

Research Article

Tailoring the Bulk Structure and Surface Chemistry of Ni-Rich NCM811 Cathodes via Polyanion Incorporation for Enhanced Electrochemical Performance up to 4.5 V

Youngmin Chi,¹ Jeseon Lee,² Hyunchul Kang,¹ Jiung Cho,³ Eunho Lim^{id},^{2,4} and Songhun Yoon^{id}¹

¹School of Integrative Engineering, Chung-Ang University, Seoul 06974, Republic of Korea

²Department of Chemical and Biochemical Engineering, Dongguk University, Seoul 04620, Republic of Korea

³Department of Materials Science and Engineering, Hongik University, Sejong, Republic of Korea

⁴Department of Energy and Materials Engineering, Dongguk University, Seoul 04620, Republic of Korea

Correspondence should be addressed to Eunho Lim; eunholim@dgu.ac.kr and Songhun Yoon; yoonsun@cau.ac.kr

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In this study, we investigate the effect of PO_4^{3-} polyanion incorporation on the physicochemical and electrochemical properties of Ni-rich layered $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ ($\text{P}_x\text{-NCM811}$, where $x = 0.0, 0.3$, and 0.5) cathode materials. A coprecipitation method with controlled polyanion injection was employed to ensure homogeneous distribution of PO_4^{3-} within the precursor particles. Comprehensive structural and morphological analyses confirmed that PO_4^{3-} incorporation led to reduced primary particle size and the formation of a compact, densely packed microstructure, particularly for the $\text{P}_{0.3}\text{-NCM811}$ cathode material. X-ray diffraction (XRD) and Rietveld refinement analyses revealed lattice expansion along the c -axis, while X-ray photoelectron spectroscopy (XPS) analysis demonstrated suppressed Ni^{2+} accumulation and surface stabilization via Li_3PO_4 formation. Electrochemical evaluation showed that $\text{P}_{0.3}\text{-NCM811}$ exhibited superior initial discharge capacity ($\sim 227 \text{ mA h g}^{-1}$), Coulombic efficiency ($\sim 92.7\%$), rate capability, and cycling stability, with approximately 86.7% capacity retention after 100 cycles at 1.0 C. Electrochemical impedance spectroscopy (EIS) further confirmed lower surface film and charge transfer resistances, as well as enhanced Li^+ diffusion kinetics in the polyanion-modified cathodes. Differential capacity analysis indicated improved structural reversibility during phase transitions for $\text{P}_{0.3}\text{-NCM811}$, with reduced polarization and minimal $\text{H2} \rightarrow \text{H3}$ transition-induced degradation. These results demonstrate that PO_4^{3-} polyanion incorporation is a promising strategy to stabilize the structure and improve the electrochemical performance of Ni-rich layered oxide cathodes under high-voltage operation (4.5 V vs. Li/Li^+).

Keywords: cathode materials; enhanced electrochemical performance; $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$; lithium-ion batteries; polyanion incorporation

1. Introduction

Lithium-ion batteries (LIBs) have become essential energy storage solutions, supporting applications ranging from portable electronics to electric vehicles (EVs) and large-scale energy storage systems (ESSs) [1, 2, 3]. As global demand intensifies, particularly for EVs, significant research efforts have been dedicated to enhancing LIB performance metrics, notably energy density, rate capability, and cycle life [4, 5].

Among these, cathode materials profoundly influence battery performance due to their complex structural transformations and electrochemical instability during lithium-ion (Li^+) insertion/extraction processes [6, 7].

Achieving high energy density requires optimization of electrode material capacity and operating voltage ($E = \text{Ah} \times V$, where Ah denotes the electrode capacity and V represents the operating potential) [8]. Layered oxide cathodes, specifically Ni-rich $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})\text{O}_2$ (NCM), derived from

LiNiO₂ (LNO), have emerged as leading candidates because of their high specific capacities and reduced cobalt content, addressing both performance and economic considerations [9, 10, 11]. In particular, Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O₂ (NCM811) has attracted substantial interest owing to its high capacity, competitive cost, and potential for achieving higher energy densities required for advanced EV applications [12].

Despite these merits, NCM811 cathodes suffer from rapid capacity degradation and limited rate capability, especially under high potential conditions (~4.5 V vs. Li/Li⁺), essential for maximizing energy density. High potential operation exacerbates intrinsic structural instabilities, including Li/Ni cation disorder, irreversible layered-to-rock-salt phase transformations, and detrimental interfacial side reactions [13, 14, 15]. Additionally, structural degradation of NCM811 is prominently driven by phase transitions during charge, evolving sequentially from a hexagonal layered (H1) phase to monoclinic (M) and further to hexagonal H2 and H3 phases. Particularly, the H2 → H3 transition at approximately 4.2 V (vs. Li/Li⁺) results in anisotropic lattice contraction along the *c*-axis, generating substantial internal stresses and microcracks [16, 17]. Such microcracks accelerate electrolyte infiltration, triggering undesirable side reactions and promoting electrochemically inactive NiO phase formation, thereby dramatically compromising cycle life [18, 19].

To mitigate these challenges, numerous advanced strategies have been extensively explored. Surface modification using Li⁺ conductive coatings such as LiAlO₂, LaPO₄, LiNbO₃, LiTaO₃, and lithium phosphate-based compounds (e.g., Li₃PO₄) has proven effective in stabilizing cathode/electrolyte interfaces, reducing parasitic reactions, and enhancing interfacial Li⁺ transport kinetics [20, 21, 22, 23, 24]. Additionally, precise morphological engineering via controlled coprecipitation methods, including secondary particle alignment, radial gradient concentration designs, and nano/microstructural tuning, have been actively investigated to alleviate mechanical stress and reduce crack propagation during repeated cycling. Moreover, doping strategies employing both cationic species (e.g., Ti⁴⁺, Al³⁺, Mg²⁺, Zr⁴⁺, and Nb⁵⁺) and anionic species (e.g., F[−] and Cl[−]) have garnered significant attention [25, 26, 27, 28, 29, 30, 31]. These doping strategies effectively suppress cation mixing, enhance structural stability by modulating metal–oxygen bond strength and lattice parameters, and promote favorable electronic configurations and ionic diffusion pathways [32, 33, 34]. Among the various doping methods, PO₄^{3−} polyanion incorporation stands out due to its ability to stabilize structural transitions, reduce interfacial impedance, and improve Li⁺ diffusivity, significantly extending cycling stability and rate performance of Ni-rich NCM cathodes [35].

In this work, we present a comprehensive investigation into the structural and electrochemical enhancement of NCM811 via strategic incorporation of PO₄^{3−} polyanions (denoted as P_{*x*}-NCM811, with *x* representing the molar percentage of PO₄^{3−} incorporation: 0.0, 0.3, and 0.5 mol%). The primary objective is to reinforce the internal crystal framework of NCM811, suppress cation disorder, and alleviate the severe structural instabilities at high potentials (~4.5 V vs. Li/Li⁺). Additionally, a secondary goal is to deliberately

induce the formation of a Li₃PO₄ surface layer during synthesis, stabilizing the cathode/electrolyte interface and reducing interfacial side reactions. Among the studied materials, P_{*x*}-NCM811 with *x* = 0.3 exhibited superior electrochemical performance, including enhanced specific capacity, improved Coulombic efficiency, and substantially better cycling stability under rigorous high potential cycling conditions. To elucidate the mechanisms behind these performance improvements, we conducted extensive physicochemical and electrochemical analyses, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy, and electrochemical impedance spectroscopy (EIS). These investigations provide clear evidence of the beneficial role of PO₄^{3−} incorporation in stabilizing the internal lattice structure and mitigating the detrimental high potential structural transformations in NCM811 cathodes.

