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

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2020 DOE VTO Annual Merit Review

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Project ID: bat406

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Overview

Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 50%

Budget

- Total project funding
  - FY19 $2.55M
  - FY20 $1.8M
- 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

Relevance/Objectives

- Cathode materials based on cation-disordered Li-excess rocksalts (DRX) can deliver energy densities up to 1000 Wh/Kg.
- DRX structure allows a wide range of chemistry, providing an opportunity to develop Co-free high energy density cathode materials that are alternative to the traditional layered NMC-type cathodes.
- Fundamental understandings on what controls DRX performance characteristics, particularly rate capability, cycling stability and voltage slope, are key to enabling rational decisions on further development and commercial viability of this newer class of cathode materials.

Milestones

Date	Milestones	Status
December 2019	Electrochemical evaluation of surface processes in DRX	Completed
March 2020	Original milestone on “DRX synthesis scale-up to 50 g” replaced by “Evaluate F-solubility limit in DRX materials” (see explanation on slide 16)	Completed
June 2020	Pouch cell evaluation on power density of at least 2 DRX compositions	On schedule
September 2020	Determine key barriers in rate capability and deliver insights on mitigation	On schedule

Approach/Strategy

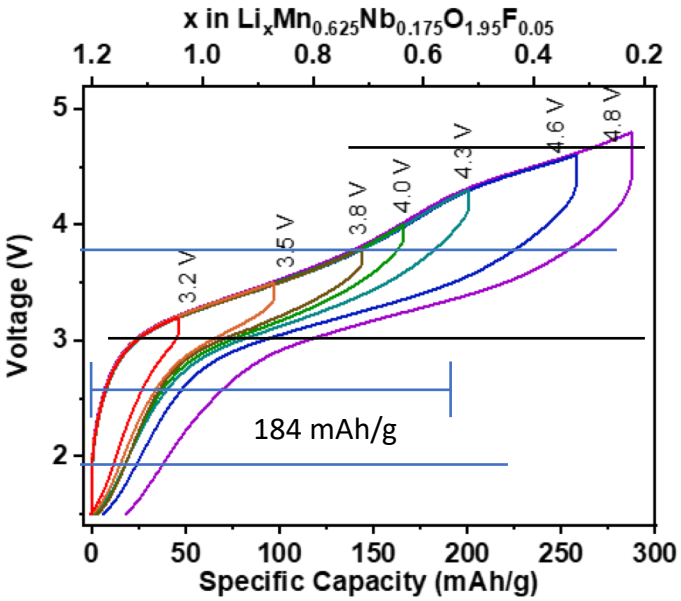
- Focus on three fluorinated DRX (F-DRX) baseline systems and their analogues: $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF), $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$(LNTMOF) and $Li_2Mn_{1/2}Ti_{1/2}O_2F$.
- Explore synthesis conditions to prepare DRX materials with optimized performance. 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.

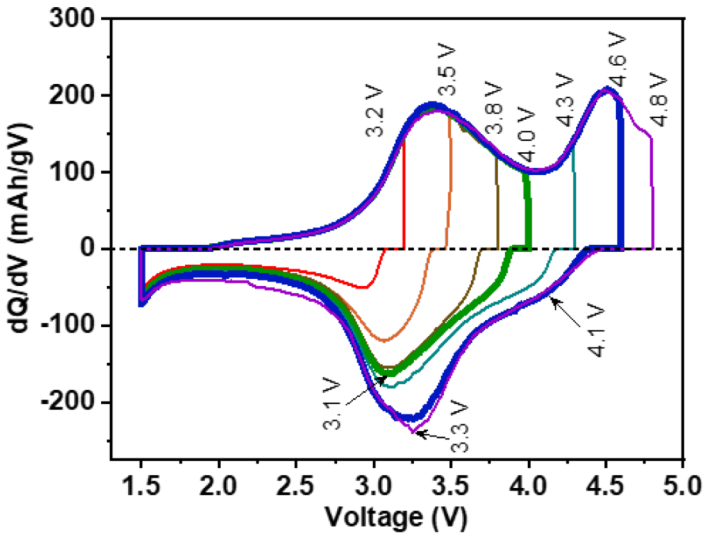
Technical Accomplishments: DRX redox activities defined

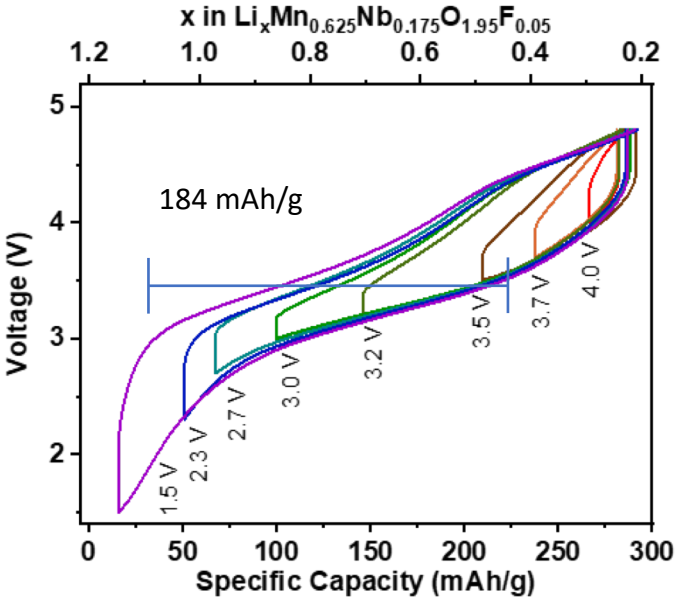
$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF)

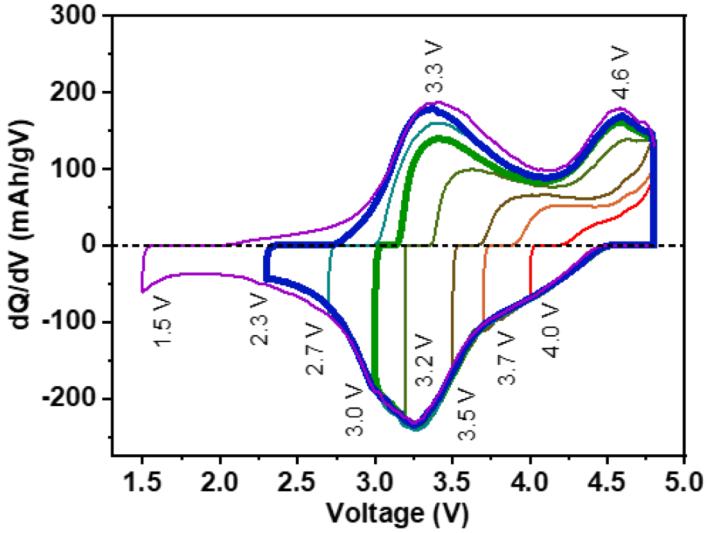
LMNOF	Theo. Cap. (mAh/g)
Mn^{3+}/Mn^{4+}	184
1 Li^{+}	294
1.2 Li^{+}	353

- Behavior of redox couples evaluated by systematically varying charge and discharge voltage window
- Mn and O redox active regimes identified





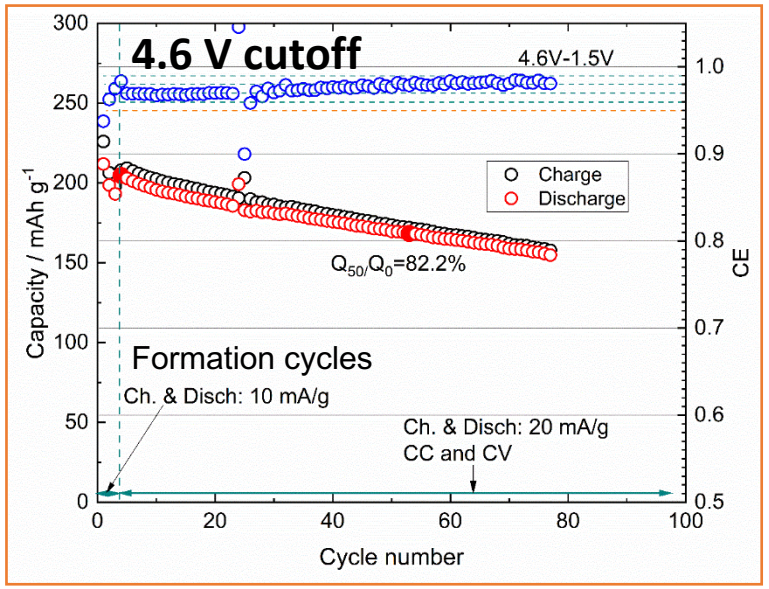


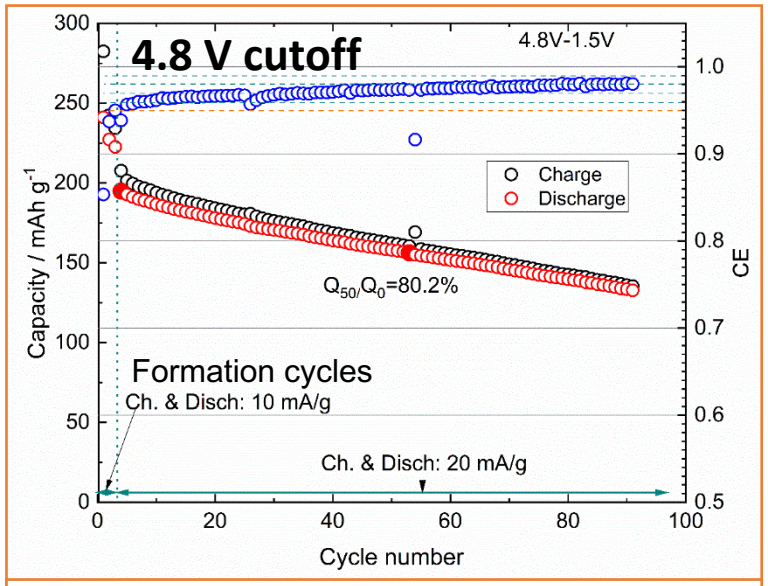


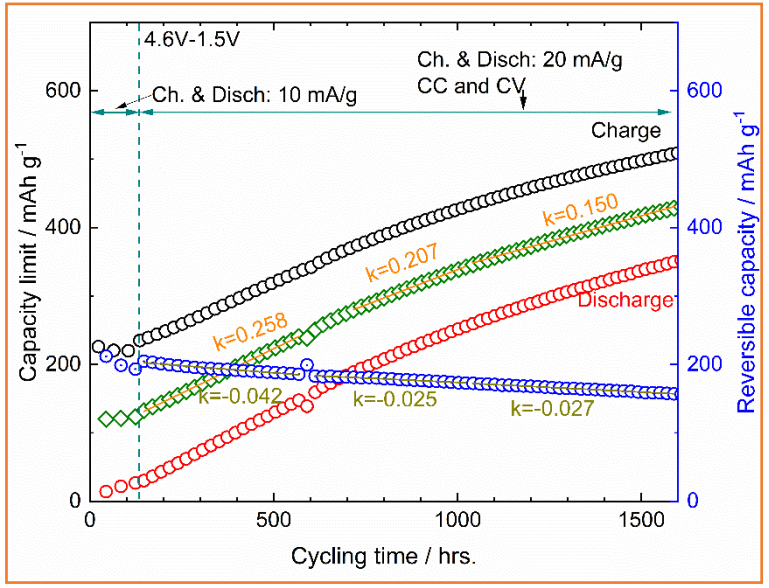
High-voltage cycling reduces stability

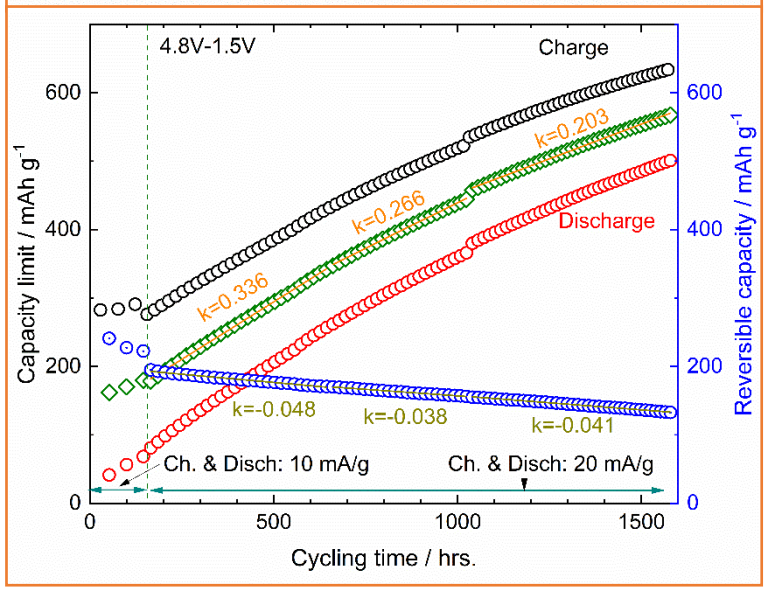
LMNOF Metrics	4.6 V Cutoff	4.8 V Cutoff
Discharge capacity (C/10) after formation (mAh/g)	208	192
Capacity retention 50th cycle (%)	82	80
Capacity fade rate 50th cycle (%/cycle)	0.27	0.41
Avg. side-reaction rate 50th cycle (mAh/g/h)	0.150	0.203
Coulombic efficiency 50th cycle	0.985	0.979

- After initial formation cycles, cycling at an upper cutoff voltage of 4.6 V delivers better long-term stability than 4.8 V.
- Subgroup formed to investigate electrolyte breakdown contribution to capacity fade at high voltages.

