Disordered Rocksalt Transition-Metal Oxides (TMOs): Synthetic Strategies

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2021 DOE VTO Annual Merit Review

June 21-25, 2021

Project ID: bat406

Overview

Timeline

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

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)

Barriers Addressed

- Energy density
- Cycle life
- Cost

Partners

- Lawrence Berkeley National Laboratory
- Oak Ridge National laboratory
- Pacific Northwest National Laboratory
- UC Santa Barbara

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Relevance/Objectives

- Cathode materials based on cation-disordered Li-excess rocksalts (DRX) can deliver energy densities up to 1000 Wh/Kg and > 3000Wh/l (cathode only)
- DRX structure allows a wide range of chemistry, providing an opportunity to develop Co-free as well as Ni-free high energy density cathode materials that are alternatives to the traditional layered NMC-type cathodes. In particular, materials with Mn-redox, and Ti as charge compensator are being investigated. These are both metals whose oxide precursors are inexpensive and abundant.
- Fundamental understanding on what controls DRX performance characteristics, particularly rate capability, cycling stability and voltage slope, are key to enabling rational decisions on further development of this newer class of cathode materials.

Milestones

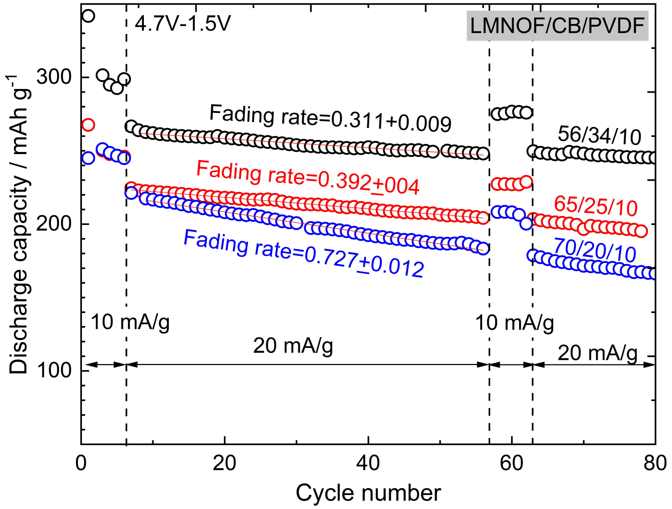
Date	Milestones	Status
December 2020	Synthesis of DRX with various short-range ordering	Completed
March 2021	Develop synthetic approaches to increase F-solubility in DRX materials	Completed
June 2021	Synthesis of enhanced material according to the modeling and characterization effort	On schedule
September 2021	Demonstration of a Co-free optimized DRX with > 200 mAh/g for at least 50 cycles at RT	On schedule

Approach/Strategy

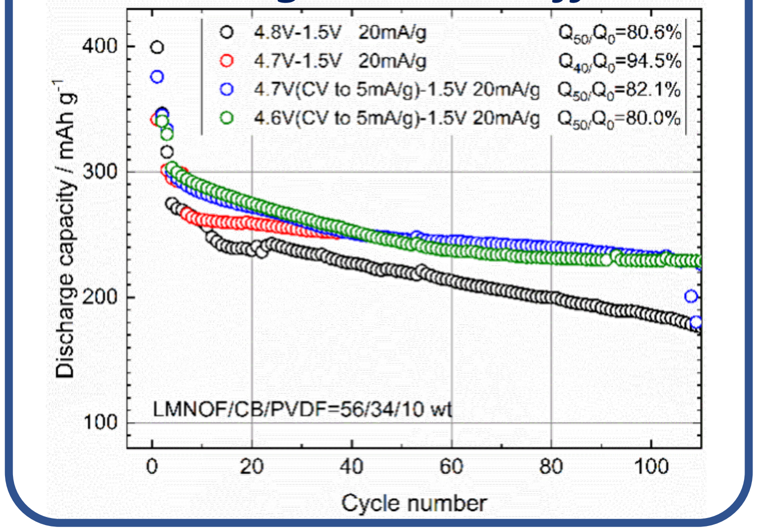
- Focus on three fluorinated DRX (F-DRX) baseline systems and their analogues: $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF), $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$(LNTMOF) and $Li_2Mn_{1/2}Ti_{1/2}O_2F$. *Note: emphasis has now shifted to the two Mn-based systems, away from the Ni-based system studied in year 1.*
- Explore synthesis conditions to prepare DRX materials with optimized performance. Establish reliable and scalable synthesis protocols and provide same-batch materials to the tasks within the DRX program.
- Fabricate quality electrodes of DRX materials. Develop electrochemical testing protocols and benchmark DRX performance metrics.
- Develop, synthesize and characterize DRX model systems for mechanistic understanding and experimental support of the modeling effort.

Cycling stability influenced by C content/V window/separator

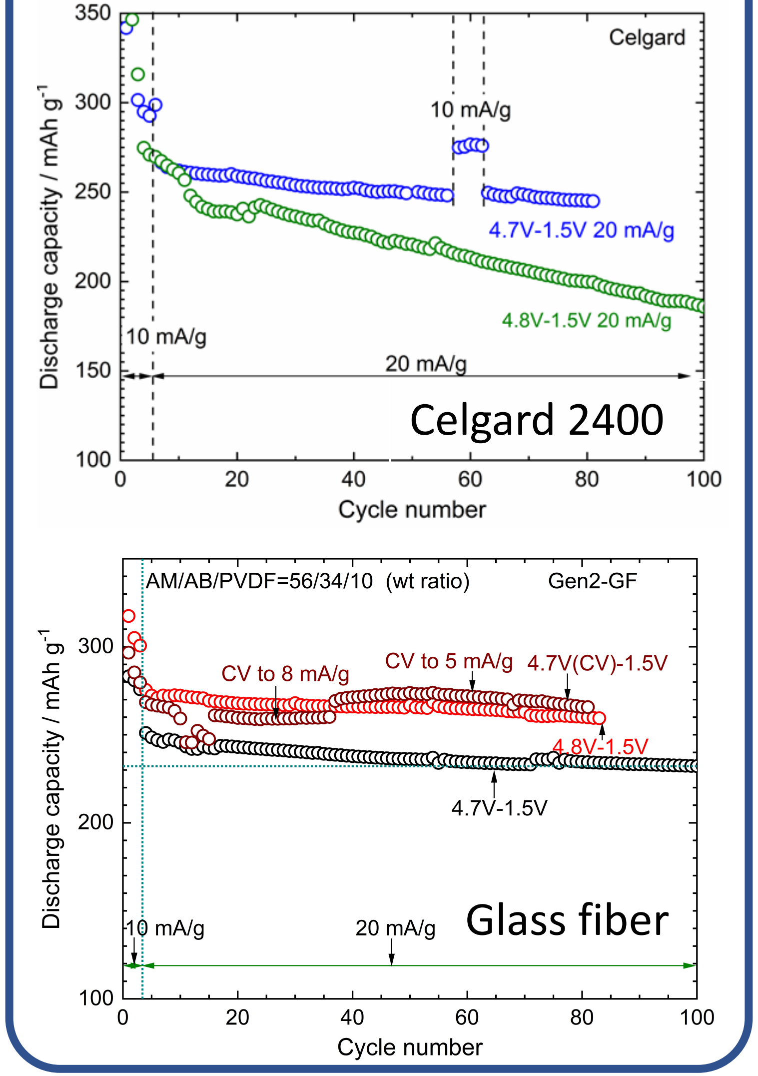
Carbon content effect



Voltage window effect

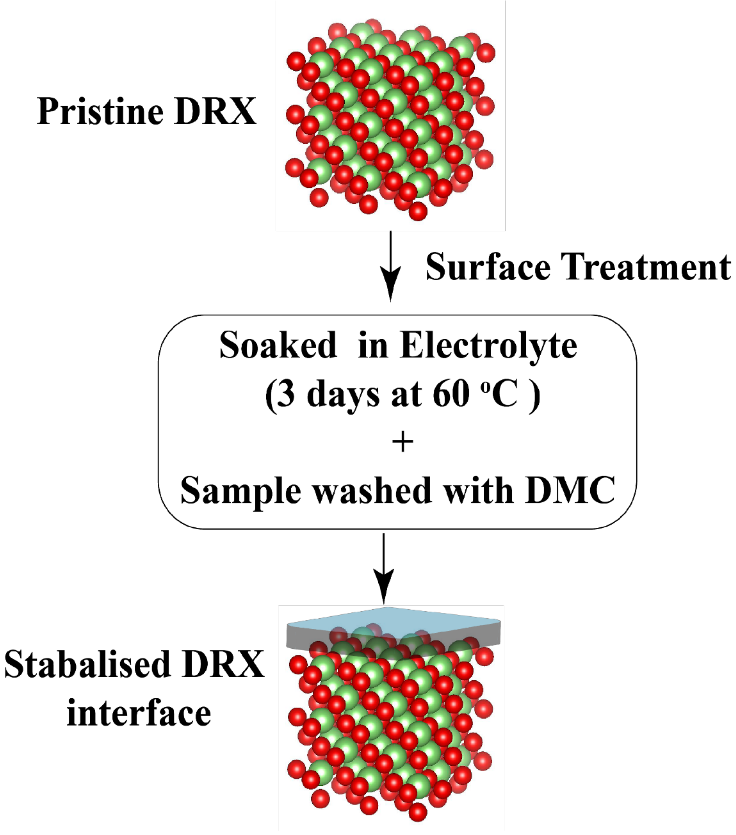


Separator effect



- DRX composition: $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF)
- Carbon effect – increasing carbon content in electrode formulation leads to less impedance, better DRX utilization and higher capacity.
- Voltage effect – cycling to higher voltage increases initial capacity but also capacity fade.
- Separator effect – capacity fade reduced by using more porous separator like glass fiber, even at high voltages (4.8 V).

