



Disordered Rocksalt Transition-Metal Oxides (TMOs): Recent Advances and Characterization

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2021 DOE VTO Annual Merit Review

June 21-25, 2021

Related posters: BAT404, BAT405 and BAT406

Project ID: bat376

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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



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	Establish the relationship between short-range order and performance	Completed
March 2021	Detailed understanding of surface chemistry, including O-loss and densification	Completed
June 2021	Modeling of enhancement strategy for cycle life and rate	On schedule
September 2021	Demonstration of a Co-free optimized DRX with > 200mAh/g at 50 cycles at room temperature	On schedule

Approach/strategy (1)

- Focus on three DRX baseline systems and their analogues:

$\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$ (LMNOF): Solid-state synthesis, Mn-redox

$\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$ (LNTMOF): Solid-state synthesis, Ni-redox

$\text{Li}_2\text{Mn}_{1/2}\text{Ti}_{1/2}\text{O}_2\text{F}$ (LMTOF): High F-content, ball-milled, $\text{Mn}^{2+}/4+$ redox

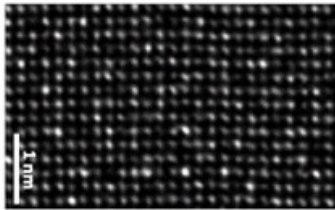
Note: emphasis has shifted away from the Ni-based system studied in year 1 to the two Mn-based systems.

- Modeling of bulk and surface cation arrangement, ion transport, and stability
- Explore synthesis conditions to prepare DRX materials with optimized performance. Establish reliable and scalable synthesis protocols for materials with high F content.
- Detailed characterization of bulk redox, surface structure and oxygen loss/oxidation to relate to impedance growth.
- Develop the characterization methods need to study these materials
- Fabricate quality electrodes of DRX materials. Develop electrochemical testing protocols and benchmark DRX performance metrics.

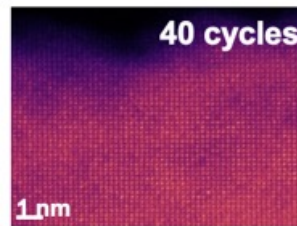
Approach/strategy (2)

At start of year 2 team was organized around six key challenges, each with a team lead

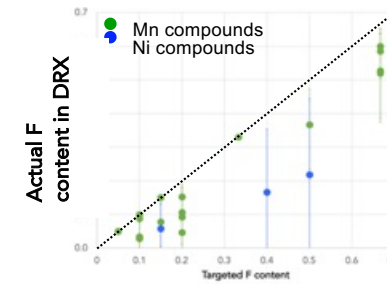
Short-range cation order



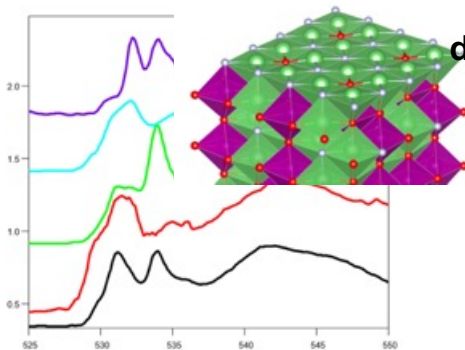
Bulk changes with cycling



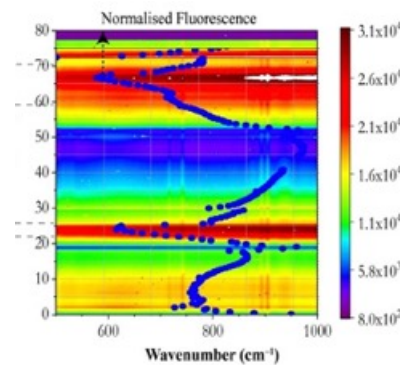
F-solubility



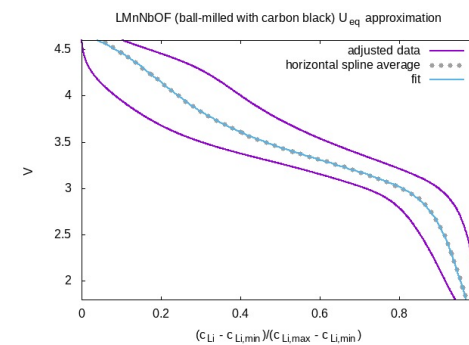
Surface processes



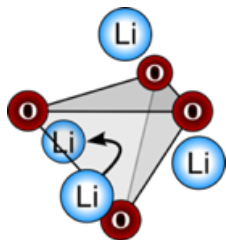
High voltage issues



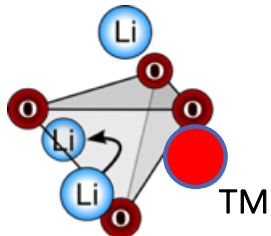
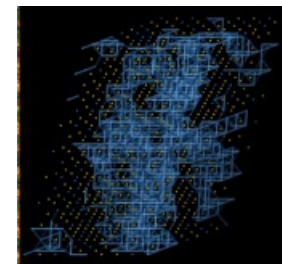
Pouch cells



Technical Accomplishment: Modeling of how cation Short Range Order Controls Rate



Background: Li diffusion is achieved through tetrahedral sites with no surrounding transition metals (TM). These “O-TM channels” form percolating diffusion pathways through the DRX materials



