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Tailoring Solid-State Reaction Pathways for Bulk Fluorination of Mn-Rich Rock-Salt Cathodes

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Abstract

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Abstract

Manganese-based cation-disordered rock-salt (DRX) cathodes offer high capacity without relying on cobalt and nickel, but maintaining that capacity over extended cycling often requires bulk fluorination. The challenge is that incorporating fluorine into Mn-rich DRX host structures is hindered by unfavorable thermodynamics and the stability of LiF, often necessitating high synthesis temperatures that promote severe lithium and fluorine volatilization. This study overcomes that limitation by manipulating the solid-state reaction pathway using unconventional Li_6MnO_4 and MnF_2 precursors in a challenging Mn-rich model system ($\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$). This precursor engineering strategy reshapes the thermodynamic landscape. Computational modeling and *in situ* X-ray diffraction reveal that by using reactive starting materials, we prevent the crystallization of unreactive kinetic dead ends, driving uniform bulk fluorination at a lower temperature. The resulting DRX retains both a high fluorine content and the lithium excess required for three-dimensional percolation, delivering improved electrochemical performance relative to material synthesized from conventional precursors.

Introduction

The global transition toward sustainable energy infrastructure has placed unprecedented demand on lithium-ion batteries. Commercial layered oxide cathodes, such as $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC), rely heavily on geochemically scarce and economically volatile transition metals like nickel and cobalt to maintain structural stability and high energy density.¹⁻⁴ With projected manufacturing targets suggesting that the demand for these elements may surpass global production capacities by 2030, developing alternative cathode chemistry based on earth-abundant, low-cost elements like manganese and iron is imperative.^{4, 5}

In this context, cation-disordered rock-salt (DRX) materials have emerged as a high-capacity, cobalt- and nickel-free platform.⁶⁻⁸ Unlike traditional layered oxides that require strict separation of lithium and transition metal sublattices to facilitate two-dimensional ion diffusion,³ DRX materials utilize a cubic rock-salt framework with randomly distributed cations.^{3, 5, 9} Percolation theory demonstrates that efficient three-dimensional lithium transport is viable within these disordered structures, provided a sufficient lithium excess is introduced to establish a continuous, low-barrier 0-TM percolation network.^{9, 10}

Among various DRX candidates, manganese-based systems (Mn-DRX) are uniquely attractive due to the natural abundance of manganese and their capability to deliver high theoretical specific energies $> 900 \text{ Wh kg}^{-1}$.^{7, 11-14} Furthermore, Mn-rich DRX compositions often undergo a beneficial structural activation during early cycling, relaxing into a spinel-like phase that optimizes 0-TM channels and boosts rate capability.¹⁵⁻¹⁷ However, severe capacity fade and large voltage hysteresis caused by irreversible anionic redox remain performance-limiting bottlenecks.^{12, 18-20} At high states of charge, the local Li-O-Li configurations inherent to Li-excess

environments leave unhybridized oxygen 2p orbitals vulnerable to oxidation, triggering oxygen loss, surface densification, and transition metal migration.^{6, 18, 21}

Partial substitution of lattice O^{2-} with F^- remains the most effective strategy to mitigate these degradation pathways.²²⁻²⁵ Incorporating monovalent, highly electronegative F^- lowers the average transition metal valence in the as-synthesized state, expanding the reversible cation redox reservoir and delaying the onset of unstable oxygen oxidation.^{4, 12, 22} Furthermore, fluorine directly stabilizes the rock-salt structure through the formation of robust, highly ionic metal-fluorine bonds that resist structural reorganization.^{26, 27}

Nevertheless, achieving uniform bulk fluorination via scalable synthesis routes presents a challenge owing to thermodynamic competition with LiF. High-energy ball milling (HEBM) can bypass thermodynamic minima to incorporate >20 mol% fluorine, but the resulting nanoscale, irregularly shaped particles suffer from low tap densities and high surface areas that accelerate detrimental electrolyte side reactions.^{4, 12, 22} Conventional high-temperature solid-state synthesis offers excellent morphological control and high tap density but is fundamentally limited by the competition with LiF,²⁸ which has low bulk solubility in DRX. Although high temperatures can often enhance solubility and diffusion, heating above 848 °C causes fluorine volatilization before effective bulk incorporation can occur, leading to substantial fluorine loss and the formation of secondary impurity phases.²⁸

To address this limitation, our previous work utilized unconventional precursors (Li_6MnO_4 and MnF_2 as Li and F sources) to synthesize fluorinated $Li_{1.2}Mn_{0.4}Ti_{0.4}O_{2-x}F_x$ compositions. We showed that by using these precursors, stable and unreactive intermediates could be avoided, leading to a three-fold increase in fluorination levels relative to conventional precursors.¹²

However, shifting toward higher manganese fractions to maximize reversible capacity and minimize reliance on inactive titanium introduces an additional challenge: as the manganese concentration increases, the thermodynamic solubility of fluorine decreases.²⁶ Cluster-expansion Monte Carlo (CEMC) simulations show that Mn-F bonds are energetically unfavorable compared to Ti-F bonds, driving Mn-rich systems to phase-separate into LiF and MnO rather than forming a homogeneous oxyfluoride.^{28, 29}

In this work, we extend the Li_6MnO_4 and MnF_2 precursor strategy to a more challenging Mn-rich DRX system for fluorination: $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$. By adjusting the Mn:Ti ratio to 3:1, we probe the boundaries of solid-state synthesis where fluorine solubility is suppressed. Through *in situ* high-temperature characterization, detailed *ex situ* characterization, and computational analyses, we evaluate how this reaction pathway governs bulk fluorination, structural stability, and battery performance, establishing a viable and design-driven route toward fluorinated Mn-rich DRX cathodes.

Experimental section

Synthesis of Li_6MnO_4

The Li_6MnO_4 precursor was prepared by solid-state synthesis using Li_2O (Alfa Aesar, 99.5%) and MnO (Alfa Aesar, 99.9%), following a previously published recipe.³⁰ Specifically, Li_2O and MnO (Li:Mn = 8.4:1) were homogeneously mixed by ball milling for 3 h using a planetary ball mill (PM200, Retsch). The mixture was pelletized in a 12 mm diameter mold. The pelletized mixed powder was then annealed at 950 °C for 12 h with continuous flow of H_2 (2%)/Ar(98%) mixed gas, followed by quenching.

Synthesis of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$

A range of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ compositions ($x = 0, 0.2, 0.4, 0.6$) were synthesized by a solid-state synthesis method. Stoichiometric amounts of Li_6MnO_4 , MnF_2 (Thermo Scientific, 99%), TiO_2 (Sigma-Aldrich, 99.8%) and Mn_2O_3 (Sigma-Aldrich, 99.9%) were homogeneously mixed by ball milling at 150 RPM for 3 h using a planetary ball mill (PM200, Retsch).

For the control group of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ compounds synthesized with conventional precursors, Li_2O (with 3 mol.% excess lithium, Alfa Aesar, 99.5%), LiF (Alfa Aesar, 99.99%), Mn_2O_3 (Sigma-Aldrich, 99.9%), MnO (Alfa Aesar, 99.99%) and TiO_2 (Sigma-Aldrich, 99.8%) were homogeneously mixed by ball milling at 150 RPM for 3 h using a planetary ball mill (PM200, Retsch). The mixtures were pelletized in a 6 mm diameter mold. The pelletized samples were then annealed for 4 h under continuous Ar gas flow (120-160 CCM) at 800 °C, 900 °C, 1000 °C, 1100 °C, followed by natural cooling. A fixed heating rate of 6.5 °C/min was used for all the synthesis attempts.