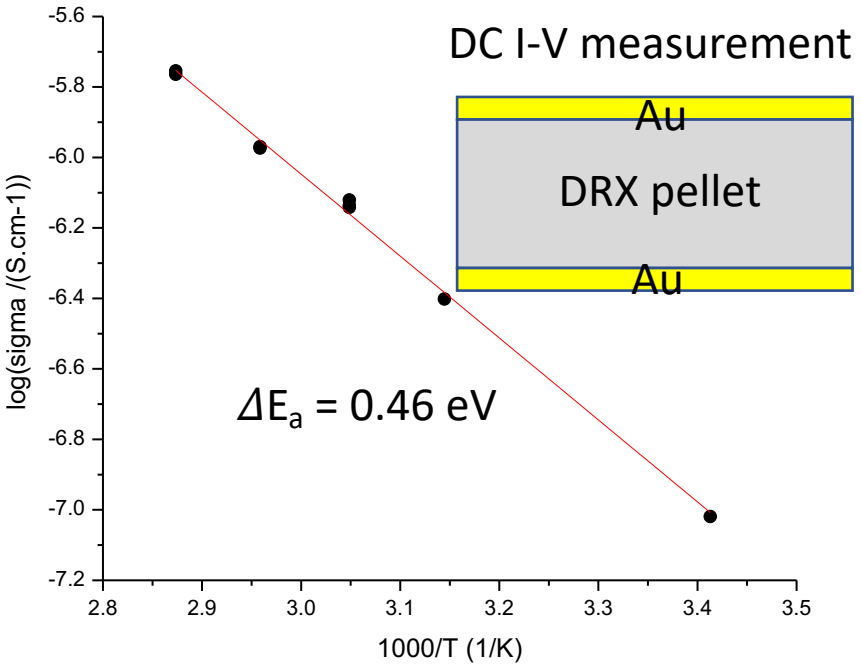


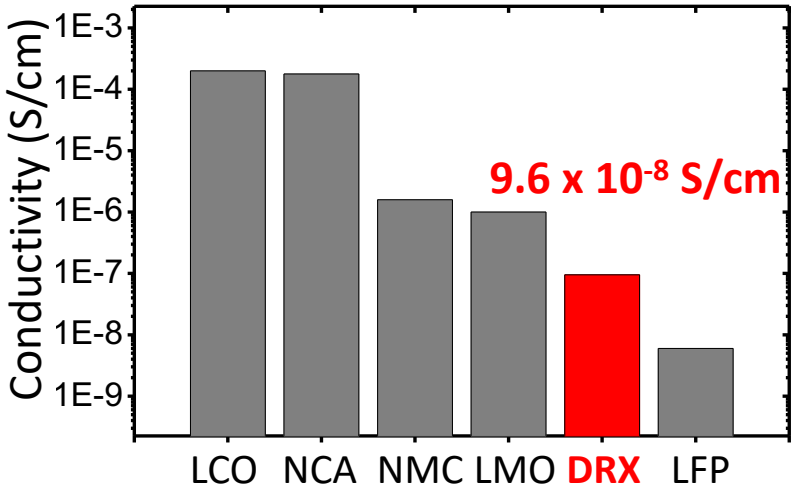


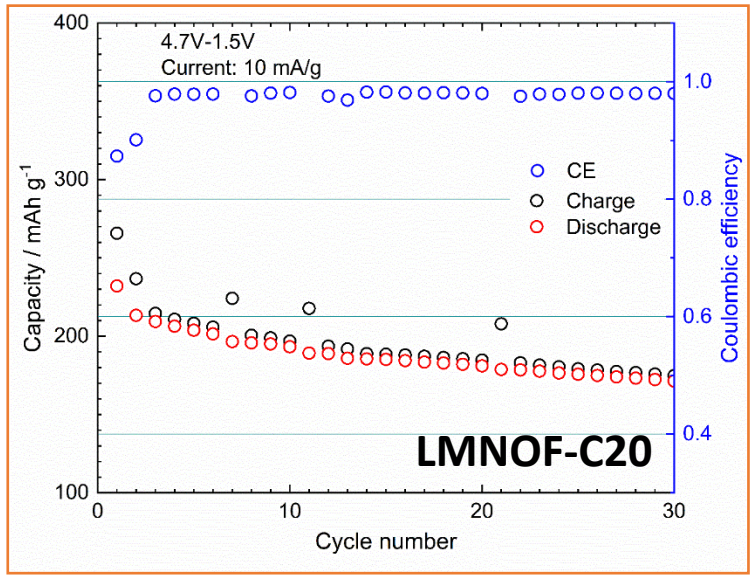


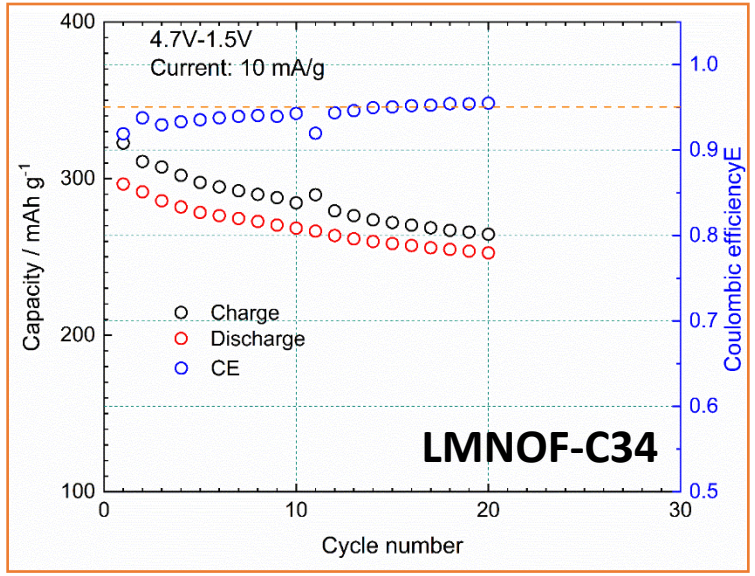


Low electronic conductivity mitigated by carbon additives





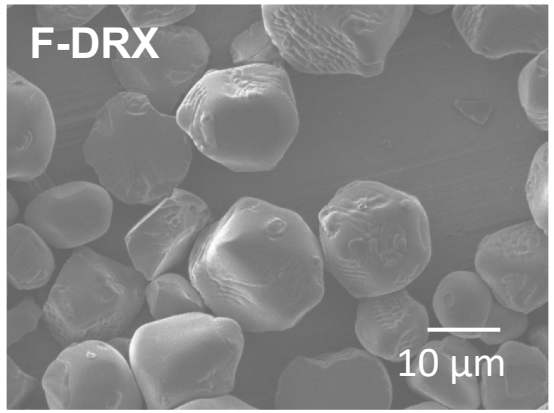




- DRX has a bulk electronic conductivity of about 10^{-7} S/cm, lower than that of layered oxides but about one order of magnitude higher than LFP.
- Electrodes formulated by changing carbon content, with active material/carbon black/binder ratio of
  - 70/20/10 in *LMNOF-C20*
  - 56/34/10 in *LMNOF-C34*
- Increasing carbon content leads to less impedance and higher capacity.

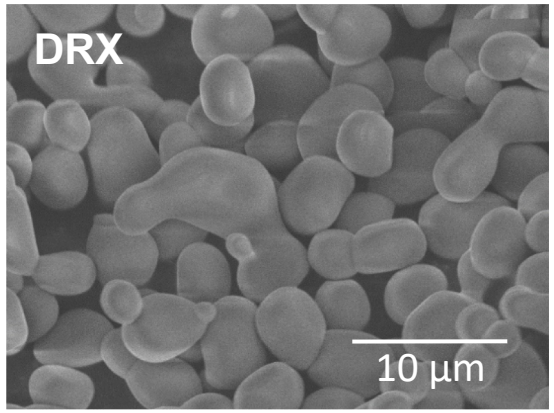
Model system for understanding DRX behavior

$Li_{1.4}Mn_{0.4}Ti_{0.2}O_{1.4}F_{0.6}$
($Li_{1.4}M_{0.4}TOF$, Li/Mn=3.5)



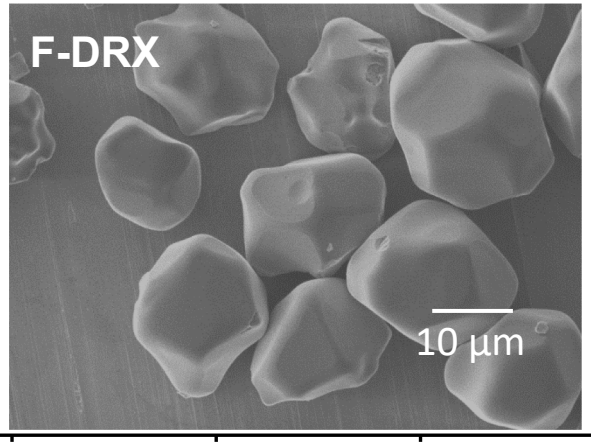
Increase Li/Mn ratio

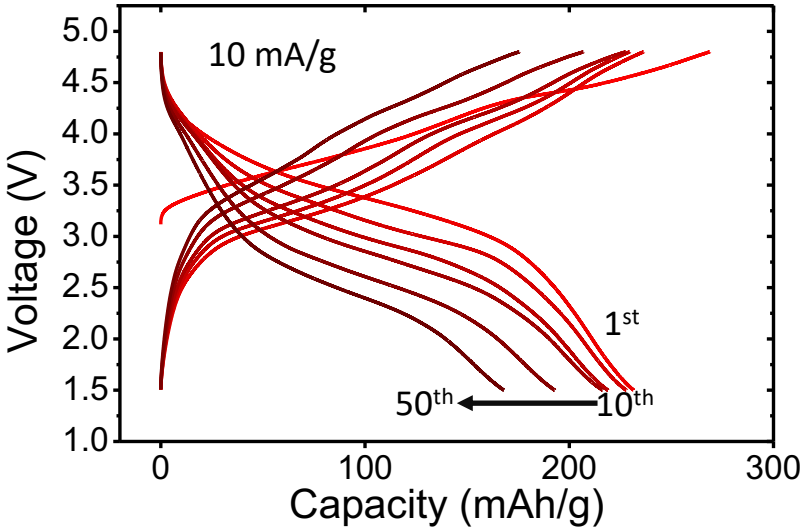
$Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$
($L_{1.2}M_{0.4}TO$, Li/Mn=3.0)

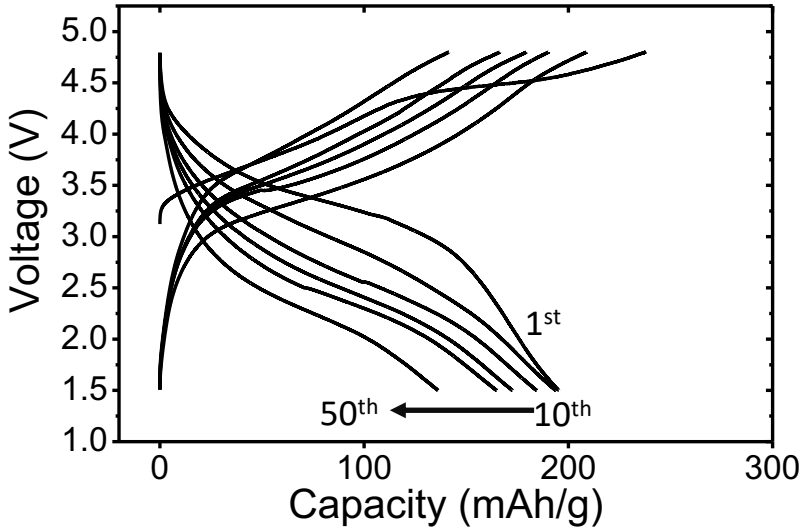


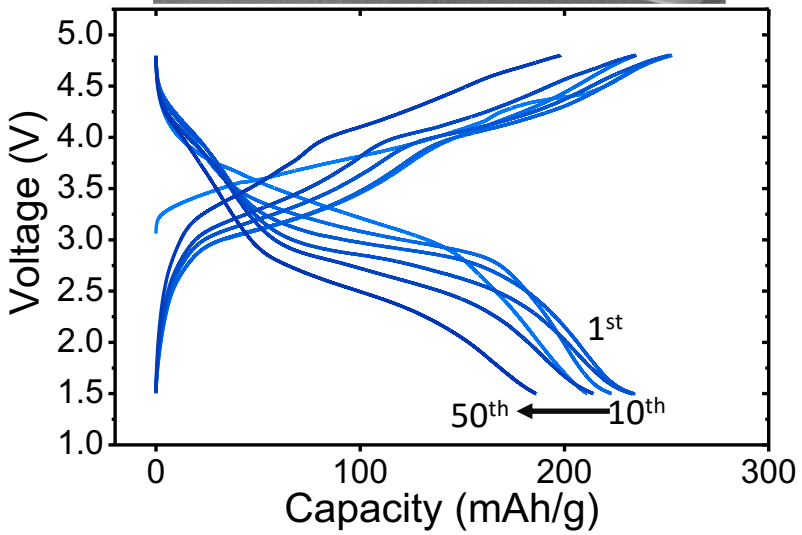
Reduce Li/Mn ratio

$Li_{1.2}Mn_{0.6}Ti_{0.2}O_{1.8}F_{0.2}$
($Li_{1.2}M_{0.6}TOF$, Li/Mn=2.0)





