Simultaneously Dual Modification of Ni-Rich Layered Oxide Cathode for High-Energy Lithium-Ion Batteries

Huiping Yang, Hong-Hui Wu, Mingyuan Ge, Lingjun Li,* Yifei Yuan, Qi Yao, Jie Chen, Lingfeng Xia, Jiangming Zheng, Zhaoyong Chen, Junfei Duan, Kim Kisslinger, Xiao Cheng Zeng, Wah-Keat Lee, Qiaobao Zhang,* and Jun Lu*

A critical challenge in the commercialization of layer-structured Ni-rich materials is the fast capacity drop and voltage fading due to the interfacial instability and bulk structural degradation of the cathodes during battery operation. Herein, with the guidance of theoretical calculations of migration energy difference between La and Ti from the surface to the inside of LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\), for the first time, Ti-doped and La\(_4\)NiLiO\(_8\)-coated LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) cathodes are rationally designed and prepared, via a simple and convenient dual-modification strategy of synchronous synthesis and in situ modification. Impressively, the dual modified materials show remarkably improved electrochemical performance and largely suppressed voltage fading, even under exertive operational conditions at elevated temperature and under extended cutoff voltage. Further studies reveal that the nanoscale structural degradation on material surfaces and the appearance of intergranular cracks associated with the inconsistent evolution of structural degradation at the particle level can be effectively suppressed by the synergetic effect of the conductive La\(_4\)NiLiO\(_8\) coating layer and the strong Ti—O bond. The present work demonstrates that our strategy can simultaneously address the two issues with respect to interfacial instability and bulk structural degradation, and it represents a significant progress in the development of advanced cathode materials for high-performance lithium-ion batteries.

1. Introduction

Layer-structured Ni-rich materials have been considered as promising cathode candidates for the next-generation lithium-ion batteries (LIBs) owing to their high energy density compared with LiFePO\(_4\) and LiCoO\(_2\).\(^{[1-3]}\) However, the commercialization of Ni-rich cathodes is still impeded by the weak interfacial stability and bulk structural degradation of the cathode particles.\(^{[4-6]}\) Numerous studies have been carried out to investigate the capacity and structural degradation mechanism of Ni-rich materials. Prior studies have shown that the direct contact between the electrode and organic electrolyte will increase the thickness of passivation layer, which is originated from the transition metal dissolution and electrolyte decomposition and therefore hinders the electrochemical kinetics and cycling stability.\(^{[7-9]}\) The electrode/electrolyte interface of Ni-rich materials is much less stable at a highly delithiated state. The transformation from the original layered to rock-salt phase (NiO) accompanied by the release of oxygen leads to the thermal runaway and induce potential safety issues.\(^{[4,10,11]}\) In addition, bulk structural degradation is another vital factor that deteriorates the electrode capacity. It was reported that Ni-rich materials suffer severe irreversible phase transition, from the layered structure (R-3m) to the spinel-like phase (Fd-3m) and rock-salt phase (Fm-3m).

H. P. Yang, Prof. L. J. Li, Q. Yao, J. Chen, L. F. Xia, Prof. Z. Y. Chen, Prof. J. F. Duan
School of Materials Science and Engineering
Changsha University of Science and Technology
Changsha 410114, P. R. China
E-mail: lingjun.li@csust.edu.cn
Prof. Q. B. Zhang
Department of Materials Science and Engineering
College of Materials
Xiamen University
Xiamen, Fujian 361005, China
E-mail: zhangqiaobao@xmu.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201808825.

DOI: 10.1002/adfm.201808825

Dr. Y. F. Yuan, Prof. J. Lu
Chemical Sciences and Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Argonne, IL 60439, USA
E-mail: junlu@anl.gov
Dr. H.-H. Wu, Prof. X. C. Zeng
Department of Chemistry
University of Nebraska-Lincoln
Lincoln, NE 68588, USA

Dr. M. Y. Ge, Dr. K. Kisslinger, Prof. W.-K. Lee
National Synchrotron Light Source II (NSLS-II)
and Center for Functional Nanomaterials
Brookhaven National Laboratory
Upton, NY 11973, USA
Dr. J. M. Zheng
Research Institute (RI)
NingDe Ampere Technology Limited
Ningde, Fujian 352100, China
due to extensive cation mixing because of the similarity of ionic radius between Li$^+$ ($0.76$ Å) and Ni$^{2+}$ ($0.69$ Å). Recently, many researchers demonstrated that the internal mechanical stress, originated from abrupt lattice shrinkage in the $c$-direction induced by the phase transition from H2 to H3, should take responsibility for the microcracks generation and propagation, which allows the penetration of electrolyte as well as exposing the internal surface where electrolyte attack and side reactions occur, and further aggravating the bulk structural and mechanical degradation of Ni-rich cathodes.\cite{15-19} More importantly, as revealed by previous studies, structural degradation of NCM during cycling always accompanies the decreasing of Ni$^{3+}$ concentration.\cite{20-22} However, the distributions of the Ni$^{3+}$ concentration at particle level, whether the degrees of such surficial chemical changes are consistent among different secondary particles or different parts of the same particle, have not been thoroughly studied so far.

To maintain stable solid–electrolyte interface and bulk structural integrity, cation substitution and surface modification have been widely adopted as promising ways to overcome these challenges and improve the electrochemical performance of cathode materials. For cation substitution, varieties of dopant ions have been employed to enhance the structural stability of Ni-rich materials.\cite{23-26} Specifically, Ti substitution has been proven effective in improving the cyclic stability by reducing the cation mixing of Li$^+/Ni^{2+}$ and alleviating the appearance of cracks in secondary particles induced by volumetric deformation.\cite{27-30} However, the Ti-doped cathodes are still directly exposed to the electrolyte. The electrolyte could potentially generate hydrofluoric acid, and dissolve the transition metal in the NCM cathode, leading to inevitable interfacial structural degradation. For surface modification, numerous coating agents including metal oxides, phosphates, fluorides, and fast ionic conductors were used to modify the surface of cathode materials.\cite{31-35} Among these surface coating materials, lanthanum-based oxides (LaMO, $M = Li$ and TM) possess good conductivity and excellent thermal stability and hence hold great potentiality for facilitating electron transfer and decreasing the heat generation by suppressing side reaction between electrode and electrolyte.\cite{36-38} However, the LaMO surface modification does not decrease the cation mixing of NCM and hardly enhance the integrity of the cathode particles.

