

Article

Tailoring Li/TMs Ratio for Enhanced Structural Stability and Rate Capability of Ni-Rich Cathodes

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Abstract

Ni-rich layered oxide $\text{LiNi}_{0.91}\text{Co}_{0.06}\text{Al}_{0.03}\text{O}_2$ (NCA91) with high specific capacity has emerged as a leading cathode candidate for advanced lithium-ion batteries (LIBs). Nevertheless, increase in Ni content triggers structural instability and fast capacity degradation, which severely impedes the practical application of Ni-rich materials. Herein, a comprehensive study is conducted to explore the structural evolution and electrochemical behaviors of NCA91 cathodes with precisely tuned Li/TMs (transition metals) molar ratios spanning from 1.01 to 1.07. Results reveal that the NCA91 electrode with an optimal Li/TMs ratio of 1.03 exhibits outstanding structural integrity, coupled with remarkable cycling durability and rate capability. Specifically, the cathode with Li/TMs = 1.03 retains 88% of its initial capacity after 100 cycles at 1 C, and maintains $\sim 130 \text{ mAh g}^{-1}$ even at 10 C. This work establishes a quantitative structure–composition–performance correlation that offers critical design principles for developing ultrahigh-nickel cathode materials.

Keywords: Ni-rich layered oxide; structural instability; capacity degradation; structure–composition–performance correlation

1. Introduction

The quest for elevated energy density in lithium-ion batteries (LIBs) has positioned nickel-rich layered oxide cathodes at the center of contemporary energy storage research [1–6]. Driven by the rapidly expanding electric vehicle (EV) market, the U.S. Department of Energy has set a target of $>300 \text{ Wh kg}^{-1}$ at the cell level by 2030, which demands cathode materials with both high specific capacity ($>200 \text{ mAh g}^{-1}$) and elevated average discharge voltage ($\sim 4.3 \text{ V vs. Li/Li}^+$). Among various compositions, Ni-rich layered oxides have established themselves as leading cathode candidates, owing to their superior gravimetric energy density that directly translates to extended driving range [7]. Nonetheless, this remarkable electrochemical performance is counterbalanced by pronounced degradation issues that are intrinsically linked to the extremely high nickel fraction ($>90\%$). A fundamental bottleneck lies in the strong coupling between bulk lattice instability and surface/interface degradation, which manifests through three interrelated failure mechanisms. First, the comparable ionic radii of Ni^{2+} ($0.69 \text{ \AA}$) and Li^+ ($0.76 \text{ \AA}$) facilitate severe $\text{Li}^+/\text{Ni}^{2+}$ cation disorder during both synthesis and cycling [8]. This antisite mixing obstructs Li^+ diffusion pathways, increases charge-transfer impedance, and progressively erodes the layered framework, resulting in a measurable reduction in accessible capacity. Second, at



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elevated states of charge (>4.2 V), the material undergoes an irreversible H2-to-H3 phase transition accompanied by a sharp c-axis collapse [9]. The resulting anisotropic strain nucleates microcracks at both inter- and intragranular levels, continuously exposing fresh surfaces to the electrolyte and establishing a detrimental positive-feedback loop of parasitic reactions. Third, highly oxidizing Ni^{4+} ions at the charged surface aggressively decompose the organic electrolyte, depleting both electrode and electrolyte [10]. Simultaneously, this drives irreversible phase transitions from the layered structure to thermodynamically stable rock-salt and spinel phases, causing permanent destruction of long-range crystal order.

Numerous strategies have been explored to mitigate these degradation pathways. Surface modification approaches, such as $\text{Ca}_3(\text{PO}_4)_2$ coating, have demonstrated concurrent suppression of cation mixing, c-axis shrinkage, and crack propagation, achieving 91.5% capacity retention at 1 C/100 cycles [11]. Bulk doping strategies, including Al/W co-doping in $\text{LiNi}_{0.65}\text{Co}_{0.15}\text{Mn}_{0.20}\text{O}_2$ (NCM), effectively suppress cation disorder, stabilize lattice oxygen, and inhibit microcrack nucleation [12]. Notwithstanding these advances, the role of Li/TM stoichiometry—arguably the most fundamental yet underexplored compositional variable—has received surprisingly limited attention. The vast majority of existing studies are confined to near-stoichiometric compositions ($\text{Li}/\text{TMs} \approx 1.00$), while systematic investigations into how off-stoichiometric Li/TMs ratios modulate the trade-off between bulk structural robustness and surface chemical reactivity remain notably absent.