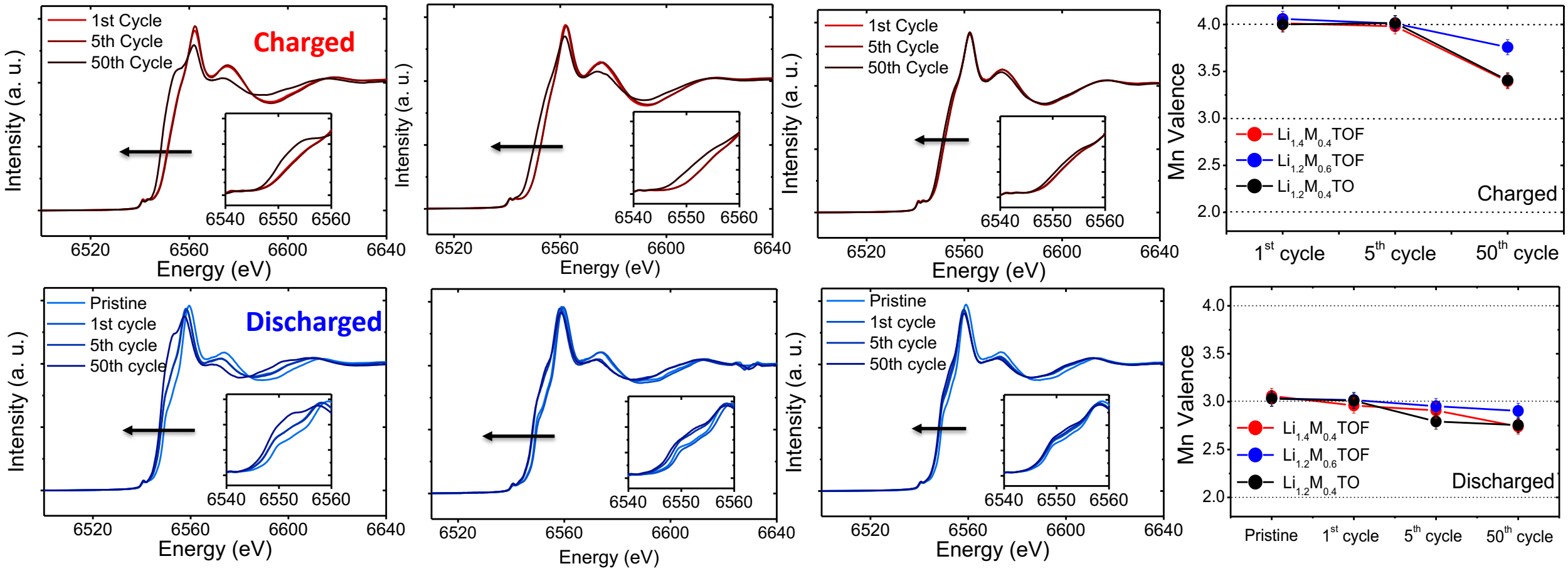




- Synthesis method developed to prepare a library of well-formed Li-Mn-Ti-O-F (LMTOF, an analogue of LMNOF baseline) crystal samples with various physical properties
- Fluorine substitution in DRX (F-DRX) and lower Li/Mn ratio improve cycling stability

Chemical changes with cycling

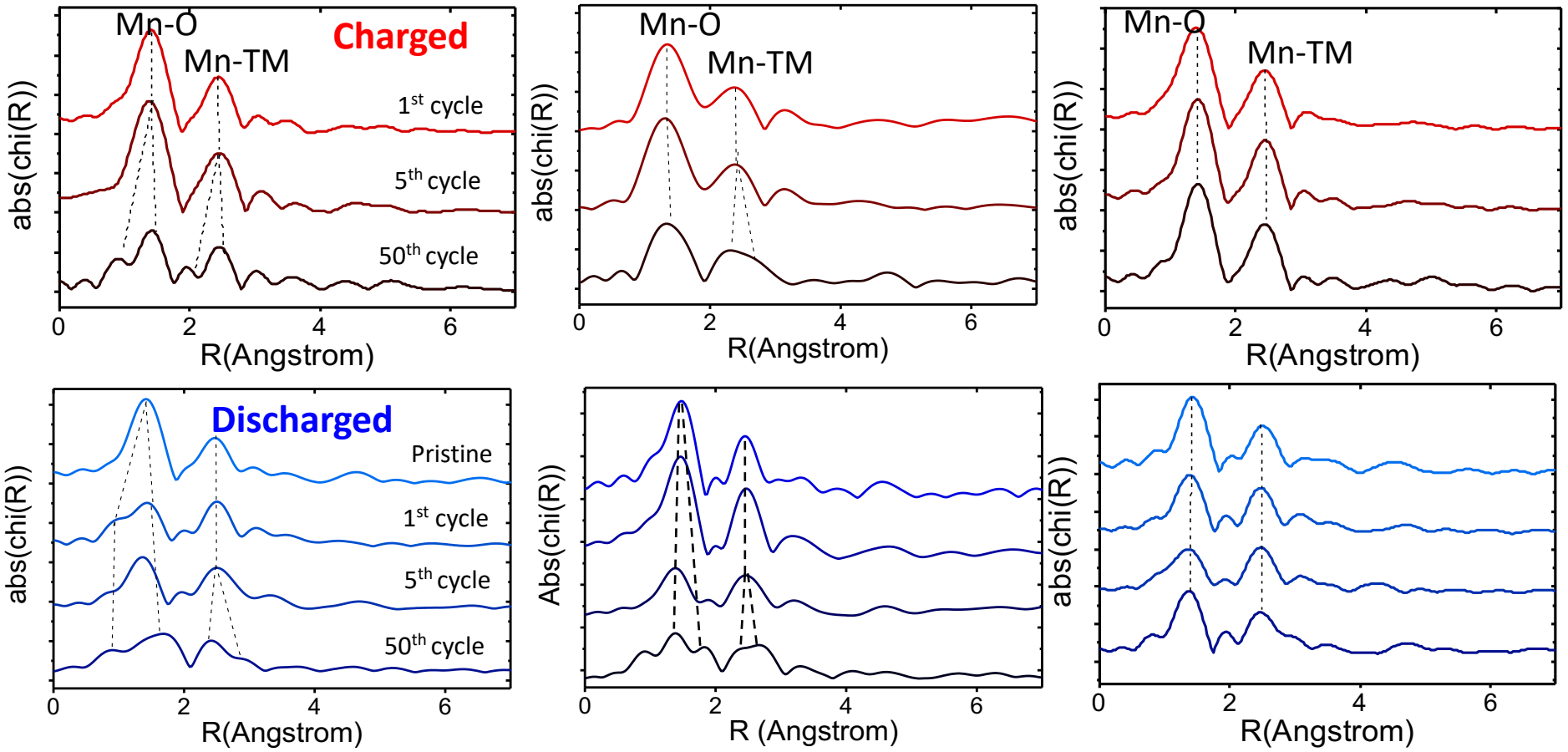
$Li_{1.4}M_{0.4}TOF$ (3.5) **$Li_{1.2}M_{0.4}TO$ (3.0)** **$Li_{1.2}M_{0.6}TOF$ (2.0)** *XANES (SSRL Beamline 2-2)*

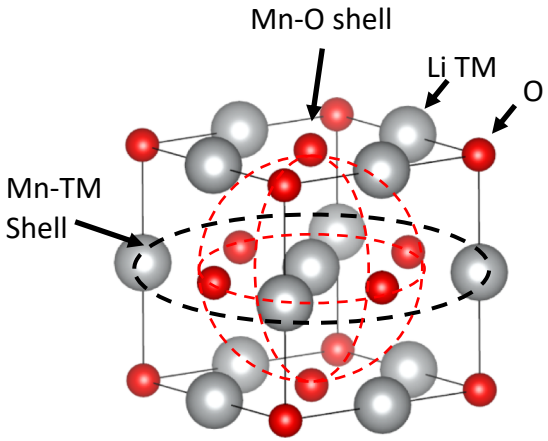


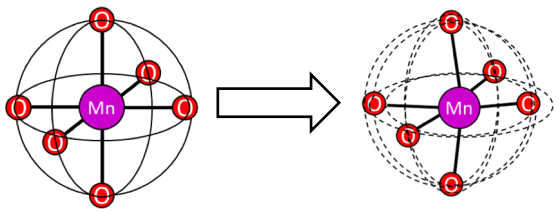
- Cycling-induced bulk Mn reduction observed, with extent of Mn reduction directly correlated to cycling stability
- Chemical changes less severe in F-DRX with lower Li/Mn ratio

Cycling-induced changes in Mn coordination environment

$Li_{1.4}M_{0.4}TOF$ (3.5) **$Li_{1.2}M_{0.4}TO$ (3.0)** **$Li_{1.2}M_{0.6}TOF$ (2.0)** *EXAFS (SSRL Beamline 2-2)*



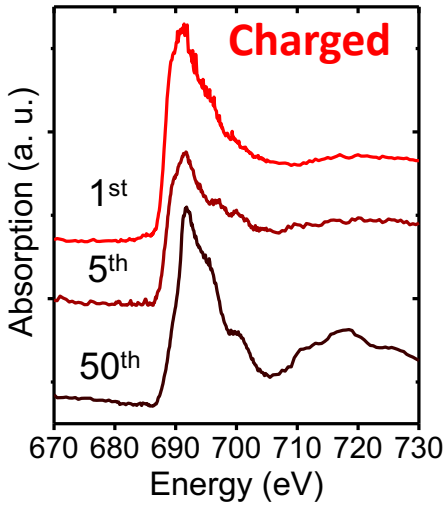




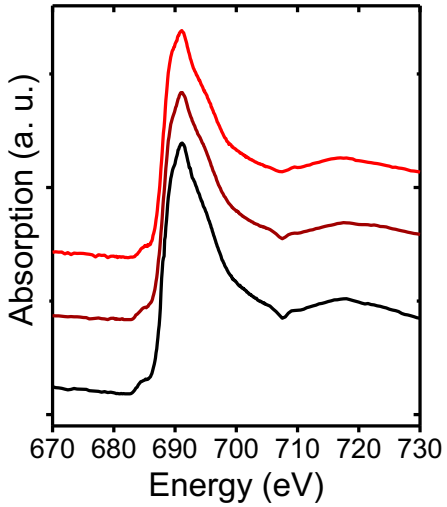
- Cycling leads to changes in Mn coordination environment but least severe on F-DRX with lower Li/Mn ratio

Cycling-induced changes in surface F chemical environment

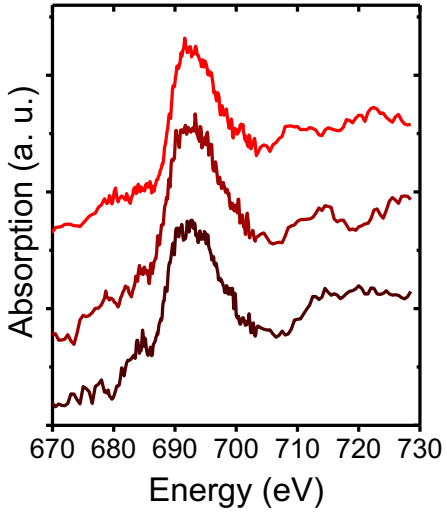
$LiPF_6$ electrolyte/PVDF



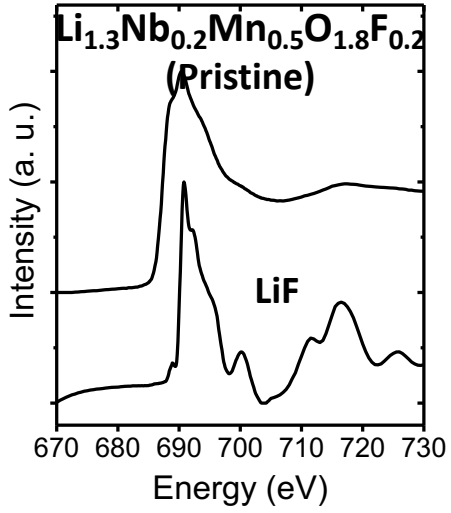
$LiClO_4$ electrolyte/PVDF

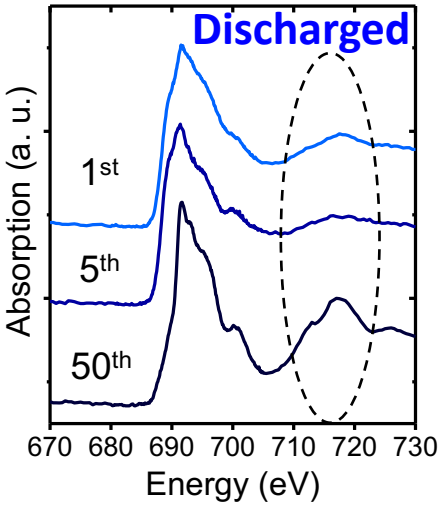


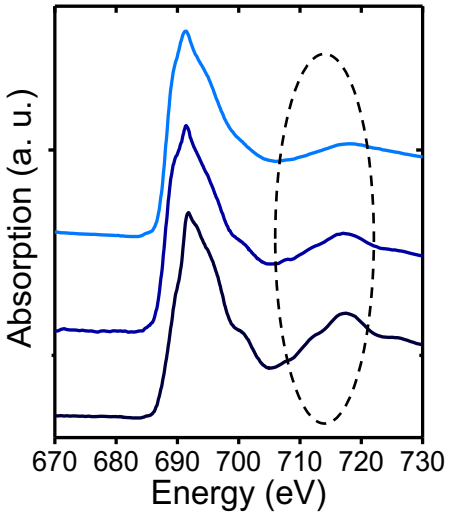
$LiClO_4$ electrolyte/no binder

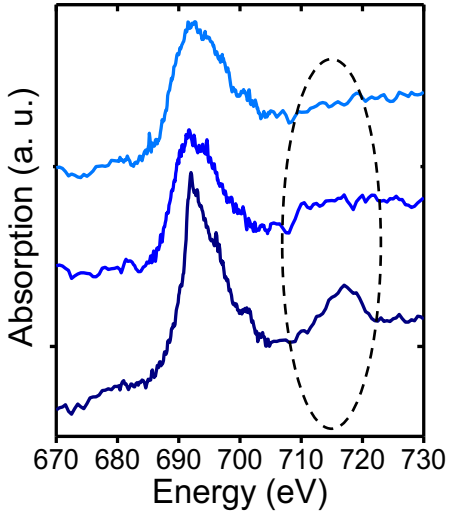


TEY sXAS (SSRL BL 8-2)