Characterization

X-ray diffraction

X-ray diffraction (XRD) analysis was conducted using a Rigaku Miniflex 600 equipped with a $\text{Cu K}\alpha$ radiation source.

Scanning electron microscopy (SEM) analysis

The surface morphology and microstructure of the samples were examined using scanning electron microscopy (SEM, FEI Quanta FEG-250). Energy dispersive X-ray spectroscopy (EDS) elemental mappings were obtained using a Bruker Quantax EDS detector.

X-ray photoelectron spectroscopy analysis

A Kratos Axis Ultra fitted with a monochromated Aluminium source ($K\alpha = 1486.6$ eV) was used for collecting the X-ray photoelectron spectra. Survey spectra were acquired employing a Pass Energy of 160 eV. High-resolution, core-level spectra for all elements were acquired with a Pass Energy of 20 eV. All spectra were referenced against the C1s peak at 284.5 eV to compensate for charging effects during acquisition.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Fluoride-Ion Selective Electrode (F-ISE) Measurement

Elemental analysis of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ compounds was determined by ICP-OES (Agilent 5110) and using F-ISE with Thermo Scientific Orion Dual Star pH/ISE Meter. For these measurements, 45 mg of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ powder was dissolved in 4 mL of aqua regia (hydrochloric acid and nitric acid in a 3:1 ratio) for 1-hour. For ICP-OES analysis, digestion solutions were diluted by factor of 1000 $\times$ before measuring. Calibration curves were generated using standard with five different concentrations from 0.5 ppm to 1000 ppm. For F-ISE analysis, digestion solutions were first diluted by a factor of 5000 $\times$. A total ionic strength adjustment buffer (TISAB II) was added to the diluted digestions at a ratio of 1:1 before measurement. F-ISE measurements were calibrated using 1 ppm F⁻ with TISAB II and 10 ppm F⁻ with TISAB II.

In situ high-temperature X-ray diffraction

In situ high-temperature XRD analysis of the synthesis process was performed using the lamp heater set-up on ALS beamline 12.2.2.³¹ The powder samples were mixed using a planetary ball mill (PM200, Retsch) at 150 RPM for 3 h and loaded into sapphire capillaries (Crytur, USA) with a 0.75-mm inner diameter. These capillaries were mounted into an infrared-heated SiC tube furnace at the beamline. The samples were heated in an Ar atmosphere up to 1000 °C at a ramp

rate of 10 °C/min, followed by a 1 h hold. Diffraction data were acquired continuously during this process with an exposure time of 30 s in angle-dispersive transmission mode using a focused 25-keV monochromatic beam ($\lambda = 0.4959 \text{ \AA}$, 15- μm spot size) and a PILATUS3 S 1M detector. The sample-to-detector distance was calibrated using LaB_6 (NIST_SRM_660a) placed at the sample position before each experimental session. For plotting and analysis, all data were converted into values of 2θ based on $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

Electrochemical measurements

For the cathode film, 280 mg of the as-synthesized active material and 80 mg of super C65 carbon black (Timcal) were mixed using shaker mill for 1 h using a SPEX8000M miller. The electrodes were prepared by hand mixing 90% of composite powder with 10% of polytetrafluoroethylene (PTFE, DuPont, Teflon 8A) using a mortar and pestle. The mixed composite was then rolled into $\sim 40 \text{ }\mu\text{m}$ free-standing thin films inside an Ar-filled glovebox. Coin-type 2032 two-electrode cells were fabricated using the composite electrode (5/16-inch diameter) containing $\sim 3 \text{ mg cm}^{-2}$ of the active material, a Li-foil (FMC) counter/reference electrode, and a glass fiber separator (Whatman, GF/D type). The electrolyte consisted of a 1 M solution (99.99%, Solvionic) of LiPF_6 in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). A glove box (VAC) filled with high-purity argon (99.999%) and equipped with oxygen and moisture sensors/absorbers (H_2O and O_2 content $< 1 \text{ ppm}$) was used for assembling the electrochemical cells. Li-ion half-cells were subjected to galvanostatic rate performance and long-term cycling testing at 20 mA g^{-1} in varied voltage ranges using an Arbin battery test instrument at 30 °C.

Computations

Reaction free energies for the formation of the DRX phases were evaluated by combining machine learning interatomic potential and density-functional theory (DFT) energies. To sample the Li-Mn-Ti-O-F configurational space, special quasi-random structures (SQS) were generated in $4\times4\times5$ rock-salt supercells (160 atoms, comprising 80 cation and 80 anion sites) using the sqsgenerator code.³² Approximately 11,500 such configurations, spanning a broad range of Li:Mn:Ti and O:F ratios around the target $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ stoichiometry, were structurally relaxed and their energies evaluated with the CHGNet universal machine learning interatomic potential.³³

Reference energies for the crystalline precursors, intermediates, and gaseous O_2 were taken from DFT calculations in the Materials Project.³⁴ These energies were computed within the generalized-gradient approximation with Hubbard-U corrections applied to the manganese 3d states (GGA/GGA+U),^{35, 36} and the Materials Project 2020 compatibility corrections were applied so that GGA and GGA+U energies could be placed on a common scale; for each phase the ground-state polymorph (lowest energy above the convex hull) was used.

To represent the high-temperature synthesis environment, the system was treated as open to oxygen exchange and a configurational entropy contribution was included. The oxygen chemical potential was referenced to O_2 gas and corrected for temperature (T) and partial pressure (p_{O_2}) using the ideal-gas expression together with the standard NIST-JANAF³⁷ heat capacity and entropy of O_2 , so that the reaction free energy depends on both T and p_{O_2} . An ideal (random) configurational entropy was evaluated separately over the cation (Li/Mn/Ti) and anion (O/F)

sublattices and included in the reaction free energy calculations. Additionally, finite-temperature free-energy contributions for all solids were approximated using the machine-learned descriptor from Bartel *et al.*, which estimates $\Delta G_f(T)$ from the atomic volume and reduced mass of each solid.³⁸

