



RESEARCH ARTICLE

Electrode Optimization using Bimodal Sized Particles in Ni-Rich NCM Cathodes for Enhanced Volumetric Energy Density and Cycle Life

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ABSTRACT

High-nickel-layered oxide cathodes have emerged as promising candidates for high-energy lithium-ion batteries, owing to their high capacity and reduced cobalt content. In this study, $\text{LiNi}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}\text{O}_2$ (NCM9334) cathode materials were synthesized through co-precipitation, including a small-particle variant ($\sim 2\ \mu\text{m}$ secondary particles) and a conventional larger-particle variant ($\sim 15\text{--}20\ \mu\text{m}$). The small-particle cathode achieved higher initial discharge capacity ($\approx 209\ \text{mAh}\cdot\text{g}^{-1}$ at 0.1C) compared with the larger-particle cathode ($\approx 190\ \text{mAh}\cdot\text{g}^{-1}$) because of the shorter lithium-ion diffusion pathways. However, small particles exhibited slightly faster capacity fading over 100 cycles (retaining $\sim 76\%$ versus $\sim 78\%$ for large particles). To combine the advantages of both materials, bimodal cathodes were prepared by blending small and large particles in various ratios. An optimal 50:50 bimodal composite achieved a high volumetric discharge capacity of $\sim 306\ \text{mAh}\cdot\text{cc}^{-1}$ at 1C with $\sim 80\%$ capacity retention over 100 cycles. All bimodal electrodes exhibited improved cycle stability compared with single-sized cathodes, with even a 5% small-particle blend yielding $\sim 85\%$ retention. The findings indicate that decreasing the dimensions of secondary particles and implementing a bimodal particle size distribution can markedly improve the performance of Ni-rich cathodes. This approach offers a promising avenue for enhancing the energy density and prolonging the lifespan of lithium-ion batteries utilized in electric vehicles.

Keywords

Lithium-ion batteries, Ni-rich NCM, Particle size effect, Secondary particle size, Cycle performance

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INTRODUCTION

Lithium-ion batteries are distinguished by their high capacity and energy density, which renders them a promising secondary battery system for modern applications [1–3]. The capacity of a lithium-ion cell is determined chiefly by the active cathode material, which is most often a transition metal oxide. It is imperative to note that the cathode must undergo reversible reactions over a wide compositional range while maintaining a flat voltage profile due to the intercalation and deintercalation of numerous Li^+ ions during the process of charge–discharge cycling. Cathode materials must also exhibit high electronic and ionic conductivity, high cycling efficiency, and chemical and electrochemical stability to prevent reactions with the electrolyte or other cell components [4]. The ideal cathode materials are composed of spherical particles with a narrow size distribution, ensuring optimal packing and consistent performance [5].

Among various cathode candidates, layered lithium transition metal oxides in the form of LiMO_2 find wide application in commercial lithium-ion cells. In these layered structures, strong repulsive forces between adjacent O_2 slabs confine Li^+ ion transport to two-dimensional pathways within the crystal lattice. Such nickel cobalt manganese oxide (NCM) cathodes offer high theoretical capacity on the order of 274 mAh g^{-1} . However, extracting more than approximately half of the lithium from the structure causes the rapid collapse of the layered structure. Therefore, the practical capacity at typical cut-off voltages is only approximately 140 mAh g^{-1} [6,7]. Moreover, Ni-rich layered oxides tend to exhibit poor thermal stability and rely on Co, a costly metal whose application is limited by rising prices and supply chain uncertainties. Moreover, the growing demand for electric vehicles, which require batteries with a high power output and long driving range, is propelling the development of cathode materials that can deliver even higher capacities and improved safety [8].

In this study, these challenges were addressed by synthesizing a nickel-rich, cobalt-lean layered oxide with the composition $\text{Li}[\text{Ni}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}]\text{O}_2$. By increasing the content of relatively inexpensive Ni and reducing the Co content, NCM9334 is expected to lower the raw material cost of the cathode [9]. Moreover, this Ni-rich composition can provide higher capacity compared with conventional NCM materials such as NCM622, NCM811, or NCM9055. Notably, this study succeeded in producing NCM9334 in the form of a “small-particle” cathode, with secondary particle diameters of $2 \mu\text{m}$ or less (referred to as NCM-sp). The morphology and characteristics of NCM-sp and its precursor were investigated in detail.

Conventional polycrystalline NCM cathodes (hereafter referred to as NCM-LP, meaning “large-particle”) typically consist of secondary particles larger than $\sim 10 \mu\text{m}$ in diameter. This large particle size results in a long diffusion path for Li^+ ions during intercalation and deintercalation, which may adversely affect the rate of electrochemical reactions and the overall performance [10]. Furthermore, NCM-LP materials undergo substantial volume changes during repeated cycles of charging and discharging, resulting in the formation of microcracks within their primary particles [11]. These microcracks have the potential to exacerbate capacity fading and impedance growth during cycling by exposing new surfaces to side reactions.

Finally, a bimodal particle size strategy was investigated to further enhance performance. By blending the standard NCM9334 material with the proposed small-particle NCM in varying proportions, a cathode with a bimodal particle size distribution was created, increasing the cell’s energy density [11]. In such a bimodal electrode structure, small NCM particles can occupy the void spaces between larger secondary particles, thereby increasing the electrode’s overall packing density. This does not only boost the volumetric energy density but also improves the battery’s power performance and cycle life, because small particles facilitate lithium transport and accommodate strain, an effect that is particularly beneficial for fast-charging cells [12]. In this study, the weight ratio of small to large particles was systematically varied in the mixture, and an optimal blend that maximized the capacity per unit volume of the electrode was identified, demonstrating a promising route to high-energy, high-power lithium-ion batteries.

In this study, two practically attainable particle-size regimes were selected within the same NCM9334 chemistry to contrast transport and packing behaviors: a conventional large secondary particle ($\sim 15\text{--}20 \mu\text{m}$) and an intentionally synthesized small secondary particle ($\leq 2 \mu\text{m}$) (Sections 2.1 and 3.1). Guided by established packing principles for binary mixtures—where fine particles can fill interstices among coarse spheres—the bimodal design was adopted to improve electrode packing and thereby volumetric energy, without introducing additional synthesis variables [13–15].

