

Structural Control of Short-Range Order in Disordered Rock Salts by a Novel Low-Temperature Solution-Based Synthesis Method

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Abstract

Disordered rock salts (DRX) have the potential to replace current Ni and Co-based cathode materials, given their high energy density as well as the cheap and abundant source of precursors, enhancing sustainability in Lithium-ion batteries (LIB). Its commercialization is impeded by detrimental short-range order (SRO) at the atomic level, which disrupts lithium percolation channels and decreases performance in batteries. SRO is promoted by high-temperature synthesis, which also limits F substitution. Here we present a novel solution-based synthesis protocol to make $\text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_2$ based DRXs at low temperatures, allowing fluoride doping and opening the door for more sustainable DRX positive electrode materials for LIB.

Research questions

- Can a phase-pure material be obtained by solution-based synthesis?
- How does temperature affect the SRO in the material?
- Can fluorination be achieved in away that promotes percolation?

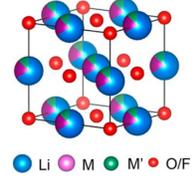


Figure 1: DRX crystal arrangement (Chen, D. et al., 2021).

Methods: Solution-based synthesis

Coprecipitation

Reactants: MnSO_4 , Ti-isopropoxide,
Precipitating agent: NaOH



Figure 2: Co-precipitation to form precursors.

Hydrothermal synthesis

Reactants: TiMnOH_x precursor, LiOH, LiF
Optional thermal treatment: 1000 °C, 2 hrs



Figure 3: Hydrothermal reactor.

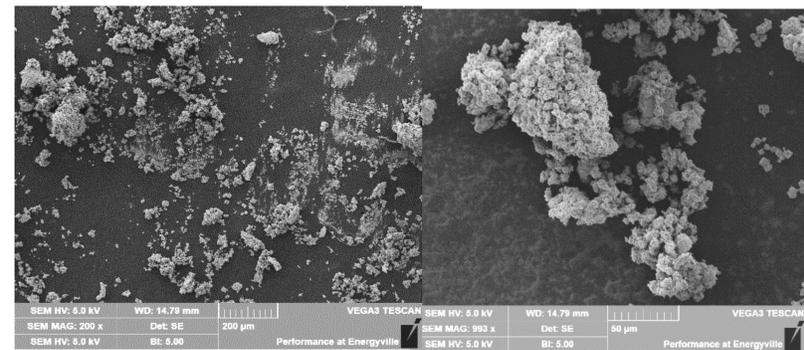


Figure 4: SEM images of LTMTO-I (80% Mn) at 200 μm and 50 μm scale. The primary particles, of around 10 μm agglomerate in large secondary particles as seen in the zoomed image.

Results

Phase purity

- A DRX phase is obtained through the proposed protocol.
- Annealing sharpens the peak, but a LiMnO_2 impurity appears.

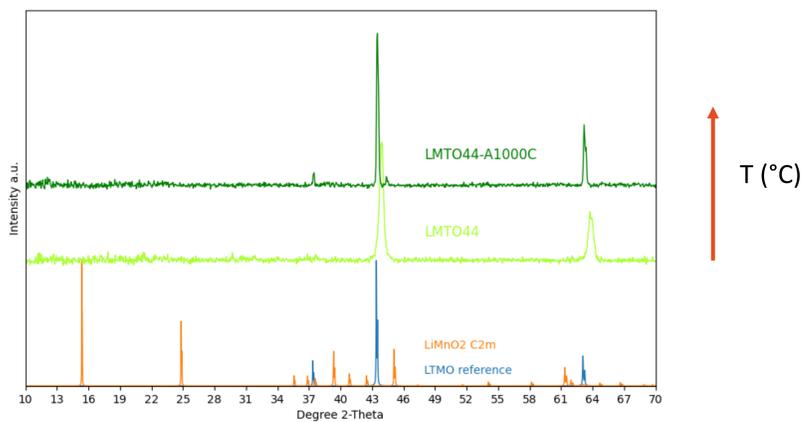


Figure 5: LMT044 before (light green) and LMT044-100C after annealing (dark green).

- 10% fluorination seems to be achieved by the lack of presence of a LiF impurity phase. F doping is confirmed by F-ISE.