Results and Discussion

Precursor-Controlled Reaction Pathways

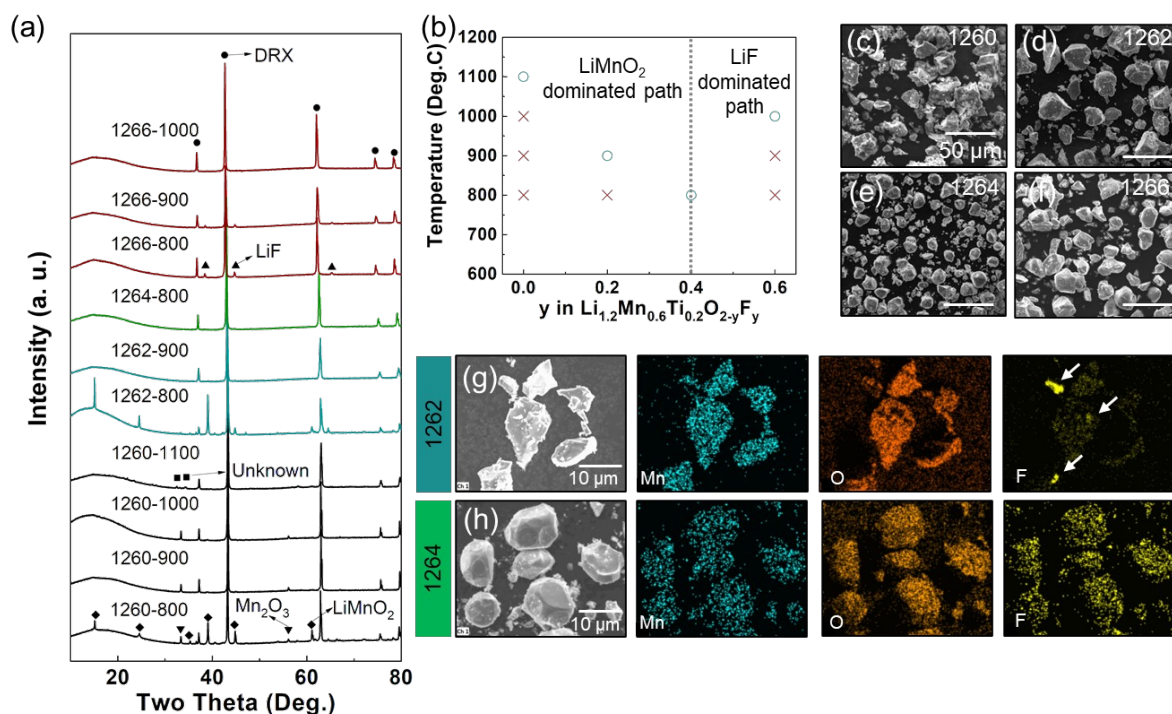


Figure 1. Structural and morphological analysis of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ ($0 \leq x \leq 0.6$) compounds, synthesized using Li_6MnO_4 and MnF_2 precursors. (a) X-ray diffraction patterns of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ ($0 \leq x \leq 0.6$) compounds. (b) Synthesis temperature threshold for pure $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ ($0 \leq x \leq 0.6$) compounds. $\circ$ indicates that a pure phase is synthesized at the selected temperature. $\times$ indicates that impurities were detected in the XRD patterns in Figure 1a at the selected temperature. Scanning electron microscopy images of (c) LMTOF-1260, (d)

LMTOF-1262, (e) LMTOF-1264, (f) LMTOF-1266. Scanning electron microscopy images and energy dispersive X-ray spectroscopy mapping results of (g) LMTOF-1262 and (h) LMTOF-1264.

To evaluate the impact of the synthesis route on the bulk fluorination of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{2-x}\text{F}_x$ ($0 \leq x \leq 0.6$) compounds, four distinct target compositions were prepared and denoted based on their nominal formulations: $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_2$ (Denoted as 1260), $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{1.8}\text{F}_{0.2}$ (Denoted as 1262), $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{1.6}\text{F}_{0.4}$ (Denoted as 1264), and $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{1.4}\text{F}_{0.6}$ (Denoted as 1266).

Figure 1a illustrates the X-ray diffraction (XRD) profiles of the target compounds synthesized across a wide temperature range. Initial synthesis trials were conducted at 800 °C, with systematic 100 °C increments up to 1100 °C upon the detection of secondary phases. For the unfluorinated baseline composition (LMTOF-1260), diffraction patterns revealed persistent secondary phases of LiMnO_2 and Mn_2O_3 at 800 °C. Elevated temperatures systematically reduced the diffraction intensities of these impurities, yet they remained present up to 1000 °C. At 1100 °C, unidentified decomposition products emerged alongside the major DRX phase, illustrating the narrow temperature window over which unfluorinated Mn-rich DRX persists.

Introducing MnF_2 as a precursor significantly modified the temperatures at which these phases were observed. For the lightly fluorinated LMTOF-1262 composition, a minor LiMnO_2 intermediate formed at 800 °C but was fully incorporated into the DRX phase at 900 °C. A phase-pure DRX material was successfully stabilized at a lower temperature of 800 °C when the fluorination target was increased to LMTOF-1264. However, further increasing the nominal fluorination to 30 mol% (LMTOF-1266) reversed this trend, requiring a higher synthesis

temperature of 1000 °C to achieve phase purity. Below this temperature, a prominent LiF impurity was present when targeting this highly fluorinated composition, and this phase volatilized and/or was partially incorporated into the bulk DRX structure upon reaching 1000 °C.

Figure 1b summarizes the temperatures at which phase-pure DRX peaks were observed across the varying fluorine targets using the Li_6MnO_4 and MnF_2 precursors. Within the low-fluorination regime (< 20 mol%, $x < 0.4$), the minimum temperature required to form a single-phase DRX structure decreases monotonically with increasing fluorine content. Here, the primary barrier is eliminating the LiMnO_2 intermediate phase. Above 20 mol%, however, the required temperature increases sharply, and the primary challenge becomes incorporating LiF. This non-monotonic trend in onset temperature indicates two distinct mechanisms at play. In low-fluorination regimes, suppressing LiMnO_2 formation appears to govern the onset, whereas in high-fluorination regimes, higher temperatures are required to overcome the thermodynamic LiF trap.

Scanning electron microscopy (SEM) was employed to monitor the morphological evolution of the synthesized products (**Figures 1c–f**). The unfluorinated LMTOF-1260 compound consists of highly irregular, agglomerated particles with dimensions of 20–30 μm . Upon fluorination up to the LMTOF-1264 composition, the particles transition into uniform, near-spherical morphologies with a refined average grain size of 10 μm . This grain refinement is directly linked to the lower processing temperature (800 °C), which successfully prunes excessive thermal sintering. For the heavily fluorinated LMTOF-1266 composition, the higher temperature required for phase integration (1000 °C) drives substantial grain growth,³⁹ increasing the particle size to approximately 20 μm .

Energy-dispersive X-ray spectroscopy (EDS) mapping was used to evaluate the elemental homogeneity of the incorporated fluorine. For the lightly fluorinated LMTOF-1262 sample, the

fluorine distribution is markedly inhomogeneous, displaying distinct particle-to-particle concentration disparities (**Figure 1g**). In sharp contrast, the LMTOF-1264 sample exhibits an exceptionally uniform, unsegregated fluorine signal across the entire particle (**Figure 1h**). For the LMTOF-1266 target composition, the fluorine signal was significantly attenuated, suggesting substantial fluorine volatilization at the elevated synthesis temperatures required for its formation.

Mechanistic Contrast with Conventional Solid-State Synthesis

To isolate the chemical advantages of the unconventional precursors (Li_6MnO_4 and MnF_2) on fluorinated DRX formation, we synthesized the fluorinated DRX with a target composition of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{1.6}\text{F}_{0.4}$ (LMTOF-1264) using conventional precursors: Li_2O , LiF , Mn_2O_3 , MnO , and TiO_2 . As shown in the *ex situ* XRD profiles (**Figure S1a**), the conventional route fails to achieve a phase-pure rock-salt oxyfluoride. At 800 °C, a primary DRX phase coexists with prominent, unreacted LiF impurities. Even as the processing temperature increases to 1100 °C, the diffraction peaks corresponding to the LiF phase persist, underscoring the thermodynamic challenges associated with dissolving F^- into the Mn-rich matrix by conventional solid-state reaction. Furthermore, SEM and EDS characterization of the 1100 °C conventional control sample (**Figures S1b–f**) reveal highly irregular particle profiles, massive grain growth, and a heavily depleted fluorine distribution.

To precisely quantify chemical compositions and final fluorine retention, inductively coupled plasma optical emission spectroscopy (ICP-OES) and fluorine ion-selective electrode (F-ISE) analyses were systematically compiled (**Table 1**). The quantified values reveal that while the baseline LMTOF-1260 sample closely mirrors its intended formulation, the fluorinated products display a clear dependence on precursor choice. Compositional analysis of LMTOF-1262 and

LMTOF-1264 synthesized using the unconventional precursors demonstrates substantial bulk fluorine retention, capturing 41% and 37% of their nominal targets ($x = 0.082$ and $x = 0.149$, respectively). Pushing the target to 30 mol% (LMTOF-1266) results in a severe drop in retention (8.5%, $x = 0.051$), confirming that the Mn-rich rock-salt structure strongly resists fluorination under solid-state synthesis conditions.