Given that the individual modification strategy (cation substitution or surface modification) can only solve partial issues of Ni-rich materials, a dual-modification strategy that combines the advantages of both cation substitution and the surface coating was proposed.\cite{39-41} Despite the traditional dual-modification routes for the Ni-rich cathodes are proven to provide enhanced electrode performance, multistep reactions involved in the experiment greatly complicate the synthesis procedure. Additionally, the traditional multistep modification processes, especially the wet processing, may also contaminate the powders and deteriorate the surface structure of Ni-rich materials. Since the as-prepared cathode Ni-rich powders are very sensitive to moisture and air, extended exposures to humid environments could result in the large-scale formation of lithium residues (LiOH, Li$_2$CO$_3$) and particle agglomeration.\cite{42-44} It is therefore highly desirable, yet quite challenging, to develop a simple but effective strategy to fabricate cathode materials with enhanced performance as well as to identify the underlying mechanism for improved performance.

In this work, informed by first-principles calculations, for the first time, we have designed and synthesized a LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM) cathode with Ti doping and La$_4$NiLiO$_8$ coating by synchronous in situ dual modification through a smart route. Based on the theoretical calculation of the migration energy difference between La and Ti from the surface to the inside of NCM, it is reasonable that compared to the La atoms, Ti atoms are more likely doped into the bulk NCM. Thus, the Ti-doped and LaMO-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ could be synchronously synthesized in situ under the same temperature ($830^\circ$C). In addition, this route avoids the detrimental exposure of NCM powders to air and water during the modification process. In contrast to previous reports, this new synchronous synthesis route is simple and robust. More importantly, the attained dual-modified architecture inherits the advantages of both La$_4$NiLiO$_8$ coating and Ti doping. The La$_4$NiLiO$_8$ coating functions as a protector and can effectively prevent the electrolyte attack, leading to a significant improvement of the NCM surficial stability and conductivity. The Ti$^{4+}$ ($0.74$ Å) ions, which pose similar ion radius with Ni$^{2+}$ ($0.69$ Å), serve as pillars and electrons accumulators that reduce the degree of cation mixing and detrimental H2–3 phase transition during cycling, and further suppress the formation of intergranular cracks. These results contribute to the significant enhancement in electrochemical performance in terms of improved rate performance, capacity retention, and largely suppressed voltage fading, even under exertive conditions such as at elevated temperature ($60^\circ$C) and under extended cutoff voltage ($4.5$ V). The cyclability of the synthesized dual-modified composite also outperforms many Ni-rich materials (Table S1, Supporting Information). By in-house designed full-field transmission X-ray microscopy (TXM) and nano-XANES, ex-nuclear magnetic resonance (NMR), ex-X-ray diffraction (XRD), and transmission electron microscopy (TEM), we elucidated the capacity degradation mechanism of NCM and revealed the inhomogeneity of Ni$^{3+}$ distribution within a particle and among particles for the NCM after cycling. Our finding in this work demonstrated that the dual-modification strategy is quite effective in suppressing bulk mechanical degradation and consistent evolution of surficial structural degradation.

2. Results and Discussion

2.1. Theoretical Design of the Roadmap for an Advanced Ti and LaMO Dual Modification

To better understand the physical picture of the Ti/La interaction in NCM, density functional theory (DFT) calculations were performed to assess the energy of doping La and Ti (Figure 1a) to the topmost surface, and to the first, second, and third Ni-rich layers, respectively. As shown in Figure 1a, doped La in the first Ni-rich layer is not structurally stable, as it tends to evade to the surface. On the other hand, the Ti on the surface is not structurally stable neither, as it tends to enter into the NCM. The structural instability is due to the much larger radius of La than that of Ni, whereas the radius of Ti is similar to that of...
The migration energy difference is defined by the energy difference between one Ti (or La) atom in the \(i\)th (\(i = 1, 2, \text{and } 3\)) Ni-rich layer of NCM and the Ti (or La) atom on the surface. As shown in Figure 1b, the DFT calculation indicates that the Ti doping is energetically favorable when the Ti atom is doped into NCM. In contrast, the energy difference for the Ti doping in the different Ni-rich layer is very small, suggesting that the Ti atom can be evenly doped into the bulk NCM matrix.

It is well known that the presence of a coating layer can greatly affect the lithium-ion diffusion and electron transport properties. Therefore, electrical conductivity stands out as a crucial figure of merit for a coating layer. To understand the electronic properties of the coated system, we calculate the electric conductivity difference of the two bulk materials, where \(S_1\) and \(S_2\) indicate the slope of the DOS at the Fermi level. The inset represents the density of states plots of the NCM and La\(_4\)NiLiO\(_8\). NCM shows half-metallic characteristics, whereas the La\(_4\)NiLiO\(_8\) displays metallic characteristics. The inset of Figure 1c indicates that the conductivity of La\(_4\)NiLiO\(_8\) is higher than that of NCM. To explore the influence of Ti doping on the NCM structures, we calculated the charge difference by using Bader charge analysis. The atomic charge difference is calculated by:

\[
\Delta \rho = \rho_{\text{total}} - \rho_{\text{atom}}
\]

where \(\rho_{\text{total}}\) and \(\rho_{\text{atom}}\) are the total charge density of the system and the superposition of each atomic charge density, respectively.

Figure 1d presents the 3D charge difference of the pristine NCM and the Ti-doped NCM (iso-surface value 0.031 eV Bohr\(^{-3}\)). In the 3D plot (upper panel), the yellow and blue regions denote charge accumulation and depletion, respectively. Figure 1e presents the 2D charge difference for a slice along the plane passing through the substituted Ni or the doped Ti.

