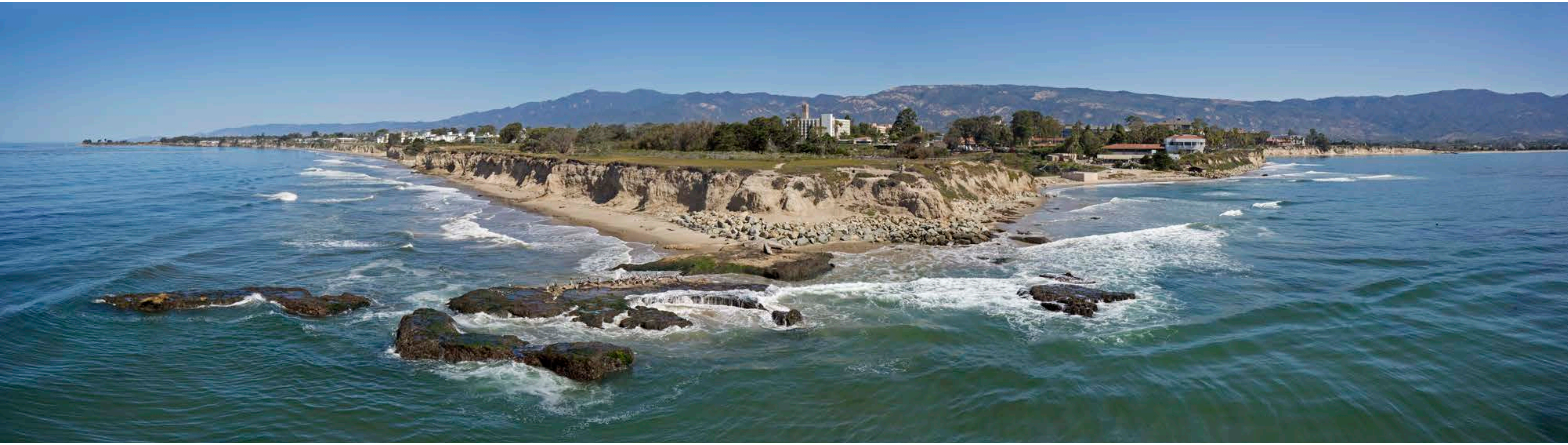
High Energy Cobalt-Free Disordered Rocksalt Lithium-ion Cathodes



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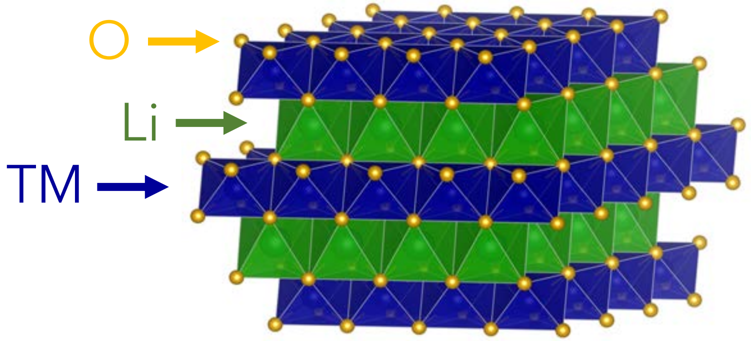
UC SANTA BARBARA MRL Materials Research Laboratory

CBMM webinar
Oct. 21st, 2020

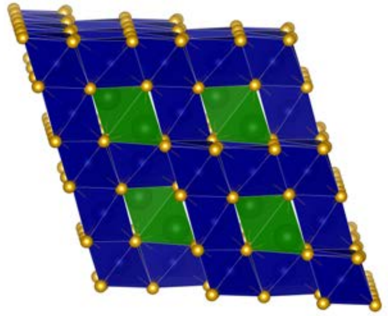
UC SANTA BARBARA MATERIALS

Current Li-ion technology relies on layered transition metal oxide cathodes based on Mn, Co, and Ni