EXPERIMENTAL

Cathode Material Synthesis

The $\text{LiNi}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}\text{O}_2$ (NCM9334) precursors were synthesized using a coprecipitation method in a continuously stirred tank reactor (CSTR; 5 L). A mixed metal sulfate solution containing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in a molar ratio of Ni:Co:Mn = 93:3:4 was prepared. This solution was pumped into the reactor simultaneously with 29 wt% NH_4OH solution as a chelating agent and 98 wt% NaOH solution as the precipitating base. Constant

reactor temperature was maintained and N_2 gas (99.99% purity) was purged to prevent the oxidation of divalent metal ions during precipitation. The metal hydroxide particles nucleated and grew under controlled stirring and addition rates. After sufficient reaction time, the precipitated spherical particles were filtered, washed repeatedly with deionized water, and dried at 80°C for ≥ 24 h to obtain the hydroxide precursor powder with the composition of $\text{Ni}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}(\text{OH})_2$. By adjusting the precipitation conditions (such as the reactant concentration and stirring rate), two precursor powders with different particle sizes were obtained: a large-particle precursor (NCM-LP precursor) with a secondary particle diameter of $\sim 15\text{--}20\ \mu\text{m}$, and a small-particle (NCM-sp) precursor with a uniform secondary particle diameter of $\leq 2\ \mu\text{m}$. Both precursor types consist of aggregated nanoscale primary particles, forming dense spherical secondary particles. The as-synthesized precursors were converted into the final Li-containing active cathode material using solid-state lithiation. The precursor powder was thoroughly mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ (lithium hydroxide monohydrate) at a Li/metal molar ratio of 1.03:1, providing a slight lithium excess. The mixture was calcined in an O_2 atmosphere at 650°C for 15 h. This relatively low calcination temperature (650°C) is lower than the typical calcination temperature for Ni-rich cathodes (which often require $\geq 700^\circ\text{C}$), but was sufficient to crystallize the layered oxide structure in the materials used in this study. The resulting $\text{Li}[\text{Ni}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}]\text{O}_2$ powders are referred to as NCM-sp (derived from the small precursor) and NCM-LP (derived from the large precursor). To prepare the bimodal cathode materials, the NCM-sp and NCM-LP precursor powders were physically blended in four different weight ratios: 5:95, 15:85, 50:50, and 85:15 (NCM-sp: NCM-LP). Subsequently, each precursor blend was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ (1.03:1 Li/metal ratio) and calcined at 650°C for 15 h in O_2 , analogous to the single-size samples. Active composite materials containing both small and large secondary particles were obtained using this process. The resulting bimodal samples were labeled as s_05, s_15, s_50, and s_85, corresponding to the weight fractions of 5%, 15%, 50%, and 85% of the small-particle component, respectively. Accordingly, the large-particle precursor ($\sim 15\text{--}20\ \mu\text{m}$) represents a conventional Ni-rich morphology from coprecipitation, while the small-particle precursor ($\leq 2\ \mu\text{m}$) was obtained by adjusting precipitation parameters (reactant concentration and stirring rate). These two representative sizes were chosen to establish a bimodal packing framework in the electrode, wherein small particles occupy interstitial voids between large particles to enhance packing/volumetric capacity [13,14].

Electrochemical characterization

Electrodes were fabricated by casting a slurry of the active material, conductive carbon, and polymer binder onto aluminum foil. Each NCM active material (single size or bimodal) was mixed with Super P carbon black (conductive additive) and poly(vinylidene difluoride) (PVdF; binder) at a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). The slurry was stirred thoroughly, and a uniform doctor blade was then coated onto the Al-foil current collectors. The coated sheets were dried at 120°C for 20 min to remove the NMP, and then calendered (roll-pressed) to enhance the electrode density. Disc electrodes with a diameter of 12 mm were punched from the sheets and dried under vacuum at 120°C for 12 h to eliminate the residual moisture. All volumetric capacities ($\text{mAh}\cdot\text{cc}^{-1}$) reported in this study represent electrode-level values, obtained by multiplying the specific discharge capacity ($\text{mAh}\cdot\text{g}^{-1}$) by the measured electrode density ($\text{g}\cdot\text{cc}^{-1}$) of the active layer after roll-pressing. The electrode thickness was measured before and after calendering to calculate the electrode density, and the Al foil current collector was excluded from the volume calculation. Thus, the reported volumetric capacity directly reflects the packing density and porosity of the electrode layer. The electrochemical performance was evaluated in 2032-type coin half-cells using lithium metal as the counter and reference electrodes. The cell assembly was carried out in an Ar-filled glove box (O_2 , H_2O < 1 ppm) to avoid contamination. A microporous polypropylene film (Celgard-type PP) served as the separator, and the electrolyte was 1 M LiPF₆ salt dissolved in a 3:7 (volume ratio) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with standard additives. After assembly, the cells were allowed to rest for approximately 12 h to ensure the thorough wetting of electrodes.

Galvanostatic charge–discharge tests were conducted using a battery cycler (Wonatech WBCS 3000 L). Cells were formed with two initial charge–discharge cycles at 0.1C (where 1C corresponds to $\sim 200\ \text{mA}\cdot\text{g}^{-1}$ for NCM) between 3.0 and 4.3 V versus Li/Li^+ . Thereafter, the cycling performance was measured at the rate of 1C for 100 cycles at 25°C (with charge/discharge voltage limits of 3.0–4.3 V). The rate capability was assessed by discharging the cells at various C-rates (0.1C, 0.2C, 0.5C, 1C, 2C, 5C) while charging at a lower rate (for example, 0.1–0.2C) to ensure full charge before each high-rate discharge. All electrochemical tests were performed at room temperature ($25 \pm 1^\circ\text{C}$).

Characterization of Materials

The morphology and particle size of the cathode powders (precursors and calcined active materials), and the microstructure of fabricated electrodes, were examined using field-emission scanning electron microscopy (FE-SEM; Zeiss Sigma 300). Through this observation technique, images of the secondary particle size and shape were

obtained, which helped verify the dispersion of small and large particles in the bimodal electrodes. The crystalline structure of the calcined cathode materials was analyzed by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.540 \text{ \AA}$). The XRD patterns were collected over $2\theta = 10^\circ - 90^\circ$ at a scan rate of $2.6^\circ \text{ min}^{-1}$. The phase identification and structural ordering were evaluated by examining the splitting of the (006/012) and (108/110) diffraction peaks and Rietveld refinement to extract the lattice parameters. Additionally, differential capacity (dQ/dV) analysis was conducted by differentiating the charge–discharge curves to elucidate the reaction plateaus and phase transitions during cycling.