Figure 1. Theoretical design of the roadmap for an advanced Ti&LaMO dual modification. Doping a) La and Ti to the surface, 1st, 2nd, and 3rd Ni-rich layer, respectively, and the corresponding migration energy difference are shown in (b). The gray, cyan, blue, pink, purple, light-blue, and sea-green balls represent Ni, Li, La, O, Ti, Co, and Mn atoms, respectively. c) The density of states plots of the NCM and La\(_4\)NiLiO\(_8\). The inset represents the electric conductivity difference of the two bulk materials, where \(S_1\) and \(S_2\) indicate the slope of the DOS at the Fermi level. d) 3D charge difference of the pristine NCM and the Ti-doped NCM (iso-surface value 0.031 eV Bohr\(^{-3}\)). In the 3D plot (upper panel), the yellow and blue regions denote charge accumulation and depletion, respectively. e) The 2D charge difference for a slice along the plane passing through the substituted Ni or the doped Ti.
Therefore, it suggests that the Ti doping will function as electron accumulators that suppress the H2–3 phase transition during cycling and stabilize the bulk structure of NCM.

2.2. Characterization of Ti-Doped and La4NiLiO8-Coated NCM Composite

In light of these theoretical analyses, we designed synchronous in situ synthesis modification strategy of Ti-doped and La4NiLiO8-coated LiNi0.8Co0.1Mn0.1O2 cathode materials via a smart one-step calcination route. As shown in Figure 2a, the raw materials were added into the anhydrous ethanol solution with continuous stirring. The mixtures were dried and the remained powders were transferred to a tube furnace to obtain the dual-modified NCM. Based on the DFT calculations, it is supposed that Ti ions prefer to diffuse into the bulk NCM, while the La ions tend to accumulate on the surface of NCM particles, and further react with surficial Ni ions to in situ form the La4NiLiO8 coating layer during calcination.

Initially, the elemental compositions of as-obtained materials are confirmed by inductively coupled plasma (ICP) analysis. As shown in Table S2 (Supporting Information), it can be found that the results are consistent with the designed stoichiometry. The crystal structures of as-prepared LiNi0.8Co0.1Mn0.1O2, 1 mol% Ti-doped LiNi0.8Co0.1Mn0.1O2 (T1), and dual-modified samples (0.5 mol% La and 1 mol% Ti abbreviated as LT1, 2.5 mol% La and 5 mol% Ti abbreviated as LT5, and 5 mol% La and 10 mol% Ti abbreviated as LT10) were analyzed via XRD analysis. The high-quality crystallinity in Figure S1 (Supporting Information) demonstrates the successful formation of one-phase layered rhombohedral structure LiTMO2 materials (NCM and T1, JCPDS No. 70-4314), and hybrid structure LiTMO2/La4NiLiO8 materials (LT1, LT5, and LT10, JCPDS No. 52-1671). Due to the appearance of the K2NiF4-type La4NiLiO8 phase, Rietveld refinements were performed assuming two phases in the R-3m and I4/mmm space group, respectively (Figure 2b,c; Figure S2, Supporting Information). In the fitting procedure, we assumed that La occupies the 3a (lithium layer) or 3b (transition metal layer) sites of the hexagonal layered phase. The calculated molar ratio of La atom was close to 0, indicating that La atom can hardly dope into the NCM layered structure, which is consistent with the analysis of the relative energy calculation (Figure 1b). Differing from La4+, the ionic radius of Ti4+ is similar to the transition metals in NCM. To determine the preferred sites for the Ti substitution, we calculate, with DFT, the energy of substituting one Li or Ni atom with Ti at nine different positions. The energy per atom (Figure 2d) clearly shows that Ti prefers to occupy the Ni position rather than Li position. In addition, Rietveld refinements confirm that Ti is mainly on the 3b sites of the layered phase, resulting in the expansion of the crystal lattice along c- and c-directions (Table S3, Supporting Information). The Li+/Ni2+ cation mixing is 4.255% in NCM and less severe 2.512% and 3.602%, respectively, in T1 (1 mol% Ti) and LT1 (1 mol% Ti and 0.5 mol% La), which could be ascribed to that optimized Ti doping (1 mol% La) suppressing the cation mixing. X-ray photoelectron spectroscopy further demonstrates the presence of Ni2+ in LT1 is less than that in the NCM (Figure S3 and Table S4, Supporting Information). Less Ni2+ means less Li+/Ni2+ disorder, and it generally infers a good structural stability, which is further confirmed by the electrochemical measurements in the later part of the paper. In the case of LT5 and LT10, because of the high Ti concentration, the oxidation state of Ni is close to Ni2+, rendering the cation mixing a more probable scenario. Based on the calculation, it is concluded that La prefers to form the La4NiLiO8 phase, while Ti successfully dopes into the layered phase. The cation mixing of T1 and LT1 samples is suppressed by Ti doping.

The morphologies of NCM, T1 and dual-modified samples are illustrated in Figure S4 (Supporting Information). SEM images reveal spherical shaped secondary particles with an average size of 12 μm, which are assembled by primary crystalline particles. Compared with the clear surface of NCM (Figure S4a, Supporting Information), these dual-modified samples (Figure S4c–e, Supporting Information) exhibit a fuzzy and rough surface. This morphology difference may come from the possible coating layer. The cross-sectional SEM images and the corresponding EDS mapping of the LT1, LT10 are given in Figure S4k–l (Supporting Information). It shows that LT10 has a lower porosity than that of LT1, which could be attributed to the Ti doping. The elemental mappings further verify that the Ti atoms are distributed homogeneously from the bulk to surface of the particles, while the La atoms are constrained to some small white primary particles on the edges of NCM bulk matrix. This further confirms the successful synthesis of Ti-doped and LaMO-coated NCM materials.