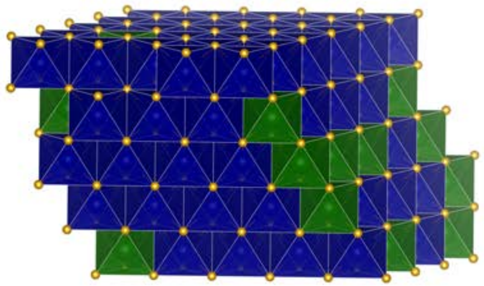
Layered rocksalt $LiMO_2$



Structural transformations on TM migration



spinel



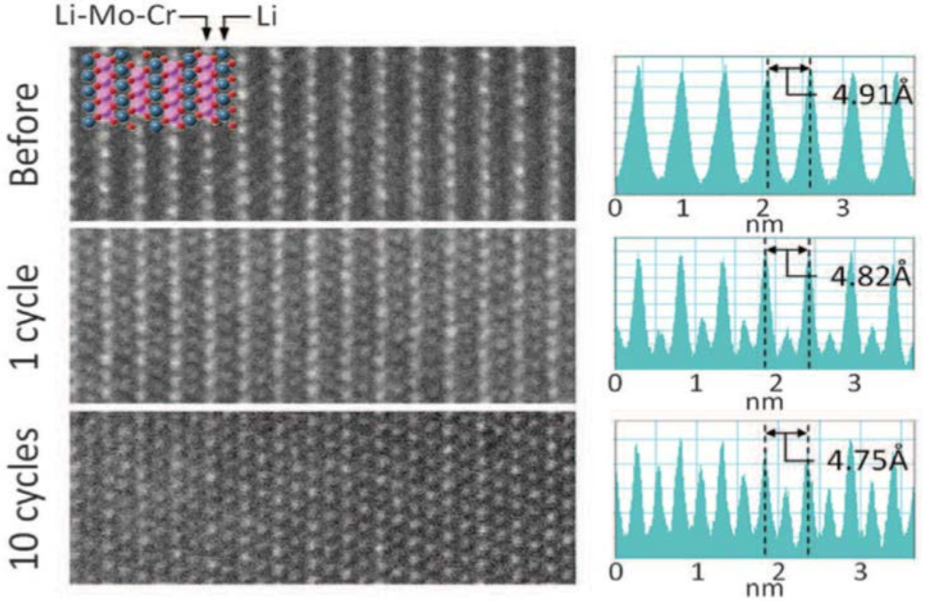
rocksalt

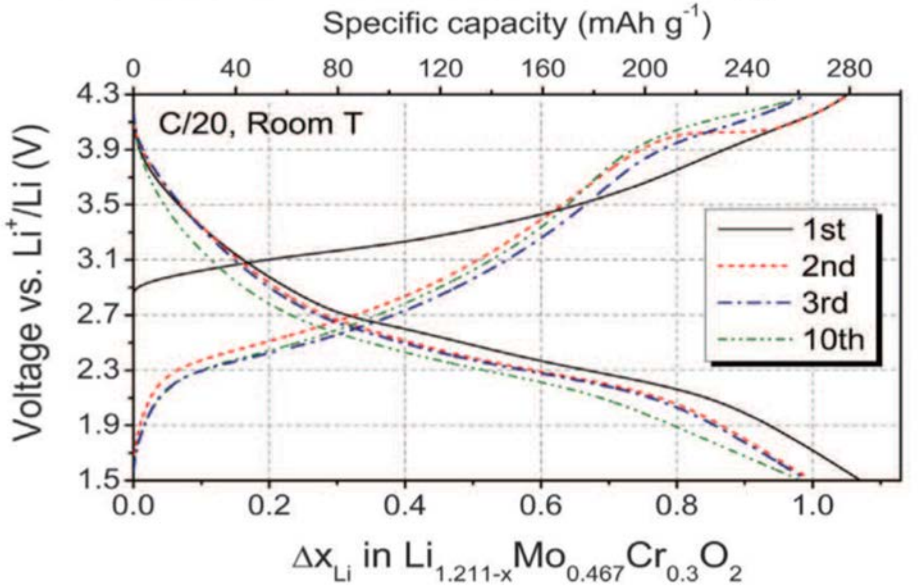
- Layered structure enables facile Li^+ extraction and reinsertion upon charge-discharge, ✓
- Large volume changes on Li^+ extraction perpendicular to the planes,
- Stable layered structure relies on presence of transition metal (TM) species with strong preference for octahedral (O_h) site occupation: Mn(IV), Co, Ni,
- TM migration at high voltage involves occupation of intermediate tetrahedral (T_d) site and can result in irreversible transformation to spinel or rocksalt structure.