RESULTS AND DISCUSSION

Morphology and Structure of NCM-sp and NCM-LP

In Fig. 1a–b, the SEM images confirm the distinct particle size distributions for the two synthesized NCM9334 cathode powders. The NCM-LP precursor consisted of approximately spherical secondary particles with a typical diameter of 15–20 μm . These large secondary particles are aggregates of numerous nanosized primary crystallites, resulting in dense polycrystalline morphology. In contrast, the NCM-sp precursor exhibited uniform spherical secondary particles, all of which had a diameter below $\sim 2 \mu\text{m}$. Despite the drastic size reduction, NCM-sp retained a spherical, aggregated morphology consisting of nano-primary particles, similar to NCM-LP. After lithiation and calcination at 650°C , both active material types (NCM-LP and NCM-sp) preserved their precursor morphologies, as shown in Fig. 1c–d, which shows the FE-SEM images of the calcined powders. Both appeared as submicron primary grains fused into spherical secondary particles, indicating that low-temperature calcination did not cause sintering into larger clumps. Notably, the secondary particle size ($\sim 2 \mu\text{m}$) of the synthesized NCM-sp is considerably small, highlighting the success of the synthesis in achieving an extremely fine secondary particle size. As shown in Fig. 1e, Powder XRD analysis revealed that both the NCM-LP and NCM-sp materials crystallize in a layered $\alpha\text{-NaFeO}_2$ type structure (space group R-3m), with no impurity peaks observed. The XRD patterns of the samples shown in Fig. 1f–g exhibit the characteristic splitting of the (006)/(012) doublet around 38° and (108)/(110) doublet around 65° , confirming a well-ordered hexagonal layered structure for both samples [16]. The degree of cation mixing (Ni^{2+} substituting in Li sites) was low for both materials, as indicated by the high intensity ratio $I(003)/I(104) > 1.2$ and the c/a lattice parameter ratio above 4.93, based on the Rietveld refinement results (Table S1) [17]. These metrics suggest that despite the lower calcination temperature, both NCM-sp

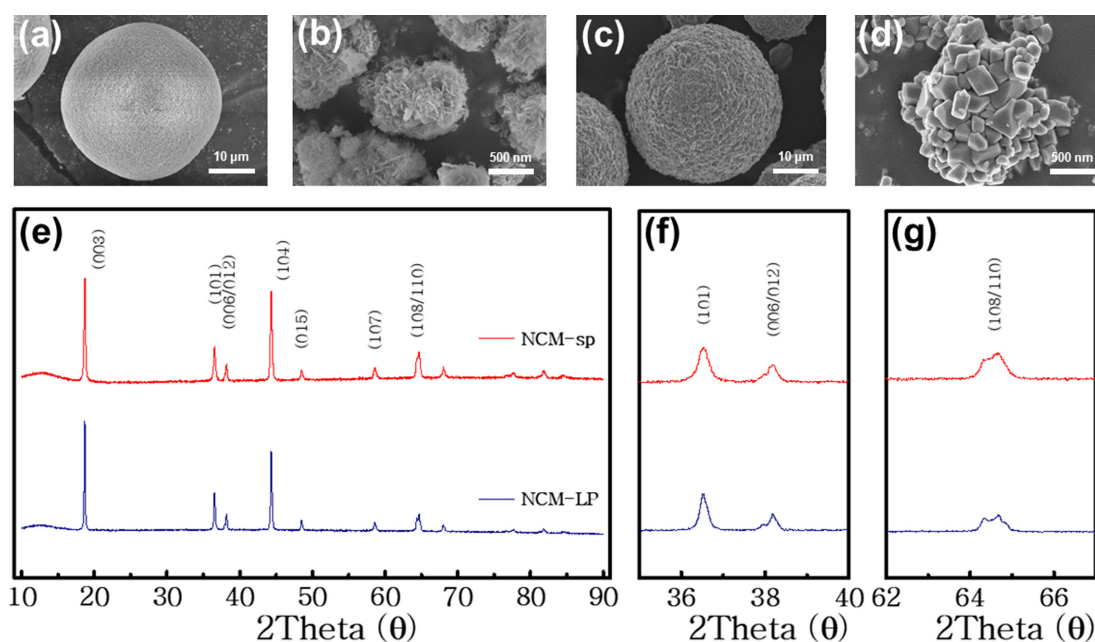


Fig. 1. FE-SEM images of precursor (a) NCM-LP and (b) NCM-sp, and active material (c) NCM-LP and (d) NCM-sp; (e) XRD analysis of both NCM-LP and NCM-sp active material. Magnifications of (f) (006)/(012) and (g) (108)/(110) peaks.

and NCM-LP achieved a well-layered structure with minimal cation disorder, comparable to that of Ni-rich cathodes calcined at higher temperatures. In summary, structural characterization confirmed that NCM-sp was phase-pure and structurally equivalent to the conventional NCM-LP, in addition to having smaller particle size.

Electrochemical Performance: Single-Size Cathodes

The first-cycle charge–discharge curves of NCM-sp and NCM-LP (at the rate of 0.1C, 3.0–4.3 V, 25°C) reveal that NCM-sp delivers higher initial discharge capacity compared with NCM-LP (Fig. 2a and Table S2). Specifically, NCM-sp achieved $\sim 208.7 \text{ mAh}\cdot\text{g}^{-1}$ on the first discharge at 0.1C, whereas NCM-LP achieved $\sim 190.3 \text{ mAh}\cdot\text{g}^{-1}$. This $\sim 10\%$ increase in the capacity of NCM-sp is attributed to its much shorter Li^+ diffusion pathways and larger surface area, which enable more complete lithium extraction/insertion within the voltage window [18]. The charge–discharge curves exhibit typical Ni-rich cathode behavior with a sloping profile and noticeable plateau above 4.0 V, corresponding to the $\text{H2} \rightarrow \text{H3}$ phase change. The NCM-sp curve lies slightly above that of NCM-LP, indicating lower polarization and higher capacity utilization. By the second formation cycle (0.1C), both electrodes stabilized at slightly lower capacity (NCM-sp: $\sim 209 \text{ mAh}\cdot\text{g}^{-1}$; NCM-LP: $\sim 193.5 \text{ mAh}\cdot\text{g}^{-1}$), suggesting good formation without excessive irreversible loss.