Cycling stability improves with surface treatment

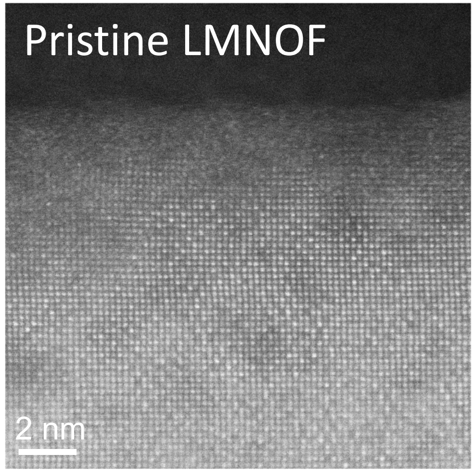


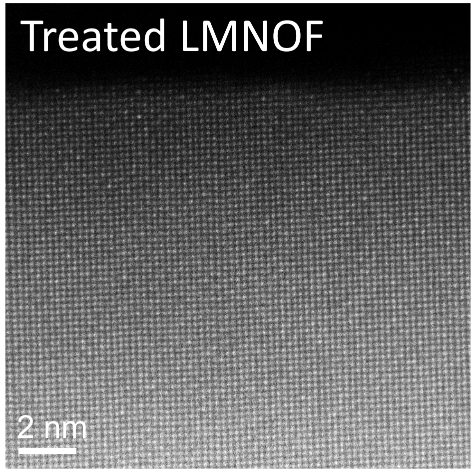
Pristine DRX

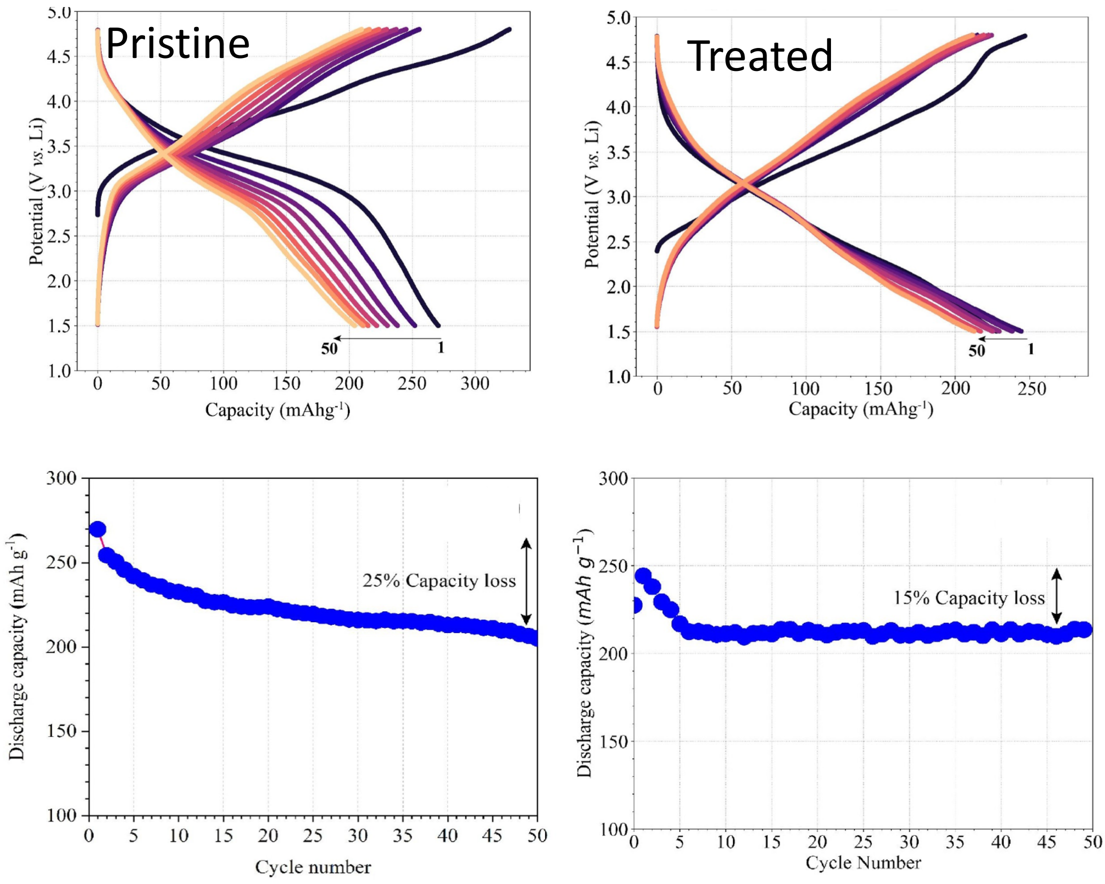
Surface Treatment

Soaked in Electrolyte
(3 days at 60 ºC)
+
Sample washed with DMC

Stabalised DRX interface



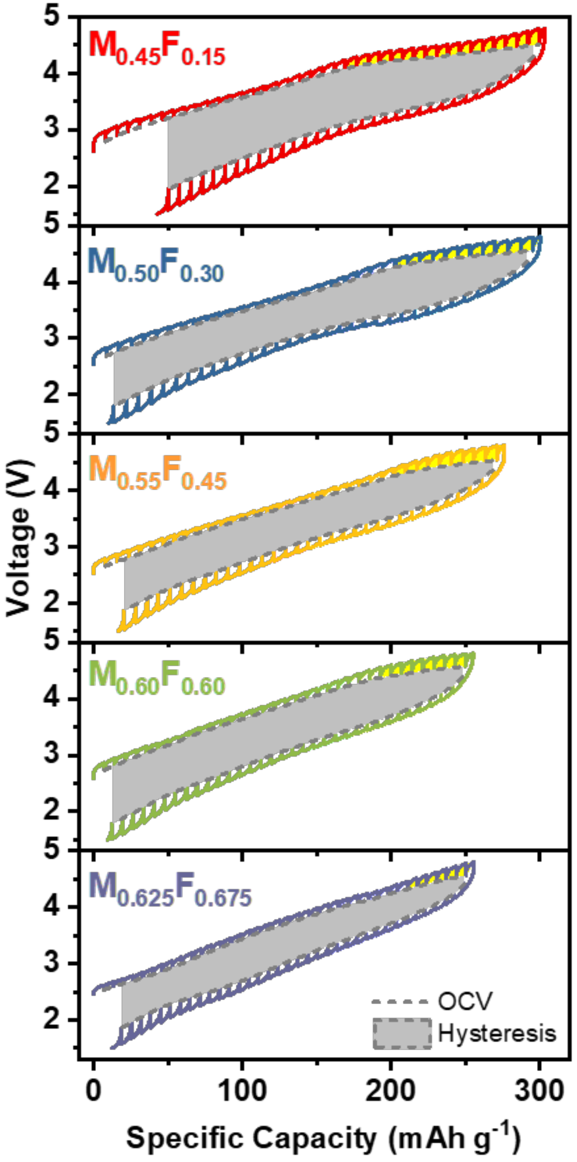




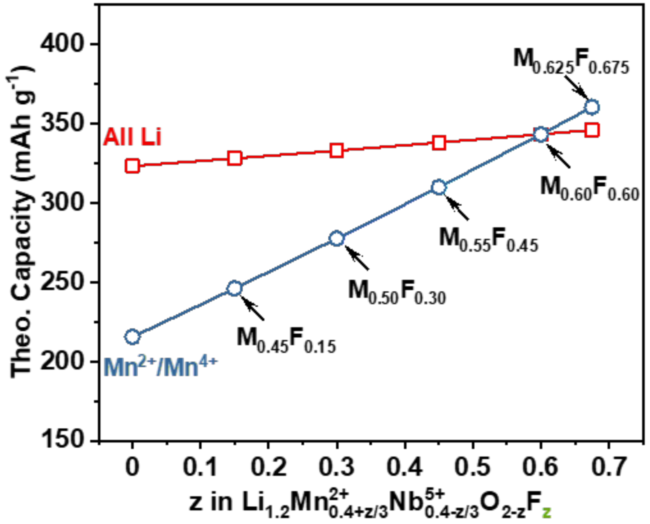
- Surface treatment improves capacity retention and cycling stability

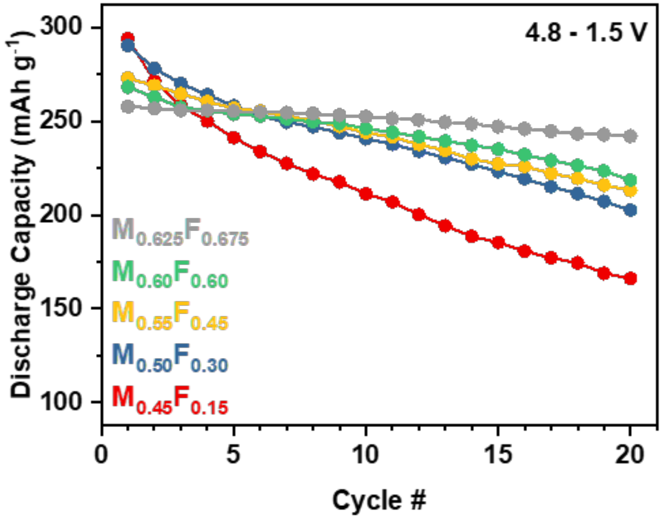
- Soaking in Gen 2 electrolyte (1.2M $LiPF_6$ in EC:EMC 3:7) at elevated temperature removes amorphous F-rich layer on the pristine surface

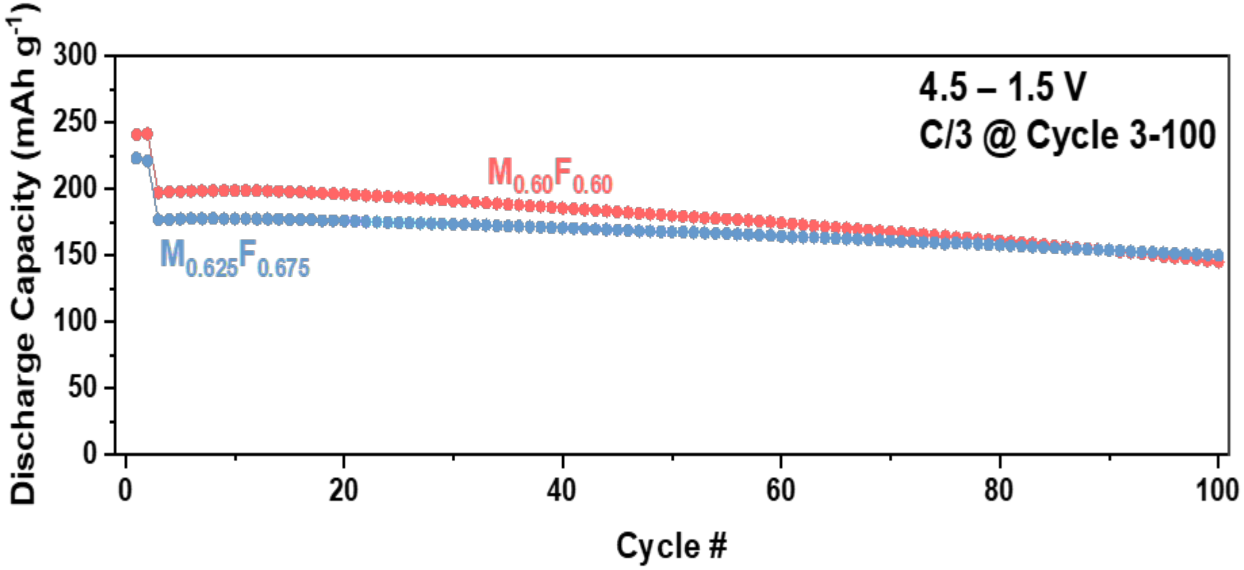
Cycling stability improves with increasing F content