Crucially, the unconventional precursor pathway outperforms the conventional route by over an order of magnitude. The control sample synthesized using conventional precursors (LMTOF-1264_LiF) achieved a meager retention of just 3.25% ($x = 0.013$). Moreover, the control sample exhibits severe lithium deficiency (Li0.966 vs. Li1.2 target), demonstrating that the high temperatures required to encourage LiF dissolution induce catastrophic lithium volatilization without driving successful bulk fluorination.

Table 1. Elemental analysis results from inductively coupled plasma optical emission spectroscopy (ICP-OES) and fluorine ion-selective electrode (F-ISE).

Sample	Li	Mn	Ti	F
LMTOF-1260_MnF ₂	1.262	0.564	0.174	N/A
LMTOF-1262_MnF ₂	1.119	0.692	0.189	0.082
LMTOF-1264_MnF ₂	1.129	0.661	0.210	0.149
LMTOF-1266_MnF ₂	0.977	0.777	0.245	0.051
LMTOF-1264_LiF	0.966	0.781	0.253	0.013

Validation of Bulk vs. Superficial Fluorination

To determine whether the incorporated fluorine is integrated within the bulk oxyfluoride material or segregated at the particle surface, X-ray photoelectron spectroscopy (XPS) depth profiling was completed across the F 1s core-level region. As demonstrated in **Figure 2a**, the LMTOF-1264_MnF₂ sample prepared via the tailored route exhibits an intense, well-defined F 1s peak that remains structurally stable and highly uniform throughout the entire sputtering sequence. This profile provides evidence of homogeneous bulk oxyfluoride formation when starting from unconventional precursors. In contrast, the conventional LMTOF-1264_LiF sample (**Figure 2b**) reveals a collapse in fluorine intensity upon sputtering past the initial surface layer, similar to a previous study.⁴⁰ This confirms that the minimal fluorine retained in the conventional synthesis is largely restricted to superficial surface anomalies or phase-segregated boundaries. This difference, tracked quantitatively via normalized intensity vs. etching time (**Figure 2c**), underscores the role of the reactive MnF₂ precursor in mediating fluorination.

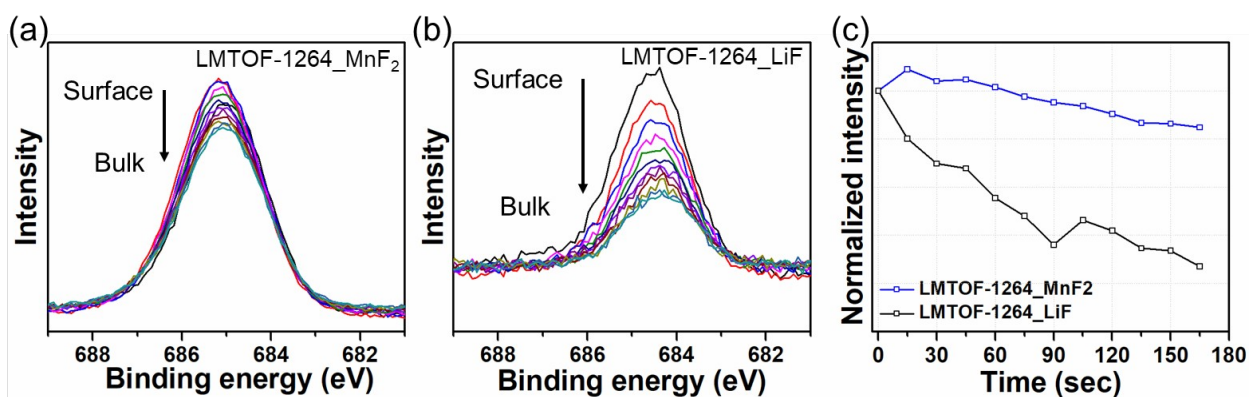


Figure 2. X-ray photoelectron spectroscopy with depth profiling of the fluorine peak. (a) Fluorine peak of LMTOF-1264_MnF₂. (b) Fluorine peak of LMTOF-1264_LiF. (c) Normalized peak intensity from the surface to the bulk for LMTOF-1264_MnF₂ and LMTOF-1264_LiF as a function of etching time.

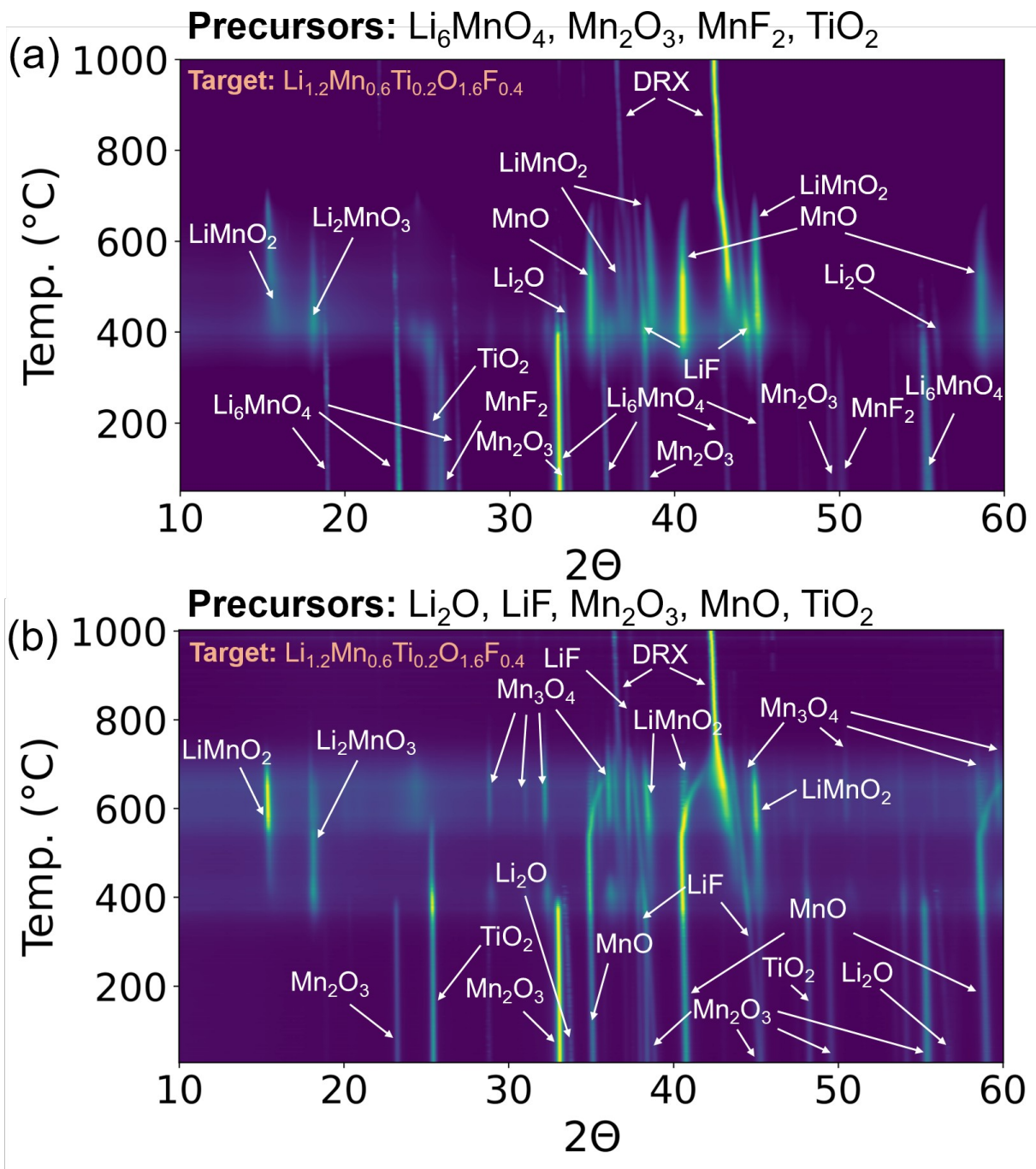


Figure 3. *In-situ* synchrotron thermal X-ray diffraction measurements (converted to Cu K for better readability) captured during the synthesis of LMTFO-1264 using precursors of (a)

Li_6MnO_4 , MnF_2 , Mn_2O_3 , TiO_2 , and (b) Li_2O , LiF , MnO , Mn_2O_3 , TiO_2 . The samples were heated in an Ar atmosphere from 100 °C to 1000 °C at a ramp rate of 10 °C/min.