Fig. 2b–c and Table S3 compare the 100-cycle performance of NCM-sp and NCM-LP in half-cells at a discharge rate of 1C (25°C). Consistent with the 0.1C results, NCM-sp exhibited higher initial capacity at 1C: $\sim 185 \text{ mAh}\cdot\text{g}^{-1}$ versus $\sim 173 \text{ mAh}\cdot\text{g}^{-1}$ for NCM-LP (measured at the first 1C cycle). This highlights the fact that, even at fast rates, the small-particle cathode can use more of its theoretical capacity, owing to efficient Li-ion transport out of the 2- μm particles. Over 100 cycles at 1C, both electrodes exhibited gradual capacity decay; however, the capacity of NCM-sp faded

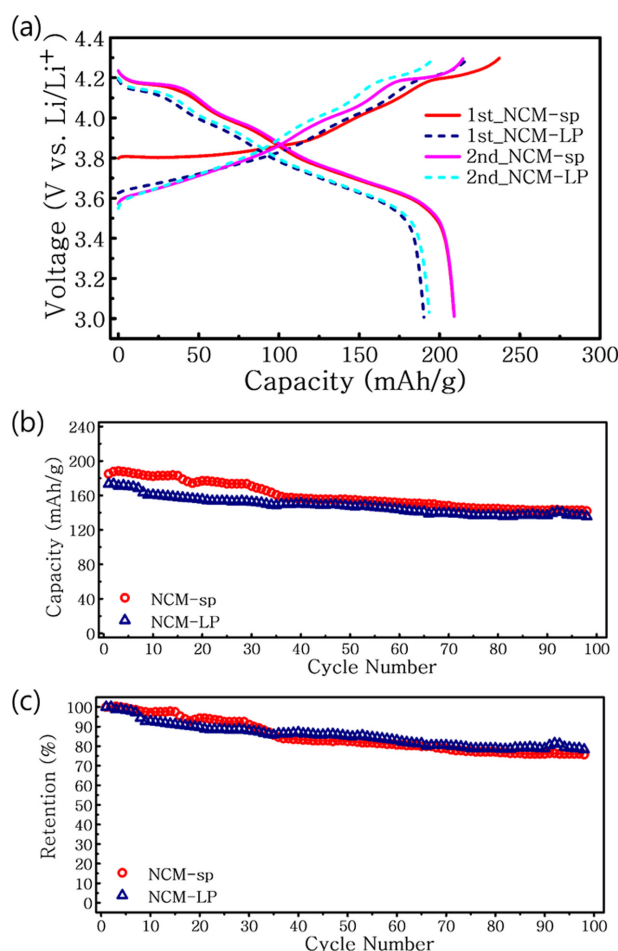


Fig. 2. (a) First-cycle charge–discharge curves of NCM-sp and NCM-LP at 0.1C; (b) capacity versus cycle number and (c) retention versus cycle number graphs at 1C.

slightly faster. After 100 cycles, NCM-sp retained $\sim 142 \text{ mAh}\cdot\text{g}^{-1}$ while NCM-LP retained $\sim 138 \text{ mAh}\cdot\text{g}^{-1}$. In terms of percentage, NCM-sp maintained 75%–76% of its initial capacity after 100 cycles, whereas NCM-LP retained $\sim 78\%$. The slightly higher capacity loss of NCM-sp is attributed to its larger surface area, which can catalyze electrolyte decomposition and parasitic reactions, leading to faster degradation. It is possible that NCM-sp forms a thicker cathode-electrolyte interphase over time and suffers more structural strain per volume, owing to the more extensive Li deintercalation in small grains. This may accelerate capacity fading compared with the inherently more stable, albeit slower, larger NCM-LP particles [19]. Nonetheless, the difference in 100-cycle retention was modest (approximately 2% in absolute terms), indicating that the small-particle approach does not significantly compromise stability. Notably, NCM-sp still achieved a higher absolute capacity compared with NCM-LP after 100 cycles (142 versus $138 \text{ mAh}\cdot\text{g}^{-1}$). This suggests that a small-particle cathode is viable for applications requiring high energy density, particularly if its surface reactivity is managed, such as through coating or electrolyte additives.

The voltage profiles during cycling (Fig. 3 and Table S4) further illustrate the behavior of each cathode. Both NCM-sp and NCM-LP exhibited a gradual decrease in the discharge voltage and capacity as the cycle number increased, but the voltage drop of NCM-sp was only slightly more pronounced. By the 80th cycle at 1C, the discharge capacity of NCM-sp had declined to $\sim 144 \text{ mAh}\cdot\text{g}^{-1}$, while that of NCM-LP was $\sim 136 \text{ mAh}\cdot\text{g}^{-1}$. The retention of high-voltage capacity is critical for energy density. Both electrodes exhibited certain reduction in the high-voltage plateau over time owing to the well-known degradation related to the $\text{H2} \rightarrow \text{H3}$ phase in Ni-rich materials.

The advantage of the smaller particle size of NCM-sp became particularly evident at high charge–discharge rates. Fig. 4a compares the discharge capacity of NCM-sp and NCM-LP at increasing C-rates (0.1C up to 5C). At low rates (0.1–0.2C), both materials approach their theoretical maximum, with NCM-sp exhibiting a slightly higher value. As the rate increased, NCM-sp retained a much larger fraction of its capacity compared with NCM-LP. For example, at 5C (a very high rate corresponding to full discharge in $\sim 12 \text{ min}$), NCM-sp retained substantial capacity, whereas the capacity of NCM-LP exhibited a sharp decline. This difference stems from the diffusion length: in the NCM-LP particles ($\sim 20 \mu\text{m}$), lithium must diffuse from deep within the particle, and during short, high-current discharges, it cannot fully reach the surface, limiting the accessible capacity [20]. In contrast, in NCM-sp ($\sim 2 \mu\text{m}$ particles), even the lithium at the particle center must only travel $\sim 1 \mu\text{m}$ to reach the surface; therefore, most Li^+ can participate in fast discharge. Therefore, NCM-sp exhibits superior power capability, making it more suitable to high-power or fast-charging applications.

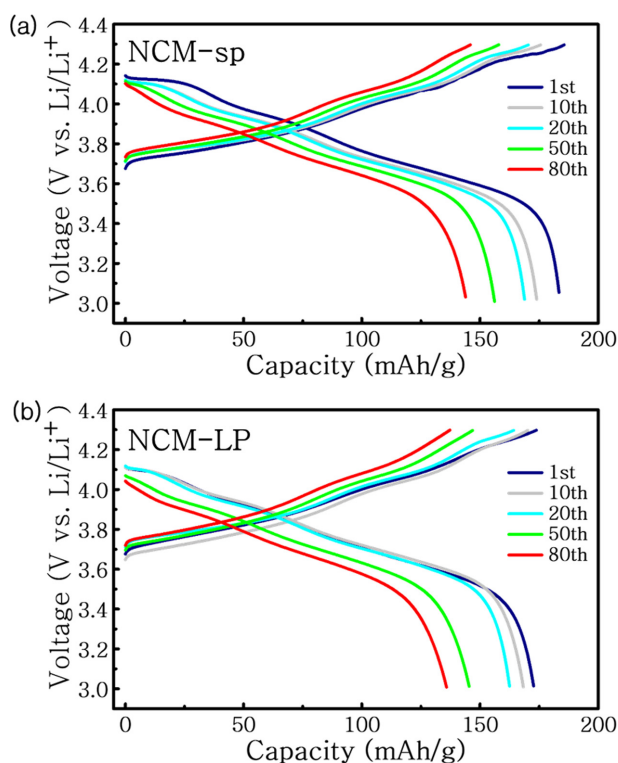


Fig. 3. Voltage–capacity profiles at 1C: (a) NCM-sp and (b) NCM-LP at 1st, 10th, 20th, 50th, and 80th cycles.