Problem: Short-range cation (SRO) order is a local statistical deviation from randomness. Typical there is an energetic preference for Li-TM nearest neighbors which shows up as SRO. This reduces the number available O-TM channels and lowers Li diffusivity

Based on this insight, three technical solutions were implemented successfully leading to high rate

- 1) Reduce SRO through high-entropy cathodes
- 2) Create spinel-like partial order as it has O-TM channels even in the ordered states (reported last year)
- 3) Non-topotacticity: Use ions that move tetrahedral at top of charge as they increase O-TM pathways

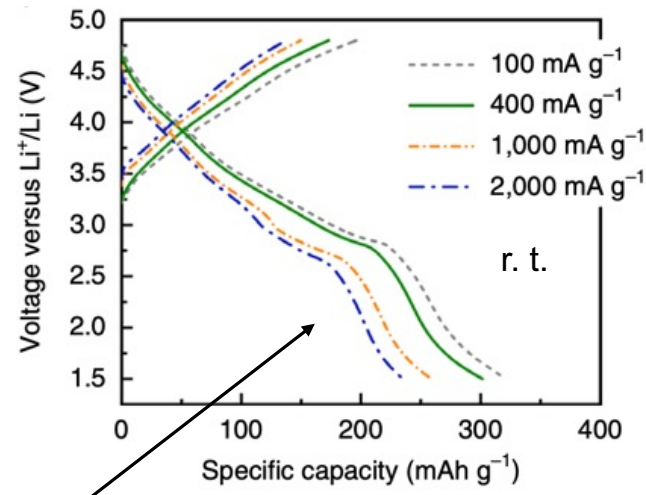
Technical Accomplishment: High rate DRX cathodes

In 2015 DRX materials had to be tested at 60°C 10 mA/g to achieve high energy densities. (N. Yabuuchi, et al. PNAS, 2015, 112, 7650). With our novel strategies in place currents up to 2A/g have been achieved at RT in DRX materials

1. High Entropy mixture

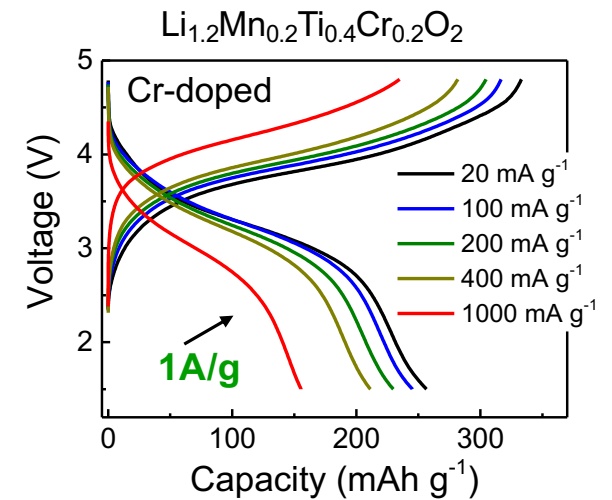
Details on next slide

2. Partial spinel order



2A/g discharge

3. Non-topotacticity.



Z. Lun, et al. Nat. Mater. 2020.

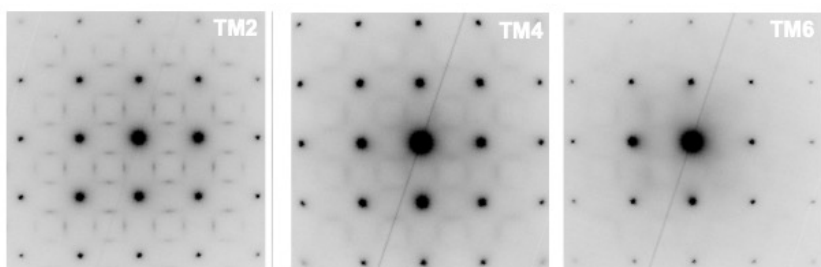
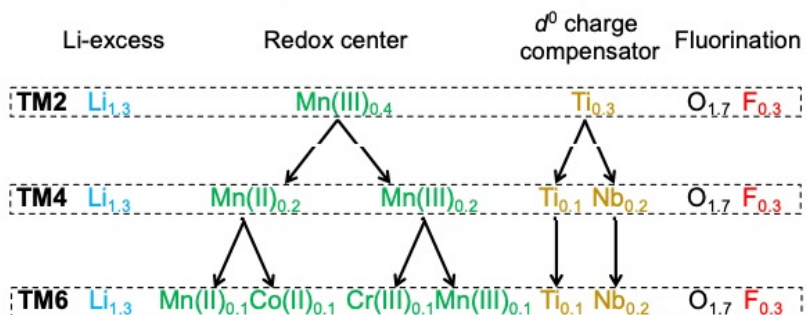
H. Ji, et al. Nat. Energy, 2020, 5, 213.

