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**U.S. DEPARTMENT OF
ENERGY**

Deep-Dive into Next Generation Cathode Materials (2B): A New Class of Materials--Disordered Rocksalt Transition-Metal Oxides

Principal Investigator: Gerbrand Ceder, Guoying Chen (co-lead)

**Lawrence Berkeley National Laboratory, Berkeley,
California 94720**

PM: Peter Faguy

June 11, 2019

Project ID: bat376

Overview

Timeline

- Start date: Oct 1, 2018
- End date: Sept 30, 2021
- Percent complete: 15 %

Budget

- Total Funding: \$6M
- Funding for FY 19:
 - \$2M

Barriers

- Barriers addressed
 - Materials resource issues
 - Capacity and energy density
 - Cathode cost

Partners

- Lead LBNL: Ceder, Chen, McCloskey, Battaglia, Kostecki, Persson, Tong, Yang
- PNNL: Chongmin Wang
- ORNL: Jagjit Nanda
- UCSB: Raphaële Clément

See also project 404, 405 and 406

Relevance

- Novel 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.

Objectives

- Improve/investigate **rate** capability
- Improve/investigate **cycling** stability
- Modify and investigate cause of **voltage slope**

Milestones

Date	Milestones	Status
December 2018	Held all-hands team meeting and agreed synthesis and testing protocols.	Completed
March 2019	Scale up: Synthesis (10 g minimal) of at least 2 DRX compositions.	Completed
June 2019	Go/No-Go: Novel method for high fluorination. No-Go if F-content cannot be $> 7.5\%$; then revert to solid-state synthesis.	On schedule
September 2019	Pouch cell evaluation of DRX materials. Report key performance metrics on one of the rocksalt materials.	On schedule

Approach/Strategy

- 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

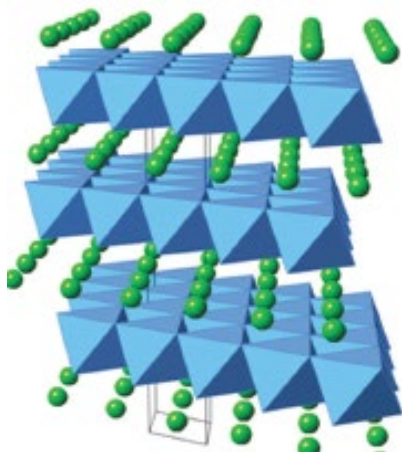
$\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$ (LNTMOF): Solid-state synthesis, Ni-redox

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

- 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.
- Fabricate quality electrodes of DRX materials. Develop electrochemical testing protocols and benchmark DRX performance metrics.

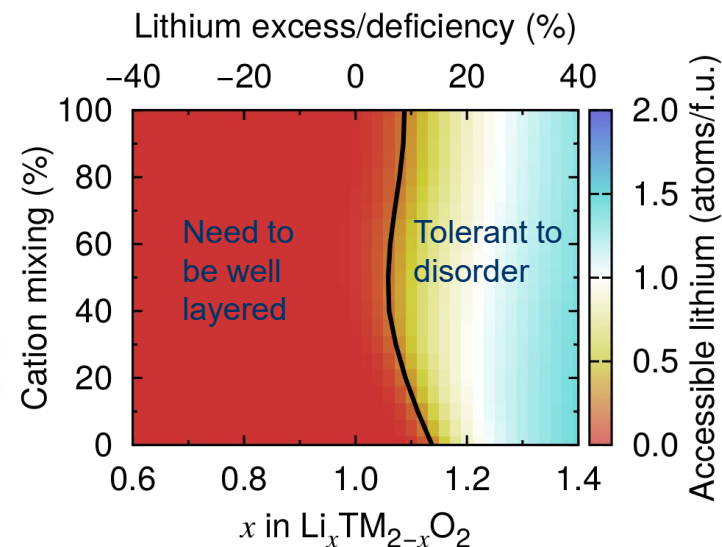
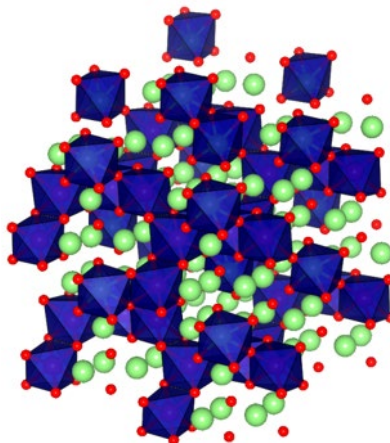
DRX - Concept

Stoichiometric layered



- Excellent commercially available cathodes
- Main components limited to Co, Ni, Al and Mn^{4+} due to need to retain layered structure upon cycling

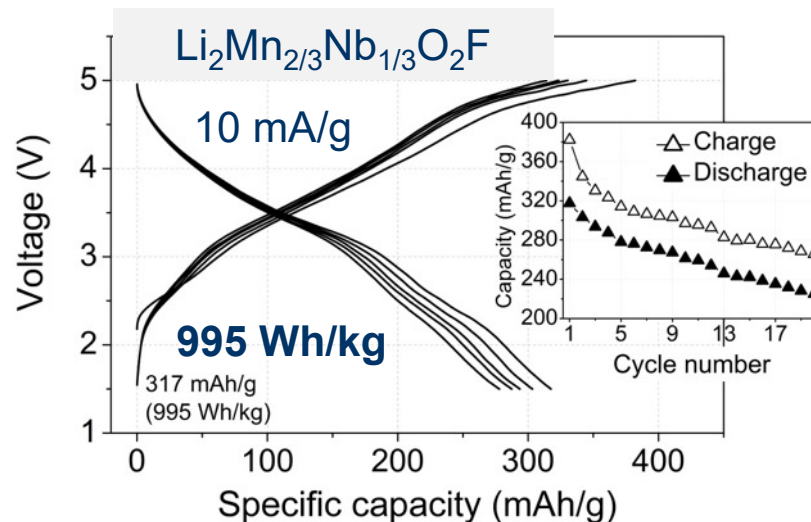
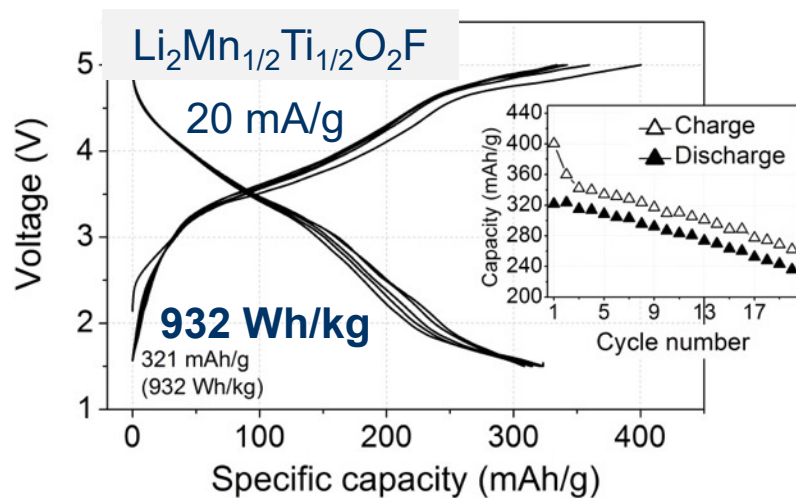
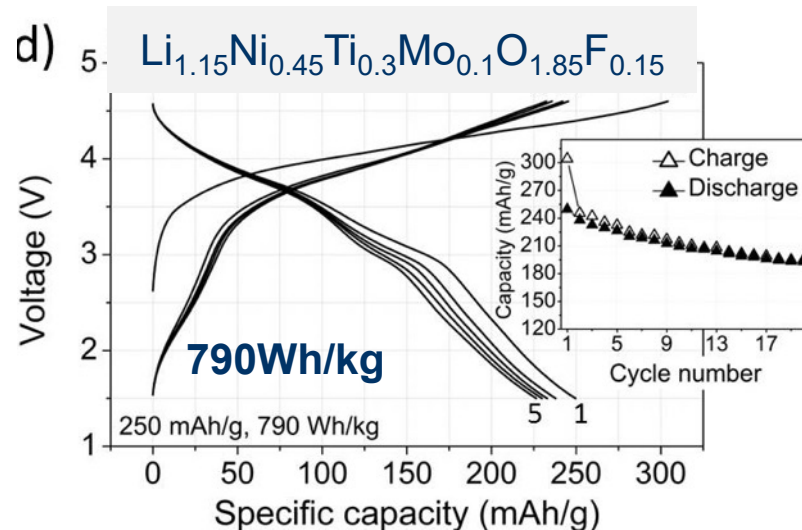
DRX



