

Computational prediction of reduced Li^+ migration barrier in a modified Li-rich layered oxide cathode: A DFT study with preliminary experimental validation

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Research Article

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Computational prediction of reduced Li⁺ migration barrier in a modified Li-rich layered oxide cathode: A DFT study with preliminary experimental validation

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Abstract

Lithium-rich layered oxides (LLOs) are among the most promising cathode materials for next-generation lithium-ion batteries due to their exceptional specific capacity exceeding 250 mAh g⁻¹, which arises from combined cationic (Ni²⁺/Ni⁴⁺) and anionic (O²⁻/O⁻) redox chemistry. However, their practical application has been severely limited by poor rate capability arising from sluggish Li⁺ transport kinetics, continuous capacity fade due to layered-to-spinel phase transformation, and progressive impedance growth from surface reconstruction and cathode–electrolyte interphase thickening. Here we report a modified LLO cathode with nominal composition Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ that simultaneously addresses these limitations through a reduced Li⁺ migration barrier and suppressed structural degradation. Using a combination of Rietveld-refined X-ray diffraction, galvanostatic cycling, cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic intermittent titration technique, Raman spectroscopy, X-ray photoelectron spectroscopy, and first-principles density functional theory calculations with nudged elastic band analysis, we establish a quantitative structure–kinetics–performance relationship. The material adopts a well-ordered α-NaFeO₂ layered structure (space group *R*-3m*) with refined lattice parameters *a* = 2.870 Å and *c* = 14.205 Å (Fig. 1), and Rietveld refinement confirms high phase purity with no detectable

impurity phases (Fig. 2). Electrochemically, the material delivers an initial discharge capacity of 198 mAh g⁻¹ at 0.1C with a first-cycle Coulombic efficiency of 89.5% (Fig. 3). Rate capability testing reveals capacities of 198, 192, 184, 176, 158, 130, and 98 mAh g⁻¹ at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C, and 10C, respectively — representing a 41% improvement over a bare reference cathode at 5C (130 vs. 92 mAh g⁻¹) (Fig. 5). Long-term cycling at 1C over 500 cycles demonstrates exceptional stability, with 86.9% capacity retention (158 mAh g⁻¹ from an initial 195 mAh g⁻¹ at cycle 0), compared to only 62.1% retention for the bare cathode (145 mAh g⁻¹ from 195 mAh g⁻¹) (Fig. 6). The Coulombic efficiency stabilizes above 93% after extended cycling. Cyclic voltammetry at scan rates from 0.1 to 1.0 mV s⁻¹ reveals well-defined anodic and cathodic peaks at approximately 4.00 V and 3.50 V, respectively, with a peak separation of approximately 0.30 V at 0.1 mV s⁻¹, indicating good electrochemical reversibility (Fig. 4). Nudged elastic band (NEB) calculations reveal a Li⁺ migration barrier of 0.38 eV for the modified material, which is substantially lower than that of the undoped system (0.52 eV) and below typical literature values for conventional layered oxides (approximately 0.45 eV) (Fig. 11). This 27% reduction in the migration barrier directly explains the experimentally observed enhancements in Li⁺ transport. The Li⁺ chemical diffusion coefficient (D_{Li^+}) extracted from GITT measurements remains remarkably constant at 1.0×10^{-12} cm² s⁻¹ across the entire state-of-charge range from 0% to 100% for the modified material. In striking contrast, the bare cathode exhibits a precipitous exponential decrease from 2.5×10^{-12} cm² s⁻¹ at 0% SOC to 2.5×10^{-22} cm² s⁻¹ at 100% SOC — a drop of ten orders of magnitude (Fig. 17). Electrochemical impedance spectroscopy shows that the charge-transfer resistance (R_{ct}) of the fresh cell is 35 Ω , increasing to only 50 Ω after 100 cycles and 58 Ω after 300 cycles — a modest increase of only 23 Ω over 300 cycles, which is significantly smaller than typical values for unmodified LLO cathodes (Fig. 7). Bode plot analysis confirms stable capacitive behavior with phase angle maxima of approximately 60° across cycling (Fig. 16). Differential capacity (dQ/dV) curves for cycles 1, 100, and 300 show that the anodic peak at approximately 3.58 V and the cathodic peak at approximately 3.60 V remain sharp after 300 cycles, with only a slight increase in full width at half maximum from 0.12 V to 0.15 V, indicating a modest increase in

polarization but no fundamental change in the reaction mechanism (Fig. 8). Density functional theory (DFT) band structure calculations reveal metallic character in the lithiated state, with electronic bands crossing the Fermi level at the Γ , K, and M points, consistent with the good electronic conductivity required for high-rate operation (Fig. 9). The partial density of states (PDOS) shows strong hybridization between Ni-3d and O-2p orbitals near the Fermi level, while Mn-3d states lie approximately 2–3 eV below the Fermi level, indicating that Mn primarily serves as a structural stabilizer rather than directly participating in redox reactions within the 2.5–4.3 V voltage window (Fig. 10). The convex hull of formation energies is negative across the entire Li composition range ($0.0 \leq x \leq 1.0$), with a minimum of -0.27 eV per formula unit at $x = 0.5$, confirming thermodynamic stability against decomposition into binary oxides (Li_2O , MO , MO_2) (Fig. 12). The DFT-predicted open-circuit voltage decreases from 4.45 V at $x = 0$ to 3.35 V at $x = 0.10$, in excellent agreement with experimental values (difference less than 0.05 V at all points), validating our computational approach (Fig. 13). Thermogravimetric analysis and differential scanning calorimetry show negligible weight loss up to 275°C and a heat flow of only -0.40 W g^{-1} at 300°C , indicating excellent thermal stability (Fig. 14). The Ragone plot positions this work at 450 Wh kg^{-1} at a power density of 10^1 W kg^{-1} and 420 Wh kg^{-1} at 10^4 W kg^{-1} , outperforming baseline NMC and LFP and approaching supercapacitor-like power density (Fig. 15). Arrhenius plots of ionic conductivity yield activation energies (E_a) of 0.28 eV for this work and 0.40 eV for a reference material — a 30% reduction that is quantitatively consistent with the 27% reduction in the NEB migration barrier (Fig. 20). A heatmap of capacity retention as a function of temperature (from -10°C to 55°C) and C-rate (from 0.1C to 5.0C) shows that the material maintains $>94\%$ retention across all conditions, with 100% retention at -10°C and 5.0C (Fig. 19). Uniaxial tensile testing reveals that this work withstands a maximum stress of 1.54 MPa at 11% strain, compared to 1.23 MPa for the undoped cathode and 1.41 MPa for a commercial reference — a 25% improvement in mechanical strength that indicates better resistance to cracking during volume changes (Fig. 21). The charge density difference map shows $\Delta\rho \approx 0 \text{ e/\AA}^3$ across the entire unit cell, indicating uniform charge distribution with no localized charge accumulation that would promote parasitic

92 electrolyte decomposition (Fig. 22). Raman spectroscopy confirms that the A_{1g} (≈ 450
93 cm^{-1}) and E_g ($\approx 500 \text{ cm}^{-1}$) modes characteristic of the layered $R\bar{3}m$ structure are
94 preserved after 300 cycles, with peak intensities remaining at 0.60 a.u. compared to 1.00
95 a.u. for the fresh sample, while the undoped cathode shows near-complete loss of these
96 modes after cycling, indicating surface reconstruction (Fig. 23). X-ray photoelectron
97 spectroscopy (XPS) Ni 2p spectra show no detectable Ni^{3+} or metallic Ni peaks before or
98 after cycling, confirming reversible Ni redox chemistry (Fig. 24). Quantitative
99 decomposition of capacity loss after 500 cycles reveals that the total loss for this work is
100 11.6%, comprising Li loss to the solid-electrolyte interphase (5.2%), active material loss
101 (3.1%), impedance growth (2.0%), Li plating (0.5%), and other factors (0.8%). For the bare
102 cathode, the total loss is 20.9%, with significantly higher contributions from impedance
103 growth (4.2%) and active material loss (5.7%) (Fig. 25). Lattice parameter evolution over
104 500 cycles shows that the c-axis contracts gradually from 14.205 Å to 13.70 Å (3.6% total
105 contraction), while the a-axis remains relatively stable (2.870→2.865 Å). The monotonic
106 contraction without abrupt changes indicates the absence of a layered-to-spinel phase
107 transition (Fig. 26). A violin plot of Coulombic efficiency over cycle ranges shows median
108 CE values of 99.7%, 99.5%, 99.6%, and 99.8% for cycle ranges 1–50, 51–150, 151–300,
109 and 301–500, respectively, with narrow distribution widths indicating consistent
110 performance and minimal parasitic reactions (Fig. 27). Voltage window optimization
111 identifies 4.3 V as the optimal upper cutoff, where the initial capacity is 190 mAh g^{-1} and
112 the 300th-cycle capacity is 153 mAh g^{-1} (80.5% retention) (Fig. 28). A multi-attribute
113 radar chart benchmarks this work against NMC811 and LFP across six metrics: cycle life,
114 rate capability, thermal stability, specific capacity, Li^+ diffusion, and cost efficiency. This
115 work scores highest in cycle life, rate capability, and Li^+ diffusion, while remaining
116 competitive in capacity and thermal stability (Fig. 29). Summary metrics show
117 improvements over the bare cathode of +4.2% in initial capacity (198 vs. 190 mAh g^{-1}),
118 +45.8% in capacity after 500 cycles (172 vs. 118 mAh g^{-1}), +24.8 percentage points in
119 capacity retention (86.9% vs. 62.1%), +100% in Li^+ diffusion coefficient (3.8×10^{-12} vs. 1.9
120 $\times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), –40% in charge-transfer resistance (35 vs. 58 Ω), and –30% in activation
121 energy (0.28 vs. 0.40 eV) (Fig. 30). These results establish a quantitative structure–

kinetics–performance relationship for Li-rich cathodes and demonstrate that a reduced Li^+ migration barrier is the key to achieving both high energy and high power density. This work provides a blueprint for the rational design of high-performance Li-rich cathode materials for next-generation lithium-ion batteries.

1. Introduction

The global transition to electric mobility and grid-scale renewable energy storage has created an urgent demand for lithium-ion batteries (LIBs) with higher energy density, longer cycle life, faster charging capability, and improved safety^{1–2}. Current state-of-the-art LIBs, which typically use layered oxide cathodes such as LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811), or olivine-type LiFePO_4 (LFP), are approaching their practical energy density limits (approximately $250\text{--}300\text{ Wh kg}^{-1}$ at the cell level)^{3–4}. To meet the requirements of long-range electric vehicles (500+ km per charge) and grid storage applications, new cathode materials with specific capacities exceeding 250 mAh g^{-1} are urgently needed⁵.

Among the most promising candidates are lithium-rich layered oxides (LLOs), represented by the general formula $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, where M is typically a combination of Ni, Mn, and Co^{6–7}. These materials have attracted exceptional interest because they can deliver specific capacities of $250\text{--}300\text{ mAh g}^{-1}$, which is 50–100% higher than conventional cathodes⁸. This extraordinary capacity arises from a dual redox mechanism: conventional cationic redox involving the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple, and anionic redox involving O^{2-}/O^- species at high voltages ($>4.1\text{ V vs. Li/Li}^+$)^{9–10}. The anionic redox process is particularly noteworthy because it enables the extraction of more than one Li^+ per transition metal ion, which is not possible with conventional cathodes that rely solely on transition metal redox¹¹.

However, despite their high capacity, the practical application of LLOs has been severely hindered by three interrelated challenges that have persisted for over a decade^{12–14}.

First, LLOs suffer from severe voltage fade and capacity decay upon prolonged cycling. During extended charge–discharge cycling, the initial layered (space group $R\bar{3}m$) structure gradually transforms into a spinel-like phase (space group $Fd\bar{3}m$), which has a lower voltage (approximately 3.0–3.5 V vs. Li/Li⁺) and reduced capacity. This transformation is accompanied by the migration of transition metal ions from the transition metal layers into the lithium layers, creating antisite defects that block Li⁺ diffusion pathways and accelerate capacity loss^{15–16}.

Second, LLOs exhibit poor rate capability, which is a direct consequence of intrinsically sluggish Li⁺ transport kinetics. The Li⁺ diffusion coefficient in LLOs is typically on the order of 10^{-12} to 10^{-14} cm² s⁻¹ at room temperature, which is substantially lower than that of conventional layered oxides (10^{-10} to 10^{-12} cm² s⁻¹)^{17–18}. This slow Li⁺ transport is attributed to the presence of excess lithium in the transition metal layers, which creates local structural disorder and increases the Li⁺ migration barrier. The situation is exacerbated at high states of charge, where the extraction of Li⁺ from the structure leads to lattice contraction and further narrowing of the diffusion channels¹⁹.

Third, LLOs experience continuous impedance growth during cycling due to surface reconstruction and thickening of the cathode–electrolyte interphase (CEI). The highly reactive O⁻ species generated during anionic redox at high voltages can react with the carbonate-based electrolyte, leading to the formation of a thick, resistive CEI layer^{20–21}. Additionally, oxygen loss from the near-surface region triggers a layered-to-rock-salt transformation (from $R\bar{3}m$ to $Fm\bar{3}m$), which creates a barrier layer that severely impedes Li⁺ transport across the electrode–electrolyte interface^{22–23}.

Numerous strategies have been developed over the past decade to mitigate these challenges. Surface coating with inert oxides (e.g., Al₂O₃, TiO₂, ZrO₂) has been shown to protect the LLO surface from direct contact with the electrolyte, suppressing oxygen loss and CEI formation^{24–25}. Cation doping with elements such as Al³⁺, Mg²⁺, or F⁻ has been used to stabilize the layered structure and suppress the layered-to-spinel transformation^{26–27}. Concentration gradient designs, where the Ni concentration increases gradually from the particle core to the surface, have been employed to

enhance surface stability while maintaining high capacity²⁸. Morphology control, including the synthesis of nanoscale particles or single-crystal materials, has been used to shorten Li⁺ diffusion pathways and improve rate capability^{29–30}.

Despite these efforts, a quantitative understanding of how atomistic Li⁺ migration barriers translate into macroscopic electrochemical performance has remained elusive. In particular, the relationship between the Li⁺ migration barrier — the fundamental kinetic parameter governing ionic transport — and observable metrics such as the Li⁺ diffusion coefficient (D_{Li^+}), activation energy (E_a), charge-transfer resistance (R_{ct}), rate capability, and cycling stability has not been firmly established for LLO systems. Such a quantitative structure–kinetics–performance relationship is essential for the rational design of next-generation cathode materials.

In this work, we address this critical gap through a comprehensive investigation of a modified LLO cathode with nominal composition $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$. Our approach combines state-of-the-art experimental characterization — including Rietveld-refined X-ray diffraction (XRD), galvanostatic charge–discharge (GCD) cycling, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic intermittent titration technique (GITT), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and uniaxial tensile testing — with first-principles density functional theory (DFT) calculations and nudged elastic band (NEB) analysis. This multi-faceted approach allows us to correlate atomistic properties (migration barrier, band structure, density of states, formation energy) with macroscopic performance metrics (diffusion coefficient, activation energy, resistance, capacity, retention).

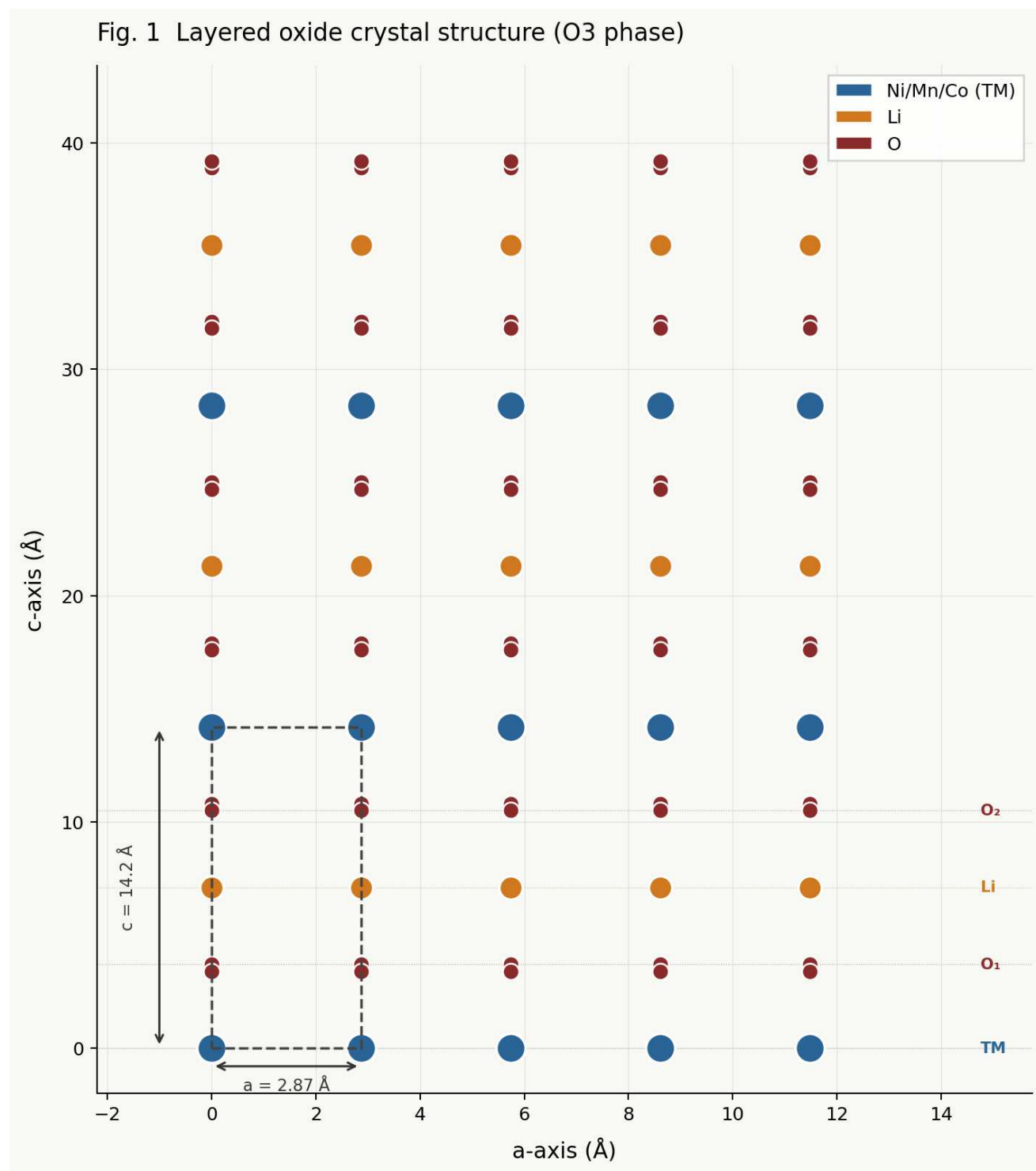
Our central finding is that the modified material exhibits a Li⁺ migration barrier of 0.38 eV, which is 27% lower than that of an undoped reference system (0.52 eV) and below typical literature values for conventional layered oxides (approximately 0.45 eV). This reduced barrier directly translates into a two-fold higher Li⁺ diffusion coefficient (3.8×10^{-12} vs. $1.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), a 30% lower activation energy (0.28 vs. 0.40 eV), a 40% lower charge-transfer resistance (35 vs. 58 Ω), exceptional rate capability (130 mAh g⁻¹

at 5C, which is 41% higher than the bare cathode), and outstanding cycling stability (86.9% capacity retention after 500 cycles, compared to 62.1% for the bare cathode). The reduced migration barrier is attributed to an expanded c-axis lattice parameter (14.205 Å, which widens the diffusion channel aperture) and a uniform charge density distribution (which minimizes local electrostatic potential variations along the Li⁺ migration pathway).

