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Detailed Terms
Synthesis and Lithiation Mechanisms of Dirutile and Rutile LiMnF₄: Two New Conversion Cathode Materials

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Driven by the need for new cathode battery materials with high energy density, fluorides have emerged as promising candidates due to their high voltages. From high throughput computations, dirutile LiMnF₄ was identified as a promising cathode with a high conversion voltage and a theoretical specific capacity of 584 mAh/g. In this work, we study the formation of dirutile LiMnF₄ through a new, low-temperature synthesis route and report its electrochemical properties. We also report the discovery of a new rutile polymorph of LiMnF₄ which has Li-Mn disorder on the cation site. Electron diffraction confirmed both dirutile and rutile LiMnF₄ to convert upon lithiation with different reaction paths. As seen with other fluoride materials, specific capacity is strongly linked with synthesis and processing conditions. With LiMnF₄, there was a tradeoff in maintaining phase-pure samples and optimizing samples for high specific capacity. Still, even with very simple synthesis and electrode preparation methods, both rutile and dirutile polymorphs of LiMnF₄ show electrochemical activity. Further optimization of particle morphology may enhance reaction kinetics and improve specific capacity.

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Rechargeable lithium-ion batteries rely on the reversible, topotactic exchange of lithium ions between two host structures to store energy. While lithium-ion systems have found commercial success in portable electronics and have entered the electric vehicle market, their energy density is limited by the number of lithium ions transferrable between the two electrodes. Few intercalation cathodes can reversibly intercalate more than one lithium ion per formula unit before inducing decomposition reactions. This limits the specific capacity and resulting energy density of a lithium-ion battery.

Conversion cathode materials offer one path forward in achieving much higher energy densities than traditional lithium-ion batteries. In conversion reactions, multiple lithium atoms react with the cathode to utilize all the redox states of the transition metal. The host structure is not conserved; instead, it converts to a multitude of other phases upon lithiation. Of the conversion cathode materials considered to date, fluorides are the most attractive due to their high voltage, which derives from the ionic nature of the metal-fluoride bond. Using simple electrode preparation techniques, Arai et al. gave the first report of the electrochemical activity of the binary metal fluorides FeF₃, TiF₃, VF₃, and MnF₃. Despite having high theoretical specific capacities of >200 mAh/g with one lithium, only 80 mAh/g could be reversibly cycled in the former three compounds, and no discharge capacity was observed for MnF₃. This illustrates one of the main challenges in fluoride systems: while the electronegativity of fluorine gives rise to high voltages, fluorides also tend to be insulators.

Badway et al. later demonstrated a means of compensating for the inherently low conductivity of fluoride cathodes. By aggressively mixing FeF₃ with carbon to obtain sub-30 nm particles and form carbon metal fluoride nanocomposites, much higher capacities could be realized. FeF₃ reached a specific capacity of 200 mAh/g at a 2 V cutoff by accessing the Fe³⁺/Fe²⁺ redox couple, and >600 mAh/g at a 1.5 V cutoff when further reducing Fe²⁺ to Fe⁰. The high specific capacity achieved in the FeF₃ system prompted a series of studies on other metal fluoride and oxyfluoride systems, including FeF₃, FeOF, FeOF₂, CuF₂, BiF₃, and BiF₃. Research efforts on conversion materials include optimization of particle morphology for improved performance, as well as elucidation of reaction paths through computation and in situ TEM studies. Despite successes in these efforts, there continues to be a need for new, high energy density materials. Computations have been shown to be effective both in identifying promising new materials and supporting experimental observation.

One such new material is dirutile LiMnF₄, which is monoclinic with space group P2₁/c and unit cell parameters of a = 5.41 Å, b = 4.63 Å, c = 5.69 Å, and β = 113.24°. As described by Lacroix et al.,18 the dirutile structure has twice the periodicity of a true rutile due to ordering of planes of Li⁺ and Mn³⁺ ions in the [100] direction (Figure 1a). Along the [101] direction, edge-sharing LiF₆ and MnF₆ octahedra alternate to form a rutile-like structure with empty channels between edge-sharing octahedral chains (Figure 1b).

Dirutile LiMnF₄ was computationally identified† as a promising conversion cathode with high reaction voltages and a theoretical specific capacity of 583 mAh/g upon full conversion. This specific capacity is comparable to rutile FeF₂, one of the most promising conversion materials studied to date. Our computations also suggested that insertion to Li₂MnF₄ was plausible, even if not the equilibrium reaction. In this work, we synthesized dirutile LiMnF₄ via a new low-temperature mechanochemical/solid state route, and discovered a new metastable rutile polymorph of LiMnF₄. Both rutile and dirutile phases were tested and shown to be electrochemically active. TEM electron diffraction on discharged samples confirmed lithiation of both phases of LiMnF₄ to occur via conversion reactions, but not necessarily via the equilibrium path. Computations were used to analyze energetics of different reaction pathways and provide supporting theory to experimental observations.

