# Solution-based synthesis of Ti-Mn DRX positive electrode materials for sustainable batteries

*Juan Guerrero, Dries De Sloovere, Jan D'Haen, Marlies Van Bael & An Hardy*

*Institute for Materials Research (imo-Imomec), UHasselt and imec, EnergyVille*

## 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 Ti-Mn 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?
- Can fluorination be achieved?
- Is it possible to control the SRO to enhance electrochemical properties?

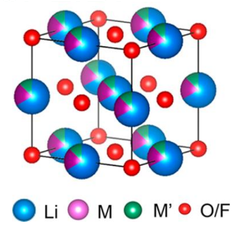


Figure 1: DRX crystal arrangement (Chen, D. et al., 2021).

## Methods: Solution-based synthesis

Reactants: $MnSO_4$, Ti-isopropoxide,
Precipitating agent: NaOH
Lithiation and fluorination: LiOH, LiF

Grinding

Drying

Figure 3: Co-precipitation to form precursors.

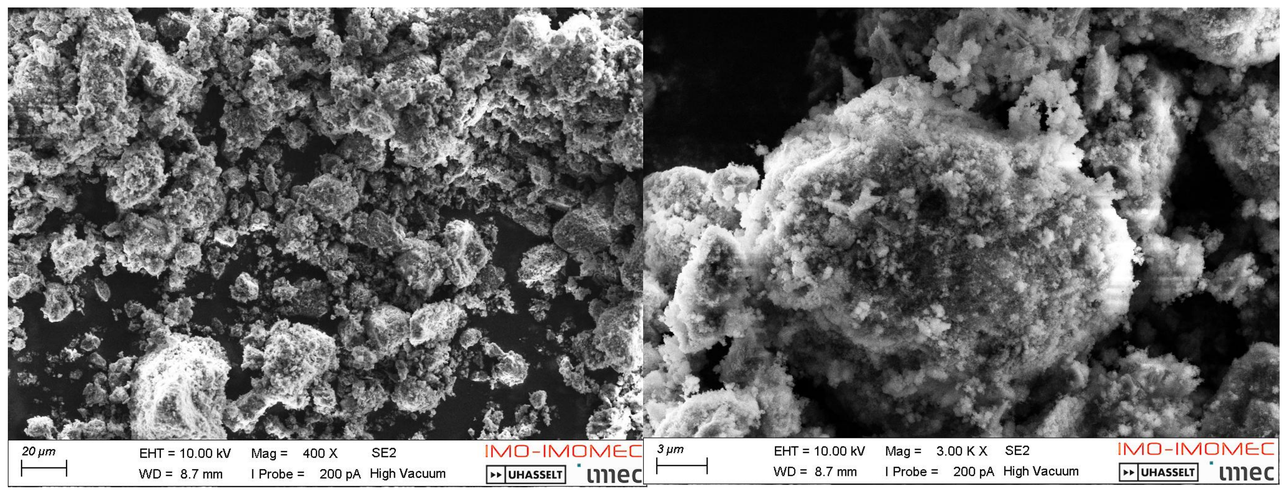


Figure 2: SEM images of LTMO-I (80% Mn) at 20 µm and 3 µm scale.

## Results

### Phase purity

- A DRX phase is obtained through the proposed protocol.
- As the Mn concentration increases, $MnO_x$ impurity phases appear on the material like $MnO_2$.

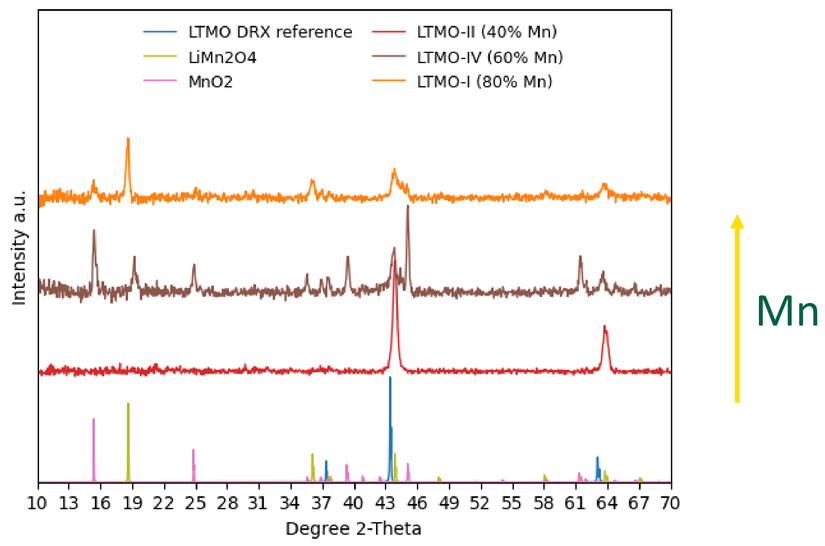


Figure 3: DRX phase at increasing Mn concentrations.