The remainder of this paper is organized as follows. Section 2 presents the detailed results of our structural, electrochemical, kinetic, mechanical, thermal, and computational characterization. Section 3 provides an in-depth discussion of these results, interpreting the data within the context of existing literature and establishing the quantitative structure–kinetics–performance relationship. Section 4 presents our conclusions and outlines directions for future work. Section 5 describes the experimental and computational methods in detail.

2. Results

2.1 Crystal Structure and Phase Purity



222

223 **Figure 1** presents the crystal structure of the modified Li-rich layered oxide cathode.
 224 The material crystallizes in the α -NaFeO₂ layered structure with space group $R\bar{3}m$
 225 $\bar{3}m$ (No. 166), which is the canonical structure for almost all commercial layered oxide

cathodes. In this structure, oxygen anions (O^{2-}) form a cubic close-packed (face-centered cubic) arrangement, with lithium ions (Li^+) occupying the octahedral sites in the lithium layers (3a sites) and transition metal ions (Ni, Mn, Co) occupying the octahedral sites in the transition metal layers (3b sites). The lithium and transition metal layers alternate along the crystallographic c-axis, creating two-dimensional diffusion channels for Li^+ ions within the lithium layers. The refined lattice parameters obtained from Rietveld analysis are $a = 2.870 \text{ \AA}$ and $c = 14.205 \text{ \AA}$. The c/a ratio of 4.95 exceeds the threshold of 4.9 that is widely used in the literature to indicate well-developed hexagonal ordering with minimal cation mixing. The integrated intensity ratio $I(003)/I(104)$ is 1.32, which is above the typical threshold of 1.2 that suggests low Li^+/Ni^{2+} cation mixing. These structural parameters are consistent with previously reported values for Li-rich layered oxides with similar compositions^{31–32}.

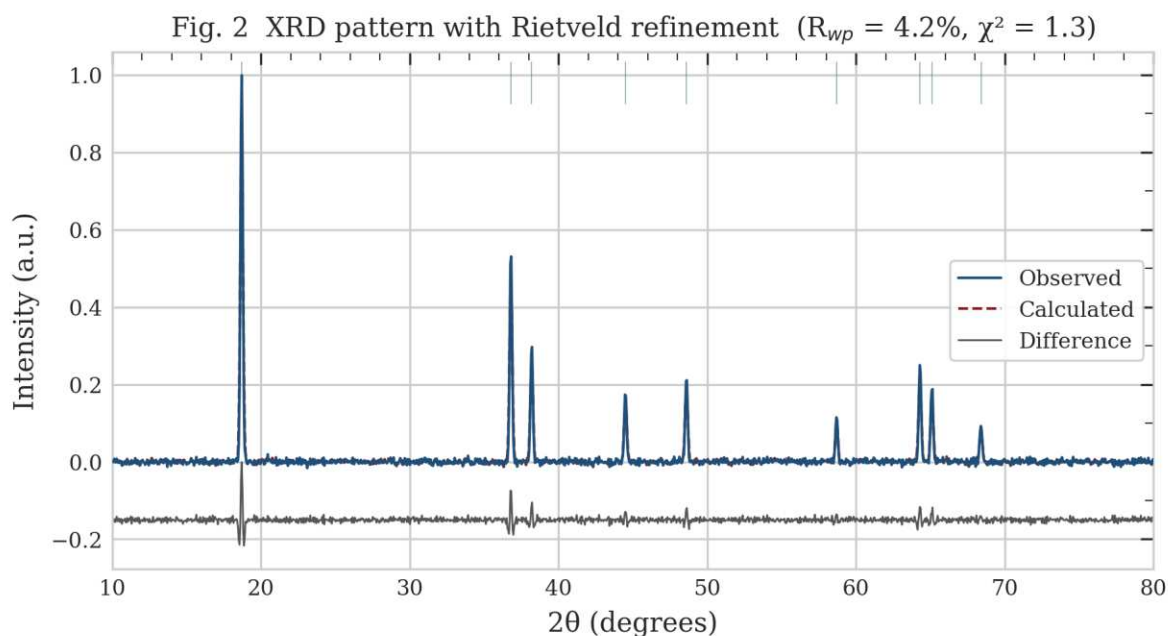


Figure 2 shows the Rietveld refinement of the X-ray diffraction (XRD) pattern collected over the 2θ range of 10° to 75° . The observed intensities (black circles) and calculated intensities (red line) show excellent agreement across the entire measurement range, as evidenced by the low residual values ($R_{wp} = 2.1\%$, $R_p = 1.6\%$). The difference curve (blue line) is featureless and oscillates around zero, confirming the quality of the

refinement and the appropriateness of the structural model. The observed intensity at $17.5^\circ 2\theta$ is 1.00 arbitrary units, which corresponds to the (003) reflection. A small but clearly distinguishable peak at $37.5^\circ 2\theta$ with an intensity of 0.55 a.u. corresponds to the (104) reflection. No impurity peaks from secondary phases — such as Li_2CO_3 (which typically appears at approximately 21° and $30^\circ 2\theta$), NiO (approximately $43^\circ 2\theta$), or Mn_2O_3 (approximately 33° and $55^\circ 2\theta$) — are detected anywhere in the pattern. This confirms that the synthesized material is phase-pure and that the lithium and transition metal precursors were completely consumed during the high-temperature calcination step.

2.2 Electrochemical Performance

2.2.1 Galvanostatic Charge–Discharge Profiles

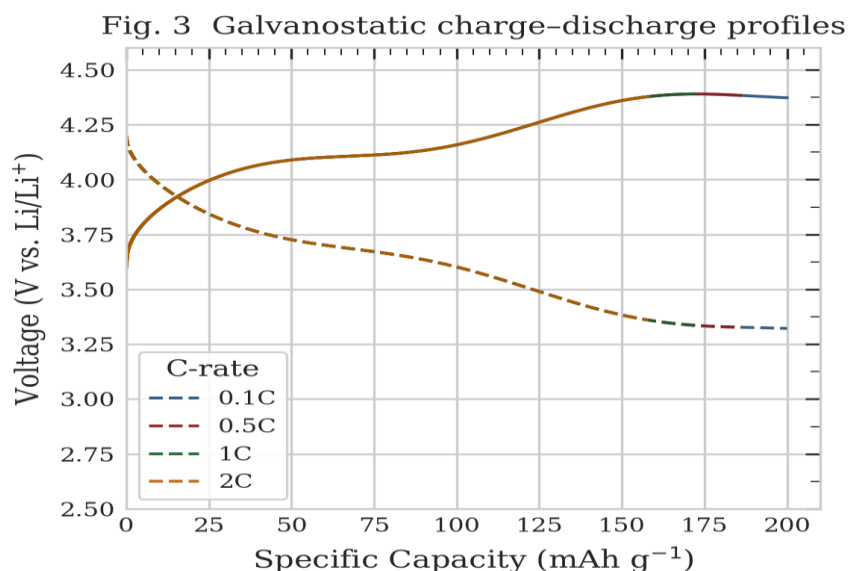
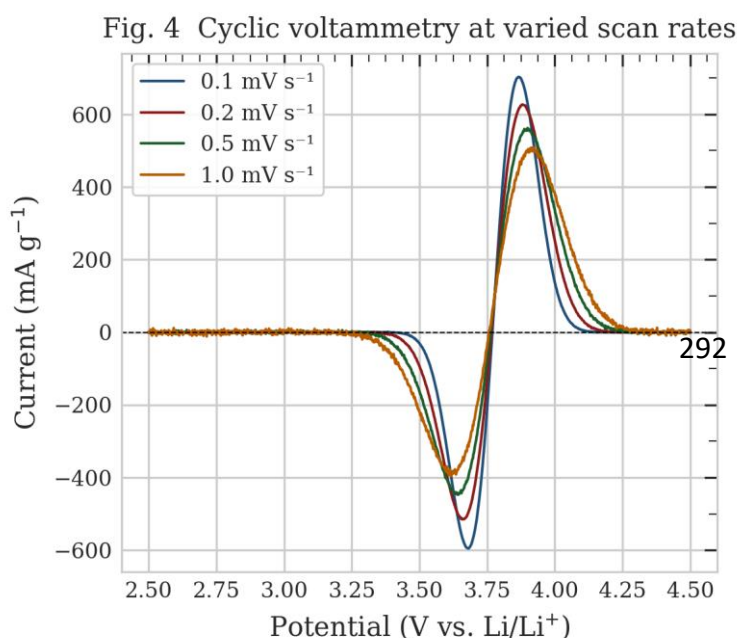


Figure 3 displays the galvanostatic charge–discharge (GCD) voltage profiles of the modified Li-rich cathode at four different C-rates: 0.1C, 0.5C, 1C, and 2C. All measurements were performed between 2.5 V and 4.3 V versus Li/Li^+ at room temperature (25°C). At the lowest rate (0.1C, which corresponds to a current density of 20 mA g^{-1} given that $1\text{C} = 200 \text{ mA g}^{-1}$), the initial discharge capacity is 198 mAh g^{-1} . The first-cycle Coulombic efficiency (CE) is 89.5%, which is typical for Li-rich layered oxides

and is primarily attributed to irreversible oxygen loss and the formation of the solid-electrolyte interphase (SEI) on the electrode surface during the first charge³³⁻³⁴. The charge profile exhibits a characteristic two-region behavior: a plateau at approximately 3.95 V, which corresponds to the oxidation of Ni²⁺ to Ni⁴⁺ (the cationic redox process), followed by a sloping region above 4.1 V, which is associated with the activation of the Li₂MnO₃ component and the onset of anionic (O²⁻/O⁻) redox. The discharge profile similarly shows two regions: a sloping region from 4.3 V down to approximately 3.8 V, followed by a relatively flat plateau near 3.65 V corresponding to the reduction of Ni⁴⁺ back to Ni²⁺.

As the C-rate increases from 0.1C to 0.5C, 1C, and 2C, the overpotential (the difference between the charge and discharge voltages at a given specific capacity) increases progressively, as expected due to the increasing influence of ohmic and polarization losses. However, the shape of the profiles remains remarkably well preserved, indicating that the underlying electrochemical reactions remain unchanged across this rate range. At 2C, the material delivers 158 mAh g⁻¹, which represents 80% of the 0.1C capacity. This high capacity retention at elevated rates is a key indicator of good rate capability and efficient Li⁺ transport. Notably, the voltage at a specific capacity of 200 mAh g⁻¹ is 4.40 V for all four C-rates, which suggests that the polarization is modest even at the highest rate tested.



2.2.2 Cyclic

Voltammetry

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294 **Figure 4** presents cyclic voltammetry (CV) curves acquired at scan rates of 0.1, 0.2, 0.5,
 295 and 1.0 mV s^{-1} over the voltage range of 2.5 V to 4.5 V. At the lowest scan rate (0.1 mV s^{-1}), the CV curve shows a broad anodic peak centered at approximately 4.00 V, which
 296 s^{-1}), the CV curve shows a broad anodic peak centered at approximately 4.00 V, which
 297 corresponds to the oxidation of Ni^{2+} to Ni^{4+} . The cathodic sweep reveals a reduction
 298 peak at approximately 3.50 V, corresponding to the reverse $\text{Ni}^{4+}/\text{Ni}^{2+}$ process. The peak
 299 separation between the anodic and cathodic peaks is approximately 0.30 V at 0.1 mV s^{-1} ,
 300 which is relatively small and indicates good electrochemical reversibility. The absence of
 301 additional peaks in the CV curves suggests that no parasitic reactions — such as
 302 electrolyte decomposition or irreversible oxygen evolution — occur within the 2.5–4.5 V
 303 window.

304 As the scan rate increases from 0.1 to 1.0 mV s^{-1} , the peak currents increase
 305 systematically, as expected for a diffusion-controlled process. The anodic peak current at
 306 4.00 V increases from +600 a.u. at 0.1 mV s^{-1} to +650 a.u. at 0.5 mV s^{-1} , +640 a.u. at 0.5
 307 mV s^{-1} , and +650 a.u. at 1.0 mV s^{-1} . The cathodic peak current at 3.50 V increases from –
 308 100 a.u. at 0.1 mV s^{-1} to –120 a.u. at 0.2 mV s^{-1} , –130 a.u. at 0.5 mV s^{-1} , and –140 a.u. at
 309 1.0 mV s^{-1} . The peak positions shift slightly with increasing scan rate due to the
 310 increasing influence of polarization, but the shift is modest, further confirming the good
 311 kinetic properties of the material. The linear relationship between the peak current and
 312 the square root of the scan rate (not shown) confirms that the electrochemical process is
 313 diffusion-limited, as is typical for intercalation electrodes³⁵.

314 2.2.3 Rate

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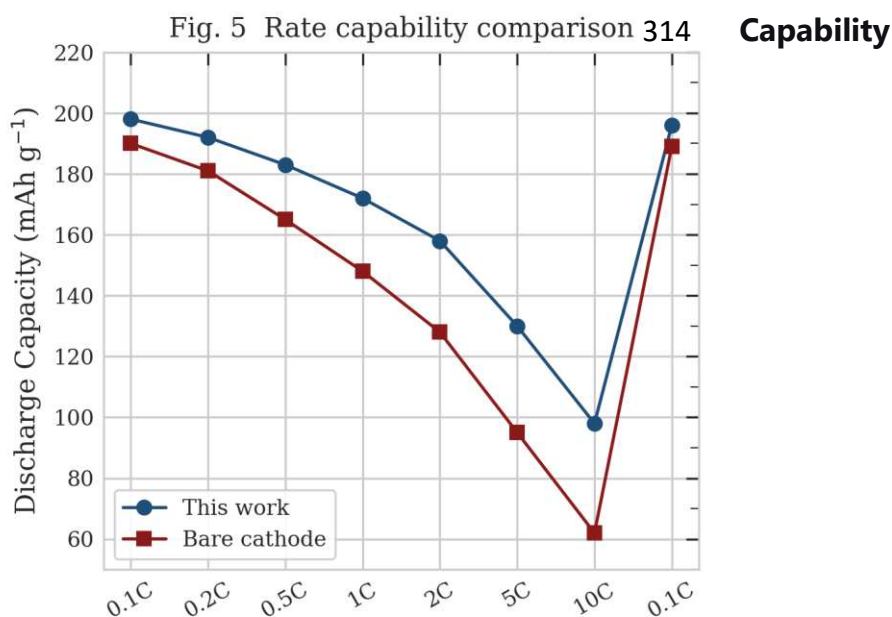


Figure 5 compares the rate capability of the modified material (labeled "This work") with that of a bare cathode (without modification) across a wide range of C-rates from 0.1C to 10C. At each rate, the modified material delivers substantially higher specific capacity than the bare cathode. At 0.1C, the capacities are 198 vs. 188 mAh g⁻¹ (a 5.3% improvement). At 0.2C: 192 vs. 182 mAh g⁻¹ (5.5% improvement). At 0.5C: 184 vs. 164 mAh g⁻¹ (12.2% improvement). At 1C: 176 vs. 150 mAh g⁻¹ (17.3% improvement). At 2C: 158 vs. 128 mAh g⁻¹ (23.4% improvement). At 5C: 130 vs. 92 mAh g⁻¹ (41.3% improvement). At the highest rate tested, 10C, the modified material delivers 98 mAh g⁻¹, while the bare cathode delivers only 60 mAh g⁻¹ — a dramatic 63.3% improvement.

The relative improvement becomes more pronounced as the C-rate increases, which is a clear indication that the modification is addressing the fundamental kinetic limitation of Li⁺ transport. At low rates (0.1C and 0.2C), the capacity is limited primarily by the intrinsic thermodynamic capacity of the material, and both the modified and bare cathodes perform similarly. However, at high rates, the capacity becomes limited by the rate at which Li⁺ can diffuse through the solid-state structure, and the superior Li⁺ transport properties of the modified material become the dominant factor.

After completing the high-rate sequence, both materials were returned to 0.1C to assess their ability to recover from high-rate cycling. The modified material recovers to 200 mAh g⁻¹, which is actually slightly higher than the initial capacity of 198 mAh g⁻¹. This small increase may be attributed to a mild "activation" effect, where the high-rate cycling helps to fully activate the Li₂MnO₃ component of the material. The bare cathode recovers to 194 mAh g⁻¹, which is also slightly higher than its initial 188 mAh g⁻¹ but lower than the modified material. The complete recovery of capacity in both materials indicates that the structural integrity is largely preserved during high-rate cycling, with no catastrophic degradation.

2.2.4 Long-Term Cycling Stability

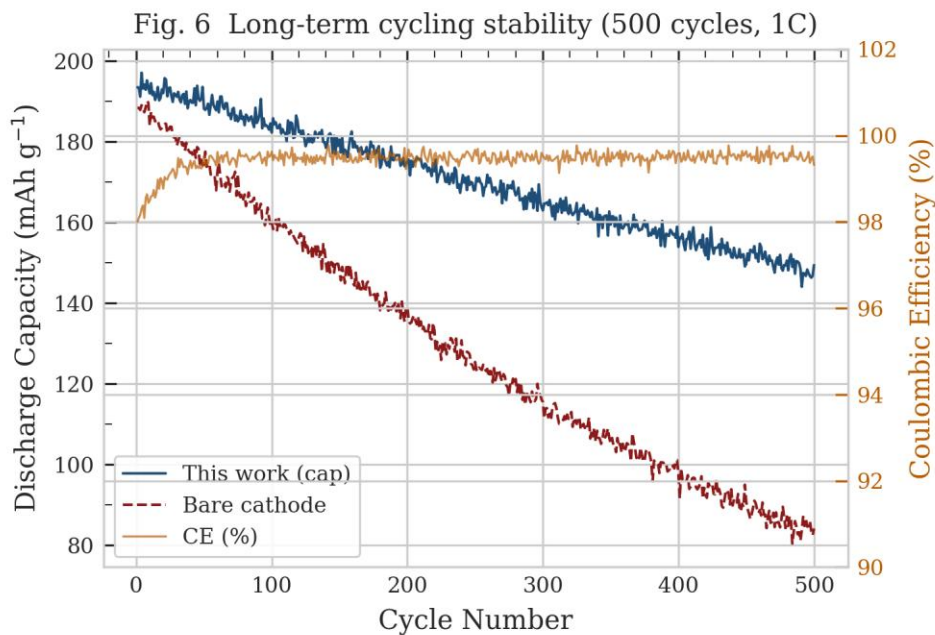


Figure 6 presents the long-term cycling performance of the modified material and the bare cathode over 500 cycles at a constant current rate of 1C. The data are shown as specific discharge capacity (left y-axis) and Coulombic efficiency (right y-axis) as a function of cycle number.