To map the reaction pathways by which these precursors yield fluorinated DRX compositions, *in situ* high-temperature XRD characterization was performed from 100 °C to 1000 °C. **Figure 3a** tracks the structural evolution of the LMTOF-1264_ MnF_2 unconventional precursor blend. Below 350 °C, the starting phases (Li_6MnO_4 , MnF_2 , Mn_2O_3 , TiO_2) remain unreacted. Above 350 °C, a rapid cascade of intermediate transitions is triggered: Li_6MnO_4 , Mn_2O_3 and MnF_2 are consumed to generate a mixture of crystalline intermediates including LiMnO_2 , Li_2MnO_3 , MnO , Li_2O , and LiF . However, it should be noted that some unreacted Li_6MnO_4 remained up to 600–650 °C. The evolution of these active manganese intermediate phases represents a distinct departure from lower-Mn target compositions,¹² showing that the high target manganese concentration alters low-temperature phase formation. Importantly, the low-temperature intermediates that form continue to undergo successive phase transformations with increasing temperature. Within 350–400 °C, the diffraction intensities of Li_6MnO_4 and MnF_2 decrease as signals for transient LiF and MnO phases increase. DRX formation initiates at ~400 °C, coinciding with the consumption of TiO_2 as well as a decrease in LiF diffraction intensity and the disappearance of the MnF_2 peak. Meanwhile, the Mn-containing intermediates (LiMnO_2 , Li_2MnO_3 , MnO) remain mostly unreacted. These results suggest the initial DRX that forms is likely Ti-rich with fluorination. Upon further heating to 700–750 °C, the intermediate oxides and transient fluorides react and yield a single-phase, bulk-fluorinated DRX. Above 850 °C, secondary diffraction peaks emerge, indicating decomposition of this oxyfluoride.

The conventional precursors exhibit a fundamentally different phase transformation sequence (**Figure 3b**). Li_2O and Mn_2O_3 react below 500 °C to yield LiMnO_2 and Li_2MnO_3 intermediates, and a Ti-rich DRX phase appears at 550 °C alongside the oxidation of MnO into Mn_3O_4 , but the primary fluoride source (LiF) remains inactive, with LiF peaks persisting up to its melting point (~900 °C). The failure to incorporate fluorine with this precursor mixture is consistent with prior reports.^{12, 28, 41} At temperatures above 900 °C, LiF peaks disappear, but the volatility of fluorine²⁸ likely leads to its escape in the gas phase rather than incorporating into the DRX phase.

In situ tracking of different fluorination targets with unconventional precursors (**Figure S2**) shows that nominal fluorine content (*i.e.*, which composition x is being targeted) changes the dominant intermediate phase and, as a result, the temperature required for DRX formation. At low fluorine content, the precursor mixtures contain a larger proportion of Mn_2O_3 , which reacts with Li_6MnO_4 to produce LiMnO_2 and Li_2MnO_3 intermediates. These Li–Mn–O phases must subsequently be consumed before a phase-pure DRX product can form. As the nominal fluorine content increases, the intensity of these oxide intermediates decreases. At highly fluorinated compositions, LiF becomes the dominant impurity phase, persisting to substantially higher temperatures. This persistence indicates that the fluorine content exceeds what can be readily incorporated into Mn-rich DRX, leaving LiF as a stable secondary phase. These results are well aligned with our *ex situ* XRD observations in **Figure 1a**.

Computational Thermodynamics of Precursor-Guided Fluorination

To establish a quantitative foundation for these experimental observations, we evaluated how precursor choices influence the thermodynamic driving forces governing DRX phase formation. Utilizing the CHGNet machine-learned interatomic potential,³³ we screened the free energies of over 11,500 disordered $\text{Li}_y\text{Mn}_z\text{Ti}_{2-y-z}\text{O}_{2-x}\text{F}_x$ configurations spanning $x \geq 0, 1 \leq y \leq 1.5, z \leq 1$. An ideal

configurational entropy term, assuming random mixing on the cation and anion sublattices, was included to account for high-temperature synthesis environments. Vibrational entropy contributions were additionally approximated using a machine-learned descriptor.³⁸ The system was treated as open to oxygen exchange, with the oxygen chemical potential referenced to O₂ gas as a function of temperature (T) and partial pressure (p_{O_2}).³⁸

Using this framework, we mapped the reaction free energy (ΔG) to form each candidate DRX composition from both precursor sets across a wide (T, p_{O_2}) processing window. At each condition, we identified the specific DRX composition with the most negative ΔG . Following previous work, this “max- ΔG ” phase is often the one nucleating first during early, low-temperature phase transformations.⁴²⁻⁴⁴ As such, the fluorine content of this composition indicates the propensity for a precursor set to deliver fluorine into the DRX phase, independent of the nominal target stoichiometry, and disregarding the effect of competing phases.

Figure 4 compares the conventional and unconventional precursor sets, both before and after the initial solid-state reactions identified in **Figure 3**. Considering first the pristine precursors (*i.e.*, before any reactions occur), the two routes show notable differences. For the conventional set (Li₂O + MnO + LiF + TiO₂), the thermodynamically favored DRX phase contains near-zero fluorine ($x < 0.1$ per O_{2-x}F_x formula unit) across a wide range of (T, p_{O_2}) (**Figure 4c**). This indicates that the system can minimize its free energy by forming a fluorine-free DRX and leaving LiF unreacted. In contrast, the unconventional set (Li₆MnO₄ + MnO + MnF₂ + TiO₂) favors substantially fluorinated DRX phases ($x \approx 0.3\text{--}0.6$ per O_{2-x}F_x formula unit) at high temperature and low p_{O_2} (**Figure 4e**).

To clarify how the unconstrained optima in the heatmaps emerge, we next resolved the same reaction energy landscape as a function of fluorine content (x) under representative conditions of 1000 °C and 1 Pa O₂ (**Figures 4a and 4b**). At each fluorine content, we identified the most favorable DRX candidate by minimizing the reaction free energy over the sampled cation compositions (y) and (z) in Li _{y} Mn _{z} Ti_{2- y - z} O_{2- x} F _{x} . These curves therefore represent lower-energy envelopes rather than reactions to a single fixed target composition. When starting from conventional precursors, ΔG is minimized at zero fluorination and rises monotonically as fluorine is added, so a fluorine-free oxide is always preferred. In contrast, unconventional precursors lead to the most driving force (most negative ΔG) occurring at a heavily fluorinated composition ($F \approx 0.4$). This change is rooted in the chemical potential of fluorine in the respective fluorine sources. LiF is a thermodynamic sink, and there is no thermodynamic incentive for it to react with a Mn-rich oxide. Replacing LiF with the more reactive MnF₂ increases the chemical potential of fluorine in the starting state, shifting the thermodynamically preferred composition to more fluorinated DRX phases.