2. Experiment

2.1. Material Synthesis. PO₄^{3−} polyanions were incorporated into Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ precursors via a coprecipitation method to synthesize polyanion-modified NCM811, denoted as P_{*x*}-NCM811 (*x* = 0.0, 0.3, and 0.5, where *x* represents the molar ratio of PO₄^{3−} incorporation). A 2.0 M metal sulfate solution was prepared by dissolving NiSO₄·6H₂O, CoSO₄·7H₂O, and MnSO₄·5H₂O in a molar ratio of 8:1:1 in deionized water. Additionally, 2.0 M NH₄OH and 4.0 M NaOH solutions were prepared as the chelating and precipitating agents, respectively. To incorporate PO₄^{3−} into the precursor structure, Na₃PO₄·12H₂O was dissolved in a NaOH solution and the concentration of Na₃PO₄·12H₂O was adjusted to control the PO₄^{3−} content. For instance, for P_{0.3}-NCM811, the concentration of Na₃PO₄·12H₂O was set to 0.3 mol% relative to the metal sulfates.

The metal sulfate solution, NH₄OH, NaOH, and Na₃PO₄·12H₂O + NaOH solutions were separately and continuously fed into a continuously stirred tank reactor using precision peristaltic pumps to ensure uniform incorporation of PO₄^{3−} throughout the precursor particles from core to surface. The reactor atmosphere was maintained under inert N₂ gas, the pH was kept at approximately 11, and the reaction temperature was maintained at 55°C. The resulting P_{*x*}-NCM811 precursors were collected by filtration, thoroughly washed with deionized water, and dried at 80°C for 24 h. The dried precursors were then mixed with LiOH·H₂O in a Li/metal molar ratio of 1.02 and calcined in an O₂ atmosphere at 780°C for 12 h to obtain the final P_{0.0}-NCM811, P_{0.3}-NCM811, and P_{0.5}-NCM811 cathode materials.

2.2. Material Characterization. The crystal structures of the synthesized cathode materials were analyzed using XRD (New D8-Advance, Bruker). The particle morphology was examined via field-emission scanning electron microscopy (FE-SEM, ZEISS Sigma), and the elemental distribution was assessed using energy-dispersive X-ray spectroscopy (EDS) mapping (ZEISS Sigma). The chemical states of the constituent elements were characterized by XPS (Thermo Scientific K-Alpha⁺).

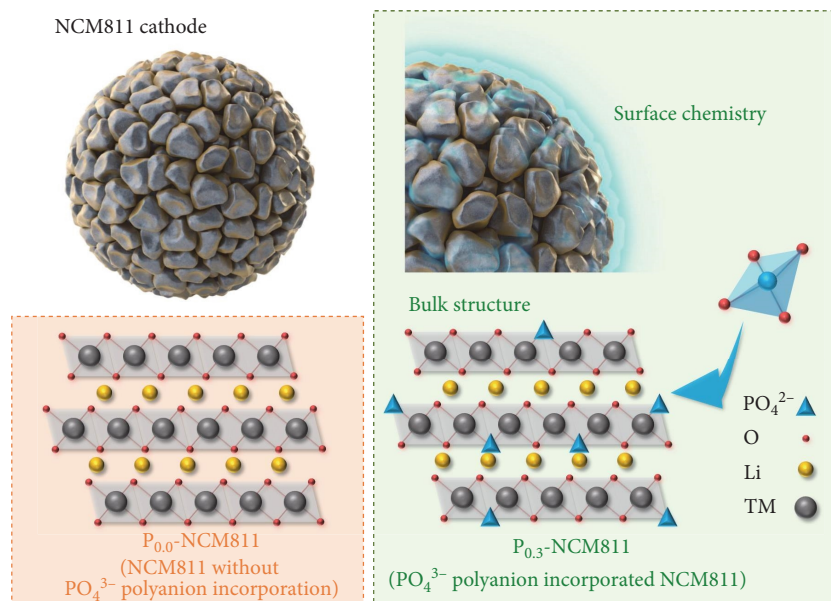


FIGURE 1: Schematic illustration comparing NCM811 without PO_4^{3-} polyanion incorporation ($\text{P}_{0.0}$ -NCM811) and with PO_4^{3-} polyanion incorporation ($\text{P}_{0.3}$ -NCM811).

2.3. Electrochemical Measurements. To evaluate the electrochemical performance, the P_x -NCM811 cathode materials were mixed with Super P (conductive agent) and polyvinylidene fluoride (PVDF, binder) in a weight ratio of 94:3:3 using N-methylpyrrolidone (NMP) as the solvent. The resulting slurry was uniformly coated onto aluminum (Al) foil and dried in an oven at 120°C for 20 min. The dried electrodes were roll-pressed, punched into circular disks (10 mm in diameter), and vacuum-dried at 120°C for 10 h. CR2032 coin cells were assembled in an argon-filled glove box using Li metal as both the counter and reference electrodes. The electrolyte consisted of 1.0 M LiPF_6 dissolved in a mixed solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in a 3:7 volume ratio.

Galvanostatic charge–discharge tests were conducted using a battery cycler (WonATech, WBCS 3000 L) within a potential range of 3.0–4.5 V (vs. Li/Li^+). A current rate of 1.0 C was defined as 180 mAh g^{-1} . All electrochemical measurements were performed at 25°C . EIS was carried out using a ZIVE SP1 workstation (WonATech) after 100 cycles at 1.0 C, with an amplitude of 10 mV over a frequency range of 0.01–100 kHz to analyze resistance evolution during cycling. The Li^+ diffusion coefficient (D_{Li^+}) was calculated using the following equation:

$$D_{\text{Li}^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}.$$

D_{Li^+} is the Li^+ diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$); R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the absolute temperature (K); A is the effective surface area of the electrode (cm^2); n is the number of electrons involved in the reaction (dimensionless); F is the Faraday constant ($96,485 \text{ C mol}^{-1}$); C is the concentration of Li^+ in the electrode (mol cm^{-3}); σ is

the Warburg coefficient (slope from low-frequency impedance, $\Omega \text{ s}^{-0.5}$).

3. Results and Discussion

3.1. Synthesis and Characterization of P_x -NCM811 Cathode Materials. $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ (referred to as P_x -NCM811, where $x = 0.0, 0.3$, and 0.5), incorporating varying amounts of PO_4^{3-} polyanions, was synthesized through a carefully controlled method that modulates the injection rate of the PO_4^{3-} polyanion source. In brief, to prepare the P_x -NCM811 cathode materials, $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ precursors (P_x -NCM811 precursors) were first synthesized using a coprecipitation method (details in Section 2). Unlike conventional methods that introduce PO_4^{3-} postsynthesis, either by reacting with surface residual Li to form a Li_3PO_4 layer or by posttreatment incorporation, we incorporated the PO_4^{3-} polyanions directly during the coprecipitation process. As illustrated in Figure 1, this strategy was deliberately designed to modulate both the surface chemistry and the bulk structure of NCM811. By precisely controlling the injection rate, we enabled a uniform distribution of PO_4^{3-} polyanions from the core to the surface of the precursors.