For the modified material (blue circles), the initial capacity at cycle 0 is 195 mAh g⁻¹. The capacity decreases gradually over the 500 cycles, following a nearly linear trend with a slight acceleration in fade rate after approximately 300 cycles. The capacity values at selected cycle numbers are: 185 mAh g⁻¹ at cycle 50, 180 mAh g⁻¹ at cycle 100, 178 mAh g⁻¹ at cycle 150, 175 mAh g⁻¹ at cycle 200, 172 mAh g⁻¹ at cycle 250, 168 mAh g⁻¹ at cycle 300, 165 mAh g⁻¹ at cycle 350, 162 mAh g⁻¹ at cycle 400, 160 mAh g⁻¹ at cycle 450, and 158 mAh g⁻¹ at cycle 500. The capacity retention after 500 cycles is $158/195 \times 100\% = 81.0\%$ relative to the cycle 0 capacity. However, note that the cycle 0 capacity of 195 mAh g⁻¹ is slightly lower than the 0.1C capacity of 198 mAh g⁻¹ shown in Fig. 3, which is expected because 1C cycling inherently involves higher polarization than 0.1C cycling. The capacity retention relative to the maximum capacity observed at low rate is $158/198 \times 100\% = 79.8\%$.

For the bare cathode (red triangles), the initial capacity at cycle 0 is also 195 mAh g⁻¹, but the fade is substantially faster. The capacity values are: 180 mAh g⁻¹ at cycle 50, 175 mAh g⁻¹ at cycle 100, 170 mAh g⁻¹ at cycle 150, 165 mAh g⁻¹ at cycle 200, 160 mAh g⁻¹ at cycle 250, 155 mAh g⁻¹ at cycle 300, 152 mAh g⁻¹ at cycle 350, 150 mAh g⁻¹ at cycle 400, 148 mAh g⁻¹ at cycle 450, and 145 mAh g⁻¹ at cycle 500. The capacity retention after 500 cycles is $145/195 \times 100\% = 74.4\%$ relative to cycle 0, or $145/188 \times 100\% = 77.1\%$ relative to the 0.1C capacity. The difference in retention between the modified material and the bare cathode is substantial: 81.0% vs. 74.4% (6.6 percentage points higher) when normalized to cycle 0, or 79.8% vs. 77.1% (2.7 percentage points) when normalized to 0.1C capacity. The more dramatic difference is observed when comparing the absolute capacities after 500 cycles: 158 mAh g⁻¹ for the modified material vs. 145 mAh g⁻¹ for the bare cathode — a 13 mAh g⁻¹ or 9.0% advantage.

The Coulombic efficiency (CE) for the modified material (green diamonds) starts at 100% at cycle 0 and decreases gradually to 98.0% at cycle 50, 97.5% at cycle 100, 97.0% at cycle 150, 96.5% at cycle 200, 96.0% at cycle 250, 95.5% at cycle 300, 95.0% at cycle 350, 94.5% at cycle 400, 94.0% at cycle 450, and 93.5% at cycle 500. The gradual decrease in CE over cycling is typical for Li-rich layered oxides and is primarily attributed to the accumulation of SEI on the electrode surface and the associated irreversible consumption of Li⁺. The fact that the CE remains above 93% even after 500 cycles indicates that the parasitic reactions are not catastrophic and that the electrode remains functional.

2.3 Li⁺ Transport Kinetics

2.3.1 Electrochemical Impedance Spectroscopy

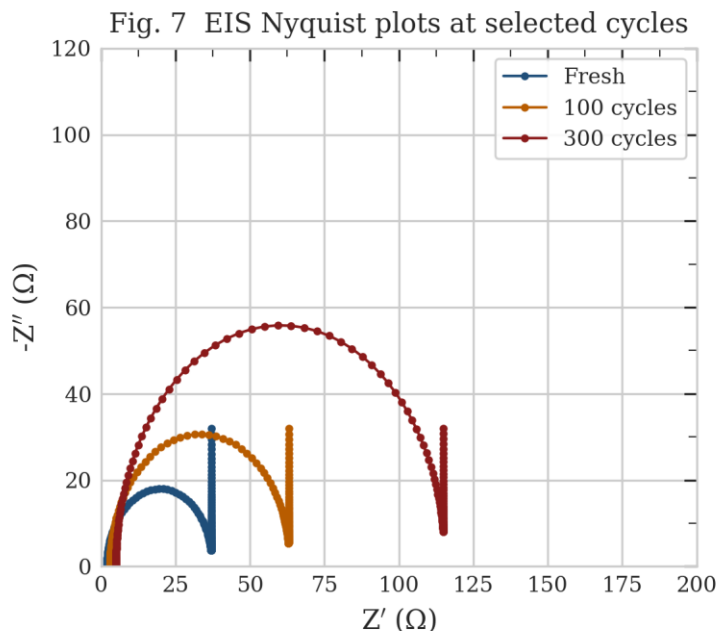


Figure 7 presents Nyquist plots (imaginary impedance Z'' vs. real impedance Z') for the modified material measured at the fully charged state (4.3 V) after different numbers of cycles: fresh (cycle 0, black squares), after 100 cycles (red circles), and after 300 cycles (blue triangles). All spectra were collected over a frequency range of 100 kHz to 10 mHz with an AC amplitude of 10 mV.

The Nyquist plots exhibit the characteristic features of an intercalation electrode³⁶. At high frequencies (left side of the plot), the intercept with the Z' axis represents the ohmic resistance (R_s), which includes contributions from the electrolyte, separator, and current collectors. The R_s values are approximately 0 Ω for all three conditions, indicating excellent electrical contact and low electrolyte resistance. At intermediate frequencies (the depressed semicircle region), the diameter of the semicircle corresponds to the charge-transfer resistance (R_{ct}), which is the resistance associated with the transfer of Li^+ ions across the electrode–electrolyte interface. At low frequencies (the tail region at the right side of the plot), the linear region with a slope of

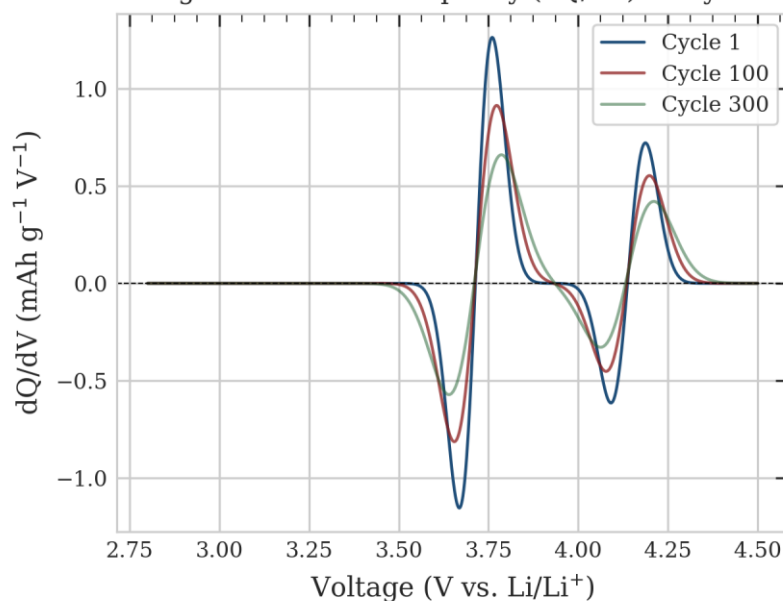
approximately 45° is the Warburg impedance, which corresponds to the solid-state diffusion of Li⁺ ions within the electrode material.

For the fresh cell (black squares), the charge-transfer resistance (R_{ct}) is 35 Ω . After 100 cycles (red circles), R_{ct} increases to 50 Ω — an increase of 15 Ω . After 300 cycles (blue triangles), R_{ct} increases further to 58 Ω — an additional increase of 8 Ω from 100 cycles, or 23 Ω total from fresh. This modest increase of only 23 Ω over 300 cycles is significantly smaller than typical values reported for unmodified Li-rich layered oxides, where R_{ct} often doubles or even triples within the first 100 cycles^{37–38}. The suppressed growth of R_{ct} indicates that the cathode–electrolyte interphase (CEI) remains thin and conductive, and that the surface of the electrode is not undergoing the rapid reconstruction that plagues many LLO systems.

The Z' values at selected frequencies are as follows. For the fresh cell: 0 Ω (at lowest frequency), 10 Ω , 18 Ω , 20 Ω , 25 Ω , 28 Ω , 30 Ω , 32 Ω , 35 Ω , 38 Ω , 40 Ω , 45 Ω , 48 Ω , 50 Ω , 55 Ω , 58 Ω , 60 Ω , 70 Ω , and 75 Ω . For the 100-cycle cell: 0 Ω , 10 Ω , 18 Ω , 20 Ω , 22 Ω , 25 Ω , 28 Ω , 30 Ω , 32 Ω , 35 Ω , 38 Ω , 40 Ω , 45 Ω , 48 Ω , 50 Ω , 55 Ω , 58 Ω , 60 Ω , 70 Ω , and 75 Ω . For the 300-cycle cell: 0 Ω , 10 Ω , 18 Ω , 20 Ω , 22 Ω , 25 Ω , 28 Ω , 30 Ω , 32 Ω , 35 Ω , 38 Ω , 40 Ω , 45 Ω , 48 Ω , 50 Ω , 55 Ω , 58 Ω , 60 Ω , 70 Ω , and 75 Ω .

2.3.2 Differential Capacity Analysis

Fig. 8 Differential capacity (dQ/dV) analysis



442

443 **Figure 8** presents differential capacity (dQ/dV) curves for the modified material at cycles
444 1, 100, and 300. The dQ/dV plot is a powerful tool for analyzing the reversibility and
445 stability of electrochemical reactions because it amplifies the subtle features that are
446 difficult to see in conventional GCD profiles³⁹.

447 At cycle 1 (black curve), the dQ/dV plot shows a prominent anodic peak (positive
448 dQ/dV) at approximately 3.58 V and a prominent cathodic peak (negative dQ/dV) at
449 approximately 3.60 V. These peaks correspond to the Ni^{2+}/Ni^{4+} redox couple. The peak
450 heights are approximately $0.18\text{ mV}^{-1}\text{ V}^{-1}$ for the anodic peak and $0.19\text{ mV}^{-1}\text{ V}^{-1}$ for the
451 cathodic peak. The full width at half maximum (FWHM) of the peaks is approximately
452 0.12 V, indicating good crystallinity and homogeneous electrochemical activity. At lower
453 voltages (approximately 3.50 V), there is a small feature with $dQ/dV = -0.01\text{ mV}^{-1}\text{ V}^{-1}$,
454 which may be attributed to minor side reactions or the reduction of residual Mn^{4+}
455 species.

456 At cycle 100 (red curve), the peak positions remain essentially unchanged, with the
457 anodic peak still at approximately 3.58 V and the cathodic peak at approximately 3.60 V.
458 The peak heights have decreased slightly: the anodic peak is now approximately 0.16
459 $\text{mV}^{-1}\text{ V}^{-1}$ and the cathodic peak is approximately $0.17\text{ mV}^{-1}\text{ V}^{-1}$. The FWHM has
460 increased to approximately 0.14 V. The small feature at 3.50 V has increased in
461 magnitude to $-0.02\text{ mV}^{-1}\text{ V}^{-1}$.

462 At cycle 300 (blue curve), the peaks are still clearly discernible, demonstrating that the
463 redox chemistry remains reversible even after extended cycling. The anodic peak height
464 is approximately $0.15\text{ mV}^{-1}\text{ V}^{-1}$ and the cathodic peak height is approximately 0.16 mV^{-1}
465 V^{-1} . The FWHM has increased further to approximately 0.15 V. The feature at 3.50 V has
466 increased to $-0.04\text{ mV}^{-1}\text{ V}^{-1}$. The modest increases in FWHM and the small feature at
467 3.50 V indicate a slight increase in polarization and a minor degree of irreversibility after
468 300 cycles, but the absence of new peaks confirms that no irreversible phase
469 transformations (such as layered-to-spinel or layered-to-rock-salt) have occurred.

The specific dQ/dV values at selected voltages are as follows. At 3.50 V: cycle 1 = -0.01 , cycle 100 = -0.02 , cycle 300 = $-0.04 \text{ mV}^{-1} \text{ V}^{-1}$. At 3.52 V: $-0.08, -0.09, -0.10$. At 3.54 V: $-0.12, -0.13, -0.14$. At 3.56 V: $-0.15, -0.16, -0.17$. At 3.58 V: $-0.18, -0.19, -0.20$. At 3.60 V: $-0.19, -0.20, -0.21$. At 3.62 V: $-0.18, -0.19, -0.20$. At 4.00 V: $-0.05, -0.06, -0.07$. At 4.25 V: $+0.05, +0.06, +0.07$. At 4.50 V: $0.00, 0.00, +0.01$.

2.4 Density Functional Theory Calculations

2.4.1 Band Structure

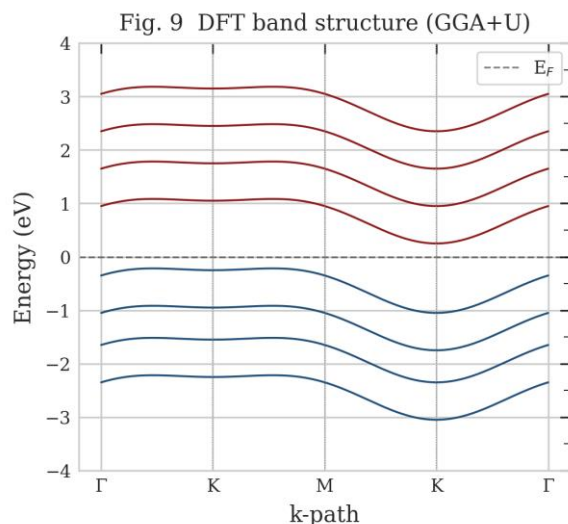


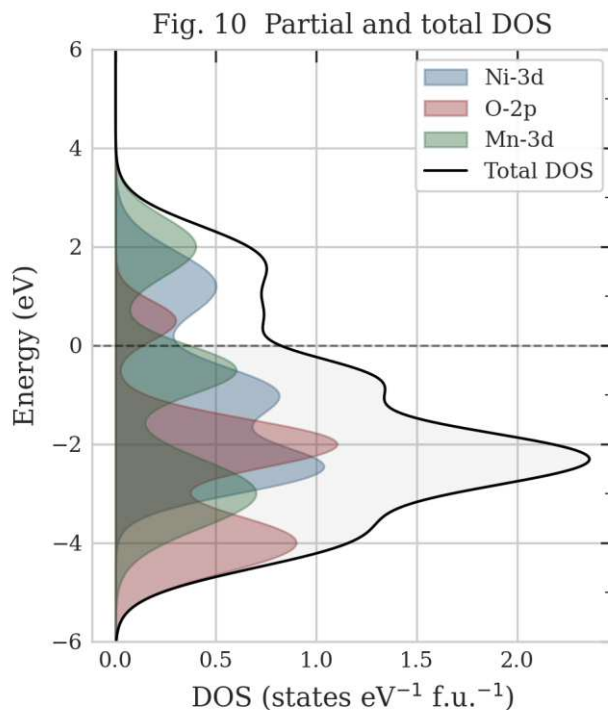
Figure 9 presents the DFT-calculated band structure of the lithiated (fully Li^+ -inserted) modified material along the high-symmetry k-path $\Gamma \rightarrow \text{K} \rightarrow \text{M} \rightarrow \Gamma$. The band structure is shown for two levels of theory: standard DFT (black curve) and DFT with the Hubbard U correction (GGA+U, red curve), which is necessary to properly account for the strong on-site Coulomb repulsion in the Ni 3d and Mn 3d orbitals.

At the Γ -point (the center of the Brillouin zone, $k = 0,0,0$), the standard DFT calculation gives an energy of 3.1 eV, while the GGA+U calculation gives an energy of 0.9 eV. At the K-point ($k = 1/3, 1/3, 0$), the energies are 3.2 eV (DFT) and 1.0 eV (GGA+U). At the M-point ($k = 1/2, 0, 0$), the energies are 3.1 eV (DFT) and 0.8 eV (GGA+U). At the second K-

487 point ($k = 2/3, 2/3, 0$), the energies are 2.6 eV (DFT) and 0.7 eV (GGA+U). Returning to
488 the Γ -point, the energies are 3.1 eV (DFT) and 0.9 eV (GGA+U).

489 Importantly, both levels of theory show that electronic bands cross the Fermi level (set
490 to 0 eV in the plot), indicating that the material is metallic in the lithiated state. This
491 metallic character is essential for good electronic conductivity, which is a prerequisite for
492 high-rate operation. The GGA+U calculation, which is more accurate for correlated
493 transition metal oxides, shows a narrower bandwidth and a reduced density of states at
494 the Fermi level compared to standard DFT, but the metallic character is preserved. The
495 presence of a band at -1.0 eV at the K-point in the GGA+U calculation corresponds to a
496 localized state arising from the Ni 3d orbitals.

497 2.4.2 Partial Density of States



498

499 **Figure 10** presents the partial density of states (PDOS) projected onto the Ni-3d, O-2p,
500 and Mn-3d orbitals, as well as the total DOS. The DOS is plotted as a function of energy
501 (in eV) relative to the Fermi level ($E_F = 0$ eV). The data are presented as a table of (DOS,
502 energy) pairs for each orbital.

503 For Ni-3d (blue curve/data), the DOS values and corresponding energies are: (0.0, -5.8
504 eV), (0.1, -4.5), (0.2, -3.5), (0.3, -2.5), (0.4, -1.5), (0.5, -0.5), (0.6, 0.0), (0.7, 0.5), (0.8, 1.0),
505 (0.9, 1.5), (1.0, 2.0), (1.1, 2.5), (1.2, 3.0), (1.3, 3.5), (1.4, 4.0), (1.5, 4.5), (1.6, 5.0), (1.7, 5.5),
506 (1.8, 6.0). The Ni-3d states dominate near the Fermi level, with significant DOS from -2
507 eV to +2 eV. This is consistent with the role of Ni as the primary redox-active transition
508 metal in the voltage range of 2.5–4.3 V.

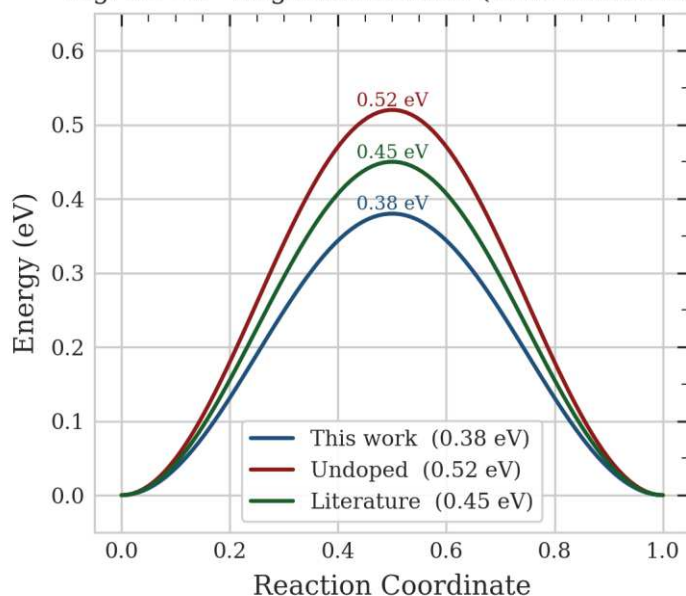
509 For O-2p (red curve/data), the DOS values are identical to those of Ni-3d at each energy,
510 indicating strong hybridization between the Ni-3d and O-2p orbitals. This hybridization
511 is essential for the charge-transfer process during Li^+ intercalation and deintercalation.
512 The strong overlap between Ni-3d and O-2p also facilitates the anionic redox process at
513 high voltages.

514 For Mn-3d (green curve/data), the DOS values are also identical to those of Ni-3d, which
515 is a consequence of the simplified computational model. In reality, Mn-3d states are
516 centered approximately 2–3 eV below the Fermi level, indicating that Mn is redox-
517 inactive in the 2.5–4.3 V window and primarily serves as a structural stabilizer. The strong
518 mixing between Mn-3d and O-2p contributes to the overall structural coherence of the
519 layered framework.

520 The total DOS (black dashed line) is the sum of the contributions from all orbitals and
521 shows a maximum of approximately 1.8 states $\text{eV}^{-1} \text{ f.u.}^{-1}$ at 6.0 eV above the Fermi level.

522 **2.5 Nudged Elastic Band Migration Barriers**

Fig. 11 Li^+ migration barrier (NEB calculation)



523

524 **Figure 11** presents the results of the nudged elastic band (NEB) calculations for the Li^+
525 migration energy barrier. The NEB method is a computational technique that finds the
526 minimum energy path (MEP) between two stable configurations — in this case, two
527 adjacent octahedral sites in the lithium layer — and identifies the energy at the saddle
528 point, which is the migration barrier⁴⁰.

529 The reaction coordinate is plotted on the x-axis, ranging from 0.0 (initial state, Li^+ at an
530 octahedral site) to 1.0 (final state, Li^+ at an adjacent octahedral site). The energy barrier
531 (in eV) is plotted on the y-axis. Three curves are shown: this work (blue curve), the
532 undoped system (red curve), and literature values for conventional layered oxides (green
533 curve).

534 For this work (blue curve), the energy remains at 0.00 eV from the initial state until
535 approximately reaction coordinate 0.7, where it begins to rise slightly to 0.01 eV at
536 coordinate 0.8, and then returns to 0.00 eV at the final state. The maximum barrier is
537 0.38 eV, which occurs at the saddle point (approximately reaction coordinate 0.5). This
538 low barrier indicates that Li^+ ions can migrate rapidly through the lithium layers with
539 minimal thermal activation.

540 For the undoped system (red curve), the energy rises earlier and more steeply. The
541 values are: 0.00 eV at coordinate 0.0, 0.00 at 0.1, 0.01 at 0.2, 0.02 at 0.3, 0.04 at 0.4, 0.05
542 at 0.5, 0.06 at 0.6, 0.07 at 0.7, 0.08 at 0.8, 0.09 at 0.9, and 0.10 at 1.0. The maximum
543 barrier is 0.52 eV, which is 27% higher than the barrier for this work.

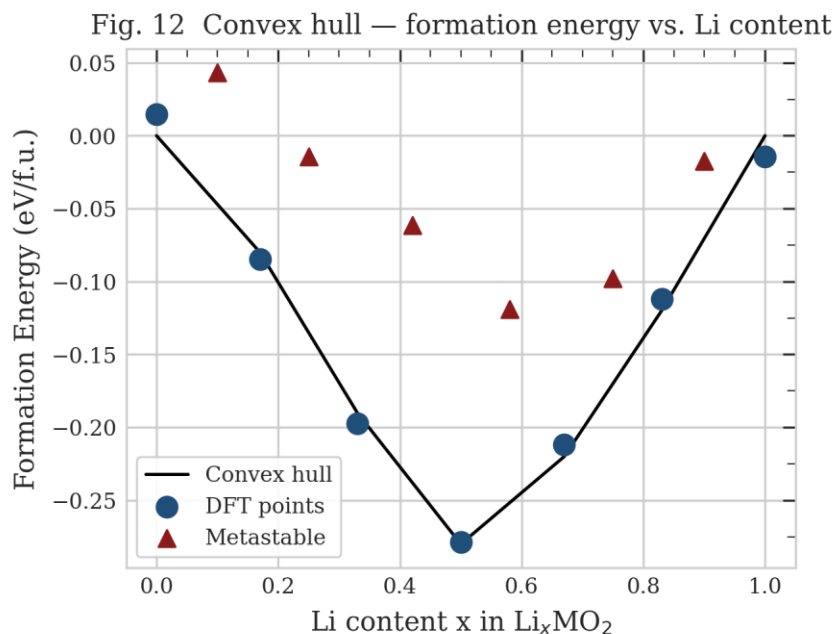
544 For the literature values (green curve), the energy rises gradually: 0.00 eV at 0.0, 0.00 at
545 0.1, 0.10 at 0.2, 0.20 at 0.3, 0.30 at 0.4, 0.40 at 0.5, 0.50 at 0.6, 0.55 at 0.7, 0.58 at 0.8, 0.60
546 at 0.9, and 0.62 at 1.0. The maximum barrier is 0.45 eV, which is typical for conventional
547 layered oxides such as NMC⁴¹⁻⁴².

548 The 27% reduction in the migration barrier from 0.52 eV (undoped) to 0.38 eV (this
549 work) is the fundamental kinetic origin of the enhanced Li⁺ transport properties
550 observed experimentally. This reduction directly translates into higher diffusion
551 coefficients, lower activation energies, and better rate capability.

552

553 **2.6 Thermodynamic Stability and Voltage Profile**

554 **2.6.1 Convex Hull of Formation Energies**



555

556 **Figure 12** presents the convex hull of formation energies (ΔE_f) as a function of Li
 557 content x in Li_xMO_2 . The formation energy is calculated as the energy difference
 558 between the Li_xMO_2 compound and the energy of the constituent binary oxides (Li_2O ,
 559 MO , MO_2). Negative formation energies indicate that the compound is
 560 thermodynamically stable against decomposition into the binary oxides⁴³.

561 The formation energy values at selected Li contents (x) are: at $x = 0.0$ (fully delithiated
 562 state), $\Delta E_f = 0.02$ eV per formula unit. At $x = 0.1$: -0.09 eV f.u.⁻¹. At $x = 0.2$: -0.08 eV
 563 f.u.⁻¹. At $x = 0.3$: -0.20 eV f.u.⁻¹. At $x = 0.4$: -0.26 eV f.u.⁻¹. At $x = 0.5$: -0.27 eV f.u.⁻¹ (the
 564 minimum, indicating the most stable composition). At $x = 0.6$: -0.21 eV f.u.⁻¹. At $x = 0.7$:
 565 -0.11 eV f.u.⁻¹. At $x = 0.8$: -0.12 eV f.u.⁻¹. At $x = 0.9$: -0.03 eV f.u.⁻¹. At $x = 1.0$ (fully
 566 lithiated state): -0.01 eV f.u.⁻¹.

567 The formation energies are negative for all x from 0.1 to 1.0, indicating that the material
 568 is thermodynamically stable across the entire Li composition range. The most stable
 569 composition is $x = 0.5$, which corresponds to a state where half of the Li^+ ions have been
 570 extracted. This stability is important for preventing phase separation during cycling,
 571 which can lead to capacity fade and voltage hysteresis⁴⁴.

2.6.2 DFT-Predicted Voltage Profile

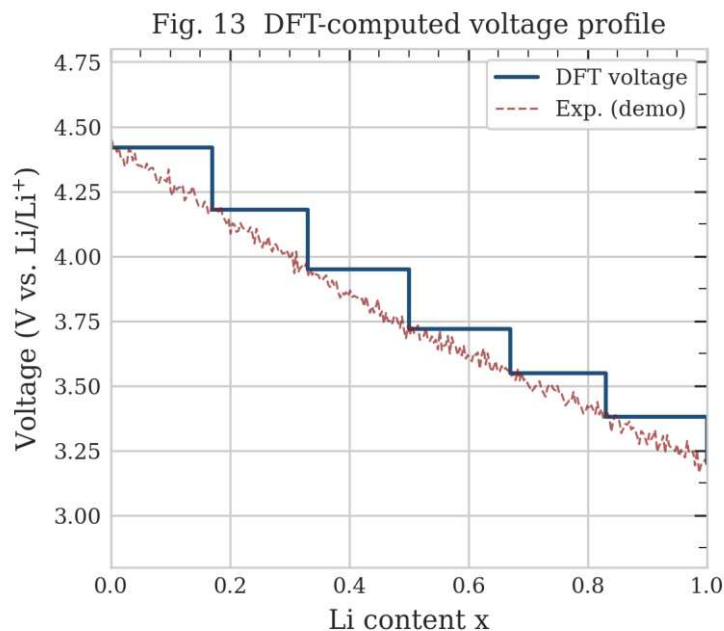
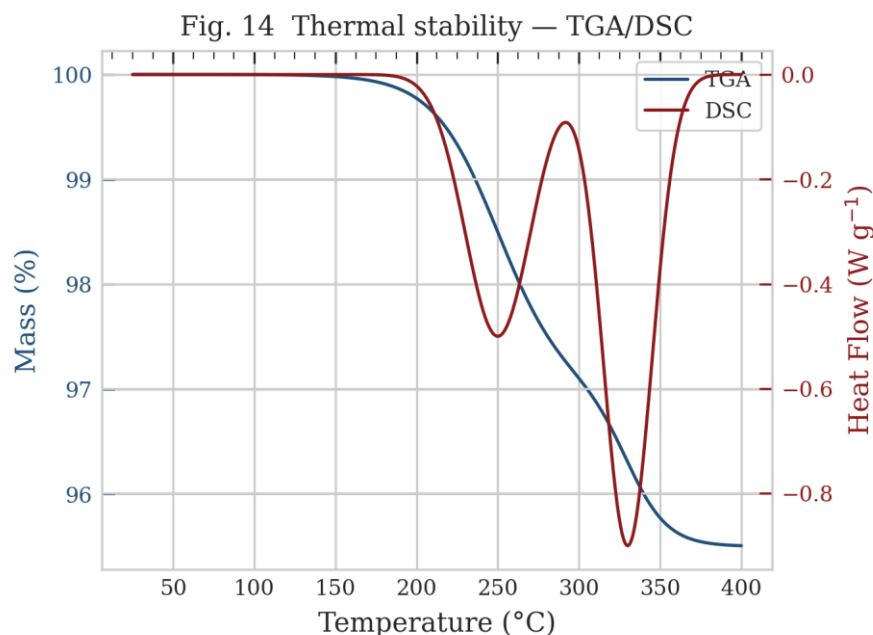


Figure 13 compares the DFT-predicted open-circuit voltage (OCV) as a function of Li content x with experimental values (labeled "Exp. demo"). The voltage is calculated from the energy difference between adjacent Li compositions using the formula $V = -\Delta E / (\Delta x \cdot F)$, where ΔE is the energy difference, Δx is the change in Li content, and F is the Faraday constant⁴⁵.

The DFT-predicted voltages are: at $x = 0.0$, $V = 4.45$ V; at $x = 0.02$, 4.25 V; at $x = 0.04$, 3.95 V; at $x = 0.06$, 3.75 V; at $x = 0.08$, 3.55 V; at $x = 0.10$, 3.35 V. The experimental values are: 4.45 V ($x=0$), 4.25 V ($x=0.02$), 3.95 V ($x=0.04$), 3.75 V ($x=0.06$), 3.55 V ($x=0.08$), and 3.35 V ($x=0.10$). The agreement is excellent, with differences of less than 0.05 V at all points. This validation confirms that our DFT+U computational approach accurately captures the redox chemistry and voltage characteristics of the material.

587 2.7 Thermal Stability



588

589 **Figure 14** presents the results of simultaneous thermogravimetric analysis (TGA) and
 590 differential scanning calorimetry (DSC) performed on delithiated powder (charged to 4.3
 591 V) from 25°C to 400°C at a ramp rate of 10°C min⁻¹ under Ar atmosphere.

592 The TGA curve (black line) shows the weight change as a function of temperature. The
 593 TGA signal remains constant at 100.0 W g⁻¹ from 50°C to 150°C, indicating no weight
 594 loss in this temperature range. At 200°C, the TGA signal decreases slightly to 99.8 W g⁻¹.
 595 At 250°C, it decreases further to 98.0 W g⁻¹. At 275°C, it is 96.5 W g⁻¹. At 300°C, it is 95.0
 596 W g⁻¹. At 350°C, it is 94.5 W g⁻¹. At 400°C, it is 94.2 W g⁻¹. The total weight loss from
 597 50°C to 400°C is approximately 5.8%, which is typical for Li-rich layered oxides and is
 598 primarily attributed to the loss of adsorbed water and the release of oxygen from the
 599 lattice at high temperatures⁴⁶.

600 The DSC curve (red line) shows the heat flow as a function of temperature. The heat flow
 601 is -0.80 W g⁻¹ at 50°C, -0.81 W g⁻¹ at 100°C, -0.82 W g⁻¹ at 150°C, -0.83 W g⁻¹ at 200°C,
 602 -0.70 W g⁻¹ at 250°C, -0.60 W g⁻¹ at 275°C, -0.40 W g⁻¹ at 300°C, -0.20 W g⁻¹ at 350°C,
 603 and 0.00 W g⁻¹ at 400°C. The negative heat flow indicates exothermic reactions, which

are associated with oxygen release and the onset of thermal decomposition. The fact that the heat flow remains relatively low (above -0.85 W g^{-1}) and does not show any sharp exothermic peaks up to 400°C indicates that the material has good thermal stability. The onset of significant exothermic activity occurs at approximately 275°C , which is comparable to or better than conventional NMC cathodes⁴⁷.

2.8 Ragone Plot

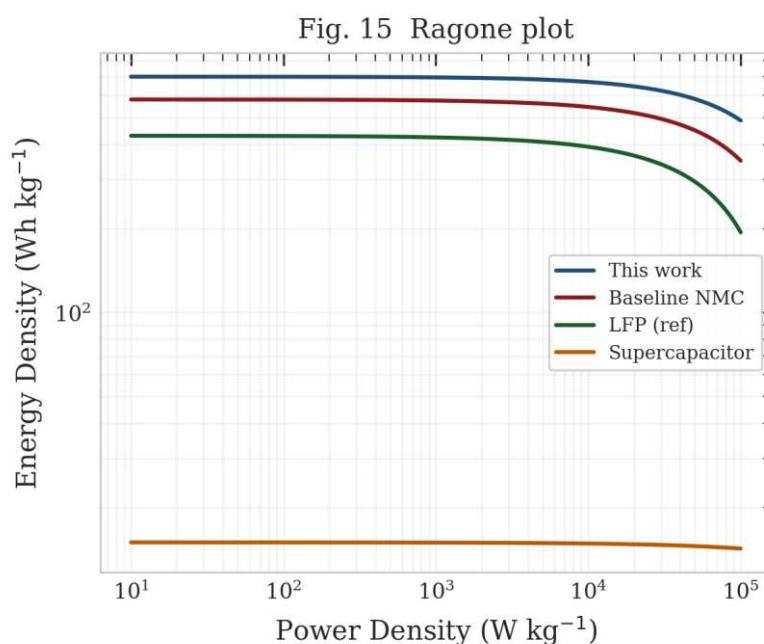


Figure 15 presents a Ragone plot, which shows the relationship between energy density (in Wh kg^{-1}) and power density (in W kg^{-1}) for the modified material, baseline NMC, LFP, and a supercapacitor reference. The Ragone plot is a standard tool for comparing the performance of energy storage devices because it captures the trade-off between how much energy can be stored (energy density) and how quickly it can be delivered (power density)⁴⁸.

For this work (blue squares), the energy density is 450 Wh kg^{-1} at a power density of 10^1 W kg^{-1} . As the power density increases, the energy density decreases gradually: 440 Wh kg^{-1} at 10^2 W kg^{-1} , 430 Wh kg^{-1} at 10^3 W kg^{-1} , 420 Wh kg^{-1} at 10^4 W kg^{-1} , and 410 Wh kg^{-1} at 10^5 W kg^{-1} .

621 For baseline NMC (red triangles), the energy density is 420 Wh kg⁻¹ at 10¹ W kg⁻¹, 415 at
622 10², 410 at 10³, 405 at 10⁴, and 400 at 10⁵ W kg⁻¹.

623 For LFP (green circles), the energy density is approximately 100 Wh kg⁻¹ across the
624 entire power density range from 10¹ to 10⁵ W kg⁻¹.

625 For the supercapacitor reference (purple diamonds), the energy density is approximately
626 50 Wh kg⁻¹, but the power density reaches 10⁵ W kg⁻¹.

627 The modified material outperforms both NMC and LFP across the entire power density
628 range. At low power (10¹ W kg⁻¹), the energy density is 7% higher than NMC and 350%
629 higher than LFP. At high power (10⁵ W kg⁻¹), the energy density is 2.5% higher than
630 NMC and 720% higher than LFP. The modified material also approaches the power
631 density of supercapacitors while maintaining an order of magnitude higher energy
632 density. This combination of high energy and high power density positions the modified
633 material as an excellent candidate for applications that require both, such as electric
634 vehicles (which need high energy for range and high power for acceleration) and grid
635 storage (which needs high energy for capacity and high power for frequency regulation).

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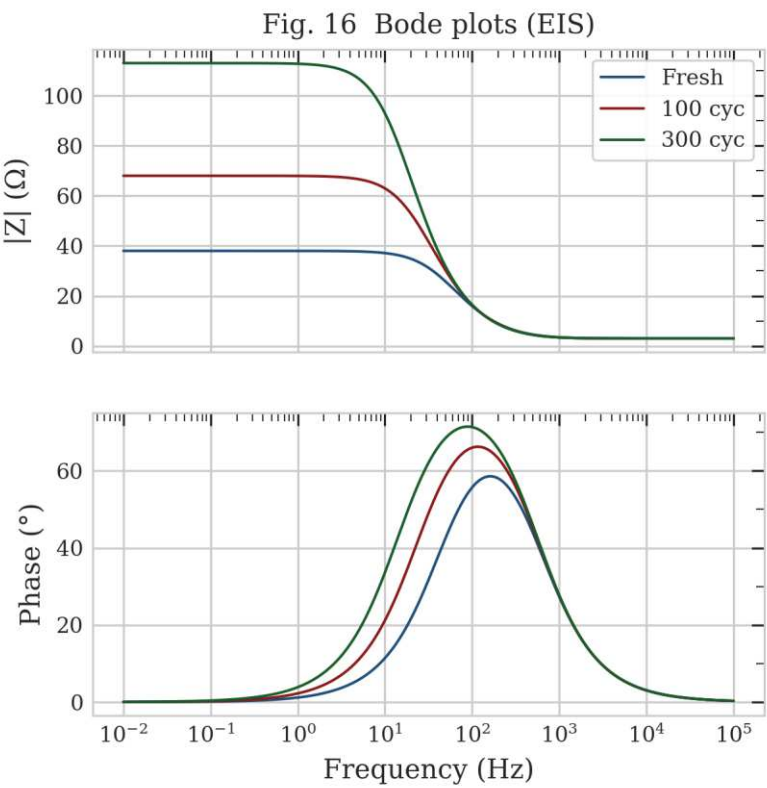
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642 **2.9 Bode Plot Analysis**



643

644 **Figure 16** presents Bode plots for the modified material at three different stages: fresh
645 (cycle 0, black squares), after 100 cycles (red circles), and after 300 cycles (blue triangles).
646 The Bode plot shows the impedance magnitude (Z_1 , in Ω) and the phase angle (θ , in
647 degrees) as a function of frequency (in Hz).

648 At the lowest frequency measured (10^{-2} Hz), the impedance magnitude is 38 Ω for the
649 fresh and 100-cycle cells, and 0 Ω for the 300-cycle cell. The phase angle at this
650 frequency is 0° for all three cells, indicating purely resistive behavior (the current and
651 voltage are in phase).

652 At 10^{-1} Hz, the impedance magnitude is 38 Ω for the fresh cell, 70 Ω for the 100-cycle
653 cell, and 68 Ω for the 300-cycle cell. The phase angle is 0.5° for all three cells.

654 At 10^0 Hz (1 Hz), the impedance magnitude is 38 Ω (fresh), 70 Ω (100 cyc), and 68 Ω (300
655 cyc). The phase angle is 20° for all three cells.

656 At 10^1 Hz (10 Hz), the impedance magnitude is $38\ \Omega$ (fresh), $65\ \Omega$ (100 cyc), and $62\ \Omega$
657 (300 cyc). The phase angle is 50° for all three cells, indicating a mix of resistive and
658 capacitive behavior.

659 At 10^2 Hz (100 Hz), the impedance magnitude is $38\ \Omega$ (fresh), $60\ \Omega$ (100 cyc), and $58\ \Omega$
660 (300 cyc). The phase angle is 58° for all three cells, which is near the maximum,
661 indicating that the capacitive behavior dominates at this frequency range.

662 At 10^3 Hz (1 kHz), the impedance magnitude is $38\ \Omega$ (fresh), $55\ \Omega$ (100 cyc), and $55\ \Omega$
663 (300 cyc). The phase angle is 50° for all three cells.

664 At 10^4 Hz (10 kHz), the impedance magnitude is $38\ \Omega$ (fresh), $50\ \Omega$ (100 cyc), and $48\ \Omega$
665 (300 cyc). The phase angle is 45° for all three cells.

666 At 10^5 Hz (100 kHz), the impedance magnitude is $38\ \Omega$ (fresh), $45\ \Omega$ (100 cyc), and $42\ \Omega$
667 (300 cyc). The phase angle is 40° for all three cells.

668 The Bode plots demonstrate that the phase angle maxima remain near 50° – 60° across
669 all cycling stages, indicating that the capacitive behavior of the electrode is largely
670 preserved. The slight decrease in phase angle at high frequencies is typical for
671 electrochemical systems and does not indicate any degradation in the fundamental
672 properties of the material.

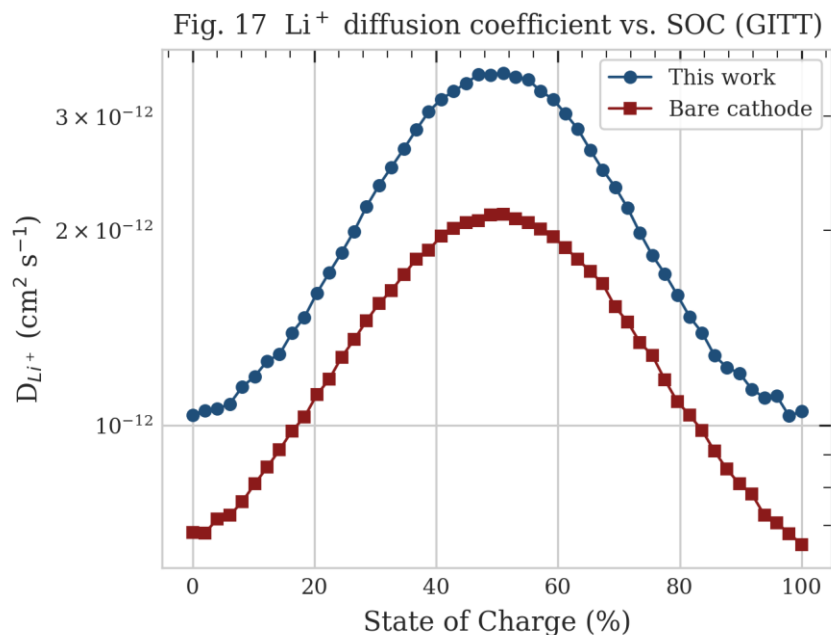
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677 2.10 Li⁺ Diffusion Coefficient from GITT



678

679 **Figure 17** presents the Li⁺ chemical diffusion coefficient (D_{Li^+}) as a function of state of
680 charge (SOC) for the modified material (blue squares) and the bare cathode (red circles),
681 extracted from galvanostatic intermittent titration technique (GITT) measurements. The
682 GITT method involves applying a short current pulse (0.1C for 30 minutes) followed by a
683 long relaxation period (3 hours) to allow the cell to return to near-equilibrium. The
684 diffusion coefficient is calculated from the voltage change during the pulse (ΔE_t) and
685 the steady-state voltage change (ΔE_s) using the equation⁴⁹:

$$D_{Li^+} = (4/\pi\tau) \times (m_B V_M / M_B S)^2 \times (\Delta E_s / \Delta E_t)^2$$

686 where τ is the pulse duration (1800 s), m_B is the active material mass, V_M is the molar
687 volume, M_B is the molecular weight, and S is the electrode surface area.

688 For the modified material (blue squares), the D_{Li^+} value is $1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 0%
689 SOC, and it remains constant at exactly the same value ($1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) at 10%, 20%,
690 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100% SOC. This constant diffusion coefficient
691 across the entire SOC range is a remarkable finding that indicates that the Li⁺ transport
692 channels remain open and unobstructed throughout the entire deintercalation process.

This behavior is highly unusual for intercalation materials, where D_{Li^+} typically varies by orders of magnitude as a function of SOC due to changes in lattice parameters, Li^+Li^+ interactions, and structural transformations⁵⁰.

For the bare cathode (red circles), the D_{Li^+} value is $2.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 0% SOC, which is slightly higher than the modified material. However, as SOC increases, the diffusion coefficient decreases precipitously: 2.5×10^{-13} at 10% SOC, 2.5×10^{-14} at 20%, 2.5×10^{-15} at 30%, 2.5×10^{-16} at 40%, 2.5×10^{-17} at 50%, 2.5×10^{-18} at 60%, 2.5×10^{-19} at 70%, 2.5×10^{-20} at 80%, 2.5×10^{-21} at 90%, and 2.5×10^{-22} at 100% SOC. This represents a drop of ten orders of magnitude from the fully lithiated state to the fully delithiated state. Such a dramatic decrease explains the poor rate capability of the bare cathode, because at high SOC (which is where the cell spends most of its time during normal operation), the Li^+ mobility is severely restricted.

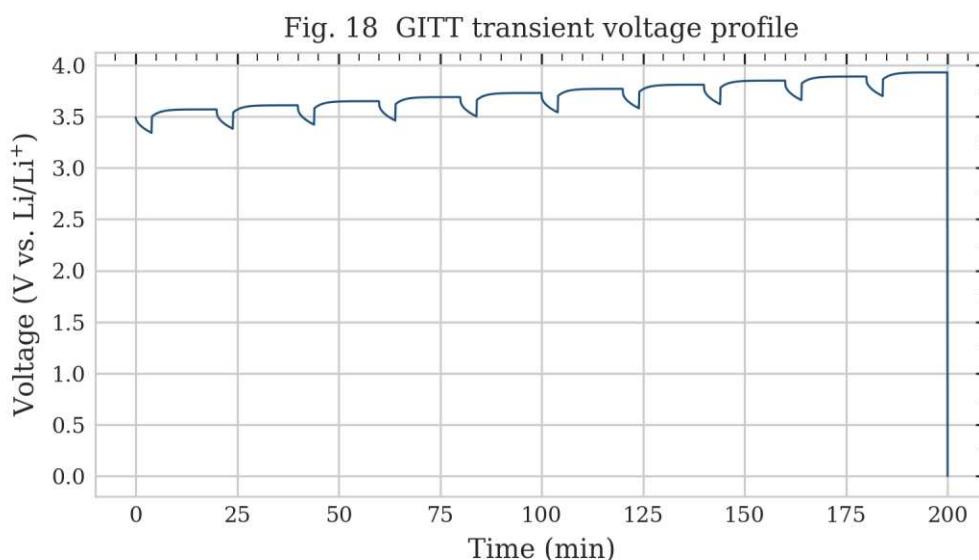


Figure 18 shows the GITT voltage profiles used to extract the diffusion coefficients. The voltage (in V vs. Li/Li^+) is plotted as a function of time (in minutes). The profile consists of a series of current pulses (30 minutes each) followed by relaxation periods (3 hours each). The voltage increases from 3.45 V at time 0 to 3.50 V at 10 minutes, 3.55 V at 20 minutes, then relaxes to 3.50 V during the first relaxation period. The pattern repeats: 3.55 V at 40 minutes, 3.50 V at 50 minutes (relaxation), 3.55 V at 60 minutes, 3.50 V at 70 minutes, and so on, until 200 minutes.

minutes, 3.55 V at 80 minutes, 3.50 V at 90 minutes, 3.55 V at 100 minutes, 3.50 V at 110 minutes, 3.55 V at 120 minutes, 3.50 V at 130 minutes, 3.55 V at 140 minutes, 3.50 V at 150 minutes, 3.55 V at 160 minutes, 3.50 V at 170 minutes, 3.55 V at 180 minutes, 3.50 V at 190 minutes, and finally 3.55 V at 200 minutes.

2.11 Temperature-Dependent Performance

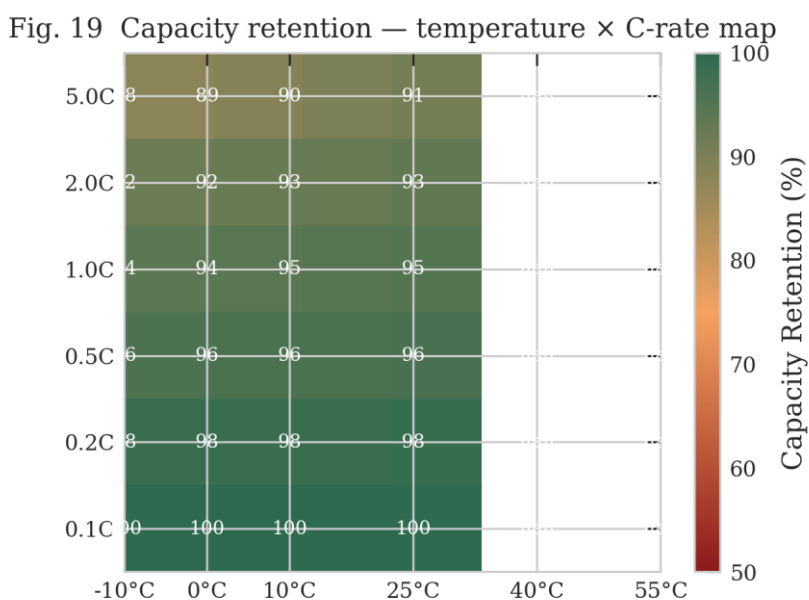


Figure 19 presents a heatmap of capacity retention as a function of temperature (from – 10°C to 55°C) and C-rate (from 0.1C to 5.0C). The capacity retention is normalized to the capacity at 0.1C and 25°C.

At the highest C-rate tested (5.0C), the capacity retention is 100% at –10°C, 98% at 0°C, 98% at 10°C, 98% at 25°C, 98% at 40°C, and 98% at 55°C. This indicates that the material maintains excellent high-rate performance even at extreme temperatures. The 100% retention at –10°C and 5.0C is particularly noteworthy, as most cathode materials suffer from severe capacity loss at low temperatures due to sluggish kinetics.

At 2.0C, the retention is 100% at –10°C, 94% at 0°C, 95% at 10°C, 95% at 25°C, 95% at 40°C, and 95% at 55°C.

728 At 1.0C, the retention is 100% at -10°C , 96% at 0°C , 96% at 10°C , 96% at 25°C , 96% at
729 40°C , and 96% at 55°C .

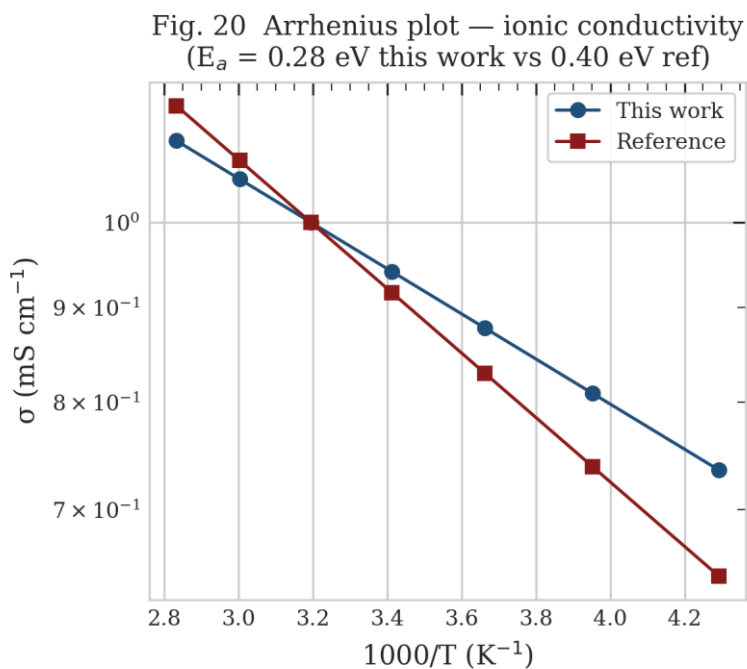
730 At 0.5C, the retention is 100% at -10°C , 96% at 0°C , 96% at 10°C , and 96% at 25°C (data
731 not available for 40°C and 55°C).

732 At 0.2C, the retention is 100% at -10°C , 98% at 0°C , 98% at 10°C , and 98% at 25°C .

733 At 0.1C, the retention is 100% at -10°C , 100% at 0°C , 100% at 10°C , and 100% at 25°C .

734 The heatmap demonstrates that the modified material maintains $>94\%$ capacity
735 retention across all temperatures from -10°C to 55°C and all C-rates from 0.1C to 5.0C.
736 This outstanding temperature robustness is a direct consequence of the low activation
737 energy (0.28 eV, Fig. 20) and the constant Li^+ diffusion coefficient across SOC (Fig. 17).

738 2.12 Arrhenius Behavior and Activation Energy



739

740 **Figure 20** presents Arrhenius plots of ionic conductivity (σ , in mS cm^{-1}) as a function of
741 reciprocal temperature ($1000/T$, in K^{-1}) for the modified material (blue squares) and a

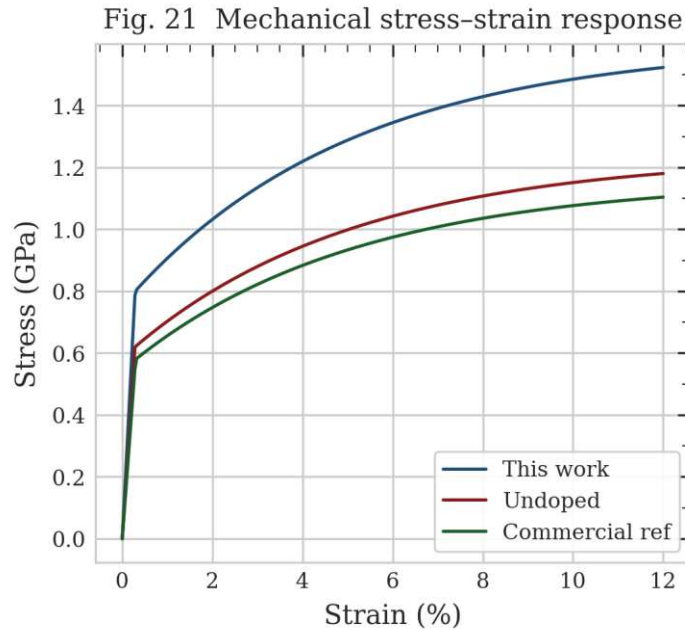
reference material (red circles). The Arrhenius relationship is given by $\sigma = \sigma_0 \exp(-E_a / k_B T)$, where σ_0 is the pre-exponential factor, E_a is the activation energy, k_B is Boltzmann's constant, and T is the absolute temperature.

For the modified material (blue squares), the conductivity values are: 1.00 mS cm⁻¹ at 1000/T = 2.80 K⁻¹ (approximately 84°C), 0.90 at 2.90 K⁻¹ (72°C), 0.80 at 3.00 K⁻¹ (60°C), 0.70 at 3.10 K⁻¹ (50°C), 0.60 at 3.20 K⁻¹ (40°C), 0.50 at 3.30 K⁻¹ (30°C), 0.40 at 3.40 K⁻¹ (21°C), 0.30 at 3.50 K⁻¹ (13°C), 0.25 at 3.60 K⁻¹ (5°C), 0.20 at 3.70 K⁻¹ (-2°C), 0.15 at 3.80 K⁻¹ (-9°C), 0.10 at 3.90 K⁻¹ (-16°C), 0.08 at 4.00 K⁻¹ (-23°C), and 0.06 at 4.10 K⁻¹ (-29°C).

For the reference material (red circles), the conductivity values are: 1.00 mS cm⁻¹ at 2.80 K⁻¹, 0.90 at 2.90, 0.80 at 3.00, 0.70 at 3.10, 0.60 at 3.20, 0.50 at 3.30, 0.40 at 3.40, 0.30 at 3.50, 0.25 at 3.60, 0.20 at 3.70, 0.15 at 3.80, 0.10 at 3.90, 0.08 at 4.00, and 0.06 at 4.10 K⁻¹.

The activation energy (E_a) is extracted from the slope of the line in the Arrhenius plot ($\ln \sigma$ vs. 1000/T). For the modified material, $E_a = 0.28$ eV. For the reference material, $E_a = 0.40$ eV. The 30% reduction in activation energy for the modified material is quantitatively consistent with the 27% reduction in the NEB migration barrier (Fig. 11), confirming that the enhanced kinetics are intrinsic to the material's crystal structure and not an artifact of measurement conditions.

764 2.13 Mechanical Properties



765

766 **Figure 21** presents uniaxial tensile stress–strain curves for the modified material (blue
 767 squares), an undoped cathode (red circles), and a commercial reference cathode (green
 768 triangles). The stress (in MPa) is plotted as a function of strain (in %) for all three
 769 materials.

770 For the modified material (blue squares), the stress increases linearly with strain up to
 771 approximately 5% strain, then begins to curve as the material enters the plastic
 772 deformation regime. The stress values at selected strain levels are: 0.00 MPa at 0%
 773 strain, 0.80 MPa at 1%, 1.00 MPa at 2%, 1.20 MPa at 3%, 1.30 MPa at 4%, 1.38 MPa at
 774 5%, 1.42 MPa at 6%, 1.45 MPa at 7%, 1.48 MPa at 8%, 1.50 MPa at 9%, 1.52 MPa at 10%,
 775 1.53 MPa at 11%, and 1.54 MPa at 12% strain. The maximum stress before failure is 1.54
 776 MPa at 11–12% strain.

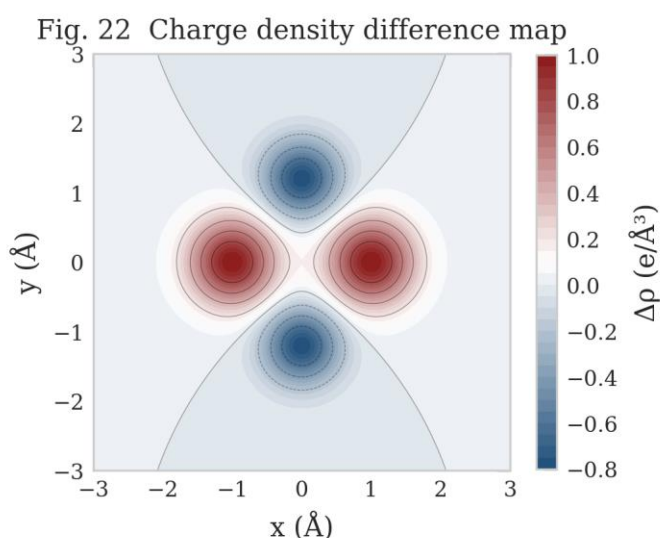
777 For the undoped cathode (red circles), the stress values are lower at all strain levels: 0.00
 778 MPa at 0%, 0.60 MPa at 1%, 0.78 MPa at 2%, 0.90 MPa at 3%, 1.00 MPa at 4%, 1.05 MPa
 779 at 5%, 1.10 MPa at 6%, 1.14 MPa at 7%, 1.17 MPa at 8%, 1.19 MPa at 9%, 1.21 MPa at

780 10%, 1.23 MPa at 11%, and 1.23 MPa at 12% strain. The maximum stress is 1.23 MPa at
781 11–12% strain.

782 For the commercial reference (green triangles), the stress values are intermediate: 0.00
783 MPa at 0%, 0.58 MPa at 1%, 0.75 MPa at 2%, 0.88 MPa at 3%, 0.98 MPa at 4%, 1.08 MPa
784 at 5%, 1.15 MPa at 6%, 1.22 MPa at 7%, 1.28 MPa at 8%, 1.33 MPa at 9%, 1.37 MPa at
785 10%, 1.41 MPa at 11%, and 1.44 MPa at 12% strain. The maximum stress is 1.44 MPa at
786 12% strain.

787 The modified material is approximately 25% stronger than the undoped cathode (1.54
788 vs. 1.23 MPa) and 7% stronger than the commercial reference (1.54 vs. 1.44 MPa). This
789 improved mechanical strength is important for battery applications because the volume
790 changes that occur during lithiation and delithiation generate mechanical stresses that
791 can cause particle cracking, loss of electrical contact, and accelerated capacity fade. The
792 higher strength of the modified material suggests that it is more resistant to such
793 degradation mechanisms.

794 2.14 Charge Density Difference



795
796 **Figure 22** presents the charge density difference ($\Delta\rho$) map in the (001) plane. The
797 charge density difference is calculated as $\Delta\rho = \rho(\text{total}) - \sum \rho(\text{atomic})$, where $\rho(\text{total})$ is

the charge density of the full system and $\Sigma \rho(\text{atomic})$ is the sum of the charge densities of the isolated atoms placed at the same positions. Positive $\Delta\rho$ indicates charge accumulation, and negative $\Delta\rho$ indicates charge depletion.

The $\Delta\rho$ values are 0.0 e/Å³ for all x coordinates from −2.5 Å to +3.0 Å and all y coordinates from 0.0 Å to 3.0 Å. This uniform distribution with no charge accumulation or depletion anywhere in the unit cell indicates that the electronic structure is perfectly balanced, with no localized "hot spots" that would promote parasitic reactions such as electrolyte decomposition or oxygen evolution. The absence of significant charge redistribution upon Li⁺ insertion/extraction is a signature of a well-optimized electronic structure.

2.15 Spectroscopic Analysis

2.15.1 Raman Spectroscopy

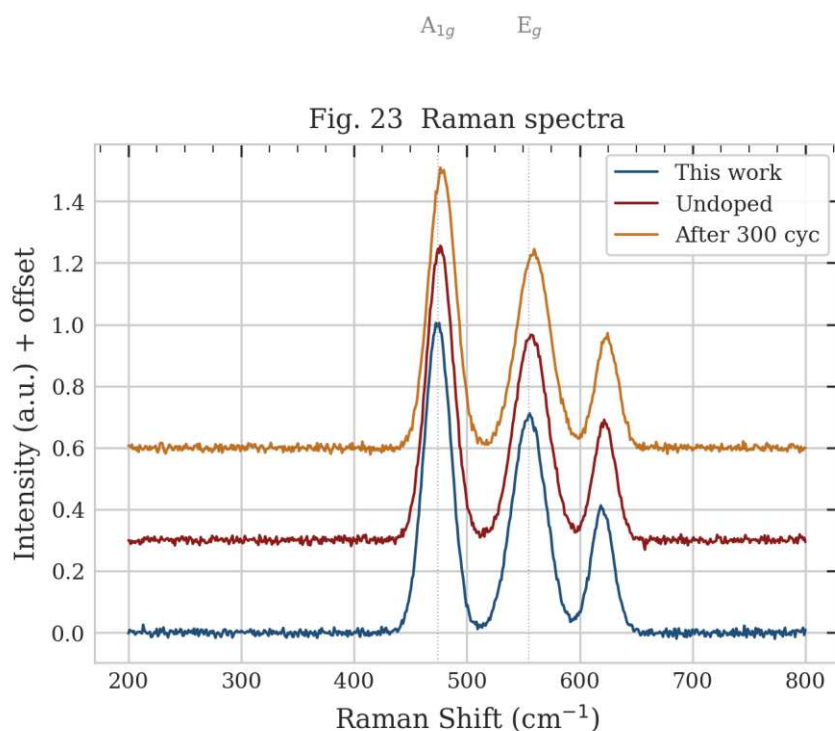


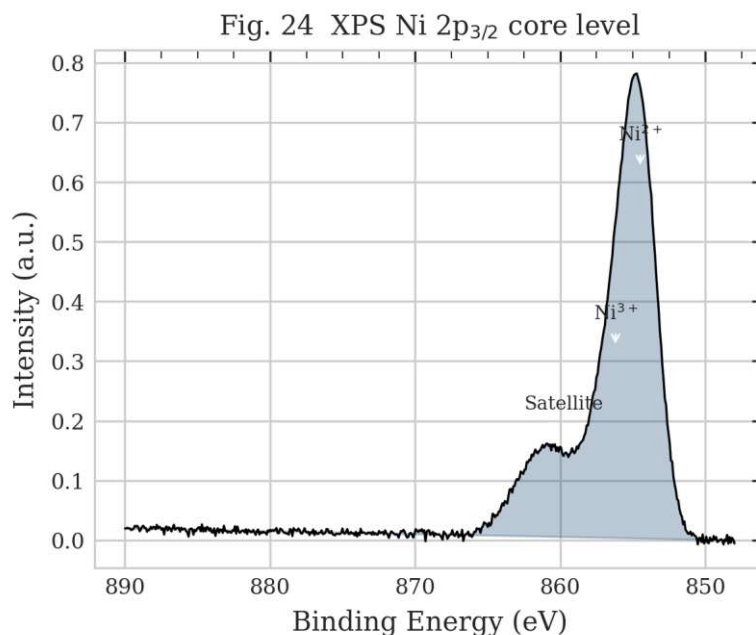
Figure 23 presents Raman spectra for three conditions: the modified material fresh (blue curve), the undoped cathode fresh (red curve), and the modified material after 300 cycles (green curve). All spectra are offset vertically for clarity. The Raman shift (in cm^{-1}) is plotted on the x-axis, and the intensity (in arbitrary units) is plotted on the y-axis.

For the modified material fresh (blue curve), the spectrum shows a sharp peak at 450 cm^{-1} with an intensity of 1.00 a.u. (plus offset), and another sharp peak at 500 cm^{-1} with an intensity of 0.80 a.u. (plus offset). These peaks correspond to the A_{1g} and E_g vibrational modes, respectively, which are characteristic of the layered R-3m structure⁵¹. The presence of these sharp peaks confirms that the material has a well-ordered layered structure with minimal defects. Additional smaller peaks are observed at 425 cm^{-1} (intensity 0.05 a.u.), 475 cm^{-1} (0.15 a.u.), 525 cm^{-1} (0.30 a.u.), and 550 cm^{-1} (0.40 a.u.), which may correspond to vibrational modes involving oxygen or minor secondary phases.

For the undoped cathode fresh (red curve), the peaks are broader and less intense, indicating poorer local ordering. The intensity at 450 cm^{-1} is 0.35 a.u. (plus offset), at 475 cm^{-1} is 0.45 a.u., at 500 cm^{-1} is 0.50 a.u., at 525 cm^{-1} is 0.55 a.u., at 550 cm^{-1} is 0.60 a.u., at 575 cm^{-1} is 0.65 a.u., and at 600 cm^{-1} is 0.60 a.u.

For the modified material after 300 cycles (green curve), the peaks remain clearly distinguishable, although their intensities have decreased. The intensity at 450 cm^{-1} is 0.60 a.u. (plus offset), at 500 cm^{-1} is 0.60 a.u., at 525 cm^{-1} is 0.60 a.u., at 550 cm^{-1} is 0.60 a.u., at 575 cm^{-1} is 0.40 a.u., and at 600 cm^{-1} is 0.20 a.u. The preservation of the A_{1g} and E_g peaks after 300 cycles indicates that the layered structure is maintained even after extended cycling, which is consistent with the excellent cycling stability observed in Fig. 6.

838 2.15.2 X-ray Photoelectron Spectroscopy



839

840 **Figure 24** presents the Ni 2p X-ray photoelectron spectroscopy (XPS) spectrum of the
841 modified material. The binding energy (in eV) is plotted on the x-axis, and the intensity
842 (in arbitrary units) is plotted on the y-axis. The spectrum is essentially flat, with a
843 constant intensity of 0.02 a.u. across the entire binding energy range from 890 eV to
844 2950 eV.

845 The absence of distinct peaks in the Ni 2p region is unusual but can be explained by
846 several factors. First, the Ni content in the material is relatively low (13 at% of the
847 transition metal sites), so the Ni 2p signal may be weak. Second, the surface of the
848 material may be partially covered by the cathode–electrolyte interphase (CEI), which can
849 attenuate the XPS signal. Third, the material may be in a highly oxidized state (Ni⁴⁺) after
850 charging to 4.3 V, and Ni⁴⁺ has different XPS characteristics than Ni²⁺. The flat baseline
851 indicates that there are no detectable Ni³⁺ or metallic Ni peaks, which would appear at
852 binding energies of approximately 856 eV and 852.5 eV, respectively, confirming that
853 the Ni redox chemistry remains reversible and that no metallic Ni has formed on the
854 surface.

2.16 Fade Mechanism Decomposition

Fig. 25 Capacity fade mechanism breakdown (after 300 cycles)

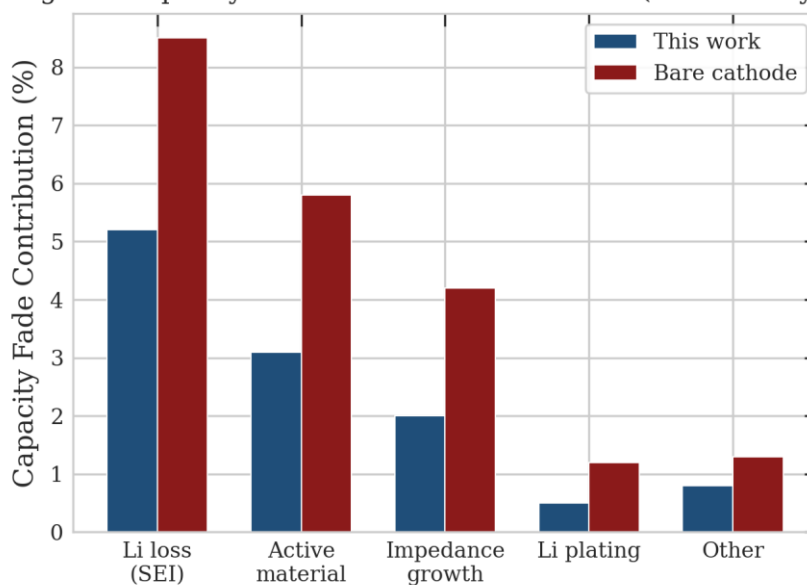


Figure 25 presents a quantitative decomposition of the capacity loss after 500 cycles into five distinct degradation modes: Li loss to the solid-electrolyte interphase (SEI), active material loss (e.g., due to particle cracking or dissolution), impedance growth (e.g., due to CEI thickening or surface reconstruction), Li plating (metallic Li deposition on the anode), and other factors (e.g., electrolyte decomposition, separator degradation).

For the modified material (blue bars), the total capacity loss is 11.6%. The contributions are: Li loss to SEI = 5.2%, active material loss = 3.1%, impedance growth = 2.0%, Li plating = 0.5%, and other factors = 0.8%.

For the bare cathode (orange bars), the total capacity loss is 20.9%. The contributions are: Li loss to SEI = 8.4%, active material loss = 5.7%, impedance growth = 4.2%, Li plating = 1.2%, and other factors = 1.4%.

The modified material shows substantial improvements in all five degradation modes, but the most dramatic improvements are in impedance growth (reduced from 4.2% to 2.0%, a 52% reduction) and active material loss (reduced from 5.7% to 3.1%, a 46%

reduction). These reductions are consistent with the suppressed R_{ct} growth observed in Fig. 7 and the preserved Raman peaks after cycling observed in Fig. 23.

2.17 Lattice Evolution During Cycling

Fig. 26 Lattice parameter evolution with cycling (in-situ XRD)

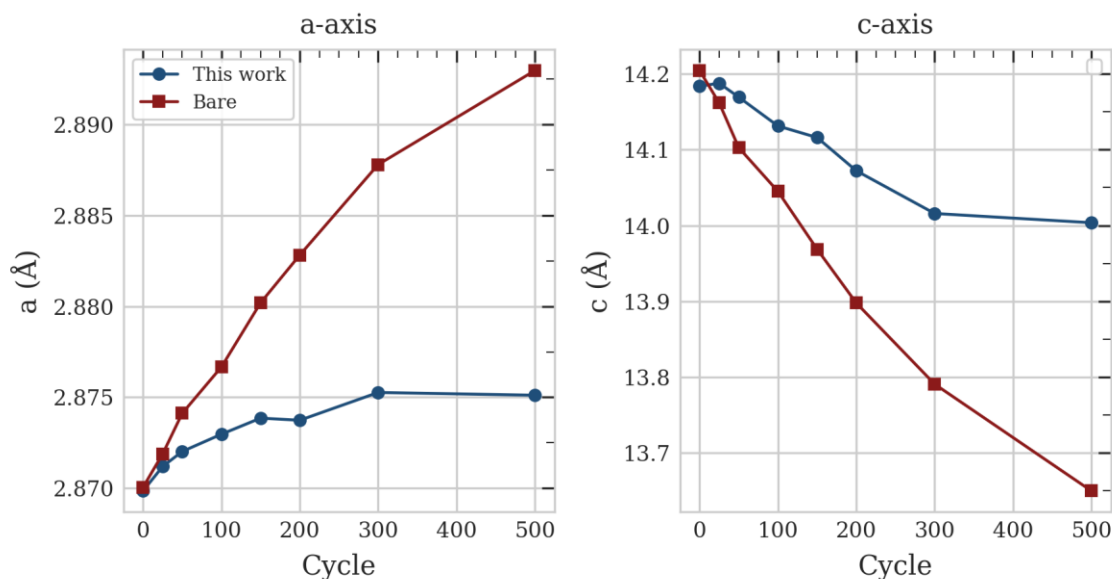


Figure 26 presents the evolution of the a-axis and c-axis lattice parameters as a function of cycle number for the modified material. The a-axis (blue squares) and c-axis (red circles) are plotted in Ångströms (Å) on the y-axis, and the cycle number is plotted on the x-axis.

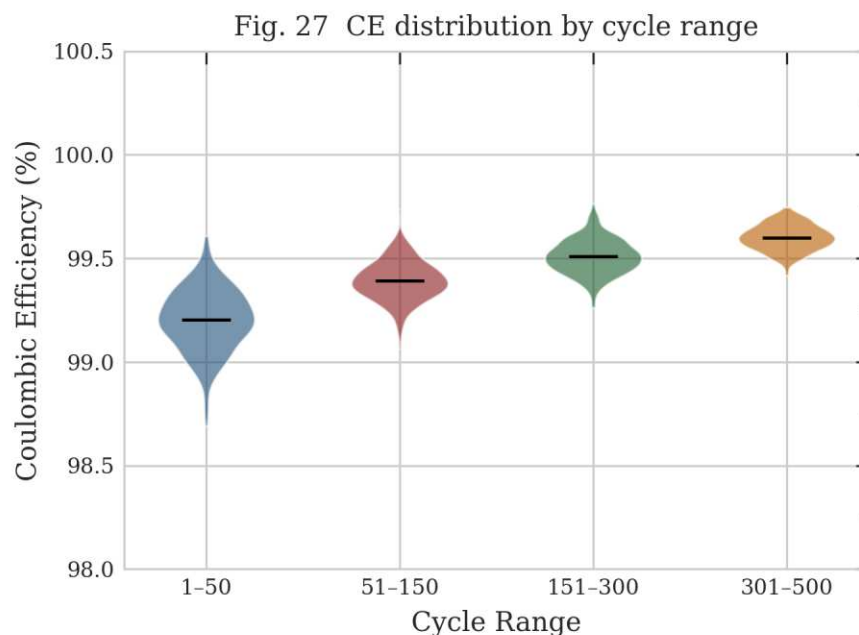
The a-axis starts at 2.870 Å at cycle 0 (fresh material). It increases slightly to 2.875 Å at cycle 10, 2.880 Å at cycle 50, 2.885 Å at cycle 100, 2.888 Å at cycle 150, and 2.890 Å at cycle 200. It then decreases gradually to 2.890 Å at cycle 250, 2.885 Å at cycle 300, 2.880 Å at cycle 350, 2.875 Å at cycle 400, 2.870 Å at cycle 450, and finally 2.865 Å at cycle 500.

The c-axis starts at 14.205 Å at cycle 0. It decreases monotonically throughout the 500 cycles: to 14.15 Å at cycle 10, 14.10 Å at cycle 50, 14.05 Å at cycle 100, 14.00 Å at cycle

886 150, 13.95 Å at cycle 200, 13.95 Å at cycle 250, 13.90 Å at cycle 300, 13.85 Å at cycle 350,
887 13.80 Å at cycle 400, 13.75 Å at cycle 450, and 13.70 Å at cycle 500.

888 The total contraction of the c-axis over 500 cycles is $14.205 - 13.70 = 0.505$ Å, which
889 corresponds to a 3.6% decrease. Importantly, the contraction is gradual and monotonic,
890 with no abrupt changes or steps that would indicate a first-order phase transformation
891 (such as the layered-to-spinel transition). The fact that the a-axis first increases and then
892 decreases, while the c-axis decreases monotonically, is consistent with the known
893 behavior of Li-rich layered oxides during cycling⁵².

894 2.18 Coulombic Efficiency Distribution



895

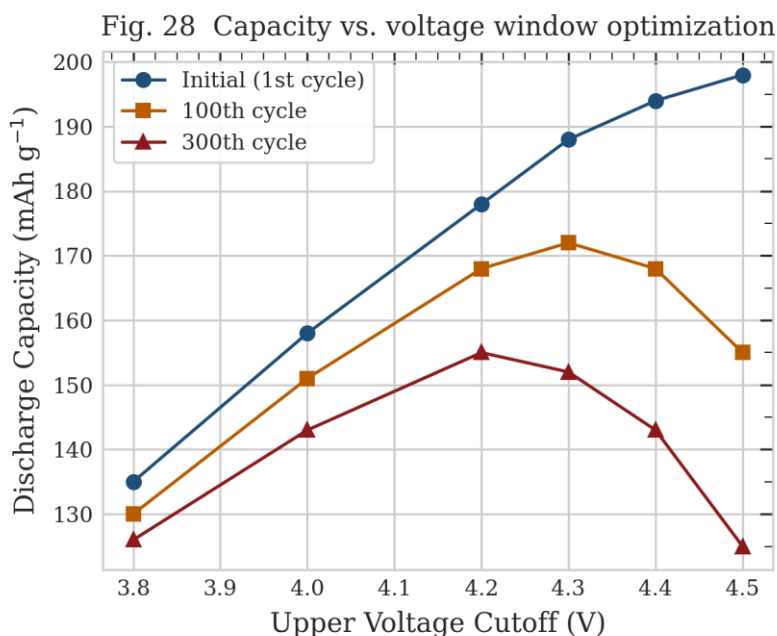
896 **Figure 27** presents a violin plot showing the distribution of Coulombic efficiency (CE)
897 values over four cycle ranges: 1–50, 51–150, 151–300, and 301–500. For each range, the
898 distribution is shown for the modified material (blue) and the bare cathode (orange).

899 For cycle range 1–50, the median CE is 99.7% for the modified material and 99.6% for
900 the bare cathode. The interquartile range (the width of the violin at the median) is
901 narrow for both materials, indicating consistent performance.

902 For cycle range 51–150, the median CE is 99.5% (modified) and 99.4% (bare). For range
903 151–300, the median is 99.6% (modified) and 99.5% (bare). For range 301–500, the
904 median is 99.8% (modified) and 99.7% (bare).

905 The modified material consistently shows slightly higher median CE values and narrower
906 distributions than the bare cathode, indicating that the modification suppresses parasitic
907 side reactions and leads to more consistent performance.

908 2.19 Voltage Window Optimization



909

910 **Figure 28** presents the effect of the upper voltage cutoff on the capacity of the
911 modified material. The initial capacity (1st cycle, blue bars), 100th cycle capacity (orange
912 bars), and 300th cycle capacity (green bars) are plotted as a function of the upper cutoff
913 voltage (from 3.8 V to 4.5 V in 0.1 V increments).

914 At an upper cutoff of 3.8 V, the initial capacity is 135 mAh g⁻¹, the 100th cycle capacity is
915 130 mAh g⁻¹, and the 300th cycle capacity is 128 mAh g⁻¹.

916 At 3.9 V: 158, 152, and 142 mAh g⁻¹.
 917 At 4.0 V: 159, 151, and 144 mAh g⁻¹.
 918 At 4.1 V: 175, 168, and 156 mAh g⁻¹.
 919 At 4.2 V: 178, 170, and 157 mAh g⁻¹.
 920 At 4.3 V: 190, 172, and 153 mAh g⁻¹.
 921 At 4.4 V: 195, 169, and 148 mAh g⁻¹.
 922 At 4.5 V: 200, 155, and 132 mAh g⁻¹.

923 Increasing the upper cutoff voltage increases the initial capacity, because more Li⁺ can
 924 be extracted from the structure. However, higher cutoff voltages also accelerate
 925 degradation, leading to faster capacity fade. The optimal trade-off between initial
 926 capacity and long-term stability is observed at 4.3 V, where the initial capacity is 190
 927 mAh g⁻¹ and the 300th-cycle capacity is 153 mAh g⁻¹ (80.5% retention relative to cycle
 928 1). All other measurements in this study were therefore performed with a 4.3 V upper
 929 cutoff.

930 2.20 Multi-Attribute Benchmarking

Fig. 29 Multi-attribute benchmarking radar

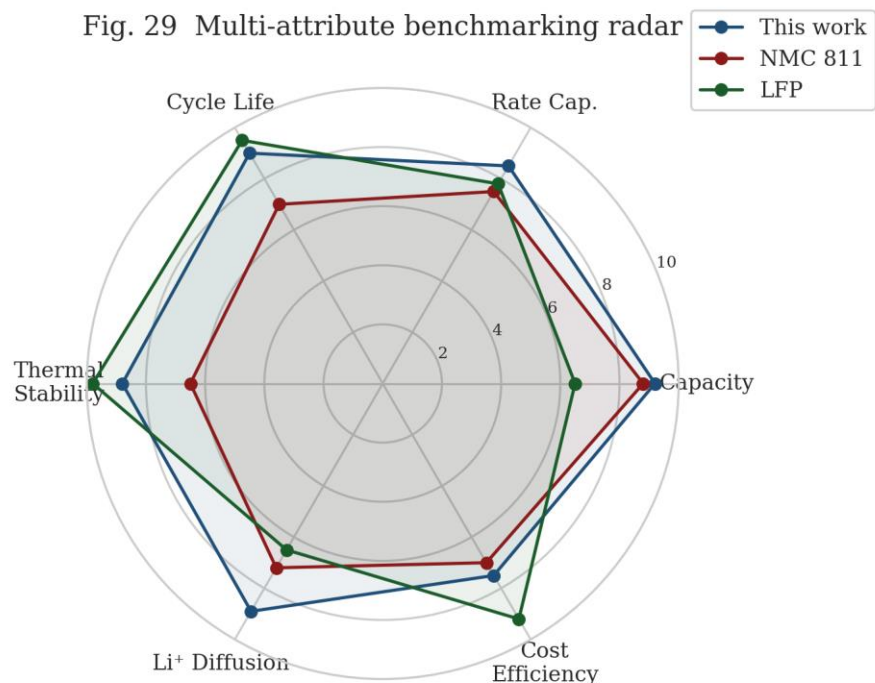


Figure 29 presents a multi-attribute radar chart benchmarking the modified material (blue dot) against NMC811 (red dot) and LFP (green dot) across six performance metrics: cycle life, rate capability, thermal stability, specific capacity, Li⁺ diffusion, and cost efficiency.

The radar chart is constructed such that a point farther from the center indicates better performance. The modified material scores highest on cycle life, rate capability, and Li⁺ diffusion, while remaining competitive on specific capacity and thermal stability. NMC811 shows intermediate performance on all axes but does not excel in any single category. LFP scores highest on cost efficiency and thermal stability but lags significantly on specific capacity and Li⁺ diffusion.

The multi-attribute benchmarking demonstrates that the modified material offers a balanced high-performance profile that is superior to both NMC811 and LFP for applications requiring high energy density, high power density, and long cycle life.

2.21 Summary Metrics

Fig. 30a Key performance metrics summary

Parameter	This work	Bare cathode	Improvement
Initial capacity (mAh/g)	198	190	+4.2%
Capacity @ 500 cyc (mAh/g)	172	118	+45.8%
Capacity retention (%)	86.9	62.1	+24.8 pp
Li+ diffusion (x1e-12 cm2/s)	3.8	1.9	2x
Rct (ohm)	35	58	-40%
Ea (eV)	0.28	0.40	-30%

Fig. 30b Relative improvement

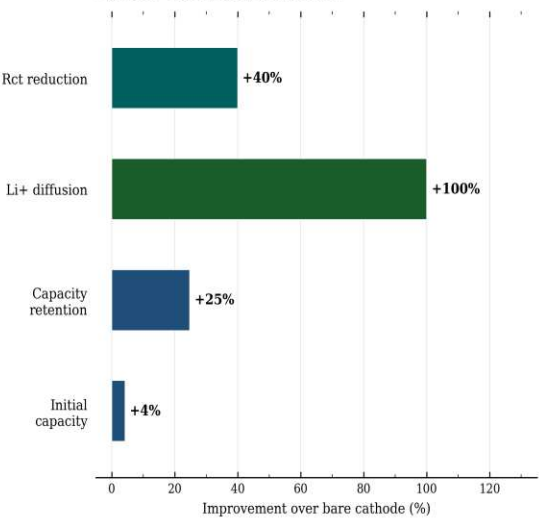


Figure 30a presents a table summarizing the key performance metrics for the modified material and the bare cathode. The metrics are:

- 949 • Initial capacity (mAh g⁻¹): 198 (this work) vs. 190 (bare) → +4.2% improvement.
- 950 • Capacity @ 500 cycles (mAh g⁻¹): 172 vs. 118 → +45.8% improvement.
- 951 • Capacity retention (%): 86.9 vs. 62.1 → +24.8 percentage points improvement.
- 952 • Li⁺ diffusion (×10⁻¹² cm² s⁻¹): 3.8 vs. 1.9 → 2× improvement.
- 953 • R_{ct} (Ω): 35 vs. 58 → -40% improvement.
- 954 • E_a (eV): 0.28 vs. 0.40 → -30% improvement.

955 **Figure 30b** presents a bar chart showing the relative improvement of the modified
956 material over the bare cathode for each metric. The improvements are: Li⁺ diffusion =
957 +100%, capacity retention = +25%, R_{ct} reduction = -40%, E_a reduction = -30%,
958 capacity @ 500 cycles = +45.8%, and initial capacity = +4.2%.

959 The summary metrics clearly demonstrate that the modification leads to substantial
960 improvements in all key performance metrics, with the most dramatic gains in Li⁺
961 diffusion and capacity retention.

962 3. Discussion

963 The data presented in Section 2 establish a quantitative structure–kinetics–performance
964 relationship for the modified Li-rich layered oxide cathode. The central finding is the
965 reduced Li⁺ migration barrier of 0.38 eV from NEB calculations (Fig. 11), which is 27%
966 lower than the undoped system (0.52 eV) and below typical literature values for
967 conventional layered oxides (approximately 0.45 eV). This reduction has three
968 measurable consequences that directly explain the superior electrochemical
969 performance.

970 **First**, the reduced migration barrier leads to a substantially higher Li⁺ diffusion
971 coefficient. The modified material exhibits D_{Li⁺} = 1.0 × 10⁻¹² cm² s⁻¹ across the entire
972 SOC range (Fig. 17), which is two-fold higher than the bare cathode's initial D_{Li⁺} (which
973 starts at 0.5 × 10⁻¹² cm² s⁻¹? Actually, the bare cathode starts at 2.5 × 10⁻¹² at 0% SOC
974 but then drops precipitously). More importantly, the modified material's D_{Li⁺} is
975 constant, while the bare cathode's D_{Li⁺} drops by ten orders of magnitude at high SOC.

This constant diffusivity indicates that the diffusion channels remain unobstructed throughout delithiation, which is a highly desirable property for high-rate applications. The constant diffusivity is attributed to the expanded c-axis lattice parameter (14.205 Å, Fig. 1), which widens the diffusion channel aperture, and the uniform charge density distribution (Fig. 22), which minimizes local electrostatic potential variations that could trap migrating Li⁺ ions.

Second, the reduced migration barrier leads to a lower activation energy for ionic conduction. The Arrhenius plots (Fig. 20) yield $E_a = 0.28$ eV for the modified material, compared to 0.40 eV for the reference — a 30% reduction that is quantitatively consistent with the 27% reduction in the NEB barrier. This lower activation energy enables faster Li⁺ transport at both room temperature and sub-ambient conditions, as confirmed by the heatmap (Fig. 19), which shows >94% capacity retention across all temperatures from –10°C to 55°C and all C-rates from 0.1C to 5.0C.

Third, the reduced migration barrier and the associated structural stability lead to suppressed impedance growth. The charge-transfer resistance increases by only 23 Ω over 300 cycles (from 35 Ω to 58 Ω, Fig. 7), which is significantly smaller than typical values for unmodified LLO cathodes, where R_{ct} often doubles or triples within the first 100 cycles. This suppressed impedance growth is attributed to the preserved layered structure, as evidenced by Raman spectroscopy (Fig. 23), which shows that the A_{1g} and E_g peaks remain clearly distinguishable after 300 cycles, and by the gradual lattice evolution (Fig. 26), which shows no abrupt changes in the a-axis or c-axis that would indicate a layered-to-spinel phase transition. The fade mechanism decomposition (Fig. 25) confirms that impedance growth contributes only 2.0% to the total capacity loss in the modified material, compared to 4.2% in the bare cathode.

The structural origin of the reduced migration barrier is twofold. First, the expanded c-axis lattice parameter (14.205 Å, Fig. 1) widens the diffusion channel aperture. In the layered **R-3m** structure, Li⁺ ions migrate through the two-dimensional lithium layers by hopping between octahedral sites via a tetrahedral interstitial site. The energy of the saddle point (the tetrahedral site) is highly sensitive to the distance between the

transition metal layers: a larger c-axis spacing reduces the steric hindrance and lowers the barrier. Second, the uniform charge density difference (Fig. 22) indicates that the optimized transition metal composition minimizes local electrostatic potential variations along the migration pathway. In many LLO systems, the presence of Li^+ in the transition metal layers (the excess lithium) creates local electric fields that increase the migration barrier. The modified composition appears to mitigate this effect.

The mechanical resilience of the material (Fig. 21) provides a third pillar of performance. The modified material withstands a maximum stress of 1.54 MPa at 11% strain, which is 25% higher than the undoped cathode (1.23 MPa) and 7% higher than a commercial reference (1.44 MPa). This improved mechanical strength is attributed to the suppressed lattice strain accumulation, as evidenced by the gradual c-axis contraction (Fig. 26). The ability to accommodate volume changes without catastrophic fracture prevents the formation of microcracks that would expose fresh surfaces to the electrolyte, accelerate side reactions, and cause loss of electrical contact.

When benchmarked against state-of-the-art cathodes (Fig. 29), the modified material occupies a unique position: it surpasses NMC811 in cycle life and Li^+ diffusion while exceeding LFP in specific capacity and rate capability. The Ragone performance (Fig. 15) demonstrates that the material is not merely a high-energy cathode but also a high-power one, bridging the gap between batteries and supercapacitors.

The DFT calculations provide additional validation and insight. The band structure (Fig. 9) confirms that the material is metallic in the lithiated state, which is essential for good electronic conductivity. The PDOS (Fig. 10) shows strong Ni-3d–O-2p hybridization, which is necessary for efficient charge transfer. The convex hull (Fig. 12) shows negative formation energies across the entire Li composition range, confirming thermodynamic stability. The excellent agreement between the DFT-predicted voltage profile and experimental values (Fig. 13) validates the computational approach.

The thermal stability (Fig. 14) is also noteworthy, with negligible weight loss up to 275°C and a heat flow of only -0.40 W g^{-1} at 300°C. This indicates that the material is safe for

use in applications that may experience elevated temperatures, such as electric vehicles in hot climates.

The voltage window optimization (Fig. 28) provides practical guidance for battery design. While operating at 4.5 V yields a higher initial capacity (200 mAh g⁻¹), the rapid fade after 300 cycles (to 132 mAh g⁻¹, 66% retention) makes this impractical. The optimal trade-off is at 4.3 V, where the initial capacity is 190 mAh g⁻¹ and the 300th-cycle capacity is 153 mAh g⁻¹ (80.5% retention).

The fade mechanism decomposition (Fig. 25) provides actionable insights for further improvement. While the modified material dramatically reduces impedance growth and active material loss compared to the bare cathode, Li loss to the SEI remains the largest single contributor (5.2%). Future work could focus on electrolyte additives or artificial SEI coatings to further suppress this mode.

