OAK RIDGE National Laboratory

Solid-State Synthesis of Fluorine-Rich Disordered Rocksalt Cathodes

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Project ID: BAT404

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

Overview

Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 86%

Barriers Addressed

- Energy density
- Cycle life
- Cost

Budget

- Total project funding
  - FY19 $3.125 M (LBNL, ORNL, PNNL, UCSB)
  - FY20 $2.375 M (LBNL, ORNL, PNNL, UCSB)
  - FY21 $3.125 M (LBNL, ORNL, PNNL, UCSB)
- BAT376, BAT404, BAT405 and BAT406 (LBNL, ORNL, PNNL, UCSB)

Partners

- Lawrence Berkeley National Laboratory (LBNL)
- Oak Ridge National Laboratory (ORNL)
- Pacific Northwest National Laboratory (PNNL)
- UC Santa Barbara (UCSB)

Relevance

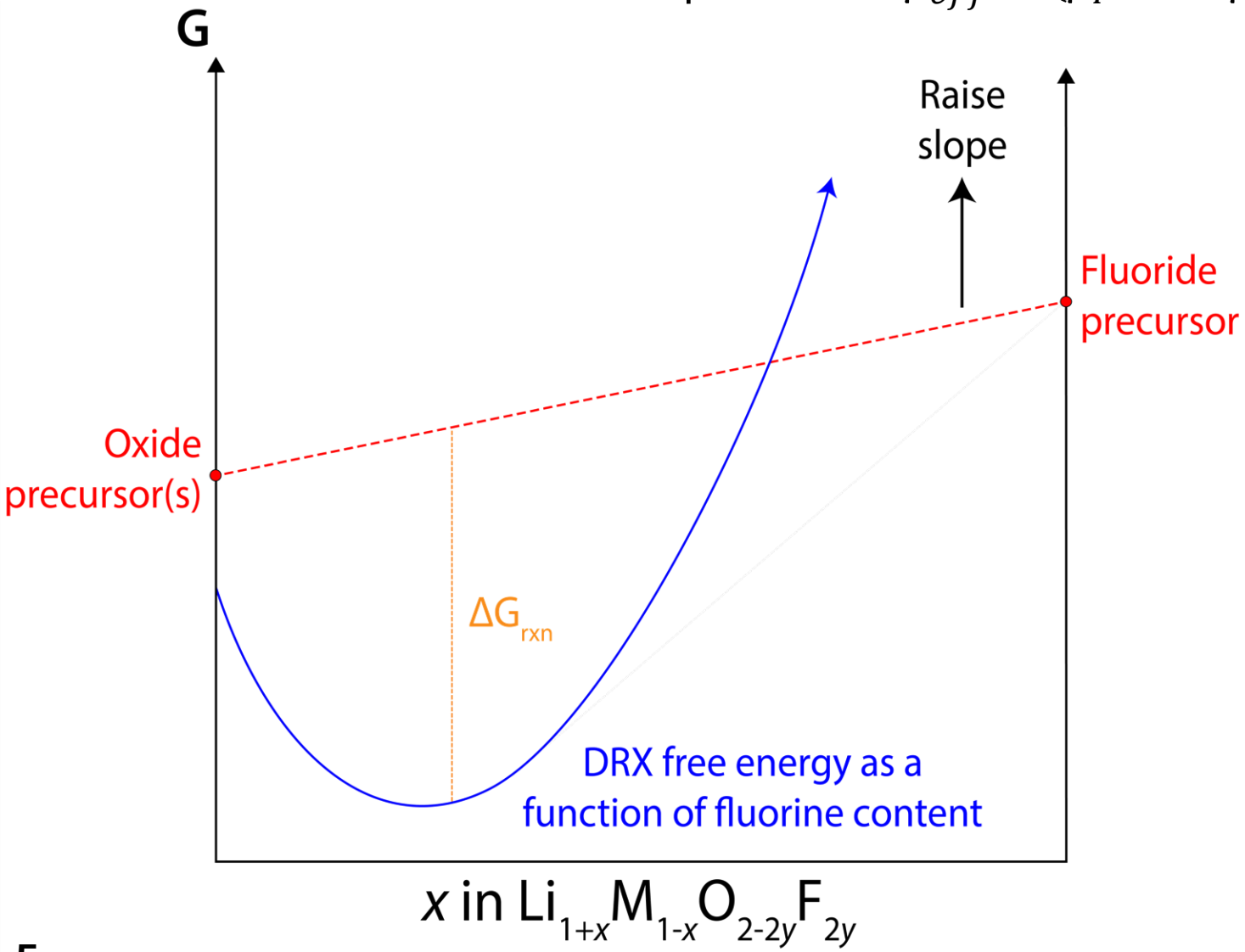
- Li-excess disordered rocksalt (DRX) cathodes can deliver specific energies up to 1000 Wh/kg.
- DRX structure is compatible with a wide range of chemistries, providing an opportunity to develop Co-free, high energy density cathodes that are alternatives to traditional layered NMC-type cathodes.
- Fundamental understanding on what controls DRX cathode performance (e.g., capacity, rate capability, cycling stability, and operating voltage) is key to enabling rational decisions on further development and assessing commercial viability.

FY21 Milestones

Due Date	Description	Status
12/31/2020	Complete synthesis and characterization of two DRX compositions using low temperature fluorination methods, $Li_{1.15}Ni_{0.533}Nb_{0.317}O_{1.8}F_{0.2}$ and $Li_{1.15}Ni_{0.533}Nb_{0.317}O_{1.8}F_{0.25}$	Completed
03/31/2021	Investigate relation between F solubility and electrochemical performance for Mn and Ni-rich DRX phases,	Completed
06/30/21	Undertake neutron PDF and NMR and analysis of relevant DRX compositions from partner laboratory PIs.	On target
09/30/21	Develop morphology control of DRX phases with specific focus on Mn-F rich by optimizing synthesis conditions and varying precursors	In progress

Shifting equilibrium toward higher F content: Thermodynamic Approach

Effective chemical potential: $\mu_{eff} = (\mu_F + 0.5\mu_{Li}) - (\mu_O + 0.25\mu_{Mn} + 0.25\mu_{Ti})$



Strategies:

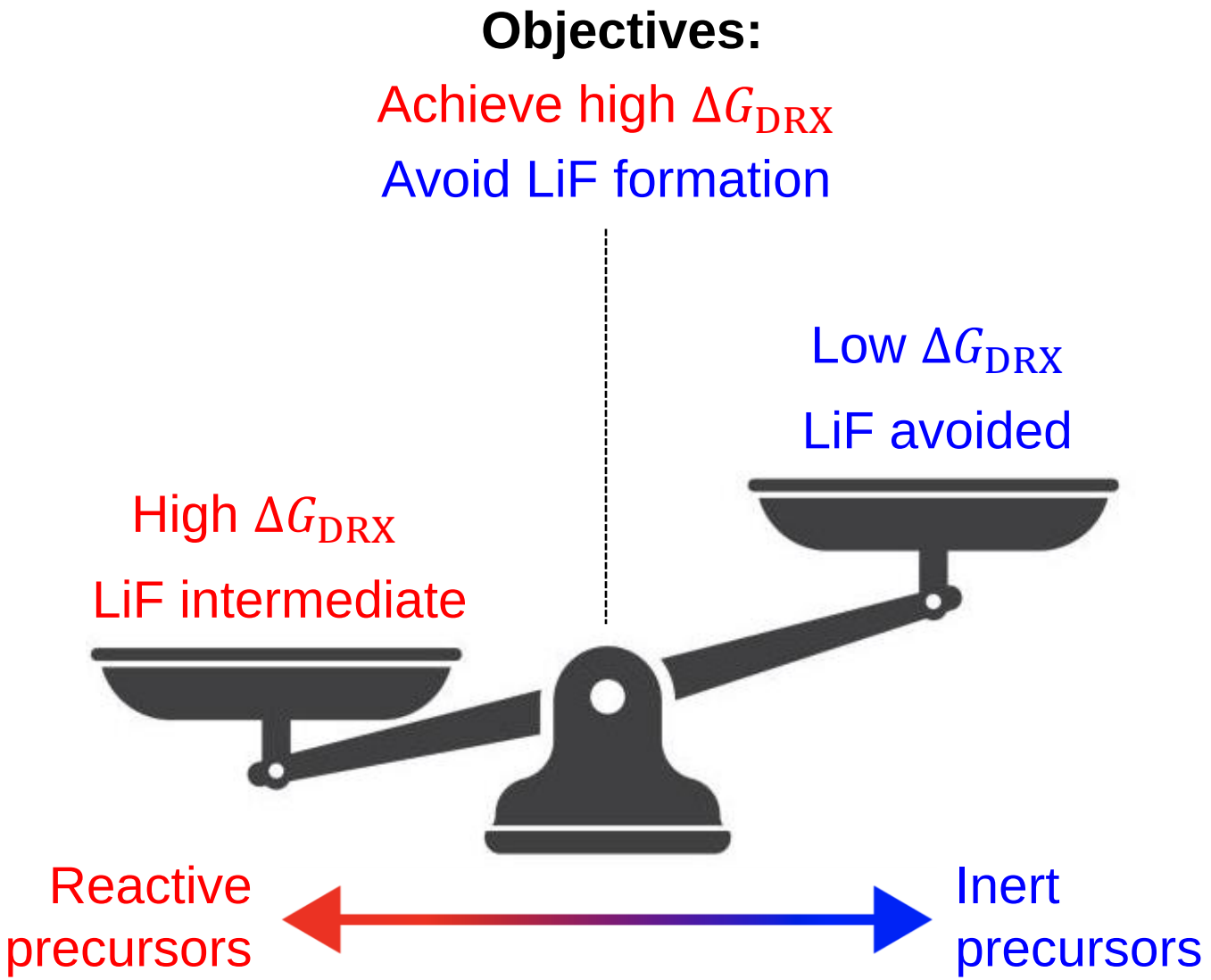
1) **Raise the fluorine chemical potential (μ_F)** by using a reactive fluoride precursor (e.g., MnF_2)

2) **Lower the oxygen chemical potential (μ_O)** with reducing conditions
   - Low p_{O_2} atmosphere
   - Add reducing agents to consume oxygen

Controlling the reaction pathway requires the right set of precursors

Achieve a balance of reactivity:

- The Li-containing precursor should not prematurely react with the F-containing precursor (i.e., we want to avoid LiF formation)
- Want to select a Li-source that "locks in" lithium and has low reactivity with MnF_2
- For example, use Li-metal-oxides as precursors rather than simple Li-salts (e.g., Li_2CO_3)



Three promising precursor sets selected for solid-state synthesis of Li-Mn-Ti-O-F

1) $Li_6MnO_4 + TiO_2 + MnF_2 \rightarrow$ DRX $(\Delta G \approx -267\ \mathrm{meV/atom})$

   No reducing agent, MnF_2 used as F-source, Li_6MnO_4 locks in Li to suppress LiF formation

2) $Li_2TiO_3 + LiMnO_2 + LiF + MnF_2 + Mn \rightarrow$ DRX $(\Delta G \approx -302\ \mathrm{meV/atom})$

   Mn acts as reducing agent, LiF|MnF_2 eutectic used as F-source

3) $Li_2TiO_3 + LiMnO_2 + LiF + MnF_2 + C \rightarrow$ DRX + CO $(\Delta G \approx -324\ \mathrm{meV/atom})$

   C acts as reducing agent, LiF|MnF_2 eutectic used as F-source

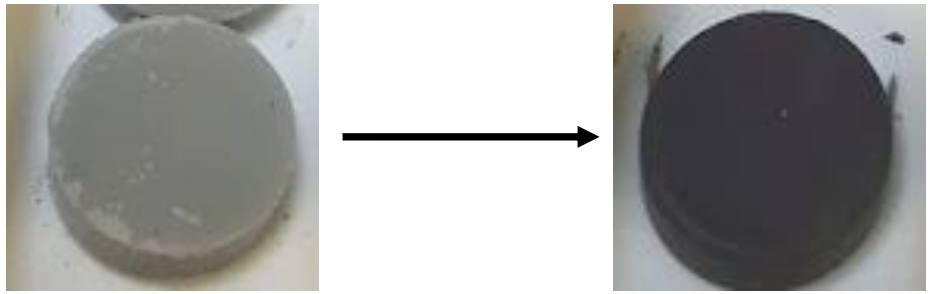
More reducing conditions → higher driving force for fluorination