As confirmed by SEM images (Figure S1), all P_x -NCM811 precursors exhibited needle-like primary particles aggregated into spherical secondary particles. In addition, EDS mapping of all P_x -NCM811 precursors revealed a homogeneous distribution of Ni, Co, and Mn throughout the particles (Figures S2–S4). Notably, the $\text{P}_{0.3}$ -NCM811 (Figure S3) and $\text{P}_{0.5}$ -NCM811 (Figure S4) precursors also exhibited a uniform distribution of phosphorus, further confirming the successful incorporation of PO_4^{3-} during the coprecipitation step. However, after calcination with a Li source to obtain the final P_x -NCM811 cathode materials, SEM images revealed a clear

variation in the primary particle sizes depending on the extent of PO_4^{3-} incorporation (Figure 2a–c). Furthermore, low-magnification SEM images of the $\text{P}_x\text{-NCM811}$ cathode materials (Figure S5) confirm that all cathode materials consist predominantly of spherical secondary particles across the samples. Elemental distributions were further examined by EDS mapping. As shown in Figure S6, the $\text{P}_{0.0}\text{-NCM811}$ cathode material exhibited a uniform distribution of Ni, Co, and Mn throughout the particles, while maintaining a spherical morphology. In contrast, both $\text{P}_{0.3}\text{-NCM811}$ and $\text{P}_{0.5}\text{-NCM811}$ samples showed homogeneously distributed P in addition to the transition metals, confirming successful polyanion incorporation (Figures S7 and S8). These results suggest that incorporation of PO_4^{3-} leads to a more uniform primary particle size distribution. To further support this observation, quantitative particle size analysis of 100 primary particles was conducted (Figure S9), which revealed a clear reduction and narrowing of particle size upon PO_4^{3-} incorporation. Notably, the $\text{P}_{0.3}\text{-NCM811}$ sample exhibited smaller and more densely packed primary particles, indicating that appropriate incorporation of PO_4^{3-} can regulate particle morphology, which may in turn positively influence the electrochemical performance.

To investigate the structural characteristics of the synthesized $\text{P}_x\text{-NCM811}$ cathode materials, XRD analysis was performed (Figure 2d–g). All samples exhibited well-defined layered structures characteristic of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$, with a rhombohedral structure belonging to the $R\bar{3}m$ space group. Despite the incorporation of PO_4^{3-} , no secondary phases or impurity peaks were detected in the XRD patterns of $\text{P}_{0.3}\text{-NCM811}$ and $\text{P}_{0.5}\text{-NCM811}$ cathode materials. Moreover, the distinct splitting of the (006)/(102) and (108)/(110) peaks demonstrates the high crystallinity of the cathode materials, further supporting the successful incorporation of PO_4^{3-} polyanions (Figure 2e,f) [36]. To gain more detailed insight into the structural variations, Rietveld refinement was conducted (Figure 2h–j), and the results are summarized in Table S1. The a -axis lattice parameter remained nearly unchanged across the series; however, a gradual increase in the c -axis lattice parameter was observed with increasing PO_4^{3-} content. This expansion can be attributed to the substitution of relatively small spherical O^{2-} anions (140 pm) with the larger PO_4^{3-} polyanions (238 pm), indicating successful incorporation into the NCM811 lattice structure [37]. This observation is further corroborated by high-resolution transmission electron microscopy (TEM) images (Figure S10), where the (003) lattice spacing increased from 0.481 nm for $\text{P}_{0.0}\text{-NCM811}$ to 0.501 nm for $\text{P}_{0.3}\text{-NCM811}$, providing direct evidence of c -axis expansion upon PO_4^{3-} incorporation. Additionally, the shift of the (003) peak toward lower angles, consistent with Rietveld results, further supports c -axis expansion (Figure 2g). Since Li^+ primarily diffuse along the (003) planes within the Li layers, an increased interslab spacing is expected to enhance Li^+ mobility, thus, potentially improving rate capability [38]. The degree of cation mixing, which can be inferred from the intensity ratio of $I_{(003)}/I_{(104)}$, also showed a favorable trend [39]. As shown in Table S1, the $I_{(003)}/I_{(104)}$ ratio increased from 1.80 to 1.92 with higher PO_4^{3-}

content, indicating a decrease in cation mixing. This structural improvement is expected to contribute to better electrochemical stability and capacity retention.

To investigate the changes in the surface valence states of $\text{P}_x\text{-NCM811}$ cathode materials induced by PO_4^{3-} polyanion incorporation, XPS analysis was conducted. As shown in Figure 3a–c, P 2p spectra of $\text{P}_{0.3}\text{-NCM811}$ and $\text{P}_{0.5}\text{-NCM811}$ display a prominent peak around 133.4 eV, which is characteristic of tetrahedral PO_4 groups. This observation confirms the successful incorporation of PO_4^{3-} polyanions into the NCM811 structure during synthesis. Although the overall intensity of the P 2p signal is relatively weak due to the intrinsically low phosphorus content, complementary evidence from XRD peak shifts (Figures 2g) and EDS elemental mapping (Figures S6–S8) consistently confirms the presence and homogeneous distribution of phosphorus. Taken together, these results substantiate the successful incorporation of PO_4^{3-} polyanions into the NCM811 lattice despite the limited signal-to-noise ratio in the XPS spectra. Figure 3d–f shows the Ni 2p spectra, where the Ni 2p_{3/2} and Ni 2p_{1/2} peaks appear at approximately 855.1 and 872.5 eV, respectively, along with their associated satellite peaks. Deconvolution of the Ni 2p_{3/2} peak reveals contributions from Ni^{2+} (854.6 eV) and Ni^{3+} (855.6 eV) species. The relative Ni^{3+} content increases from 48% ($\text{P}_{0.0}\text{-NCM811}$) to 60% ($\text{P}_{0.3}\text{-NCM811}$) and 63% ($\text{P}_{0.5}\text{-NCM811}$) with increasing polyanion incorporation, as summarized in Table S2. This trend suggests that PO_4^{3-} incorporation effectively suppresses the surface accumulation of Ni^{2+} , thereby reducing the degree of cation mixing—consistent with the findings from Rietveld refinement analysis. C 1s spectra for all samples are shown in Figure 3g–i. Peaks observed at approximately 284.8 and 289.8 eV correspond to hydrocarbon species and Li_2CO_3 , respectively [40]. The Li_2CO_3 commonly originates from residual lithium compounds that react with atmospheric CO_2 and moisture during sample handling, which is frequently observed in Ni-rich NCM cathodes. Compared to $\text{P}_{0.0}\text{-NCM811}$, both the intensity and relative area of the Li_2CO_3 peak decrease significantly in the $\text{P}_{0.3}\text{-NCM811}$ and $\text{P}_{0.5}\text{-NCM811}$ cathode materials (Table S2), indicating that PO_4^{3-} incorporation reduces the formation of Li residuals. This result suggests that during the high-temperature synthesis process, residual Li on the precursor surface reacts with PO_4^{3-} species to form a Li_3PO_4 surface layer. Although the absolute quantification of residual lithium is experimentally challenging due to its inherently low concentration, the systematic decrease in the Li_2CO_3 signal observed in the XPS C 1s spectra provides reliable indirect evidence of reduced surface Li. This interpretation is further supported by complementary structural and compositional analyses, which consistently indicate the stabilizing effect of PO_4^{3-} incorporation.

These physicochemical characterizations collectively demonstrate that PO_4^{3-} polyanions are not only incorporated into the NCM811 lattice, but may also exist as Li_3PO_4 on the particle surface. Such dual effects are expected to significantly influence the electrochemical performance of NCM811 cathode materials, particularly in terms of capacity retention, rate capability, and long-term cycling stability.