To understand the microstructure of the potential coating layer, TEM, high-resolution transmission electron microscopy (HRTEM), and the corresponding fast Fourier transformation (FFT) of the selected area were conducted for the NCM (Figure S5a, Supporting Information), T1 (Figure S5b, Supporting Information), LT1 (Figure 2e,f), and LT5 (Figure 2g,h). The FFT patterns of NCM and T1 confirm that the LiTMO2 layered phase is successfully formed. As shown in Figure 2e–h, the LT1 and LT5 samples show rough edges and the thickness of coating layers increases with the increase of La concentration. Corresponding FFT images based on the marked regions (Figure 2f-I,II,h-I,II) demonstrate that the bulk region exhibits a LiTMO2 layered phase (space group R-3m), whereas the nanomembrane on the surface of the LT1 and LT5 particles are indexed as (006, 114, 112, and 105) facets of La4NiLiO8, which is characterized as “highway” for rapid electrons transport. It is well documented that interfacial binding energy is highly dependent on the terminated surfaces.[48–50] We calculated nine possible configurations with different surface terminations of La4NiLiO8 and NCM, and the four relatively stable configurations are shown in Figure S6 (Supporting Information). The most stable epitaxial and chemical binding at the...
interface can be achieved between the La-terminated La₄NiLiO₈ nanocoating and O-terminated NCM materials. Upon the XPS analysis (Figure S3, Supporting Information), higher intensity peak corresponding to the lattice oxygen for LT1 relative to that of NCM further confirms that La₄NiLiO₈ adhered strongly on the surface of NCM particles.[51,52] Moreover, the Co, Mn XPS spectra indicate that there is no change in the valence states in the NCM and LT1 surface. The valence states of LT1 are determined to be Ti⁴⁺ and La³⁺. All the analysis and characterization strongly confirm that the Ti-doped and La₄NiLiO₈-coated LiNi₀.₈Co₀.₁Mn₀.₁O₂ composite has been successfully synthesized via a smart one-step synchronously calcination route.

2.3. Electrochemical Performance of Pristine, Ti-Doped, and Dual-Modified NCM Electrodes

The electrochemical performance of each sample was examined in 2025R coin-type half-cell with a lithium metal anode cycled. As shown in **Figure 3a**, under the voltage range of 2.7–4.3 V, the initial discharge capacity of NCM, T1, and LT1 electrodes at a rate of 0.1 C was 210.21, 203.21, and 200.34 mAh g⁻¹, respectively. The Coulombic efficiency of T1 and LT1 are superior to that of NCM, because 1 mol% Ti doping can prevent Li⁺/Ni²⁺ mixing and reduce the irreversible capacity loss due to the formation of the passivation layer. The initial discharge curves for the different samples are illustrated in Figure S7 (Supporting Information), 174 and 120.9 mAh g⁻¹ for LT5 and LT10, respectively. Obviously, the high cation mixing degree and the thick coating layer are responsible for such a large irreversible capacity of LT5 and LT10.

To understand the phase transition behavior during initial charge–discharge process, the corresponding dQ/dV curves of NCM, T1 and LT1 samples are exhibited in Figure 3b. All dQ/dV curves display three redox peaks related with phase transitions from hexagonal to monoclinic (H₁ to M), monoclinic to hexagonal (M to H₂) and hexagonal to hexagonal (H₂ to H₃). It was reported that the H₂–₃ phase transition tends to result in the generating and propagating of bulk microcracks.[15–19] As shown in Figure 3b, for the T1 and LT1 samples, which were doped by 1% Ti, the intensity of detrimental H₂ to H₃ phase transition become weaker than that of the NCM sample. More critically, as shown in Figure S8 (Supporting Information), the H₂–₃ phase transition disappears gradually with increasing

|Figure 3. Electrochemical performance of NCM, T1, and LT1 in the voltage range of 2.7–4.3 V at room temperature: a) Initial charge–discharge curves at 0.1 C. b) The dQ/dV curves of NCM, T1, and LT1 based on (a). c) Rate capability. d) Cyclic ability at a current density of 1 C (180 mA g⁻¹). e) Charge– discharge curves of NCM, T1, and LT1 based on (d).|
Ti concentration. Therefore, it could be concluded that Ti$^{4+}$ doping could suppress the detrimental H2–3 phase transition, which is in accordance well with our DFT calculations.

The rate performances of all samples (Figure 3c; Figure S9, Supporting Information) within a voltage window of 2.7–4.3 V. Comparing to the NCM, the T1 and LT1 samples show improved rate capability, especially at high current rates. For example, the LT1 cathodes maintain a reversible specific capacity of 157.1 mAh g$^{-1}$ at 10 C, while the NCM cathodes deliver a specific capacity of only 110.92 mAh g$^{-1}$. It is worth noting that the capacity of LT1 is also higher than that of T1 at 5 C and 10 C, respectively. The excellent rate property of LT1 could ascribe to the conductive La$_4$NiLO$_8$ coating layer, which benefits the fast electron transportation.

The cyclic properties of NCM, T1, and the dual-modified samples, tested at 1 C between 2.7 and 4.3 V, were compared in Figure 3d and Figure S10 (Supporting Information). It is obviously the bare NCM exhibits the worst cycling performance among all samples. The capacity rapidly fades from 177.52 to 133.21 mAh g$^{-1}$ after 200 cycles with a 0.125% decay per cycle. The T1 sample maintains a reversible capacity of 144.1 mAh g$^{-1}$ after 200 cycles with 0.0866% decay per cycle. The LT1 sample maintains a reversible capacity of 158.3 mAh g$^{-1}$ after 200 cycles with 0.0472% decay per cycle. The evolution of charge–discharge profiles and corresponding midpoint voltages are shown in Figure 3e and Figure S11 (Supporting Information), respectively. Apparently, NCM exhibits much increase in cell overpotential compared to that of T1 and LT1. More critically, it can be seen that the gravimetric energy density of the LT1 was also superior to those of the T1 and NCM after 200 cycles. The cyclic performances under the elevated charge cutoff potential of 4.5 V at 1 C are illustrated in Figure S12 (Supporting Information). The discharge capacity of NCM dropped rapidly, from 181.40 to 111.86 mAh g$^{-1}$ after 160 cycles with 0.2396% decay per cycle. In contrast, the capacity retention is improved for the T1 and LT1, which achieves 0.1834% and 0.1464% decay per cycle, respectively.