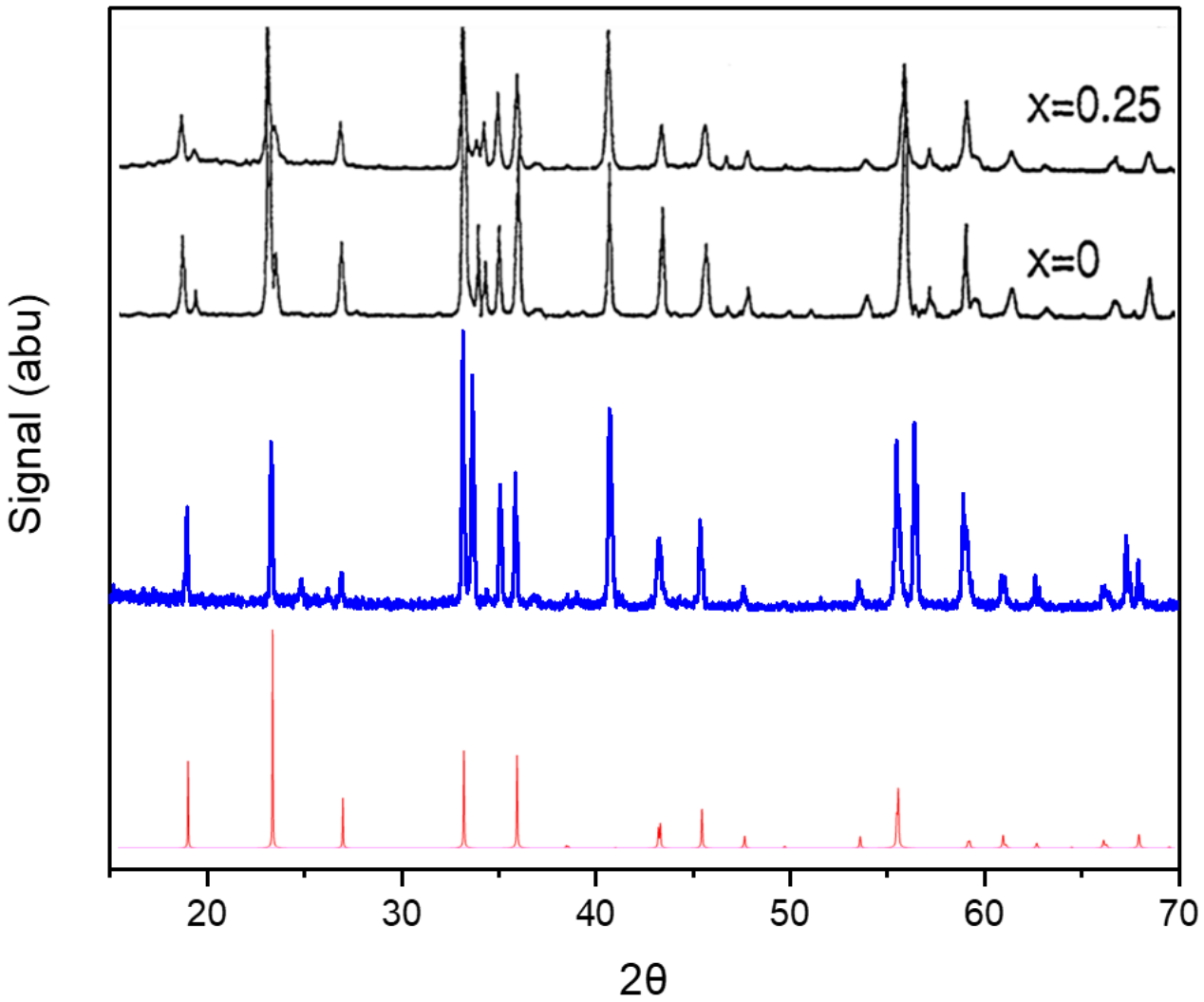
Possibility of side reactions (does MnF_2 react prematurely?)

- For (1): $Li_6MnO_4 + MnF_2 \rightarrow LiF + MnO$ $(\Delta G \approx -228\ \mathrm{meV/atom})$
- For (2) and (3): $LiMnO_2 + MnF_2 \rightarrow Mn_3O_4 + LiF$ $(\Delta G \approx -76\ \mathrm{meV/atom})$

Li_6MnO_4 precursor was produced for solid state synthesis of $Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$

$$Li_2O + MnO \xrightarrow{\text{950 °C, 12 hr; 4\% } H_2/Ar} Li_6MnO_4$$

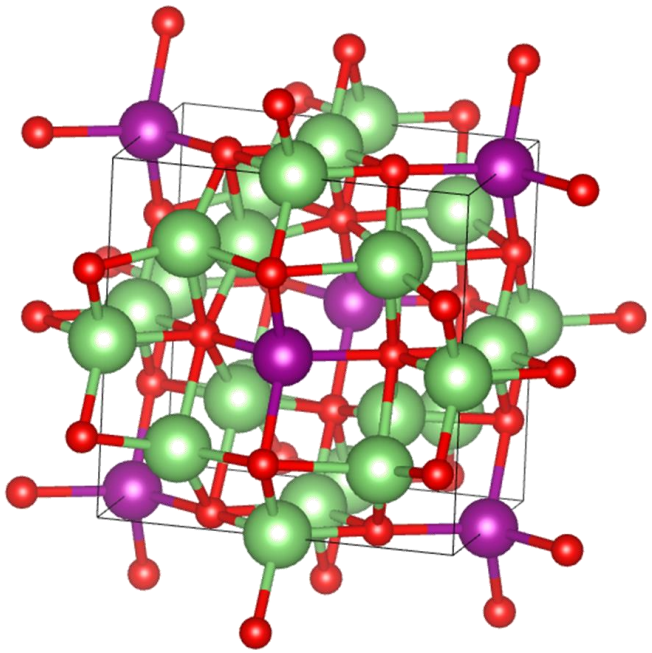




Reported pattern of **$Li_{6-x}MnO_4$** (Narukawa et al. 1999)