- **Dense** crystalline rocksalt-structured materials with cations disordered over octahedral sites.
- Percolate Li-ion transport for **Li-excess** > 10%
- **High** capacity and **energy** content
- Can use a **wide variety of metals**
- **Low volume expansion**
- Can be partially **F-substituted** (for O) enhancing stability and capacity
- **New direction** for dense cathodes

DRX - Concept

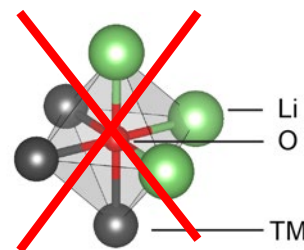
Compound	Capacity
$\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$	280 mAh/g
$\text{Li}_2\text{VO}_2\text{F}$	320 mAh/g
$\text{Li}_{1.3}\text{Nb}_x\text{M}_{0.7-x}\text{O}_2$ (M = Mn, Ni, Co, Fe)	300 mAh/g
$\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$	290 mAh/g
$\text{Li}_{1.2}\text{Ni}_{0.333}\text{Ti}_{0.333}\text{Mo}_{0.133}\text{O}_2$	230 mAh/g
$\text{Li}_x\text{Ni}_{2-4x/3}\text{Sb}_{x/3}\text{O}_2$	150 mAh/g
$\text{Li}_{1+x}\text{Ti}_{2x}\text{Fe}_{1-3x}\text{O}_2$	250 mAh/g
$\text{Li}_4\text{Mn}_2\text{O}_5$	350 mAh/g
$\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{0.4}\text{O}_2$	270 mAh/g
$\text{Li}_{4/3}\text{Mo}^{6+}_{2/9}\text{Mo}^{3+}_{4/9}\text{O}_2$	330 mAh/g
$\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$	250 mAh/g
$\text{LiMoO}_{2-x} - \text{LiF}$ ($0 \leq x \leq 2$)	320 mAh/g
$\text{Li}_2\text{MnO}_2\text{F}$	280 mAh/g



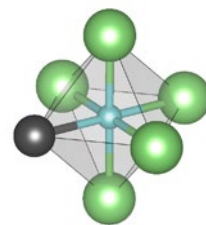
DRX – Concept: Fluorination $\text{Li}_{1+x}\text{M}_{1-x}(\text{O}_y\text{F}_{2-y})$

Some O in DRX materials can be substituted by F

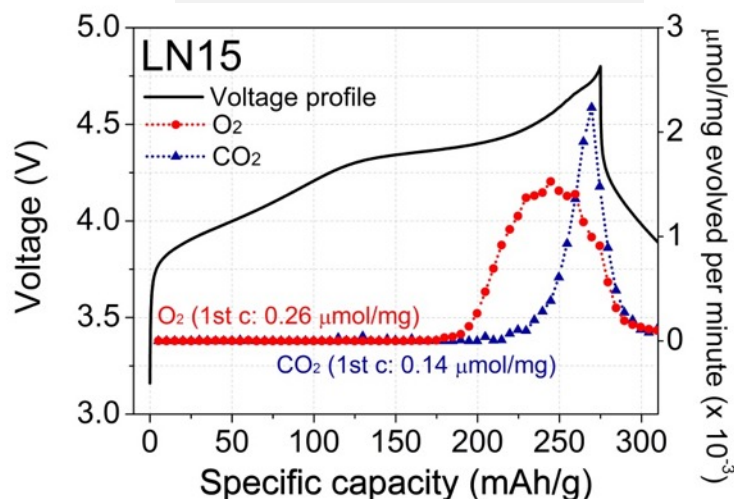
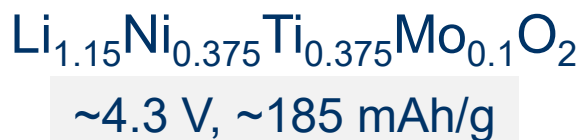
- reduces valence on the metal
- reduces O-loss at high charge
- reduces impedance growth
- increases capacity