Has the cation ordering paradigm become obsolete?

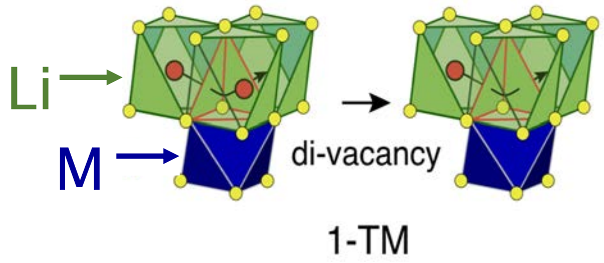
"Having well-ordered structures where there is little or no intermixing between the Li and the TM sublattice is generally considered important for obtaining high-capacity cathode materials with good cycle life".

- $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ disorders upon cycling and Li layer spacing decreases from ~2.63 Å to ~2.39 Å.
- Yet, high energy density (660 Wh/kg between 1.5 and 4.3V) and little capacity fade observed for C coated cathodes.
- This entails good Li^+ diffusion despite disorder. Hence, unlike layered oxides, Li^+ diffusion mechanism does not depend on height of intermediate tetrahedral site.

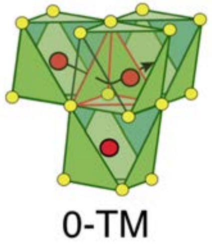




layered oxides

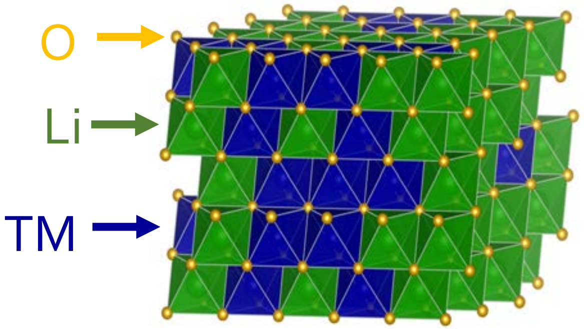


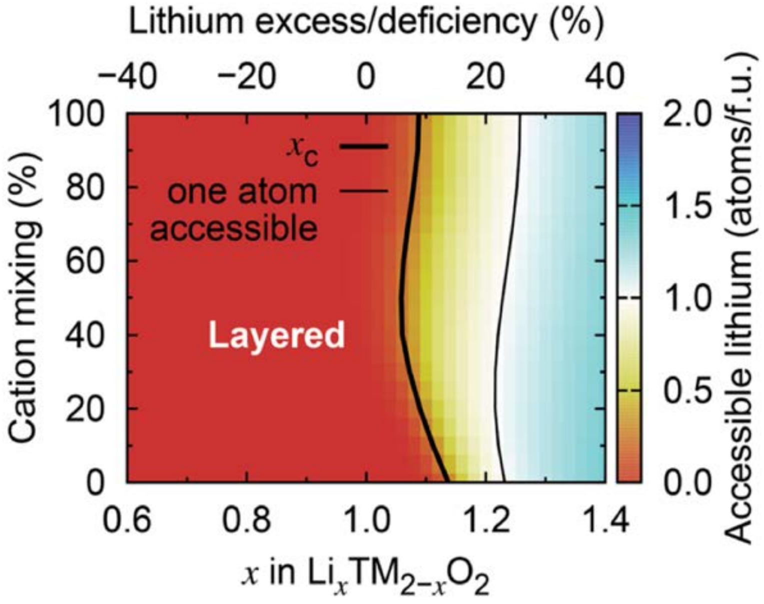
disordered rocksalt



Lee, Urban, Li, Su, Hautier, Ceder, Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Batteries, *Science* **343**(6170), 519 (2014)

Several design criteria have been identified for high performance disordered rocksalt (DRX) cathodes





- Stabilization of disordered rocksalt (DRX) oxide structure relies on presence of d^0 TM species (Mo^{6+}, Nb^{5+}, Ti^{4+}, Zr^{4+}) that can accommodate highly distorted O_h sites.
- Redox-active species occupy more regular O_h sites in structure.
- Li excess ($Li_xTM_{2-x}O_2$ with $x \geq 1.1$) needed for Li percolation upon cation disordering.