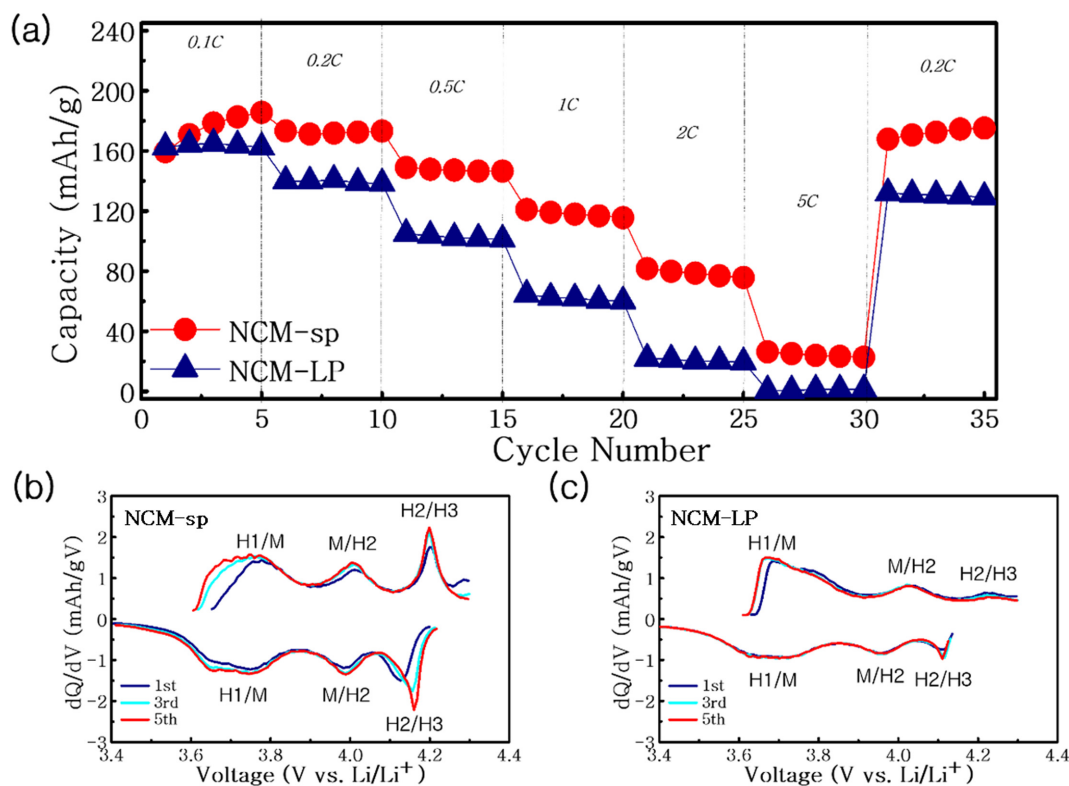


Fig. 4. (a) Rate capability of NCM-sp and NCM-LP from 0.1C to 5C; differential capacity (dQ/dV) plot of (b) NCM-sp and (c) NCM-LP.

The differential capacity (dQ/dV) plots (Fig. 4b–c) for the initial cycles provide further insights. Specifically, NCM-sp exhibits sharper and more intense redox peaks compared with NCM-LP at the same number of cycles. The higher peak intensity indicates more facile and complete phase transitions (for example, $Ni^{2+/3+/4+}$ redox) in the small particle cathode, consistent with its higher capacity delivery [21]. Particularly, the peaks associated with the main Ni^{2+}/Ni^{4+} oxidation–reduction couple were more pronounced for NCM-sp, reflecting better utilization of the active material during the charge–discharge process [22].

In summary, the results for the single-size cathode reveal that downsizing the secondary particle to $\sim 2\ \mu\text{m}$ significantly boosts the initial capacity and rate performance, at the cost of a slightly accelerated capacity fade. This tradeoff motivated the investigation of bimodal cathodes, with the objective of capturing the benefits of both particle sizes.

Bimodal Cathode Performance (Mixing Small and Large Particles)

For reference, the large-particle-only electrode discussed in Section 3.2 (NCM-LP) corresponds to the 0% small-particle (s_{00}) composition and serves as the baseline for all bimodal comparisons. Therefore, the subsequent data sets (s_{05} , s_{15} , s_{50} , and s_{85}) represent incremental additions of the small-particle component relative to this baseline.

The SEM examination of the bimodal electrodes (s_{05} , s_{15} , s_{50} , and s_{85}) confirmed that the small and large NCM9334 particles were uniformly distributed throughout the electrode, with evenly mixed conductive carbon and binder (Fig. 5). For example, in the s_{50} electrode (50% small and 50% large by weight), the $\sim 2\ \mu\text{m}$ NCM-sp particles were visibly nestled in the interstitial spaces between the $\sim 15\ \mu\text{m}$ NCM-LP particles. This efficient packing arrangement confirms that small particles are able to occupy voids between larger particles, thereby increasing the overall tap density of the electrode [15]. Electrodes with higher fractions of small particles appeared to be more densely packed. However, extremely high fractions of small particles (such as s_{85} with 85% small particles) also led to the agglomeration of fine particles and potentially less efficient conductive network percolation through large particles.

All four bimodal compositions maintained a layered crystal structure with no detectable secondary phases, as revealed by XRD (Fig. 6a–c). Specifically, their structure closely resembled the superposition of the patterns of pure NCM-sp and NCM-LP. Rietveld analysis (Table S5) revealed that all bimodal samples had $c/a > 4.9$ and $I(003)/I(104) > 1.2$, similar to the single-compo-