$Li_{1.2}Mn^{2+}_{0.4+z/3}Nb^{5+}_{0.4-z/3}O_{2-z}F_z$



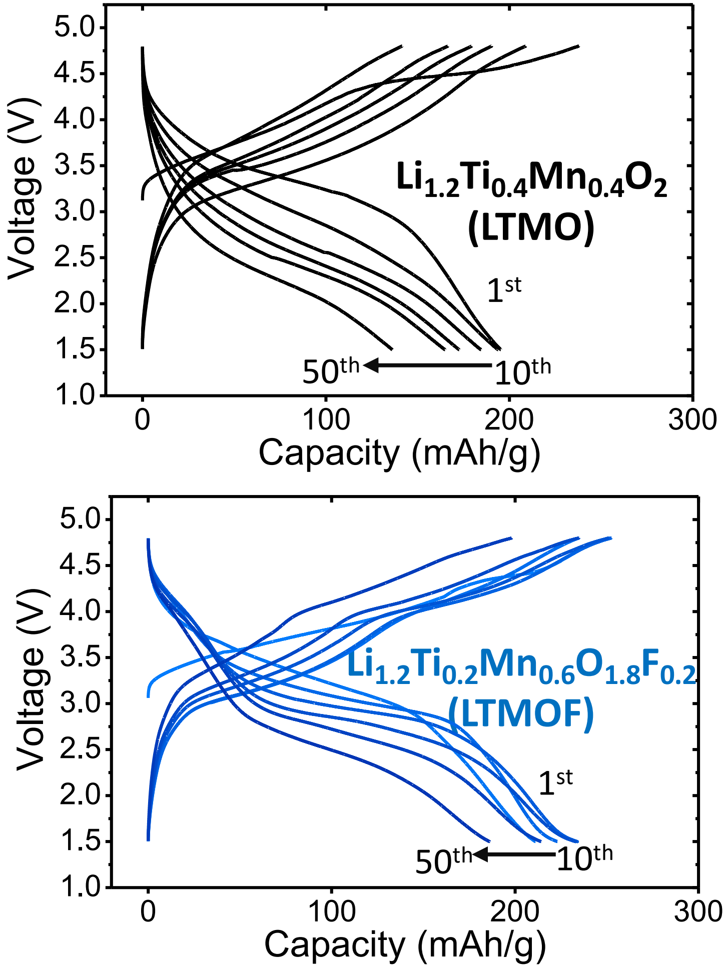




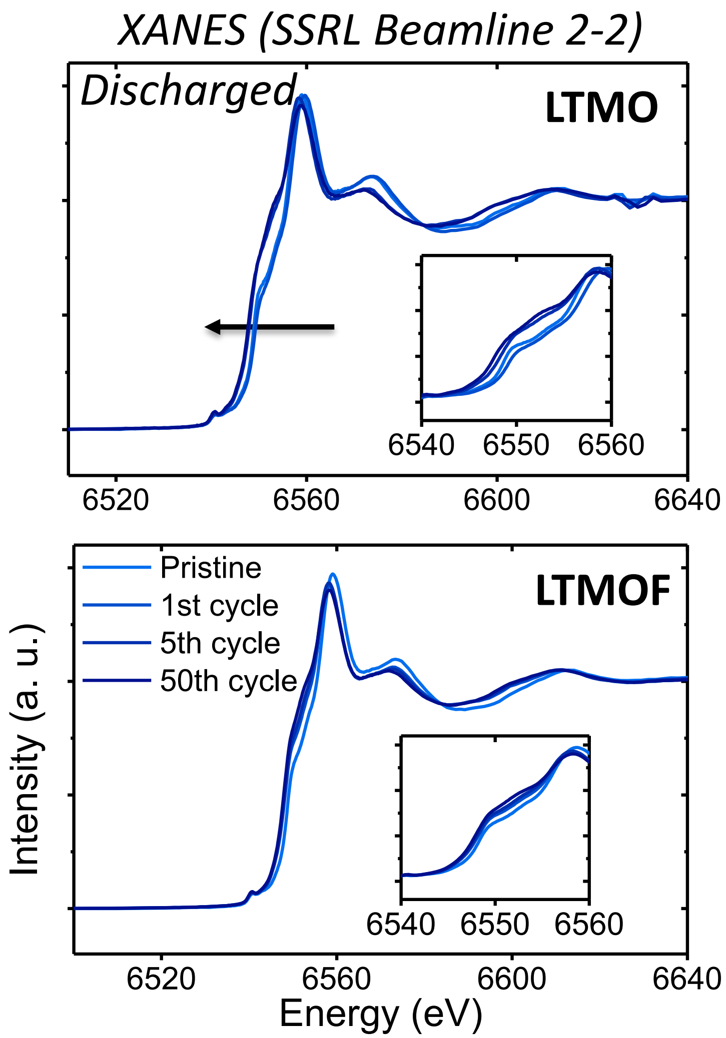
- All samples prepared by high-energy ball milling method
- DRX cycling utilizing Mn double redox delivers high capacity
- Higher F-content improves cycle life even at high V charge cutoff

Yue et al. Adv. Funct. Mater., 2021, 31, 2008696

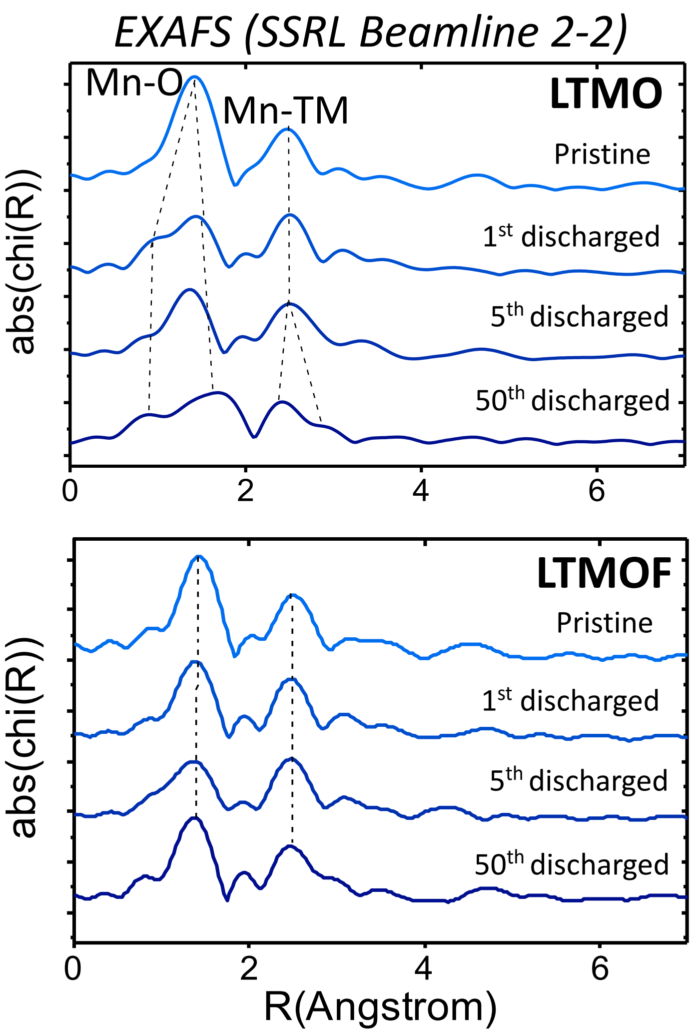
F substitution enhances chemical and structural stability



Chen et al., J. Mater. Chem. A **9**, 7826 (2021)



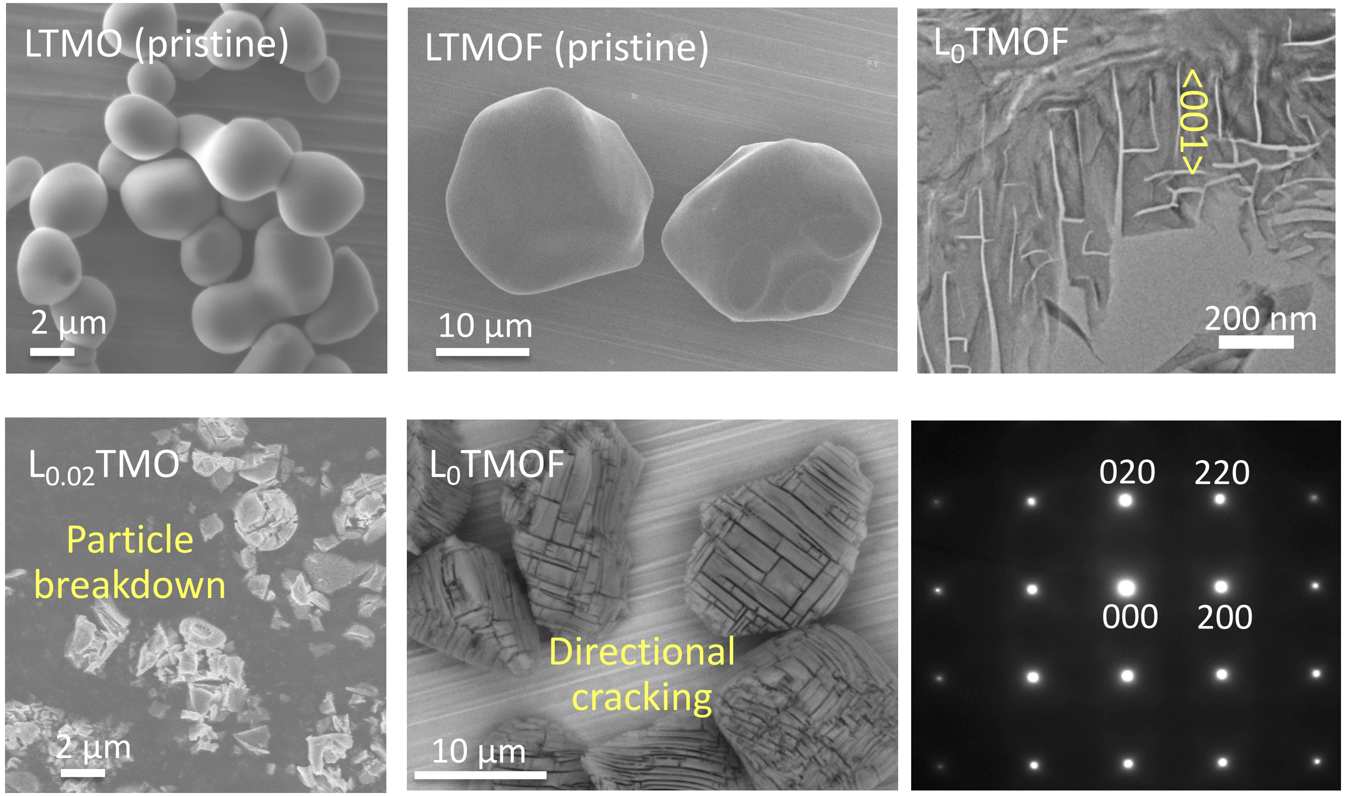
- F improves chemical stability of redox-active Mn during cycling



- F improves local structural stability (Mn coordination)

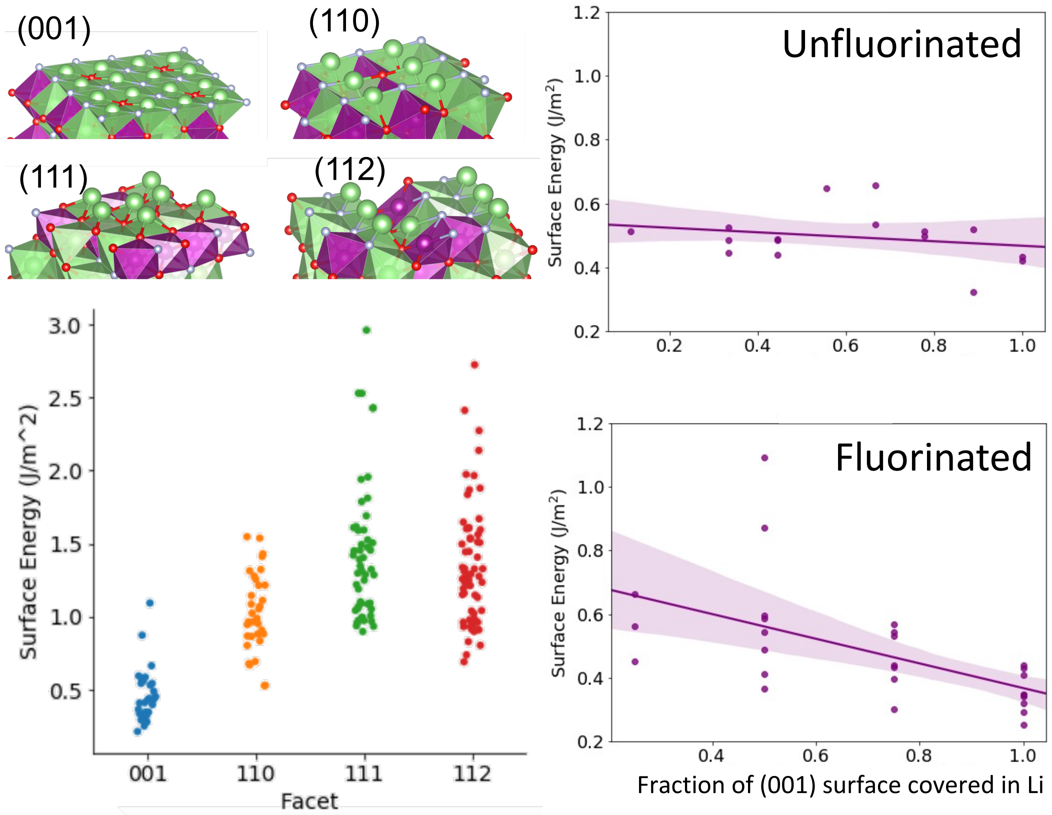
F substitution improves chemomechanical behavior