Li excess ($x \geq 1.1$) for percolation → $Li_xTM_{2-x-y}TM'_yO_2$

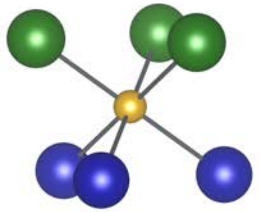
redox-active high valent, d^0 metal

- Reduction in average cation valence (Li excess) compensated by high-valent d^0 TM' species.
- Reduction in TM content compensated by reduction in redox-active TM valence upon incorporation of high-valent d^0 species.

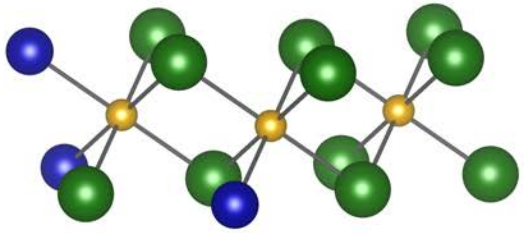
Urban, Lee, Ceder, The configurational space of rocksalt-type oxides for high-capacity lithium battery electrodes, *AEM* **4**(13), 1400478 (2014);
Urban, … Ceder, Electronic-structure origin of cation disorder in transition-metal oxides, *PRL* **119**(17), 176402 (2017).

Cation disorder enables fluorination and significant improvements in performance for DRX cathodes

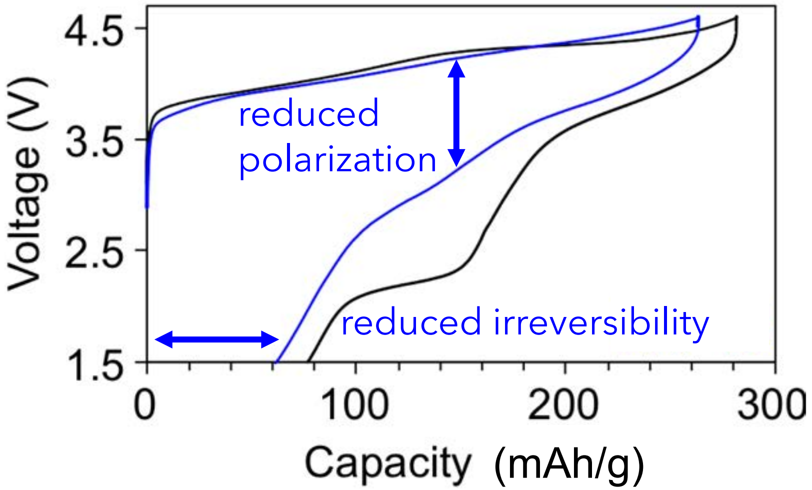
- F substitution for O in layered oxides prohibited by large TM-F bond formation energy. Predicted F solubilities < 0.8% for typical TM oxides.
- E_f(Li-F)<<E_f(TM-F): cation disorder results in Li-rich anion environments amenable to F substitution.