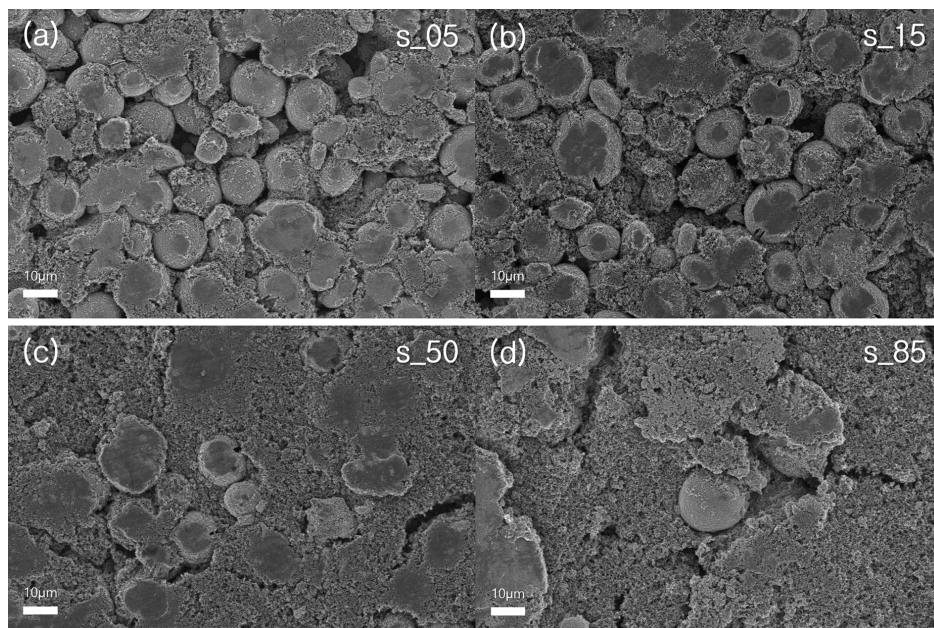


Fig. 5. SEM images of bimodal electrodes: (a) s_05, (b) s_15, (c) s_50, and (d) s_85.

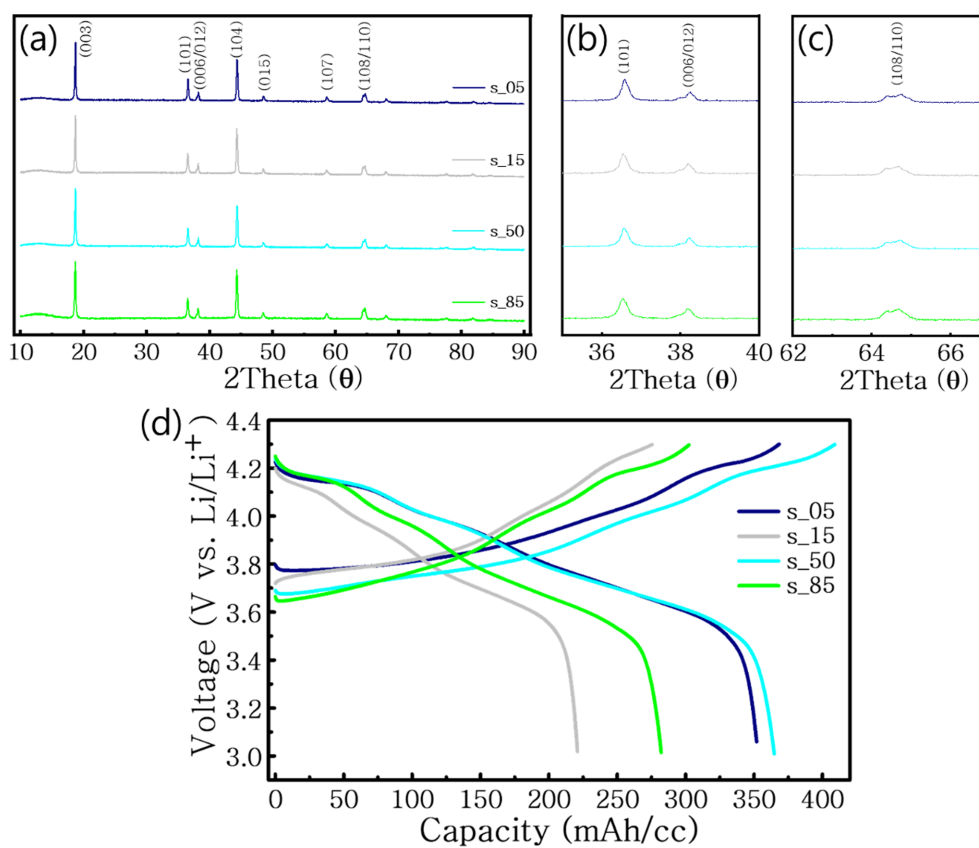


Fig. 6. (a) XRD patterns of bimodal electrodes over 10°–90° 2θ range; (b) (101), (006)/(012) and (c) (108)/(110) reflections; (d) initial voltage–capacity profiles of bimodal electrodes (capacity in mAh·cc⁻¹).

nent powders, suggesting that mixing and co-calcination did not degrade structural ordering [23].

The primary motivation for using bimodal cathodes is to enhance their volumetric energy density. To assess this, the discharge capacity per unit volume of electrode ($\text{mAh}\cdot\text{cc}^{-1}$) was measured for each composition, including the initial capacities at a low rate of 0.1C (Fig. 6d and Table S6). At a low rate (0.1C, first cycle), all bimodal electrodes delivered substantially higher volumetric capacities compared with the single-size electrodes, owing to improved packing. For example, s_50 (50% small) yielded $\sim 364.7 \text{ mAh}\cdot\text{cc}^{-1}$ on the first discharge at 0.1C, compared with $\sim 282.1 \text{ mAh}\cdot\text{cc}^{-1}$ for s_85 and $\sim 275.4 \text{ mAh}\cdot\text{cc}^{-1}$ for s_15. Even the s_05 (5% small) electrode, which is dominated by large particles, exhibited $\sim 351.9 \text{ mAh}\cdot\text{cc}^{-1}$ initially, which is significantly higher than what a pure NCM-LP electrode can achieve (because pure NCM-LP is essentially s_00, presumably with more void space). These results confirm that introducing a minor fraction of small particles dramatically increases the electrode's volumetric capacity by filling the voids. Among the tested ratios, the s_50 composition exhibited the highest initial volumetric energy delivery ($\sim 365 \text{ mAh}\cdot\text{cc}^{-1}$ at 0.1C), indicating optimal packing efficiency when small and large particles are balanced in equal proportion. A similar trend