J. Huang, et al. Nature Energy 2021

Technical Accomplishment : High Entropy Cathodes for High Rate

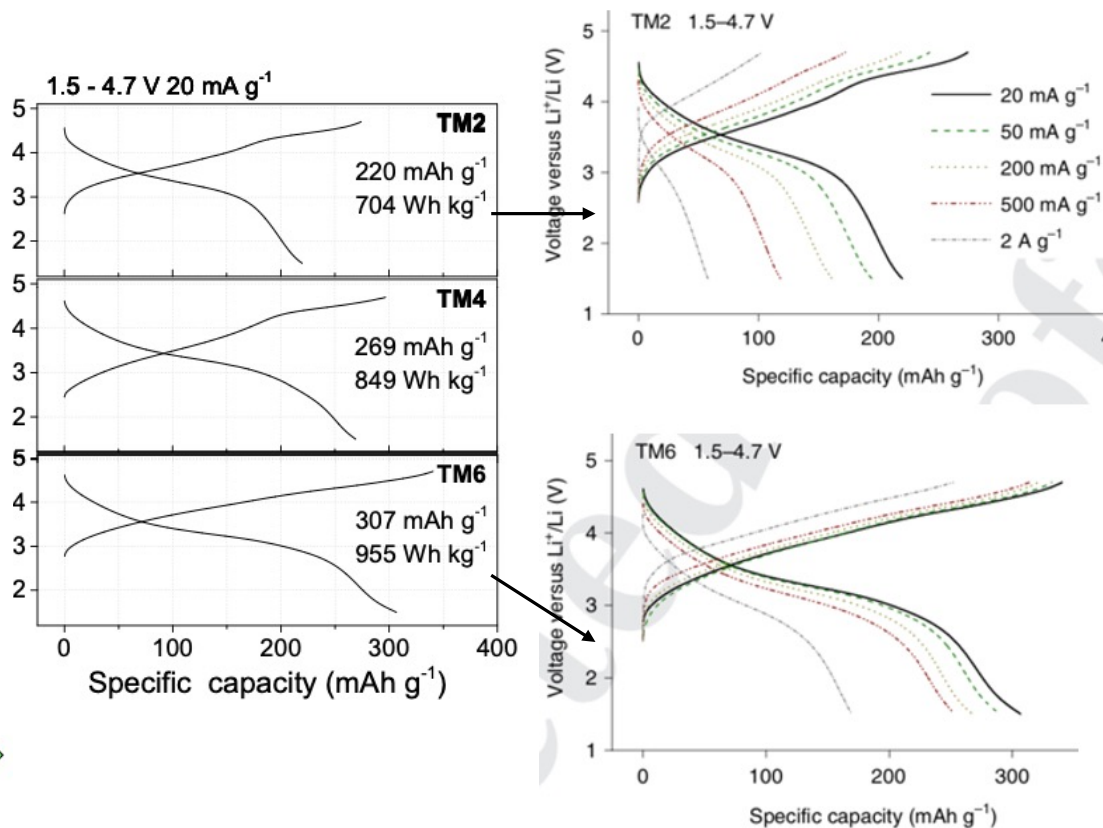
High entropy is created by introducing more metals. This creates more randomness, decreases SRO, and increases specific energy and rate

Prototype composition design



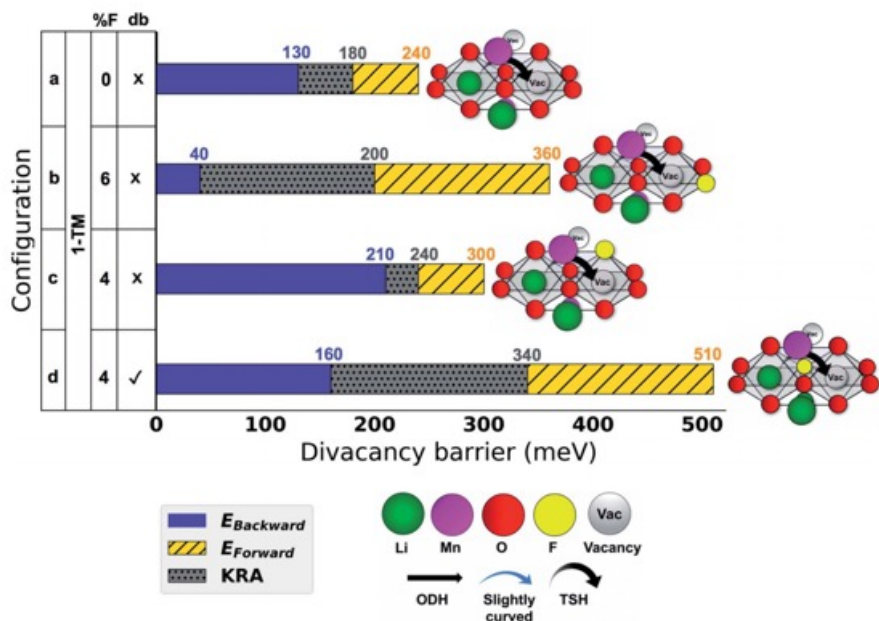
SRO (diffuse scattering) decreases; rate increases

Z. Lun, et al. Nat. Mater. 2020.



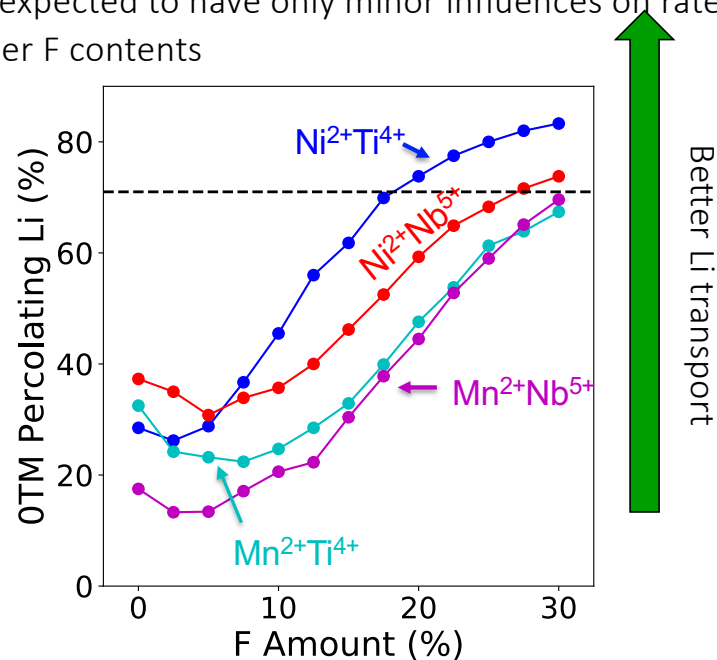
Technical Accomplishment: Modeling effect of Fluorine on rate performance