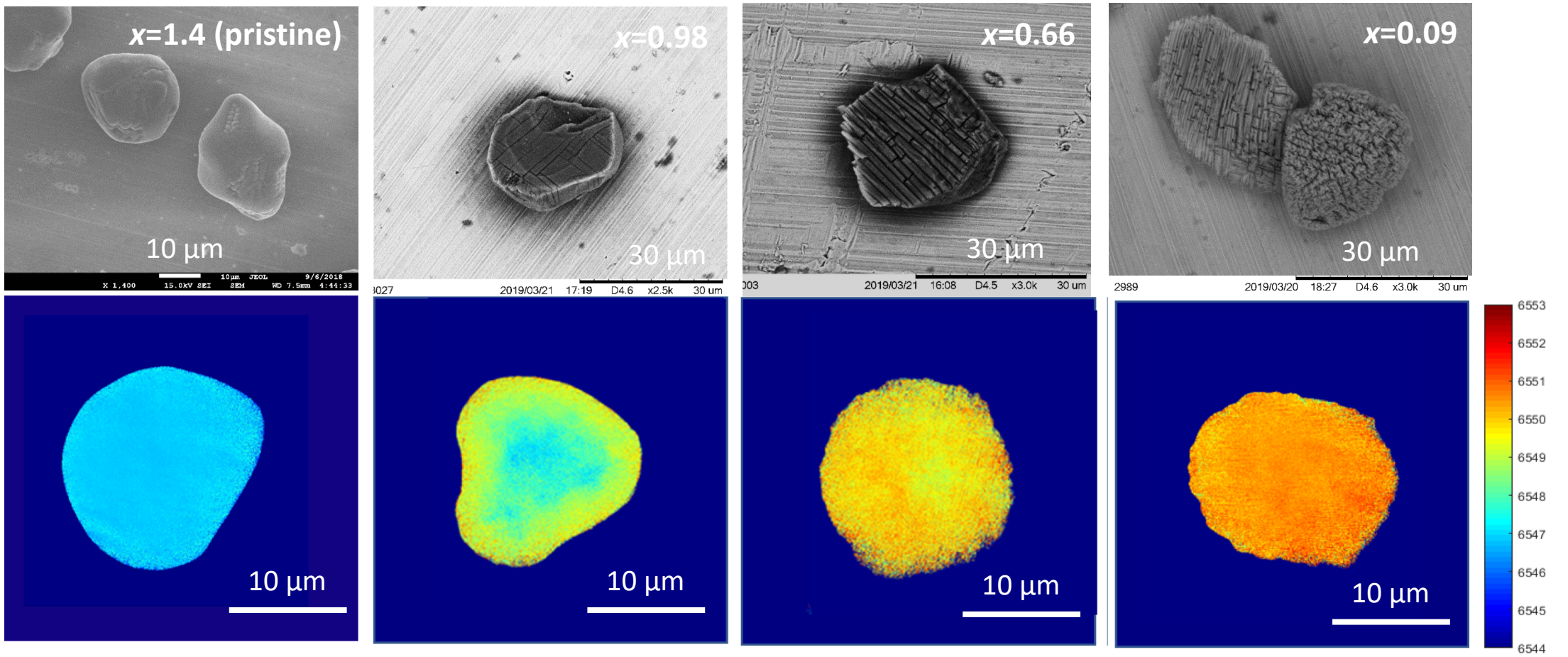
- By comparing electrodes made with and without F-containing binders as well as cycling in both $LiPF_6$ and $LiClO_4$ electrolytes, changes in F intrinsic to DRX confirmed.
- Cycling leads to increase in ionic characteristics of surface F in DRX, with chemical environment resembling that of LiF

Chemo-mechanical behavior in DRX

$Li_xMn_{0.4}Ti_{0.2}O_{1.4}F_{0.6}$ ($Li_xM_{0.4}TOF$) single particles

SEM

2D XANES chemical mapping (SSRL BL 6-2c)

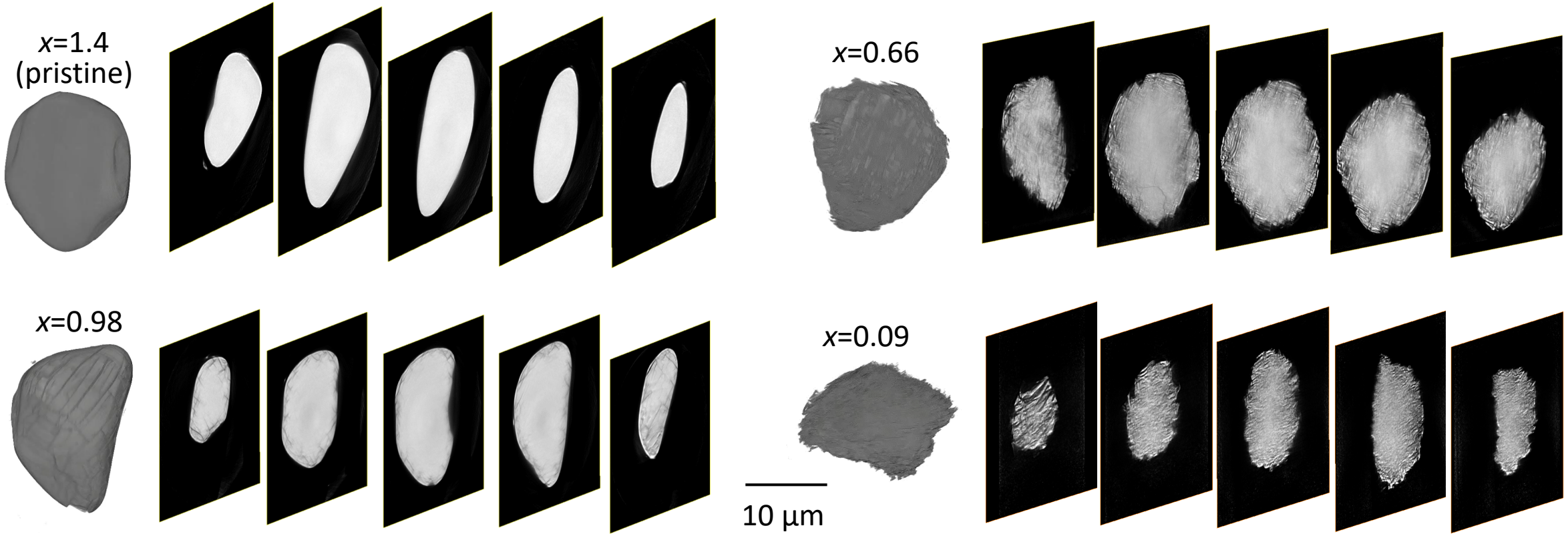


Mn E_0 energy

- Evolution in particle-level chemical and mechanical properties revealed in studies carried out on large crystals
- Redox processes inhomogeneous in large grains.

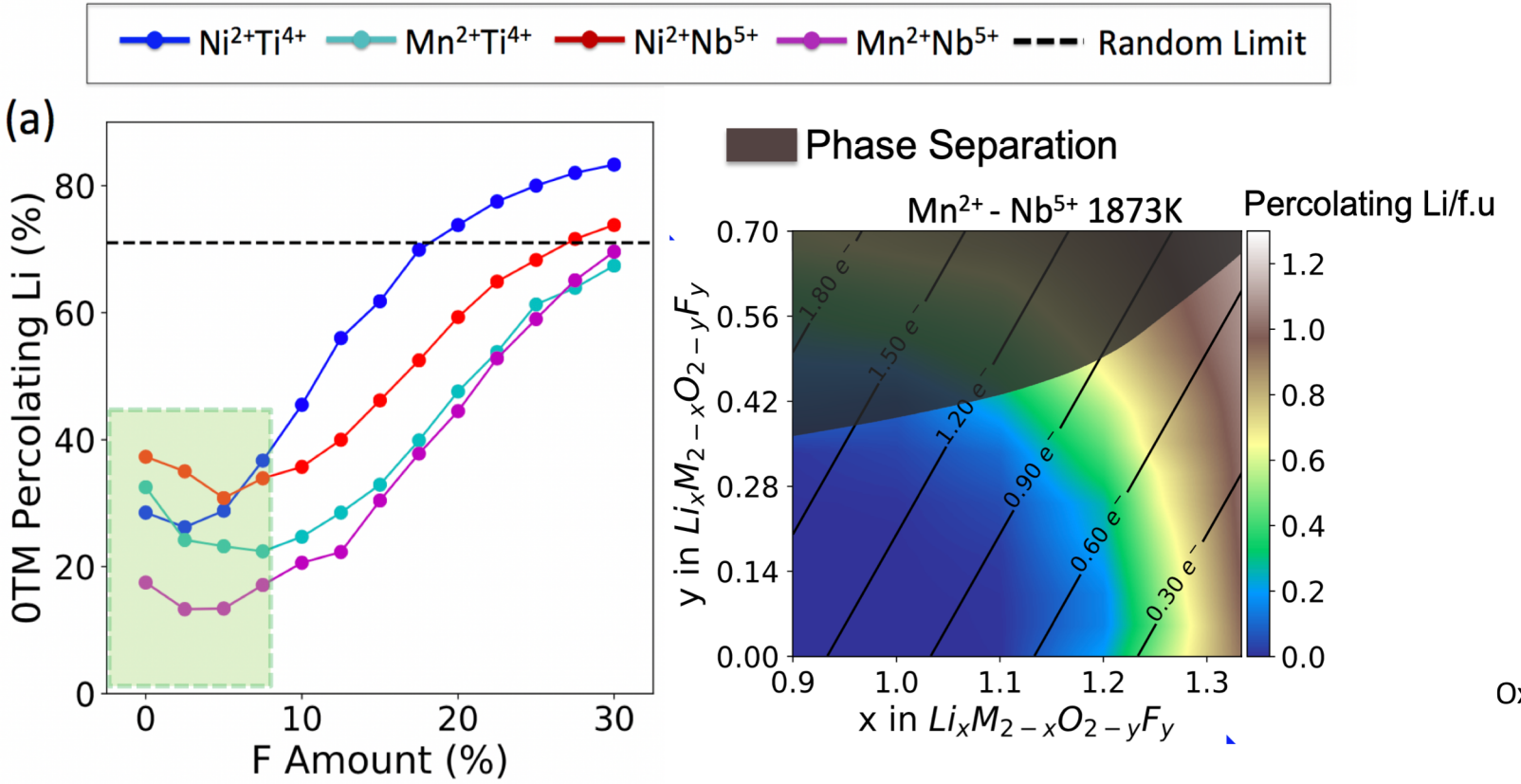
Single-particle tomography reveals morphological evolution

Computed tomography (CT) of $Li_xM_{0.4}TOF$ single particles (SSRL BL 6-2c)



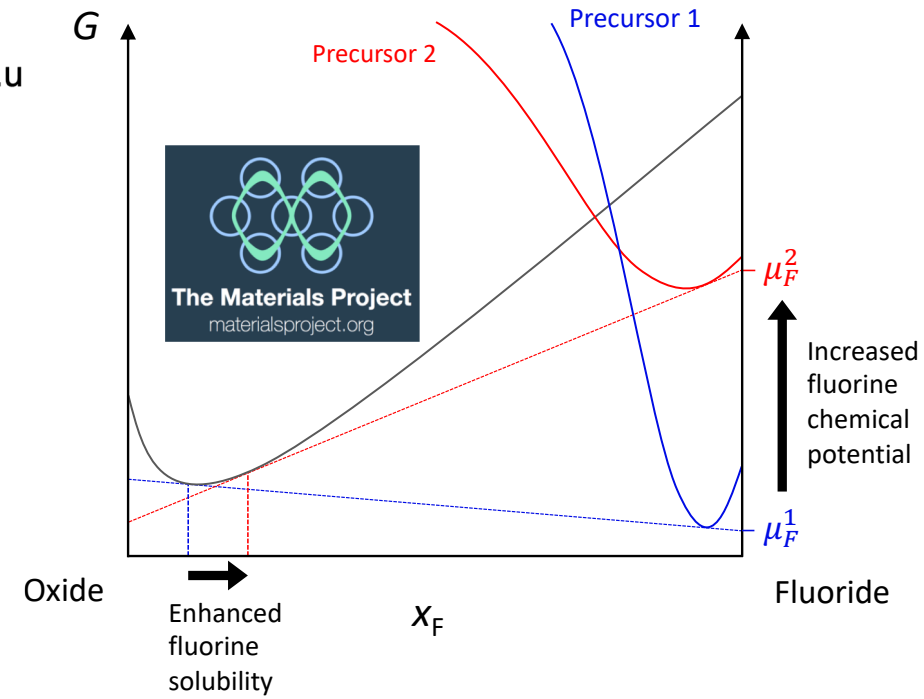
- Nano-CT allows for non-destructive evaluation of microstructures at the particle-level
- Particle cracking appears along (001) direction and progresses from the surface towards the bulk with increasing level of delithiation in F-DRX

DRX improvement strategy – high F and low Li/TM ratio



$Li_{1.2}(M, M')_{0.8}O_{2-y}F_y$

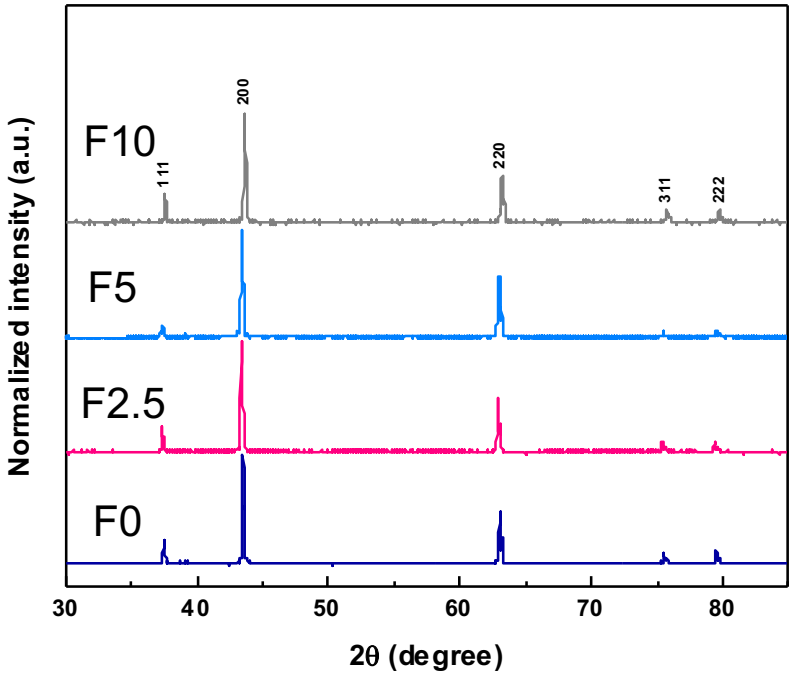
Ouyang et al., *Adv. Energy. Mat.* (2020)