The reactivity of the precursors complicates this picture, however, because the starting materials undergo partial phase transformations before DRX crystallization. **Figures 4a and 4b**, therefore, also report the driving force to form DRX from the intermediate phases that these precursors produce on heating (*i.e.*, after initial reactions but before DRX formation). For the conventional route, Li₂O and MnO react to form stable Li-Mn-O ternaries (*e.g.*, Li₂MnO₃), from which there is essentially no driving force to form DRX, and the little DRX they can form remains fluorine-free. Whether one considers the pristine precursors or their intermediates, the conventional route thus offers no viable thermodynamic path to a fluorinated DRX.

The unconventional route behaves very differently. Although the reactive MnF_2 is partially consumed and converted to LiF at low temperature, the persistence of Li_6MnO_4 helps maintain a significant driving force to form DRX across a wide range of fluorine contents ($\Delta G < 0$ throughout). Once MnF_2 has been fully converted to LiF , the fluorine-free oxide again becomes the preferred product, but any MnF_2 surviving into the DRX-forming window continues to favor fluorine incorporation; the shaded region between the “before” and “after” curves in **Figure 4b** represents this intermediate regime.

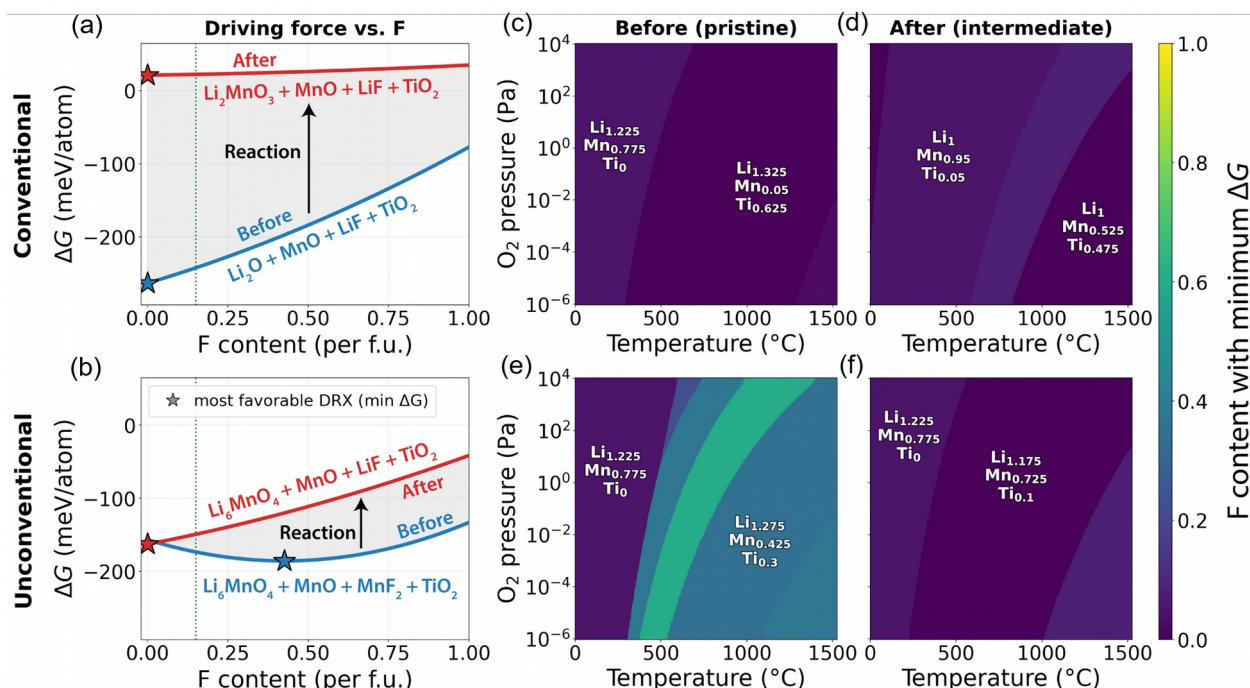


Figure 4. Thermodynamic driving force for DRX formation before and after the initial reaction of the precursors, for the conventional and unconventional routes. Reaction free energy (ΔG) to form DRX as a function of fluorine content at 1000 °C and 1 Pa O_2 , evaluated both for the pristine precursors (“before”) and for the intermediate phases they form on heating (“after”); stars mark the most favorable (minimum ΔG) composition for (a) conventional and (b) unconventional precursors. Fluorine content of the most thermodynamically favored DRX phase

as a function of temperature and oxygen partial pressure, for (c) the pristine precursors and (d) their intermediates in the case of conventional precursors. Fluorine content of the most thermodynamically favored DRX phase as a function of temperature and oxygen partial pressure, for (e) the pristine precursors and (f) their intermediates in the case of unconventional precursors.

The Role of Manganese Precursors in Governing Intermediate Phase Formation

The synthesis experiments targeting increasingly fluorinated DRX compositions (**Figure 1**) revealed a non-monotonic relationship between target fluorine content and the temperature required to achieve phase-pure DRX. Below 20 mol% fluorine ($x = 0.4$ in O_{2-x}F_x), phase-pure DRX formation is limited primarily by the formation of Li–Mn–O intermediates. The lower-fluorine precursor mixtures contain a larger proportion of Mn_2O_3 that leads to greater amounts of LiMnO_2 and Li_2MnO_3 intermediates, which are limited in their reaction with the DRX phase unless high temperature ($> 800\text{ }^\circ\text{C}$) is used. Increasing the target fluorine content reduces the formation of these stable intermediates, thereby lowering the temperature required to achieve phase-pure DRX.

In addition, *in situ* measurements (**Figures 3 and S2**) confirm that these Li–Mn–O ternaries originate from reactions between the Li_6MnO_4 and the supplemental manganese oxide (Mn_2O_3) precursors. This raises a fundamental mechanistic question: why do these stable ternaries form so readily, and how does the choice of manganese precursor dictate the thermodynamics associated with DRX formation?

Li_6MnO_4 (nominally $3\text{Li}_2\text{O} + \text{MnO}$) acts as a highly reactive lithium source. Upon contact with manganese oxides, this lithium precursor can react with manganese oxide to form stable Li–Mn–O ternaries as observed in the *in situ* XRD analysis (**Figure 3**). Therefore, we hypothesize that the specific ternary phase formed can be strictly governed by the initial oxidation state of the

manganese precursor. When Mn_2O_3 was used as a supplementary manganese source along with Li_6MnO_4 and MnF_2 to synthesize LMTOP-1264 (**Figure 1a**), the pure DRX phase was synthesized at 800 °C. However, substituting Mn_2O_3 with the more oxidized MnO_2 precursor results in the formation of LiMnO_2 at 800 °C and necessitates significantly higher synthesis temperatures (**Figure 5a**). In contrast, utilizing a more reduced MnO precursor allows for the synthesis of phase-pure DRX at 800 °C as shown in **Figure 5 b**.