Herein, we address this critical gap by comprehensively examining NCA91 cathode materials with precisely controlled Li/TMs molar ratios spanning 1.01–1.07. By integrating structural characterization with systematic electrochemical evaluation, we elucidate the competitive effects of Li-deficient and Li-excessive compositions on cation ordering, phase evolution, and surface stability. This work establishes a quantitative structure–composition–performance correlation that provides actionable design principles for developing next-generation ultrahigh-nickel cathode materials.

2. Results and Discussion

The crystal structures of NCA91 cathode materials with Li/TMs ratios of 1.01, 1.03, 1.05, and 1.07 were characterized using X-ray diffraction (XRD), and the corresponding XRD patterns are presented in Figure 1a–d. All these cathode materials exhibit a hexagonal $\alpha\text{-NaFeO}_2$ layered structure, conforming to the $R3m$ space group [13,14]. Notably, no extraneous impurity peaks were detected in any of the XRD patterns, confirming the high purity of the synthesized materials. The XRD patterns of these cathodes display a set of characteristic peaks, including (003), (101), (104), (006)/(102), and (018)/(110), etc., which are typical of layered transition metal oxide cathode materials (Figure 1a). Among these peaks, the (003) peak is of particular significance as it reflects the stacking arrangement of lithium layers and transition metal layers along the c-axis within the layered structure. In contrast, the (104) peak is associated with the atomic arrangement within the transition metal layer. Altering the Li/transition metals (Li/TMs) stoichiometry leads to noticeable variations in both the intensities and angular positions of characteristic reflections in the XRD profiles. Among various structural indicators, the $I_{(003)}/I_{(104)}$ intensity ratio is widely employed to quantify cation disordering—namely, the migration of TM ions into Li layers [15]. A ratio above 1.2 is conventionally taken as evidence of minimal cation mixing and a well-ordered layered framework. In contrast, insufficient Li content intensifies antisite defects, which compromise layer integrity, hinder Li^+ migration, and consequently deteriorate the electrochemical behavior. Apart from the lack of foreign-phase reflections, all diffraction patterns display distinct peak splitting for the (006)/(102) and (018)/(110) pairs centered at $\sim 37.5^\circ$ and $\sim 64.0^\circ$, respectively—a fingerprint of superior crystallinity and robust layered ordering. Quantitative analysis of the $I_{(003)}/I_{(104)}$ ratios is shown in Figure 1b.

The measured values follow the order: 0.78 (Li/TMs = 1.01) < 1.20 (Li/TMs = 1.07) < 1.34 (Li/TMs = 1.05) < 1.57 (Li/TMs = 1.03). A pronounced increase from 0.78 to 1.57 is observed as the Li/TMs ratio rises from 1.01 to 1.03, reflecting a substantial suppression of cation disorder and enhanced layer coherence. Beyond Li/TMs = 1.03, however, the ratio gradually decreases to 1.34 and 1.20 at Li/TMs = 1.05 and 1.07, respectively, revealing that excess Li is likewise unfavorable for cation ordering. Hence, Li/TMs = 1.03 represents the optimal stoichiometry for achieving the lowest degree of antisite mixing. This inference is further substantiated by the peak-splitting behavior. For the Li/TMs = 1.01 specimen, the (006)/(102) and (018)/(110) splitting is significantly weaker than that of the other samples (Figure 1c,d), indicating a less coherent layered arrangement. Such a finding aligns well with its lowest $I_{(003)}/I_{(104)}$ value, confirming that pronounced cation mixing under Li-deficient conditions undermines the overall structural regularity of the cathode material.