Anion environment in layered oxides: 3 x TM-F bonds



Li-rich anion environments obtained upon cation disordering



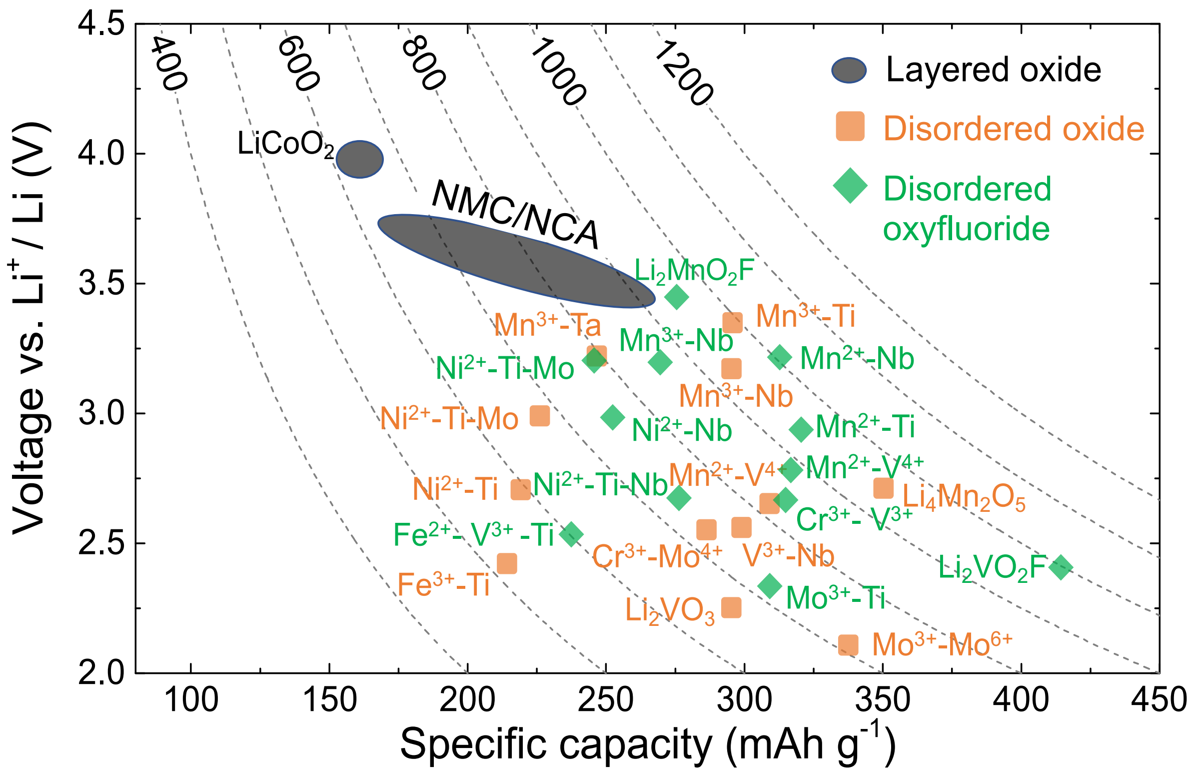
LNF15: $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

LN15: $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$

- Fluorination increases TM-based redox capacity. High voltage electrochemical processes more reversible than in oxides.
- Fluorination also increases the average potential (3V → 3.2V).
- Energy density:
  - 587 Wh/kg for LN15,
  - 790 Wh/kg for LNF15.

Richards, Dacek, Kitchaev, Ceder, Fluorination of lithium-excess transition metal oxide cathode materials, *AEM*, 1701533 (2017); Lee, Papp, Clément, …, Ceder, Mitigating oxygen loss to improve the cycling performance of high capacity cathode materials, *Nat. Commun.*, **8**(1), 981 (2017).

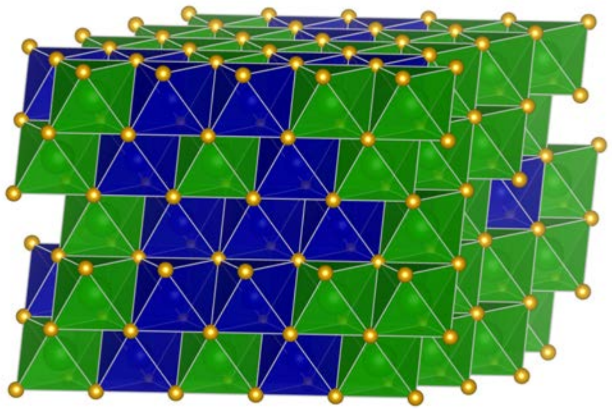
High energy density at a lower cost



Can reach ~1000 Wh/kg of energy density!