As synthesized **Li_6MnO_4**

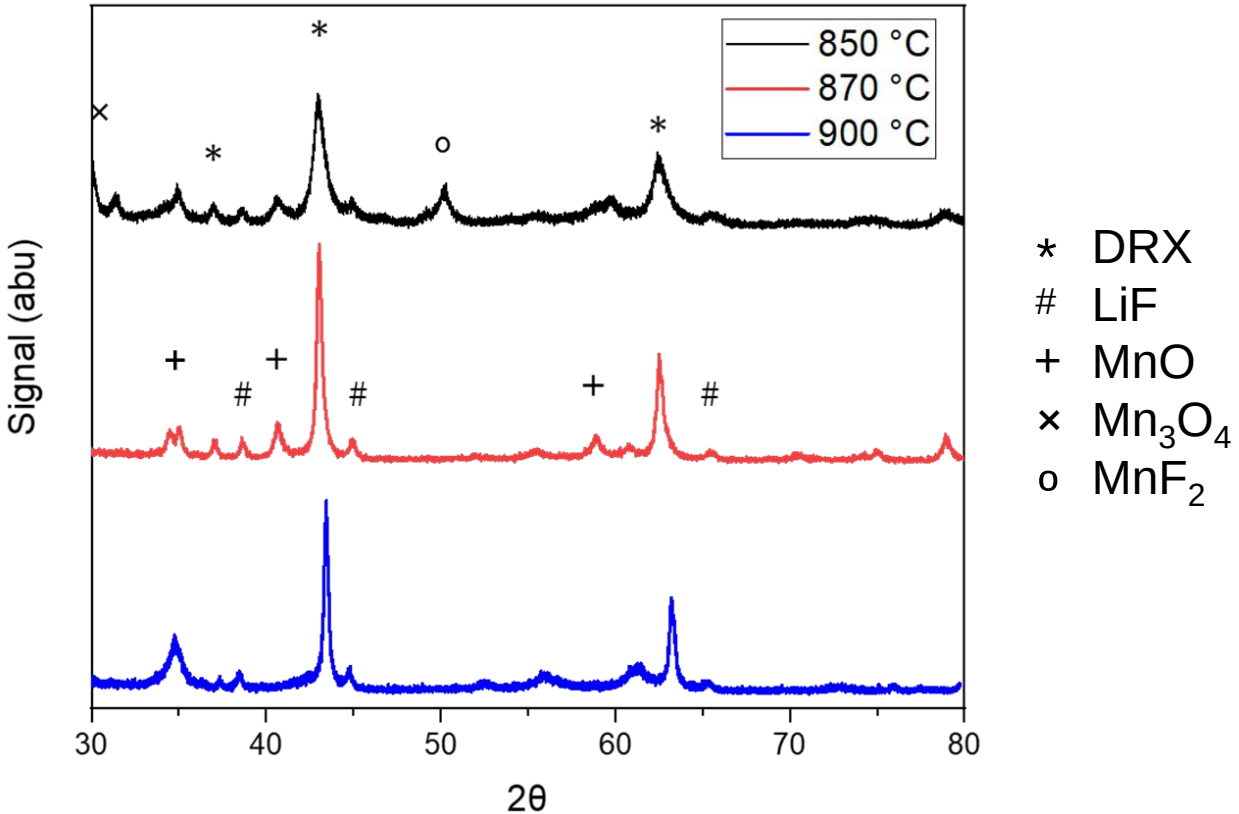
Simulated pattern



Temperature and mixing process have significant impact on phase purity.

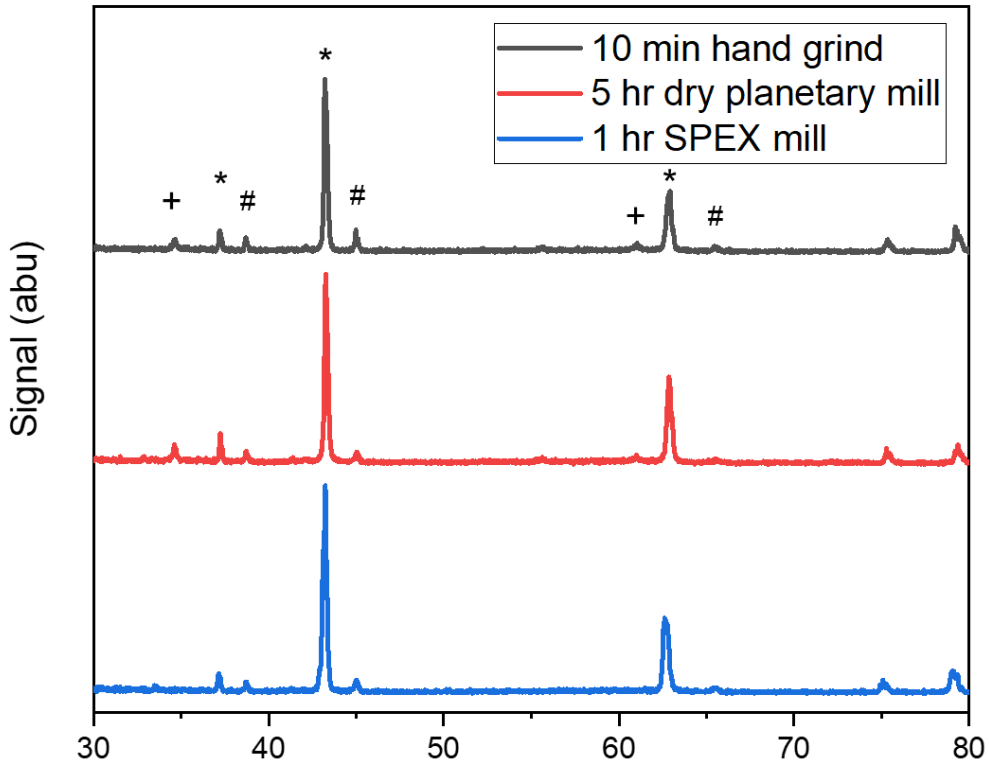
$$Li_6MnO_4 + MnF_2 + TiO_2 \longrightarrow Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$$

- Significant impurity phases remain even after melting MnF_2 (856 °C)
- Heating at 900 °C reduces amount of impurities



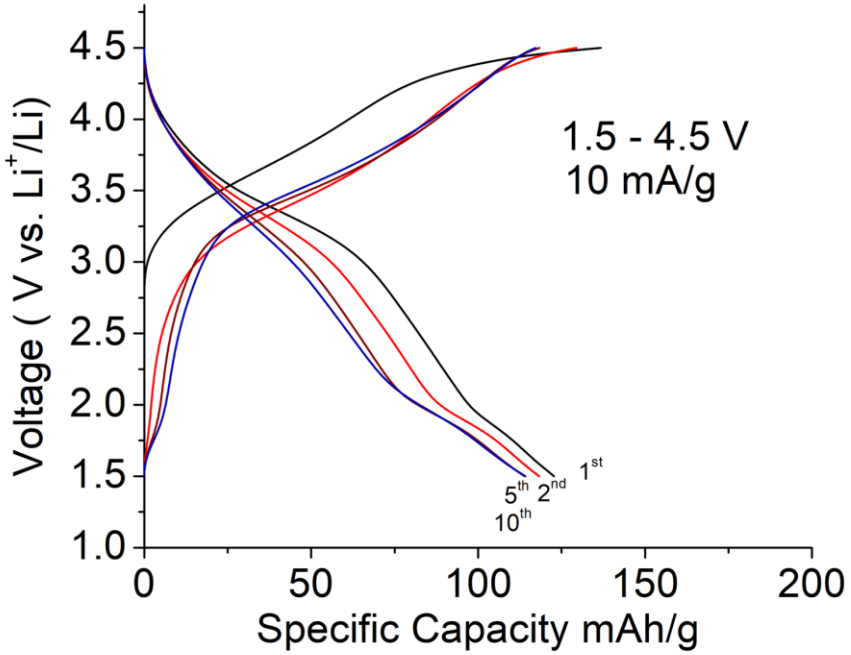
$Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$ (4 hr firing, 850–900 °C)