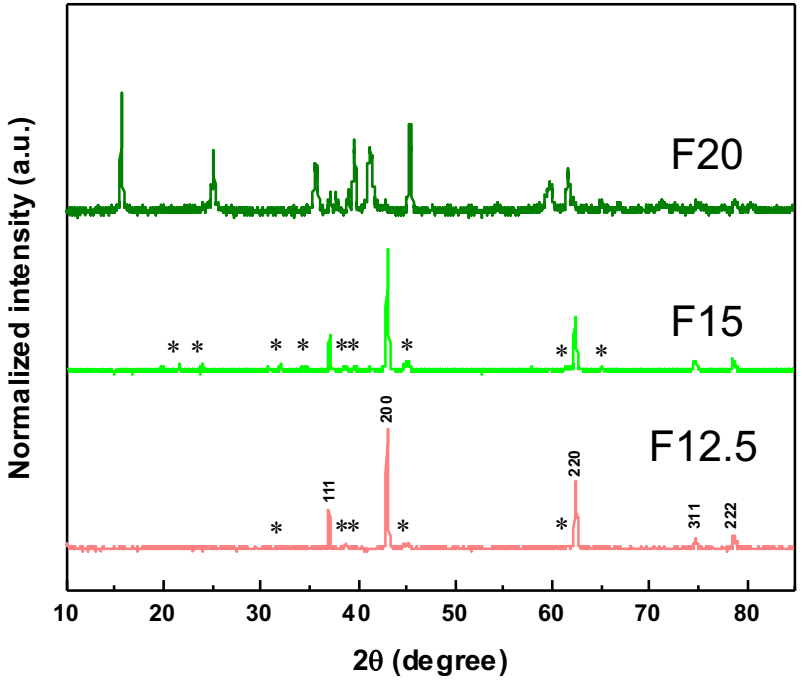


- Theory indicates better Li-transport and cyclability with higher level of fluorination in DRX
- F solubility can be tuned by modifying competing phases present in the system
- Precursors with higher F chemical potential (μ_F) than currently used LiF desirable in achieving higher F solubility limit

Synthesis approach to increase F content in DRX developed

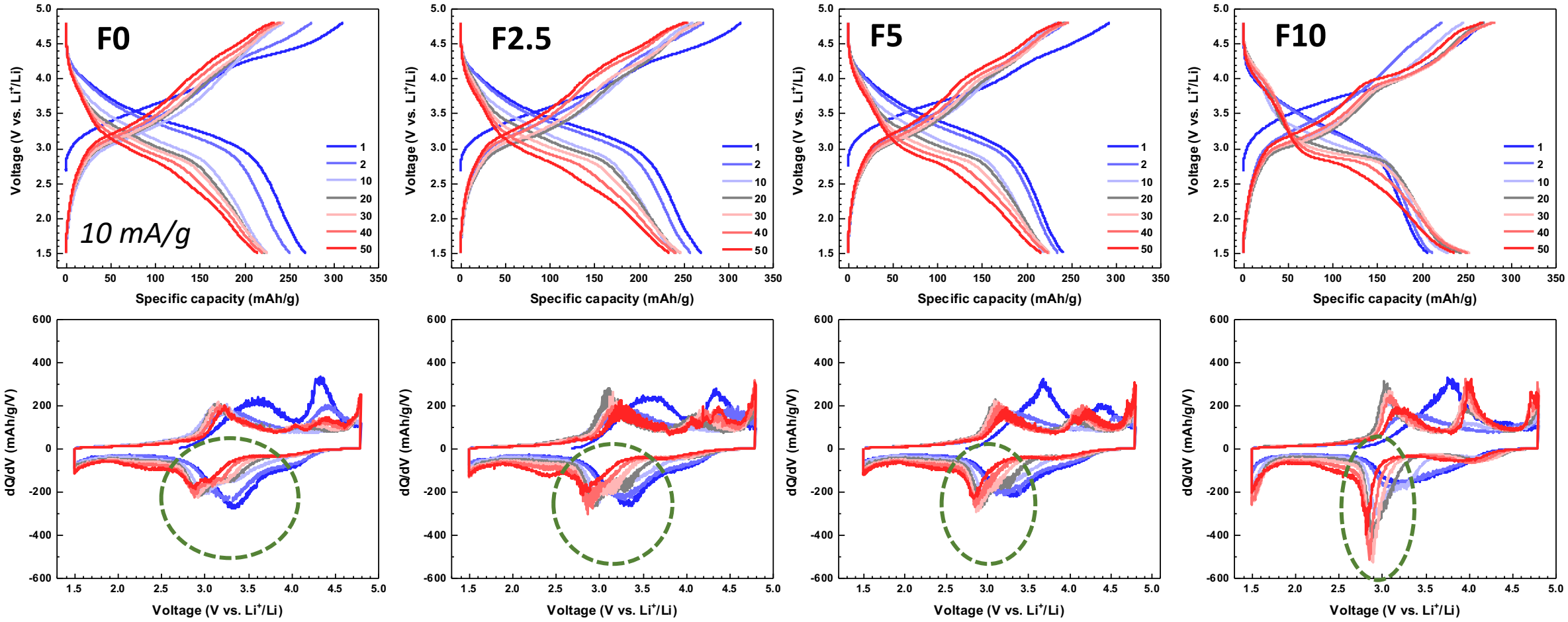
Label (Li/ Mn ratio)	Targeted Composition
F0 (2.0)	$Li_{1.2}Mn_{0.6}Nb_{0.2}O_2$
F2.5 (1.9)	$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
F5 (1.85)	$Li_{1.2}Mn_{0.65}Nb_{0.15}O_{1.9}F_{0.1}$
F10 (1.7)	$Li_{1.2}Mn_{0.7}Nb_{0.1}O_{1.8}F_{0.2}$
F12.5 (1.65)	$Li_{1.2}Mn_{0.725}Nb_{0.075}O_{1.75}F_{0.25}$
F15 (1.6)	$Li_{1.2}Mn_{0.75}Nb_{0.05}O_{1.7}F_{0.3}$
F20 (1.5)	$Li_{1.2}Mn_{0.8}O_{1.6}F_{0.4}$





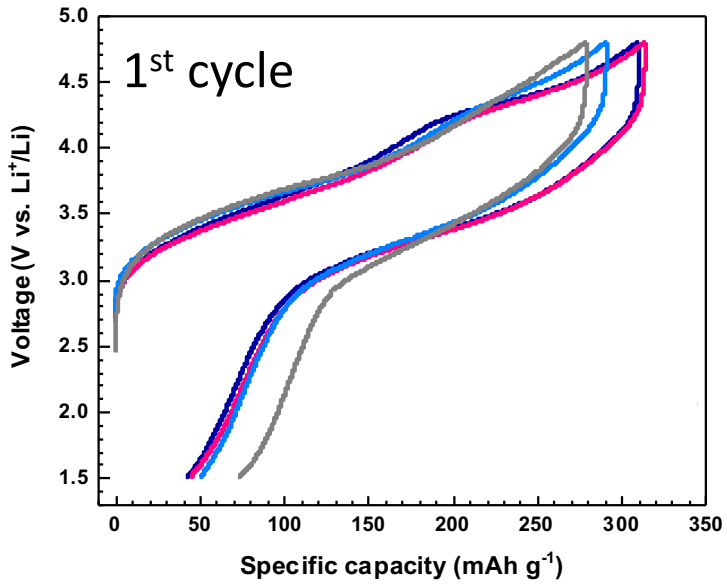
- Considering the important role of F in DRX, management decision was made to shift the synthesis focus to maximize F solubility in DRX. The original milestone on “DRX synthesis scale-up to 50 g” (due in March 2020) was accordingly replaced by “Evaluate F-solubility limit in DRX materials”.
- New synthesis route developed – a fluoropolymer polytetrafluoroethylene (PTFE) was used to replace LiF as F precursor.
- Phase pure rocksalt F-DRX obtained up to 10 at.% of F in the LMNOF system.
- Impurities detected on XRD upon further increasing F content to 12.5 at.%, notably LiF.

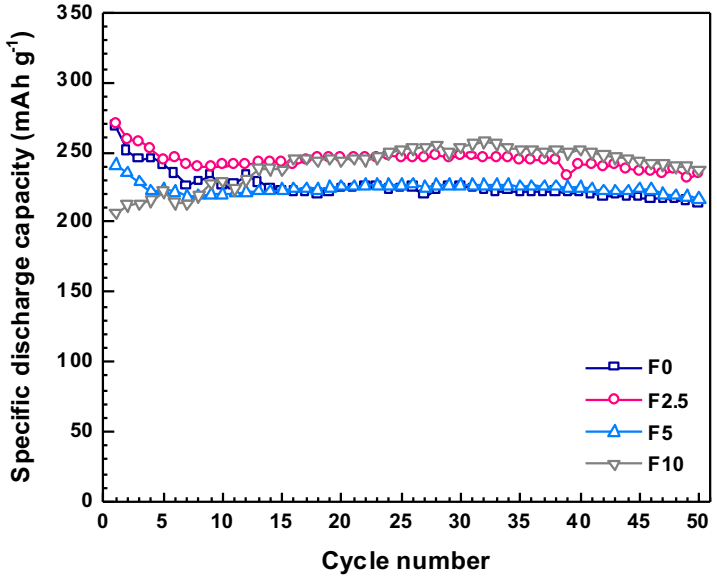
Effect of F content – electrochemical performance

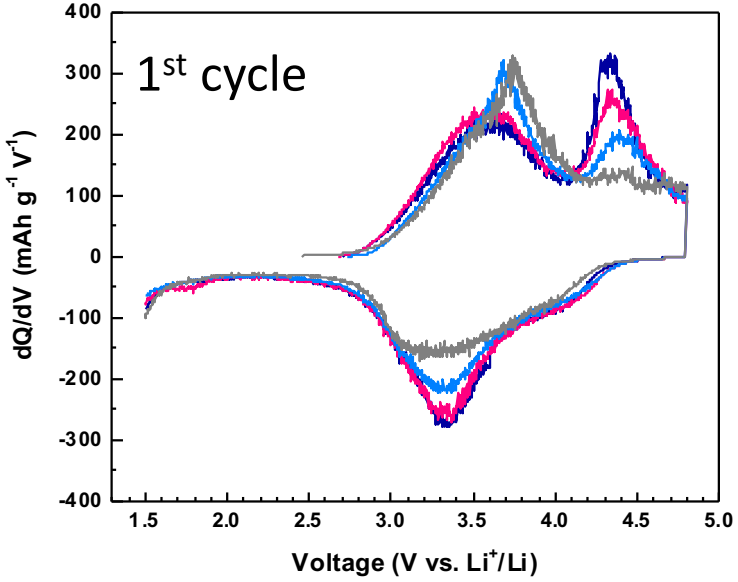


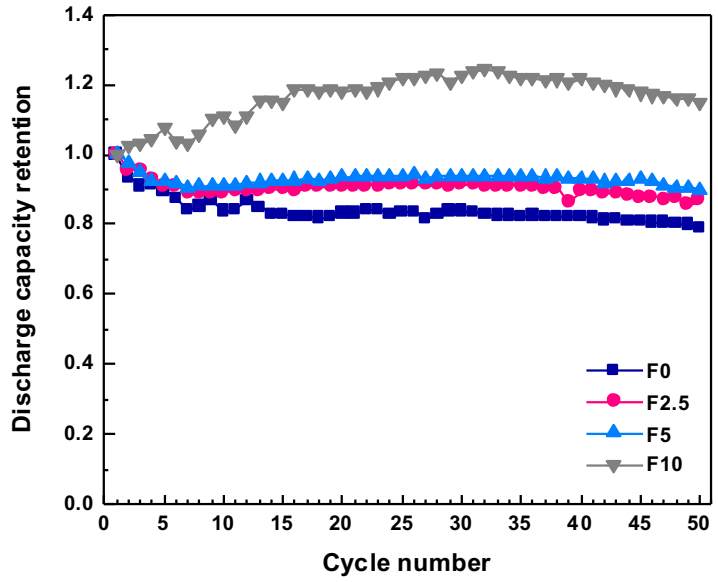
- Capacity fade observed upon long-term cycling but less severe with increasing F substitution in DRX
- Increase in F content leads to more defined and more reversible redox features after initial cycling