The enhanced cyclic ability of Ti-doped sample and dual-modified samples suggest that Ti$^{4+}$ doping can improve the structural stability of NCM, while the La$_4$NiLO$_8$ coating layer will protect the NCM from reacting with electrolyte and enhance the structural/interfacial stability, even under the extended operational potential windows. Thus, the optimized Ti and LaMO dual-modified sample exhibit the best cycling performance.

To further evaluate the performance and thermal stability of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ system at elevated temperature, differential scanning calorimetry (DSC) profiles of the NCM and LT1 charged to 4.3 V are presented in Figure 4a. The initial exothermic peaks can be indexed to SEI layer decomposition and there is no significant difference between NCM and LT1. The second exothermic peak is indexed to the cathode decomposition, accompanied by the amount of oxygen generated from the structure of electrode materials.$^{[53–55]}$ The NCM sample exhibits a broad exothermal peak around 228.58 °C with a heat generation of 1141 J g$^{-1}$, while the LT1 sample shifts to a higher temperature (243.97 °C) and overall heat generation was reduced to 655.8 J g$^{-1}$. The six oxygen atoms around the substituted Ni and doped Ti are shown in Table S6 (Supporting Information), it clearly shows that the Ti doping share more electrons to the oxygen around, which agrees well with the charge difference analysis in Figure 1d, suggesting stronger bond

---

**Figure 4.** a) Differential scanning calorimetry profiles of the NCM an LT1 charged to 4.3 V. b) Cyclic ability of NCM and LT1 in the voltage range of 2.7–4.3 V at 60 °C. The charge–discharge curves of c) NCM and d) LT1 based on (b).
strength of Ti–O than that of Ni–O.\textsuperscript{[29,56,57]} Owing to the stable structure, the modified sample shows an enhanced thermal stability at elevated temperature.

To explore capacity and cyclability of those aggressively tested NCM and LT1, cells were cycled under 1 C within a voltage window of 2.7–4.3 V at 60 °C. Compared to the cells cycled at room temperature, these aggressively tested cells exhibit worse capacity retention. This is because high temperature would lead to the release of molecular oxygen from the NCM host lattice, accelerating structural degradation.\textsuperscript{[31,58,59]} As shown in Figure 4b, the capacity of the NCM drops from 195.6 to 85.2 mAh g\textsuperscript{−1} after 150 cycles, with capacity retention of 43.55%. While the LT1 maintains 159.9 mAh g\textsuperscript{−1} after 150 cycles with capacity retention of 83.28%. It is worth mentioning that the capacity and cyclability of LT1 are superior to those of NCM. The galvanostatic discharge curves of NCM and LT1 are depicted in Figure 4c,d, respectively. The voltage hysteresis of both materials gradually increases during extend cycling, which may reflect the increasing impedance and structural degradation.\textsuperscript{[60,61]} The results demonstrate NCM sample suffers serious voltage decay and hysteresis compared to LT1, and also confirm that the layered structural stability is enhanced by Ti\textsuperscript{4+} doping and La\textsubscript{4}NiLiO\textsubscript{8} surface modification.

### 2.4. Evaluation of the Structural Degradation

To further analyze kinetic behavior and resistance parameters, electrochemical impedance spectroscopy (EIS) of NCM and LT1 in the charged state of 4.3 V were conducted and shown in Figure 5a–c. All curves are constituted with two semicircles and a sloped line. The intercept on the real axis (Z') represents the solution resistance (R\textsubscript{sol}). The first semicircle is related to the surface-film resistance (R\textsubscript{f}), the second semicircle can be assigned charge transfer resistance (R\textsubscript{ct}) and the followed sloped line, Warburg impedance, corresponding to Li\textsuperscript{+} ions diffusion in the interior active material.\textsuperscript{[33,62–65]} The value of D\textsubscript{Li}\textsuperscript{+} is calculated by the relationships between Z'\textsubscript{re} and ω\textsuperscript{−1/2} in the low-frequency region. The fitted EIS results and D\textsubscript{Li}\textsuperscript{+} values are listed in Table 1. Notably, after 200 cycles, the D\textsubscript{Li}\textsuperscript{+} value of NCM and LT1 reduces to 9.717 × 10\textsuperscript{−12} and 1.014 × 10\textsuperscript{−12} cm\textsuperscript{2} s\textsuperscript{−1}, respectively. The LT1 shows higher D\textsubscript{Li}\textsuperscript{+} values and lower R\textsubscript{ct} values than those of the NCM electrode. The results suggest that the conductive coating layer, La\textsubscript{4}NiLiO\textsubscript{8}, could reduce the interfacial resistance and prevent the surficial structural degradation of the cathode during cycles.