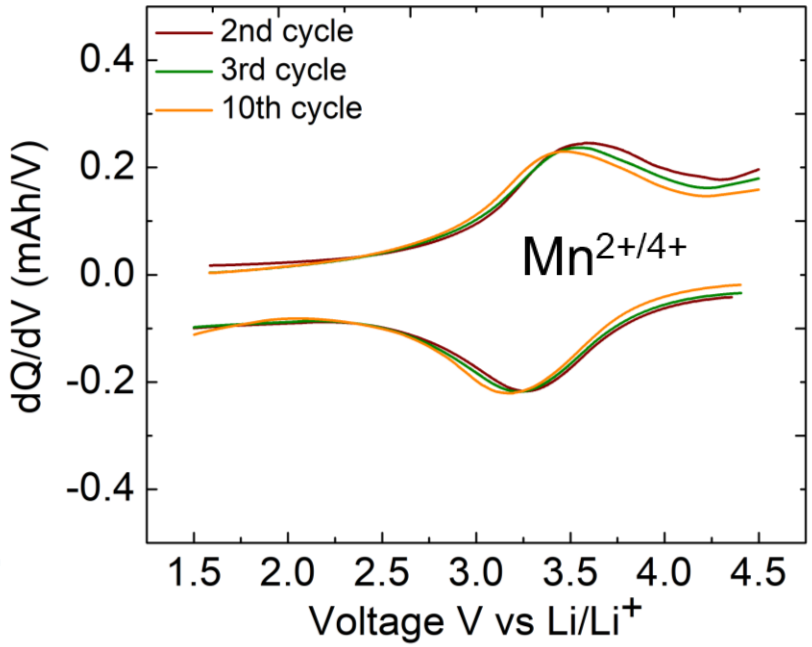
- Extensive planetary ball milling is often used prior to the firing step
- High energy premixing of reactants is vital to ensure intimate contact for phase pure formation

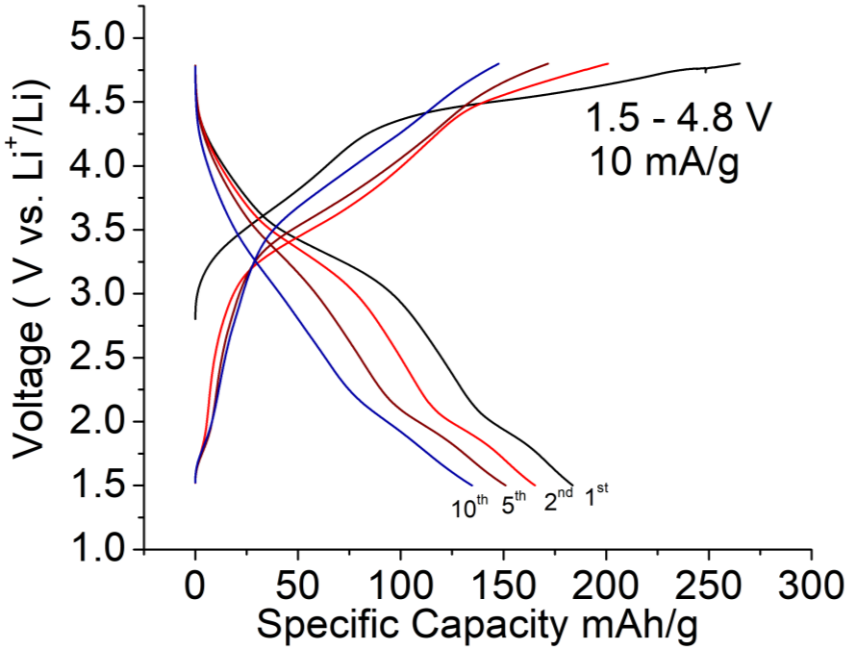


$Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$ (6 hr firing, 900 °C)

Preliminary electrochemical results on $Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$ are encouraging. Further optimization of the synthesis conditions and electrode processing are needed.