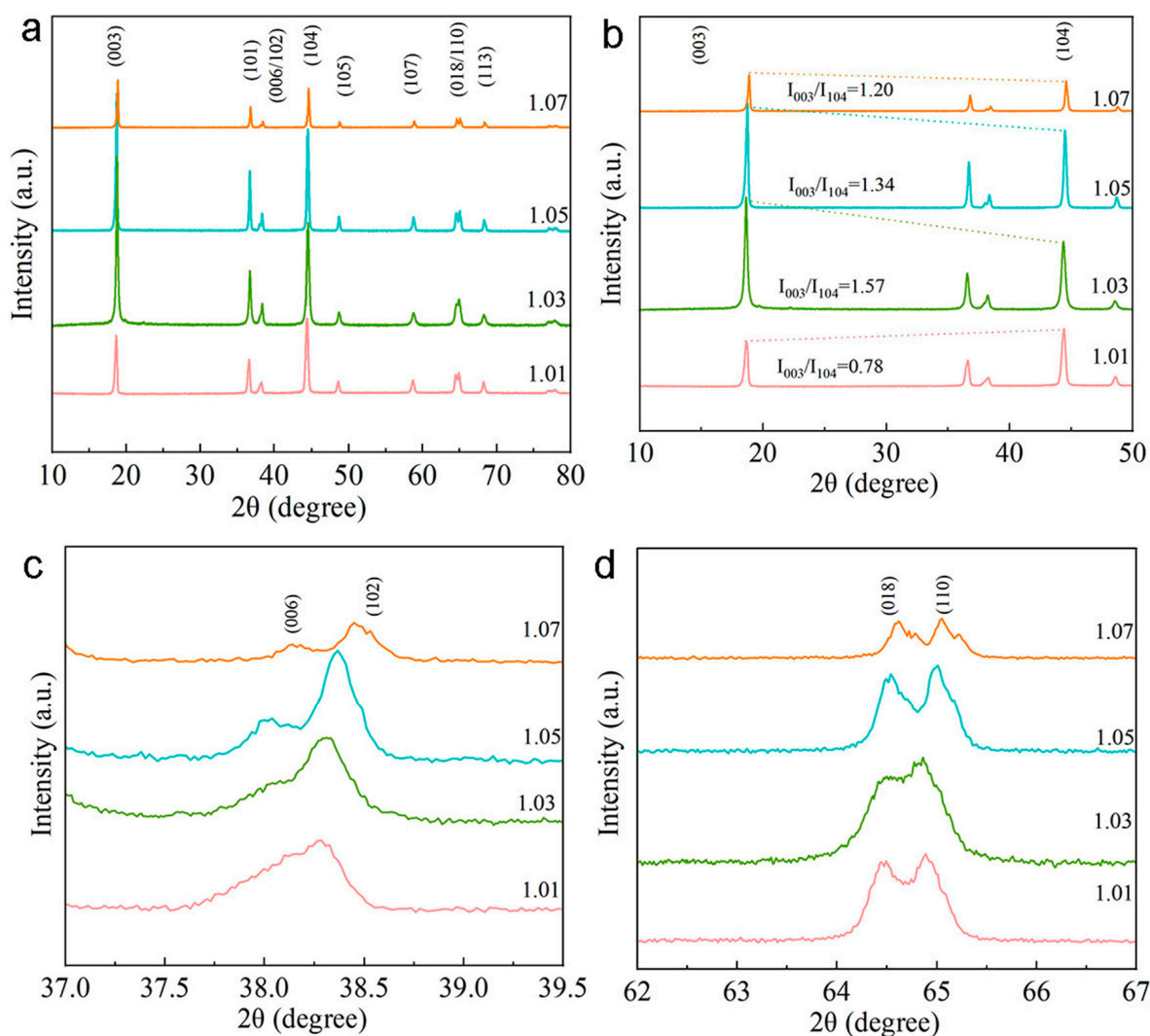


Figure 1. (a) XRD results of NCA91 with Li/TMs ratio of 1.01, 1.03, 1.05 and 1.07. (b) Amplified (003) peak and (104) peak. (c) Amplified (006)/(102) peaks. (d) Amplified (018)/(110) peaks.

The surface morphology of NCA91 cathodes synthesized at Li/TMs ratios of 1.01, 1.03, 1.05, and 1.07 was characterized via SEM (Figure 2a–h). Each composition exhibits well-defined spherical secondary particles with a mean diameter of ~11 μm, comprising densely packed primary crystallites of approximately 200 nm. No significant morphological differences are observed among the four samples, suggesting that the Li/TM stoichiometry exerts a minimal influence on the microstructural development. Supplementary EDS

elemental mapping performed on the Li/TMs = 1.03 specimen (Figure 2i–m) further confirms a homogeneous spatial distribution of Ni, Co, Al, and O over the particle surface, corroborating the compositional uniformity of the as-prepared cathode. In addition, the HRTEM of the sample with Li/TMs of 1.03 indicates that the synthesized sample has a layered structure, as shown in Figure S1.