Fluorine has beneficial effects on high voltage stability, but could potentially modify the Li diffusion in two ways: 1) By locally modifying the barrier for Li hopping; 2) By modifying the percolation of 0-TM channels through the structure. Both of these were investigated separately. Our conclusion is that F is expected to have only minor influences on rate performance: Minor negative for < 5-7% F, and minor positive for higher F contents



Ab initio computation of hopping barriers shows only marginal effect of F in the environment of barriers

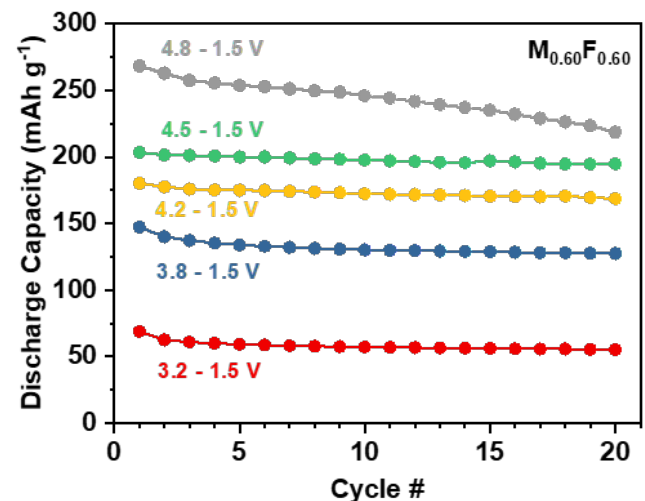
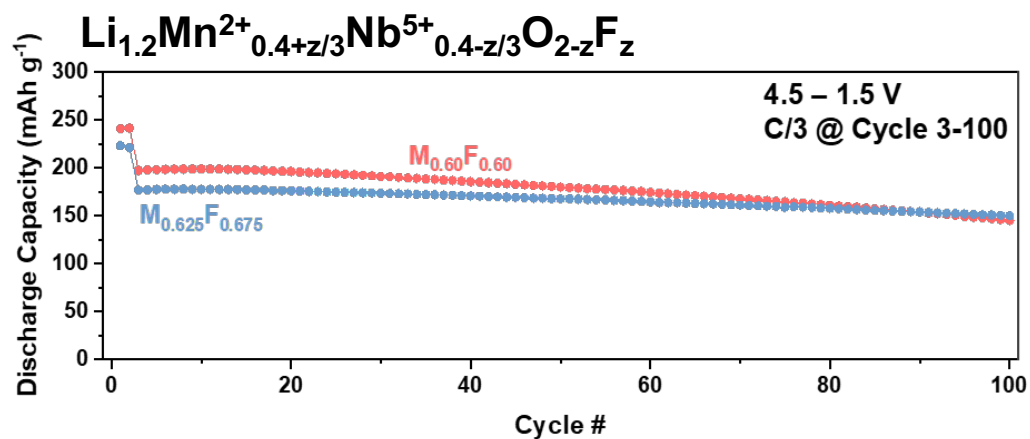
Z. Jadidi et al., J. Mater. Chem. A, 8, DOI: 10.1039/d0ta06415g (2020)



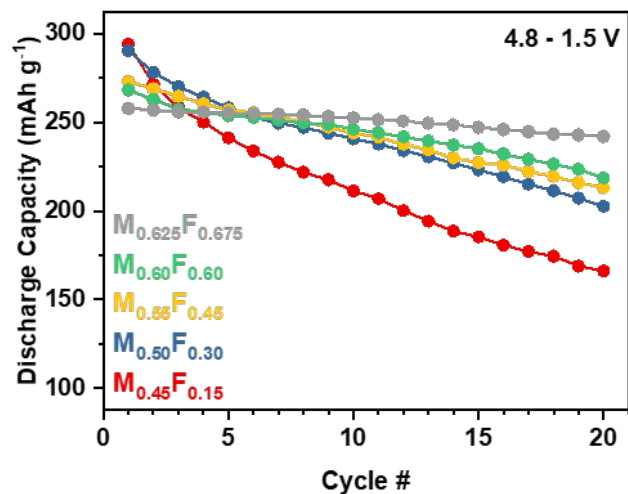
Modeling shows that a small amount of F-substitution decreases Li-percolation but higher amounts significantly improve it.