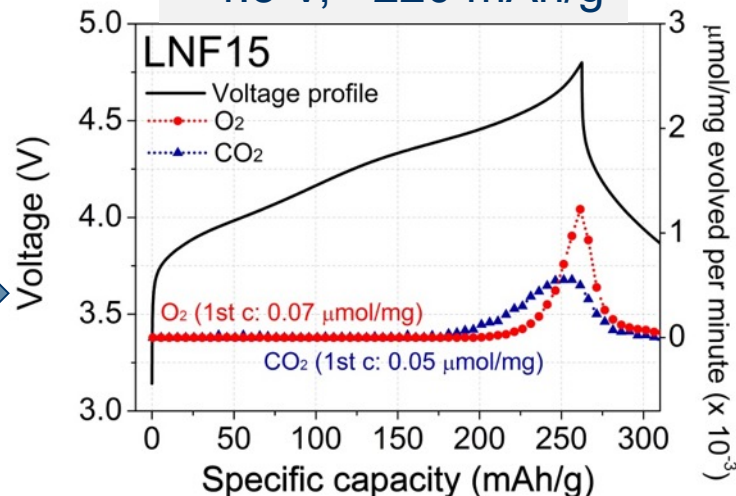
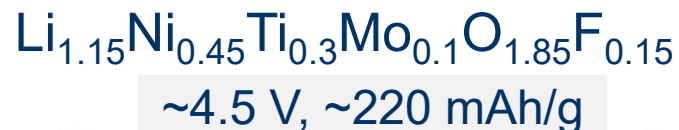
O-environment in layered cathodes



Statistically occurring environment in DRX cathodes that can be fluorinated

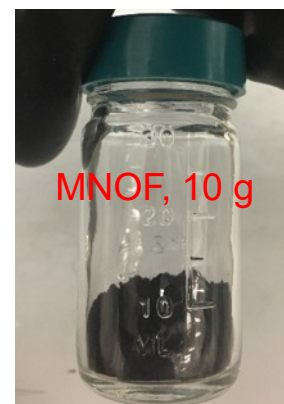
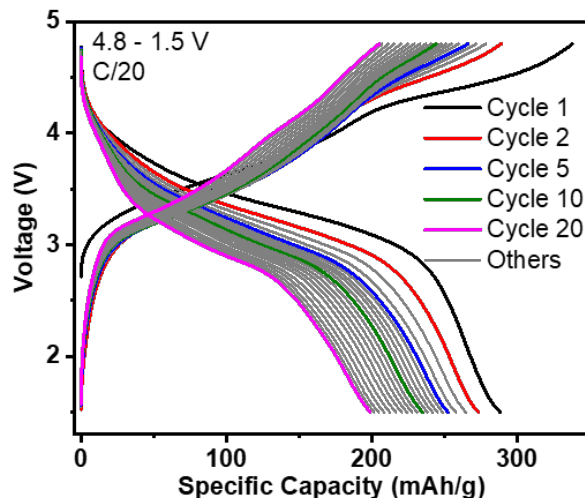
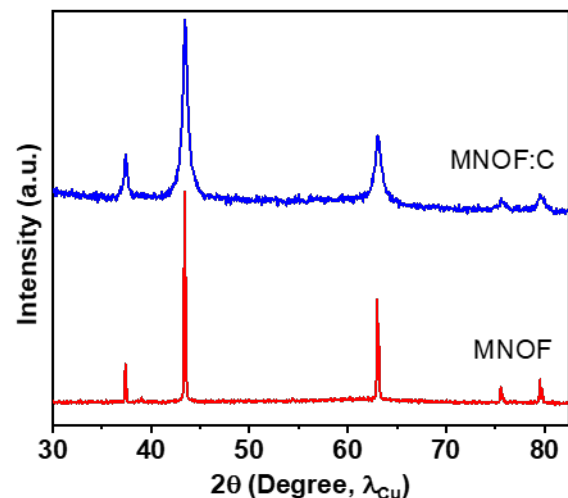


Reduced
O₂ loss



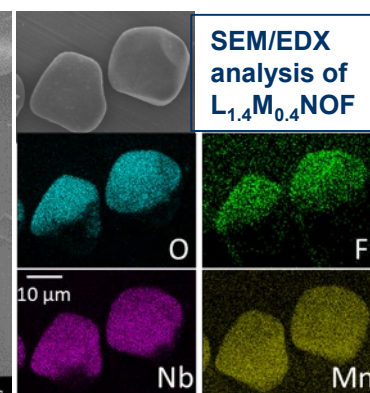
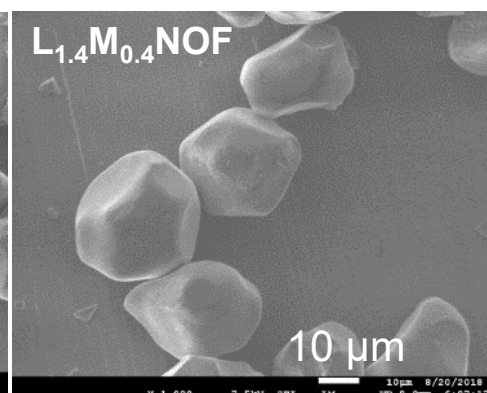
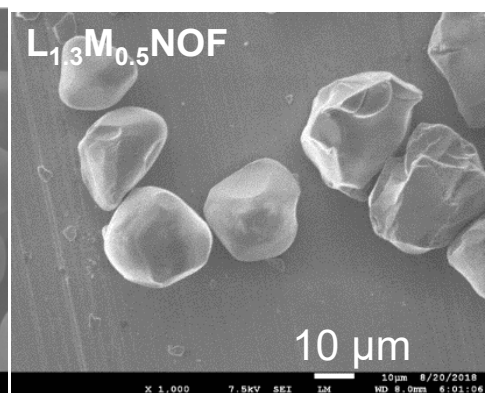
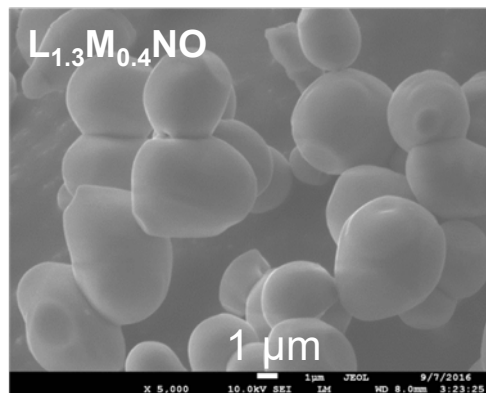
Approach/Accomplishment (1a): Controlled and scalable synthesis of fluorinated compounds