The resistance behaviors are probably related to the electrochemically inactive layer such as rock-salt phase on the surface of cathodes. To further confirm our hypothesis, the interfacial microstructure and local atomic composition of NCM, T1, and LT1 after 200 cycles were investigated in detail. As shown in Figure 5d–f, NCM sample shows a rough and fuzzy surface, whereas T1 and LT1 sample exhibits a high-quality surface. Three representative regions from the bulk to surface have been selected, respectively. In the bulk region of cathodes (Figure 5d-I,e-I,f-I), the initial layered structure is still retained with the R-3m space group. Region II locates in the middle region between the bulk and the surface of cathodes. As shown in Figure 5d-II, for NCM sample, the (200) facet and (220) facet of NiO (JCPDS No. 47-1049) with Fm-3m space group are detected, demonstrating Ni\textsuperscript{2+} ions generate from the reduction of unstable Ni\textsuperscript{4+} ions.\textsuperscript{[13,21,66]} In Figure 5e-II, the spinel phase from the diffraction spots of the T1 sample is detected. In sharp contrast, the diffraction spots of LT1 sample (Figure 5f-II) are indexed as (101, 006) facets of NCM (JCPDS No. 70-4314), demonstrating that the well-ordered layered structure is well conserved, and no structural damage appears in the middle region of LT1. Moreover, for NCM and T1 samples in Figure 5d-III,e-III, the presence of rock-salt phase and spinel-like phase indicate that the original layered structure is fully transformed into NiO phase and LiNi\textsubscript{2}O\textsubscript{4} phase, respectively, which is critical for the increase in the electrode impedance, resulting in the deterioration of the electrochemical performance. As expected, for the LT1 sample (Figure 5f-III), the surface layer is composed of La\textsubscript{4}NiLiO\textsubscript{8} phase. To further elucidate the structural changes of these cycled electrodes, XRD analysis was performed. As shown in Figure S15 (Supporting Information), after 200 cycles, the (003) peak of NCM obviously shifts to lower degree and Li\textsubscript{2}CO\textsubscript{3} impurity phase appears. Notably, the T1 and LT1 samples exhibit layered rhombohedral structure. All these results confirm that suitable Ti doping could enhance the layered structural stability, while the La\textsubscript{4}NiLiO\textsubscript{8} coating layer could protect the cathode particles from corroding by electrolyte during charge/discharge processes.

To examine the change of the local Li environments, the \textsuperscript{7}Li MAS NMR spectra obtained before and after cycling of the NCM and LT1 are shown in Figure 6a,b. The peak at 0 ppm can be referred to the SEI film. The bulk of Li environment before and after cycling has a large change in NCM. In contrast, the change in LT1 is very limited, indicating a good reversibility of Li intercalation and deintercalation.

To further evaluate the functionality of double modification, the capture of the morphology and chemical state evolution at the nanoscale is highly desirable. The in-house designed full-field transmission X-ray microscopy at NSLS-II (FXI, 18ID) is capable of imaging a larger field of view (40 × 40 μm\textsuperscript{2}), which can reconstruct a 3D tomographic morphology as well as providing a mapping of elemental information by using nano-XANES with high spatial resolution (30 nm).\textsuperscript{[67]} Figure 6c–x

<table>
<thead>
<tr>
<th>Sample</th>
<th>NCM</th>
<th>LT1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle number</td>
<td>R\textsubscript{re} (Ω)</td>
<td>R\textsubscript{ct} (Ω)</td>
</tr>
<tr>
<td>5th</td>
<td>71.24</td>
<td>212.7</td>
</tr>
<tr>
<td>100th</td>
<td>91</td>
<td>299.2</td>
</tr>
<tr>
<td>200th</td>
<td>100</td>
<td>1320</td>
</tr>
</tbody>
</table>

Figure 5. Nyquist plots of a) NCM and b) LT1, and c) the relationships between Z'\textsubscript{re} and ω\textsuperscript{−1/2} based on the 5th, 100th, and 200th cycles. HRTEM and corresponding FFT images of d) NCM, e) LT1, and f) LT1 after 200 cycles at 1 C rate between 2.7 and 4.3 V.
Figure 6. $^7$Li MAS NMR spectra obtained before cycling and after cycling of a) NCM and b) LT1. Morphology characterization of NCM and LT1 using TXM: c–e) Reconstruction of single NCM particle, specifically; c) 3D reconstruction of single NCM particle. d) Slice view of NCM particle. e) An enlarged view of (d) showing multiple cracks. Similarly, f–h) 3D morphology of NCM particles after cycling. i–l) 3D morphology of single LT1 particle, and m–n) 3D morphology of LT1 particle after cycling. o) 2D XANES mapping showing the Ni$^{3+}$ concentration of NCM particle after cycling. The color scheme indicates the Ni$^{3+}$ percentage: Ni$^{3+}$ / (Ni$^{3+}$ + Ni$^{2+}$). Raw data of the XANES spectra together with their fitting curves for this sample are illustrated at four different locations p–s), as indicated by the arrow in (o). t) 2D XANES mapping showing the Ni$^{3+}$ concentration of LT1 after cycling. The color scheme indicates the Ni$^{3+}$ percentage. Raw data of the XANES spectra together with their fitting curves for this sample are presented at four different locations u–x), as indicated by the arrow in (t).

compares the TXM measurements of bare NCM and LT1 particles. Figure 6c shows the 3D representation of a typical secondary NCM particle. Close examination of the particle indicates that there are multiple microcracks embedded inside the particles (indicated by the arrow in Figure 6d), which are the remaining gaps among the primary particles owing to the inhomogeneous diffusion during its preparation process. These cracks are easy to distinguish from the enlarged view, as
shown in Figure 6e. It is noticed that cracks are well distributed over the whole particle, and the width of the cracks are between 100 and 200 nm. In comparison, the LT1 particle shows low porosity and no noticeable cracks (Figure 6l–k), indicating that the Ti doping helps eliminate the particle-to-particle gap and enhance the secondary particle integrity, which offers great advantages over the pristine NCM particle.

After being charged/discharged for 200 cycles between 2.7 and 4.3 V at 1 C, Figure 6–f and Figure 6–n present the 3D morphology of the two types of particles NCM (f–h) and LT1 (l–n). The cracks in the after-cycle NCM particle were propagated to the surface (indicated by the arrow in Figure 6h), providing channels for electrolyte penetration, exposing the internal surface as well as leading to poor electrical conductivity and further accelerating the structural degradation of electrode materials. The microcrack propagation could be further ascribed to the large bulk mechanical stress caused by H2 to H3 phase transition during cycling. In contrast, the LT1 particle retains its integrity after cycling, contributing to the reduced detrimental phase transition from H2 to H3, which are consistent with the results of DFT calculations and dQ/dV analysis.