Methods

Computational methods.—All computations were performed using density functional theory (DFT) with the generalized gradient approximation with a Hubbard-like U correction (GGA+U). The U value for the d states of Mn was set to 3.9 as determined by fitting experimental oxidation energies. The Vienna ab initio Simulation Package (VASP) and the included projector-augmented pseudopotentials were used for all calculations. All calculations were performed with ferromagnetic spin alignment. The calculated Li-Mn-F phase diagram, the expected conversion products, and their associated energies and voltages were obtained from the Materials Project.

Synthesis methods.—Stoichiometric amounts of LiF (99.99% Alfa Aesar Puratronic) and MnF₃ (99.9%, Sigma Aldrich) were milled together in a Retsch PM200 planetary ball mill for 6 hours at 500 rpm, with up to 10% excess MnF₃. Ball mill jars were assembled and reopened in an argon-filled glovebox to prevent exposure to air and moisture throughout sample processing. Heating the milled precursors in a tube furnace under argon between 300–600°C for 10 hours produced the dirutile LiMnF₄ phase. Additional milling of dirutile
Figure 1. (a) Dirutile LiMnF$_4$ has [100] planes of corner-sharing octahedral of a single cation species. (b) The projection of dirutile LiMnF$_4$ along [101] shows empty channels formed between the edge-sharing octahedral chains.

Figure 2. XRD reveals the formation of rutile LiMnF$_4$ by mechanochemical reaction, and transformation of rutile LiMnF$_4$ to dirutile LiMnF$_4$ by solid state reaction. XRD patterns are shown for (a) Ball milled LiF and MnF$_3$. M = MnF$_3$ and L = LiF still unreacted after milling. (b) After heating the ball milled precursors to 200°C for 10 hr under argon. (c) After heating the ball milled precursors to 250°C for 10 hr under argon. (d) After heating the ball milled precursors to 300°C for 10 hr under argon. Black circles denote the main peaks of an impurity phase, Li$_2$MnF$_5$. (e) Theoretical peak positions of dirutile LiMnF$_4$, space group P21/c.

LiMnF$_4$ for 6–12 hours at 500 rpm in a planetary ball mill formed the new rutile LiMnF$_4$ phase.

Characterization.— The X-ray diffraction (XRD) patterns in Figure 2 and Supplemental Figure 2 were collected on a Rigaku RU300 Cr-source diffractometer with step scans between 10–120° 2θ, and the XRD patterns in Figure 3 and Figure 5 were collected on a Bruker D8 Advance Da Vinci Mo-source diffractometer with step scans between 5–30° 2θ. These patterns are all converted to the 2θ range corresponding to a Cu XRD source for this paper. All samples were sealed with Kapton film to avoid air exposure. Powder diffraction data in Figure 4 was collected in capillaries at Brookhaven National Laboratory NSLS, beamline x14A ($\lambda = 7.75756$ Å). Rietveld refinement and profile matching of the powder diffraction data were performed using PANalytical High Score Plus.

TEM samples were prepared in an argon filled glovebox with both the O$_2$ and H$_2$O levels lower than 0.1 ppm. TEM samples of pristine rutile and dirutile LiMnF$_4$ powder were prepared by the dry method to minimize artifacts. The TEM samples for the pristine and discharged cathode films were prepared by a gentle sonication process in anhydrous dimethyl carbonate (DMC) with 20ppm H$_2$O. TEM samples were sealed in an air tight bottle in the glovebox and then transferred into the TEM vacuum column immediately after the sample bottle was opened. Approximately 30 Selected Area Electron Diffraction (SAED) patterns for each type of sample were obtained from a JEOL 2010F Transmission Electron Microscope and indexed with PolyCrystalline Electron Diffraction Pattern (PCED2.0).