B. Ouyang et al., Adv. Energy Mater. 2020, 1903240, DOI: 10.1002/aenm.201903240 (2020)

Technical Accomplishment: F enhances cycle life even when charging to high voltage

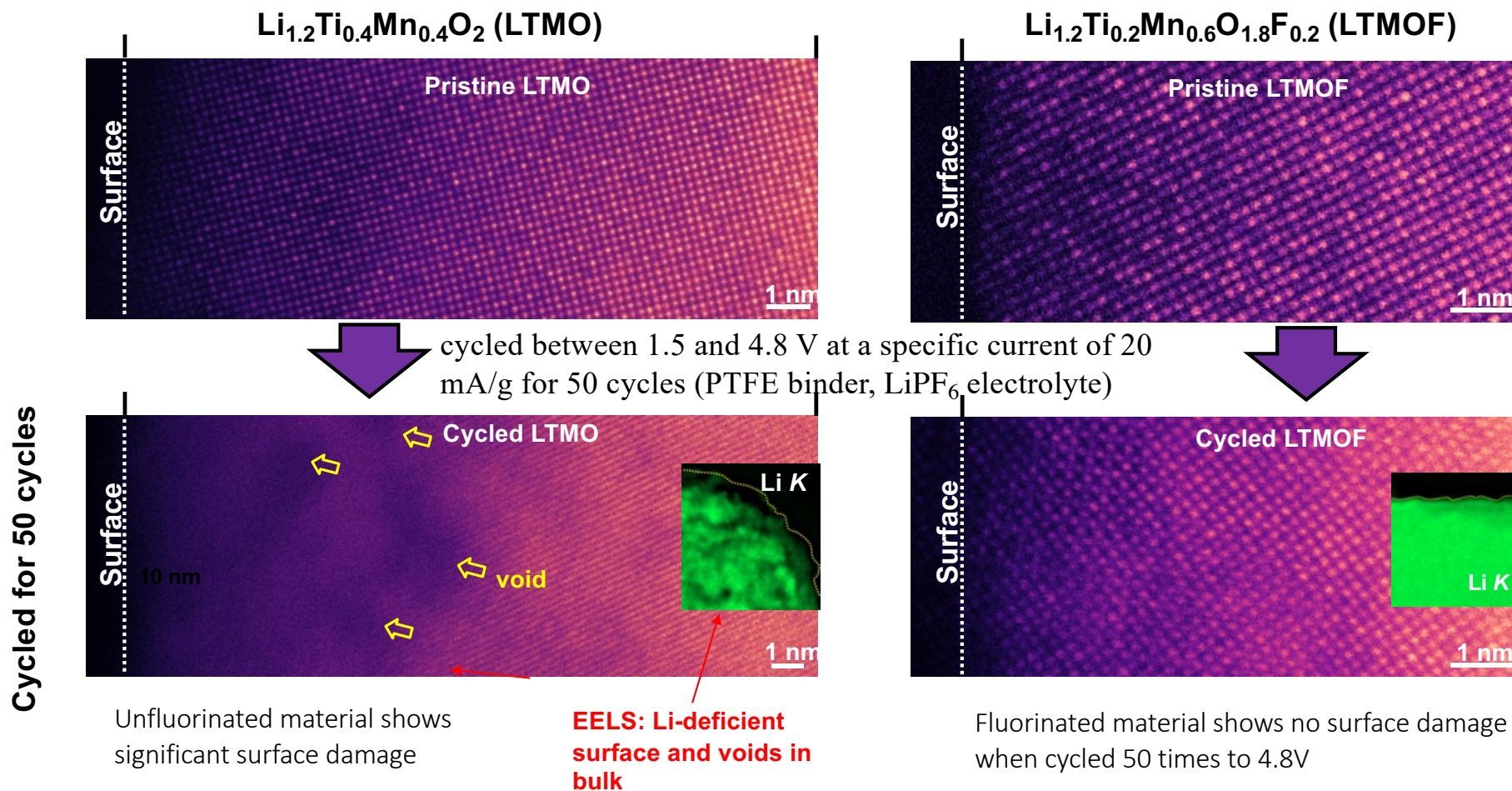


Charge cutoff > 4.5 reduces cycle life



Higher F-content gives better cycle life even at high V charge cutoff

Technical Accomplishment: F protects against surface degradation

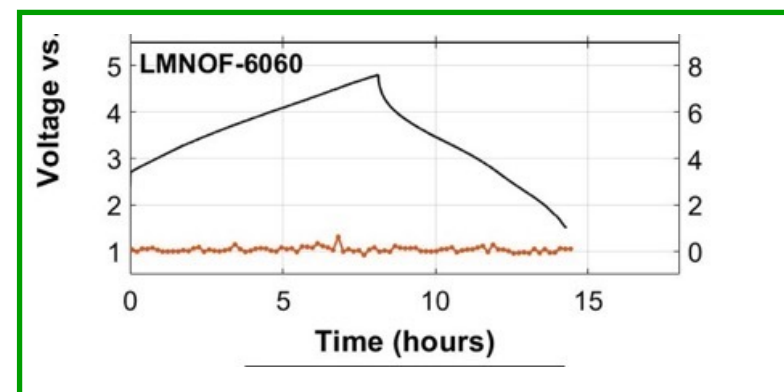
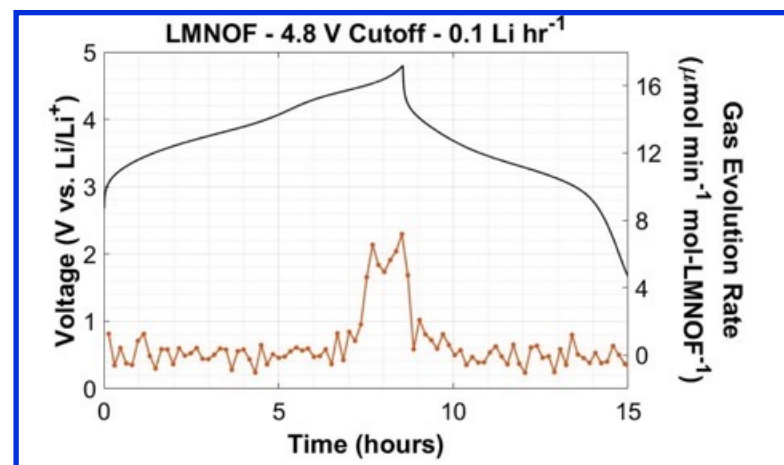