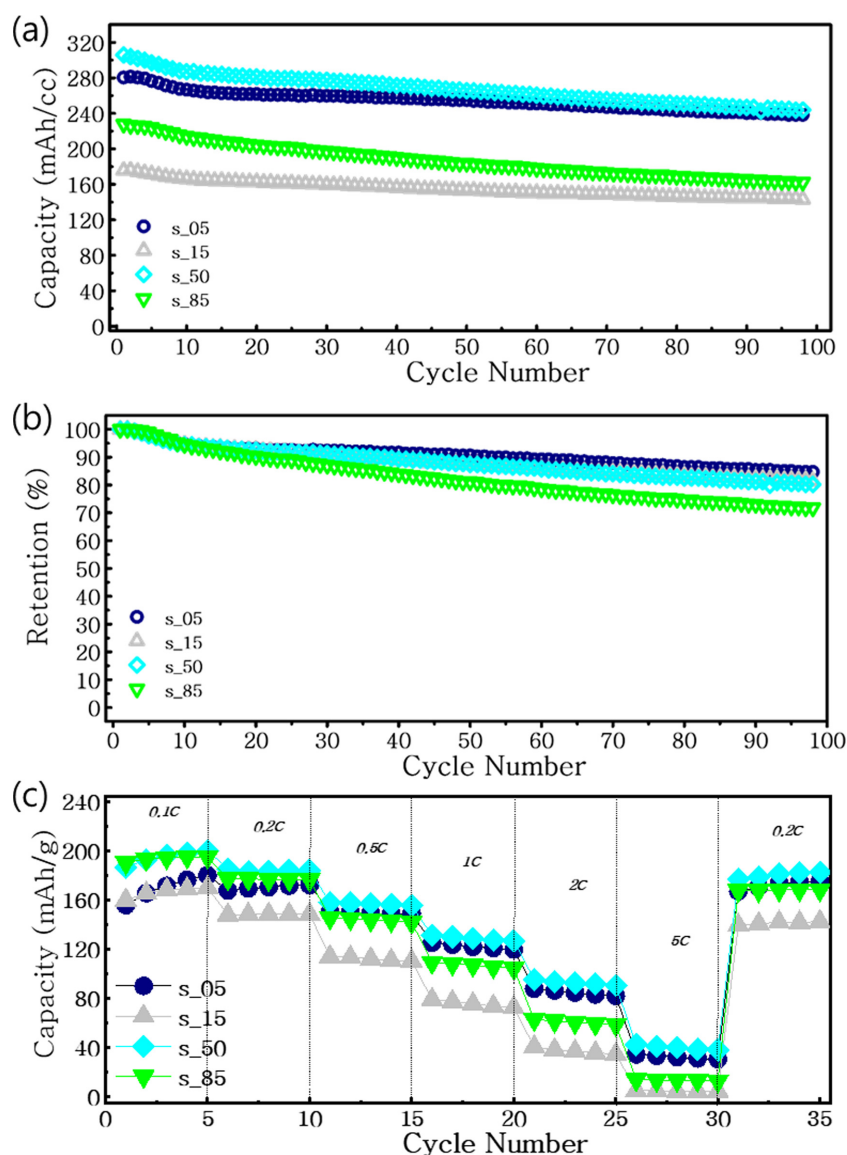


Fig. 7. (a) Capacity–cycle number graph ($\text{mAh}\cdot\text{cc}^{-1}$); (b) retention–cycle number graph of bimodal electrodes; (c) C-rate performance of bimodal electrodes.

was observed at the practical 1C rate. The initial 1C discharge capacity (volumetric) for s_50 was $\sim 305.9 \text{ mAh}\cdot\text{cc}^{-1}$, the highest in the group. The s_05 electrode also performed well at 1C, with an initial value of $\sim 280.4 \text{ mAh}\cdot\text{cc}^{-1}$, whereas s_85 and s_15 exhibited lower values (~ 227.8 and $\sim 175.7 \text{ mAh}\cdot\text{cc}^{-1}$, respectively) owing to their less optimal packing or electronic connectivity. Thus, a 50% small + 50% large blend achieved the optimal balance of high initial capacity and dense packing, outperforming even the predominantly small s_85 in volumetric terms. This is likely because s_85, despite its abundance of small particles, may have a less effective conductive network or require more binder to wet the high surface area [24].

All bimodal electrodes exhibited improved cycle stability relative to the pure small-particle cathode, and some even rivaled or exceeded the pure large-particle cathode in terms of retention. After 100 cycles at 1C (25°C), the capacity retention was $\sim 84.7\%$ for s_05, $\sim 81.5\%$ for s_15, $\sim 80.2\%$ for s_50, and $\sim 75.7\%$ for s_85 (Fig. 7a–b and Table S7). Notably, even the worst performer among them (s_85) retained $\sim 75.7\%$ after 100 cycles, which is consistent with the retention of pure NCM-sp ($\sim 75\%$ – 76%). The best cycling durability was observed for the s_05 electrode (only 5% small particles), retaining 84.7% after 100 cycles, which is significantly higher than that of either NCM-sp or NCM-LP alone ($\sim 78\%$ maximum). This suggests that incorporating only a small fraction of fine particles can improve long-term stability, possibly by filling gaps and maintaining better contact between the active material and the conductive matrix as the electrode expands/contracts during cycling. However, as the fraction of small particles increased, the cycle retention tended to decrease (s_85 had the lowest retention), indicating that an excessively high surface area exacerbates side reactions despite the packing benefits. The s_50 electrode, which had a slightly lower retention ($\sim 80\%$) compared with the s_05 electrode still exhibited good stability with the highest capacity. All bimodal compositions exhibited a higher retained volumetric capacity after 100 cycles compared with the pure NCM-LP electrode, owing to their initial high loading.

The bimodal electrodes exhibited excellent rate capabilities (Fig. 7c). Even those with a high small-particle content (s_85) maintained better high-rate performance compared with the pure large-particle cathode, owing to the presence of short diffusion pathways through small particles [18]. Moreover, those with predominantly large particles (s_05) still benefited from the small amount of NCM-sp, slightly boosting rate performance compared with pure NCM-LP. Thus, the bimodal approach can be tuned to achieve the desired balance between power and energy density.

Differential voltage analysis provided insights into the mechanistic advantages of bimodal design. The dQ/dV plots (Fig. 8) for the first cycle reveal that s_05 had the highest peak intensity among the four mixes, indicating very effective capacity utilization, nearly as good as that of pure NCM-sp, despite having mostly large particles. Over 80 cycles, the decline in the dQ/dV peak corresponding to the H2 $\rightarrow$ H3 transition was more gradual in the bimodal electrodes compared with that in single-size electrodes. Particularly, the pure NCM-sp and NCM-LP cathodes exhibited sharper reduction in the high-voltage peak intensity (which is linked to capacity loss at a high state of charge) compared with