SEM/TEM/EDX



- Large single crystals used to understand intrinsic DRX behavior
- Random cracking in LTMO leads to particle breakdown while directional cracking along <001> directions enables integrity

DFT calculations



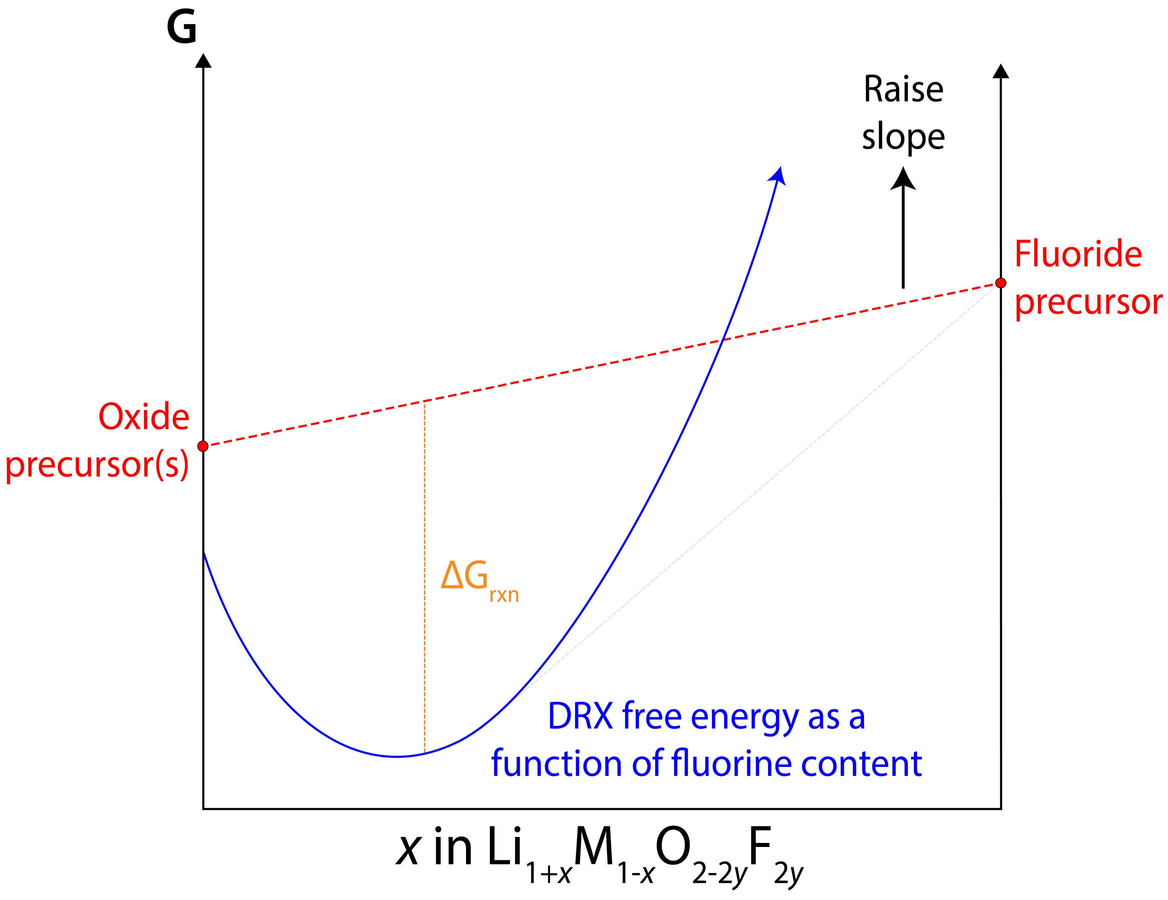
- Directional cracking correlated to Li enrichment on (001) surface upon fluorination

Strategies to increase F content in scalable synthesis

- **Shifting chemical equilibrium toward higher F content**

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 more reactive fluoride precursor than LiF

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

Synthesis routes being investigated (see Poster bat404)

Less reducing

1) $Li_6MnO_4 + TiO_2 + MnF_2 \rightarrow$ DRX
($\Delta G \approx -267$ meV/atom)
- No reducing agent, MnF_2 as F-source

2) $Li_2TiO_3 + LiMnO_2 + LiF + MnF_2 + Mn \rightarrow$ DRX
($\Delta G \approx -302$ meV/atom)
- Mn as reducing agent, LiF|MnF_2 eutectic as F-source

3) $Li_2TiO_3 + LiMnO_2 + LiF + MnF_2 + C \rightarrow$ DRX + CO
($\Delta G \approx -324$ meV/atom)
- C as reducing agent, LiF|MnF_2 eutectic as F-source

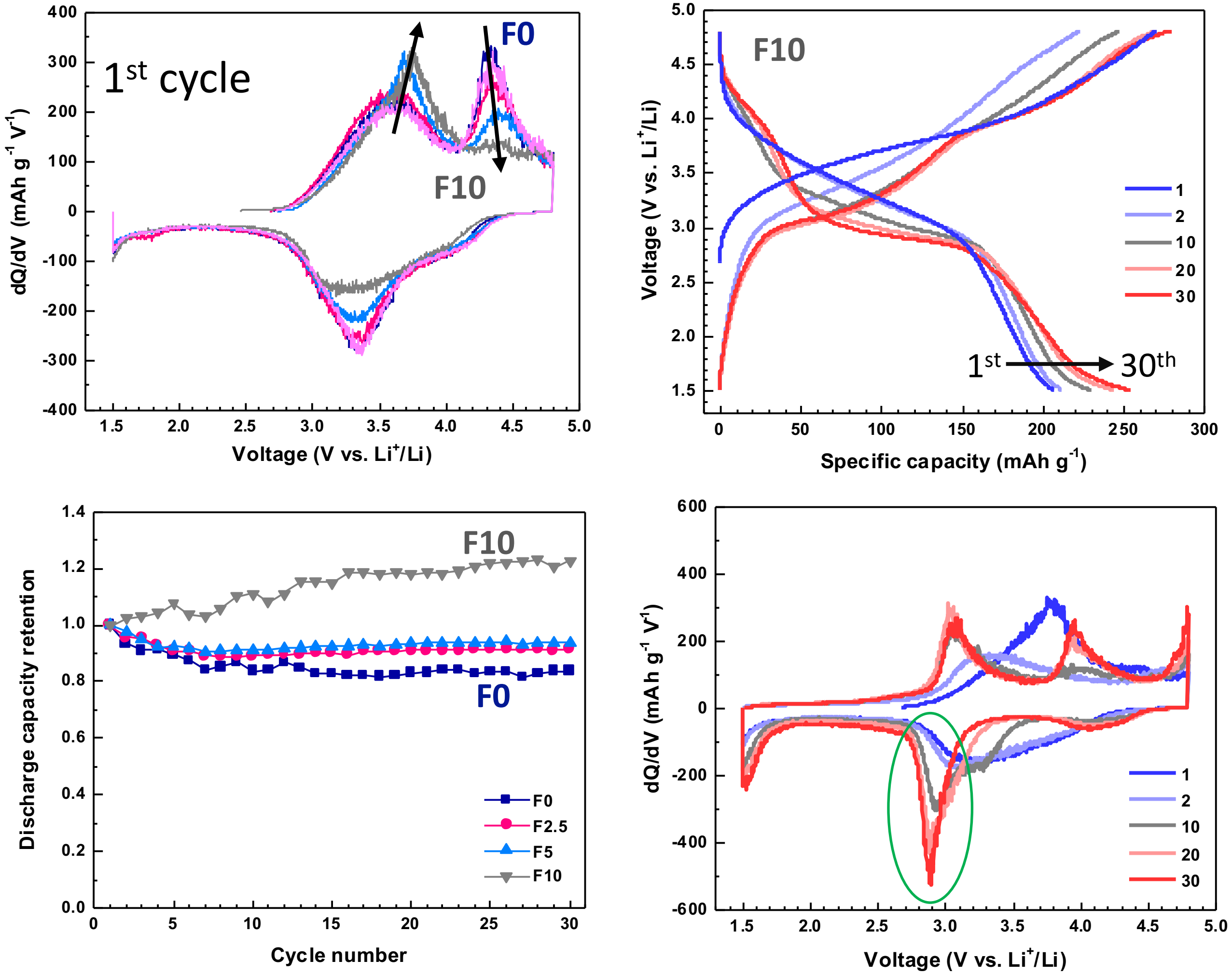
More reducing

Strategies to increase F content in scalable synthesis

- **Synthesis with PTFE as F precursor**

Sample	Composition	Capacity (mAh/g)	
		Mn	Li
F0	$Li_{1.2}Mn_{0.6}Nb_{0.2}O_2$	175	350
F2.5	$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$	184	353
F5	$Li_{1.2}Mn_{0.65}Nb_{0.15}O_{1.9}F_{0.1}$	193	356
F10	$Li_{1.2}Mn_{0.7}Nb_{0.1}O_{1.8}F_{0.2}$	212	363

- PTFE precursor has higher μ_F than LiF, enabling higher F solubility in Mn-Nb based DRX
- Higher F content enables more Mn content and redox contribution.
- Mn-rich DRX shows unique behavior
  - ○ Capacity increases with cycling
  - ○ Development of cathodic peak at ~ 2.9 V contributes to stable large capacity

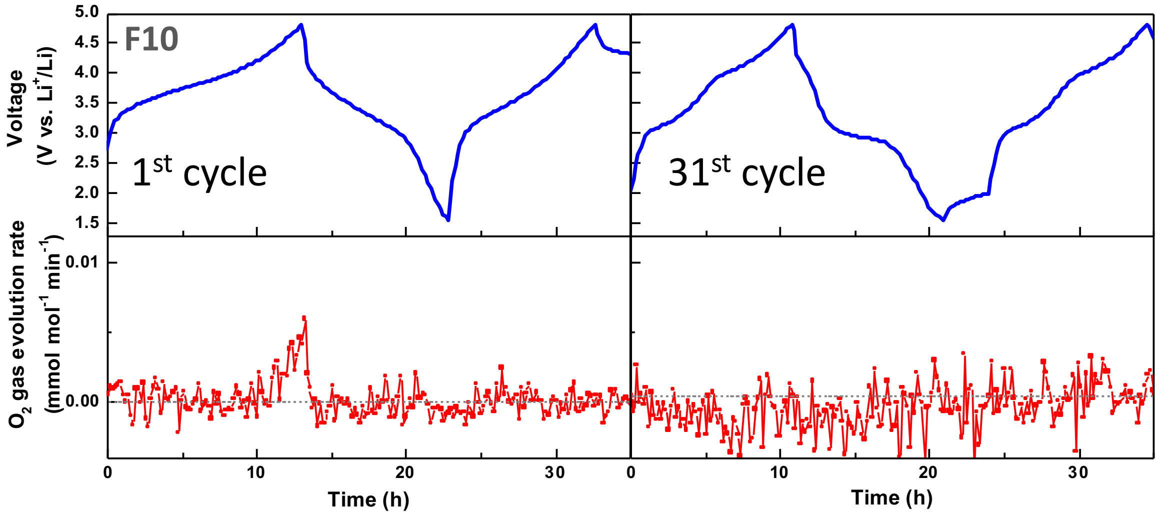


Ahn et al., Adv. Energy Mate., 2001671 (2020)

