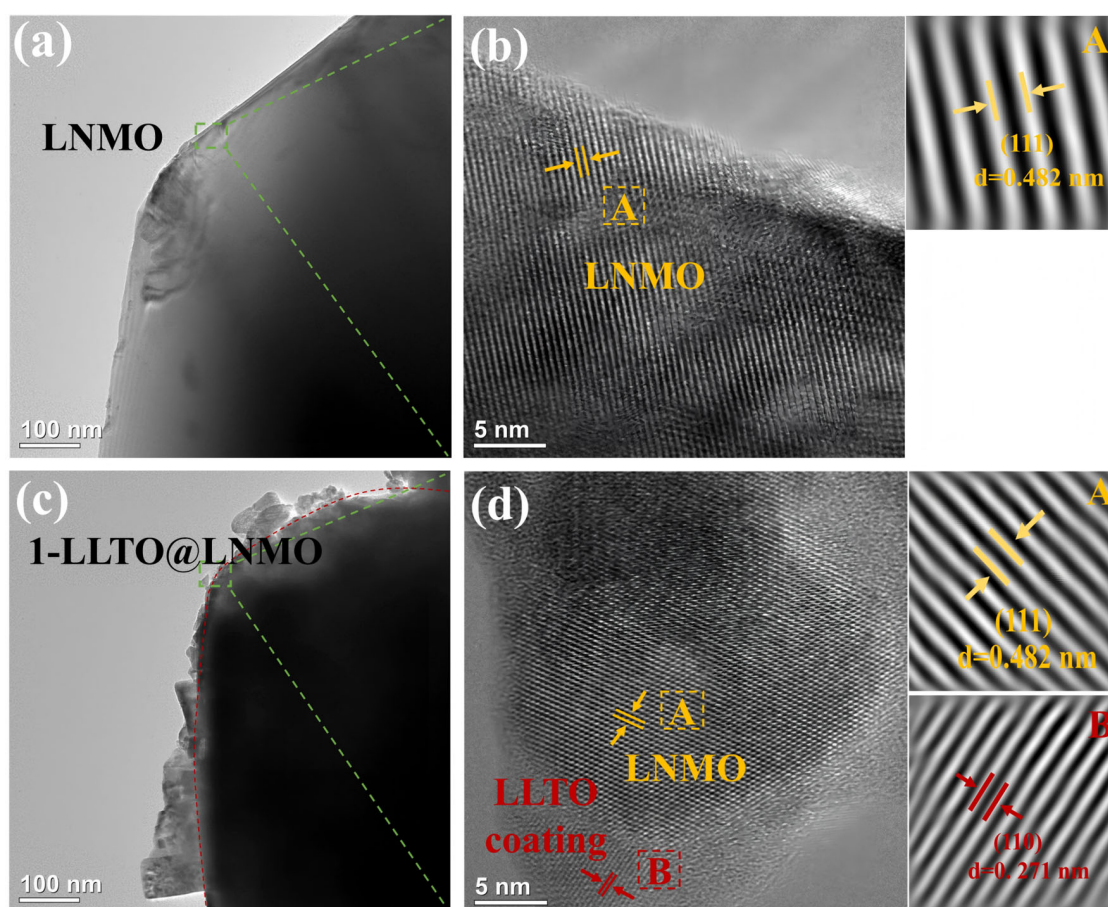


Figure 3. HRTEM and FFT images confirming the crystalline nature of the coating. (a,b) Reference LLTO structure. (c,d) 1-LLTO@LNMO sample, showing lattice fringes corresponding to spinel LNMO and a crystalline LLTO coating layer (~6–8 nm thick) on the surface, indicative of a coherent interface.

The surface chemical composition and elemental oxidation states were studied using XPS. As depicted in Figures 4a–c and S4a–c, the survey spectrum of the LNMO@LLTO samples exhibits distinct peaks associated with La 3d and Ti 2p [45]. In the high-resolution Ti 2p spectrum, well-defined peaks are observed at 463.6 eV (Ti 2p_{1/2}) and 457.9 eV (Ti 2p_{3/2}), which are characteristic of Ti⁴⁺. Similarly, the La 3d spectrum features the peaks at 854.6 and 834.8 eV, assigned to the La 3d component of La³⁺. These findings further verify the presence of LLTO coating on the LNMO surface [47].