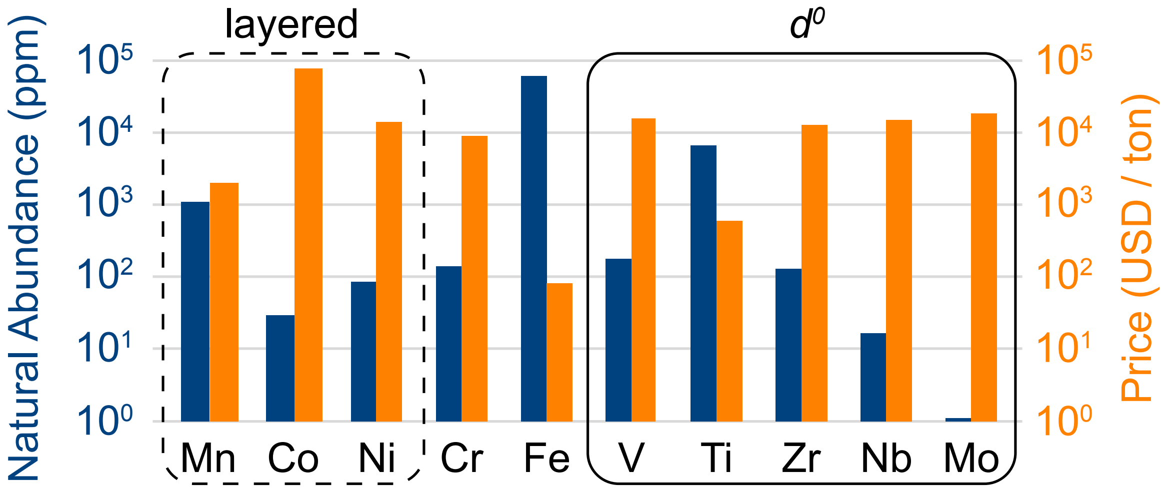
NMC: Li-Ni-Co-Mn-O_2

NCA: Li-Ni-Co-Al-O_2



$Li_xTM_{2-x-y}TM'_yO_2$ DRX cathodes

Enable the use of cheap and abundant metals.

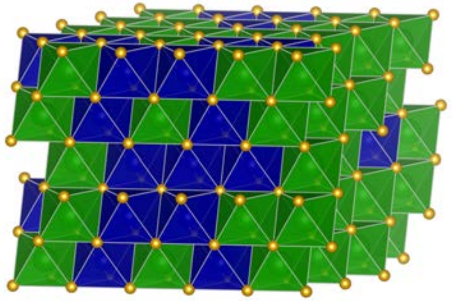


Clément, Lun, Ceder, Cation Disordered Rocksalt Transition Metal Oxides and Oxyfluorides for High Energy Li-ion Cathodes, *Energy & Environ. Sci.*, **13**(2), 345 (2019); www.webelements.com, www.metallary.com, U.S. Geological Survey, 2019

Processes at play in DRX cathodes are far from understood

- Characterization of DRX compounds is particularly tricky.
  - Cation disorder leads to several TM environments with different redox potentials → classical characterization tools (XAS) are not suited for the study of local electrochemical properties.
  - O and F cannot be distinguished with X-ray nor neutron diffraction.
  - Combination of ^{7}Li and ^{19}F solid-state nuclear magnetic resonance (NMR) and first principles calculations can provide insight into local structure and local redox processes.