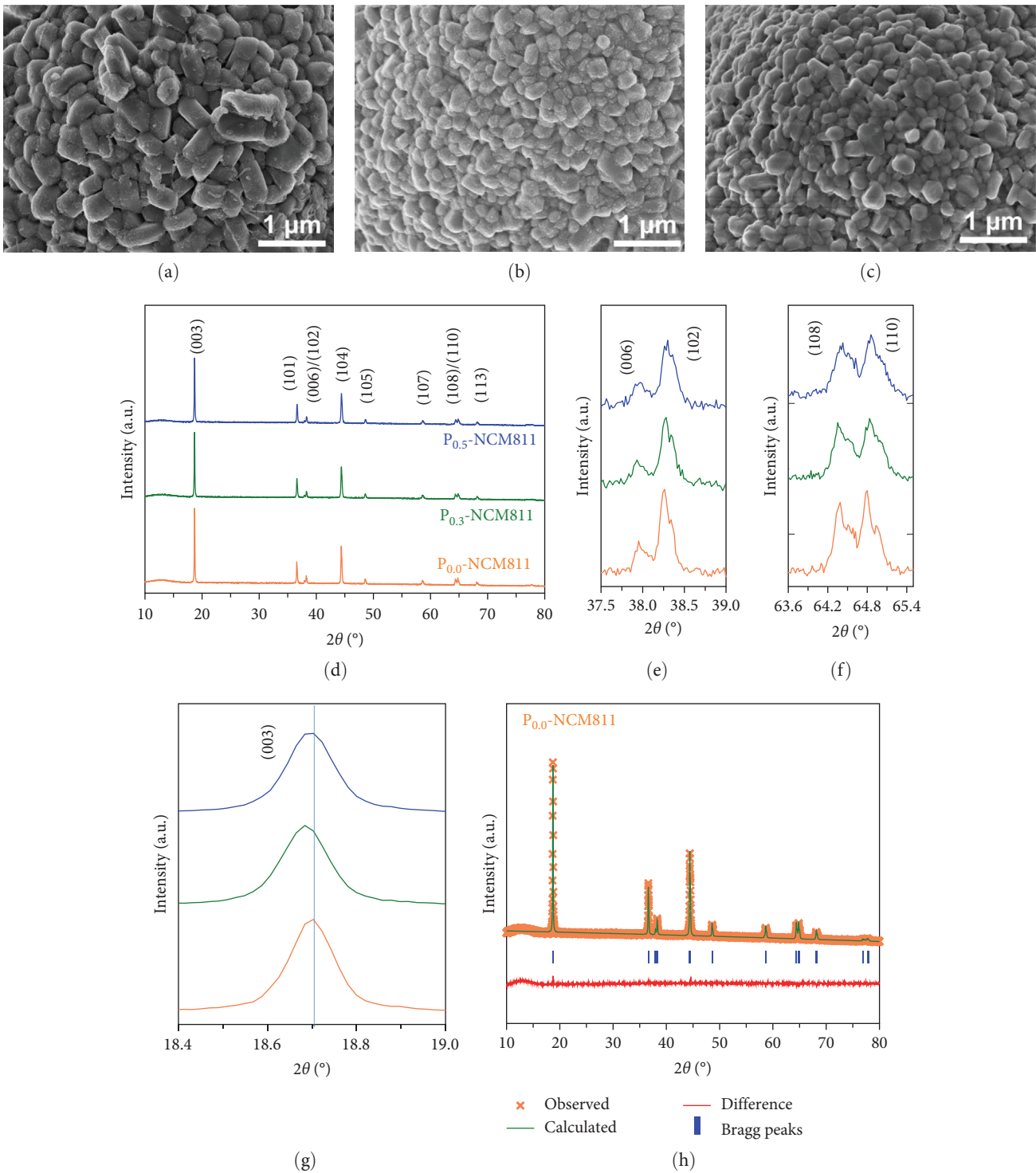


FIGURE 2: Continued.

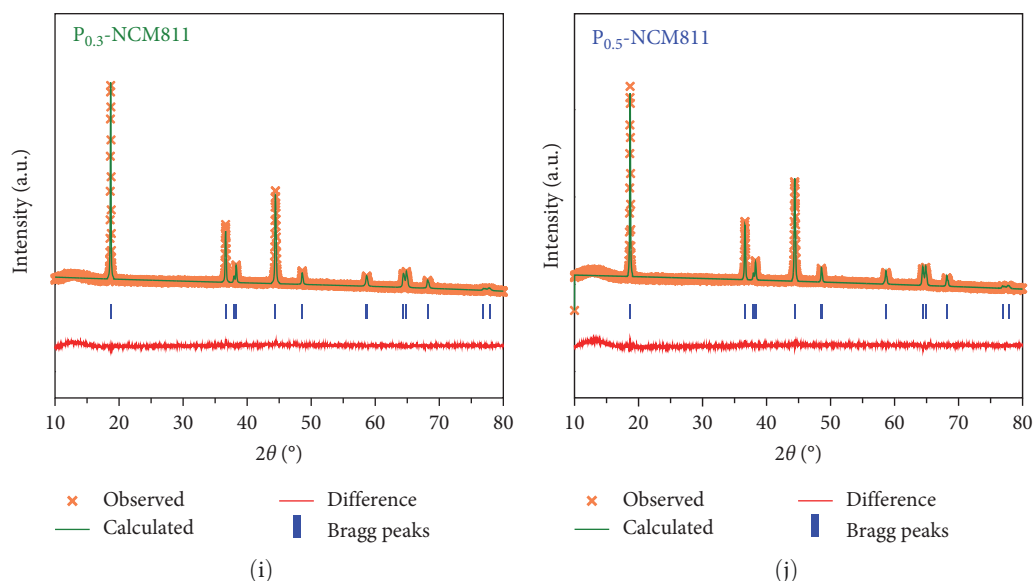


FIGURE 2: SEM images of (a) $P_{0.0}$ -NCM811, (b) $P_{0.3}$ -NCM811, and (c) $P_{0.5}$ -NCM811 cathode materials. (d–g) XRD patterns of P_x -NCM811 cathode materials. Rietveld refinement results for (h) $P_{0.0}$ -NCM811, (i) $P_{0.3}$ -NCM811, and (j) $P_{0.5}$ -NCM811 cathode materials.

3.2. Electrochemical Performance Evaluation of P_x -NCM811 Cathode Materials. The electrochemical performance of the synthesized P_x -NCM811 cathode materials was evaluated using half-cells assembled with Li metal serving as both the counter and reference electrodes. Galvanostatic charge–discharge tests were conducted at 25°C within a potential range of 3.0–4.5 V (vs. Li/Li^+). Figure 4a–d displays the initial charge–discharge curves measured at a current density of 0.1 C (1.0 C = 180 mA h g^{-1}). Although all P_x -NCM811 cathode materials exhibited similar voltage profiles, notable differences in their initial discharge capacities were observed. Specifically, the pristine $P_{0.0}$ -NCM811 and $P_{0.5}$ -NCM811 cathode materials delivered an initial discharge capacity of approximately 216 and 215 mA h g^{-1} , respectively, while the $P_{0.3}$ -NCM811 cathode material, incorporating an optimal amount of PO_4^{3-} polyanions, showed enhanced capacities of approximately 227 mA h g^{-1} . Coulombic efficiency also improved with the incorporation of an appropriate amount of polyanions. The first-cycle efficiencies of $P_{0.0}$ -NCM811, $P_{0.3}$ -NCM811, and $P_{0.5}$ -NCM811 were approximately 90.7%, 92.8%, and 90.1%, respectively, indicating that the incorporation of an optimal amount of PO_4^{3-} positively influences the electrochemical behavior of the cathode. Among the cathode materials, $P_{0.3}$ -NCM811 cathode material exhibited the most favorable combination of initial capacity and efficiency. This enhancement can be correlated with the XPS results discussed previously. The reduction in Ni^{2+} concentration, achieved through PO_4^{3-} incorporation, is likely to suppress the formation of electrochemically inactive NiO species on the particle surface, thereby reducing irreversible capacity loss and improving initial Coulombic efficiency.