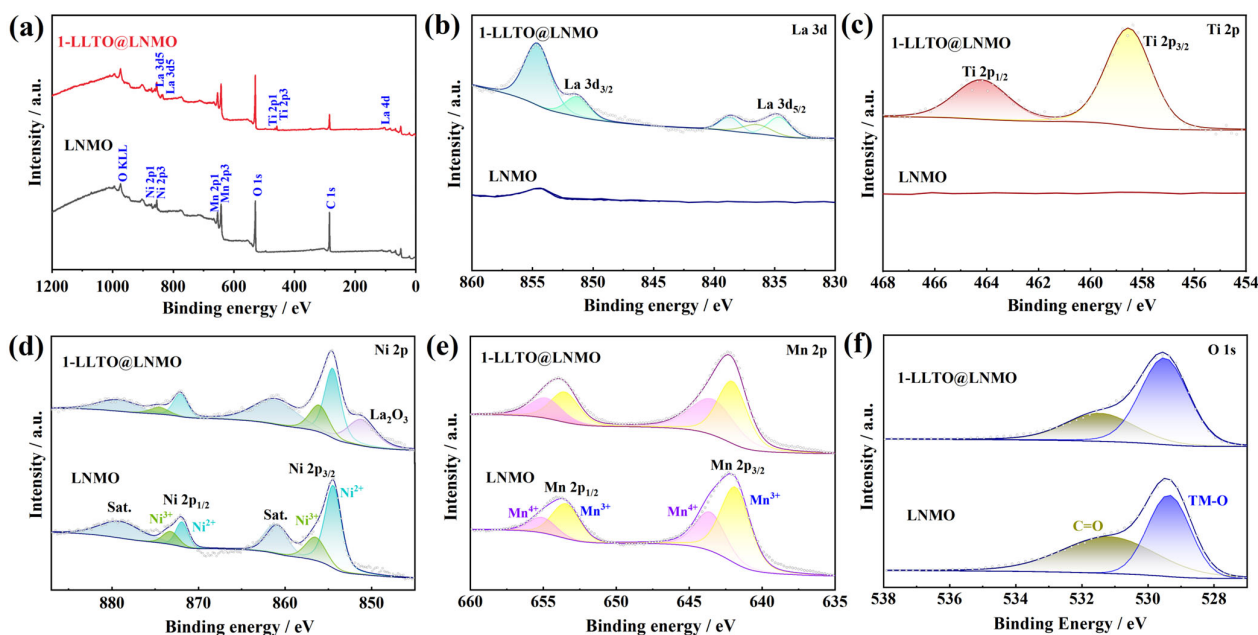


Figure 4. XPS spectra comparing the surface chemistry of pristine LNMO and 1-LLTO@LNMO. (a) Survey scan showing the presence of La and Ti from the coating. High-resolution spectra of (b) La 3d, (c) Ti 2p, (d) Ni 2p, (e) Mn 2p, and (f) O 1s, revealing changes in surface oxidation states and confirming the formation of the LLTO coating.

The oxidation states of nickel were analyzed utilizing the Ni 2p spectra (Figures 4d and S4d). Three peaks located at 854.5 eV (Ni 2p_{3/2}) and 872.1 eV (Ni 2p_{1/2}) confirm the coexistence of Ni²⁺ and Ni³⁺ oxidation states on the cathode surface [48]. Quantitative deconvolution results indicate that the relative proportion of Ni²⁺ decreases gradually, with values of 44.84%, 34.29%, 31.61%, and 31.05% for pristine LNMO, 1-LNMO@LLTO, 2-LNMO@LLTO, and 3-LNMO@LLTO, respectively. It should be noted that these values reflect the chemical states in the near-surface region probed by XPS. The elevated Ni³⁺ content can lower the polarization voltage throughout cycling, which in turn enhances the cycling performance of coated LNMO samples [44]. Moreover, the La 3d_{3/2} peak with a binding energy of 851.4 eV is identified near the Ni 2p_{3/2} peak, further confirming the successful formation of the coating [49].