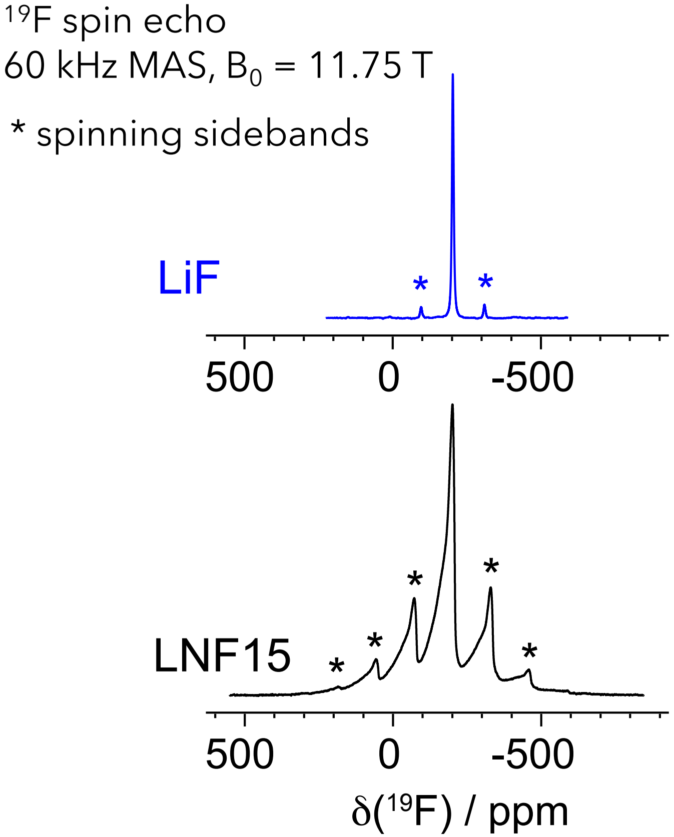
$Li_xTM_{2-x-y}TM'_yO_2$
DRX cathodes

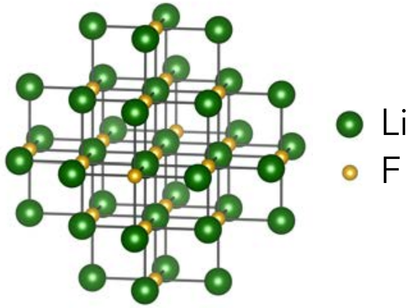


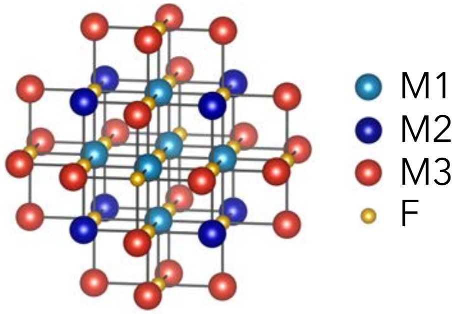
- Several questions remain unanswered, *e.g.*:
  - Does F incorporate the bulk DRX structure? What is the F solubility limit in DRX?
  - Extent and type of cation short-range order in DRX? How does is impact Li$^+$ diffusion and electrochemical properties?
  - How does fluorination affect short-range order? Li$^+$ diffusion? Overall performance?

^{19}F solid-state NMR of paramagnetic DRX cathodes

- Solid-state NMR is a local structure probe and the chemical shift (δ) provides information on the local environment of the nuclear species under investigation.







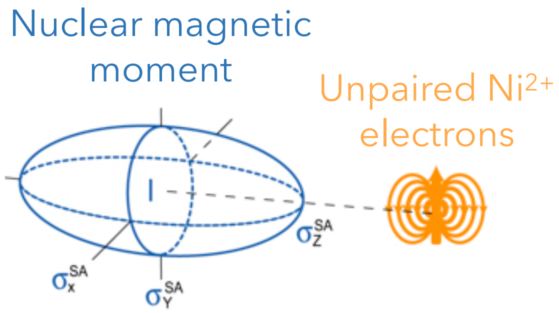
LNF15: $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

- In LiF: single F environment, where F surrounded by diamagnetic F/Li species.

  → single, sharp resonance at δ = -204 ppm.

- In LNF15: wide range of F environments, surrounded by Li^+, Ni^{2+}, Mo^{6+}, Ti^{4+} species distributed amongst M1, M2, M3 sites.

  → paramagnetic Ni^{2+} results in signal broadening and large shift of resonance away from δ = -204 ppm.


Nuclear magnetic moment

Unpaired Ni^{2+} electrons

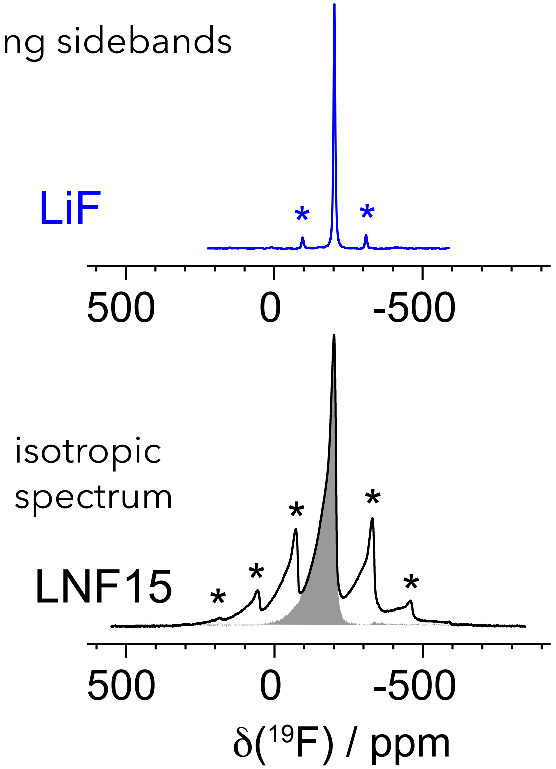
  → large number of F environments results in overlapping NMR signals and distribution of chemical shifts.