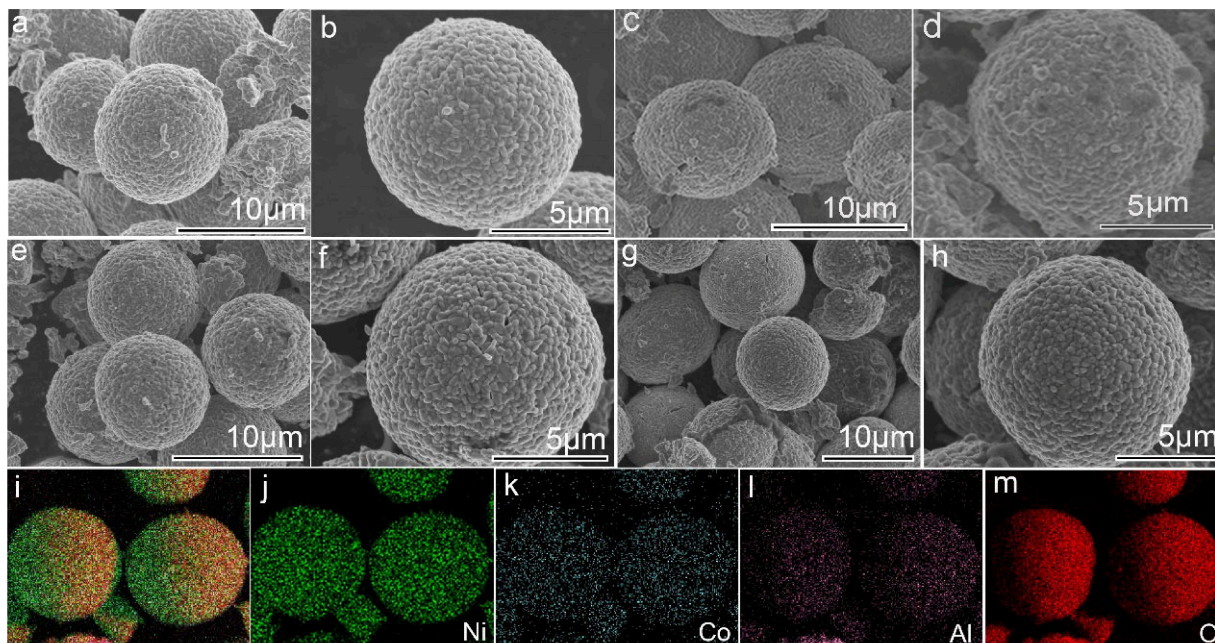


Figure 2. SEM images of NCA91 with Li/TMs ratio of 1.01 (a,b), 1.03 (c,d), 1.05 (e,f) and 1.07 (g,h). EDS mapping of Ni, Co, Al and O in NCA91 with Li/TMs ratio of 1.03 (i–m).

The electrochemical behavior of NCA91 cathodes with Li/TM ratios of 1.01, 1.03, 1.05, and 1.07 was systematically assessed in coin-type half cells (vs. Li/Li^+), with the corresponding results presented in Figure 3. Figure 3a–d display the charge–discharge voltage profiles of the four compositions cycled at 1 C within the 2.7–4.5 V for 100 cycles. All four samples exhibit distinct voltage plateaus in the 10th cycle, attributable to the sequential $\text{H1} \rightarrow \text{H2} \rightarrow \text{H3}$ phase transitions [16]. Notably, the plateaus of the Li/TMs = 1.01 electrode fade markedly faster than those of the other three compositions upon prolonged cycling. After 100 cycles, the average charge–discharge voltage hysteresis of the Li/TMs = 1.01 sample reaches 0.726 V, substantially exceeding the values of 0.442 V, 0.449 V, and 0.637 V recorded for the Li/TM = 1.03, 1.05, and 1.07 electrodes, respectively. Among all samples, the voltage profiles of the Li/TMs = 1.03 cathode remain remarkably stable throughout 100 cycles with only marginal shifts, indicating a minimal impedance growth and superior structural resilience compared to the other compositions. Notably, during the trickle-charge stage (i.e., constant-voltage charging at 4.5 V), the current progressively diminishes, enabling partial recovery of the capacity lost to polarization. This manifests as a distinct voltage plateau at 4.5 V in the charge profiles, which is directly associated with the over-potential arising from electrode polarization. For the Li/TMs = 1.01 electrode (Figure 3a), the capacity contribution of this plateau decreases from 67.2 mA h g^{-1} after 10 cycles to $36.22 \text{ mA h g}^{-1}$ after 100 cycles, reflecting persistent and severe polarization even after extended cycling. In stark contrast, the corresponding plateau capacities for the Li/TMs = 1.03, 1.05, and 1.07 electrodes are substantially lower: 29.3 and 35.6 mA h g^{-1} (10/100 cycles), 7.89 and $28.48 \text{ mA h g}^{-1}$ (10/100 cycles), 21.88 and $36.61 \text{ mA h g}^{-1}$ (10/100 cycles), respectively (Figure 3b–d). These results clearly demonstrate that optimizing the Li/TMs stoichiometry effectively suppresses the growth of electrode polarization during long-term