The morphology differences between two types of particles before and after cycling suggest that particle integrity is a major factor contributing to their cycling performance differences. Figure 6–x illustrates the oxidation states of Ni for bare NCM and LT1 after 200 cycles. Derived from nano-XANES, Figure 6o displays a 2D map of Ni+3 concentration (percentage of Ni+2+/Ni+3+ + Ni+2+) for the NCM particles. It is clear to identify the inhomogeneity of Ni+3 distribution within a particle and among particles. For instance, position 1 shows a high Ni+3 concentration (>96%, Figure 6p) in the center of the particle; whereas at particle periphery, Ni+3 concentration drops to <80% at position 2 (Figure 6q). If we look at another particle, e.g., positions 3 and 4 (Figure 6r–s), a significant amount of Ni+3 has been converted to Ni+2. This inhomogeneity of Ni oxidation states and a large amount of Ni+2 existence indicate the structural instability of the NCM during battery cycling, e.g., side reactions, and cation mixing. In comparison, the majority of LT1 particles retain high Ni+3 concentration (Figure 6t–x) that is uniformly distributed across the particles. The lowest measured Ni+3 percentage in LT1 (85%, Figure 6y) is still larger than most of the regions of the NCM sample (Figure 6o). These results demonstrate that Ti and LaMO double modification can suppress the intergranular cracks and the inconsistent evolution of structural degradation, enhancing the structural stability of Ni-rich materials.

3. Conclusion

In summary, we have theoretically predicted and successfully synthesized a Ti-doped and La4NiLiO4-coated LiNi0.8Co0.1Mn0.1O2 composite cathode via a simple one-step calcination approach. The main finding of this work is the significant enhancement of electrochemical performance in terms of rate capability and cycling stability of the optimized Ti and LaMO dual-modified sample as compared to that of the bare LiNi0.8Co0.1Mn0.1O2 electrode at 25 and 60 °C. The remarkably enhanced rate property and cycling stability can be ascribed to three aspects: 1) the attained La4NiLiO4 coating layer contributes to the better surficial stability and interfacial kinetic behavior; 2) the Ti doping serves as pillars and electrons accumulators, suppressing the cation-mixing degree and detrimental phase transition; 3) More importantly, the intergranular cracks and the inconsistent evolution of structural degradation of LiNi0.8Co0.1Mn0.1O2 are successfully suppressed by the Ti and LaMO dual modification, which could be attributed to the synergistic effect of reduced phase transition and enhanced surficial stability on NCM. The proposed strategy of dual-modified route provides a rational approach for the development of advanced cathode material for high-performance lithium-ion batteries, which could also be extended to other high capacity cathode materials to achieve enhanced performance.

4. Experimental Section

Computational Methods: Density functional theory calculations were carried out by using the projector-augmented plane-wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP).[69] The exchange-correlation function was described by the Perdew–Burke–Ernzerhof generalized gradient approximation with the Hubbard U corrections (PBE-GGA+U).[69] The U–J value for Ni, Mn, Co was set to 6.2, 3.9, and 3.32 eV, respectively.[70] The kinetic energy cutoff at 520 eV for PAW was adopted for all bulk and surface structures. The conjugated gradient method was employed to the geometry optimization and all the atomic coordinates were fully relaxed till the Hellmann–Feynman force on each atom was less than 0.01 eV Å−1, and the convergence criteria for total energy was 10−5 eV. The reciprocal space was sampled on the Gamma-centered meshes with a density larger than 10 Å−1. The spin-polarized ordering was employed and a vacuum space more than 15 Å was introduced to the simulated model with a surface. For all energy calculations, the setups were consistent with the materials project. To compare the preferred location of La and Ti, we take one Ti and La on the surface as a reference. We exchanged the La/Ti atom with one Ni atom from the different Ni-rich layer, and finally obtained the migration energy difference of La and Ti in different layers, respectively.

Materials Synthesis—NCM Sample: Spherical LiNi0.8Co0.1Mn0.1O2 (labeled NCM) layered materials were synthesized by solid-state reaction. The mixture of LiOH·H2O, and commercial Ni0.8Co0.1Mn0.1(OH)2 hydroxide precursors (molar ratio of lithium to transition metal = 1.10) was preheated at 480 °C for 5 h, then calcined at 830 °C for 12 h under oxygen condition with a heating rate of 5 °C min−1.

Materials Synthesis—Single-Modified NCM Sample: To prepare Ti-doped LiNi0.8Co0.1Mn0.1O2 (labeled T1) powders, C16H36O4Ti was dissolved into 60 mL anhydrous ethanol by continuous stirring at a temperature of 60 °C. Then, the LiOH·H2O was added to the solution and kept stirring for 30 min, followed by the addition of Ni0.8Co0.1Mn0.1(OH)2. The resulting solution was dried at 120 °C until the ethanol was evaporated. Later, the powder was transferred to a tube furnace and calcined at the same condition as NCM to obtain T1 sample.

Materials Synthesis—Dual-Modified NCM Sample: Dual-modified LiNi0.8Co0.1Mn0.1O2 materials, labeled LT1 (0.5 mol% La and 1 mol% Ti), LT5 (2.5 mol% La and 5 mol% Ti), LT10 (5 mol% La and 10 mol% Ti), were synthesized by the following steps. 1) C6H9O6La · H2O and C16H36O4Ti dissolved into 60 mL anhydrous ethanol under stirring at a temperature of 60 °C. Then, the LiOH·H2O was added to the solution and kept stirring for 30 min, followed by the addition of Ni0.8Co0.1Mn0.1(OH)2. The resulting solution was dried at 120 °C until the ethanol was evaporated. Later, the powder was transferred to a tube furnace and calcined at the same condition as NCM to obtain T1 sample.