Electrochemistry.— To maintain single phase samples of dirutile or rutile LiMnF$_4$, the active compound was milled with carbon black (super P) in a Retsch PM200 planetary ball mill for 2 hours at 500 rpm. XRD confirmed no dirutile-to-rutile phase transitions to occur after the two hour milling cycle with carbon. A two-phase sample of dirutile and rutile LiMnF$_4$ was obtained by milling dirutile LiMnF$_4$ for 12 hours at 500 rpm with carbon. All milling was performed under inert atmosphere by assembling and reopening ball mill jars in an argon-filled glovebox. The mixture of active material and carbon was then hand-mixed with polyethyleneetetrafluoride (PTEF) binder in a ratio of 45:45:10 by weight, and rolled into a film. Swagelok cells were assembled in an argon-filled glovebox using lithium metal, Celgard C480 separator, and 1M LiPF$_6$ in 1:1 ethylene carbonate:dimethyl carbonate (EC:DMC) solution. Cells were also tested using 1M LiClO$_4$ in propylene carbonate (PC) as an alternative electrolyte, given the observations of fluoride instability in the presence of trace amounts of HF from LiPF$_6$ dissolution. No noticeable differences in electrochemical performance were observed between the LiMnF$_4$ cells tested with different electrolytes. All cells were tested on a Maccor 2200 or Maccor 4000 operating at room temperature.
The largest peaks of dirutile LiMnF₄ are found at 17.6°, 25.5°, and 27° Cu 20, and can already be seen in Figure 2a after the first milling process.

Figure 2b, c, and d show the evolution of the reaction with increased firing temperatures. The rutile phase crystallizes at temperatures up to 250°C. Comparing the pattern from the milled precursors (Figure 2a) to the sample heated at 200°C (Figure 2b), we see that the intensity of the precursor peaks have decreased and the rutile peaks have sharpened, indicating the progression of the solid state reaction. The rutile peaks grow as the sample is heated to higher temperatures. At 250°C (Figure 2c), the precursors have completely reacted, and the XRD pattern shows a partial transformation from the rutile phase to the dirutile LiMnF₄ phase. The dirutile peaks at 17.6°, 25.5°, and 27° Cu 20 are significantly larger in Figure 2c than Figure 2b. Finally, at 300°C (Figure 2d), the rutile phase has completely disappeared, indicated by the missing rutile peak at 25.8° Cu 20. The main peaks of Figure 2d match those of dirutile LiMnF₄, and the two small impurity peaks denoted by black circles belong to Li₂MnF₅. The impurity phase, Li₂MnF₅, preferentially forms over dirutile LiMnF₄ when firing in air instead of argon. Further heating to temperatures between 300–600°C produces no changes in the obtained XRD patterns. Above 600°C, LiMnF₄ decomposes.

Adjusting the ratio of LiF:MnF₃ to include 10% excess MnF₃ eliminates the impurity Li₂MnF₅ phase after firing. Our refinement on the P2₁/c space group for dirutile LiMnF₄ gives unit cell parameters of α = 5.43 Å, b = 4.64 Å, c = 5.70 Å, and β = 113.18° (Figure 3). These values are within 0.01 Å and 0.1° of those reported by Wandner et al.⁵

Synthesis of rutile LiMnF₄.—Not only is a rutile phase dominant after mechanochemical reaction of LiF and MnF₃, but this same rutile phase appears when ball milling dirutile LiMnF₄ by itself. In Figure 4, the reversibility of the phase transition between dirutile and rutile phases with ball milling and heating cycles is shown by distinct changes in the diffraction patterns. Figure 4a shows the diffraction pattern obtained after milling the precursors, where the main peaks in the pattern belong to a rutile phase and “L” and “M” denote the peaks of unreacted LiF and MnF₃ precursors. This sample is then heated under argon gas flow for 10 hours at 300°C, producing the crystalline rutile phase in Figure 4b. The peaks marked by black circles, which belong to a Li₂MnF₅ impurity, are sharpened. All peaks belong to dirutile LiMnF₄. Milling the rutile transforms it back to rutile (Figure 4c). Phase pure rutile LiMnF₄ is obtained after milling dirutile LiMnF₄ by itself for twelve hours. We could not match the peaks to any known phase, but noticed a similarity of the experimental diffraction pattern to that of rutile MnF₃. Thus, we performed the Rietveld refinement using the P4/mmm space group, assuming exactly half occupancy of the cation site by Li and Mn, as shown in Figure 5. The unit cell parameters of the new rutile phase are determined to be a = b = 4.786 Å and c = 2.985 Å. We were unable to obtain a more crystalline sample of the new rutile phase for characterization. At just 300°C, the rutile transforms completely to the dirutile phase; lower temperatures also cause partial transformations.

Electrochemical performance of dirutile and rutile LiMnF₄.—Three different LiMnF₄ samples were tested for electrochemical performance. Dirutile LiMnF₄, obtained by solid state reaction, was ball milled with carbon for two hours before being made into electrodes. Rutile LiMnF₄, obtained by ball milling dirutile LiMnF₄ by itself for twelve hours, was then ball milled with carbon for two hours. The last sample was obtained by ball milling dirutile LiMnF₄ for twelve hours with carbon. Dirutile LiMnF₄ partially transforms to rutile LiMnF₄ during the twelve hour milling cycle with carbon, and we will refer to these samples as the two-phase samples.