To quantify these effects, we performed two complementary thermodynamic calculations (**Figure 5c**). First, we computed the driving force for the reaction between Li_6MnO_4 and various manganese oxides to form Li-Mn-O intermediates. Second, we calculated the driving force for these intermediates to convert into the target DRX phase, assuming the concurrent conversion of MnF_2 into MnO and LiF . Our results demonstrate that the propensity to form Li-Mn-O ternaries scales linearly with the oxidation state of the manganese precursor. MnO_2 (Mn^{4+}) is oxidation-state matched to Li_2MnO_3 , forming this highly stable ternary with a significant driving force (-230 meV/atom) at 1000 °C. Mn_2O_3 (Mn^{3+}) leads to LiMnO_2 and MnO intermediates (-114 meV/atom), whereas MnO (Mn^{2+}) exhibits no thermodynamic driving force to react with Li_6MnO_4 in a closed system. Essentially, more oxidized manganese precursors lower the energy of the system through non-fluorinating reactions with Li_6MnO_4 , inhibiting fluorination of the resulting lower energy Li-Mn-O ternary phases.

Figure 5d illustrates that these MnO_2 -derived intermediates ($\text{LiMnO}_2 + \text{Li}_2\text{MnO}_3$, red curve) provide significantly less driving force for DRX formation than the Mn_2O_3 -derived intermediates ($\text{LiMnO}_2 + \text{MnO}$, blue curve). Specifically, the exceptional thermodynamic stability of Li_2MnO_3 inhibits subsequent reactions at moderate temperatures.

These calculations explain the non-monotonic temperature trend observed in **Figure 1** through two competing thermodynamic regimes. At low fluorine targets, higher proportions of oxide precursors (relative to MnF_2) are required, promoting the formation of stable Li-Mn-O ternaries, which require high temperature to initiate reaction. Consequently, increasing the fluorine content initially lowers the required temperature by decreasing the proportion of these less reactive intermediates. At high fluorine targets, however, excess fluorine accumulates as LiF, which primarily leaves the system by volatilization at temperatures exceeding $848\text{ }^\circ\text{C}$,²⁸ rather than incorporating into the DRX phase. The required synthesis temperature thus rises again, creating a minimum at 20 mol% ($x = 0.4$ in O_{2-x}F_x) fluorine where the penalties of stable ternary formation and LiF trapping are simultaneously minimized.

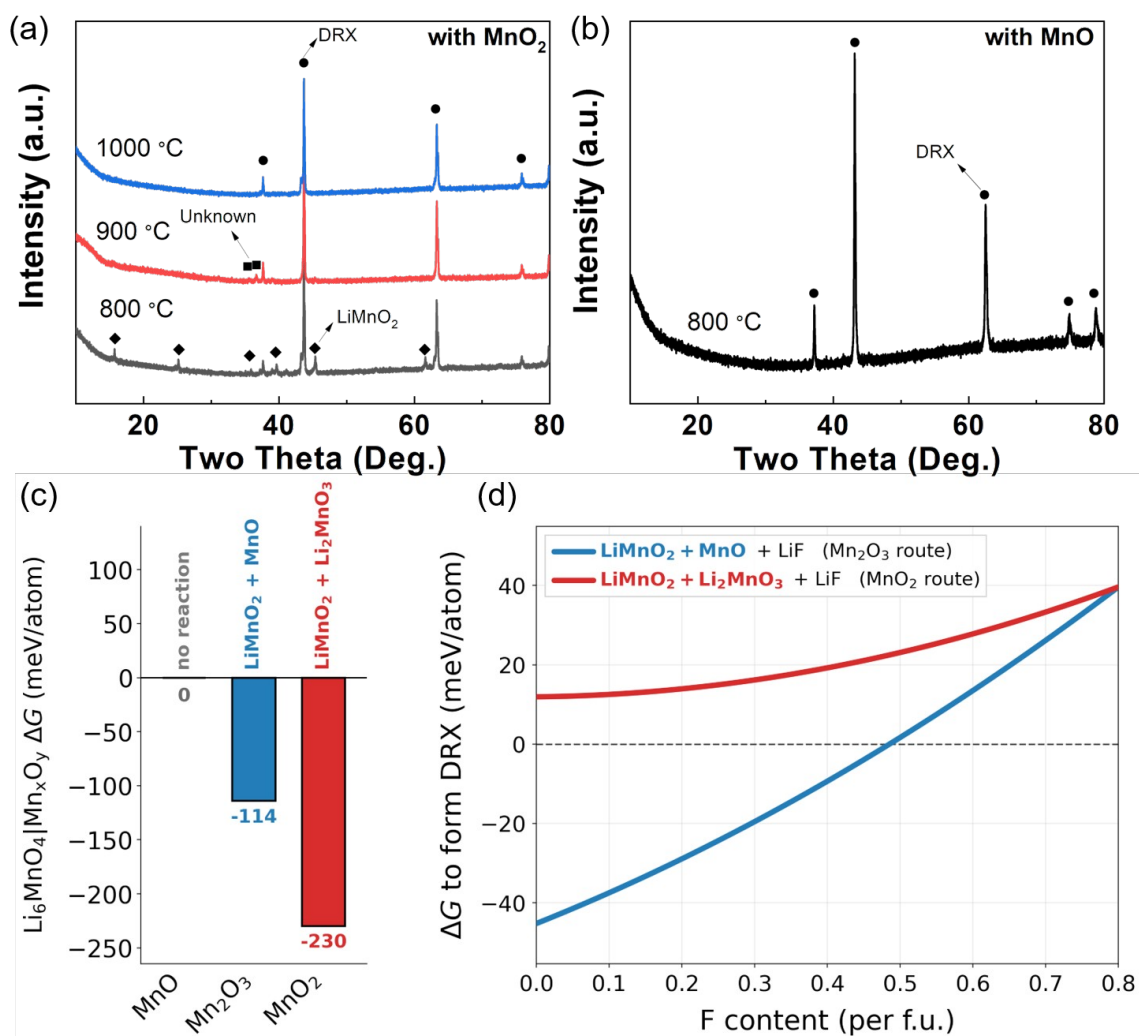


Figure 5. (a) X-ray diffraction patterns of LMTOF-1264 synthesized with Li_6MnO_4 , MnF_2 , TiO_2 and MnO_2 . (b) X-ray diffraction patterns of LMTOF-1264 synthesized with Li_6MnO_4 , MnF_2 , TiO_2 and MnO . Thermodynamic origin of Li-Mn-O intermediate formation and its effect on DRX fluorination. (c) Driving force for Li_6MnO_4 to react with different manganese oxides and form Li-Mn-O ternaries. (d) Driving force to form DRX phases from Li-Mn-O intermediates, plotted as a function of fluorine content.

Electrochemical property evaluation of LMTOF-1264 synthesized by different precursors