Figure 4e presents the rate capability of P_x -NCM811 cathode materials tested at various current densities (0.2, 0.5, 1.0, 2.0, and 4.0 C). Compared to the pristine $P_{0.0}$ -NCM811, both $P_{0.3}$ -NCM811 and $P_{0.5}$ -NCM811 cathode materials exhibited significantly improved rate performance, with $P_{0.3}$ -NCM811 demonstrating the most superior

behavior among the series, despite having a lower PO_4^{3-} content than $P_{0.5}$ -NCM811. Specifically, the $P_{0.3}$ -NCM811 cathode delivered discharge capacities of approximately 218, 207, 199, 190, and 178 mA h g^{-1} at current rates of 0.2, 0.5, 1.0, 2.0, and 4.0 C, respectively, corresponding to capacity retentions of approximately 95.8% (0.5 C), 92.6% (1.0 C), 88.0% (2.0 C), and 82.9% (4.0 C), as shown in Figure 4f and Figure S11a. Furthermore, as illustrated in Figure S11b, the $P_{0.3}$ -NCM811 cathode exhibited superior discharge specific capacities across all tested C-rates. This excellent rate performance is attributed to the smaller and more uniformly distributed primary particles in $P_{0.3}$ -NCM811, which shorten the Li^+ diffusion paths. In addition, the expanded *c*-axis resulting from PO_4^{3-} incorporation likely reduces Li^+ diffusion resistance, facilitating more efficient Li^+ insertion and extraction during charge–discharge cycles.

Figure 4g illustrates the cycling stability of P_x -NCM811 cathodes over 100 cycles at 1.0 C. While all cathode materials exhibited Coulombic efficiencies close to approximately 100%, $P_{0.3}$ -NCM811 and $P_{0.5}$ -NCM811 maintained relatively higher efficiencies throughout the test. Notably, even under a high cut-off voltage of 4.5 V (vs. Li/Li^+), $P_{0.3}$ -NCM811 retained a discharge capacity of approximately 171 mA h g^{-1} after 100 cycles, compared to approximately 146 and 167 mA h g^{-1} for $P_{0.0}$ -NCM811 and $P_{0.5}$ -NCM811, respectively. The corresponding capacity retentions were approximately 74.7%, 86.7%, and 83.2%, further highlighting the superior cycling stability of $P_{0.3}$ -NCM811. The enhanced long-term stability of $P_{0.3}$ -NCM811 can be attributed to the reduced cation mixing and suppression of inactive NiO phase formation, as supported by both XPS and structural analysis. These synergistic effects of polyanion incorporation underscore its critical role in improving both the kinetics and structural stability of Ni-rich layered cathode materials under high-voltage operation.

To further investigate the effect of PO_4^{3-} polyanion incorporation on the interfacial and charge transport

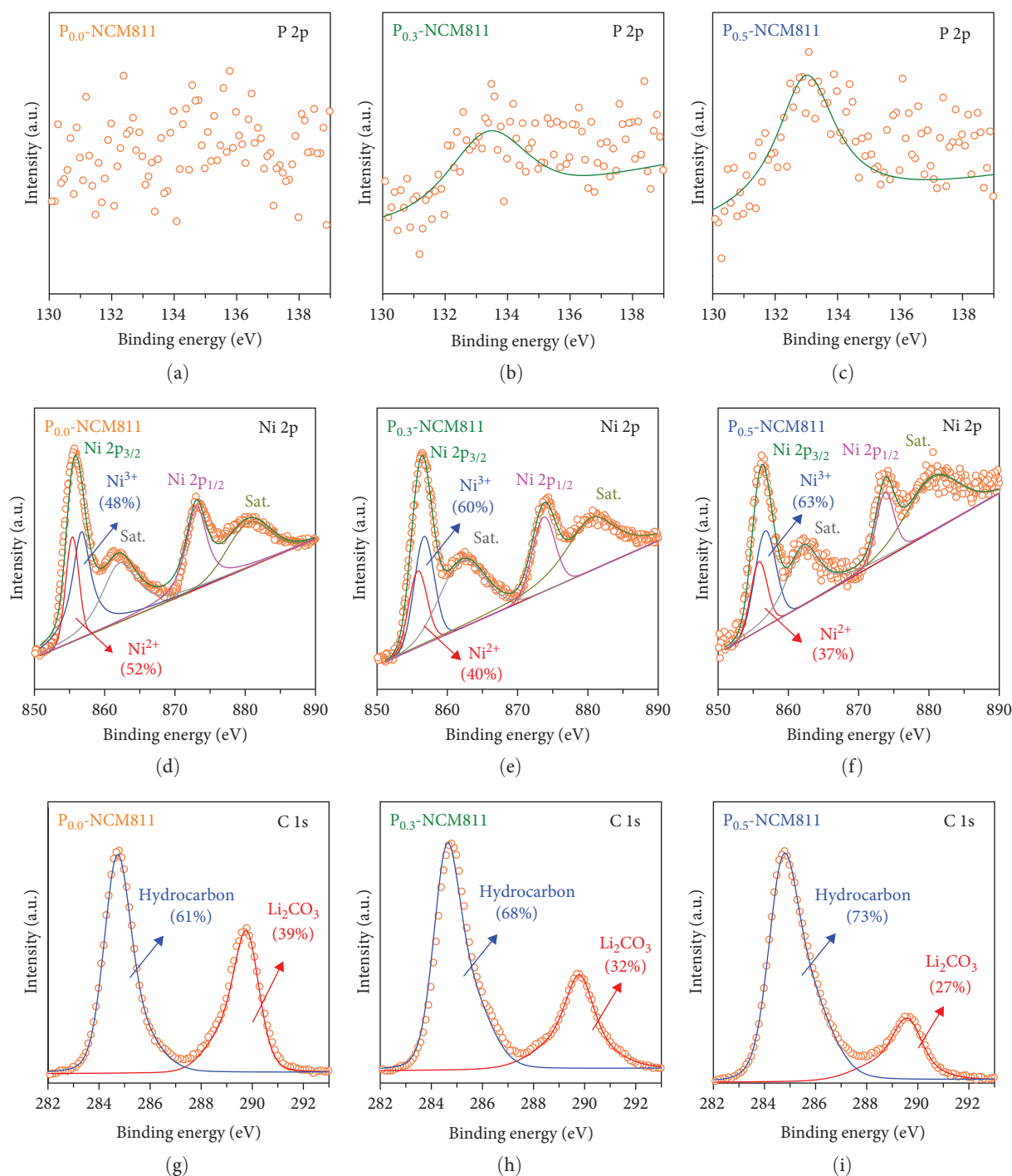


FIGURE 3: XPS P 2p spectra of (a) $P_{0.0}$ -NCM811, (b) $P_{0.3}$ -NCM811, and (c) $P_{0.5}$ -NCM811 cathode materials. XPS Ni 2p spectra of (d) $P_{0.0}$ -NCM811, (e) $P_{0.3}$ -NCM811, and (f) $P_{0.5}$ -NCM811 cathode materials. XPS C 1s spectra of (g) $P_{0.0}$ -NCM811, (h) $P_{0.3}$ -NCM811, and (i) $P_{0.5}$ -NCM811 cathode materials.

properties of P_x -NCM811 cathode materials, EIS measurements were performed after 100 charge/discharge cycles at 1.0 C. The corresponding Nyquist plots are shown in Figure 4h, and the results are summarized in Table S3. The first semicircle in the high-frequency region corresponds to the resistance of the solid electrolyte interphase (SEI) layer (R_{sf}). Among the cathode materials, $P_{0.0}$ -NCM811 exhibited the highest R_{sf} value of $8.10\ \Omega$, whereas $P_{0.3}$ -NCM811 and

$P_{0.5}$ -NCM811, which contain incorporated PO_4^{3-} , displayed significantly lower values of 5.30 and $5.53\ \Omega$, respectively. This reduction in surface resistance is attributed to the formation of a Li_3PO_4 -based surface coating layer, which enhances the surface stability of the cathode particles during prolonged cycling. The second semicircle in the mid-frequency region represents the charge transfer resistance (R_{ct}). $P_{0.0}$ -NCM811 exhibited an R_{ct} of $11.85\ \Omega$, while $P_{0.5}$ -