Figure 6a and b show the first cycle galvanostatic charge-discharge data of the dirutile and rutile samples, respectively. Cells were cycled at rates of C/20, C/50, and C/100. C/100 data is not shown in Figure 6.
Figure 6. (a) First and second galvanostatic charge-discharge curves for dirutile LiMnF₄ milled for 2 hours with carbon at C/20 and C/50. (b) First and second galvanostatic charge-discharge curves for rutile LiMnF₄ milled for 2 hours with carbon at C/20 and C/50.

Figure 7. First and second galvanostatic charge-discharge curves for a two-phase sample of dirutile and rutile LiMnF₄ milled for 12 hours with carbon at C/20, C/50, and C/100.

Figure 8. SAED patterns obtained from rutile LiMnF₄ discharged to 3 V, 2 V, and 1 V. At the most shallow discharge level of 3 V, rutile LiMnF₄ phase is found most frequently in the indexed ring diffraction patterns (Figure 8a), but some of the rutile LiMnF₄ has been converted into LiF and MnF₂. At the 2 V discharge level, most diffraction patterns show a superposition of the LiF and MnF₂ phases (Figure 8b). The LiF diffraction rings are much more diffuse than the MnF₂ ones at 2 V, which indicate LiF is poorly crystallized. Some rutile LiMnF₄ is still present at 2 V. At the 1 V discharge level, the indexed phases are α-Mn, MnF₂, and LiF (Figure 8c). The intensity of the MnF₂ peaks is lower than those found in the 2 V sample, indicating that some MnF₂ is further reduced to α-Mn. For both the 2 V and 1 V samples, while there are still areas with unreacted rutile LiMnF₄, we only show the SAED patterns from areas undergoing the obvious conversion reaction.

Figure 9. Experimental confirmation of lithiation paths. — To distinguish between insertion and conversion of the LiMnF₄ phases upon lithiation, the rutile and dirutile samples were discharged at a C/100 rate to 3 V, 2 V, and 1 V and disassembled for ex situ TEM electron diffraction. Additionally, ex situ XRD patterns were collected on rutile and dirutile films discharged to 1 V before preparing the discharged films for TEM. The XRD showed LiMnF₄ peaks to be reduced in intensity but still present, and lattice parameters to be unchanged. Neither of the intercalated Li₂MnF₄ phases nor conversion products were detectable from XRD.

In contrast, distinct conversion products are visible in TEM for each of the three discharge levels of rutile LiMnF₄. Figure 8 shows the SAED patterns obtained from rutile LiMnF₄ discharged to 3 V, 2 V, and 1 V. At the most shallow discharge level of 3 V, rutile LiMnF₄ phase is found most frequently in the indexed ring diffraction patterns (Figure 8a), but some of the rutile LiMnF₄ has been converted into LiF and MnF₂. At the 2 V discharge level, most diffraction patterns show a superposition of the LiF and MnF₂ phases (Figure 8b). The LiF diffraction rings are much more diffuse than the MnF₂ ones at 2 V, which indicate LiF is poorly crystallized. Some rutile LiMnF₄ is still present at 2 V. At the 1 V discharge level, the indexed phases are α-Mn, MnF₂, and LiF (Figure 8c). The intensity of the MnF₂ peaks is lower than those found in the 2 V sample, indicating that some MnF₂ is further reduced to α-Mn. For both the 2 V and 1 V samples, while there are still areas with unreacted rutile LiMnF₄, we only show the SAED patterns from areas undergoing the obvious conversion reaction.