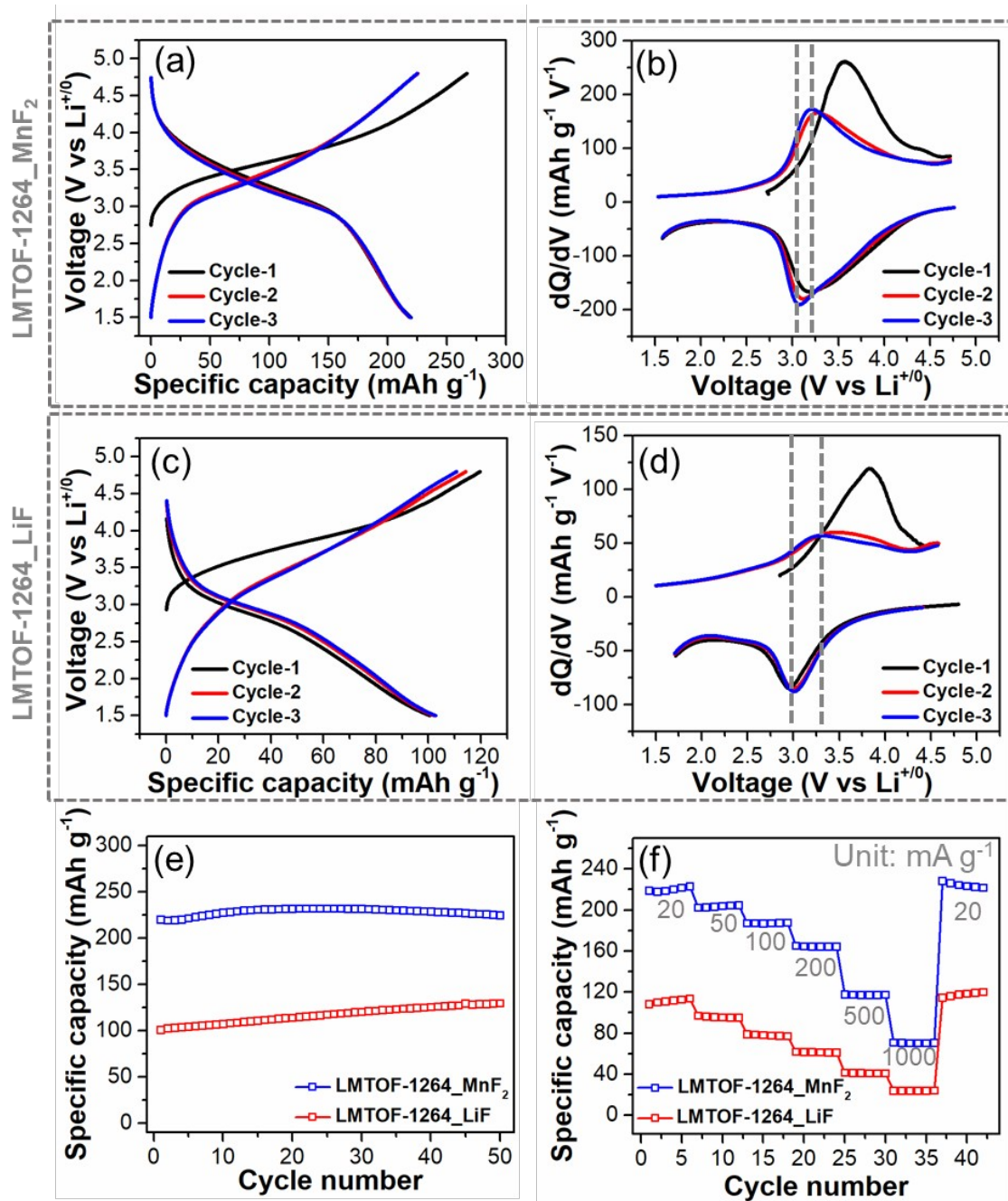


Figure 6. Electrochemical performance of LMTOF-1264 compounds synthesized using conventional (LMTOF-1264_LiF) and unconventional (LMTOF-1264_MnF₂) precursors.

(a) Galvanostatic charge–discharge profiles and (b) dQ dV⁻¹ plot of LMTOF-1264_MnF₂ cycled

at 20 mA g⁻¹ (c) Galvanostatic charge–discharge profiles and (d) dQ dV⁻¹ plot of LMTOF-1264_LiF cycled at 20 mA g⁻¹ (e) Cycling performance of LMTOF-1264_MnF₂ and LMTOF-1264_LiF at 20 mA g⁻¹. (f) Rate performance of LMTOF-1264_MnF₂ and LMTOF-1264_LiF.

To evaluate how the synthesis pathway influences electrochemical behavior, we compared the performance of the bulk-fluorinated LMOTF-1264_MnF₂ sample against the conventionally synthesized LMTOF-1264_LiF control system. **Figures 6a and 6c** display the typical galvanostatic charge–discharge profiles of both materials cycled at a current density of 20 mA g⁻¹. Notably, the bulk-fluorinated LMTOF-1264_MnF₂ cathode delivers a substantially higher specific discharge capacity of ~220 mAh g⁻¹, more than doubling the ~101 mAh g⁻¹ achieved by the conventional LMTOF-1264_LiF control. Furthermore, the tailored precursor route yields a significantly higher average discharge voltage (3.1 V vs. 2.5 V for the conventional sample) and a markedly suppressed voltage polarization (0.7 V vs. 1.4 V), where polarization is quantified as the difference between the average charge and discharge voltages ($\Delta V = \bar{V}_{\text{charge}} - \bar{V}_{\text{discharge}}$). This reduced polarization is further validated by the differential capacity (dQ dV⁻¹) profiles shown in **Figures 6b and 6d**. The LMTOF-1264_MnF₂ electrode demonstrates a much tighter voltage gap between its main anodic (oxidation) and cathodic (reduction) peaks compared to the broad, shifted peaks of the conventional control.

The weaker performance of the conventional LMTOF-1264_LiF sample can be attributed to the bulk lithium deficiency previously confirmed by elemental analysis (**Table 1**). In a conventional solid-state process, driving fluorine incorporation from a stable LiF source requires extreme sintering temperatures (> 1000° C), which triggers the simultaneous volatilization and loss of both

lithium and fluorine.²⁸ Because three-dimensional transport in cation-disordered systems relies on a threshold concentration of lithium excess to maintain an active 0-TM percolation network,⁹ the observed lithium deficiency for materials made by the conventional synthesis method can severely restrict reversible lithium extraction and reinsertion.

The cycling stability of both cathodes at 20 mA g⁻¹ is compared in **Figure 6e**. While the conventional LMTOF-1264_LiF control displays a gradual, incremental capacity increase over cycles, it remains non-competitive. Conversely, the bulk-fluorinated LMTOF-1264_MnF₂ cathode exhibits stable cycling performance, maintaining 96.5% of its highest capacity after 50 cycles.

Finally, **Figure 6f** highlights the rate capabilities evaluated across a broad range of current densities (20, 50, 100, 200, 500, and 1000 mA g⁻¹). The LMTOF-1264_MnF₂ electrode consistently outperforms the conventional control at every current rate. This superior kinetic response underscores the efficacy of the tailored synthesis pathway, which results in DRX compositions closer to ideal targets by way of higher fluorine incorporation at lower temperature than conventional precursor choices.

Summary

This work demonstrates a strategy to address the challenge of synthesizing Mn- and F-rich DRX cathodes by engineering reaction pathways starting from unconventional Li₆MnO₄ and MnF₂ precursors. While conventional solid-state routes are fundamentally inhibited by the stability of LiF, our tailored reaction pathway reshapes the energy landscape associated with fluorination and DRX formation. Integrated computational modeling and *in situ* diffraction reveal that these reactive precursors bypass the persistent thermodynamic traps of conventional solid-state routes,

facilitating a low-temperature pathway that drives uniform bulk fluorination before the onset of fluorine loss due to volatilization. Consequently, the resulting bulk-fluorinated $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ti}_{0.2}\text{O}_{1.6}\text{F}_{0.4}$ cathode preserves lithium excess, delivering a high specific capacity of $\sim 220 \text{ mAh g}^{-1}$, reduced voltage polarization, and superior rate capability. This work demonstrates how careful selection of precursors can overcome synthetic challenges associated with the development of high-performance, earth-abundant, next-generation energy storage systems.

Author Information and Notes

The authors declare the following competing interests: H. K. and V.S.A. are co-inventors on US nonprovisional patent application 19/457,356 submitted by Lawrence Berkeley National Laboratory that covers the synthesis effort of fluorinated disordered rocksalt cathode using unconventional precursors in this work. The authors used Gemini and ChatGPT to assist with grammar correction, language polishing, and enhancement of manuscript consistency. All content was carefully reviewed and revised by the authors to ensure accuracy, and the authors take full responsibility for the final manuscript.

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