Cycling stability improves with increasing F content



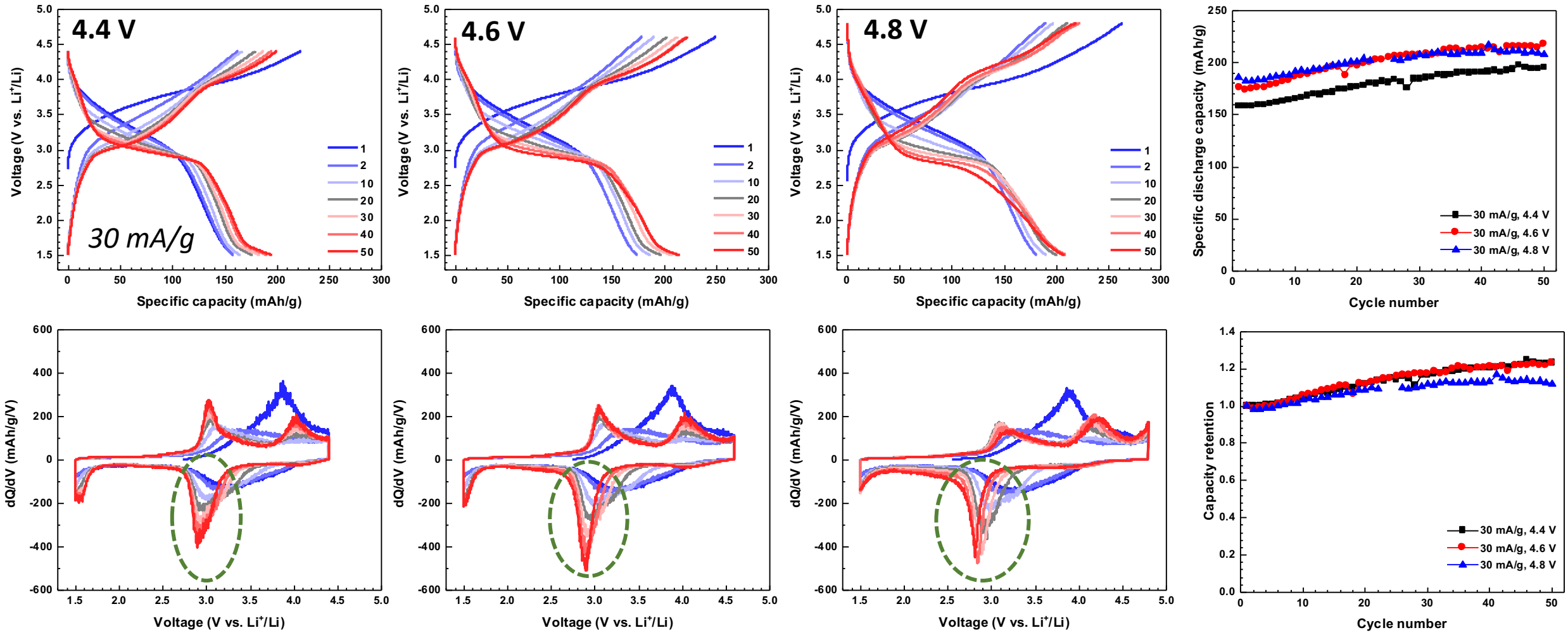






- Cycling stability follows the trend of increase in F content
- F10 with a low Li/Mn ratio of 1.7 showed the unique feature of capacity increase with cycling
- F10 delivered the best performance with improved stability, capable of continuous cycling with > 200 mAh/g of discharge capacity

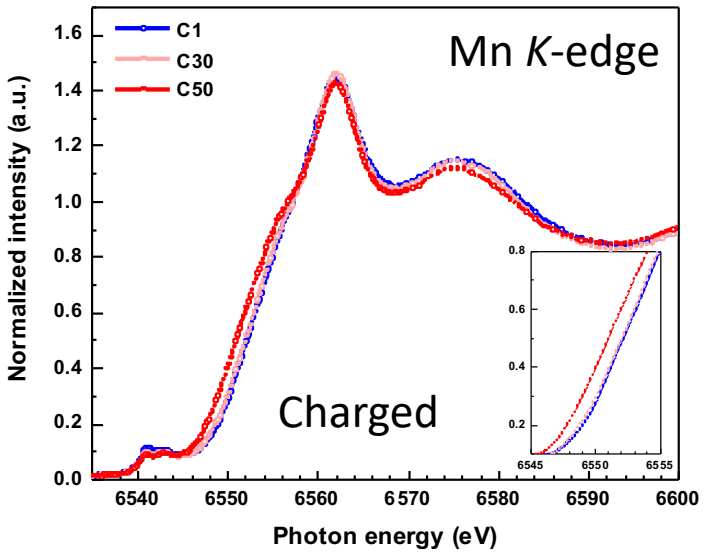
F10 DRX – more stable high-voltage cycling

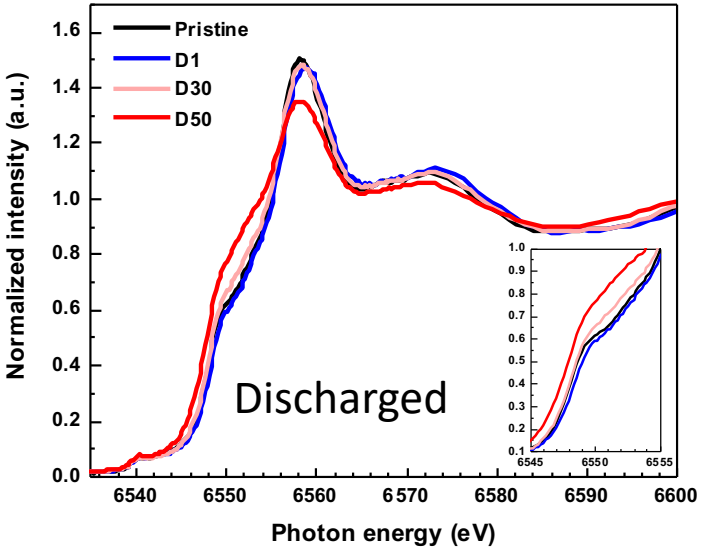


- Cycling stability of F10 DRX decreases with increasing upper cutoff voltage but less severe compared to DRX with lower F content
- Balanced capacity and stability achieved by cycling to a cutoff voltage of 4.6 V

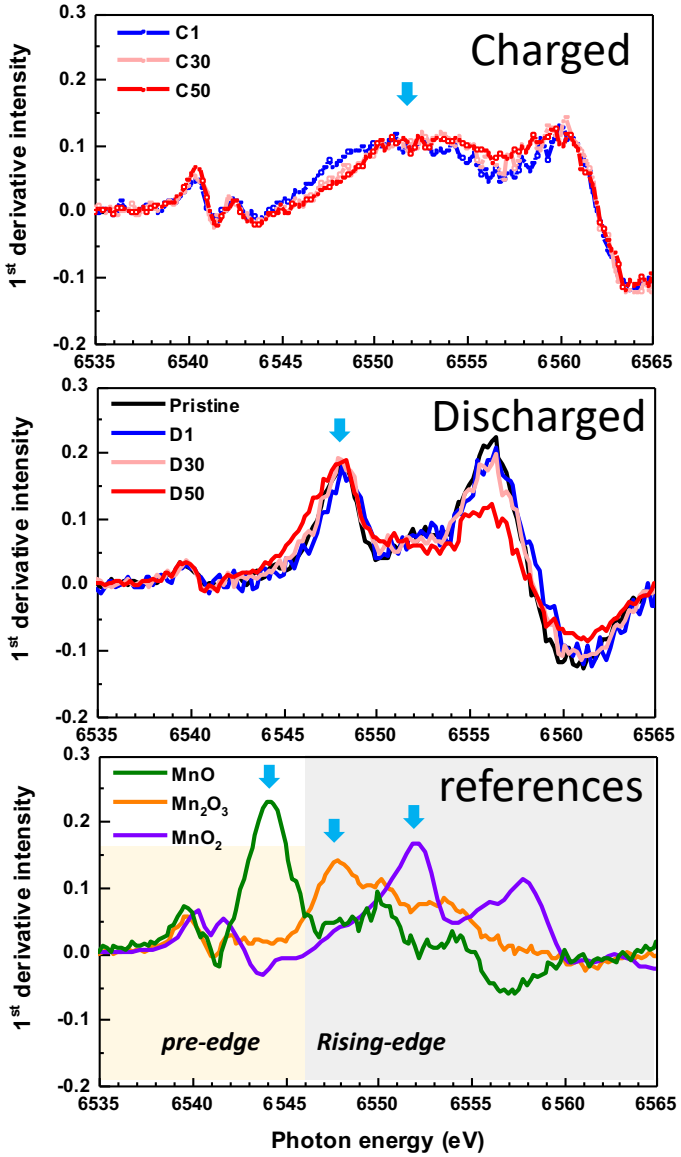
F10 DRX – less bulk chemical changes

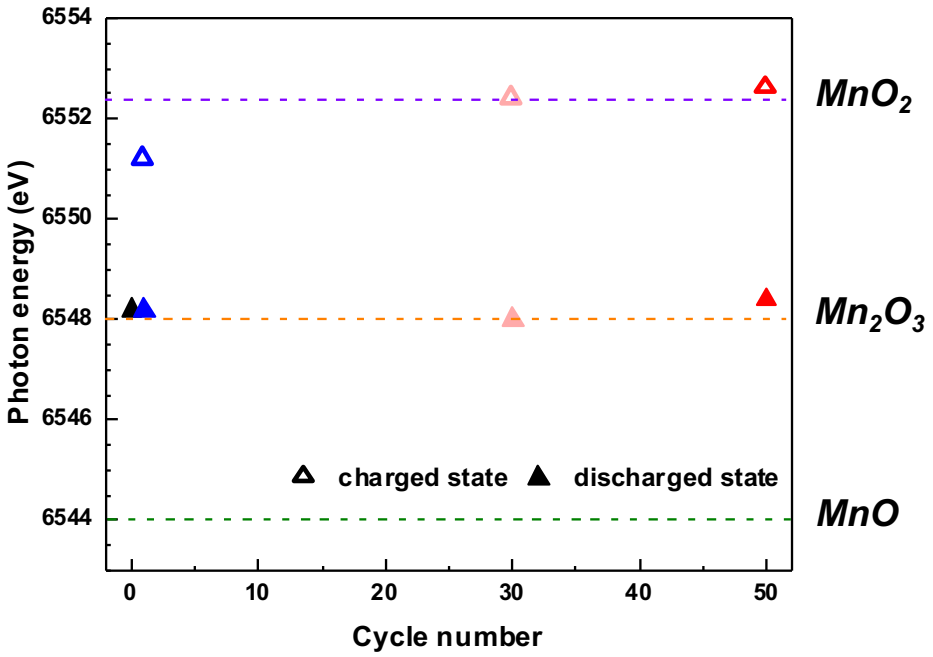
XANES (SSRL Beamline 2-2)





K-edge 1st derivative intensity

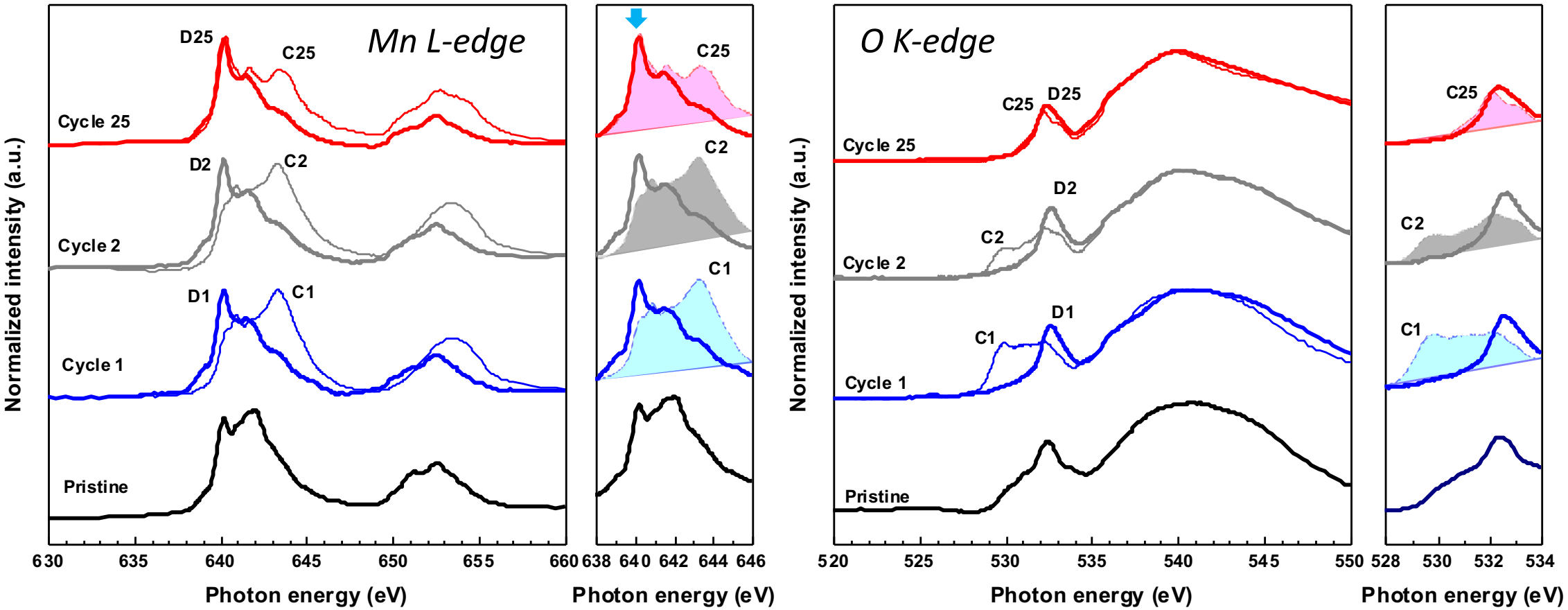




- Cycling-induced bulk Mn reduction was no longer observed in low Li/Mn F-DRX.
- Slight increase in Mn oxidation state suggests different redox processes are involved. Further investigation ongoing.

F10 DRX – less surface chemical changes

TEY sXAS (SSRL Beamline 10-1)



- Cycling-induced surface Mn reduction mostly observed in the first cycle, likely a result of side reaction with electrolyte.
- Changes in O pre-edge peak significant – further investigation by RIXS planned.