Technical Accomplishment: Very low O₂ release from fluorinated DRX

DEMS Results

Material	1 st cycle O ₂ evolved* (mmol gas/mol mat'l)
NMC-622	0.4
Li-rich NMC	1.1
$\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$	0.50
$\text{Li}_{1.2}\text{Mn}_{0.60}\text{Nb}_{0.2}\text{O}_{1.40}\text{F}_{0.60}$	0

- Compared to a commercial NMC-622 and Li-rich NMC DRX materials exhibit less O₂ evolution
- Low fluorinated DRX shows similar O₂ release than a commercial NMC, even though its particle size is much smaller and the material is unoptimized
- High F-content DRX releases NO oxygen

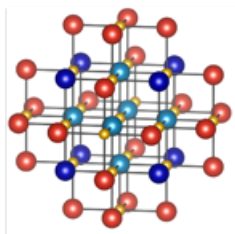


Technical Accomplishment: Atomic-level characterization of DRX

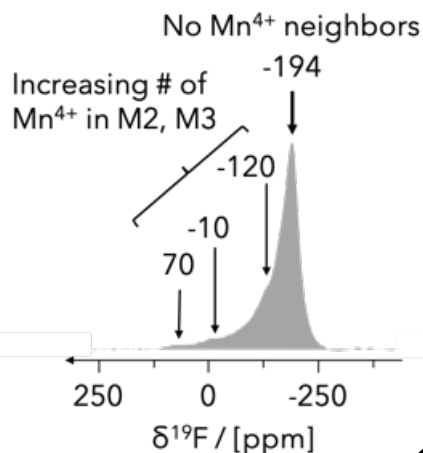
Because DRX materials have a cation-disordered long-range structure, XRD provides minimal information on the atomic-level arrangements. This team has developed novel methods to characterize short-range order and F-content of the materials

New methods to study SRO

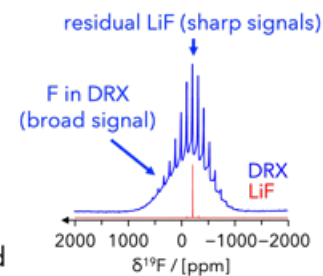
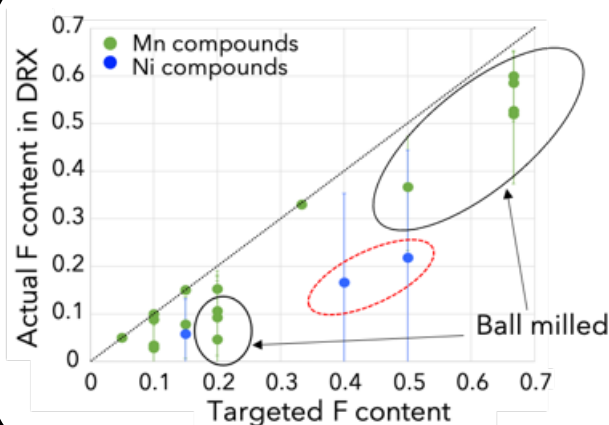
Position of, e.g., Mn^{4+} in local shell around F affects ^{19}F chemical shift:



● M1
● M2
● M3
● F

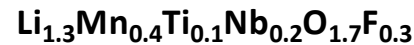
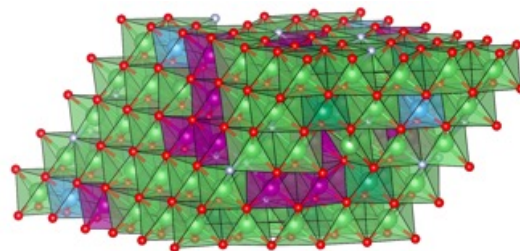
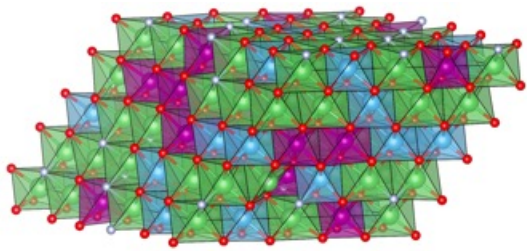