Wei Tong: Optimization of precursors, calcining conditions and cooling rate



See
poster
406

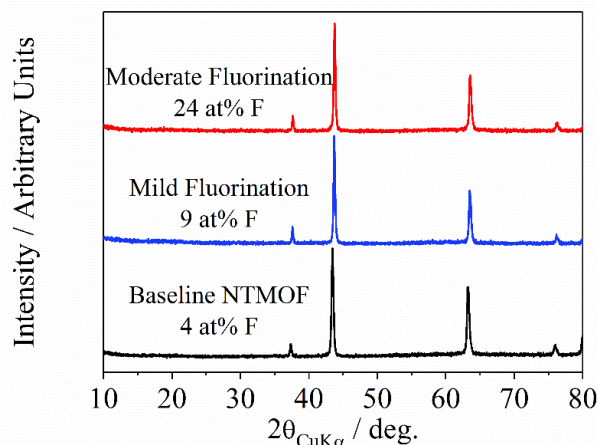
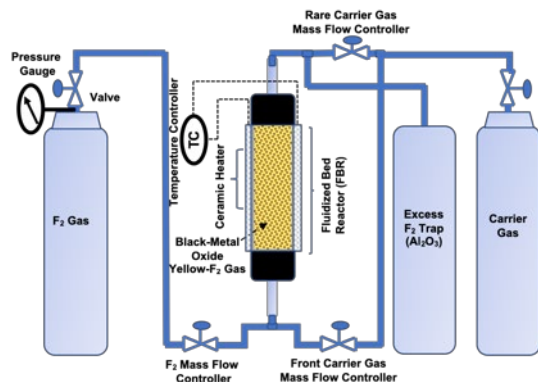
Guoying Chen: Molten Salt grown large particles for detailed characterization



Approach/Accomplishment (1b): Novel ways to bring Fluorine into the compound

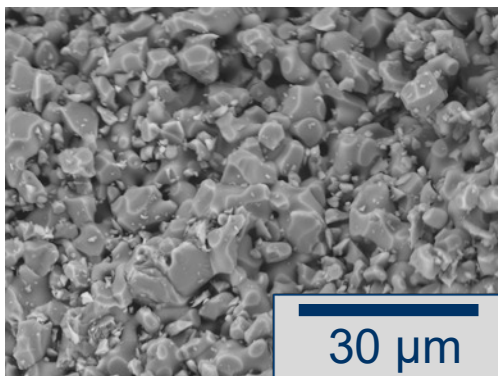
Chen/Ceder: Evaluating solubility limit when using different precursors

Nanda (ORNL): Fluorination of DRX-oxides or precursors

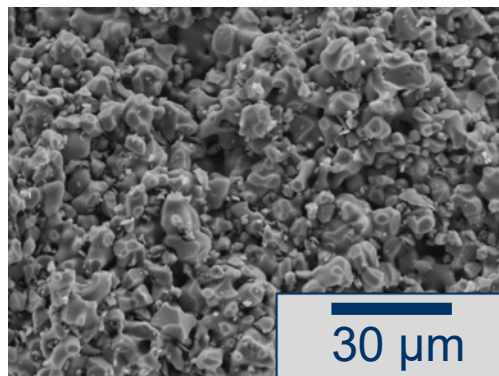


Already shown that can increase F-content of mildly fluorinated starting materials

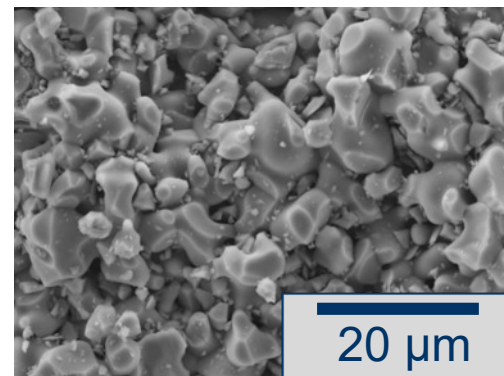
Unmodified LMNOF



Mild Fluorination



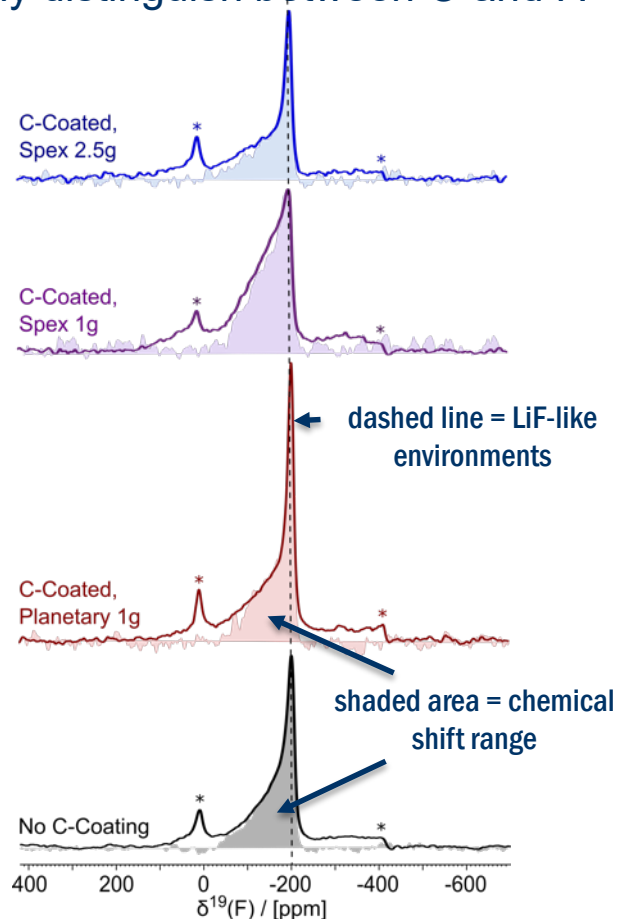
Moderate Fluorination



Approach/Accomplishment (2): Characterization

F-content and location: Clement (UCSB):

NMR is best probe to detect F in cathode bulk as unlike neutrons or Xrays, NMR can easily distinguish between O and F.



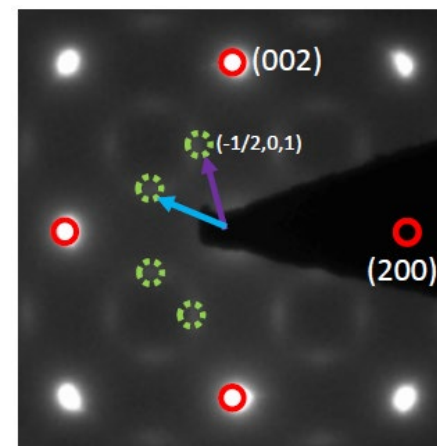
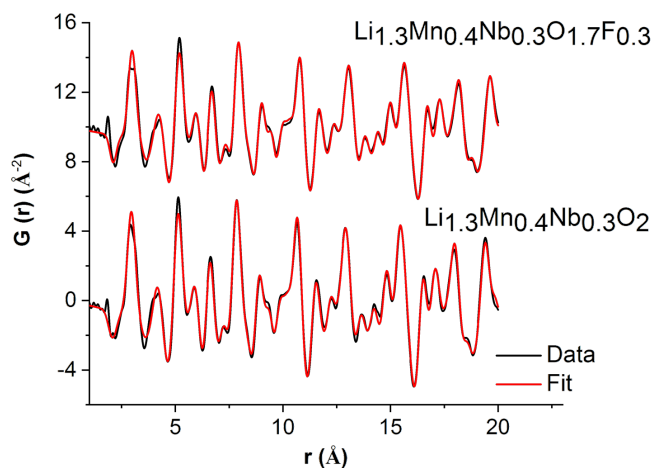
Evaluation of samples with various C-coating approaches