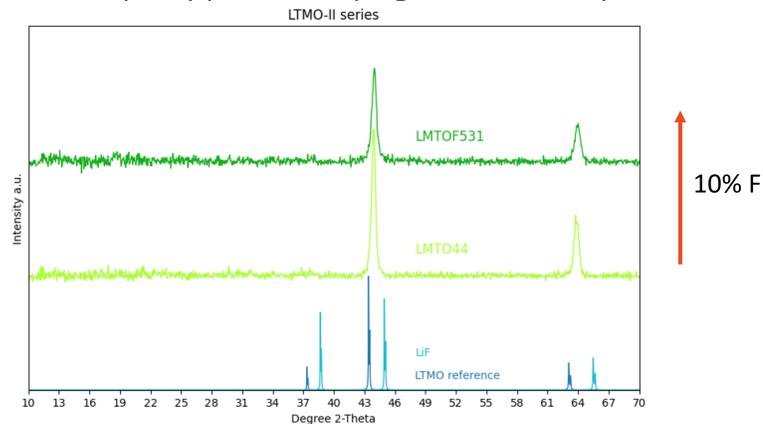


Figure 6: LMT044(light green) and the fluorinated stoichiometry LMT0531, $\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{0.9}\text{F}_{0.1}$ (dark green).

ICP: Stoichiometry check

Sample	Expected comp.	Precursor actual ratio (Mn:Ti)	Material actual composition
LMT044	$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ (Mn:Ti = 1:1)	0.98	$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.43}\text{O}_x$
Fluorination: LMT0531	$\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{F}_{0.1}$ (Mn:Ti = 1,67)	2.1	$\text{Li}_{0.97}\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_x\text{F}_{0.1}$

Cycling

- Cycling improved after fluorination but not after annealing.
- Galvanostatic cycling shows evidence of oxygen redox reactions at high voltages. Cycled between 2 and 5 V.

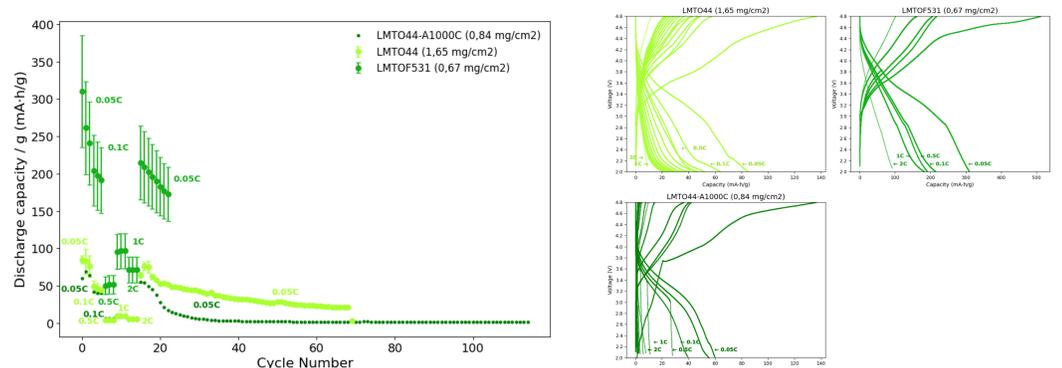


Figure 7: Cycling results of LMT044, LMT044-A100C and LMT0531.

Surface impurities

- Synchrotron XRD shows the presence of Li_2CO_3 impurities at all conditions.
- TGA results show that thorough washing reduces the impurity amount.

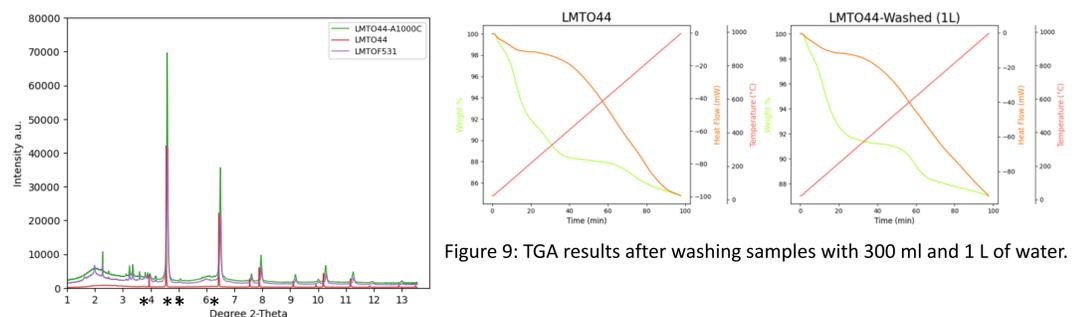


Figure 8: Synchrotron results on LMT044, LMT044-A1000C and LMT0531. Asterisks represent LiCO_3 peaks.

Conclusions & Future Work

- A DRX phase is successfully synthesized at low temperatures. Annealing at promotes the DRX phase but also the appearance of a monoclinic impurity phase.
- The XRD results and F-ISE show that fluorination seems possible. It also drastically improves the cycling results, while annealing has a poor performance.
- Further impurities in the sample and the effect of washing will be investigated with TGA-IR and ICP to check for lithium loss.
- SRO will be investigated with Li and F NMR as well as the pair distribution function.

References: Chen, D. et al. (2021), ACS Energy Letters