cycling. Figure 3e,f present the long-term cycling stability of the four compositions at 1 C. After the initial cycle, the Li/TMs = 1.01, 1.03, 1.05, and 1.07 cathodes deliver discharge capacities of 164.9, 197.1, 190.1, and 199 mA h g⁻¹, respectively. Following 100 cycles, these values decrease to 132.8, 173.5, 164.4, and 146.1 mA h g⁻¹, corresponding to capacity retentions of 80.7%, 88.0%, 86.5%, and 73.4%, respectively. The Li/TMs = 1.03 composition consistently outperforms the others in both absolute capacity and retention. The rate capabilities of all four samples were further evaluated at various current densities within the 2.7–4.5 V (Figure 3g–i). At low rates (0.2 C, 0.5 C, and 1 C), the Li/TMs = 1.01 cathode delivers notably lower specific capacities, likely attributable to its inferior layered ordering, whereas the Li/TMs = 1.03, 1.05, and 1.07 electrodes exhibit comparable performance. At high rates (≥ 10 C), however, the Li/TMs = 1.03 sample clearly surpasses the other three compositions. Specifically, at 10 C, it maintains a discharge capacity of ~ 130 mA h g⁻¹—approximately 63% of its 0.2 C capacity—significantly exceeding those of the Li/TMs = 1.01, 1.05, and 1.07 counterparts. The voltage profiles of the Li/TMs = 1.05 and 1.07 electrodes at different rates are provided in Figures S2 and S3. Given the excellent electrochemical performance of the as-prepared Li/TMs = 1.03 cathode in half-cells, it was assembled into coin-type full-cells with a graphite anode to evaluate its practical application potential. The test results demonstrated that the samples with Li/TMs ratios of 1.03 maintained a capacity retention rate of $\sim 80\%$ after 100 cycles at 2 C in the range of 2.7–4.3 V, significantly surpassing the values of $\sim 57\%$, $\sim 60\%$ and $\sim 70\%$ for the samples with Li/TMs ratios of 1.01, 1.05 and 1.07 (Figure 3j). Cyclic voltammetry analysis revealed that the sample with a Li/TMs ratio of 1.03 exhibited an initial oxidation-reduction peak spacing (ΔV) of 0.22 V. For comparison, the corresponding ΔV values for samples with Li/TMs ratios of 1.01, 1.05, and 1.07 were 0.22, 0.24, and 0.22 V, respectively. The narrower peak separation observed at the 1.03 ratio signifies diminished electrochemical polarization and enhanced interfacial reversibility. Integrating these findings with complementary characterization results confirms that the Li/TMs ratio of 1.03 yields the optimal overall electrochemical performance (Figures 3k and S4–S6). Galvanostatic intermittent titration technique (GITT) measurements revealed that the average lithium-ion diffusion coefficient of the sample with a Li/TMs ratio of 1.03 was significantly higher than that of the other three samples, indicating superior lithium-ion transport kinetics (Figure 3l).

Differential capacity (dQ/dV) analysis was further performed to elucidate the redox processes and phase evolution of the four cathodes upon cycling. As illustrated in Figure 4a–d, all samples exhibit three pairs of characteristic redox peaks, corresponding to the sequential phase transformations: hexagonal (H1) $\rightarrow$ monoclinic (M) $\rightarrow$ hexagonal (H2) $\rightarrow$ hexagonal (H3) during charge (delithiation), and the reverse sequence during discharge (lithiation) [17–20]. The peaks located at approximately 4.1–4.35 V are attributed to the H2 $\rightarrow$ H3 transition, which is widely recognized as a primary contributor to capacity degradation. This final phase transition induces an abrupt contraction of the c-axis, subjecting the cathode particles to significant mechanical stress that progressively undermines their electrochemical reversibility. For the Li/TMs = 1.01 electrode, the delithiation peaks progressively diminish in intensity with extended cycling, accompanied by a pronounced widening of the delithiation/lithiation voltage gap—particularly for the H2 $\rightarrow$ H3 transition. After 100 cycles, the phase transition features are almost completely smeared out, signifying severely compromised reversibility, in good agreement with the charge–discharge voltage profiles discussed above.