Mn-rich DRX – understanding capacity increase

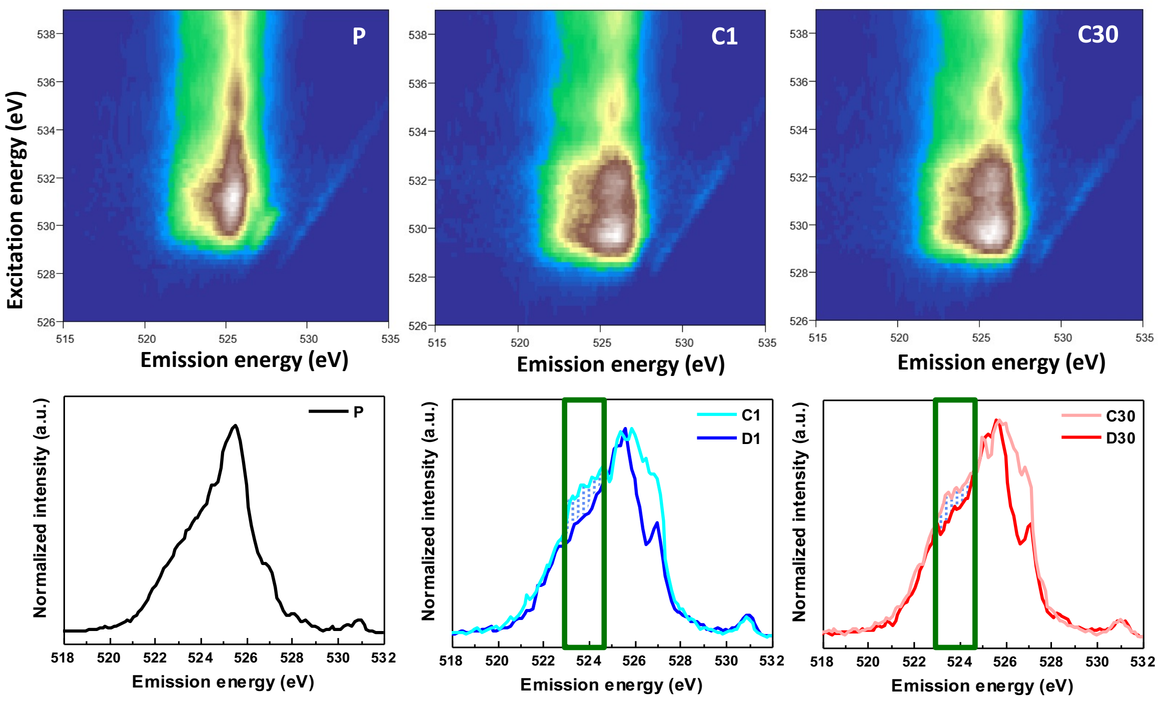
- **Capacity increase not a result of increased O redox contribution**

Operando DEMS



- O_2 gas evolution detected upon 1st charge but not after 30 cycles.

O K-edge RIXS (ALS)

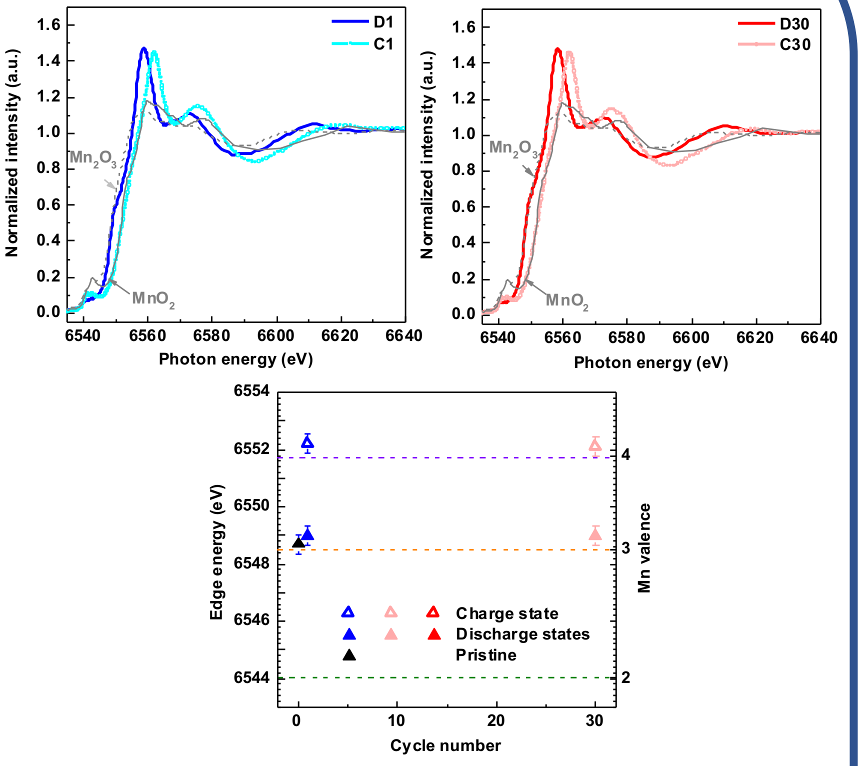


- An overall relatively small oxidized oxygen features detected on RIXS but no changes with cycling.

Mn-rich DRX – understanding capacity increase

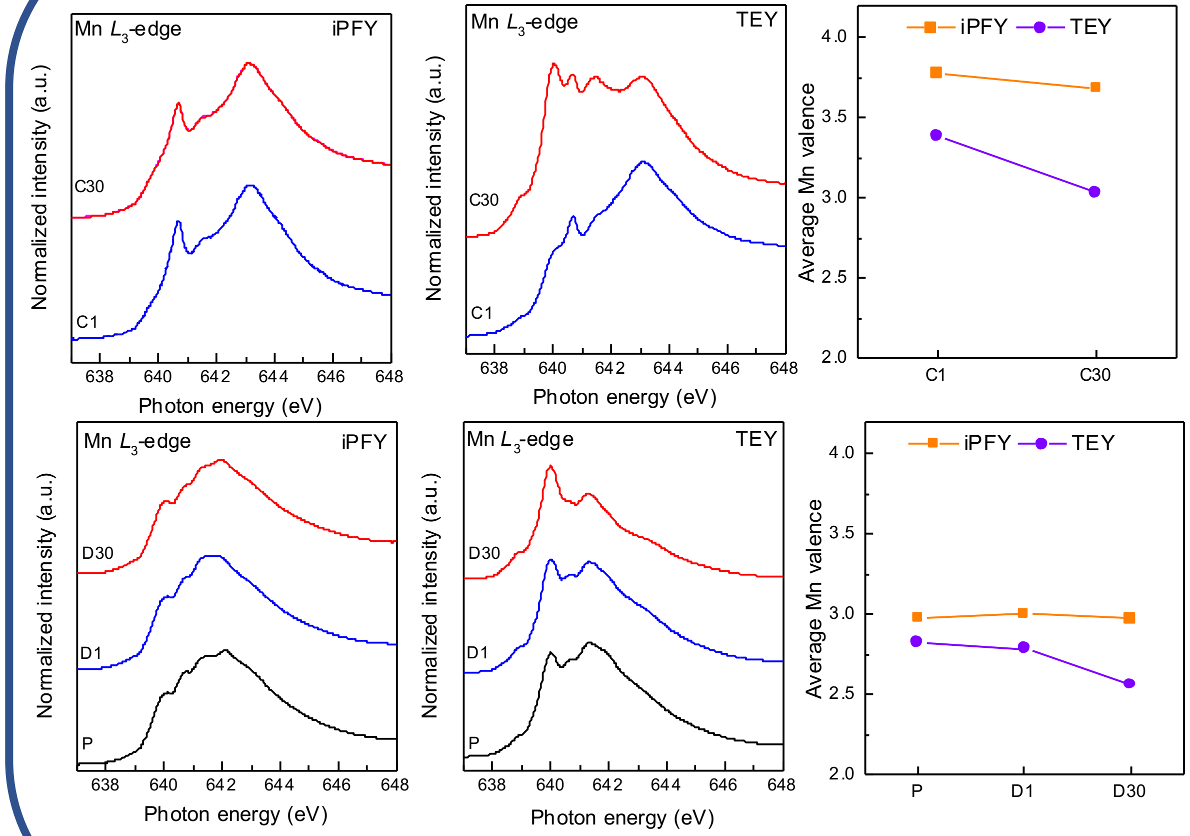
- **Surface and subsurface Mn^{2+} species detected after cycling**

Mn K-edge hard XAS (SSRL)



Bulk Mn redox remains primarily Mn^{3+}/Mn^{4+}

Mn L-edge soft XAS (ALS)