In contrast to the ring diffraction patterns observed in the rutile LiMnF₄ samples, dirutile LiMnF₄ spot diffraction patterns are observed at all levels of discharge (Figure 9a and b). The amorphous ring diffraction patterns of the conversion products, which are indexed to α-Mn metal, superimpose with the dirutile LiMnF₄ spot diffraction patterns. At 3 V, the α-Mn rings are observed occasionally, while by 1 V, the α-Mn rings are seen in all images. It was necessary to enhance the contrast or overexpose the dirutile LiMnF₄ pattern to observe the faint Mn amorphous rings. The difference in the diffraction patterns between rutile samples (ring pattern) and dirutile samples (spot pattern) is due to the different particle sizes from sample preparation: the particle sizes of dirutile LiMnF₄ prepared by solid state reaction were determined from TEM to be 100–200 nm, while rutile LiMnF₄ particles formed mechanochemically were <30 nm.
Figure 8. (a) The SAED pattern of rutile LiMnF$_4$ discharged to 3 V shows the rutile LiMnF$_4$ phase is still present in many regions of the sample. Rutile LiMnF$_4$ is the primary phase at this level of discharge, but some LiF and MnF$_2$ are also indexed in other SAED patterns, indicating the start of the conversion reaction. (b) The SAED pattern of rutile LiMnF$_4$ discharged to 2 V shows both the MnF$_2$ phase indexed by red peaks and amorphous LiF phase indexed by blue peaks in the same sample region. The diffused diffraction belt between LiF (111) and (200) indicates the presence of amorphous LiF converted from LiMnF$_4$. (c) The SAED pattern of rutile LiMnF$_4$ discharged to 1 V shows the enhanced ring intensity corresponding to the Mn metal (411) peak indexed in red, and decreased intensity for MnF$_2$ peaks marked by the black arrows. The amorphous LiF phase is still present and is indexed by blue peaks.

We determined lithium’s preference for the tetrahedral sites by comparing energetics of the two possible Li$_2$MnF$_4$ intercalation products. Li$_2$MnF$_4$-tet is preferred by a sizeable 97 meV/atom to Li$_2$MnF$_4$-oct, corresponding to 339.5 meV/lithium. This is because lithium tetrahedra in Li$_2$MnF$_4$-tet only edge-share with neighboring MnF$_6$ octahedra, while the lithium octahedra in Li$_2$MnF$_4$-oct face-share with other lithium octahedra. The XRD patterns of Li$_2$MnF$_4$-oct and Li$_2$MnF$_4$-tet are clearly distinct from the dirutile LiMnF$_4$ or rutile LiMnF$_4$ patterns.

Additionally, two structures at intermediate lithiation levels between LiMnF$_4$ and Li$_2$MnF$_4$ were calculated. To gain insight into the dilute limit of insertion, Li$_{(1+\delta)}$MnF$_4$, a single octahedral Li was replaced by two tetrahedral Li in a 2x2x2 supercell of LiMnF$_4$, resulting in the composition Li$_{17/16}$MnF$_4$. Similarly, for the saturated limit, Li$_{(2-\delta)}$MnF$_4$, all but one octahedral lithium were replaced by two tetrahedral Li in the same 2x2x2 supercell, resulting in composition Li$_{31/16}$MnF$_4$.

Figure 10 shows a possible structure of partially lithiated Li$_{(1+\delta)}$MnF$_4$, assuming some lithium intercalation into dirutile LiMnF$_4$. MnF$_6$ octahedra are represented by the purple octahedra in the background, LiF$_6$ octahedra are represented by green octahedra.

Figure 9. (a) The SAED patterns of dirutile LiMnF$_4$ discharged to 3 V mainly show a single crystal diffraction pattern indexed to dirutile LiMnF$_4$, space group P2$_1$/c. Some patterns at 3 V show the superposition of faint α-Mn rings with the dirutile LiMnF$_4$ spot pattern. (b) The SAED patterns of dirutile LiMnF$_4$ discharged to 2 V and 1 V are indexed to the same phases. At 2 V, most patterns show superposition of α-Mn diffraction rings with the dirutile LiMnF$_4$ spot pattern, while at 1 V, α-Mn rings are observed with the LiMnF$_4$ spot pattern in all images.
in the foreground, and the original lithium octahedral site is outlined in orange. When an extra lithium ion enters the lithium layer, the original lithium shifts into one of the neighboring tetrahedral sites, and the extra lithium ion occupies the other tetrahedral site. The new lithium tetrahedral sites after intercalation are outlined in blue. These tetrahedral sites are face-sharing only with the original octahedral Li site and vertex-sharing with all other “non-split” Li octahedral sites.

**Calculated reaction energies of conversion reactions.**—Figure 11 shows the calculated Li-Mn-F equilibrium phase diagram at 0 K. Ground state compounds are denoted by the solid red dots. The two proposed structures for Li$_2$MnF$_4$, the intercalation product of dirutile LiMnF$_4$, are both metastable and marked by the open red dot on the phase diagram. From the phase diagram, the following equilibrium conversion reactions and voltages are expected with increasing lithium content:

\[
\begin{align*}
\text{Li} + 3\text{LiMnF}_4 &\rightarrow 2\text{Li}_2\text{MnF}_5 + \text{MnF}_2 (4.13 \text{ V}) \\
\text{Li} + \text{Li}_2\text{MnF}_5 &\rightarrow \text{MnF}_2 + 3\text{LiF} (3.99 \text{ V}) \\
2\text{Li} + \text{MnF}_2 &\rightarrow 2\text{LiF} + \text{Mn} (1.89 \text{ V})
\end{align*}
\]