Protocols for assessing F solubility in DRX and impact on electrochemistry

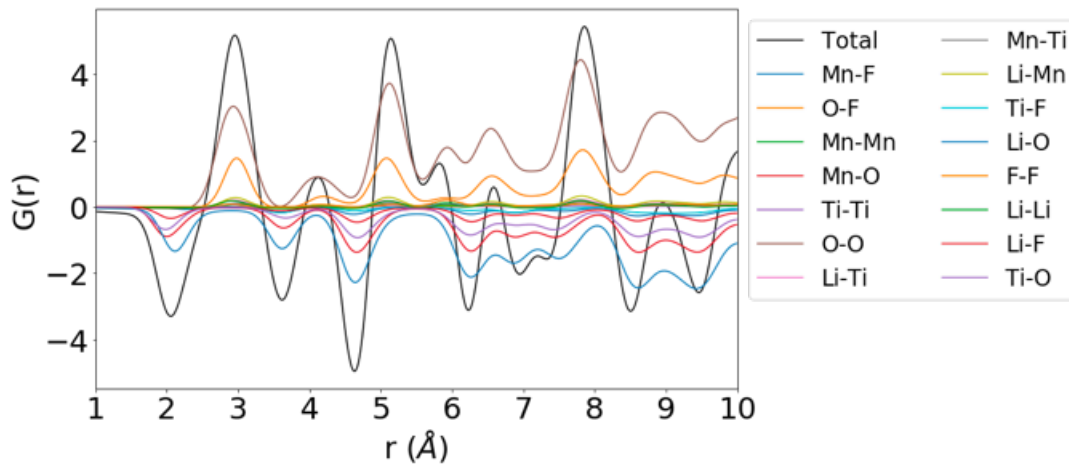


- Quantitative.
- Applicable to range of DRX chemistries.
- Compare various DRX chemistries and determine impact of d^0 TM composition and F content on SRO.
- Complementary bulk and surface characterization to determine F solubility limit in DRX.
- Gentle DRX powder washing procedure and electrochemical testing to identify impact of impurity phases on electrochemistry.

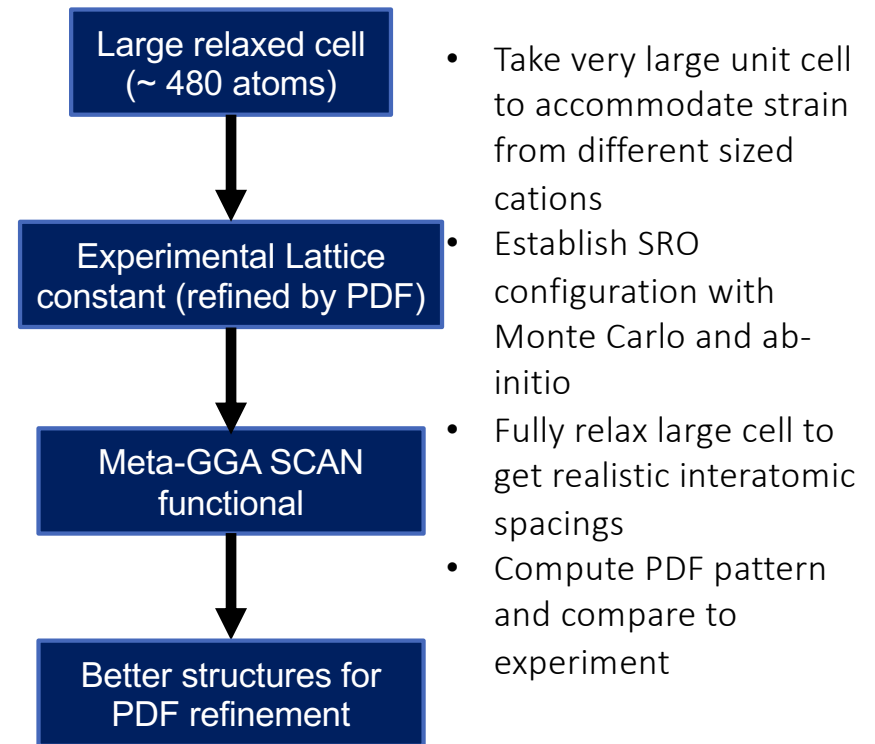
Technical Accomplishment: Developed approach to obtain cation SRO information from Neutron PDF



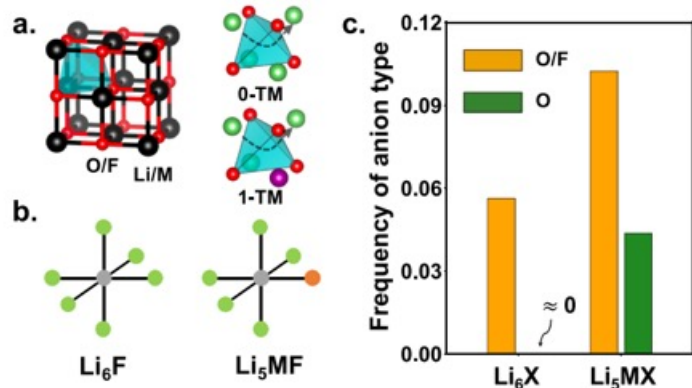
Example of simulated PDF for $\text{Li}_{1.3}\text{Mn}_{0.4}\text{Ti}_{0.3}\text{O}_{2-x}\text{F}$