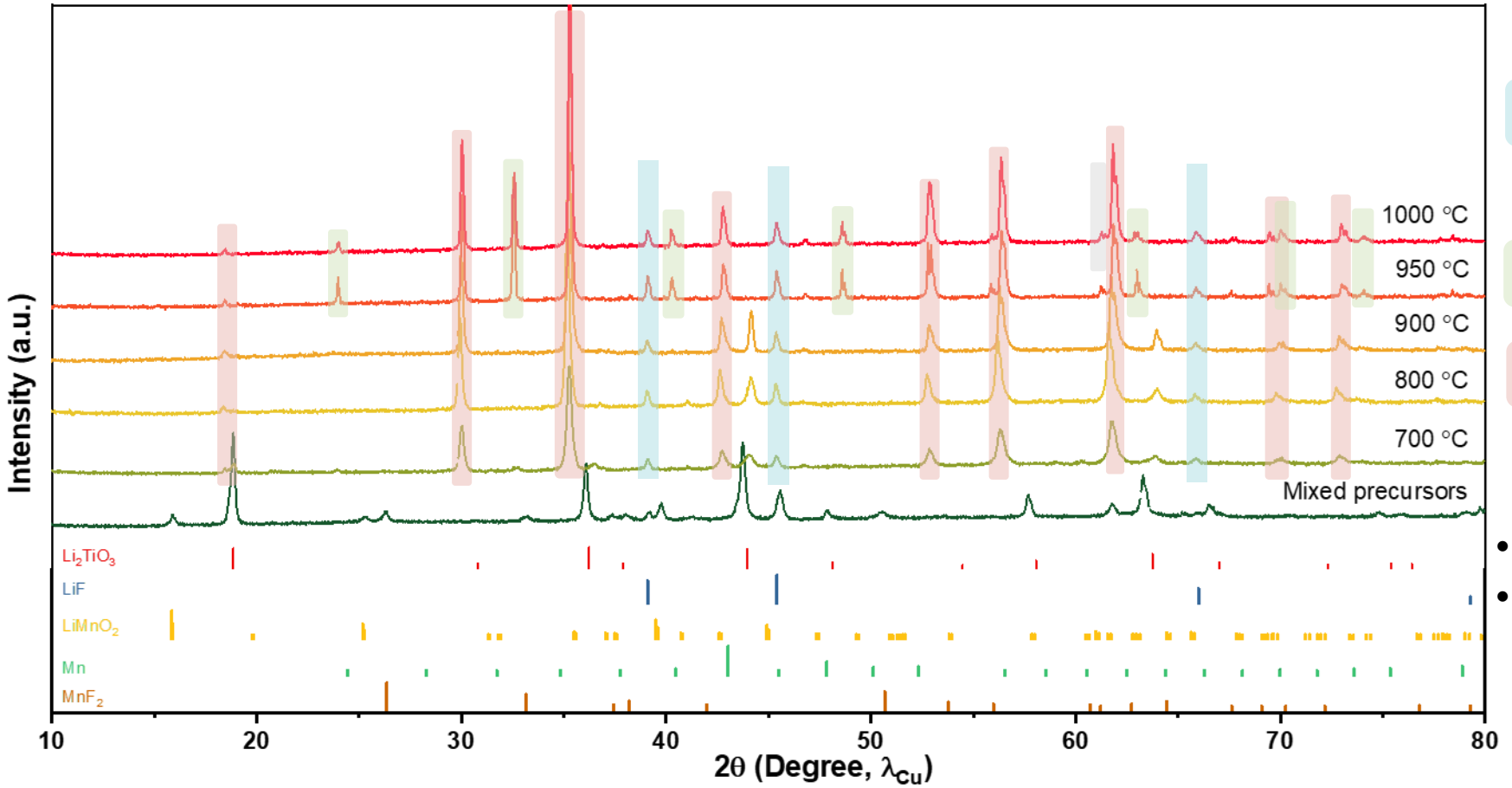


- Cycling up to 4.5 V enables initial discharge capacities of 125 mAh/g, with redox activity corresponding to the $Mn^{2+/4+}$ transition.
- Cycling up to 4.8 V increases discharge capacity at the expense of cycling stability.
- Performance may be improved by optimizing carbon content, particle size/morphology, electrolyte composition, and processing conditions.

Using reactive Mn as reducing agent for synthesis of F-rich DRX

$$0.4\ Li_2TiO_3 + 0.2\ LiMnO_2 + 0.2\ LiF + 0.1\ MnF_2 + 0.1\ Mn \rightarrow Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$$

- Mn metal is reactive, must choose precursors with low reactivity toward Mn
- Reducing Mn balances with Mn^{3+} in $LiMnO_2$ to achieve Mn^{2+} in the targeted DRX phase



LiF MnO

Partially convert to hexagonal $R\bar{3}$

Cubic $Fd\bar{3}m$

- $LiMnO_2 + MnF_2 \rightarrow Mn_3O_4 + LiF$
- $Mn_3O_4 + Mn \rightarrow 4\ MnO$

Using carbon to drive fluorination

$LiF + MnF_2 + LiMnO_2 + Li_2TiO_3 + C \rightarrow Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4} + CO$

Eutectic melt at 600°C enables DRX formation

Reducing agent

Gives large free energy gain at high temperatures

Strong driving force for DRX formation from these precursors:

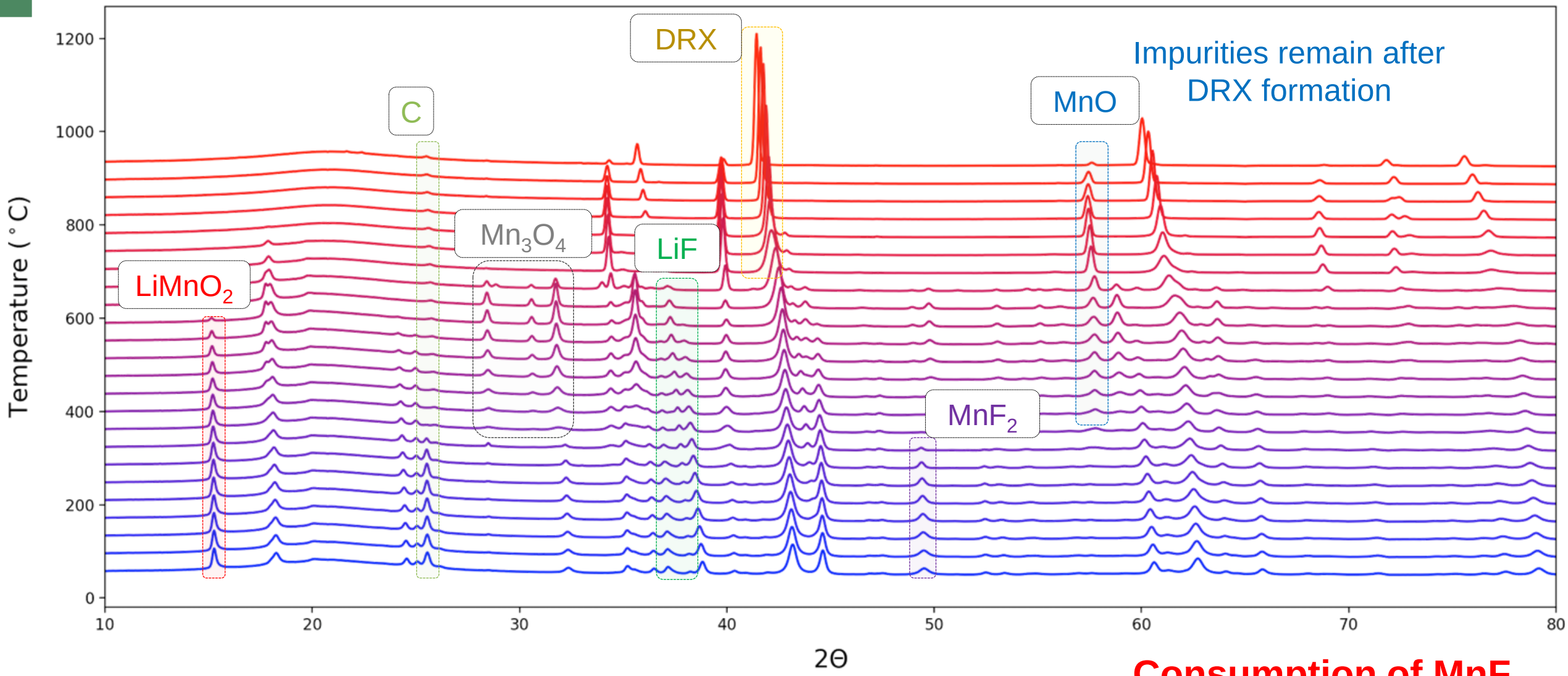
$LiF + MnF_2 + LiMnO_2 + Li_2TiO_3 + C \rightarrow Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4} + CO$ $(\Delta G_{800\,^\circ C} \approx -324\ \mathrm{meV/atom})$

However, do any side reactions occur beforehand?