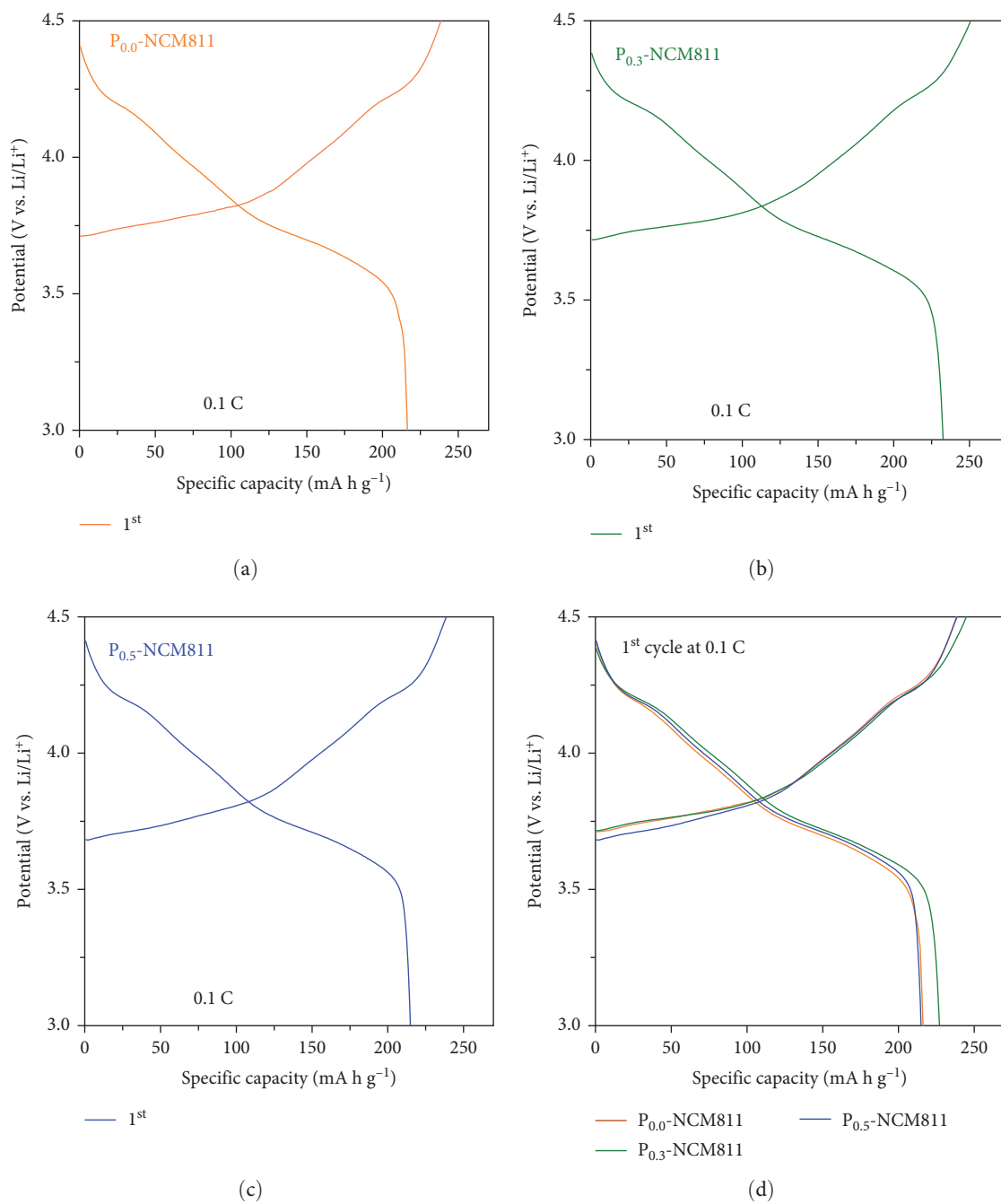


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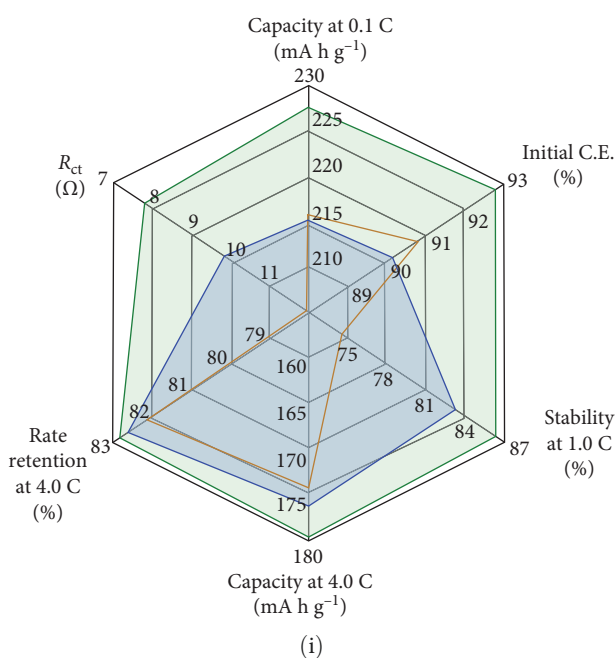
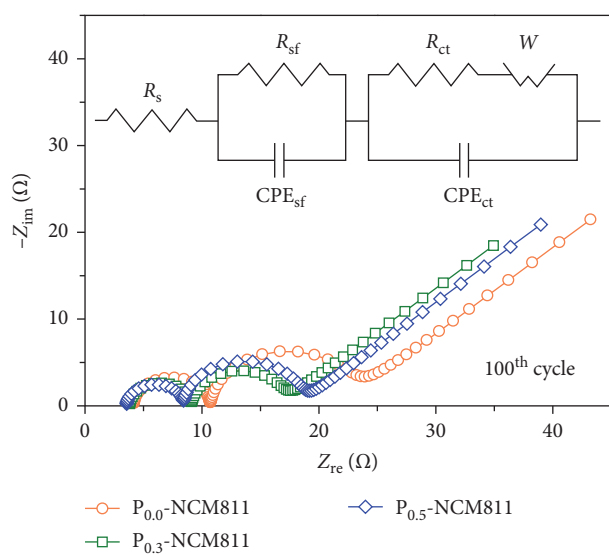
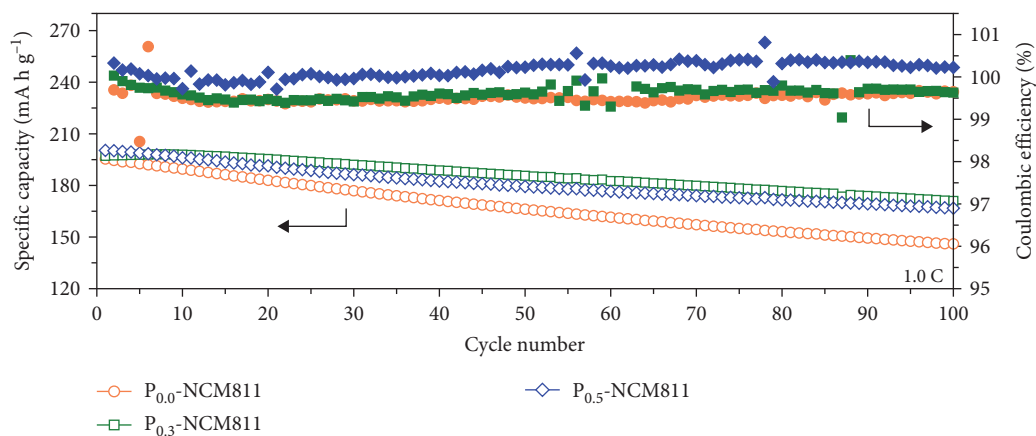
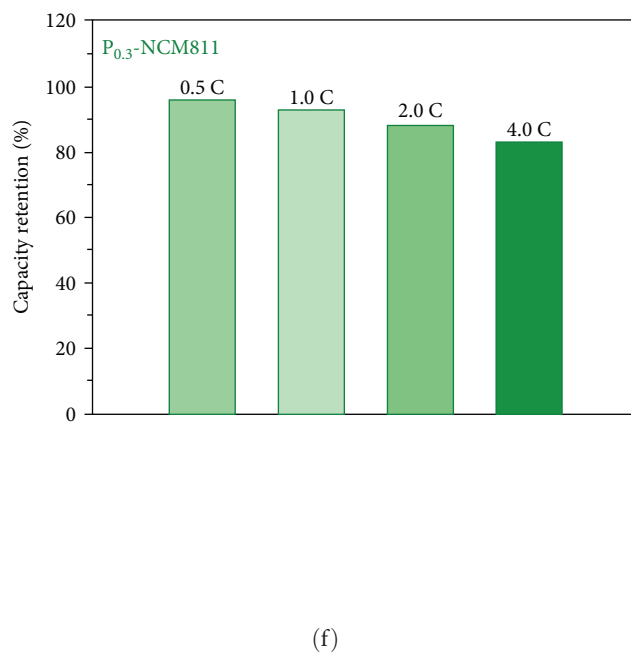
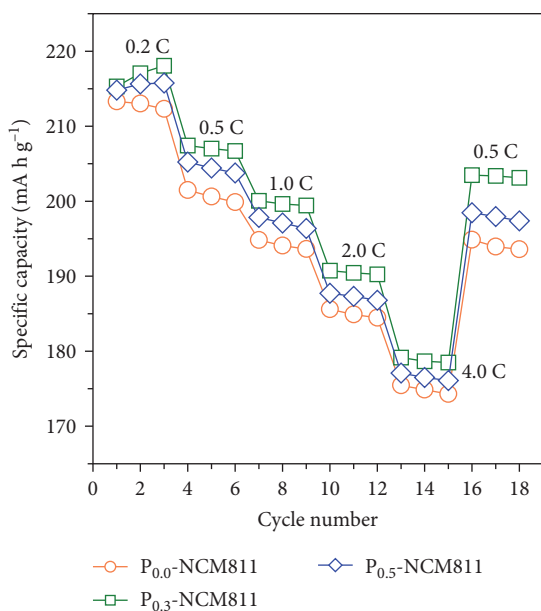