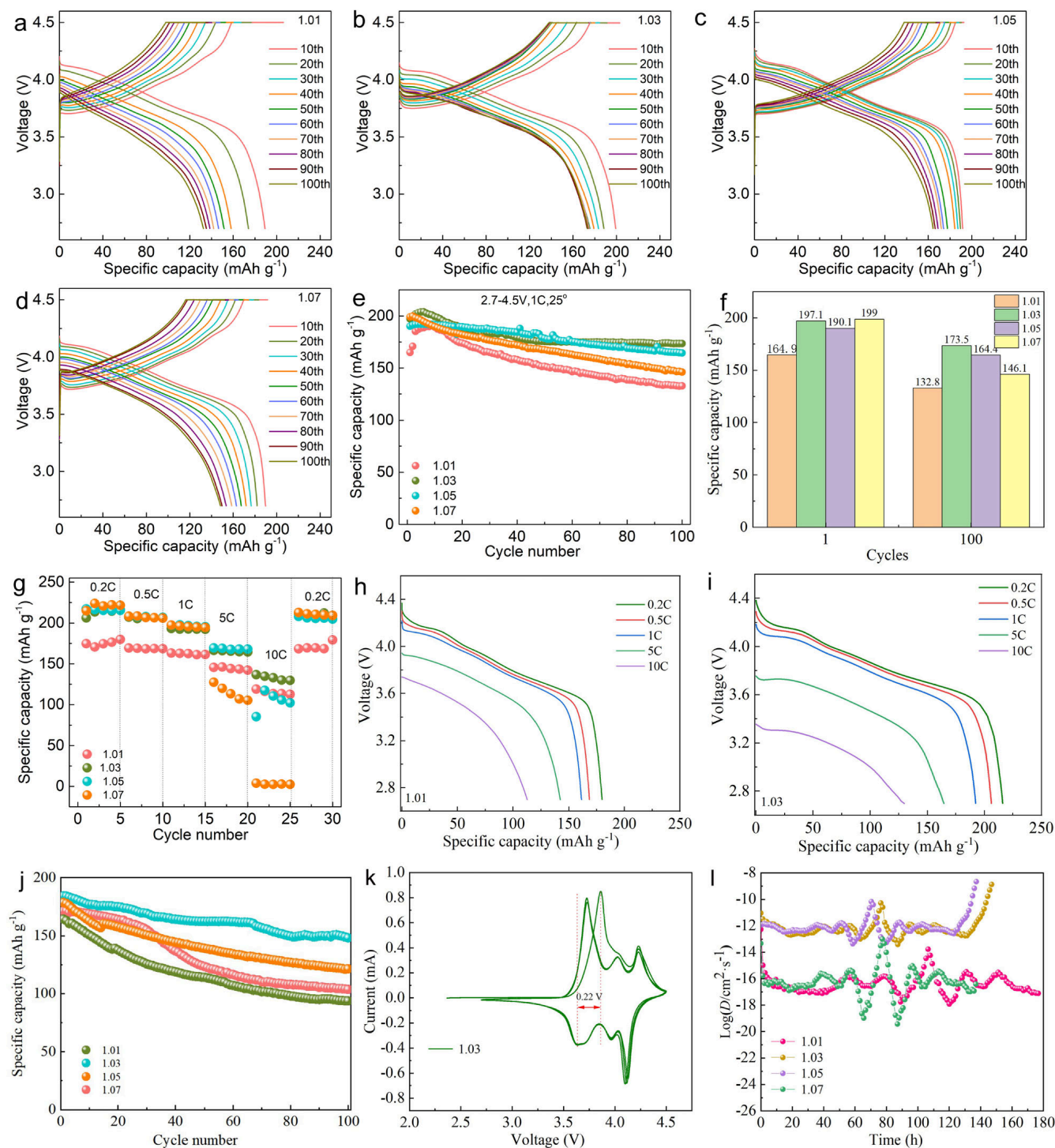


Figure 3. (a–d) Voltage curves of NCA91 with Li/TMs ratios of 1.01 (a), 1.03 (b), 1.05 (c) and 1.07 (d) at 1 C. (e) Cycling performance of NCA91 with Li/TMs ratios of 1.01, 1.03, 1.05 and 1.07 at 1 C in the range of 2.7–4.5 V. (f) Specific capacity after 1 cycle and 100 cycles of NCA91 with Li/TMs ratios of 1.01, 1.03, 1.05 and 1.07. (g) Rate performance in the range of 2.7–4.5 V. Voltage curves of NCA91 with Li/TMs ratios of 1.01 (h) and 1.03 (i) at different rates. (j) Cycling performance at 2 C in full-cells in the range of 2.7–4.3 V. (k) CV curves of NCA91 with Li/TMs ratio of 1.03 during the first three cycles. (l) Li⁺ diffusion coefficients calculated from GITT measurements.