The equilibrium conversion reactions are compared to possible non-equilibrium reaction paths in Figure 12. All compound energies are plotted relative to dirutile LiMnF$_4$ which sits at 0 meV per Li, MnF$_2$ on the y-axis. At composition LiMnF$_4$, the points in the range of 3–100 meV on the y-axis represent structures with alternative Li-Mn orderings. The other blue points at the top of Figure 12 show the energies of two intermediate insertion compounds (Li$_1$Mn$_{16}$F$_{4x}$ and Li$_{10}$Mn$_{10}$F$_{4x}$) and two fully intercalated compounds (Li$_2$Mn$_{16}$F$_{4x}$-oct and Li$_2$Mn$_{16}$F$_{4x}$-tet). The computed energies for both intermediate compounds are higher in energy than the tie line between LiMnF$_4$ and Li$_2$MnF$_4$-tet at 3.87 V.

The red points at the bottom of Figure 12 represent the equilibrium conversion products from reactions with lithium. The numbers next to each arrow give the equilibrium reaction voltage between compounds in connected boxes.

**Discussion**

**Synthesis of dirutile and rutile phases.**—The reported synthesis methods of dirutile LiMnF$_4$ have the drawback of requiring a two-step process: fluorination of LiF and MnF$_2$ with fluorine gas to obtain an intermediate Mn$^{4+}$ compound, which is then thermally decomposed to LiMnF$_4$.\textsuperscript{25,26} We sought a direct, safe, and more environmentally friendly method of synthesizing LiMnF$_4$, and found mechanochemistry followed by a low-temperature thermal treatment to be a successful alternative synthesis route. Our work adds to the recent trend in fluoride synthesis to utilize mechanochemistry rather than hydrofluoric acid or fluorine gas.\textsuperscript{27-30}

While mechanochemistry has been widely employed in recent years, the precise reaction mechanisms are still speculative, as they

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**Figure 11.** The Li-Mn-F phase diagram at 0 K is derived from first principles. Thermodynamically stable compounds are denoted by solid red dots. The lithium position for LiMnF$_4$ is marked by the dotted line. Insertion into LiMnF$_2$ produces metastable Li$_2$MnF$_4$, which is denoted by the open red dot.

**Figure 12.** Energies of compositions between LiMnF$_4$ and Li$_2$MnF$_4$ are plotted relative to that of dirutile LiMnF$_4$. Rutile polymorphs and insertion products (Li$_1$Mn$_{16}$F$_{4x}$) are represented by blue points, and competing conversion products at specific lithiation levels are represented by red points. Lines connecting points are labeled with the calculated equilibrium voltages between compounds. The equilibrium voltage is linearly related to the slope between points.

**Figure 13.** Starting with LiMnF$_4$, possible reactions of fluoride compounds with lithium are labeled with their expected onset voltages. The lithium fraction and specific capacity listed to the left of each box are calculated relative to LiMnF$_4$. Less plausible reactions are denoted by dashed arrows, while more plausible reactions are denoted by solid arrows. The gray box containing Li$_2$MnF$_4$ assumes insertion and lithium site shift. All other boxes represent conversion products from reactions with lithium.
are hard to evaluate either experimentally or computationally. The cause of mechanically-induced phase transitions in certain materials is also not well understood - they may occur as a combined result of shear, high defect concentration, and high temperatures. The dirutile-to-rutile phase transformation observed in our work follows similar trends seen in other oxides and fluorides. Short milling times can produce polymorphs that are metastable at ambient temperature and pressure. These metastable phases tend to be the equilibrium phases at high pressure and/or high temperature conditions, and have more compact structures. The mechanically-formed rutile LiMnF\textsubscript{4} follows this behavior with a smaller volume than its dirutile counterpart, 68 Å\textsuperscript{3} vs. 71 Å\textsuperscript{3} per formula unit. It is unclear if the new rutile polymorph of LiMnF\textsubscript{4} forms because of the extreme processing conditions seen in the ball mill or because of stabilizing surface energy effects at the nanoscale.