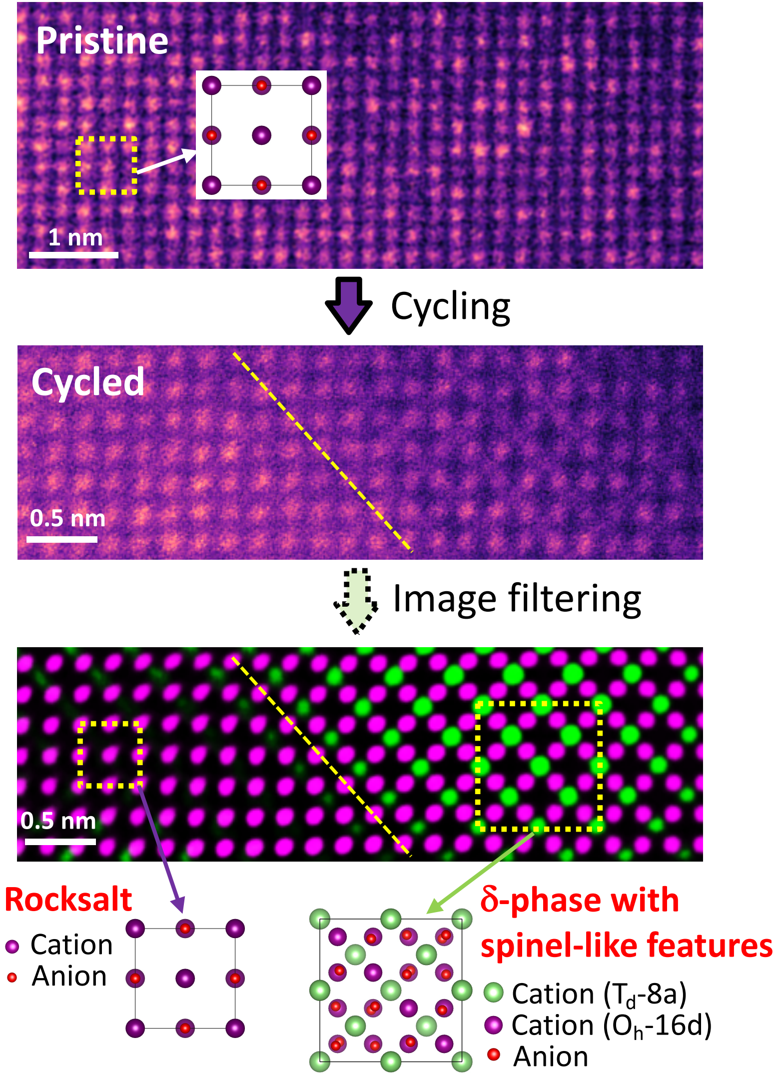


Cycling increases surface and subsurface Mn^{2+} presence

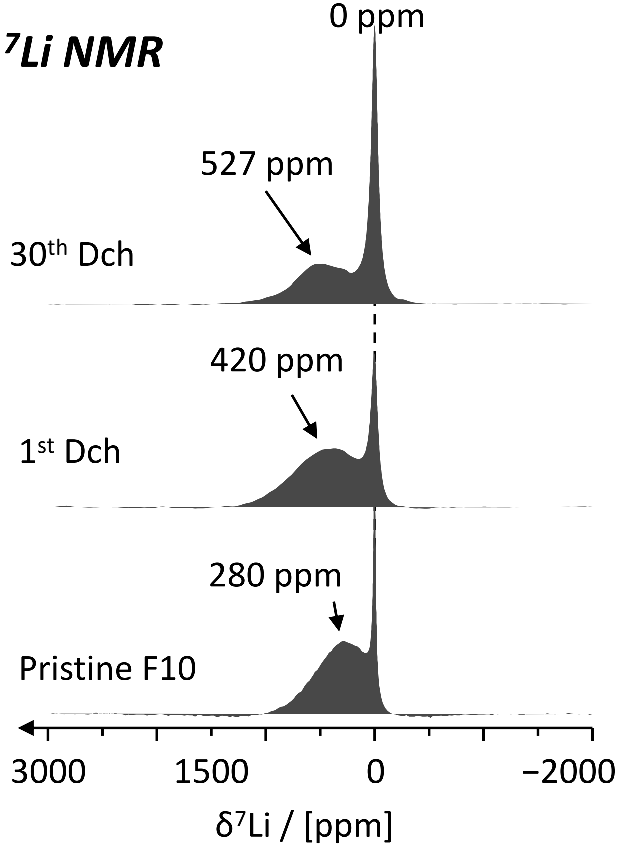
Mn-rich DRX – understanding capacity increase

- **Formation of δ-phase with spinel-like features cause of capacity increase with cycling**

STEM imaging

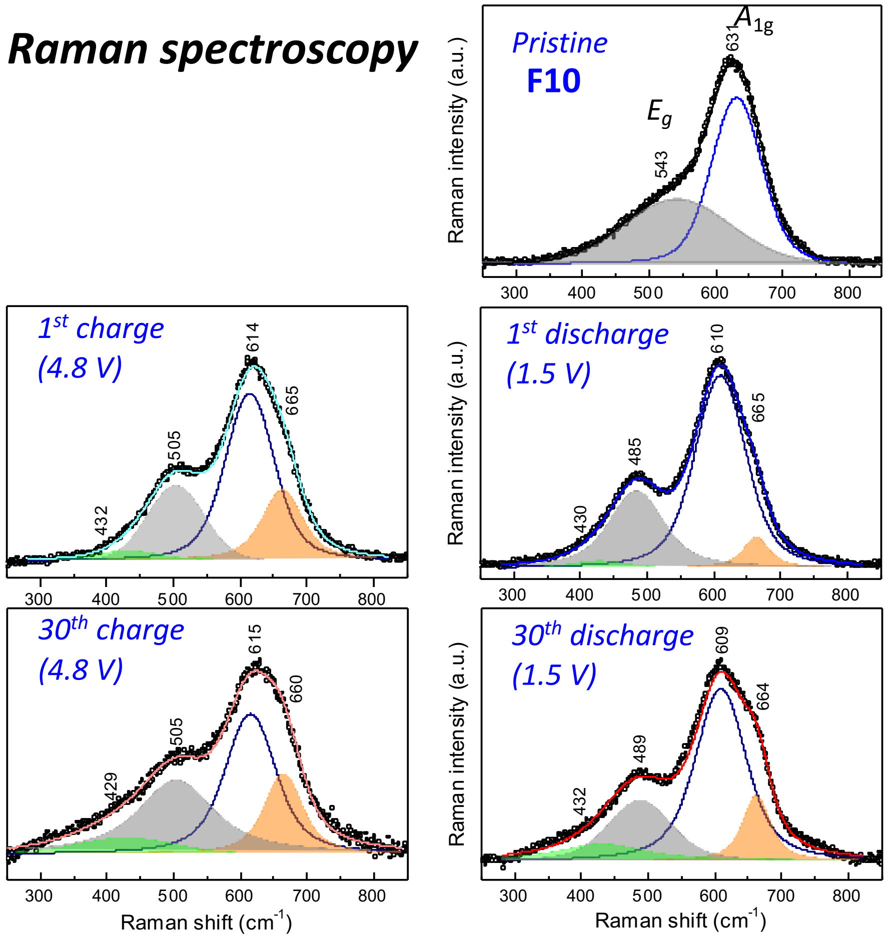


^{7}Li NMR



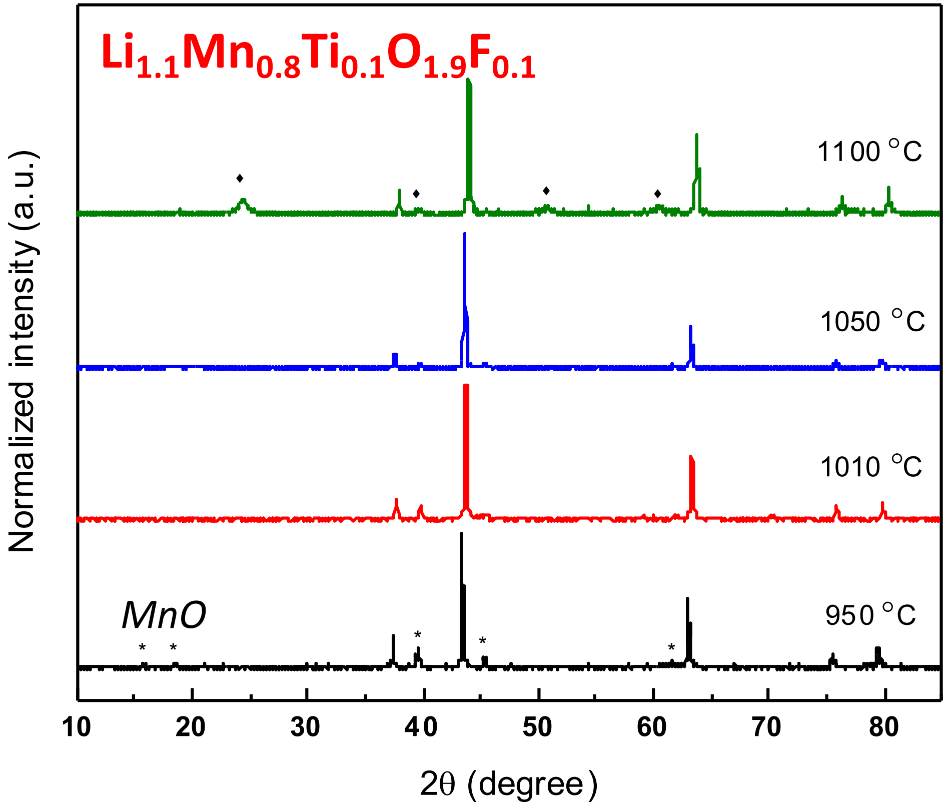
Gradual increase in average $\delta_{iso}(^7Li)$ from 280 to 527 ppm corresponds to partial transformation to δ-phase with spinel-like features.

Raman spectroscopy

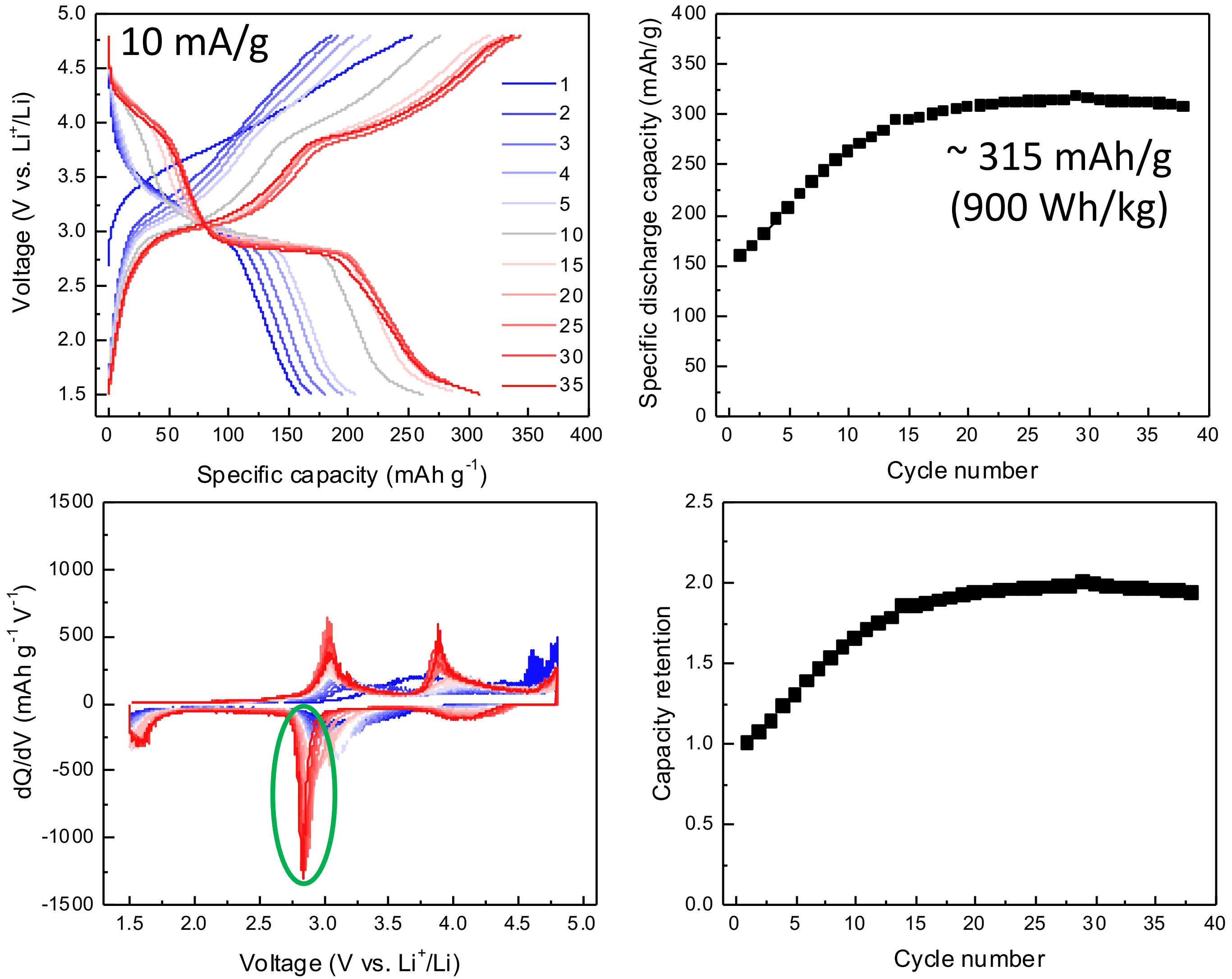


Local presence of spinel-like features confirmed. Content increases continuously with cycling.

Improved DRX with Mn-enrichment



- Highest Mn-content DRX made in phase pure with best performance in the series so far
- Higher Mn leads to faster development of cathodic peak at ~ 2.9 V



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:

Recommendation/Comment: The material does provide an alternative to the Co-containing NMC cathode. However, for the new elements, the reviewer asserted that the PI needs to make sure that they are sustainable (e.g., Nb supply concerns).
Response/Action: One of the main advantages of DRX is that they consist of earth abundant metals. Nb-based DRXs were selected as baseline mainly for material understanding purpose. This year our focus largely shifted towards the Mn/Ti-based systems.