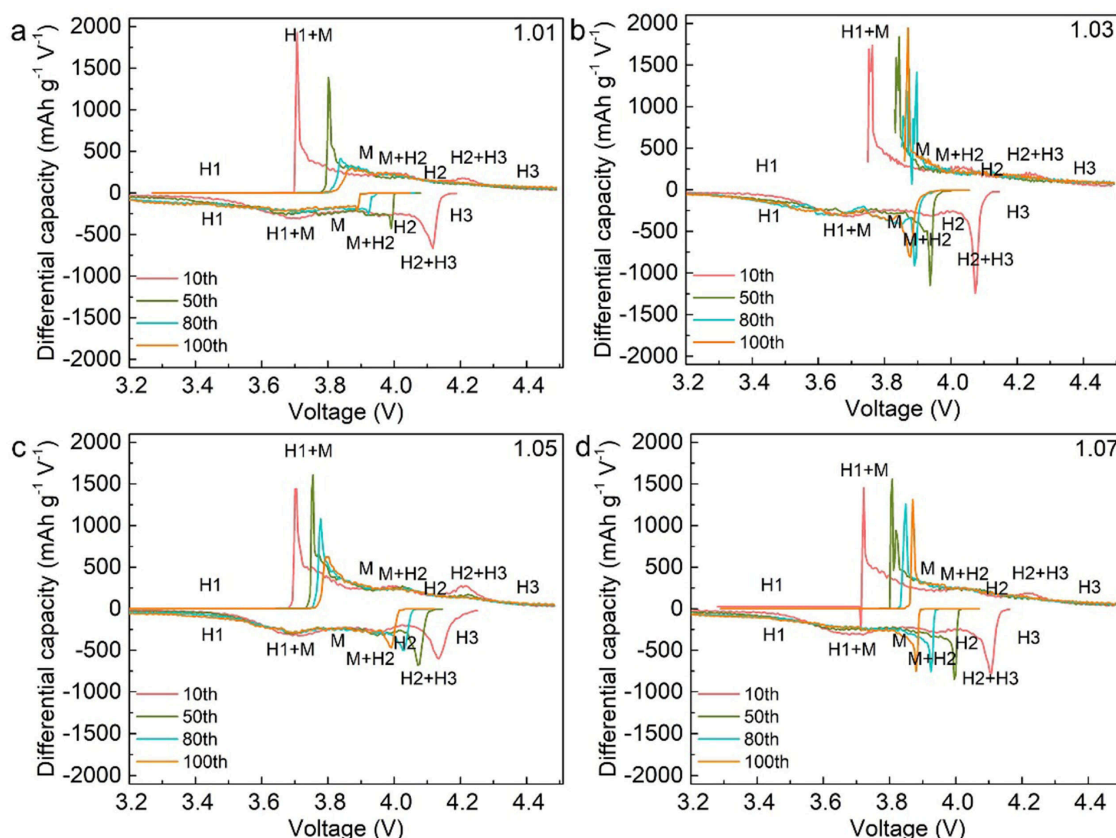


Figure 4. Corresponding differential capacity profiles of Li/TMs = 1.01 (a), 1.03 (b), 1.05 (c), and 1.07 (d).

3. Materials and Methods

3.1. Materials Preparation:

All reagents employed in this work were utilized without further purification unless otherwise specified. The hydroxide precursor $\text{Ni}_{0.91}\text{Co}_{0.06}\text{Al}_{0.03}(\text{OH})_2$ was procured from Shaanxi Coal & Chemical Industry Co., Ltd (Xian, Shanxi, China). Lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, 98%, analytical reagent) was obtained from Aladdin Reagent Co., Ltd (Shanghai, China). To fabricate the $\text{LiNi}_{0.91}\text{Co}_{0.06}\text{Al}_{0.03}\text{O}_2$ (referred to as NCA91) cathode material, stoichiometric quantities of the hydroxide precursor and $\text{LiOH}\cdot\text{H}_2\text{O}$ were weighed according to a Li-to-transition-metal molar ratio of 1.01:1, 1.03:1, 1.05:1, and 1.07:1, respectively. The two powders were subjected to hand-grinding for 20 min beneath an infrared drying lamp to ensure homogeneous blending. Subsequently, the blended mixture underwent high-temperature treatment at 730 °C for 10 h under a flowing oxygen atmosphere, yielding the final layered oxide product NCA91.