$LiMnO_2 + MnF_2 \rightarrow Mn_3O_4 + LiF$ $(\Delta G \approx -76\ \mathrm{meV/atom})$

→ **Probe reaction sequence *in situ*** ←

In-situ XRD studies reveal the reactivity of $LiMnO_2$

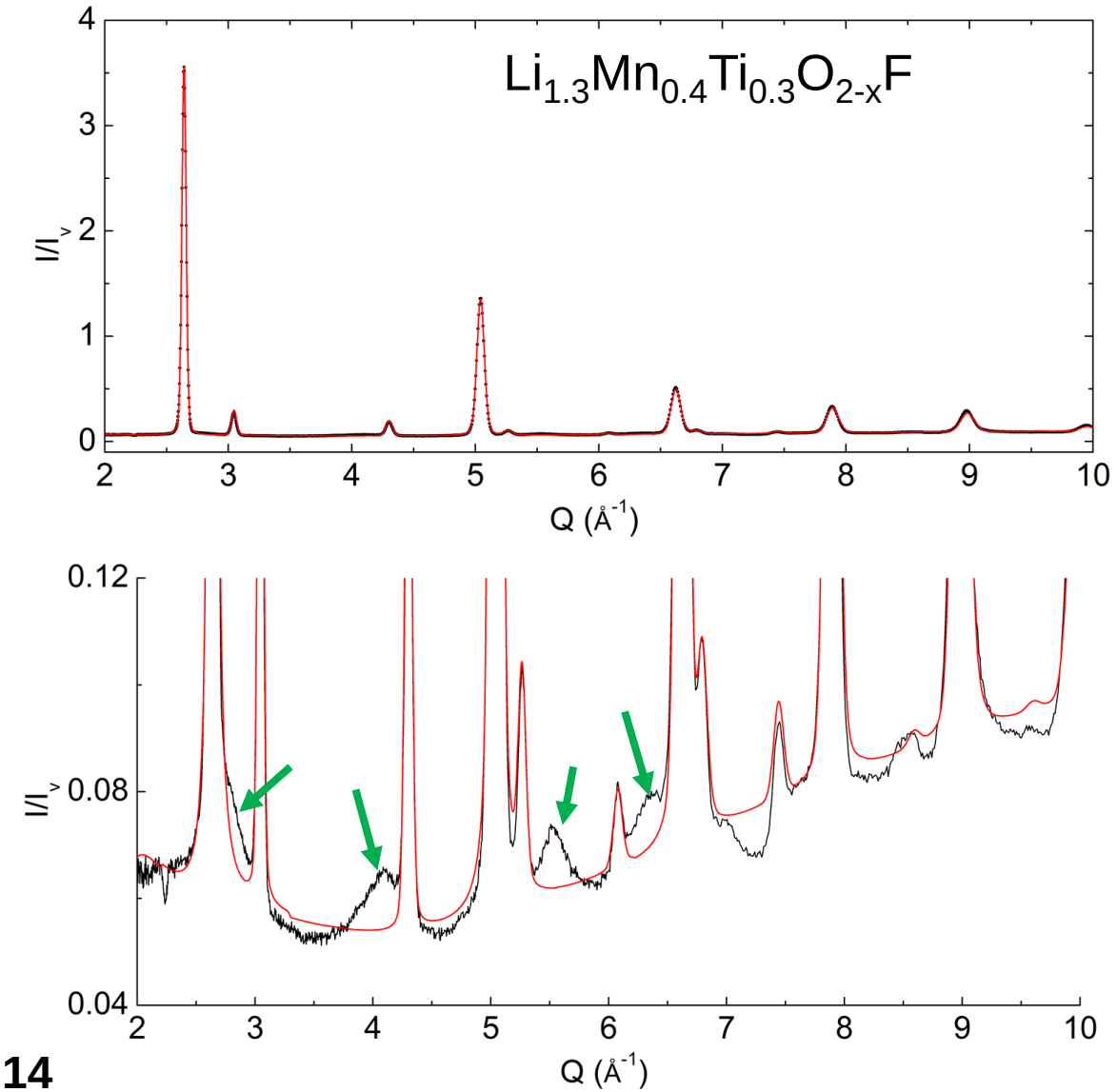


Observed reactions < 600 ºC: $LiMnO_2 + MnF_2 \rightarrow LiF + Mn_3O_4$

$Mn_3O_4 + C \rightarrow MnO + CO_2$

Consumption of MnF_2 leads to limited DRX solubility

The short-range order (SRO) of DRX compositions deviate from the long-range structure (Fm-3m) indicating different Li-TM coordination. Neutron pair distribution function (PDF) analysis is a powerful method to probe SRO.



- Average DRX structural model fits overall neutron pattern well, but the presence of diffuse scattering features indicates short-range cation ordering and/or clustering.

- The average structure (disordered rock salt) fits the PDF well above 5 Å, but the structure fits the short-range PDF (<5 Å) very poorly.
  1. The first PDF peak splits into two peaks (two drastically different M-O/F bond distances)
  2. The peak around 4 Å also splits into two peaks (the secondary nearest M-M or anion-anion distances).

Please see **BAT-405** for more Neutron PDF analysis to elucidate SRO

Responses to Previous Year Reviewers' Comments

A total of four reviewers evaluated the project. Overall, the reviewers' feedback was very positive. Specific comments and suggestions are addressed below:

Recommendations/Comments: Direct fluorination of DRX cathode oxides is an interesting new approach, according to the reviewer; The PI indicated the collaboration and contributions from other team members is going well; that was clear to the reviewer in following the presentation. However, as the overall DRX project moves across several teams, the development process can be improved by stronger coordination that effectively utilizes and integrates learnings from other team members.
Response/Action:. We appreciate the feedback. Reviewers can see better coordination and teaming in the work presented this year. Please see posters Bat-405 and Bat-406 that points to joint teamwork and sharing results.