For the Mn 2p spectra (Figures 4e and S4e), the peaks at locations 641.9, 643.7, 653.3, and 655.1 eV are identified to be Mn³⁺ and Mn⁴⁺ [50]. The area calculations indicate that the relative ratio of Mn³⁺ reduces from 67% in pristine LNMO to 45.36%, 42.12%, and 37.44% as the LLTO coating content increases. This reduction indicates that the LLTO coating promotes surface oxidation of manganese, which is consistent with previous reports [44]. The enhanced oxidation is attributed to the hydrothermal treatment, which improves structural ordering and raises the proportion of ordered to disordered phase in LNMO [44]. This reduction in the relative surface concentration of Mn³⁺, which is more susceptible to dissolution and Jahn-Teller distortion, is considered a favorable condition that may contribute to the improved electrochemical stability observed for the coated samples [51]. Although increased structural ordering may slow down ion transport in the bulk and thus limit rate performance, the LLTO coating compensates by facilitating the migration rate of Li⁺ across the interface. Consequently, the synergistic combination between surface coating and hydrothermal treatment is expected to enhance both rate capability and cycling stability.

Lastly, the O 1s spectra display peaks at 529.3, 530.9, and 532.7 eV, attributing to lattice oxygen bonded with transition metals in LNMO and adsorbed oxygen on the surface,

respectively (Figures 4f and S4f) [52]. The proportion of adsorbed O increases from 34.9% for pristine LNMO to 39.7%, 39.89%, and 40.43% with increasing LLTO coating content, attributable to the interaction between surface oxygen sites on LNMO and the LLTO coating layer.

3.2. Electrochemical Performance

Systematically evaluated the electrochemical properties of the pristine and LLTO-modified LNMO cathodes. Figure 5a displays the initial constant current charge–discharge profiles at a voltage of 3.0 to 5.0 V. Long-term cycling was first evaluated at 0.1 C to assess the intrinsic stability of the electrodes under high-voltage conditions with minimized polarization and kinetic stress. They exhibit characteristic features of LNMO. The long plateau at approximately 4.7 V is related to the redox reaction of the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple, while a short plateau near 4 V is associated with the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox pair in the disordered phases [46]. Further kinetic insight is gained from CV (Figure S5). All curves present distinct redox pairs, with $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{4+}$ located at 4.0 and 4.7 V, consistent with the galvanostatic results. The overpotential (ΔE), defined as the potential difference between the oxidation and reduction peaks, is a key indicator of the polarization degree during charge and discharge processes [53]. The calculated ΔE values are 0.30, 0.24, 0.26, and 0.25 V for pristine LNMO, 1-LLTO@LNMO, 2-LLTO@LNMO, and 3-LLTO@LNMO, respectively. Notably, 1-LLTO@LNMO displays the lowest ΔE value, demonstrating that the optimal LLTO coating can mitigate electrochemical polarization in the electrode. Furthermore, the redox peaks of 1-LLTO@LNMO show minimal shift upon repeated cycling, suggesting a highly reversible $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction. This observation underscores the critical role of the LLTO coating in mitigating Mn dissolution and promoting reaction reversibility of the LNMO cathode.