3.2. Material Characterization

The crystallographic features of all cathode samples were examined by powder X-ray diffraction (Bruker D8 Advance diffractometer, Karlsruhe, Germany) over a 2θ scanning window spanning from 10° to 80° with a scanning speed of 5° min^{−1}. Surface topographies and cross-sectional microstructures of the electrodes were captured via field-emission scanning electron microscopy (HITACHI SU8010, Tokyo, Japan). Additionally, high-resolution transmission electron microscopy (HRTEM, TecnaiG2 F30, FEI Company, Hillsboro, OR, USA) was used to observe the detailed morphology and crystal structure of the cathodes.

3.3. Electrochemical Measurements

For electrode fabrication, cathode slurries were prepared by dispersing the as-synthesized active material, conductive carbon black (Super-P), and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) solvent at a mass proportion of 8:1:1. The resulting homogeneous slurry was cast onto aluminum foil using a doctor blade and then transferred to a vacuum drying chamber maintained at 120 °C for 12 h to completely evaporate the solvent. Coin-type CR2032 (Canrd Technology Co.Ltd., Shenzhen, Guangdong, China) half-cells were constructed inside an argon-filled glove box (H_2O and $\text{O}_2 < 0.1$ ppm). Lithium metal foil served as the counter/reference electrode, while a microporous Celgard 2325 membrane functioned as the separator. The liquid electrolyte consisted of 1.2 M LiPF_6 dissolved in a binary carbonate solvent comprising ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a weight ratio of 3:7, supplemented with 2 wt% vinylene carbonate (VC) as a film-forming additive. The cycling performance was performed on Land (CT3001A, Wuhan, Hubei, China) at 1 C in 2.7–4.5 V at 25 °C. The rate performance was evaluated by cycling at various rates (C/5, C/2, 1 C, 5 C and 10 C) for 5 cycles, respectively. Cyclic voltammetry (CV) profiles were recorded on an electrochemical workstation (CHI760E, Shanghai, China) at a scanning rate of 0.2 mV s^{-1} within a voltage range of 2.7–4.5 V.

4. Conclusions

In summary, this work presents a systematic investigation into the influence of Li/TMs stoichiometry on the structural evolution and electrochemical performance of Ni-rich NCA91 cathodes. By precisely tuning the Li/TMs molar ratio from 1.01 to 1.07, a non-monotonic dependence of cation ordering, phase reversibility, and interfacial stability on the Li content is revealed. The NCA91 cathode with a Li/TMs ratio of 1.03 exhibits the optimal balance between suppressed cation mixing and minimal antisite disorder, thereby preserving the layered structural integrity during prolonged cycling. Consequently, this composition delivers superior cycling stability (88.0% capacity retention after 100 cycles at 1 C) and exceptional rate capability ($\sim 130 \text{ mAh g}^{-1}$ at 10 C, retaining $\sim 63\%$ of its 0.2 C capacity), significantly outperforming both Li-deficient and Li-excessive counterparts. The underlying mechanism is attributed to the mitigation of the irreversible $\text{H}_2 \rightarrow \text{H}_3$ phase transition and the alleviation of electrode polarization, as corroborated by differential capacity analysis and voltage hysteresis evaluation. Overall, this study establishes a quantitative structure–composition–performance relationship for NCA91, providing critical design guidelines for the rational development of next-generation ultrahigh-nickel cathode materials with enhanced durability and rate performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14070186/s1>, Figure S1. HRTEM image of NCA91 with Li/TMs ratio of 1.03; Figure S2. Voltage curves of NCA91 with Li/TMs ratio of 1.05 at different rates; Figure S3. Voltage curves of NCA91 with Li/TMs ratio of 1.07 at different rates; Figure S4. CV curves of NCA91 with Li/TMs ratio of 1.01 during the first three cycles; Figure S5. CV curves of NCA91 with Li/TMs ratio of 1.05 during the first three cycles; Figure S6. CV curves of NCA91 with Li/TMs ratio of 1.07 during the first three cycles.

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