Recommendation/Comment: It would be interesting to know if morphology would be a factor impacting material and electrochemical properties, such as surface properties, packing density, or long-term stability.
Response/Action: We thank the reviewer for the excellent suggestion. This year DFT calculation revealed the lowest energy facets in DRX are (100) and (110) families. Both modeling and experimental efforts are ongoing in this area and more results will be reported in the future.

Recommendation/Comment: As the team mentioned, the electrolyte could be a factor to optimize the performance and surface characteristics on DRX materials; this could be a future study or collaboration with an electrolyte expert group in the future.
Response/Action: Electrolyte plays an important role in high voltage stability. Some preliminary work was performed this year but in depth exploration on different electrolytes and how they interact with DRX will be an important part in the next stage of DRX research.

Recommendation/Comment: It would be great to know if the synthesis approach is optimized based on the feedback from the other project teams.
Response/Action: The synthesis team works closely with the modelling and diagnostics teams. This is clearly shown in this year's effort in increasing F solubility as well as improving short-range ordering, among others. More details on coordinated DRX research can be found in posters BAT376, BAT404 and BAT405.

Recommendation/Comment: In the synthesis area the synthesis approach mainly uses the solid-state method to obtain the DRX structure. Would the team consider the solution method in the future? The solution-based synthesis approach cold be easier to scale up in the future.
Response/Action: We thank the reviewer for the suggestion. Solution-based synthesis is worth exploring and this may be pursued in the next stage of DRX research.

Contributors and Acknowledgement

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Remaining Challenges and Barriers

- DRX cycling stability at high voltages
    - Fluorinated materials are surface-stable at high voltage, but it appears that electrolyte degradation is present at high voltage and leads to impedance growth.
- DRX compositional optimization
    - While this deep-dive program has led to understanding and mitigation of several of the early issues with DRX materials (rate capability, fade, voltage slope), understanding and solutions for each problem have been demonstrated, but not in a single material. Compositional optimization is needed to put all these solutions together in a single material or group of materials.
- High Mn-content compounds are very attractive due to their very high energy density, and potential low cost, but bulk changes with cycling need to be better understood (and harnessed).
- While achievable fluorine contents in solid-state synthesis already leads to significant improvement in stability, further benefits could be derived from a higher F content in the material. This will require scalable synthesis methods that can lead to a higher F uptake.

Proposed Future Work

- **Compositional Optimization**
  - Starting from the Li-Mn-Ti-O-F base composition, further optimize composition based on what we have learned, to improve rate, stability, and energy density
- **Investigation of δ-phase**
  - Very high Mn-content DRX materials have promising energy density. Upon cycling they increase in capacity as bulk transformation to a δ-phase is observed. Since this phase has higher energy density and a flatter voltage profile, we will characterize this phase and attempt to synthesize it directly.
- **Investigation of F uptake mechanism and different synthesis approaches**
  - We will investigate the mechanism by which DRX materials form by using in-situ diffraction during synthesis, and modify the synthesis protocol and precursors to increase F-uptake
- **Understand the origin of DRX cycling stability**
  - Evaluate in more detail cycle life as a function of low and high voltage cutoff in pouch cells

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

Summary

- DRX cycling stability depends on cathode carbon content, voltage window and separator porosity.
- Cycling can be improved by increasing F content as well surface electrolyte treatment of the pristine.
- F substitution improves chemical and structural stabilities as well as DRX chemomechanical behavior upon cycling
- Strategies to increase F content in scalable synthesis developed
- Formation of δ-phase with spinel-like features leads to unique behavior of capacity increase in Mn-rich DRX cycling
- New DRX with enhanced performance developed

Technical Back-Up Slides

DRX electrode fabrication process

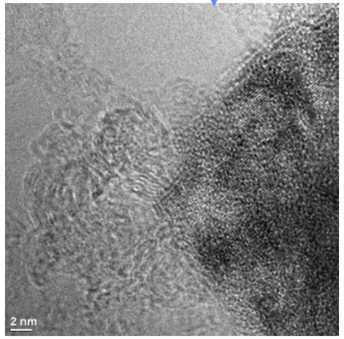
DRX ball-milled with carbon→AM/C

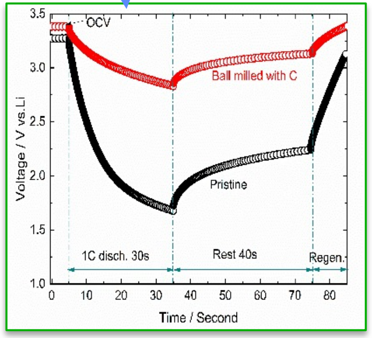
Mortar pestle grinding of AM/C (+ Carbon) + binder

Slurry making *via* homogenizer

Doctor blade coating and drying

Laminate calendering

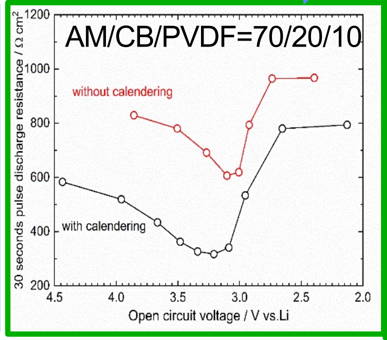


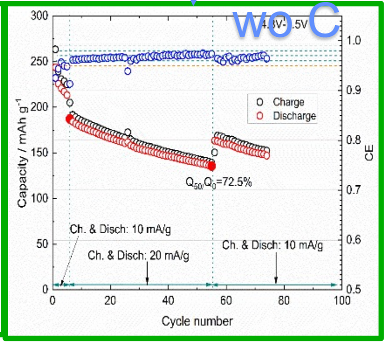


Improves uniformity, breaks down agglomerates

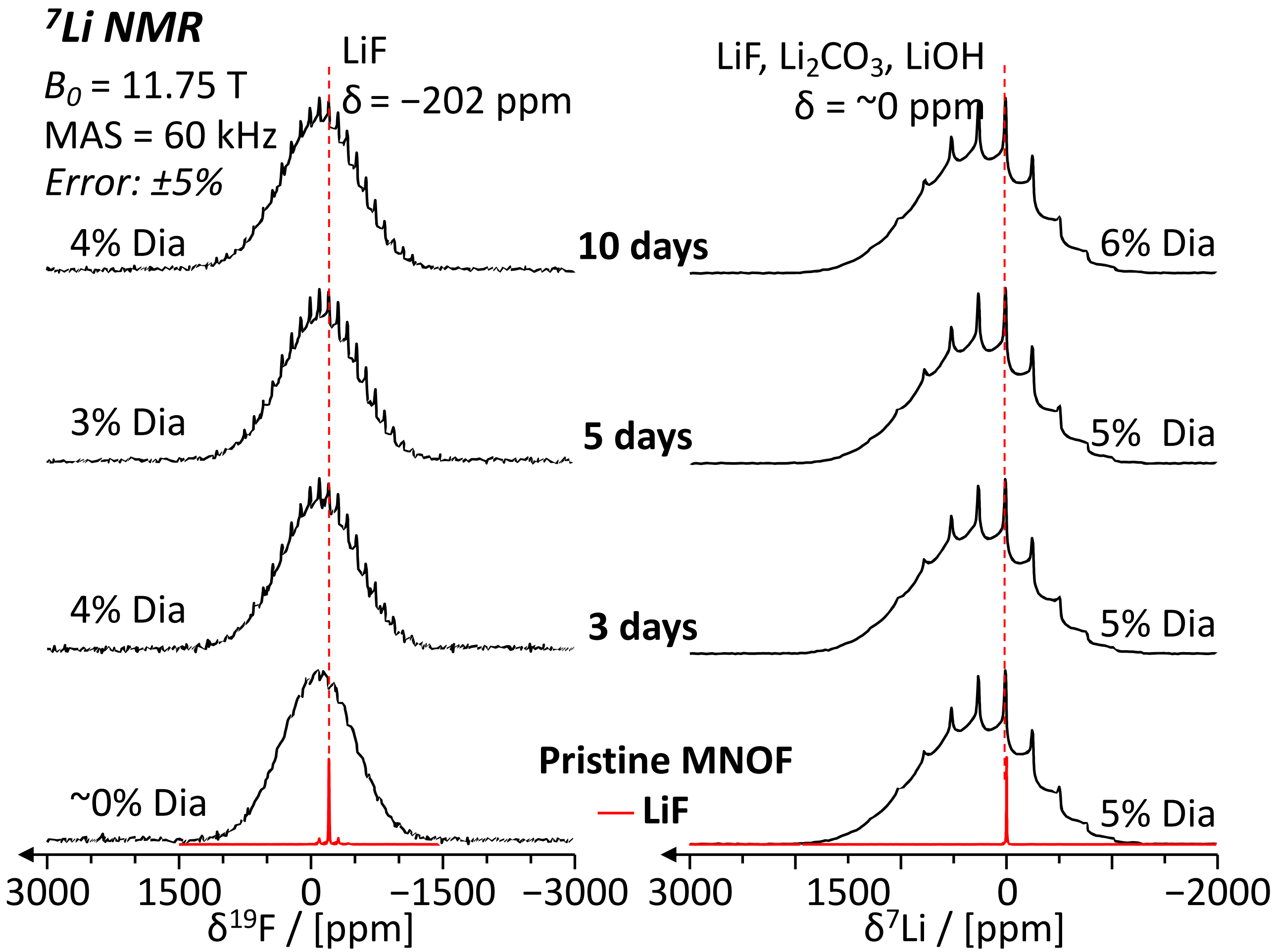
Total weight of solids needed < 1 *gram*