Materials Synthesis—Material Characterizations: The elemental compositions of the samples were determined by inductively coupled plasma (Thermo Electron Corporation). The crystalline phase of all powder samples was characterized by X-ray diffraction (Rigaku, Ultima VI).
using Cu Kα radiation operated at 40 kV, 2θ = 10°–90° with a scan speed of 2° min⁻¹. The surface valence states were determined by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) measurements with Al Kα radiation and all spectra were calibrated by C 1s (284.8 eV) as a reference. Scanning electron microscopy (SEM, Nova NanoSEM-230) and high-resolution transmission electron microscopy (FEI Talso 200s) were performed to examine the particle morphologies and microstructures of as-prepared samples. To determine the thermal stability of cathode material, the assembled cells were at the delithiated state of 4.3 V (third cycle) and disassembled in an Ar-filled glove box, followed by removing the wet cathode and sealing it into a stainless-steel crucible with a perforated lid and a gold foil seal. The differential scanning calorimetry analysis is conducted by an STA 409 PC (NETZSCH, Germany) at a heating speed of 5 °C min⁻¹ under Ar atmosphere. For the ⁷Li MAS-NMR experiments, the pristine samples were collected by mixing the cathodes, acetylene black and polyvinylidene difluoride in N-methyl-2-pyrrolidone (NMP) and then dried at 120 °C in a vacuum oven for 4 h. For the ⁷Li MAS-NMR and TXM experiments, the postcycling cathodes were collected via carefully disassembling the cycled electrodes (200h) from the cells, washing with DMC for five times and drying in the Ar-filled glove box. ⁷Li MAS-NMR experiments were performed with a Bruker Avance III 400 MHz spectrometer. TXM measurements were performed at FXI beamline (18-ID) at National Synchrotron Light Source-II (NSLS-II). For 3D reconstruction, 1200 projection images was taken at 0–180 rotational degrees in a fly-scan mode. The pixel size of each 2D image is 30 nm. The “Gridrec” algorithm implemented in Tomopy package was used to reconstruct the 3D structure.[7] For nano-XANES measurement, 2D images were taken at different energies across the Ni absorption edge (8.29–8.43 keV, 1 eV interval). Standard samples (NiO, and LiNiO₂) were used to extract the reference absorption spectra for Ni²⁺ and Ni³⁺ oxidation states.

Materials Synthesis—Electrochemical Measurement: The electrochemical performances were measured using a coin-type 2025R cell. The slurry, prepared by mixing 80% active materials, 10% acetylene black and 10% polyvinylidene difluoride in a 1:1:1 (v/v/v) mixture of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and ethylene carbonate (EC) was used as electrolyte. Cells using a lithium metal anode were assembled in a steel crucible with a perforated lid and a gold foil seal. The differential scanning calorimetry analysis is conducted by an STA 409 PC (NETZSCH, Germany) at a heating speed of 5 °C min⁻¹ under Ar atmosphere. For the ⁷Li MAS-NMR experiments, the pristine samples were collected by mixing the cathodes, acetylene black and polyvinylidene difluoride in N-methyl-2-pyrrolidone (NMP) and then dried at 120 °C in a vacuum oven for 4 h. For the ⁷Li MAS-NMR and TXM experiments, the postcycling cathodes were collected via carefully disassembling the cycled electrodes (200h) from the cells, washing with DMC for five times and drying in the Ar-filled glove box. ⁷Li MAS-NMR experiments were performed with a Bruker Avance III 400 MHz spectrometer. TXM measurements were performed at FXI beamline (18-ID) at National Synchrotron Light Source-II (NSLS-II). For 3D reconstruction, 1200 projection images was taken at 0–180 rotational degrees in a fly-scan mode. The pixel size of each 2D image is 30 nm. The “Gridrec” algorithm implemented in Tomopy package was used to reconstruct the 3D structure.[7] For nano-XANES measurement, 2D images were taken at different energies across the Ni absorption edge (8.29–8.43 keV, 1 eV interval). Standard samples (NiO, and LiNiO₂) were used to extract the reference absorption spectra for Ni²⁺ and Ni³⁺ oxidation states.

Materials Synthesis—Electrochemical Measurement: The electrochemical performances were measured using a coin-type 2025R cell. The slurry, prepared by mixing 80% active materials, 10% acetylene black and 10% polyvinylidene difluoride and dispersing with an appropriate amount of N-methyl-2-pyrrolidone (NMP) and then dried at 120 °C in a vacuum oven for 4 h. Discs with 12 mm in diameter were used and typical positive electrode loadings are about 2.3 mg cm⁻². L1P6 (1 %) in a 1:1:1 (v/v/v) mixture of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and ethylene carbonate (EC) was used as electrolyte. Cells using a lithium metal anode were assembled in a dry Ar-filled glove box where the oxygen and moisture content is under 1 ppm; Electrochemical tests were performed with constant current (CC) between 2.7 and 4.3 V. After 2 cycles at 0.1 C (18 mA g⁻¹) to activate the electrode, the cycle performance at 25 and 60 °C was conducted at a current density of 1 C. After the 5, 100, 200 cycles at 1 C at 25 °C, in the charge state of 4.3 V, electrochemical impedance spectroscopy measurements were performed using (Solartron 1470E) in the frequency range of 10⁻¹–10⁵ Hz.

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

Acknowledgements
H.P.Y., H.-H.W., and M.Y.C. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Grant Nos. 51774051, 51304031, and 21703185), National Key R&D Program of China (Grant No. 2018YFB0800500). This work was also supported by the Changsha City Fund for Distinguished and Innovative Young Scholars (Grant No. KQ1707014) and the Hunan Provincial Natural Science Foundation of China (Grant No. 2018J2428). J. Lu gratefully acknowledges support from the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office. Argonne National Laboratory is operated for DOE Office of Science by UChicago Argonne, LLC, under Contract No. DE-AC02-06CH11357. This research used resources at FXI beamline (18-ID) of the National Synchrotron Light Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886. We thank Karen Chen of BNL/Stony Brook for use of the Cu-Fe alloy sample. The authors also thank Prof. Huolin Xin and Dr. Ruojian Lin from Center for Functional Nanomaterials, Brookhaven National Laboratory, for her assistance with TEM analyses.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
DFT calculation, dual-modification strategy, lithium-ion batteries, Ni-rich materials, synchronous synthesis

Received: December 12, 2018
Revised: January 11, 2019
Published online: