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Near-Micron Single-Crystalline Mn-Rich Cathodes With Exceptional Cycling Stability

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ABSTRACT

Achieving high-energy-density and long-term cycling stability in Mn-redox-based cathodes is a critical step toward advancing Ni- and Co-free Li-ion chemistries to diversify supply chains and lower battery costs. Here, we demonstrate an unusually high performance benchmark for Mn-redox cathodes using near-micron single-crystalline δ -phase cation-disordered rocksalt (δ -DRX), derived from Mn-rich DRX, delivering $\approx 640 \text{ Wh kg}^{-1}$ with $\approx 97\%$ capacity retention over 400 cycles. The very high energy density and cycle life were achieved by using a high Mn content, to suppress oxygen redox activity, and careful control of the synthesis parameters to tune single crystal particle size. Using high-throughput automated electron microscopy, we identify interparticle compositional heterogeneity present in the early stage of phase-pure DRX formation as the origin of orthorhombic LiMnO_2 impurity formation during cooling, a finding that rationalizes the long high-temperature dwell times required and the associated particle coarsening in conventional synthesis. We demonstrate that an accelerated cooling strategy kinetically suppresses localized impurity formation, reducing long high-temperature exposure, and enables downsizing of single-crystalline Mn-rich DRX particles to the near-micron regime ($D_{50} = 1.5 \text{ }\mu\text{m}$). This work provides a mechanistic basis for particle-size control in Mn-rich DRX synthesis, and presents δ -DRX as a stable, sustainable, high-performance, Ni- and Co-free cathode material.

1 | Introduction

Lithium-ion batteries (LIBs) have become indispensable in modern society, powering applications that range from portable electronics to large-scale energy storage systems [1, 2]. This widespread integration into daily life has intensified the demand

for battery materials that are both resource-efficient and sustainable. However, state-of-the-art cathode materials, the component that largely determines battery cost and energy density in LIBs, rely heavily on redox-active nickel (Ni) and cobalt (Co), elements that are scarce and geographically concentrated, raising concerns regarding long-term supply stability [3]. The shift to mining

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low-grade Ni ores has also significantly increased the CO₂ intensity associated with the production of high Ni cathode materials [4].

Manganese (Mn) is particularly attractive as a more sustainable redox-active transition metal, being both earth-abundant and widely distributed. Additionally, it is well-suited as the basis for a Li-ion cathode due to its high redox potential (3–4 V vs Li/Li⁺ for Mn^{3+/4+} in an oxide), low toxicity, and robust structural and thermal stability arising from the electronic stability of Mn⁴⁺ in the charged state [5]. These attributes have motivated extensive efforts to develop Mn-redox-based cathodes, such as spinel LiMn₂O₄ and olivine LiMn_xFe_{1-x}PO₄ (LMFP) [6, 7].

Spinel LiMn₂O₄ was commercialized in the early years of Li-ion technology, but its limited theoretical capacity of 148 mAh g⁻¹ and Mn dissolution at elevated temperatures led to its replacement by Ni- and Co-based layered cathodes [8]. In principle, the capacity of LiMn₂O₄ could be doubled by lithiation to Li₂Mn₂O₄ [9, 10], but the strong cooperative Jahn-Teller distortion and the concomitant two-phase region create challenges for stable material cycling [11, 12].

Cation-disordered rocksalt (DRX) oxides have therefore been proposed as a potential candidate to address the issues in conventional Mn-based cathodes [13, 14]. Because their structures lack long-range cation order and retain only nanometer-scale short-range correlations, DRX phases disrupt long-range Mn³⁺ ordering, thereby mitigating bulk structural instabilities associated with cooperative Jahn-Teller distortions [15–17]. However, the inherently poor Li-ion transport in DRXs remains a critical barrier to their practical application as Mn-redox-based cathode materials [16–18].

Recently, a new class of Mn-based cathodes, referred to as the δ -phase cation-disordered rocksalt (δ -DRX), has been reported as a promising solution that bridges the advantages of both conventional Mn-based cathodes and DRX systems [12, 19, 20]. In a Mn-rich DRX parent structure (Mn $\geq$ 0.6 per formula unit), the δ -phase microstructure readily forms through the migration of low-valent Mn ions upon cycling, driven by a thermodynamically favored transformation toward spinel-like cation ordering in lithium-deficient (charged) compositions [12, 20]. This transformation to the δ -phase was reported to be accelerated through either in situ electrochemical pulsing or by heating a chemically delithiated state [12, 19].

Unlike fully ordered spinel phases that exhibit a continuous, long-range spinel ordering, the δ -phase consists of nanoscale domains of eight different spinel variants with short coherence lengths ($\approx$ 5 nm), which impinge on each other at antiphase boundaries [12, 19, 20]. This nanoscale structural motif disrupts long-range Mn³⁺ ordering and effectively suppresses cooperative Jahn-Teller distortions responsible for capacity fade, thereby enabling solid-solution-like behavior near 3 V instead of a two-phase reaction [12]. Thus, δ -DRX exhibits stable electrochemical cycling with negligible voltage decay over extended cycling [12, 19, 20].

δ -DRX uniquely enables operation with micron-scale single-crystalline particles, an ability inaccessible to conventional DRX systems. The interconnected spinel-like framework between

domains in δ -DRX provides better Li-ion transport pathways, resulting in enhanced Li⁺ diffusivity ($D \approx 10^{-13}$ – 10^{-14} cm² s⁻¹) compared to that of the conventional DRXs ($D \approx 10^{-14}$ – 10^{-16} cm² s⁻¹) [19]. This enhanced transport enables micron-scale single-crystalline δ -DRX particles to sustain high reversible capacities ($\approx$ 170 mAh g⁻¹). This is in contrast with conventional DRXs, which require an additional milling step to produce nanosized particles that compensate for their intrinsic kinetic limitations [19]. As demonstrated in Ni- and Co-based layered cathodes, adopting the single-crystalline strategy confers multiple practical advantages at the cell level [21–23]. These include the mitigation of surface-driven parasitic reactions through reduced specific surface area, a decreased reliance on conductive carbon additives, and an effective increase in active material packing density, which directly translates into improved volumetric energy density. The ability of δ -DRX to accommodate micron-scale single-crystalline architecture offers a strategic advantage for high-energy-density, Ni- and Co-free Mn-based cathode materials from a practical standpoint.

Despite these promising attributes, critical synthesis challenges remain that restrict the full potential of single-crystalline Mn-rich DRX/ δ -DRX. To thermodynamically stabilize DRX structures with respect to ordered phases such as orthorhombic LiMnO₂ (*o*-LiMnO₂), *d*⁰ elements such as Ti⁴⁺ are used on account of their greater tolerance for occupying the heavily distorted octahedra that arise in disordered oxides [17, 24]. Increasing the Mn content in DRX to prevent detrimental oxygen redox and promote the δ -phase transition comes at the cost of a lower Ti⁴⁺ content. The resulting decreased *d*⁰-stabilization of the disordered structure elevates the order-disorder transition temperature required to stabilize the DRX phase over *o*-LiMnO₂ [17, 25–27]. Therefore, Mn-rich DRX compositions typically require high synthesis temperature ($\approx$ 1100°C) and/or prolonged dwell times compared with their lower-Mn counterparts, conditions that inevitably promote rapid particle coarsening. This synthesis constraint produces large Mn-rich DRX particles, which increase Li-ion diffusion lengths and exacerbate poor Li-ion transport kinetics [12, 19, 20, 28], ultimately hindering both the kinetics of the electrochemical conversion to the δ -phase and the rate capability of δ -DRX [19]. Overcoming the challenge of particle-size control is essential to unlock the electrochemical performance of δ -DRX and establish it as a viable Mn-based cathode, as demonstrated by the commercial success of the LiFePO₄ cathode through particle-size engineering [29, 30].

Here, we identify an interparticle compositional heterogeneity present in the early stages of phase-pure DRX formation as a hidden kinetic constraint that limits particle-size reduction in Mn-rich DRX systems. We show that the interparticle heterogeneity promotes the localized formation of *o*-LiMnO₂ impurities in Ti-lean particles during cooling. However, eliminating it requires extensive interparticle diffusion, achievable only through long-duration high-temperature annealing, which drives severe particle coarsening. As an alternative, a rapid cooling strategy is introduced to kinetically suppress this cooling-induced localized impurity formation, obviating the need for excessive thermal exposure. This enables particle-size reduction to the near-micron regime in the rapid-cooled DRX (RC-DRX; median size $\approx$ 1.5 μ m), compared with the 3.5 μ m limit of the slow-cooled DRX (SC-DRX) prepared by the conventional protocol.

The δ -DRX cathode, derived from near-micron single-crystalline Mn-rich DRX by pulsing, demonstrates markedly improved electrochemical kinetics while maintaining exceptional cycling stability, with $\approx 97\%$ capacity retention at an energy density of ≈ 640 Wh kg^{-1} over 400 cycles. These results establish a new performance benchmark among Mn-redox-based cathodes and highlight the strong potential of single-crystalline δ -DRXs as sustainable, high-performance, Ni- and Co-free Li-ion cathodes.

2 | Results

2.1 | Synthesis of Single-Crystalline Mn-Rich DRX Using a Conventional Annealing Route

Several studies have been devoted to synthesizing single-crystalline Mn-DRX particles via molten-salt-assisted methods. Early work by Chen et al. first demonstrated highly uniform single-crystalline $\text{Li}_{1.3}\text{Mn}_{0.4}\text{Nb}_{0.3}\text{O}_2$ DRX with a large particle size of 5–8 μm synthesized using a KCl flux and long annealing (12 h) at 950°C [31]. More recently, Lee et al. reported a nucleation-promoted strategy that enabled the formation of much smaller single-crystalline $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ DRX particles (≈ 500 nm) at 800°C to partially alleviate the poor Li-ion transport of the DRX phase [32].

Importantly, however, particle-size control strategies that may work for these representative low-Mn compositions nonetheless remain challenging in Mn-rich DRX compositions due to their higher disordering temperature ($>1000^\circ\text{C}$). This is evidenced by previous work on $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$, showing that phase-pure Mn-rich DRX is achieved at a much higher reaction temperature with a prolonged dwell time (1100°C for 20 min), which inevitably induces pronounced coarsening to particle sizes of several microns ($> 3 \mu\text{m}$) [19]. Although these micrometer-sized particles delivered a discharge capacity of ≈ 170 mAh g^{-1} after an electrochemical pulsing activation protocol designed to induce the δ -phase transformation [19], their rate capability remains constrained. In particular, the accessible capacity reached only $\approx 76\%$ of that achieved in ball-milled counterparts (≈ 220 mAh g^{-1}) [19].

Achieving particle-size reduction in Mn-rich DRXs hinges on suppressing rapid coarsening during high-temperature synthesis, as particle growth accelerates dramatically at the elevated temperature typical of solid-state synthesis ($> \approx 800^\circ\text{C}$) [32, 33]. Accordingly, we first directly probe the lower bound of the thermal window required for phase-pure DRX formation in a representative Mn-rich composition, $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$. Synthesis was carried out using a conventional protocol consisting of a heating ramp of $10^\circ\text{C min}^{-1}$, an isothermal dwell at the target temperature, and subsequent natural (or slow) cooling inside the furnace (Figure 1a). All reactions were conducted in a KCl-based molten-salt medium with a salt-to-precursor mass ratio (STP) of 3.

To probe the lowest temperature at which DRX forms, the peak temperature was first set to 1000°C with a dwell time of 1 min. Under this condition, XRD patterns in Figure 1b display dominant DRX reflections, including the characteristic (200) peak, alongside substantial *o*-LiMnO₂ reflections (marked in

orange), confirming a DRX phase with a significant amount of *o*-LiMnO₂ impurity [34, 35]. We show in Figure S1 that increasing the peak temperature to 1100°C reduces the impurity fraction, but minor orthorhombic peaks between 30° and 60° persist even after extending the dwell time to 10 min. The bottom panel of Figure 1c shows that complete suppression of the orthorhombic phase and the formation of phase-pure DRX are achieved only when the dwell time is further prolonged to 20 min at 1100°C , representing the minimum annealing condition attainable under a conventional heating protocol. This sample is hereafter referred to as slow-cooled DRX (SC-DRX) (Figure 1c). Inductively coupled plasma mass spectrometry (ICP-MS) confirms that the metal ratios of as-synthesized SC-DRX are close to the target stoichiometry (Table S1).

Scanning electron microscopy (SEM) combined with laser diffraction particle-size analysis was employed to evaluate the particle size of the SC-DRX. The SEM image in Figure 1d shows that SC-DRX comprises single-crystalline particles with a uniform size distribution on the micrometer scale, in contrast to the solid-state-synthesized $\text{Li}_{1.2}\text{Mn}_{0.65}\text{Ti}_{0.15}\text{O}_{1.9}\text{F}_{0.1}$ DRX particles, reported by Hau et al., which exhibit a broad size distribution ranging from nanoparticles to tens of micrometers [12]. Despite improved homogeneity in particle diameter, the prolonged high-temperature dwell required to eliminate orthorhombic phase impurities inevitably induces substantial grain coarsening, yielding a median particle size (D50) of 3.5 μm , as corroborated by SEM observations and laser diffraction particle-size analysis (Figure 1d,e). These results reveal an intrinsic limitation of the conventional annealing protocol in achieving effective particle-size reduction for Mn-rich DRX.

2.2 | Evolution of Long-/Medium-/Short-Range Mn-Rich DRX Structures During Cooling

In the previous section, our synthesis experiments identified annealing at 1100°C for 20 min (at a heating ramp of $10^\circ\text{C min}^{-1}$) as the minimum annealing condition required to obtain phase-pure $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$ DRX under a conventional annealing protocol. This requirement appears inconsistent with recent *in situ* XRD results reported by Liang et al., who investigated the synthesis pathway of the same Mn-rich DRX composition under comparable heating conditions [36]. In that study, the orthorhombic intermediate phase was observed to disappear near 1000°C , accompanied by the emergence of a phase-pure DRX during continuous heating.

This apparent discrepancy is nontrivial. While *in situ* XRD indicates that the pure DRX phase becomes thermodynamically accessible near 1000°C during continuous heating, our synthesis shows that phase purity is achieved and retained only after annealing at substantially higher temperatures and for longer dwell times. Notably, unlike *in situ* measurements that track phase evolution exclusively during heating, recovering *ex situ* samples from synthesis inherently involves an additional cooling process, in which structural evolution may occur. Reconciling the contrasting observations in the early stage of phase-pure DRX formation is essential, as it directly impacts the true minimum annealing requirement for Mn-rich DRX synthesis

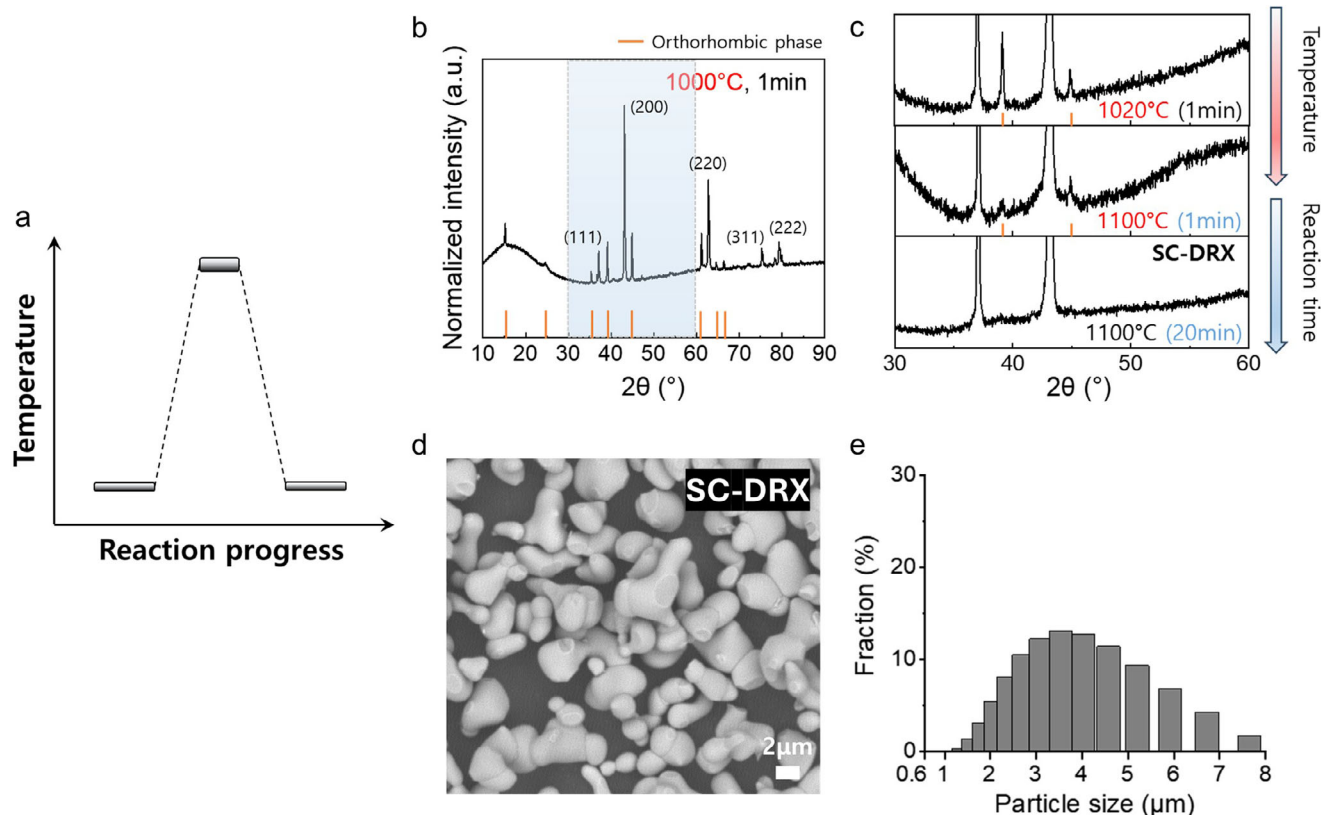


FIGURE 1 | Characterization of Mn-rich DRXs through molten-salt synthesis. (a) Schematic illustration of the conventional heating profile, including ramping, dwelling, and cooling, in solid-state or molten-salt synthesis. (b) XRD result between 10° and 90° for a sample ramped to 1000°C at a ramping rate of $10^\circ\text{C min}^{-1}$, followed by holding for 1 min and natural cooling. Miller indices correspond to a DRX phase (Fm-3m space group), and additional peaks marked with orange indicate an $o\text{-LiMnO}_2$ impurity phase (Pmmn space group). (c) XRD results between 30° and 60° for samples ramped to either 1020°C or 1100°C , followed by holding for 1 min, and a sample ramped to 1100°C , followed by holding for 20 min and natural cooling. The last condition yields phase-pure DRX (SC-DRX). (d) SEM images (scale bar, $2\text{ }\mu\text{m}$) and (e) laser diffraction particle size analysis of the SC-DRX powder ($D_{50} = 3.5\text{ }\mu\text{m}$).

and, consequently, the extent to which particle coarsening can be minimized.

We address this issue using a set of synchrotron-based complementary characterization techniques that probe the cooling-induced structural evolution of Mn-rich DRX across multiple length scales. Short- and medium-range ordering was probed with synchrotron pair distribution function (sPDF), while synchrotron XRD was used to assess long-range ordering. As a model condition representative of the early stage of phase-pure DRX formation, a $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$ sample was heated to 1100°C at a ramp rate of $10^\circ\text{C min}^{-1}$ and held for 1 min, and then cooled under three distinct protocols to isolate cooling-induced structural evolution: (i) water quenching, where the sample was immediately immersed in deionized water (corresponding to a cooling rate of well over $1100^\circ\text{C min}^{-1}$) [28]; (ii) air quenching, where the sample was cooled in ambient air within approximately 1 min, using a strong fan; and (iii) natural cooling inside the furnace, where the sample was allowed to cool gradually (staying above 800°C for ≈ 20 min or ≈ 2 h cool to room temperature in furnace).

Figure 2a–e show the PDF data which can be used to evaluate the short- and medium-range structural evolutions during cooling. The degree of short- and medium-range ordering at

different cooling modes (or speeds) was qualitatively evaluated by fitting the sPDF results at low r values (between 1.8 and $15\text{ }\text{\AA}$) using a special quasi-random structure (SQS) model that approximates statistically random cation distributions [37]. In this framework, a lower weighted residual factor (R_w) indicates closer agreement with a random local structure. This approach is adapted from the prior work by Cai et al., which demonstrated that the local structure of DRX materials is highly sensitive to thermal history, including dwell times and cooling rate [38].

Figure 2a–c show the sPDF fitting results for samples subjected to water quenching, air quenching, or natural cooling, respectively. The water-quenched sample shows the best fit with the computed sPDF of the fully disordered structure, with an R_w value of 15.5% (Figure 2a), whereas the air-quenched and naturally cooled samples show slightly higher values of 16.6% (Figure 2b) and 16.4% (Figure 2c), respectively, showing a greater deviation from randomness with decreasing cooling rate. Distinct spectral differences are observed in the water-quenched sample, particularly in the $2.1\text{--}2.8\text{ }\text{\AA}$ and $6.9\text{--}7.5\text{ }\text{\AA}$ regions (Figure 2d,e), where its profile deviates clearly from those of the air-quenched and naturally cooled samples. This is interpreted along with the lower R_w value to mean that short- and medium-range ordering develops rapidly during cooling and reaches a quasi-equilibrated state within tens

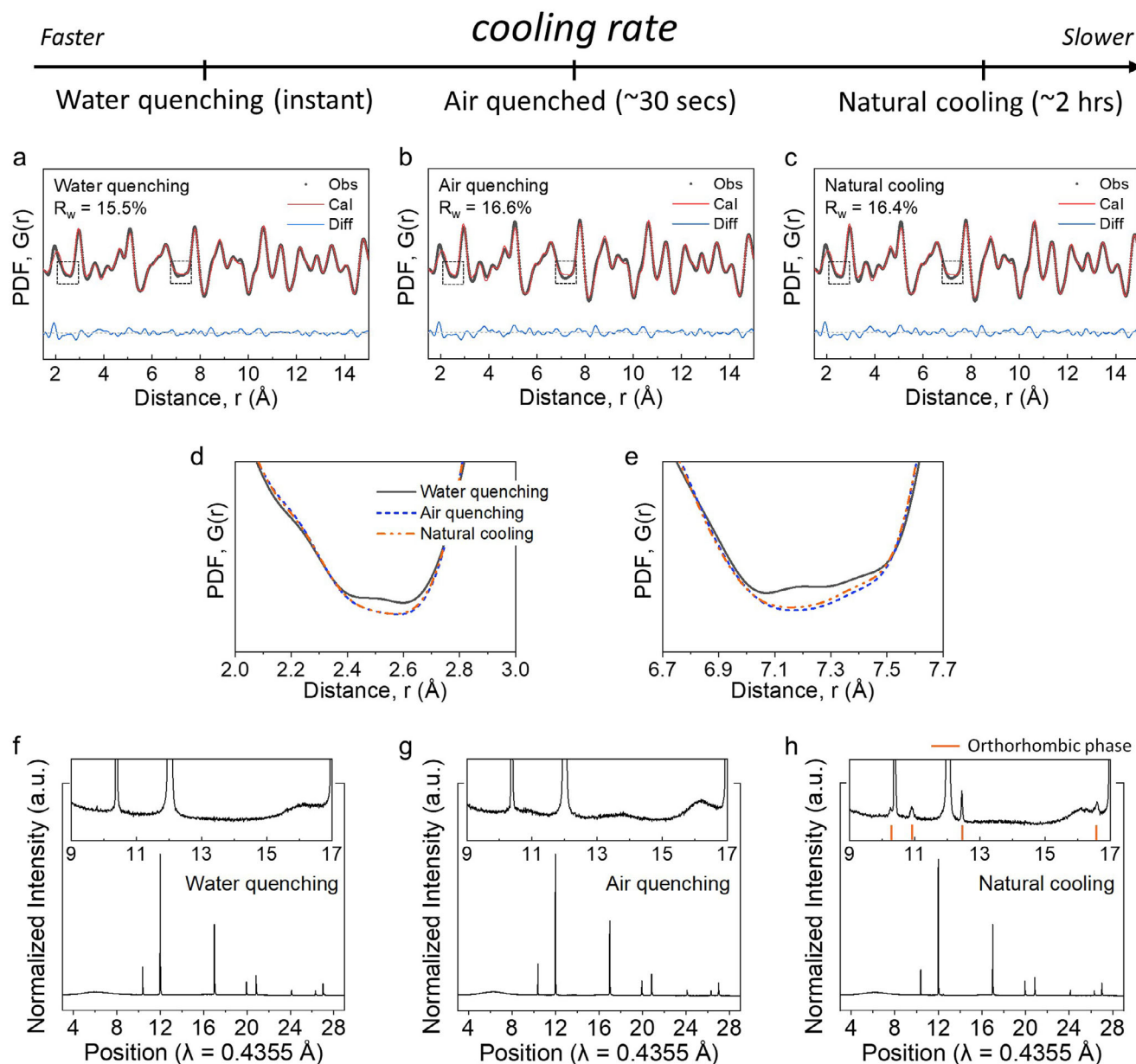


FIGURE 2 | Effect of cooling rate on long/medium/short-range ordering of Mn-rich DRX. (a–c) sPDF fitting results of samples sintered at 1100°C for 1 min with (a) water quenching, (b) air quenching, and (c) natural cooling, using a DRX structure with fully randomized cation occupation. The experimental data are plotted as black open circles, the fittings are plotted as solid red lines, and the difference between observation and calculation is plotted as solid blue lines. (d,e) Zoomed-in sPDF plots of the samples with either water quenching (black), air quenching (blue), or natural cooling (orange) are included for a comparison in a distance range of (d) 2.0–3.0 Å and (e) 6.7–7.7 Å. (f–h) Synchrotron XRD results ($\lambda = 0.4355$ Å) with different cooling strategies after being ramped to 1100°C with 1 min holding: (f) water quenching, (g) air quenching, and (h) natural cooling. Insets represent enlarged diffraction patterns.

of seconds and can only be minimized or avoided with very rapid cooling, as in a water quench.

The impact of cooling rate on long-range structural evolution was examined using synchrotron XRD (Figure 2f–h). The synchrotron XRD patterns of the water-quenched and air-quenched samples in Figure 2f,g exhibit only the characteristic DRX reflections without any additional peaks, indicating that both samples retain a phase-pure DRX structure in the long-range regime despite the measurable differences in their local ordering revealed by sPDF

analysis. In stark contrast, the XRD pattern of the naturally cooled sample (Figure 2h) shows distinct orthorhombic reflections upon cooling to room temperature, consistent with Figure 1. We note that the comparable sPDF trends of the air-quenched and naturally cooled samples, with a small difference in R_w , despite only the latter containing *o*-LiMnO₂ in XRD, can arise because a minority phase possibly appears as independent Bragg reflections in XRD but is largely masked in the PDF, where the contributions of all phases are superimposed on the same *r*-axis and dominated by the majority DRX matrix.

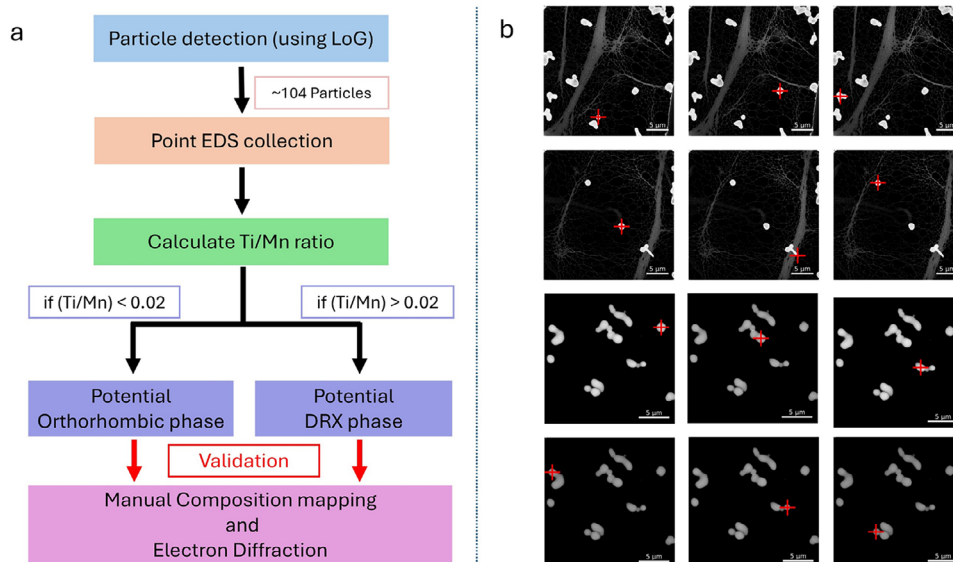


FIGURE 3 | High-throughput electron microscopy for investigating particle-level compositional variations (a) Decision-based automated workflow for high-throughput transmission electron microscopy to determine the presence of Ti-lean particles. (b) Typical high-throughput HAADF-STEM micrographs with the beam positions marked (red-cross hairs) for the point EDS measurements post automatic particle detection.

The combined synchrotron-based PDF and XRD analyses unequivocally demonstrate that the cooling rate plays a decisive role in governing the structural evolution of Mn-rich DRXs. These findings highlight cooling-stage control as a critical lever for suppressing impurity formation in synthesis, thereby allowing the improved particle-size control in Mn-rich DRX.

2.3 | Observation of Interparticle Compositional Heterogeneity in the Early Stage of Phase-Pure DRX Formation Using Automated Electron Microscopy

The synchrotron-based structural analyses establish that orthorhombic impurities emerge during the cooling stage, but the mechanistic origin of this transformation remains unresolved. Notably, the fraction of the *o*-LiMnO₂ phase remains very small, with the majority of the material retaining the DRX structure even after slow cooling. In addition, while the short- and medium-range ordering probed by sPDF stabilizes very rapidly, the long-range structural evolution continues during cooling, ultimately giving rise to detectable orthorhombic reflections in XRD results.

To rationalize these observations, we propose that the emergence of this *o*-LiMnO₂ impurity phase does not occur homogeneously across all particles but is rather a localized process occurring in a limited subset of particles or regions. This hypothesis motivates a particle-resolved investigation into compositional and structural heterogeneity during the early stage of phase-pure DRX formation.

To this end, we developed an automated high-throughput electron microscopy workflow designed to resolve interparticle compositional and structural heterogeneity in Mn-rich DRX systems (Figure 3a). Unlike conventional weight-averaged characterization methods, this workflow enables large-scale, particle-resolved

analysis by automatically identifying and interrogating individual particles, thereby allowing statistically meaningful investigation of initial phase-pure DRX formation at the level of single particles.

Specifically, we used an automated workflow to collect 104 high-angle annular dark-field scanning transmission electron microscopy (STEM-HAADF) micrographs from the naturally cooled sample used in Figure 2c,h, which contains a small fraction of *o*-LiMnO₂ impurity. Individual particles, appearing as bright regions of high Z-contrast in HAADF micrographs, were automatically detected based on the Laplacian-of-Gaussian (LoG) algorithm (Figure 3b). This automated particle recognition eliminates user bias and provides high-throughput statistical sampling that is challenging through conventional manual electron microscopy analysis. Point energy-dispersive X-ray spectroscopy (EDS) spectra were subsequently acquired from the projected centers of the identified particles, and the Ti/Mn ratio of each particle was quantified by integrating the corresponding K α peaks. Based on this high-throughput compositional screening, particles with a Ti/Mn ratio below 0.02 (the target DRX having a Ti/Mn ratio of 0.125) were classified as Ti-lean and assigned to a potential orthorhombic phase group, whereas particles with a Ti/Mn ratio above 0.02 were assigned to a potential DRX phase group. This classification criterion is grounded in the mechanistic framework outlined in the Introduction, where a sufficient concentration of *d*⁰ transition metals, such as Ti⁴⁺, is required to stabilize the cation-disordered rocksalt phase [24]. To validate this classification, manual compositional mapping was further performed on representative particles to confirm their Ti deficiency. Microprobe electron diffraction (ED) analysis was then conducted to establish a direct relation between compositional heterogeneity and phase formation by comparing particles with Ti-lean compositions (Ti/Mn < 0.02) and near-target compositions (Ti/Mn $\geq$ 0.02).

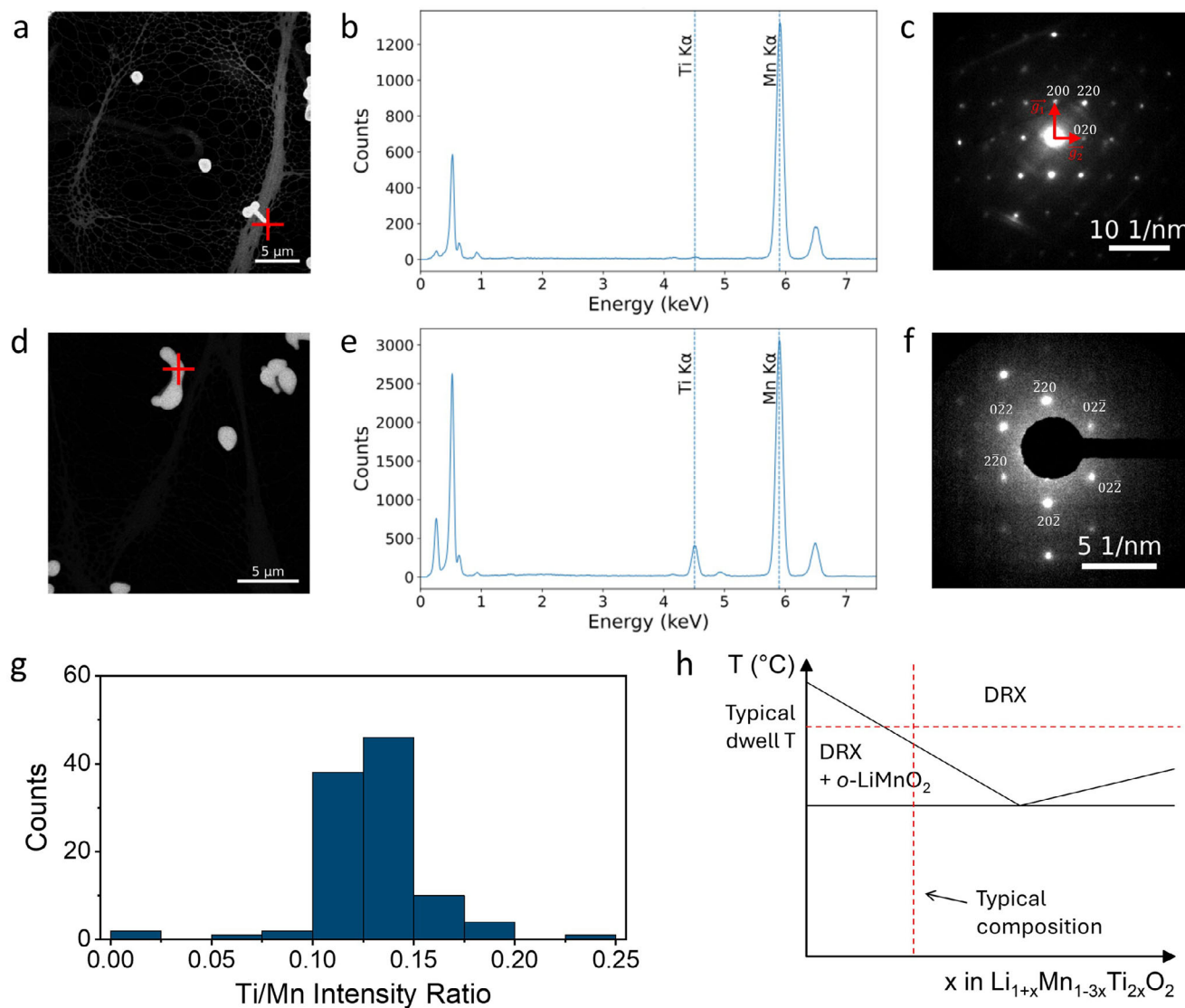


FIGURE 4 | Interparticle compositional heterogeneity. (a) STEM-HAADF image showing the particles classified as *o*-LiMnO₂. (b) STEM-EDS point spectrum obtained from the region marked in panel (a). (c) Electron diffraction pattern obtained from the region marked in panel (a). (d) STEM-HAADF image showing the particle classified as DRX. (e) STEM-EDS point spectrum obtained from the region marked with a red cross in panel (d). (f) Electron diffraction pattern obtained from the region marked by a red cross in panel (d). (g) Histogram of the Ti/Mn ratio from different particles in the naturally cooled DRX sample. (h) Schematic of the Li-Mn-Ti-O phase diagram reproduced from Kam et al. [39]. The red dashed lines indicate the typical composition and dwell temperature in Mn-rich DRX synthesis.

Figure 4a–f present TEM images, STEM-EDS point spectra, and ED patterns of representative particles identified from the automated workflow as either Ti-lean (Figure 4a–c) or near-target (Figure 4d–f) in Ti/Mn composition. The STEM images in Figure 4a and Figure S2 show that Ti-lean particles, provisionally classified as the *o*-LiMnO₂ group based on composition through the automated workflow, exhibit elongated, rod-like morphologies along with a strongly suppressed Ti K α signal relative to the Mn K α signal in point EDS spectra (Figure 4b). Manual EDS mapping of these particles in Figure S3 further visually confirms their Ti-poor composition relative to Mn. Selected-area electron diffraction (ED) patterns acquired from rod-like particles along the [100] zone axis (Figure 4c) show anisotropic lattice spacings ($d_{200} \neq d_{020}$, $d_{200} = 2 \text{ \AA}$ and $d_{020} = 1.7 \text{ \AA}$), indicative of the orthorhombic distortion of *o*-LiMnO₂.

In contrast, the TEM images of particles with near-target Ti/Mn composition (Figure 4d), classified as the potential DRX group, display more equiaxed, spherical morphologies along with pronounced K α peaks for both Ti and Mn in their EDS spectra (Figure 4e), consistent with the intended composition (Ti/Mn $\approx$ 0.125). Unlike the rod-type Ti-lean particles, manual EDS mapping of the spherical particles in Figure S3 shows a substantial and spatially uniform Ti distribution. Their ED patterns exhibit isotropic lattice spacings ($d_{220} = 1.5 \text{ \AA}$; Figure 4f), allowing unambiguous indexing to the cubic structure of a DRX phase. These combined analyses reveal that particle-level heterogeneity is present during the early stage of phase-pure DRX formation with distinct morphologies (rod-like vs spherical) corresponding to different crystal structures (orthorhombic vs DRX).

The results of a statistical compositional survey based on point EDS analysis of 104 particles in the automated dataset are shown in Figure 4g. The ensemble-averaged Ti/Mn ratio (≈ 0.128) extracted from this population closely matches the nominal target composition (Ti/Mn = 0.125), indicating that the overall stoichiometry during synthesis is well controlled. In contrast, particle-resolved analysis reveals a pronounced interparticle compositional heterogeneity (Figure 4g). While the majority of particles cluster near the target Ti/Mn ratio, a fraction exhibits substantial deviations, including Ti-lean (Mn-dominant) particles (2%, 2 out of 104 particles) with strongly suppressed Ti content, as well as Ti-enriched particles (1%, 1 out of 104 particles).

By enabling direct correlation between particle-scale composition, morphology, and crystal structure, our newly developed automated electron microscopy workflow suggests that *o*-LiMnO₂ preferentially nucleates in localized Ti-lean particles during slow cooling. These results provide mechanistic evidence that cooling-induced impurity formation is governed by interparticle compositional heterogeneity in Mn-rich DRX systems.

A recent computational study by Kam et al. [39] provides a thermodynamic framework that supports our experimental observations. In Figure 4h, we schematically reproduced the Li-Mn-Ti-O phase diagram computed by Kam et al. [39]. With increasing Li and Ti content, the disordering temperature rapidly decreases. Any inhomogeneity that creates particles with low Ti content will, during the cooling, create regions that reorder into *o*-LiMnO₂ at temperatures high enough to provide sufficient kinetics for this ordering process and the associated two-phase separation. This result provides a thermodynamic rationale for the behavior that orthorhombic impurities preferentially emerge during cooling and underscores the importance of homogeneity and careful temperature control in stabilizing phase-pure DRX without resorting to extended annealing times.

2.4 | Accelerated Cooling Strategy for Size Reduction of Mn-Rich DRX Particles

Building on the identification of cooling-induced, particle-localized orthorhombic precipitation in Ti-lean particles, we next translate this mechanistic insight into a practical synthesis strategy. In Figure 2, accelerating the cooling process kinetically suppresses *o*-LiMnO₂ impurity formation during cooling and preserves the DRX phase, eliminating the need for high-temperature annealing that would otherwise be required to homogenize composition across a minor subset of particles. Accordingly, we adopted this accelerated cooling strategy to mitigate particle coarsening and thereby enable particle-size reduction in Mn-rich DRX systems.

Air quenching was employed as the primary accelerated cooling method while maintaining a constant heating ramp rate of 10°C min⁻¹ (Figure 5a). We chose air over water quenching, as the latter may degrade the cathode material due to proton-exchange reactions [40, 41]. Based on this approach, we systematically explored the new lower bound of the thermal window required to obtain phase-pure Li_{1.1}Mn_{0.8}Ti_{0.1}O_{1.9}F_{0.1} DRX in Figure 5.

Figure 5b shows the XRD patterns of samples dwelled at temperatures below 1100°C (1080, 1060, and 1040°C) for 1 min, followed by air quenching at STP = 3. As demonstrated in Figure 2g, air quenching enables a significant reduction in dwell time at 1100°C from 20 min to 1 min. Notably, it also allows the formation of phase-pure DRX at reduced temperatures of 1080 and 1060°C, whereas at 1040°C, two clear *o*-LiMnO₂ impurity peaks emerge between 30° and 60°. Figure 5c shows that increasing STP to 12 (STP = 12) leads to the disappearance of the *o*-LiMnO₂ impurity peaks in the XRD pattern at 1040°C, further reducing the minimum synthesis temperature for phase-pure DRX. This behavior can be attributed to the flux-assisted nature of the molten salt, which enhances reactant dissolution and mass transport, while rapid quenching kinetically suppresses the transformation of Ti-lean DRX particles into the *o*-LiMnO₂ phase during cooling [42–44].

Through this rapid cooling strategy, the cumulative high-temperature exposure time above 800°C was reduced from approximately 50 min to 25 min. The sample synthesized under these conditions, annealed at 1040°C for 1 min with STP = 12 followed by rapid air quenching, is hereafter referred to as rapid-cooled DRX (RC-DRX) (Figure 5d). Elemental analysis (Table S1) confirms that the RC-DRX exhibits metal ratios close to the target stoichiometry. Importantly, the optimized annealing condition enables the formation of single-crystalline DRX particles with a D50 particle size of 1.5 μm, compared to the 3.5 μm lower limit achievable under conventional slow cooling (Figure 1d,e), as confirmed by SEM imaging and laser diffraction particle-size analysis (Figure 5d,e).

2.5 | Electrochemistry of Particle-Size-Engineered δ -DRX

The electrochemical performance of SC-DRX and RC-DRX was evaluated within the voltage window of 2.0–4.8 V at room temperature (RT, 30°C), as shown in Figure 6. The electrode films were prepared with a composition of DRX: Super P: Polyvinylidene fluoride (PVDF) = 7: 2: 1 (by weight). As discussed in the Introduction, Mn-rich DRXs serve as parent phases for the formation of δ -DRX upon activation. To induce the δ -phase transition, an optimized electrochemical pulsing protocol [19] was applied to both SC-DRX and RC-DRX electrodes (see Methods).

Prior to pulsing, the RC-DRX electrode exhibited a slightly higher initial discharge capacity (≈ 78 mAh g⁻¹) than SC-DRX (≈ 66 mAh g⁻¹) at a current density of 20 mA g⁻¹ (Figure 6a), which can be attributed to the shorter Li-ion transport path in the particle-size-reduced RC-DRX. More importantly, RC-DRX completed the δ -phase transformation within approximately 20 pulses (≈ 12 h), whereas SC-DRX required nearly 60 pulses to reach capacity saturation, corresponding to a three-fold acceleration in transformation kinetics for the particle-size-reduced material (Figure 6a). Ex situ synchrotron XRD of the SC-DRX and RC-DRX cathodes after 80 pulses, hereafter denoted SC- δ and RC- δ , shows the emergence of a spinel signature near $2\theta \approx 2.6^\circ$ ($\lambda = 0.1811$ Å), indicating the δ -phase transformation (Figure S4a). The spinel signature peaks of the two samples nearly overlap with comparable broadness, and Rietveld refinement (Figure S4b and c) yields similar short coherence lengths of 4.43 and 4.81 nm for

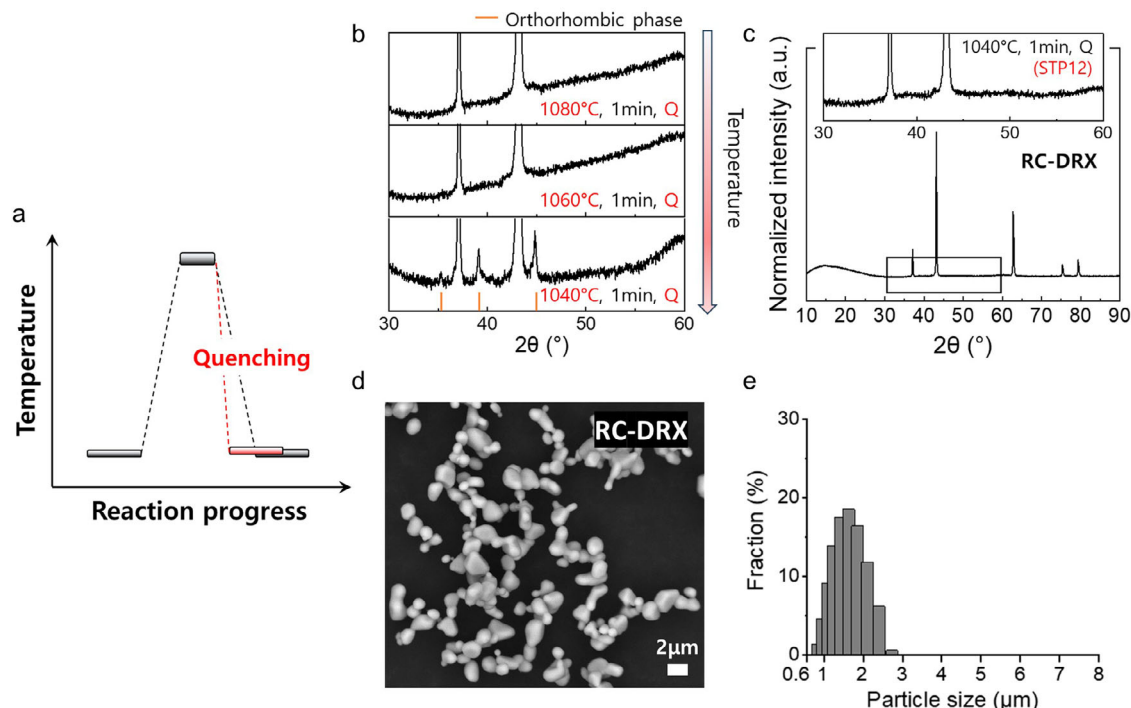


FIGURE 5 | Particle size reduction through the rapid cooling approach. (a) Schematic illustration of a heating profile, including ramping, dwelling, and rapid cooling (quenching, Q). (b) XRD results between 30° and 60° for samples ramped to 1080°C, 1060°C, or 1040°C, followed by holding for 1 min at STP = 3. Peak positions marked in orange indicate an orthorhombic impurity phase (c) XRD result between 10° and 90° for a sample ramped to 1040°C, followed by holding for 1 min at STP = 12, which yields the RC-DRX powder. The inset represents an enlarged XRD profile between 30° and 60°. (d) SEM images (scale bar, 2 μm) and (e) laser diffraction particle size analysis of the RC-DRX powder ($D_{50} = 1.5 \mu\text{m}$).

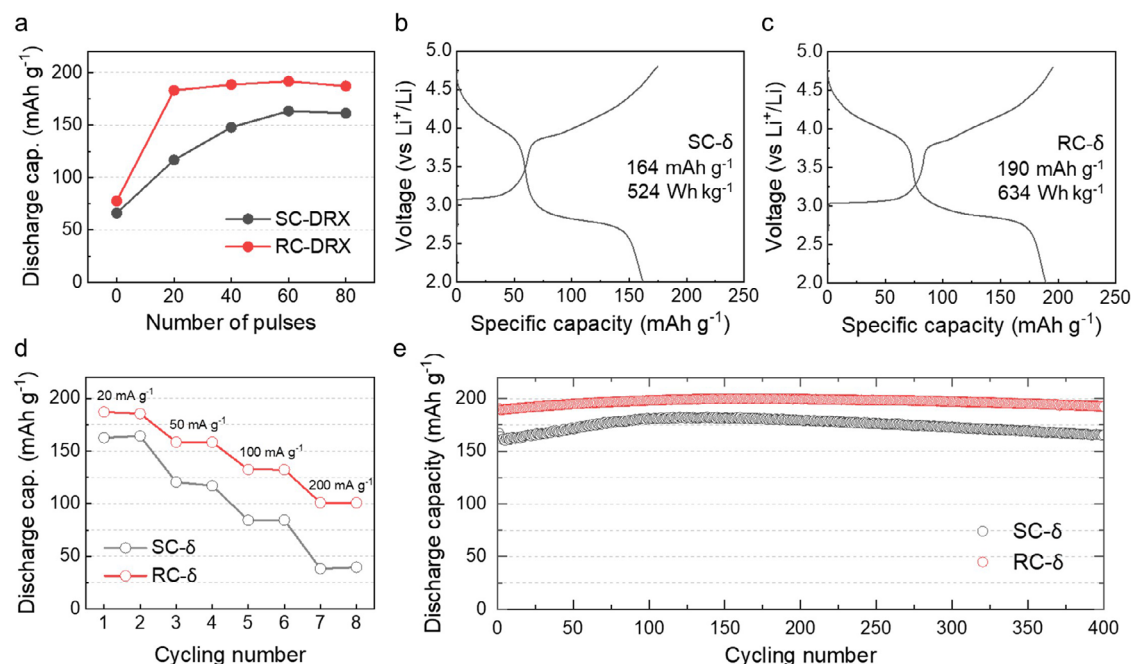


FIGURE 6 | Electrochemical performance of single-crystal δ -DRX cathodes after transformation. (a) Discharge capacity of SC-DRX (black) and RC-DRX (red) cathodes with different pulsing numbers, 0, 20, 40, 60, and 80 pulses for transformation of DRX to δ -DRX, within the voltage window of 2.0–4.8 V at 20 mA g^{-1} and 30°C. (b, c) Voltage profiles of (b) SC- δ and (c) RC- δ cathodes in the second cycle within the voltage window of 2.0–4.8 V at 20 mA g^{-1} and 30°C after 80 pulses on SC-DRX and RC-DRX. (d) Discharge capacity of SC- δ (black) and RC- δ (red) cathodes in rate capability test when cycled between 2.0 and 4.8 V at 20, 50, 100, and 200 mA g^{-1} . Two cycles are tested in each current step at 30°C. (e) Cycling performances of SC- δ (black) and RC- δ (red) cathodes when cycled between 2.0 and 4.8 V at 20 mA g^{-1} and 30°C.

SC- δ and RC- δ , respectively, close to the value reported previously for the δ phase (< 5 nm) [19]. RC- δ delivered a discharge capacity of 190 mAh g⁻¹ (≈ 634 Wh kg⁻¹) at 20 mA g⁻¹, representing a 21% enhancement in energy density compared with SC- δ , which exhibited 164 mAh g⁻¹ (≈ 524 Wh kg⁻¹) (Figure 6b,c).

Rate capability measurements further highlight the benefits of particle-size engineering. RC- δ consistently delivered higher reversible capacities across all tested current densities (Figure 6d). In particular, at a high current density of 200 mA g⁻¹, RC- δ achieved a discharge capacity of ≈ 101 mAh g⁻¹, approximately three times higher than that of SC- δ (≈ 39 mAh g⁻¹), reflecting substantially improved high-rate performance in RC- δ .

Figure 6e presents the long-term cycling performance of SC- δ and RC- δ cells measured at a current density of 20 mA g⁻¹ over 400 cycles. The RC- δ electrode retains $\approx 97\%$ of its maximum discharge capacity after 400 cycles, compared with $\approx 91\%$ for the SC- δ electrode. Both electrodes exhibit stable cycling behavior with negligible capacity decay, indicating the intrinsic robustness of the δ -phase materials. The Coulombic efficiency of the RC- δ electrode exhibits an initial value of $\approx 97\%$ and stabilizes above $\approx 99\%$ within the first fifty cycles, whereas that of the SC- δ electrode starts at $\approx 92\%$ and reaches a comparable level only after ≈ 300 cycles (Figure S5). Notably, the average discharge voltage of the RC- δ electrode decreases by 0.139 V over 400 cycles (≈ 0.3 mV per cycle), demonstrating only marginal voltage fading in long-term cycling (Figure S6), a behavior rarely observed in Mn-redox-based cathodes. We further evaluated the cycling performance of both SC- δ and RC- δ electrodes at 200 mA g⁻¹, which retain 96.8 and 98.0% of their first-cycle capacity, respectively, over 100 cycles (Figure S7). Such remarkably stable cycling performance is also demonstrated in a concentrated cathode configuration with multi-walled carbon nanotube (MWCNT) (active material: MWCNT: PTFE = 90:5:5), as shown in Figure S8 [45].