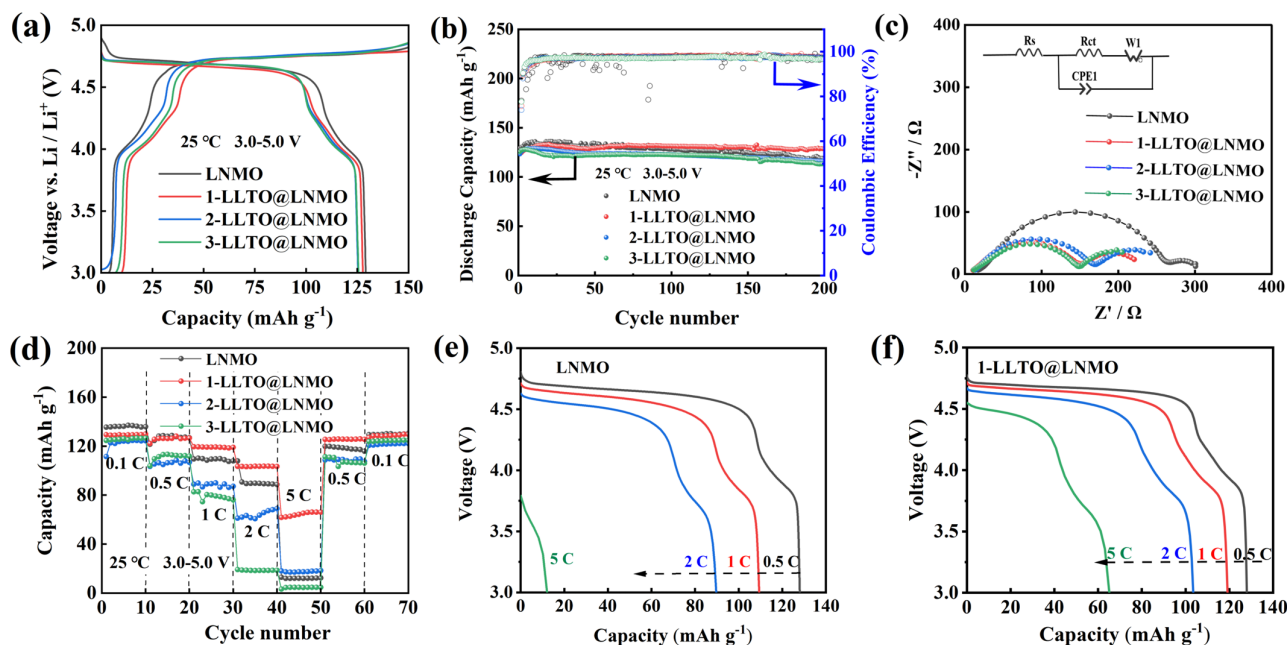


Figure 5. Electrochemical performance of pristine and LLTO-coated LNMO. (a) Initial charge/discharge profiles at 0.1 C, showing characteristic LNMO plateaus. (b) Cycling performance and Coulombic efficiency at 0.1 C, highlighting the superior capacity retention of the 1 wt% LLTO-coated sample. (c) EIS Nyquist plots after 200 cycles, showing reduced charge-transfer resistance for coated electrodes. (d) Rate capability from 0.1 C to 5 C, demonstrating the excellent high-rate performance of 1-LLTO@LNMO. (e,f) Discharge voltage profiles at different rates for pristine LNMO and 1-LLTO@LNMO, illustrating better voltage stability for the coated sample.

Figure 5b presents the cycling stability of all samples tested at 0.1 C within 3.0–5.0 V. The pristine LNMO electrode offers a higher initial discharge capacity of 129.2 mAh g^{-1} , whereas the initial capacities of 1-LLTO@LNMO, 2-LLTO@LNMO and 3-LLTO@LNMO are 127.8 , 125.7 , and 125.7 mAh g^{-1} , respectively. The LLTO-modified samples show slightly lower initial capacity, attributable to the partial coverage of active reaction sites on the LNMO surface by the non-active LLTO coating layer, and the minor lithium-ion consumption associated with the construction of a stable solid electrolyte interphase (SEI) during the initial charge–discharge cycles [54,55]. After 200 cycles, the 1-LLTO@LNMO electrode achieves the highest capacity retention rate of 96.5%, which significantly outperforms the 86.83% retention rate of pristine LNMO. The 2-LLTO@LNMO and 3-LLTO@LNMO samples also exhibit improved cycling retention, with values of 89.85% and 88.42%, respectively. Furthermore, it can be observed that the initial Coulomb efficiency of all the samples is very low, which is common for high-voltage LNMO due to interfacial side reactions. However, the 1-LLTO@LNMO displays a higher average Coulombic efficiency than that of the LNMO electrode in subsequent cycles. The enhanced cycling stability of the LLTO-coated electrodes may be ascribed to the LLTO layer, which acts as a robust physical barrier that suppresses side reactions under high-voltage conditions.

EIS measurements were performed after 200 cycles to further explore the evolution elucidate of interface impedance due to the LLTO coating (Figure 5c). The Nyquist plots obtained after 200 cycles are characterized by two depressed semicircles in the high-to-medium frequency range and an inclined line in the low-frequency range, which refer to surface film resistance (R_{sf}), charge-transfer resistance (R_{ct}), and Warburg impedance (Z_w), respectively, associated with Li^+ diffusion in the electrode [56]. The EIS data were fitted using a corresponding equivalent circuit, and the derived parameters are summarized in Table S2. The R_{ct} values for the 1/2/3 wt% LLTO@LNMO electrodes are 210.93, 241, and 137Ω , respectively, all markedly lower than the 759.6Ω for pristine LNMO. Additionally, the lithium-ion diffusion coefficient can be calculated through the relationship between Z' and $\omega^{-1/2}$ in the low-frequency region (Figure S6). The results are presented in Table S3. The LLTO@LNMO samples exhibit high D_{Li^+} values of 10.06×10^{-16} , 3.25×10^{-16} and $7.017 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, respectively. This pronounced reduction in R_{ct} and augmentation in D_{Li^+} confirm that the LLTO coating accelerates interfacial charge-transfer kinetics and enhances structural stability [57,58]. Especially, owing to its optimal amount of LLTO coating, the 1-LLTO@LNMO electrode has the lowest R_{ct} and highest D_{Li^+} value, aligning perfectly with the enhanced cycling.

Rate capability measurements were performed to assess the high-current performance at different rates (0.1 C–5 C) (Figure 5d). The initial discharge capacities of the LLTO-coated LNMO samples are similar, in the range of 123–128 mAh g^{-1} . However, the 1-LLTO@LNMO electrode represents distinctly preferable performance at current rates above 0.5 C. Its reversible specific capacity is 119.5, 103.5, and 61.8 mAh g^{-1} at 1, 2, and 5 C, respectively, remarkably exceeding those of pristine LNMO (109.5 , 90.7 , and 12.9 mAh g^{-1}). The discharge profiles of the samples at various rates (Figures 5e,f and S7) further highlight the performance advantage of 1-LLTO@LNMO. For the pristine LNMO electrode, the discharge voltage plateaus associated with the $\text{Ni}^{4+}/\text{Ni}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox reactions underwent a dramatic decline with increasing current density. This indicates that the structure has been severely damaged and the internal polarization has increased. In contrast, for the 1-LNMO@LLTO sample, its voltage distribution maintains good plateau stability under the same conditions, with a high ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox capacity even at 5 C [45]. It is worth noting that both 2-LLTO@LNMO and 3-LLTO@LNMO exhibit inferior rate capability relative to 1-LNMO@LLTO, which can be attributed to the reduced electronic conductivity caused by the excessively thick LLTO coating layer. After cycling at

various high rates and returning to 0.1 C, the capacity retention rates of pristine LNMO, 1-LLTO@LNMO, 2-LLTO@LNMO, and 3-LLTO@LNMO are 96.2%, 100%, 99.5%, and 99.4%, respectively. These results indicate that 1-LNMO@LLTO possesses the highest stability both during high-rate cycling and after returning to 0.1 C, confirming that an optimal amount of LLTO coating enables the interface region between electrode and electrolyte to be stable and thus enhances the rate performance of LNMO.

The effect of the LLTO coating on Li^+ transport kinetics was evaluated by using CV at varied scan rates, with results presented in Figure 6. All samples display two distinct pairs of redox peaks, which are consistent with the results from the galvanostatic charge/discharge tests. We can see that the peak current density increases with increasing scan rate. The oxidation peaks associated with the $\text{Mn}^{3+}/\text{Mn}^{4+}$, $\text{Ni}^{2+}/\text{Ni}^{3+}$, and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox pairs move toward more positive potentials, whereas the reduction peaks associated with $\text{Ni}^{4+}/\text{Ni}^{3+}$, $\text{Ni}^{3+}/\text{Ni}^{2+}$, and $\text{Mn}^{4+}/\text{Mn}^{3+}$ shift toward more negative potentials. In addition, the redox peaks related to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{4+}/\text{Ni}^{3+}$ gradually weaken as the scan rate elevates, implying a trend that the Ni^{2+} is directly oxidized to Ni^{4+} . The Li^+ diffusion coefficient (D_{Li^+}), a critical parameter for evaluating electrode kinetics behavior, can be determined according to the Randles-Sevcik equation [59,60].

$$i_p = (2.69 \times 10^5) n^{3/2} A C_0 D_{\text{Li}^+}^{1/2} v^{1/2} \quad (1)$$

In this equation, i_p denotes the peak current (A), n represents the number of transferred electrons, A is the electrode area (cm^2), D_{Li^+} is the Li^+ diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), v is the scan rate (V s^{-1}), and C_0 is the bulk concentration of lithium-ion (mol cm^{-3}).

The calculated lithium-ion diffusion coefficients (D_{Li^+}) values are summarized in Table S4. It is acknowledged that the calculated D_{Li^+} values are approximate, as the underlying models assume conditions that may not be fully satisfied in solid-state intercalation electrodes. These values are therefore discussed primarily for comparative purposes to highlight trends among the samples. The 1-LLTO@LNMO electrode exhibits the highest D_{Li^+} values, with $1.026 \times 10^{-11} \text{ cm}^2 \text{s}^{-1}$ for extraction and $8.24 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$ for insertion, respectively.

These findings confirm that the coating layer of LLTO can simultaneously boost both ionic and electronic migration rates, thereby enhancing the cycling stability and rate capability of LNMO. The fundamental mechanisms underlying these improved properties may include the following aspects [61,62]: (1) By constructing a physical protective interface, LLTO inhibits Mn^{3+} dissolution and stabilizes the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple, thus preserving structural reversibility and mitigating electrode degradation. (2) Owing to the LLTO modification, the interphase likely creates a more kinetically favorable environment for charge transfer between electrode and electrolyte, relieving the interfacial ion concentration gradient and emerging as a key factor in enhancing the rate performance. (3) The coherent bonding between the LLTO lattice and the LNMO surface can help to maintain the crystallographic integrity of the near-surface region of LNMO particles during repeated lithium (de)intercalation. A stable interface facilitates Li^+ insertion/extraction, significantly boosting the cycle stability.

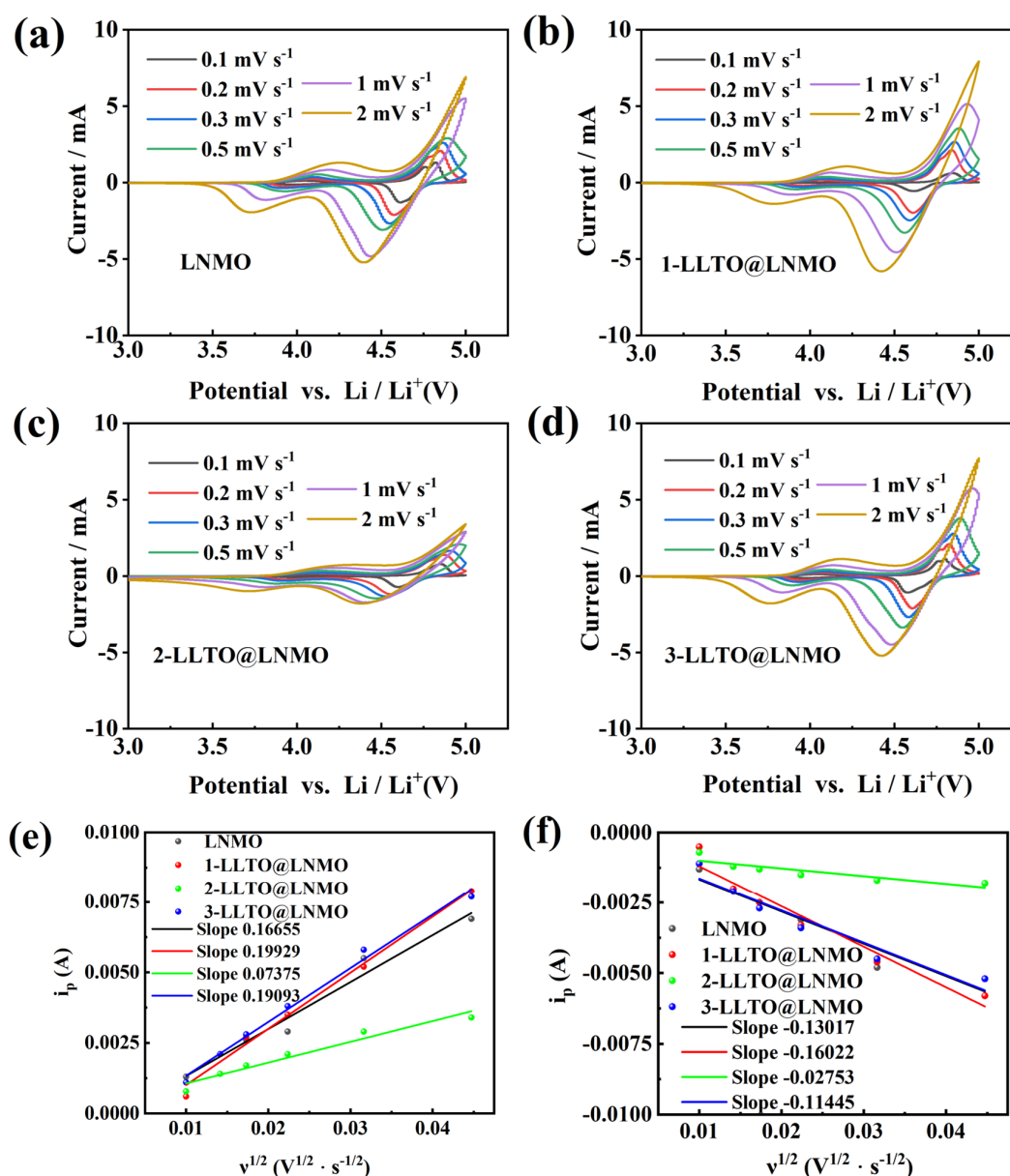


Figure 6. CV profiles at varied scan rates for (a) LNMO, (b) 1-LLTO@LNMO, (c) 2-LLTO@LNMO, and (d) 3-LLTO@LNMO, used to evaluate Li⁺ transport kinetics. (e,f) The corresponding calculated lithium-ion diffusion coefficients (D_{Li^+}), presented for comparative analysis of interfacial kinetics among samples.

4. Conclusions

In the present study, we successfully fabricated a variety of LLTO-coated LNMO cathodes through a hybrid sol-gel and hydrothermal synthesis method. Comprehensive characterization confirms the existence of an LLTO layer on the LNMO surface. The electrochemical performance indicates that the optimized 1 wt% LLTO@LNMO composite delivers a high specific capacity of 127.8 mAh g⁻¹ at 0.1 C, excellent cycling stability with 96.5% capacity retention after 200 cycles at high operating voltages, and rate capability (65.2 mAh g⁻¹ at 5 C), significantly outperforming pristine LNMO. The observed enhancement might be attributed to the LLTO layer. It functions as a multifunctional protective layer, which not only inhibits electrolyte decomposition and transition metal dissolution but also accelerates interfacial ion migration kinetics. The main strengths of this approach include the facile coating process and the identification of an optimal coating content. Fu-

ture efforts could focus on optimizing the coating uniformity and exploring the long-term stability of LNMO. Overall, employing an ion-conductive LLTO coating presents a valuable strategy for developing next-generation, cobalt-free lithium-ion batteries.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries12020044/s1>. Figure S1: Rietveld refinement of (a) 2-LLTO@LNMO, and (b) 3-LLTO@LNMO; Figure S2: FESEM image of (a) 2-LLTO@LNMO, and (b) 3-LLTO@LNMO; Figure S3: HRTEM and FFT images of (a)–(b) 2-LLTO@LNMO and (c)–(d) 3-LLTO@LNMO; Figure S4: XPS spectra comparison between 2-LLTO@LNMO and 3-LLTO@LNMO (a) Survey Scan, (b) Ni 2p, (c) Mn 2p, (d) O 1s, (e) La 3d, and (f) Ti 2p; Figure S5: CV curves at scan rate of 0.1 mV s^{−1} of (a) LNMO, (b) 1-LLTO@LNMO, (c) 2-LLTO@LNMO, (d) 3-LLTO@LNMO; Figure S6: The relationship between Z' and $\omega^{-1/2}$ in the low-frequency obtained from EIS measurement; Figure S7: The discharge curves at the current densities for (a) 2-LLTO@LNMO and (b) 3-LLTO@LNMO; Table S1: Results of the Rietveld refinement for all samples; Table S2: Impedance parameters for all samples after 200 cycles at 0.1 C; Table S3: The Warburg factor and diffusion coefficient for all samples; Table S4: Results of diffusion coefficients for all samples. References [33,63] are cited in the Supplementary Materials.

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