Recommendation/Comment: While the findings in the direct fluorination on lithiated DRX are not all encouraging, the team proposed two different routes to fluorinate the DRX materials. In the solution-based method, the material can benefit from better mixing at the atomic level, but the fluorination process was still unclear to the reviewer. The solution-based method has the potential to control the morphology. It would be interesting to know if the direct fluorination changes the morphology of DRX or forms the coating on the surface.
Response/Action: We agree that direct fluorination had unintended consequences in terms of the cathode's electrochemical performance. Solution processes like sol-gel enable better mixing at the atomic level, but it's difficult to find an appropriate F-precursor. Direct fluorination of DRX particles yielded thin LiF surface films but did not have a notable impact on the particle morphology.

Recommendation/Comment: The reviewer remarked that the resources may not be sufficient in the future if a scale-up of one of the productions processes has to be implemented.

Response/Action: Scale-up of some successful DRX compositions will be pursued at the BMF at ORNL and MERF at Argonne National Laboratory.

Contributors, Collaborators, and Acknowledgements

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Yiman Zhang

Remaining Challenges and Barriers

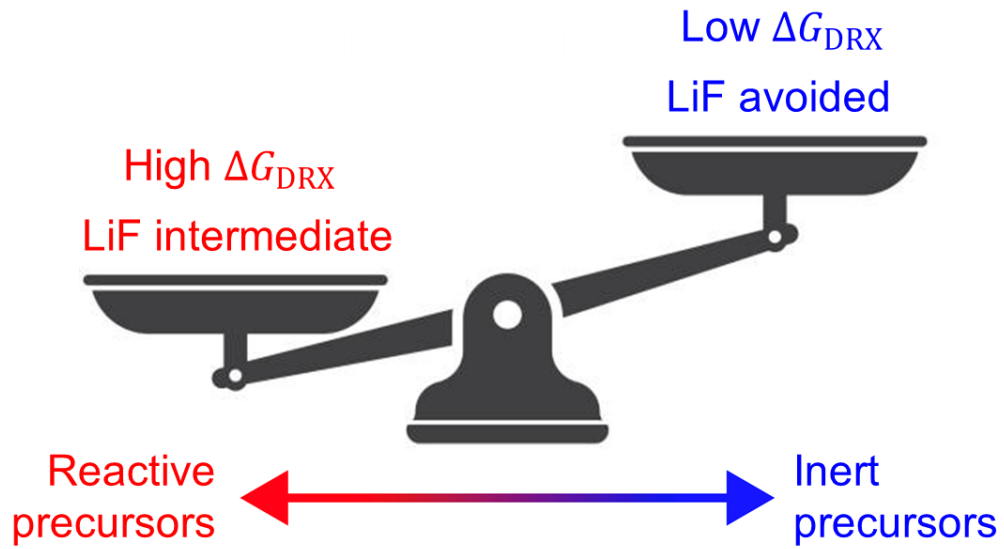
- Scalable synthesis of DRX with high F content
- Addressing high voltage instabilities (e.g., oxygen evolution)
- Intrinsic low electronic conductivity of DRX composition affecting capacity utilization and rate capability
- Optimization of DRX composition and synthesis conditions

Proposed Future Research

- Improve cathode cycling stability and rate capabilities through synthesis control
  - Higher F content
  - SRO optimization
  - Hybrid structure – ordered/disordered, spinel/rocksalt
  - Particle engineering (size, morphology, surface chemistry, etc.)
- Improve electronic conductivity of DRX cathodes by carbon coating (e.g., CVD processes)
- Full cell testing

“Any proposed future work is subject to changes based on funding levels.”

Summary



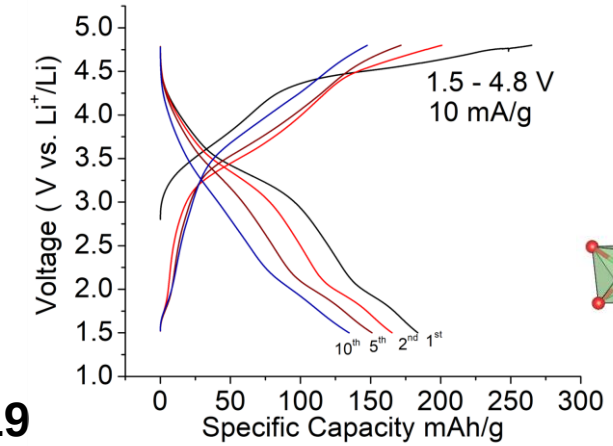
Technical Approach:

- Novel precursor sets were identified to synthesize Li-Mn-Ti-O-F DRX cathodes while mitigating undesired reactions
- Synthesis efforts guided by modeling and thermodynamic calculations

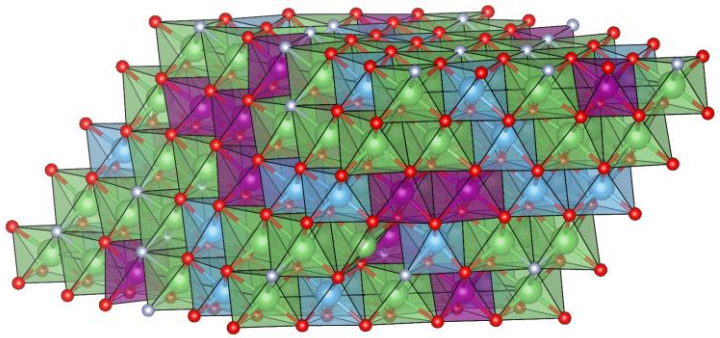
Accomplishments:

- Fluorinated $Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$ cathodes were produced with initial capacities near 200 mAh/g
- *In-situ* XRD measurements identified intermediate reactions which occur during calcination
- Neutron diffraction and pair distribution function analysis provide key insights on short-range ordering of DRX cathodes.

$Li_{1.2}Mn_{0.4}Ti_{0.4}O_{1.6}F_{0.4}$



Simulated DRX Structure



Ongoing Work:

- Optimizing synthesis conditions to eliminate impurity phases (e.g., LiF)
- Developing CVD processes to apply carbon coatings to DRX particles
- Improving understanding of F distribution in fluorinated DRX cathodes