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Contributors and Acknowledgement

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Remaining Challenges and Barriers

- DRX cycling stability at high voltages
  - Contribution of detrimental electrode/electrolyte interactions
  - How to balance the trade offs in stability and capacity at high voltages
- DRX rate capability
  - What roles do the intrinsic ionic and electronic conductivities play?
  - Can DRX materials with improved rate capability be engineered?
- How to control DRX voltage profile through materials design and synthesis

Proposed Future Work

- Further develop synthesis approaches and disseminate established synthesis protocols
  - Maximize F content in DRX – explore different reaction precursors and dopants
  - Promote beneficial short-range ordering in DRX structure – explore synthesis conditions
- Investigate ways to improve DRX cycling stability and rate capability
  - Investigate materials engineering strategies to improve stability and rate capability.
  - Investigate the effect of electrolyte and additives on high-voltage cycling stability
  - Investigate changes in electronic/ionic conductivities and DRX kinetics with cycling. Gain knowledge on what controls DRX rate capability
- Develop pouch cell evaluation of DRX compounds. Establish testing protocols.

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

Summary

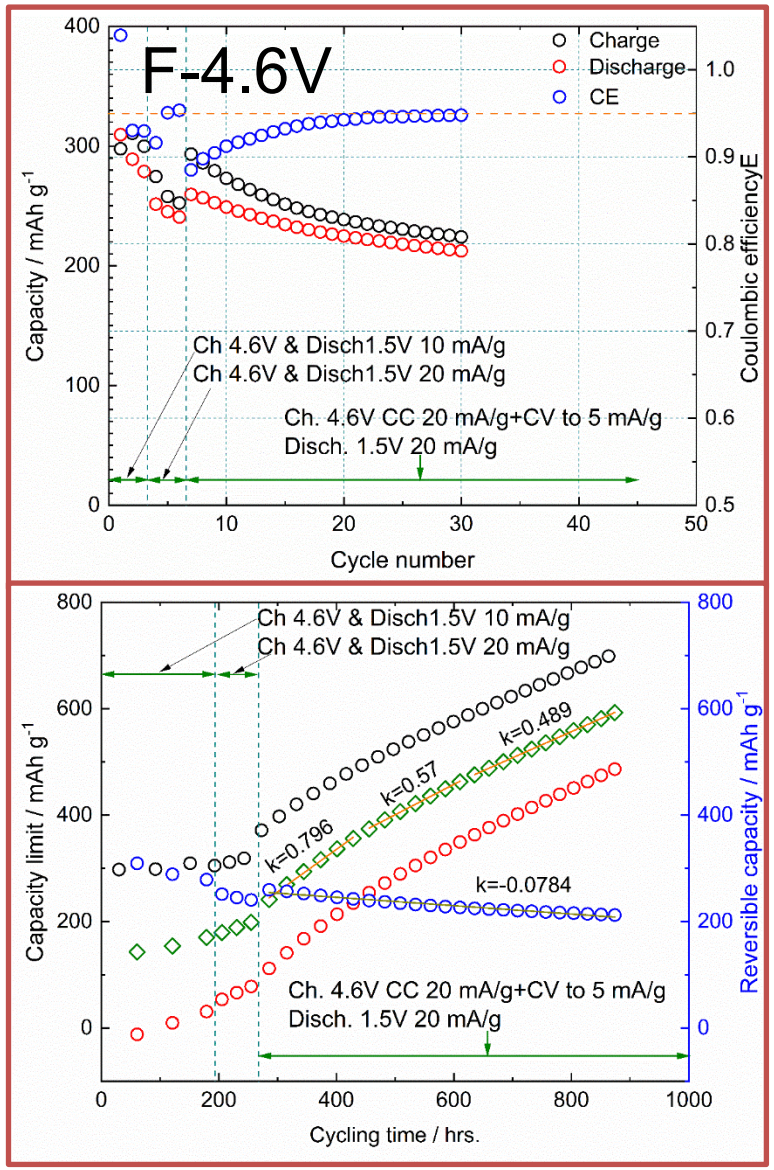
- Physical and electrochemical properties of LMNOF DRX baseline materials were evaluated
  - Cycling to an upper cutoff voltage of 4.6 V improves stability while maintaining high capacity
- LMTOF model system with systematically varied properties were prepared to understand DRX degradation mechanisms and their controlling factors
  - Composition optimization important – better performance obtained on DRX materials with high F content and lower Li/TM ratio
- A synthesis approach utilizing PTFE precursor was developed to achieved higher F solubility and reduced Li/Mn ratio in LMNOF
  - New DRX material capable of stable cycling with a discharge capacity over 200 mAh/g was developed

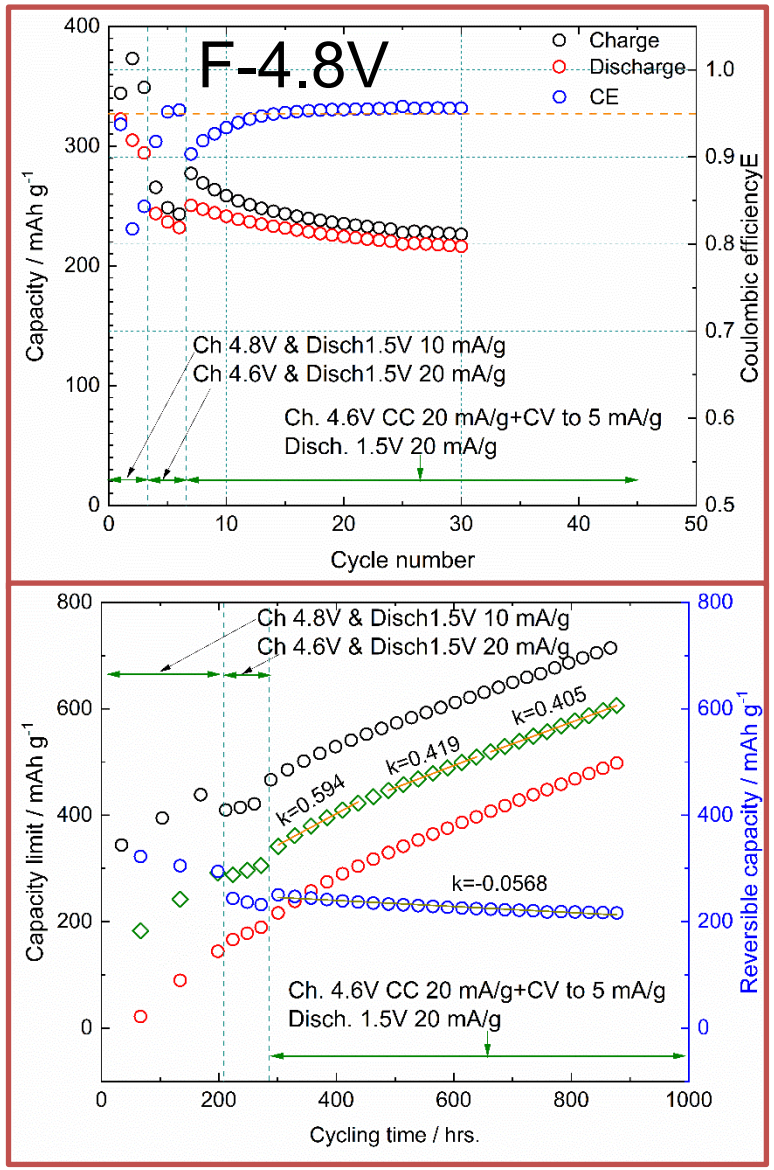
Technical Back-Up Slides

Effect of formation cutoff voltage on LMNOF cycling

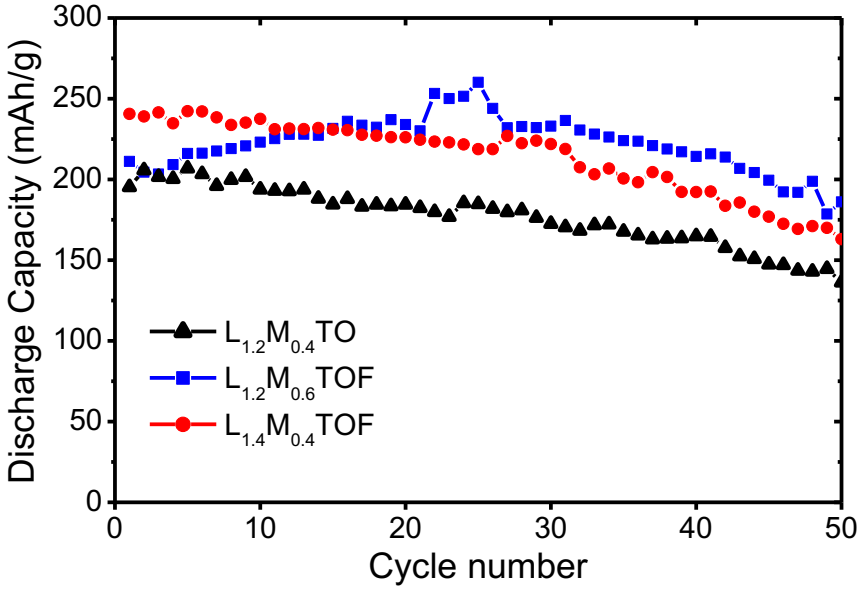
LMNOF Metrics	F-4.6 V	F-4.8 V
Discharge capacity (C/10) after formation (mAh/g)	260	250
Capacity retention 30th cycle (%)	82	86
Capacity fade rate 30th cycle (%/cycle)	0.78	0.57
Avg. side-reaction rate 30th cycle (mAh/g/h)	0.489	0.405
Coulombic efficiency 30th cycle	0.976	0.980

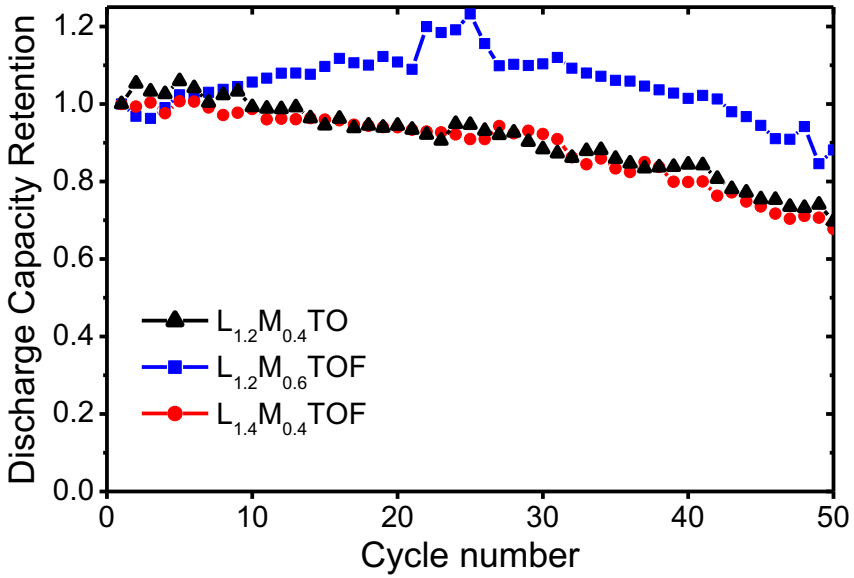
- Formation cycles with 4.8 V upper voltage cutoff provides protection for long-term cycling

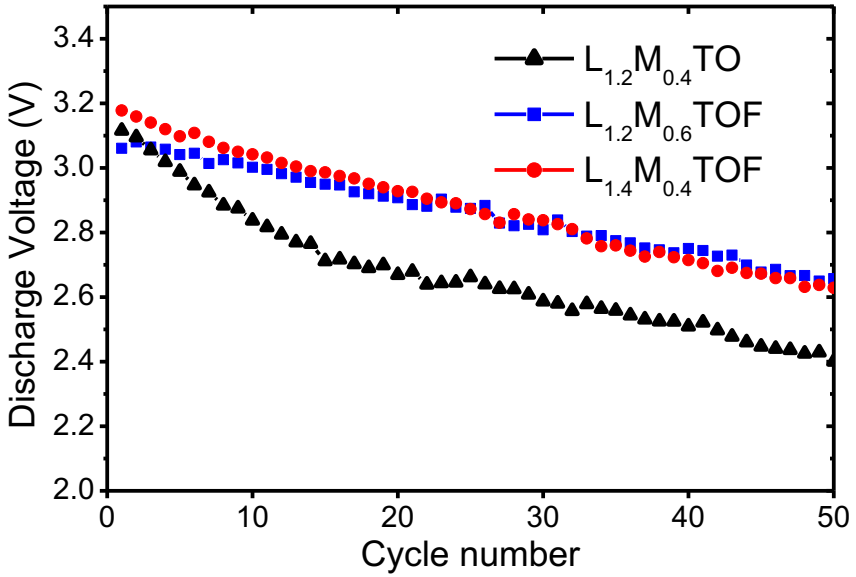


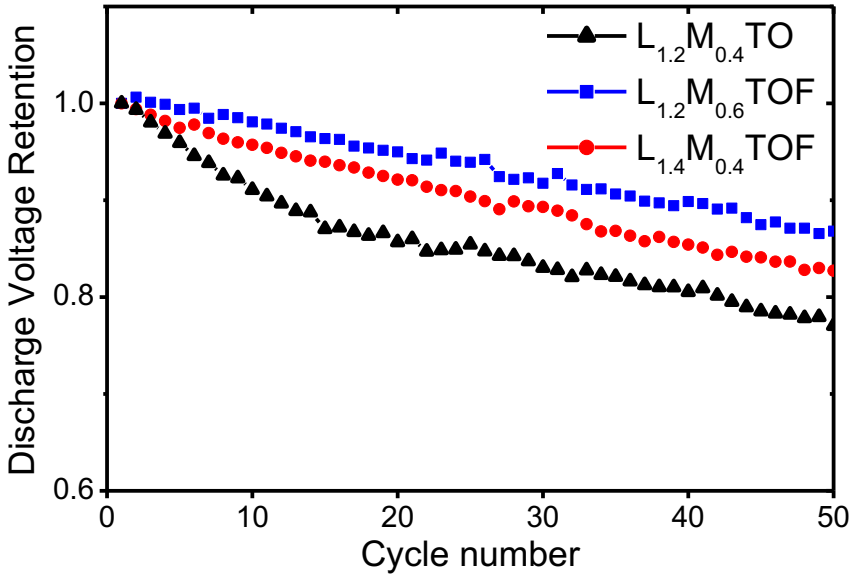


Electrochemical performance of LMTOF samples









$Li_{1.4}Mn_{0.4}Ti_{0.2}O_{1.4}F_{0.6}$
($Li_{1.4}M_{0.4}TOF$, Li/Mn=3.5)