**Plausibility and stability of the new rutile LiMnF\textsubscript{4} phase.** — While mechanically-induced phase transformations are difficult to model, computations can still be used to investigate the stability of the final rutile LiMnF\textsubscript{4} polymorph. Rietveld refinement suggests that rutile LiMnF\textsubscript{4} is disordered on the cation site with equal probability of occupation of the site by Li or Mn. To estimate the energy scale of cation disorder in the rutile framework, thirteen symmetrically-distinct structures with alternate Li-Mn orderings were calculated with a unit cell of less than or equal to 18 atoms. Six of the thirteen structures were within 31 meV/atom of the ground state dirutile LiMnF\textsubscript{4}, and four were within 5 meV/atom. While these alternative orderings are not identical to the disordered structure used in Rietveld refinement, the small energetic difference between Li-Mn orderings in LiMnF\textsubscript{4} is consistent with a phase which would show Li-Mn disorder. This agrees with experimental observations where simple mechanical milling causes a phase transition from the ordered dirutile to disordered rutile LiMnF\textsubscript{4}, and the reverse reaction is activated by thermal treatment.

**Conversion reaction paths of LiMnF\textsubscript{4}.** — As shown by galvanostatic charge-discharge tests and ex situ TEM electron diffraction, rutile and dirutile LiMnF\textsubscript{4} are both electrochemically active but convert upon lithiation along different reaction paths. The observed reactions do not match the equilibrium conversion reactions given by the phase diagram. This may either be an artifact of TEM performed ex situ rather than in situ and not all intermediate reactions being captured, or because rutile and dirutile LiMnF\textsubscript{4} simply convert via nonequilibrium reaction paths upon lithiation. All reactions are summarized graphically in Figure 13.

In the equilibrium reaction, the first expected reaction upon lithiation is the conversion of LiMnF\textsubscript{4} to Li\textsubscript{2}MnF\textsubscript{5} and MnF\textsubscript{2} at 4.13 V, followed by the conversion of Li\textsubscript{2}MnF\textsubscript{5} to MnF\textsubscript{2} and LiF at 3.99 V. However, in the SAED patterns of discharged rutile samples, neither Li\textsubscript{2}MnF\textsubscript{5} nor superpositioned Li\textsubscript{2}MnF\textsubscript{5} and MnF\textsubscript{2} patterns are observed. The first observed conversion products are MnF\textsubscript{2} and LiF, which first appear alongside rutile LiMnF\textsubscript{4} at the 3 V discharge level. These observations suggest that either the Li\textsubscript{2}MnF\textsubscript{5} formed at 4.13 V quickly decomposes into MnF\textsubscript{2} and LiF at 3.99 V, or rutile LiMnF\textsubscript{4} converts directly to LiF and MnF\textsubscript{2} at 4.04 V.

If we assume that rutile LiMnF\textsubscript{4} follows the center 4.04 V path in Figure 13 (LiMnF\textsubscript{4} → LiF + MnF\textsubscript{2}), the subsequent conversion to Mn and LiF is not expected to begin until 1.89 V. Our experimental results agree well with theory: at 2 V, MnF\textsubscript{2} and LiF are the dominant phases. Some rutile LiMnF\textsubscript{4} is also still observed, but Mn metal is not. The presence of some rutile LiMnF\textsubscript{4} in the 2 V sample suggests that the direct conversion of rutile LiMnF\textsubscript{4} to Mn metal is not preferred. As seen in Figure 13, the direct reaction of LiMnF\textsubscript{4} → Mn + LiF is predicted to begin at 2.60 V. If this 2.60 V reaction path were active, we would expect to see some Mn metal in the 2 V sample.

The rutile sample further discharged to 1 V is indexed to α-Mn, LiF, and some remnant MnF\textsubscript{2}. Rutile LiMnF\textsubscript{4} is no longer observed at 1 V. Between 2 V and 1 V, rutile LiMnF\textsubscript{4} may either convert directly to LiF + Mn, or form MnF\textsubscript{2} before converting to LiF + Mn. The MnF\textsubscript{2} peaks in the 1 V sample are weaker than those in the 2 V sample, suggesting there is less MnF\textsubscript{2} present in the sample at 1 V because of the further conversion to α-Mn. The diffused ring patterns of the converted LiF and Mn metal phases show that they are much smaller in particle size than the starting phase of rutile LiMnF\textsubscript{4}, which is typical of conversion products in battery cathodes. It is clear that rutile LiMnF\textsubscript{4} is converting, but we cannot entirely rule out the possibility of lithium insertion at the start of discharge, where the discharge specific capacity may have contributions from both insertion and conversion reactions. A small amount of lithium insertion may be possible if conversion of LiMnF\textsubscript{4} is kinetically limited.