FIGURE 4: Initial galvanostatic charge–discharge curves at 0.1 C for (a) P_{0.0}-NCM811, (b) P_{0.3}-NCM811, and (c) P_{0.5}-NCM811 cathode materials. (d) Comparative analysis of initial charge–discharge curves at 0.1 C for P_x-NCM811 cathode materials. (e) Rate capability

comparison of P_x -NCM811 cathode materials. (f) Capacity retention of $P_{0.3}$ -NCM811 cathode material at various C-rates. (g) Cycling stability of P_x -NCM811 cathode materials at 1.0 C over 100 cycles. (h) Nyquist plots of P_x -NCM811 cathode materials after 100 cycles at 1.0 C. (i) Spider chart summarizing key electrochemical performance metrics.

NCM811 showed a reduced value of $9.86\ \Omega$. Notably, $P_{0.3}$ -NCM811 exhibited the lowest R_{ct} of $7.79\ \Omega$. Since R_{ct} is closely related to the penetration of electrolyte into microcracks and the charge transfer kinetics at the electrode/electrolyte interface, the significantly reduced R_{ct} of $P_{0.3}$ -NCM811 suggests a suppression of microcrack formation and improved interfacial charge transfer, correlating well with its superior long-term cycling performance. Furthermore, the Li^+ diffusion coefficient (D_{Li^+}) was calculated from the low-frequency region of the Nyquist plots. $P_{0.3}$ -NCM811 exhibited the highest diffusion coefficient of $9.84 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$, in comparison to $5.21 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$ for $P_{0.0}$ -NCM811 and $7.12 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$ for $P_{0.5}$ -NCM811. This result confirms that the superior rate capability of $P_{0.3}$ -NCM811 can be attributed to both its reduced interfacial resistance and enhanced Li^+ transport kinetics. As summarized in Figure 4i, the $P_{0.3}$ -NCM811 cathode incorporating an optimal amount of PO_4^{3-} polyanions exhibits the best overall electrochemical performance in terms of initial discharge specific capacity and Coulombic efficiency at 0.1 C, cycling stability at 1.0 C, discharge specific capacity at 4.0 C, rate retention, and R_{ct} .

3.3. Mechanistic Insights Into the Influence of PO_4^{3-} Polyanion Incorporation on the Electrochemical Behavior of P_x -NCM811 Cathode Materials. To elucidate the mechanisms underlying the enhanced electrochemical performance of P_x -NCM811 cathode materials upon PO_4^{3-} polyanion incorporation, a more in-depth comparative analysis was conducted between $P_{0.0}$ -NCM811 (without PO_4^{3-}) and $P_{0.3}$ -NCM811, the composition that exhibited the best capacity, rate capability, and cycling stability. Cross-sectional SEM images of the two cathode materials in the pristine state (before electrochemical cycling) are shown in Figure 5a,b. The $P_{0.0}$ -NCM811 cathode material exhibited noticeable particle fracture and a loosely packed core structure, indicating lower internal density (Figure 5a). In contrast, the $P_{0.3}$ -NCM811 cathode material showed no apparent particle cracking and featured a denser and more compact microstructure throughout the particle cross section (Figure 5b). These observations suggest that PO_4^{3-} incorporation led to a reduction in the size of primary particles, resulting in a more densely packed secondary particle architecture. This compact microstructure is expected to suppress particle degradation and microcrack formation during cycling, contributing to the improved structural stability observed in $P_{0.3}$ -NCM811. Furthermore, such dense particle arrangements can reduce interparticle distances and enhance electronic and ionic conductivity, which likely played a key role in the superior rate performance exhibited by this composition. Taken together, these results provide strong evidence that the incorporation of PO_4^{3-} polyanions not only modifies the bulk lattice structure and surface chemistry of NCM811, but also significantly influences the internal particle architecture—ultimately

enhancing both the mechanical integrity and electrochemical performance of the cathode material.