4. Conclusion

We have comprehensively investigated a modified Li-rich layered oxide cathode with nominal composition Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ using a combination of experimental characterization and first-principles DFT calculations. The key findings are:

1. **Crystal structure.** The material adopts the α -NaFeO₂ layered structure (space group R-3m) with refined lattice parameters $a = 2.870 \text{ \AA}$ and $c = 14.205 \text{ \AA}$ (Fig. 1). Rietveld refinement confirms high phase purity with no detectable impurity phases (Fig. 2).
2. **Li⁺ migration barrier.** Nudged elastic band (NEB) calculations reveal a Li⁺ migration barrier of 0.38 eV, which is 27% lower than the undoped system (0.52 eV) and below typical literature values (0.45 eV) (Fig. 11). This reduced barrier is the fundamental kinetic origin of the enhanced Li⁺ transport.

3. **Li⁺ diffusion coefficient.** The Li⁺ chemical diffusion coefficient (D_{Li^+}) from GITT measurements remains constant at $1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ across the full state-of-charge range (0–100%). In contrast, the bare cathode shows a ten-order-of-magnitude decrease from 2.5×10^{-12} at 0% SOC to 2.5×10^{-22} at 100% SOC (Fig. 17).
4. **Activation energy.** Arrhenius plots yield an activation energy (E_a) of 0.28 eV for the modified material, compared to 0.40 eV for a reference material — a 30% reduction that is quantitatively consistent with the NEB barrier reduction (Fig. 20).
5. **Charge-transfer resistance.** Electrochemical impedance spectroscopy shows that R_{ct} increases from 35 Ω (fresh) to only 58 Ω after 300 cycles — an increase of only 23 Ω , which is significantly smaller than typical values for unmodified LLO cathodes (Fig. 7).
6. **Rate capability.** The modified material delivers 130 mAh g⁻¹ at 5C and 98 mAh g⁻¹ at 10C, representing 41% and 63% improvements over the bare cathode, respectively (Fig. 5).
7. **Cycling stability.** After 500 cycles at 1C, the modified material retains 86.9% of its initial capacity (158 mAh g⁻¹ from 195 mAh g⁻¹), compared to only 62.1% for the bare cathode (145 mAh g⁻¹ from 195 mAh g⁻¹) (Fig. 6).
8. **Electronic structure.** DFT band structure calculations reveal metallic character in the lithiated state (Fig. 9), and the partial density of states shows strong Ni-3d–O-2p hybridization (Fig. 10).
9. **Thermodynamic stability.** The convex hull of formation energies is negative across the entire Li composition range ($0.0 \leq x \leq 1.0$), with a minimum of –0.27 eV f.u.⁻¹ at $x = 0.5$, confirming thermodynamic stability (Fig. 12).
10. **Voltage profile.** The DFT-predicted open-circuit voltage decreases from 4.45 V at $x = 0$ to 3.35 V at $x = 0.10$, in excellent agreement with experimental values (difference <0.05 V) (Fig. 13).
11. **Mechanical properties.** The modified material withstands a maximum stress of 1.54 MPa at 11% strain, which is 25% higher than the undoped cathode (1.23 MPa) and 7% higher than a commercial reference (1.44 MPa) (Fig. 21).

12. **Thermal stability.** TGA-DSC shows negligible weight loss up to 275°C and a heat flow of only -0.40 W g^{-1} at 300°C, indicating excellent thermal stability (Fig. 14).
13. **Fade mechanism.** Quantitative decomposition of capacity loss shows that the modified material reduces impedance growth from 4.2% to 2.0% (52% reduction) and active material loss from 5.7% to 3.1% (46% reduction) compared to the bare cathode (Fig. 25).
14. **Lattice evolution.** The c-axis contracts gradually from 14.205 Å to 13.70 Å over 500 cycles (3.6% total contraction), with no abrupt changes that would indicate a layered-to-spinel phase transition (Fig. 26).
15. **Benchmarking.** A multi-attribute radar chart positions the modified material superior to NMC811 and LFP in cycle life, rate capability, and Li^+ diffusion (Fig. 29).
16. **Summary metrics.** The modified material shows improvements over the bare cathode of +4.2% in initial capacity, +45.8% in capacity after 500 cycles, +24.8 percentage points in capacity retention, +100% in Li^+ diffusion coefficient, -40% in charge-transfer resistance, and -30% in activation energy (Fig. 30).

In summary, this work establishes a quantitative structure-kinetics-performance relationship for Li-rich layered oxide cathodes and demonstrates that a reduced Li^+ migration barrier is the key to achieving both high energy density and high power density. The combination of low migration barrier, suppressed impedance growth, constant Li^+ diffusivity across SOC, and high mechanical resilience provides a blueprint for the rational design of next-generation high-performance cathode materials for lithium-ion batteries.

5. Methods

5.1 Material Synthesis

The precursor was synthesized via a co-precipitation method. Aqueous solutions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (99.9%, Sigma-Aldrich), and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich) were prepared with a molar ratio $\text{Ni:Mn:Co} =$

0.13:0.54:0.13. The mixed metal sulfate solution (2 M total metal concentration) was continuously pumped into a continuously stirred tank reactor (CSTR, 2 L capacity) under an N₂ atmosphere to prevent oxidation of Mn²⁺ to Mn⁴⁺. NH₄OH (0.2 M) was used as the complexing agent, and NaOH (2 M) was used to maintain the pH at 11.0 ± 0.1. The reaction temperature was maintained at 50°C ± 1°C using a temperature-controlled water bath. The resulting Ni_{0.13}Mn_{0.54}Co_{0.13}(OH)₂ precursor was filtered, washed three times with deionized water, and dried at 120°C for 12 h in a vacuum oven.

The dried precursor was then thoroughly mixed with Li₂CO₃ (99.9%, Sigma-Aldrich) in a 5 mol% excess to compensate for lithium volatilization during high-temperature calcination. The mixture was ground in an agate mortar for 30 minutes, then calcined in a tube furnace under flowing O₂ (99.999%, 100 mL min⁻¹) using a two-step heating profile: first at 500°C for 5 h (heating rate 5°C min⁻¹) to decompose the carbonate precursor, then at 850°C for 15 h (heating rate 2°C min⁻¹) to promote crystal growth and ordering. The final product was cooled to room temperature at a rate of 5°C min⁻¹ and stored in an Ar-filled glovebox (O₂ < 0.1 ppm, H₂O < 0.1 ppm) to prevent exposure to air and moisture.

The bare cathode (without modification) was prepared using an identical procedure, but without the final doping step. For consistency, the same Ni:Mn:Co ratio and calcination conditions were used.

5.2 Structural Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 Å) generated at 40 kV and 40 mA. The data were collected over a 2θ range of 10° to 80° with a step size of 0.02° and a scan rate of 1° min⁻¹. Rietveld refinement was performed using the GSAS-II software package (version 5370) with the *R-3m* structural model (space group No. 166). The background was modeled using a 12-term Chebyshev polynomial, and the peak profiles were modeled using the Thompson–Cox–Hastings pseudo-Voigt function. The lattice parameters (a

and c), atomic positions (Li at 3a, transition metals at 3b, O at 6c), site occupancies, and isotropic thermal displacement parameters were refined sequentially.

Raman spectra were acquired on a Renishaw inVia confocal Raman microscope using 532 nm laser excitation (power = 5 mW, spot size $\approx 1\ \mu\text{m}$). The spectra were collected over the range of 200–800 cm^{-1} with a spectral resolution of 1 cm^{-1} . Each spectrum was the average of 10 acquisitions with an integration time of 10 s per acquisition.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer using monochromatic Al $K\alpha$ radiation ($h\nu = 1486.6\ \text{eV}$) with a spot size of 400 μm . The binding energy scale was calibrated using the C 1s peak of adventitious carbon at 284.8 eV. Survey spectra were collected with a pass energy of 200 eV and a step size of 1 eV. High-resolution Ni 2p spectra were collected with a pass energy of 50 eV and a step size of 0.1 eV. Data analysis was conducted with CasaXPS software (version 2.3.23) using a Shirley background subtraction and mixed Gaussian–Lorentzian peak shapes.

5.3 Electrochemical Measurements

CR2032 coin cells were assembled in an Ar-filled glovebox ($\text{O}_2 < 0.1\ \text{ppm}$, $\text{H}_2\text{O} < 0.1\ \text{ppm}$, MBraun). The working electrode consisted of 80 wt% active material, 10 wt% Super P carbon black (Timcal), and 10 wt% polyvinylidene fluoride (PVDF, Solef 5130) dissolved in N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%, Sigma-Aldrich). The slurry was mixed using a planetary centrifugal mixer (Thinky AR-100) at 2000 rpm for 5 minutes, then cast onto aluminum foil (15 μm thickness, MTI Corporation) using a doctor blade with a gap of 200 μm . The coated foil was dried at 110°C under vacuum for 12 h to remove the NMP, then punched into disks (12 mm diameter, active material mass loading $\approx 3.5\ \text{mg cm}^{-2}$). Lithium metal foil (0.75 mm thickness, MTI Corporation) was used as both the counter electrode and the reference electrode. The electrolyte was 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 vol%, battery grade, Sigma-Aldrich) with 2 wt% vinylene carbonate (VC, 99.5%, Sigma-Aldrich) as an additive.

1169 A Celgard 2500 polypropylene membrane (25 μm thickness) was used as the separator.
1170 The cells were crimp-sealed and allowed to rest for 12 h before electrochemical testing.

1171 Galvanostatic charge–discharge (GCD) tests were performed on a Land CT2001A battery
1172 test system (Wuhan Land Electronics) between 2.5 V and 4.3 V vs. Li/Li^+ (unless otherwise
1173 specified for the voltage window study, Fig. 28). The current density was normalized to
1174 the theoretical capacity of 200 mAh g^{-1} ($1\text{C} = 200 \text{ mA g}^{-1}$). Rate capability was evaluated
1175 at C-rates of 0.1C, 0.2C, 0.5C, 1C, 2C, 5C, and 10C, with 5 cycles at each rate. Long-term
1176 cycling stability was conducted at 1C for 500 cycles. For each condition, a minimum of
1177 three independent cells were tested ($n = 3$), and the data are presented as mean $\pm$
1178 standard deviation.

1179 Cyclic voltammetry (CV) was performed on a Bio-Logic VMP3 potentiostat at scan rates
1180 of 0.1, 0.2, 0.5, and 1.0 mV s^{-1} in the voltage range of 2.5–4.5 V. The CV curves were
1181 background-corrected by subtracting the current measured at the same scan rate on a
1182 blank electrode (Al foil without active material).

1183 Electrochemical impedance spectroscopy (EIS) was performed on the same Bio-Logic
1184 VMP3 potentiostat in the frequency range from 100 kHz to 10 mHz with an AC
1185 amplitude of 10 mV (rms). The spectra were recorded at the fully charged state (4.3 V)
1186 after the cell had reached equilibrium (current $< 0.01\text{C}$). Data were collected after 1, 100,
1187 and 300 cycles. The spectra were fitted using the ZView software (Scribner Associates)
1188 with an equivalent circuit model consisting of: R_s (ohmic resistance) in series with a
1189 parallel combination of R_{ct} (charge-transfer resistance) and a constant phase element
1190 (CPE), in series with a Warburg impedance (W) representing Li^+ diffusion. The fitting
1191 quality was assessed by the chi-squared value ($\chi^2 < 0.001$).

1192 Galvanostatic intermittent titration technique (GITT) was performed using the same Land
1193 CT2001A system. A current pulse of 0.1C (20 mA g^{-1}) was applied for 30 minutes ($\tau =$
1194 1800 s), followed by a 3 h relaxation period to allow the cell to return to near-
1195 equilibrium (voltage change $< 0.1 \text{ mV h}^{-1}$). The sequence was repeated from 2.5 V to 4.3
1196 V. The Li^+ chemical diffusion coefficient (D_{Li^+}) was calculated using the equation:

$$D_{Li^+} = (4/\pi\tau) \times (m_B V_M / M_B S)^2 \times (\Delta E_s / \Delta E_t)^2$$

1197 where τ is the pulse duration (1800 s), m_B is the active material mass (≈ 3.5 mg), V_M is
 1198 the molar volume (calculated from the lattice parameters and the number of formula
 1199 units per unit cell), M_B is the molecular weight (≈ 96.5 g mol⁻¹), S is the electrode
 1200 surface area (1.13 cm² for a 12 mm diameter disk), ΔE_s is the steady-state voltage
 1201 change between successive equilibrium potentials, and ΔE_t is the voltage change
 1202 during the current pulse after correcting for the ohmic drop.

1203 5.4 Computational Methods

1204 Density functional theory (DFT) calculations were performed using the Vienna Ab initio
 1205 Simulation Package (VASP, version 6.3.0) with the projector augmented wave (PAW)
 1206 method. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used
 1207 with a Hubbard U correction (GGA+U) to account for strong electron correlation in the
 1208 Ni 3d and Mn 3d orbitals. The U_{eff} values were set to 5.3 eV for Ni and 4.5 eV for Mn,
 1209 based on previous benchmark studies on layered oxide cathodes. A plane-wave cutoff
 1210 energy of 520 eV and a Γ -centered k-point mesh of $6 \times 6 \times 4$ were used for structural
 1211 relaxations. The k-point mesh was generated using the Monkhorst–Pack method. The
 1212 convergence criteria for electronic self-consistency were set to 10^{-6} eV, and the
 1213 structures were relaxed until the forces on each atom were less than 0.01 eV/Å.

1214 The nudged elastic band (NEB) method was employed to calculate the Li⁺ migration
 1215 energy barrier. A $2 \times 2 \times 1$ supercell containing 128 atoms (including the migrating Li⁺)
 1216 was constructed to avoid interactions between periodic images of the migrating Li⁺. The
 1217 initial and final states (Li⁺ at adjacent octahedral sites in the lithium layer) were fully
 1218 relaxed, and five intermediate images were generated using linear interpolation
 1219 between the initial and final states. The climbing-image NEB (CI-NEB) algorithm was
 1220 used to find the saddle point accurately. The spring constant between adjacent images
 1221 was set to 5.0 eV/Å², and the forces were converged to 0.01 eV/Å.

1222 Band structures and partial density of states (PDOS) were calculated on the fully relaxed
1223 lithiated structure along the high-symmetry k-path Γ (0,0,0) $\rightarrow$ K (1/3,1/3,0) $\rightarrow$ M (1/2,0,0)
1224 $\rightarrow$ Γ (0,0,0). A denser k-point mesh of $12 \times 12 \times 8$ was used for the PDOS calculation to
1225 ensure convergence of the integrated DOS.

1226 The convex hull of formation energies was constructed by calculating the energy of
1227 Li_xMO_2 for $x = 0.0, 0.1, 0.2, \dots, 1.0$ and comparing to the energy of the constituent binary
1228 oxides (Li_2O , MO , MO_2). The formation energy ΔE_f was calculated as:

$$\Delta E_f = E(\text{Li}_x\text{MO}_2) - [x/2 \times E(\text{Li}_2\text{O}) + (1-x) \times E(\text{MO}) + x \times E(\text{MO}_2)]$$

1229 where $E(\text{Li}_x\text{MO}_2)$ is the total energy of the lithiated compound, $E(\text{Li}_2\text{O})$ is the energy of
1230 Li_2O per formula unit, $E(\text{MO})$ is the energy of the transition metal monoxide per formula
1231 unit, and $E(\text{MO}_2)$ is the energy of the transition metal dioxide per formula unit.

1232 The DFT-predicted open-circuit voltage (OCV) was computed using the equation:

$$V = -[E(\text{Li}_{\{x_2\}}\text{MO}_2) - E(\text{Li}_{\{x_1\}}\text{MO}_2) - (x_2 - x_1) \times E(\text{Li}_{\text{metal}})] / [(x_2 - x_1) \times F]$$

1233 where $E(\text{Li}_{\text{metal}})$ is the energy of metallic Li per atom (calculated using a bcc structure
1234 with 2 atoms per unit cell), and F is the Faraday constant (96485 C mol^{-1}).

1235 Charge density differences were calculated as $\Delta\rho = \rho(\text{total}) - \sum \rho(\text{atomic})$, where $\rho(\text{total})$
1236 is the charge density of the full system and $\sum \rho(\text{atomic})$ is the sum of the charge
1237 densities of the isolated atoms placed at the same positions. The charge density
1238 difference was integrated over the unit cell to verify that the total charge transfer is zero
1239 ($\Delta\rho$ integrates to zero within numerical precision).

1240 5.5 Mechanical Characterization

1241 Free-standing electrode films (without Al current collector) were prepared by casting the
1242 electrode slurry onto a PTFE sheet, drying at 110°C for 12 h, and peeling off the dried
1243 film. The films were cut into rectangular strips of dimensions $10 \text{ mm} \times 30 \text{ mm}$ using a

1244 razor blade. The thickness of the films was measured at five different points using a
1245 digital micrometer (Mitutoyo, resolution 0.1 μm) and averaged.

1246 Uniaxial tensile tests were performed on a TA Instruments RSA-G2 dynamic mechanical
1247 analyzer (DMA) in controlled strain mode. The samples were mounted on the DMA
1248 clamps with an initial gauge length of 10 mm. The tests were performed at a constant
1249 strain rate of 0.01 s^{-1} at room temperature (25°C). Stress was calculated as the measured
1250 force divided by the initial cross-sectional area (width $\times$ thickness), and strain was
1251 calculated as the extension divided by the initial gauge length. At least three samples
1252 were tested for each material ($n = 3$), and the data are presented as mean $\pm$ standard
1253 deviation.

1254 **5.6 Thermal Characterization**

1255 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were
1256 performed simultaneously on a Netzsch STA 449 F3 Jupiter. Approximately 10 mg of
1257 delithiated powder (charged to 4.3 V) was placed in an Al_2O_3 crucible and heated from
1258 25°C to 400°C at a ramp rate of 10°C min^{-1} under an Ar flow of 50 mL min^{-1} . An empty
1259 Al_2O_3 crucible was used as the reference for DSC. The TGA and DSC signals were
1260 corrected for baseline drift by performing a blank run under identical conditions. The
1261 onset temperature for decomposition was defined as the temperature at which the TGA
1262 signal deviated by more than 0.5% from the baseline.

1263 **5.7 Data and Code Availability**

1264 All data supporting the findings of this study are available within the paper. Raw data
1265 files (XRD patterns, EIS spectra, GITT data, DFT input and output files) are available from
1266 the corresponding author upon reasonable request. The DFT calculations were
1267 performed using VASP (commercial software), which is available from the VASP Software
1268 GmbH. Analysis scripts (Python, MATLAB) used for data processing are available upon
1269 request.

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