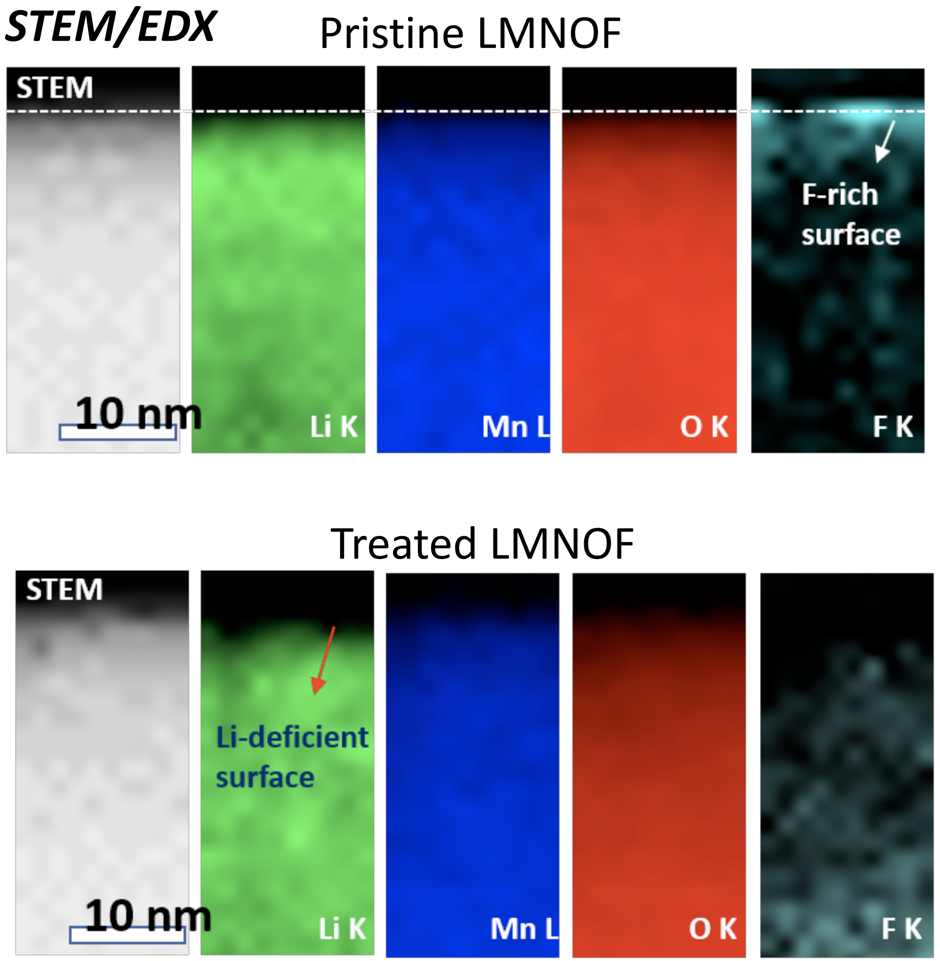
Fast drying, uniform, no cracks





DRX properties before and after surface treatment

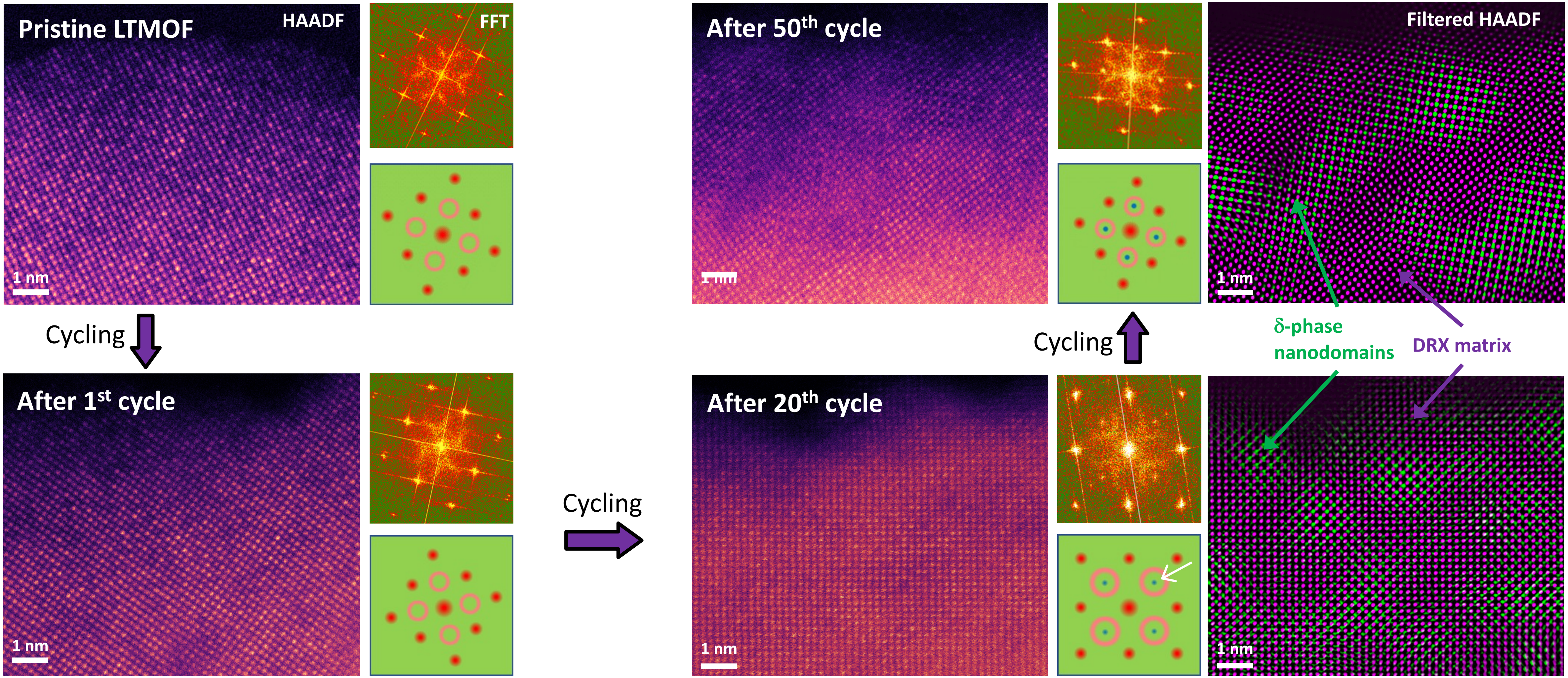




- Bulk DRX structure not impacted by electrolyte soaking
- Slight increase of Li diamagnetic phases with soaking time
- T_1 of diamagnetic ^{7}Li signal increases with soaking time: reduced Mn concentration at surface.

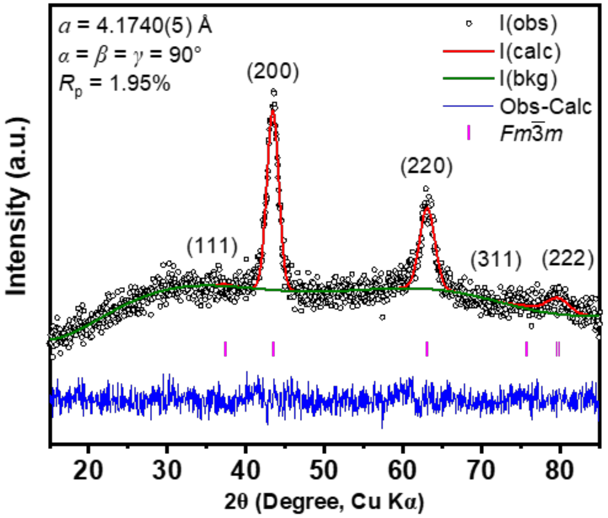
- Surface treatment removes F-rich surface amorphous layer on the pristine, leaving behind Li-depleted crystalline surface.

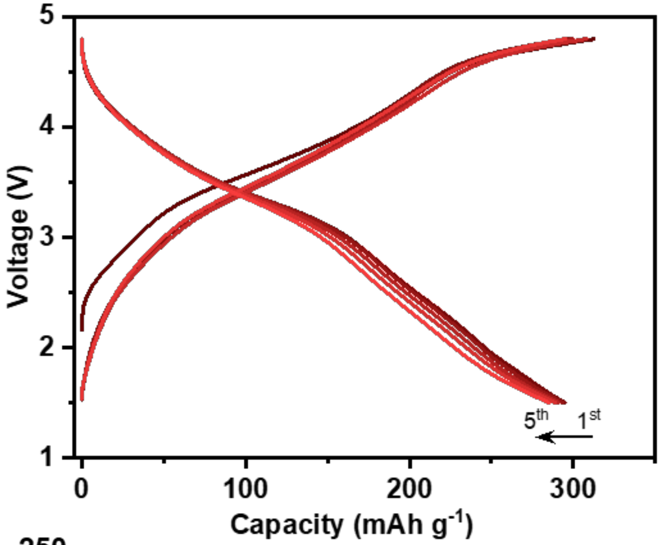
Understanding capacity increase in Mn-rich DRX – Local structure evolution

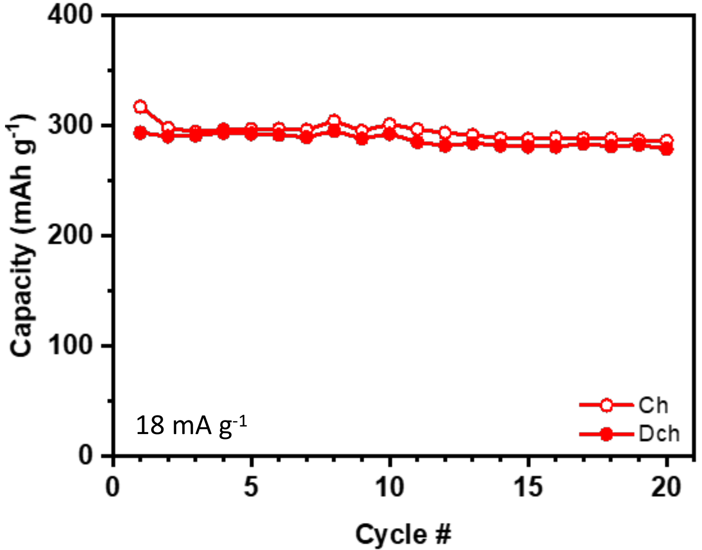


- Cycling leads to continuous growth of δ-phase nanodomains with spinel-like features within the rocksalt DRX matrix

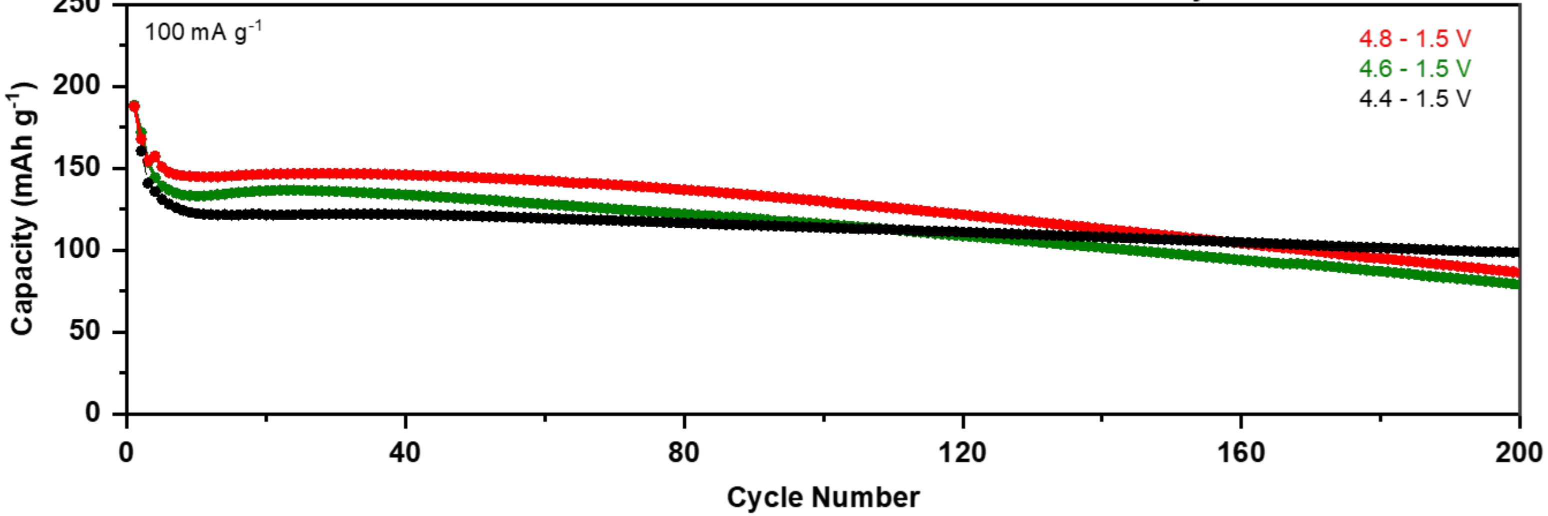
Evaluating $Li_2Mn_{1/2}Ti_{1/2}O_2F$ baseline system







$Li_2Mn_{1/2}Ti_{1/2}O_2F$	Theo. Cap. (mAh g^{-1})
Mn^{2+}/Mn^{4+}	230
1 Li^+	346
All Li^+	461



- Phase pure highly fluorinated Mn^{2+}-Ti^{4+} DRX synthesized by mechanochemical reaction
- Mn^{2+}-Ti^{4+} DRX delivers a high capacity of 300 mAh g^{-1} at a slow rate and stable cycling at 4.4 V charge voltage, but capacity decay observed at increased charging voltages