To further elucidate the impact of PO_4^{3-} polyanion incorporation on the electrochemical behavior of P_x -NCM811 cathode materials, differential capacity (dQ/dV) analysis was performed for $P_{0.0}$ -NCM811 and $P_{0.3}$ -NCM811 at the 25th, 50th, 75th, and 100th cycles during 1.0 C cycling. As shown in Figure 5c,d, layered NCM cathode materials undergo sequential phase transitions during Li^+ insertion and extraction, following a characteristic sequence from the original hexagonal phase (H1) to a monoclinic phase (M), then, to a second hexagonal phase (H2), and finally to a third hexagonal phase (H3) ($\text{H1} \rightarrow \text{M} \rightarrow \text{H2} \rightarrow \text{H3}$) [41]. In Ni-rich NCM systems, the $\text{H2} \rightarrow \text{H3}$ transition occurring around approximately 4.2 V (vs. Li/Li^+) is particularly critical, often associated with severe structural collapse and significant capacity fading. In the case of $P_{0.0}$ -NCM811, the anodic peak corresponding to the $\text{H2} \rightarrow \text{H3}$ transition progressively shifts to higher potentials with cycling, while the current intensity notably decreases (Figure 5c). Concurrently, the corresponding cathodic peak shifts to lower potentials, resulting in a voltage gap of approximately 0.27 V between the anodic and cathodic peaks by the 100th cycle. This increasing polarization is indicative of *c*-axis lattice shrinkage and elevated internal resistance, likely arising from particle cracking and interfacial degradation during repeated cycling. These structural changes may also promote side reactions between the electrolyte and electrode or the formation of electrochemically inactive NiO phases. In contrast, the $P_{0.3}$ -NCM811 cathode exhibited remarkable stability. As shown in Figure 5d, the anodic peak position remained nearly unchanged even after 100 cycles, and the associated current decay was minimal. Moreover, the voltage difference between the anodic and cathodic peaks was significantly smaller, around 0.15 V, indicating reduced polarization. These observations strongly suggest that PO_4^{3-} polyanion incorporation improves the structural reversibility of the phase transitions, particularly mitigating the detrimental effects of the $\text{H2} \rightarrow \text{H3}$ transition. This enhanced phase stability is consistent with the improved cycling performance and reduced impedance observed for $P_{0.3}$ -NCM811, underscoring the effectiveness of polyanion engineering in stabilizing Ni-rich layered cathode materials. Figure 5e schematically illustrates how the enhanced structural stability and electrochemical performance of $P_{0.3}$ -NCM811 cathode material, achieved through the appropriate incorporation of PO_4^{3-} polyanions, arise from their functional effects within the cathode material system.

4. Conclusion

We have demonstrated that strategic incorporation of PO_4^{3-} polyanions into Ni-rich layered $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})$

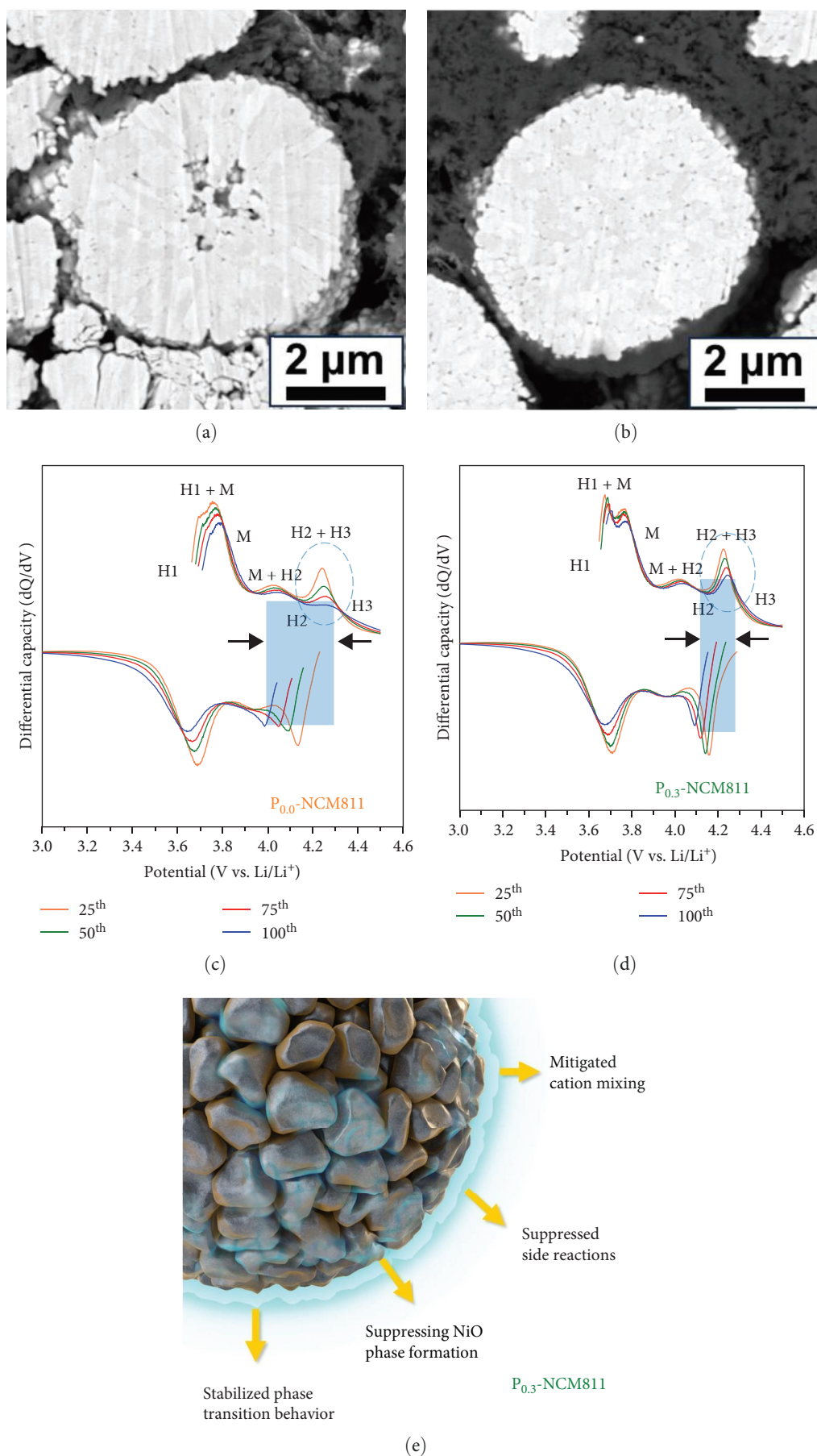


FIGURE 5: Cross-sectional SEM images of (a) $P_{0.0}$ -NCM811 and (b) $P_{0.3}$ -NCM811 cathode materials in the pristine state (before electrochemical cycling). Differential capacity (dQ/dV) plots of the 25th, 50th, 75th, and 100th charge-discharge cycles for (c) $P_{0.0}$ -NCM811 and (d) $P_{0.3}$ -

NCM811 cathode materials. (e) Schematic illustration highlighting the functional effects of PO_4^{3-} polyanion incorporation in $\text{P}_{0.3}$ -NCM811 cathode material.

O_2 significantly enhances the electrochemical performance and structural stability of the resulting cathode materials. The coprecipitation synthesis approach enabled uniform polyanion distribution, resulting in reduced primary particle size, denser microstructure, and suppressed surface degradation. Among the cathode materials studied, $\text{P}_{0.3}$ -NCM811 cathode material exhibited the most balanced and superior performance, delivering high initial discharge specific capacity, excellent rate capability, and long-term cycling stability. Detailed electrochemical and structural analyses revealed that PO_4^{3-} incorporation mitigated cation mixing, reduced interfacial resistances, and improved Li^+ diffusion. Furthermore, the reduced polarization and stabilized phase transition behavior observed in differential capacity analysis confirm the beneficial role of PO_4^{3-} in suppressing structural degradation during extended cycling. Overall, our findings highlight the effectiveness of polyanion-assisted structural and surface engineering in advancing the practical application of high energy Ni-rich layered cathode materials in next-generation LIBs.

Data Availability Statement

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

Conflicts of Interest

The authors declare no conflicts of interest.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. (*Supporting Information*) Figures S1–S5 present SEM images of P_x -NCM811 precursors and cathode materials. Figures S6–S8 provide corresponding EDS elemental maps. Figure S9 reports primary particle size distributions ($n = 100$ per sample). Figure S10 shows high-resolution TEM images highlighting (003) lattice fringes. Figure S11 compares capacity retention and discharge specific capacity at various C rates. Tables S1–S3 summarize lattice parameters, XPS (Ni 2p and C 1s) fitting results, and electrochemical parameters (R_{sf} , R_{ct}) with Li^+ diffusion coefficients (D_{Li^+}).

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