Cation short-range order characterization by Neutron pdf and TEM: (Nanda (ORNL), Ceder/Chen (LBNL), Wang (PNNL))

Long-Range Structure: Fm-3m

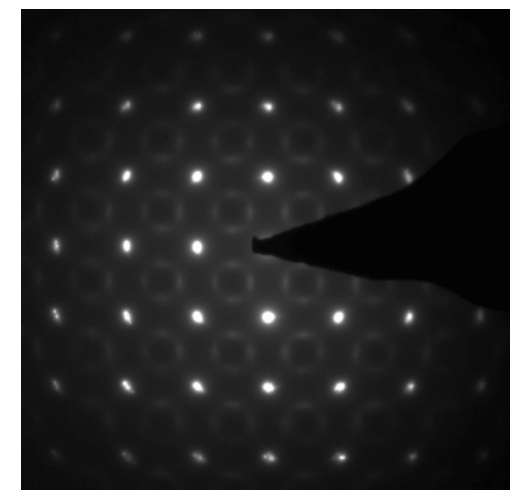
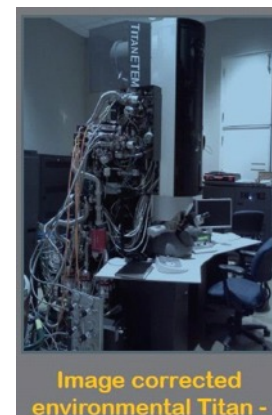
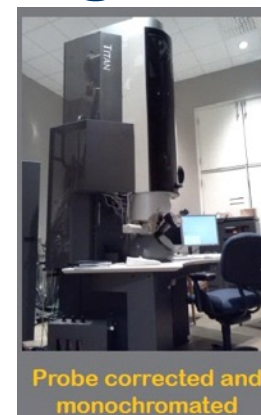
Short-Range Structure (< 5 Å)

Short-range ordering deviates from randomly disordered rock-salt structure. Fluorination changes short-range order



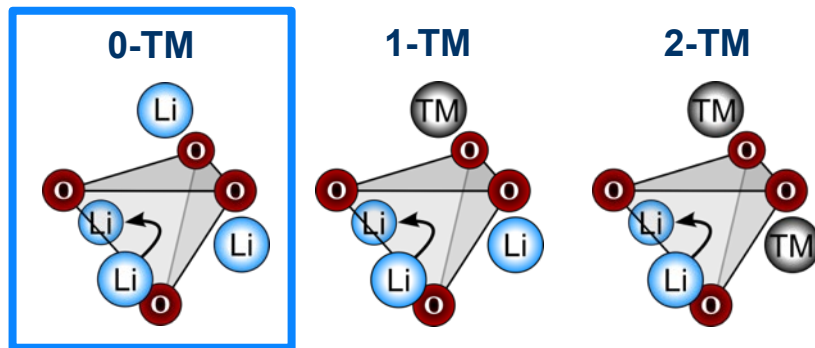
Approach/Accomplishment (3): TEM visualization of short-range cation-ordering

Chongmin Wang (PNNL)



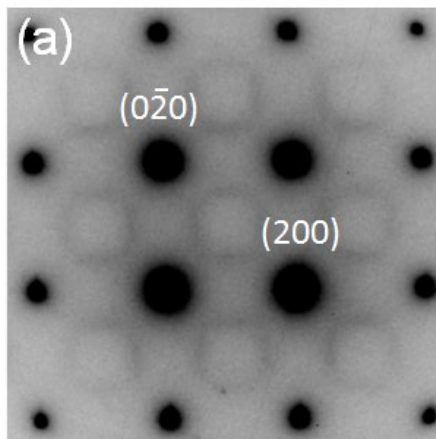
STEM-HAADF image reveals short range order in $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$ (MNOF)

Accomplishment: Why SRO is important

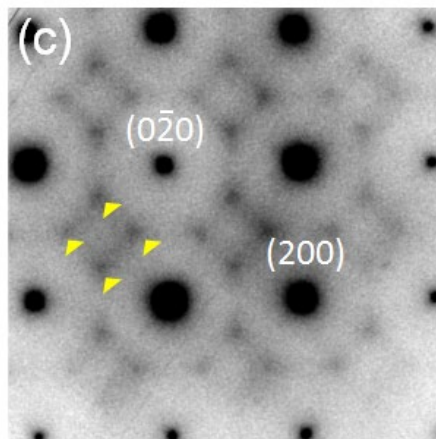


Cation SRO modifies the local arrangement of cations to modify the occurrence of 0-TM clusters. This changes the Li diffusion