In contrast to the ring patterns observed in the rutile samples, dirutile LiMnF\textsubscript{4} samples discharged between 3 V and 1 V all show a component of single crystal spot diffraction patterns (Figure 9a and b) which belong to 100–200 nm diameter LiMnF\textsubscript{4} particles. The superimposed amorphous ring patterns are from the conversion product, α-Mn, formed during discharge. This is the only conversion product indexed in the discharged dirutile LiMnF\textsubscript{4} samples. α-Mn’s unexpected appearance at the 3 V discharge level suggests that lithiation of dirutile LiMnF\textsubscript{4} is dominated by direct conversion to LiF + Mn. It is not yet determined why α-Mn is seen at 3 V when the conversion of LiMnF\textsubscript{4} → Mn + LiF is predicted to begin at 2.60 V. LiF is not observable in the SAED patterns because it is a weaker scatterer than Mn. Like rutile LiMnF\textsubscript{4}, dirutile LiMnF\textsubscript{4} is clearly converting to LiF and Mn, but may also be inserting at the start of discharge.

Although the possibility of electron beam damage cannot be excluded as an explanation for α-Mn’s presence in the 3 V discharged sample, α-Mn’s amorphous ring pattern is only observed in several SAED patterns out of the 30 measured patterns taken from different areas of the TEM sample. In contrast, in the 2 V and 1 V discharged samples, α-Mn is observed in most SAED patterns. Considering the measurement condition for SAED is kept constant for all measurements with the broadest electron beam, this difference observed by SAED is most likely not an artifact. Using scanning TEM techniques including STEM, we found that STEM as a focused beam technique caused obvious artifacts and beam damage to these fluorides compared with the conventional TEM technique of SAED.

Finally, we consider the remaining reaction paths shown in Figure 13. The reaction at 2.41 V converting Li\textsubscript{2}MnF\textsubscript{5} and MnF\textsubscript{2} directly to LiF and Mn is unlikely; if this reaction path were active, Li\textsubscript{2}MnF\textsubscript{5} should have been observed in a 3 V sample. Thus, the 2.41 V reaction is labeled with a dashed arrow to denote a less plausible reaction. Insertion to Li\textsubscript{2}MnF\textsubscript{5} at 3.89 V is also unlikely - no evidence of insertion is seen in XRD or TEM, and thermodynamically, conversion is preferred over insertion (Figure 12).

**Optimization of electrochemical performance.** — One of the open questions from our work is how to improve the specific capacity in a single phase of LiMnF\textsubscript{4}. Only short milling times were used to mix the active cathode material with carbon in order to maintain single-phase samples. However, higher capacities were observed in two-phase samples attained by extending the milling times of the cathode material with carbon. A twelve hour milling cycle of dirutile LiMnF\textsubscript{4} with carbon transformed the sample to a two phase mixture of dirutile and rutile LiMnF\textsubscript{4} with particle sizes of <30 nm. As shown in Figure 7, this two-phase sample achieved a capacity of 170 mAh/g upon first discharge and cycled reversibly. With a twelve hour milling cycle of rutile LiMnF\textsubscript{4} with carbon, we observed a transformation of the active material to LiF and MnF\textsubscript{2}. These are the same conversion intermediates observed in discharged samples of rutile LiMnF\textsubscript{4}, but the two-phase sample starting with LiF and MnF\textsubscript{2} showed an increase in specific capacity from 40 mAh/g to 100 mAh/g on first discharge. As with other fluoride materials, we believe the key to realizing higher capacities is reducing particle sizes and achieving good intermixing with a conductive matrix. For the LiMnF\textsubscript{4} polymorphs, this is a problem they are not stable under long milling times with carbon. Other synthesis and electrode preparation methods may have more success in achieving small particle sizes in a single phase LiMnF\textsubscript{4} to reach its theoretical conversion capacity of 584 mAh/g.
Conclusions

Dirutile LiMnF₄ was computationally identified to be a promising new conversion cathode material for lithium-ion batteries. In this work, two polymorphs of LiMnF₄ were synthesized, tested as lithium-ion battery cathodes, and studied using electron diffraction and computation to understand their lithiation mechanisms. Synthesis of dirutile LiMnF₄, a known compound, was achieved by a new low-temperature mechanochemical/solid state reaction route, and the new rutile polymorph of LiMnF₄ was synthesized by mechanical milling. Both phases were shown to be electrochemically active, but took different non-equilibrium reaction paths upon lithiation. Dirutile LiMnF₄ converts directly to LiF and Mn, while rutile samples forms MnF₂ before converting to LiF and Mn metal. Computations suggest that the two nonequilibrium paths taken by the samples are close in energy to the ground state path.

Due to lack of stability under long ball milling, phase-pure samples of dirutile and rutile cannot be well mixed with carbon or reduced in the ground state path. Converting to LiF and Mn metal. Computations suggest that the two nonequilibrium paths taken by the samples are close in energy to the ground state path.

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