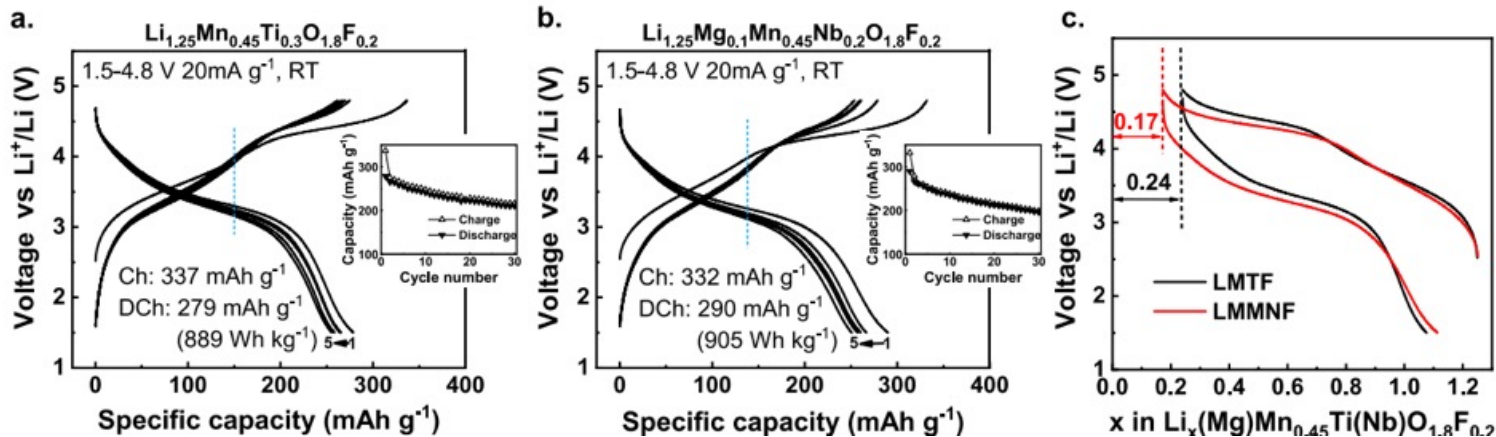
Combined ab-initio – neutron PDF approach confirms short range cation order



Technical Accomplishment: Mg doping to increase specific energy



- Modeling has shown that F doping, while beneficial for capacity retention, can reduce capacity by locking up some Li which only be removed at very high voltage
- Modeling indicated that Mg doping can displace some of the Li around F and make it available for extraction.
- Experiments confirm increase in discharge capacity with Mg doping



Responses to Previous Year Reviewers' Comments

Most reviewer comments were very positive and highlighted the collaborative nature of the team. Some specific questions are addressed below

Reviewer: DRX materials provide attractive alternatives to NMC-type cathodes. The reviewer remarked that it is good that whole team is working on the selected three materials. Co replacement by Nb or Ti may be even more problematic in terms of the material sustainability. Another concern is the high content of reactive F, which may be significantly problematic when batteries catch fire and result in the release of hydrofluoric acid (HF).

Response: Ti is not a resource problem as the precursor used is TiO₂ which is highly abundant. Nb can indeed be more problematic. Its current world production is similar to Co, but can be increased rather easily according to our conversations with the leading producer of Nb. Nonetheless, current focus is on Mn-Ti based DRX compounds which will have no resource problem. We currently have no answer to the question as to whether HF will form, but we point out that F is much more strongly bonded in the DRX than it is in the PF₆ salt.

Reviewer: the reviewer observed that it would be interesting to correlate with bulk imaging for structural analysis to understand the dissolution and structure change.

Response: We have indeed focused much more on structural characterization this year. Some of the new work is shown in posters 406 and 405.

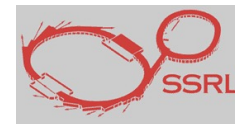
Work is relevant to the program, but it was not clear to the reviewer if the proposed cathode material is environmentally sustainable.

Response: DRX materials enable the use of the Mn redox couple, which is a highly sustainable resource. For stabilizers one can chose from Ti, Nb, Mo. The DRX program has focused in its current year heavily on Mn-Ti systems because TiO₂ is a very abundant resource.

Contributors and Acknowledgement

Juhyeon Ahn
Vincent Battaglia
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Yang Ha
Kenny Higa
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Bryan McCloskey
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Joseph Papp
Kristin Persson
Rohit Satish
Ethan C. Self
Wei Tong
Chongmin Wang
Wanli Yang
Tyler Bennet
P. M. Ajayan
Ganguli Babu



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**

- Investigate further electrode/electrolyte interactions at high voltage
- Explore alternative electrolytes
- Evaluate in more detail cycle life as function of low and high voltage cutoff in pouch cells

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

Summary of Findings

Short-range cation order and Rate capability

We have identified short-range cation order (SRO) in the DRX as a key controlling factor for Li conductivity. Three strategies to reduce SRO have been implemented all leading to high-rate capable cathodes at room temperature

Surface processes and cycle life

We have demonstrated and characterized that the mechanism by which F incorporation improves cycle life is the protection of the cathode particle surface at high voltage charge.

F-solubility and effects of fluorination

We have developed techniques to accurately quantify the amount of F in bulk DRX materials and determined the F-solubility as a function of chemistry. We have identified LiF formation early in the synthesis process as the problem for the uptake of more than 7-10% F in solid-state synthesis methods. We have established that there are no negative effects of F on rate capability

Bulk changes with cycling

We identified changes in bulk structure for DRX compounds with very high Mn content. These changes lead to an increase in capacity with cycling. We are currently investigating this structural change in more detail

High voltage issues

We have demonstrated very low oxygen loss from fluorinated DRX cathodes even when charged to high voltage. But CO₂ evolution, indicative of electrolyte decomposition at high voltage, is present. We have identified surface treatment appears as a viable technique to reduce the high voltage fade.

Characterization

We have developed several novel approaches to characterize the structural details of DRX compounds