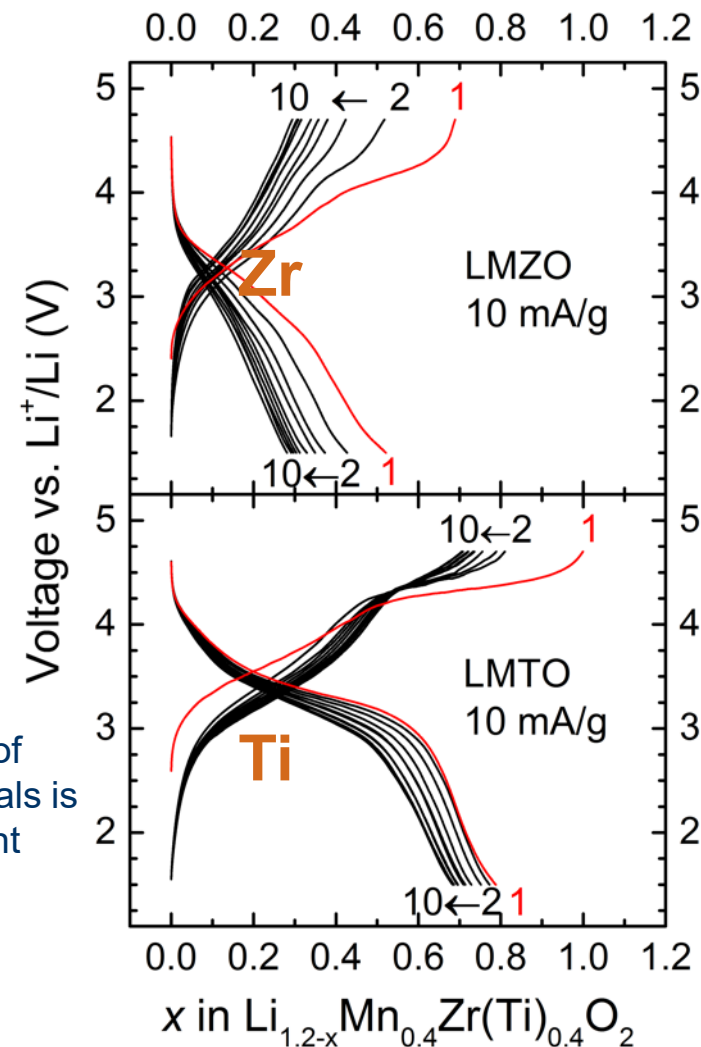
LMTO [100]
Observed



LMZO [100]
Observed

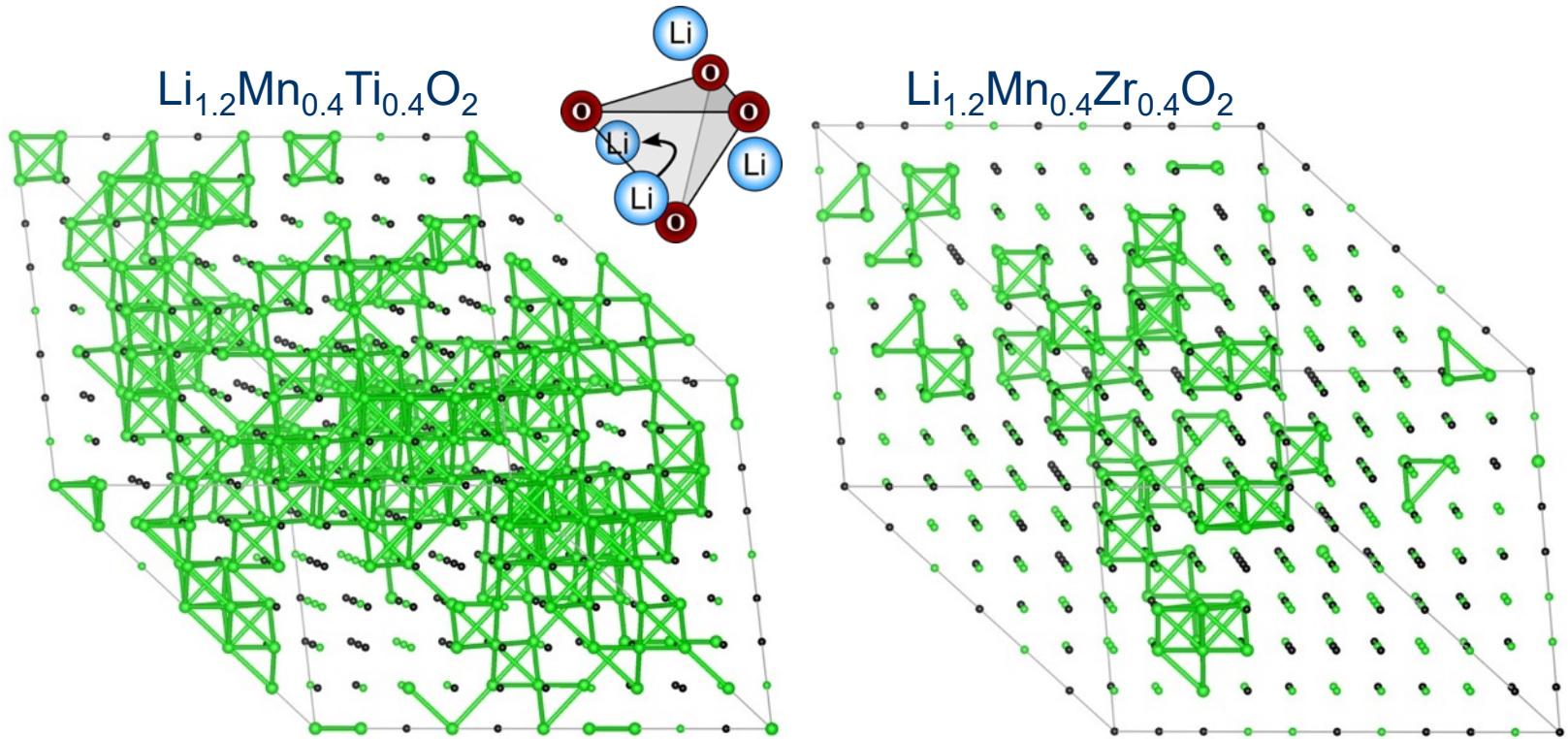


Different performance of similar materials is due to different SRO



Accomplishment: Modeling SRO

Percolation path from computed Short Range Order (SRO)



Percolation path in compound is much better than in Zr compound, consistent with the performance difference between the two compounds

Approach/Accomplishment (3): Soft-Xrays

Wanli Yang

Understanding/control of redox activity between anion/transition-metal is important for limiting hysteresis and capacity loss

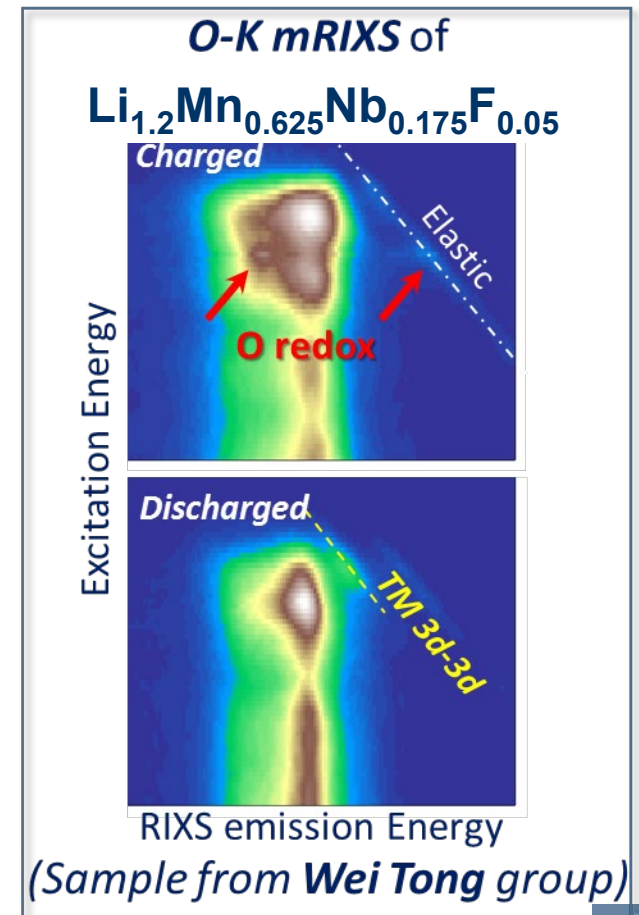
An ultimate probe of both **transition-metal** (mRIXS-iPFY) and **oxygen** (mRIXS-sPFY) redox mechanism:

- On the surface & in the bulk
- Upon transition-metal doping/stoichiometry
- Upon F-doping
- Upon electrochemical potentials and cycles

Some questions to answer:

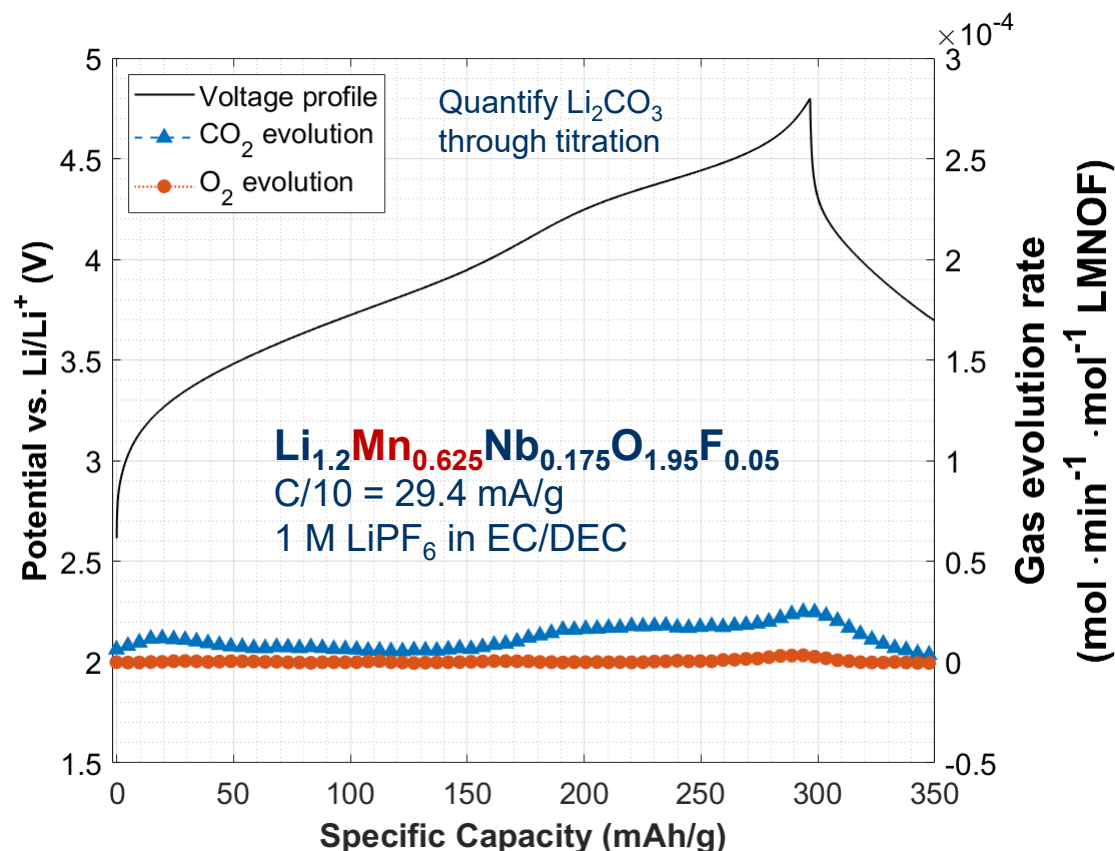
- Reversibility lattice oxygen redox in DRX
- Evolution of transition-metal redox in DRX
- F effects on transition-metal states
- F effects on oxygen activities
- F effects on surface states (TMs & O)

➤ *Complement other materials, structural, gas release experiments and calculations in the program*



Approach/Accomplishment (3): Measurement and modeling of oxygen release at surface

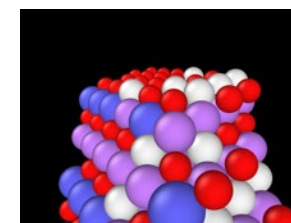
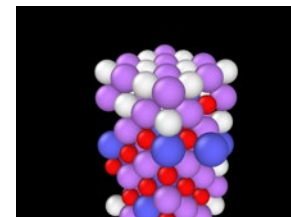
McCloskey: DEMS



Persson: surface modeling

Surface chemistry impact

Impact of F/Nb/Mn/Ti content on surface on oxygen release

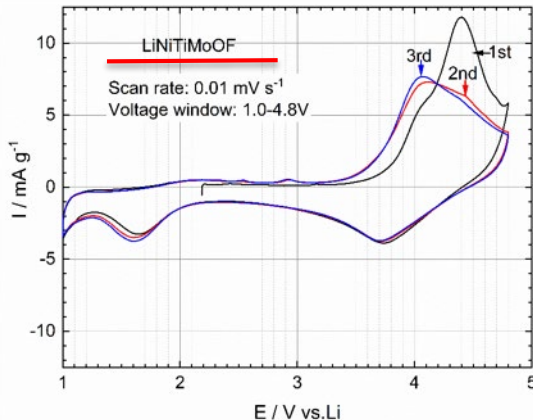
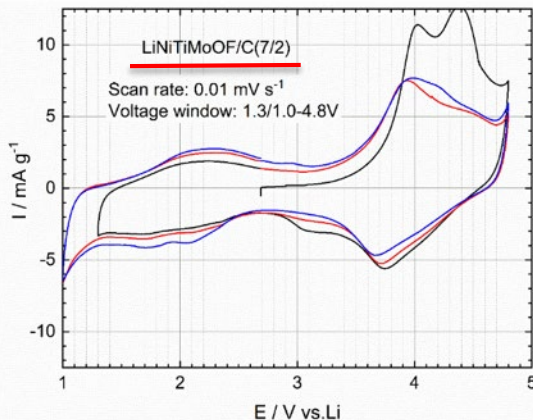


Accomplishment: Benchmark performance established with small materials quantities

Battaglia (LBNL)