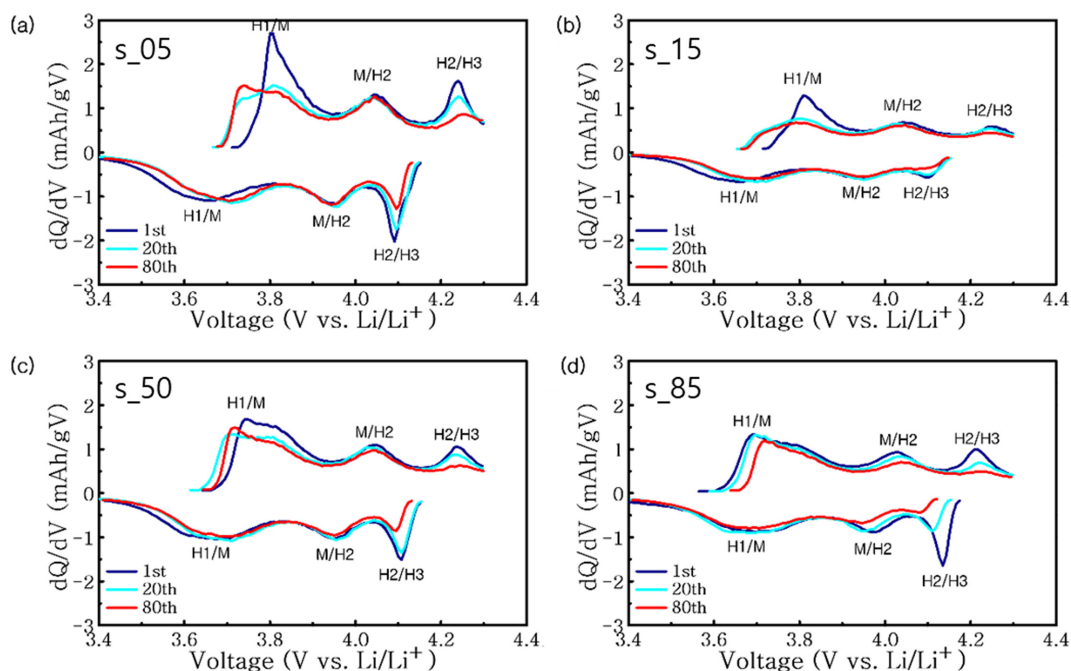


Fig. 8. Differential capacity (dQ/dV) curves of bimodal electrodes: (a) s_05, (b) s_15, (c) s_50, and (d) s_85.

the bimodal blends. This suggests that mixing particle sizes can mitigate the structural degradation associated with the H2 → H3 phase transition, possibly by alleviating localized stress and preventing continuous crack propagation. Among the bimodal samples, s_85 (highest small-particle content) exhibited the largest increase in peak separation (ΔV between charge/discharge peaks) over cycling, implying increasing polarization owing to its higher surface-driven reactivity. In contrast, s_05 maintained the lowest polarization growth, consistent with its superior capacity retention. These trends reinforce the idea that incorporating a moderate fraction of small particles (5%–50%) is beneficial, whereas an excessively small fraction can reintroduce instability.

In summary, bimodal cathodes can achieve high volumetric energy with sustained cycle life. Among the tested compositions, s_50 most closely approached the optimal trade-off, delivering the highest energy per volume with acceptable longevity. Moreover, even a small number of fine particles (s_05) significantly improved cycle stability and increased the volumetric capacity over the baseline. The results of this study clearly demonstrate that a bimodal particle size distribution in Ni-rich cathodes can outperform the single-particle-size approach by synergistically combining the merits of both small and large particles.

CONCLUSION

In this study, a high-Ni-layered cathode material, $\text{LiNi}_{0.93}\text{Co}_{0.03}\text{Mn}_{0.04}\text{O}_2$ (NCM9334), was successfully synthesized through co-precipitation and low-temperature calcination, and the effects of particle size on performance were elucidated. A small-particle NCM9334 cathode with a secondary particle size $\leq 2 \mu\text{m}$, which is significantly smaller than that in conventional Ni-rich cathode particles, was developed. The NCM-sp material exhibited a well-ordered layered structure and achieved higher initial capacity and better high-rate capability compared with a standard $\sim 15\text{-}\mu\text{m}$ particle NCM9334 cathode (NCM-LP). The short Li-ion diffusion distances in NCM-sp enabled superior discharge capacity and power performance. However, NCM-SP demonstrated slightly accelerated capacity degradation during prolonged cycling in comparison with NCM-LP, likely attributable to its augmented surface area and facilitated side reactions. Notwithstanding, the small-particle cathode exhibited a capacity retention of approximately 76% after 100 cycles at 1C, which approaches 78% of that observed for the large-particle cathode. These findings suggest that high-Ni small-polycrystalline cathodes could serve as a viable substitute for Ni-rich single-crystal cathodes, providing enhanced capacity without compromising stability to an unacceptable extent. Furthermore, by blending small and large particles, bimodal cathodes were fabricated, delivering even greater overall performance than either particle type alone. Bimodal electrodes exploit the ability of small particles to fill the interstitial voids among large particles, improving the packing density and sustaining the electrode's structural integrity. Among the tested compositions, the 50% small + 50% large (s_50) electrode delivered the highest volumetric capacity ($\sim 305\text{--}365 \text{ mAh}\cdot\text{cc}^{-1}$) and still maintained $\sim 80\%$ capacity after 100 cycles. Notably, all bimodal configurations exhibited $\geq 75\%$ retention after 100 cycles, outperforming the pure small-particle cathode in terms of longevity. The presence of even a small fraction of fine particles (for example, s_05) improved the cycle life to $\sim 85\%$ retention, presumably by enhancing electronic connectivity and reducing the mechanical strain in the electrode. Rate testing confirmed that bimodal electrodes can deliver high power because small particles facilitate rapid lithium transport, whereas large particles ensure robust network formation. A comprehensive analysis, encompassing SEM, XRD, and electrochemical methods, was employed to elucidate the findings of this study. The results indicate that particle size engineering serves as a potent strategy to optimize the performance of Ni-rich cathodes. The utilization of NCM9334, a material characterized by its small-particle size, enables the attainment of elevated energy output, thereby satisfying the demands associated with high-power applications. The incorporation of a bimodal particle size distribution within the material configuration facilitates the optimization of volumetric energy density and cycle life, surpassing the capabilities of materials with a single-sized composition. These findings signify substantial progress in meeting the rigorous performance criteria of next-generation lithium-ion batteries for electric vehicles and other energy storage applications. The utilization of a bimodal cathode architecture is a strategy that can be applied to a variety of battery systems, particularly those that necessitate a balance between energy density and stability.

CRedit AUTHORSHIP CONTRIBUTION STATEMENT

So-yeon Kim: Conceptualization, Formal analysis, Investigation, Visualization, Writing – original draft. **Junyeob Lim:** Investigation, Data curation, Conceptualization. **Dong Chul Kang:** Investigation, Data curation. **Sangwon Nam:** Investigation, Data curation. **Jaegyun Heo:** Investigation, Data curation. **Tae-jun Koh:** Investigation, Data curation. **Hyun Chul Kang:** Data curation. **Sung-Gyu Pyo:** Writing – Review and editing. **Songhun Yoon:** Writing – Review and editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this paper.

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APPENDIX A. SUPPORTING INFORMATION

Supplementary data associated with this study can be found in the online version of this paper: [<https://doi.org/10.33961/jecst.2025.00843>].

Data availability

Data are available upon reasonable request.

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