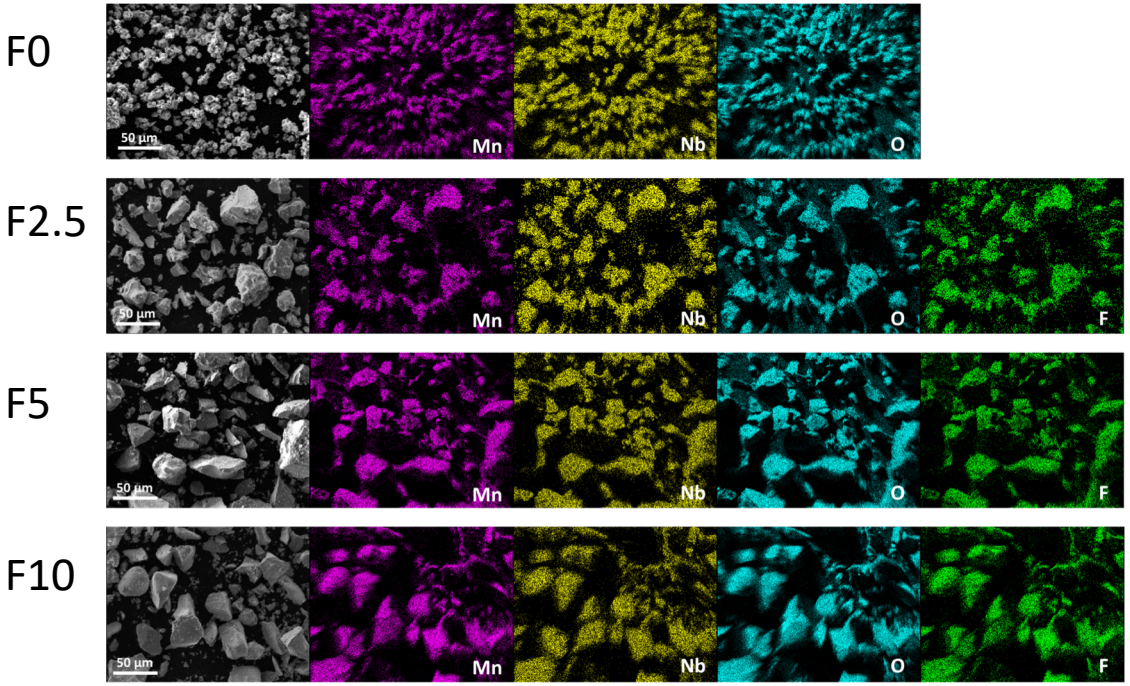
$Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ ($L_{1.2}M_{0.4}TO$, Li/Mn=3.0)

$Li_{1.2}Mn_{0.6}Ti_{0.2}O_{1.8}F_{0.2}$
($Li_{1.2}M_{0.6}TOF$, Li/Mn=2.0)

- Fluorine substitution improves cycling stability
- More significant in F-DRX with lower Li/Mn ratio

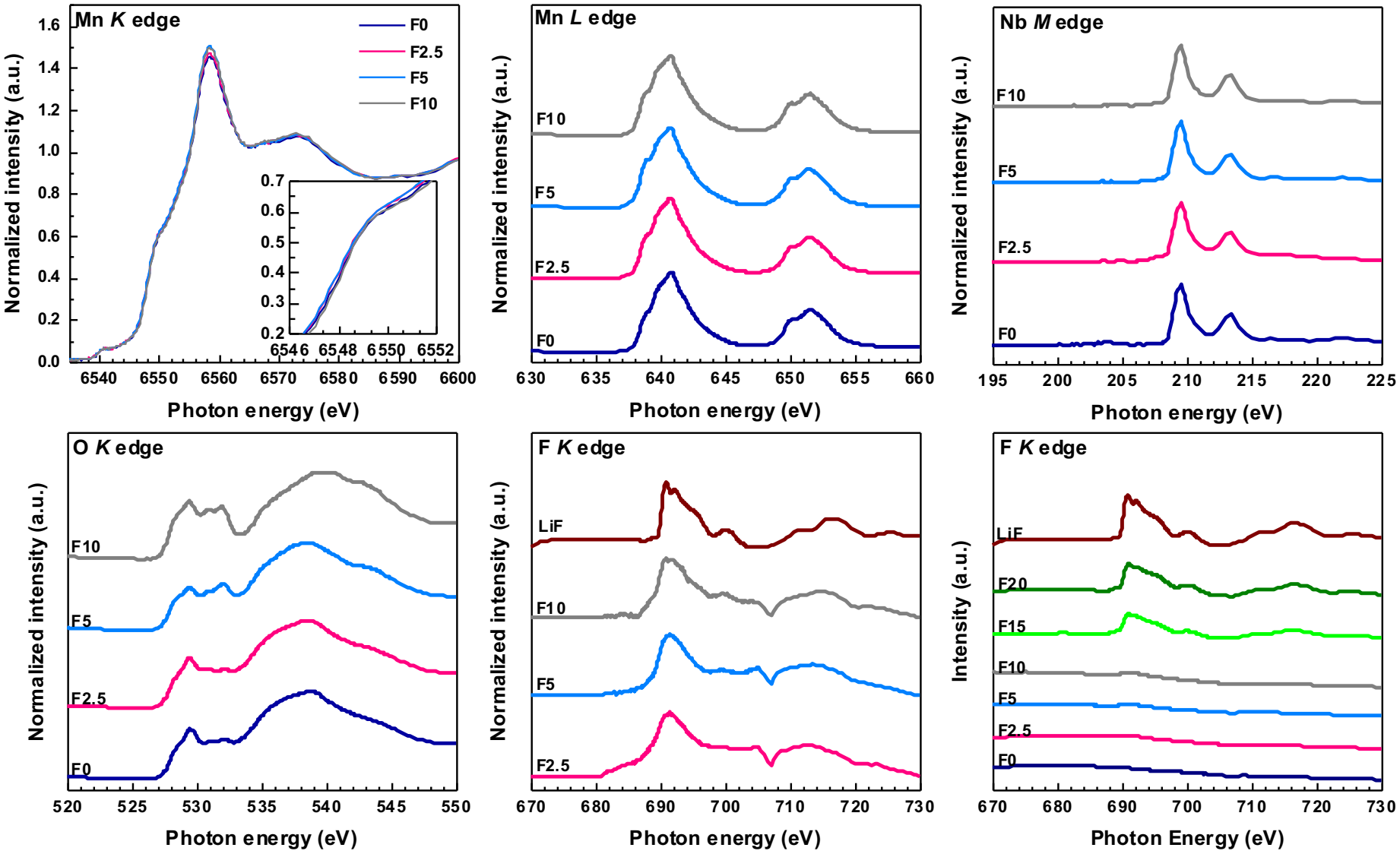
Characterization of LMNOF with various F contents

Samples	Compositions	Theoretical capacity (mAh/g)	
		Mn^{3+}/Mn^{4+}	Li content
F0	$Li^{1.2}Mn^{0.6}Nb^{0.2}O^{2}$	175	292
F2.5	$Li^{1.2}Mn^{0.625}Nb^{0.175}O^{1.95}F^{0.05}$	184	294
F5	$Li^{1.2}Mn^{0.65}Nb^{0.15}O^{1.9}F^{0.1}$	193	297
F10	$Li^{1.2}Mn^{0.7}Nb^{0.1}O^{1.8}F^{0.2}$	212	302



- Theoretical capacity contribution from Mn redox couple increases with the increase in F content and decrease in Li/Mn ratio
- Uniform elemental distribution on synthesized DRX and F-DRX samples

Characterization of LMNOF with various F contents

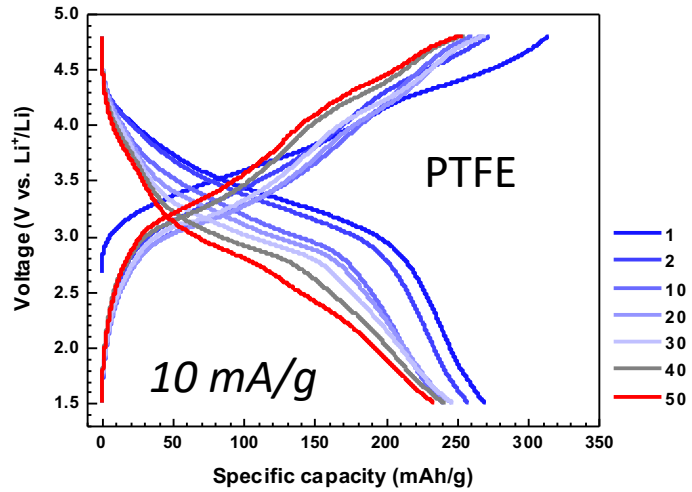


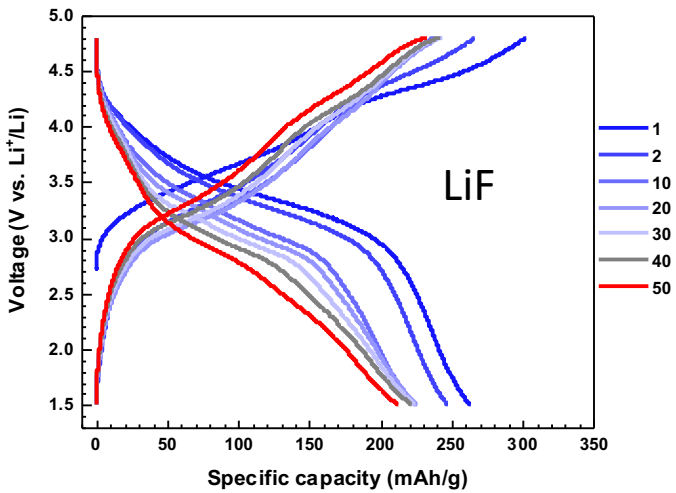
Mn K-edge hard XAS (SSRL BL 2-2)

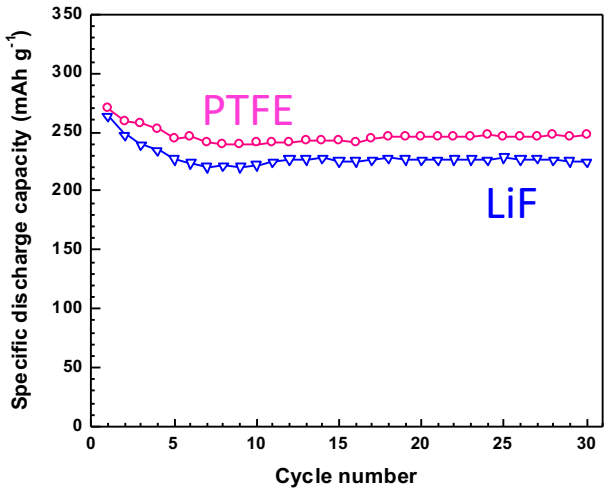
TEY soft XAS (SSRL BL 10-1)

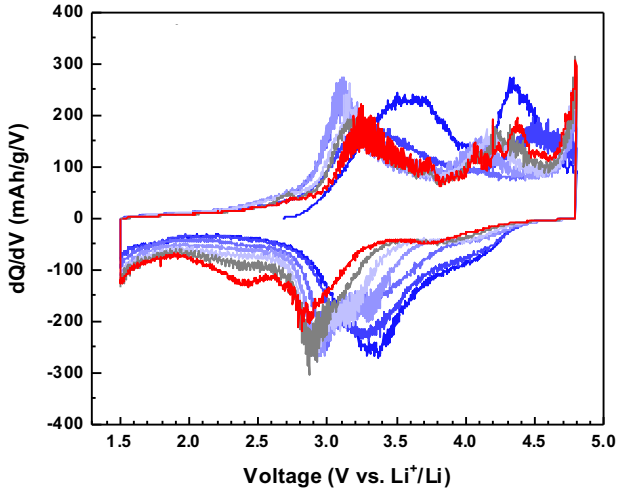
- Bulk Mn at 3+ in all samples
- Surface Mn and Nb consistent with 3+ and 5+ oxidation states
- No LiF detected until F content reaches 12.5 at.%

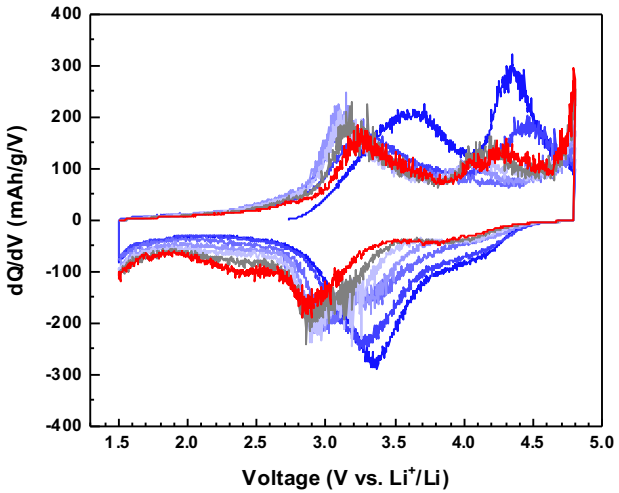
Performance comparison of DRX synthesized with PTFE and LiF











- F2.5 synthesized by using PTFE and LiF as F precursors, respectively
- Slightly improved cycling performance obtained on F-DRX made with PTFE