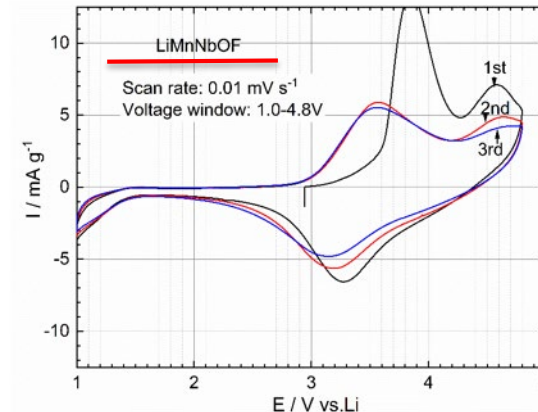
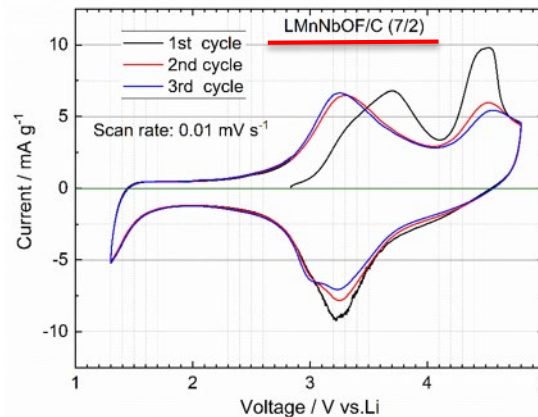
LiNiTiMoOF

w/ and w/o CB ball milling



LiMnNbOF

w/ and w/o CB ball milling



The first anodic sweep is different than the following anodic sweeps.

All sweeps after the first anodic sweep are similar.

- All changes to capacity occur in first anodic sweep.

There is less voltage hysteresis in cells with ball-milled carbon-black (less resistance)

LiNiTiMoOF shows more voltage hysteresis than LiMnNbOF.

Based on the results of the CV, to access most of the capacity while avoiding side reactions, cycle:

- LiNiTiMoOF between 1.3 and 4.6 V
- LiMnNbOF between 1.6 and 4.7 V

Summary

DRX compounds are promising dense cathodes with flexible cation and anion chemistry and high energy density

Fluor substitution of oxygen improves cycle life, reduces oxygen loss and polarization. High F-content can be used for double redox $\text{Mn}^{2+/4+}$, creating a low-cost, high capacity double redox couple

This “deep-dive” program has assembled the necessary technical strengths to investigate the key issues in DRX compounds: maximize F-content in a scalable synthesis method, characterize and model short-range cation structure to understand and optimize Li-ion transport, characterize and model surface structure after cycling to understand and mitigate oxygen loss, establish baseline performance in real pouch cells.

DRX compounds are a viable direction to create high energy density Co-free cathode materials

Remaining Challenges and Barriers

❑ **Improve cycle life**

- ❖ Cycle life is very good when voltage window is limited. But higher charge voltage gives higher energy density, but reduces life.
- ❖ Our strategy is to reduce oxygen loss and surface densification by increasing fluorine and transition metal content which reduces the oxygen activity

❑ **Improve rate capability**

- ❖ We need to understand if the rate limit is intrinsic to the material or related to surface densification as each has different mitigation strategies

❑ **Process control on synthesis to tailor and control cation short range order (SRO)**

- ❖ Cation SRO is a useful handle to modify the voltage profile and Li-ion mobility. Need to optimize it through modeling and selected heat treatments

Proposed Future Research

❑ Task 1: Synthesis

- ❖ Assess limits of fluorine substitution by solid-state methods by using different precursors, doping, after-treatment

❑ Task 2: Characterization/Modeling

- ❖ Better understand bulk and surface structure to understand origin of rate limitation

❑ Task 3: Cell making

- ❖ Develop pouch cells of DRX compounds. Optimize binder, carbon an coating method for these materials.

Partners and Collaborations

Chongmin Wang (PNNL)

Jagjit Nanda (ORNL)

Raphael Clement (UCSB)

Feng Wang (BNL)

LBNL: Kristin Persson, Guoying Chen, Wei Tong, Vince Battaglia, Wanli Yang (ALS), R. Kostecki, Huiwen Ji



UC SANTA BARBARA

Responses to Reviewers' Comments

This is a new project – no previous comments

Publications and Presentations

Publications

- E. Zhao, Q. Li, F. Meng, J. Liu, J. Wang, L. He, Z. Jiang, Q. Zhang, X. Yu*, L. Gu*, W. Yang*, H. Li, F. Wang*, X. Huang, Stabilizing the Oxygen Lattice and Reversible Oxygen Redox Chemistry through Structural Dimensionality in Lithium-Rich Cathode Oxides , **Angew. Chem. Int. Ed.** **58**, 4323–4327 (2019)
- J. Xu, M. Sun, R. Qiao, S. E. Renfrew, L. Ma, T. Wu, S. Hwang, D. Nordlund, D. Su, K. Amine, J. Lu, B. D. McCloskey, W. Yang, W. Tong*, “Elucidating Anionic Oxygen Activity in Li-Rich Layered Oxides,” **Nature Communications** **9**, 947 (2018).
- Y. Shin, W. H. Kan, M. Aykol, J. K. Papp, B. McCloskey, G. Chen and K. A. Persson, “Alleviating Oxygen Evolution from Li-excess Oxide Materials through Theory-guided Surface Protection,” **Nature Communications** **9**, 4597 (2018). DOI: 10.1038/s41467-018-07080-6.
- W. H. Kan, C. Wei, D. Chen, T. Bo, B.-T. Wang, Y. Zhang, Y. Tian, J.-S. Lee, Y. Liu and G. Chen, “Evolution of Local Structural Ordering and Chemical Distribution upon Delithiation of Rock-Salt Structured $\text{Li}_{1.3}\text{Ta}_{0.3}\text{Mn}_{0.4}\text{O}_2$ Cathode,” **Advanced Functional Materials**, 1808294 (2019). DOI: 10.1002/adfm.201808294.
- W. H. Kan, B. Deng, Y. Xu, A. K. Shukla, T. Bo, S. Zhang, J. Liu, P. Pianetta, B.-T. Wang, Y. Liu and G. Chen, “Visualizing the Effect of Local Short-Range Ordering on Lithium-Ion Diffusion in $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ Single-Crystal Cathode,” **Chem**, **4** (9), 2108 (2018). DOI:10.1016/j.chempr.2018.05.008
- C. Deng, P. Skinner, Y. Liu, R. Hunt, M. Lau, M. Sun, C. Ma, W. Tong, J. Xu, and H. Xiong, “Li-Substituted Layered-Spinel Cathode Material for Sodium-Ion Batteries,” **Chemistry of Materials** **30**, 8145-8154 (2018)

Presentations:

(MROP) 2019, UCSB, Jan 30th-31st, 2019: "Cation-Disordered Lithium Transition Metal Oxyfluoride Cathodes".

- UCSB-Grenoble workshop, April 18th-19th, 2019: "Redox in rocksalt oxyfluorides approached by solid-state NMR and theory"

Critical Assumptions and Issues

- ❖ Cycle life can be improved
- ❖ Rate capability can be improved