- Annealing at 1000 °C promotes the DRX phase.

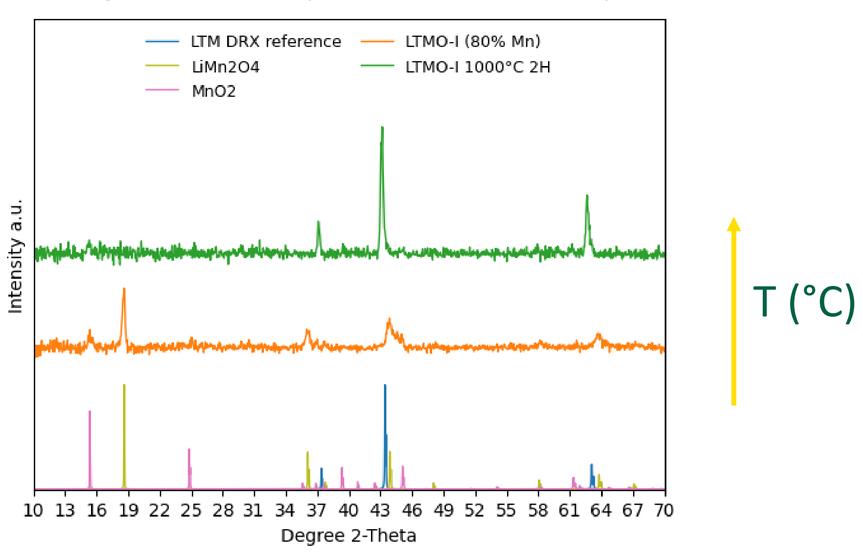


Figure 4: The effect of increasing annealing temperatures on phase purity.

## Fluorination

- 10% fluorination can be achieved through the proposed synthesis method as no LiF side phase has been detected with XRD.
- Low F content do not improve cycling performance.

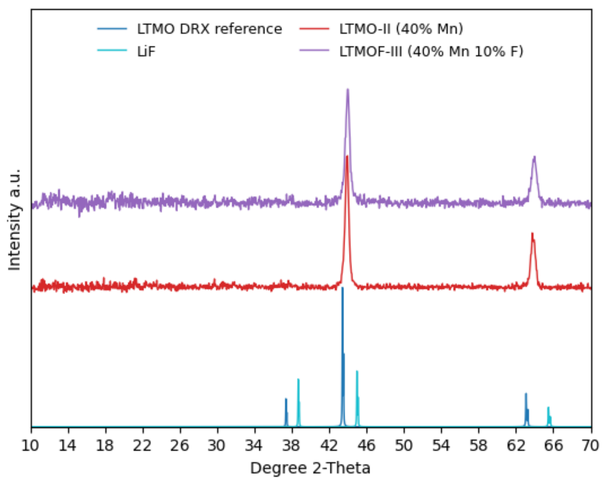


Figure 5: Phase identification for fluorinated LTMO-II.

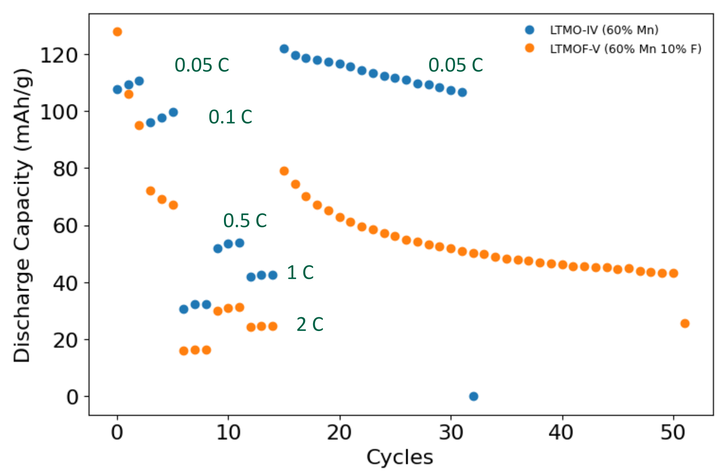


Figure 6: The effect of 10% fluorination on performance for LTMO-IV (60% Mn).

## Conclusions & Future Work

- A DRX phase is successfully synthesized at low temperatures and low Mn concentrations.
- Annealing at 1000 °C promotes the formation of a phase-pure DRX phase of samples with a high amount of Mn.
- Ti-Mn DRX samples have been successfully fluorinated at low temperatures through a solution-based protocol. Higher levels of fluorination will be investigated to promote good SRO, thus Li percolation channels to improve cycling performance.

## References

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