3 | Discussion

Mn-rich DRX/ δ -DRX cathodes, an emerging and promising subset of the DRX class [46], are based on the earth-abundant Mn element and offer a substantial cost advantage over Ni- and Co-based oxides, making them a compelling class of sustainable, Ni- and Co-free cathodes. They not only have the highest specific energy of any cathode material operating on the Mn redox couple [16, 17, 46], but also show exceptional cycling stability and can be synthesized through solid-state methods without ball milling [19]. However, the high stability of the *o*-LiMnO₂ phase in Mn-rich, low-Ti compositions elevates the order-disorder transition temperature. This thermodynamic constraint necessitates high-temperature, long-dwell synthesis to achieve cation disorder, which inevitably promotes severe particle coarsening. As the coarsened particles suffer from poor Li-ion kinetics, leading to limited electrochemical performance, a rational synthesis strategy for particle-size control is essential to avoid conventional milling-induced pulverization.

In this work, we identify the cooling-induced phase transformation of Ti-lean particles as the key origin of this synthesis challenge. Using a newly developed particle-resolved automated STEM-EDS workflow, we demonstrate interparticle composi-

tional heterogeneity that emerges in the early stage of phase-pure DRX formation. Ti-lean particles specifically are found to be highly susceptible to transformation to *o*-LiMnO₂ during a conventional slow cooling environment, consistent with our understanding that *d*⁰ elements, such as Ti, help stabilize DRX [24]. To eliminate these localized impurities, conventional synthesis routes have relied on long annealing to promote interparticle compositional homogenization, which inevitably drives severe particle coarsening. This previously unrecognized kinetic mechanism accounts for the reliance on excessive annealing to achieve phase-pure Mn-rich DRX in the literature and the persistent difficulty in reducing particle size.

We demonstrate that accelerated cooling is an effective method to kinetically suppress this cooling-induced transformation. This route acts on a different timescale, in that rapid cooling outruns the nucleation of *o*-LiMnO₂ rather than requiring the additional dwell time needed to remove the Ti-lean particles by interparticle diffusion in conventional slow cooling. Phase-pure DRX is thus obtained with substantially less time at high temperature (from dwelling at 1100°C for 20 min, followed by slow cooling to dwelling at 1040°C for 1 min, followed by quenching). This modified thermal regime enables an effective particle-size reduction from 3.5 μ m (D50) to the near-micron regime (1.5 μ m). The particle-size-engineered Mn-rich DRX readily undergoes rapid transformation into the δ -phase (≈ 12 h) upon electrochemical pulsing, and the resulting material displays markedly improved electrochemical performance. Notably, the optimized δ -DRX electrode delivers a discharge capacity of ≈ 200 mAh g⁻¹ and a gravimetric energy density of ≈ 640 Wh kg⁻¹, showing its potential as a promising Ni- and Co-free cathode material.

Crucially, the near-micron single-crystalline Li_{1.1}Mn_{0.8}Ti_{0.1}O_{1.9}F_{0.1} δ -DRX exhibits exceptional cycling stability with negligible voltage fading, retaining $\approx 97\%$ of its capacity over 400 cycles without any electrolyte modification, surface coating, or special doping. Figure S9 presents the energy density and capacity retention of δ -DRX in comparison with representative Mn-redox cathodes, such as spinel LiMn₂O₄ [47–49], olivine LiMn_xFe_{1-x}PO₄ [50–52], and DRX Li_{1+x}TM_{1-x}O₂ (TM = transition metal) [40, 53] analogues, both without (Figure S9a) and with (Figure S9b) compositional modifications or surface coating. While leaving substantial scope for further optimization through compositional design, the achieved energy density and cycling stability of δ -DRX surpasses those of other Mn-rich cathodes without (Spinel [47]: $\approx 90\%$ after 200 cycles at 541 Wh kg⁻¹, olivine [50]: $\approx 93\%$ after 100 cycles at 500 Wh kg⁻¹, DRX [40]: $\approx 84\%$ after 100 cycles at 620 Wh kg⁻¹) or with (Spinel [48, 49]: $\approx 94\%$ after 400 cycles at 410 Wh kg⁻¹ (Al-doped) and $\approx 91\%$ after 400 cycles at 488 Wh kg⁻¹ (La-Mn-Sr-O-coated), olivine [51, 52]: $\approx 94\%$ after 200 cycles at 535 Wh kg⁻¹ (Mg-doped) and $\approx 97\%$ after 400 cycles at 532 Wh kg⁻¹ (C-coated), DRX [53]: $\approx 88\%$ after 200 cycles at 754 Wh kg⁻¹ (High F-doped)) any modifications. We note that the literature data compared here were selected under broadly comparable conditions, such as half-cell configurations, room temperature, and rates at or below 1C. Although differences in finer experimental details warrant some caution in direct comparison, the comparison shows the strong potential of near-micron single-crystalline δ -DRX among Mn-redox cathodes. This remarkable performance of δ -DRX can be understood as a combined effect of the suppressed two-phase reaction in Mn nanodomains within

the δ -phase, together with an optimized balance between reduced surface-driven degradation and efficient Li-ion transport kinetics in the near-micron regime.

Mn-based cathodes are well known to exhibit a complex phase-stability landscape, in which multiple intermediate or secondary phases can form during heating depending on composition and temperature [54–56]. Our results extend this consideration to the cooling stage, demonstrating that thermal control governs phase evolution not only during heating but also during cooling. While the electrochemical performance of $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$ DRX/ δ -DRX was significantly enhanced through the implementation of quenching, a processing strategy employed across industries such as metallurgical and ceramic systems, the critical cooling rate depends sensitively on composition. In DRX compositions with reduced d^0 -metal content, the thermodynamic driving force toward ordered orthorhombic o - LiMnO_2 formation is stronger (Figure S10), implying that more rapid cooling may be required to kinetically suppress impurity precipitation during cooling. Under such conditions, quenching approaches of a more aggressive nature than air-quenching, including water quenching with appropriate mitigation of proton-exchange effects or liquid-nitrogen quenching, could be necessary to fully suppress orthorhombic impurity formation. Importantly, however, the reliance on these quenching protocols could be fundamentally reduced or even eliminated if novel synthesis strategies capable of suppressing interparticle compositional heterogeneity are developed in future studies.

Overall, this work identifies cooling-induced o - LiMnO_2 impurity precipitation imposed by interparticle compositional heterogeneity as a key kinetic constraint on particle-size control in Mn-rich DRX/ δ -DRX cathode materials. By kinetically suppressing this precipitation with accelerated cooling, we establish a general synthesis framework that decouples phase purity from particle coarsening and enables particle-size reduction to the near-micron regime. Importantly, this mechanistic control allows δ -DRX to be optimized in both energy density and cycling performance, demonstrating its strong potential as a sustainable, high-performance, Ni- and Co-free cathode material for lithium-ion batteries.

Author Contributions

E.L. and G.C. conceived the project. G.C. supervised all aspects of the research. E.L. carried out the experimental work and interpreted the results. T.H., M.M., and H.K. assisted in designing experiments and interpreting the results. T.M., P.E., and A.P. developed and implemented automated electron microscopy. S.W. conducted elemental analysis of the synthesized powders. S.H., K.O., and A.M. carried out synchrotron-based characterization. Y.F. and V.B. collected particle size distribution data using laser diffraction analysis. E.L. and G.C. wrote the initial draft, and the manuscript was revised and finalized with input from all authors.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The datasets generated and analyzed during this study are available from the corresponding author or the first author upon request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: aenm71701-sup-0001-SuppMat.docx.