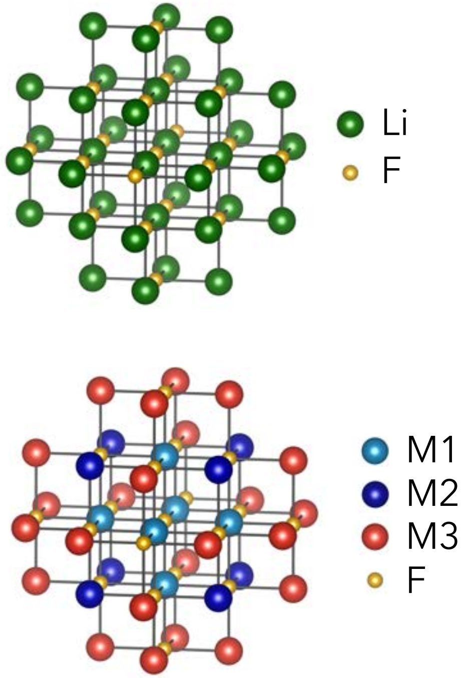
Clément, Kitchaev, Lee, Ceder, Short-range Order and Unusual Modes of Ni Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode, *Chem. Mater.*, **30**(19), 6945 (2018)

^{19}F indicates incorporation of F into the bulk cathode, but a detailed assignment requires simulations

^{19}F spin echo
60 kHz MAS, $B_0 = 11.75$ T

* spinning sidebands





LNF15: $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

What does ^{19}F NMR reveal about the nature of F environments in the DRX cathode?

Paramagnetic contributions to the ^{19}F NMR shift?

→ paramagnetic NMR calculations.

Distribution of F environments in the material?

→ Monte Carlo simulations & DFT calculations.

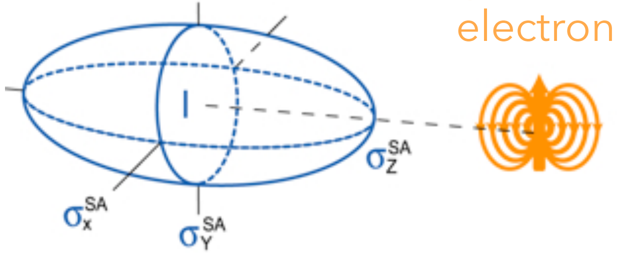
Clément, Kitchaev, Lee, Ceder, Short-range Order and Unusual Modes of Ni Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode, *Chem. Mater.*, **30**(19), 6945 (2018)

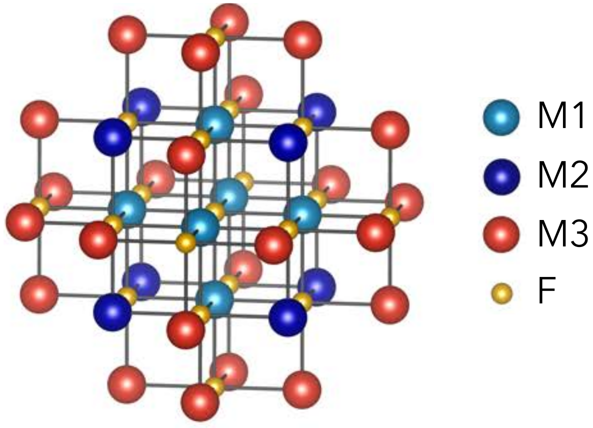
First principles predictions of ^{19}F NMR parameters

- Paramagnetic chemical shift results from delocalization of electron spin density from the Ni^{2+} *d* orbitals to the ^{19}F nucleus.

Nuclear magnetic moment

Unpaired Ni^{2+} electrons





$$\delta \propto \rho(r = 0)$$

↑

Unpaired spin density at nuclear position obtained from first principles.

Shift contributions for Ni^{2+} in M_1, M_2 and M_3 positions:

Interaction type	δ(Ni^{2+}) / ppm*
M1 (~2.1 Å)	5521
M2 (~3.6 Å)	-27
M3 (~4.6 Å)	13

nearest-neighbor Ni^{2+} leads to very large shift

Paramagnetic linebroadening:

# nn Ni	$\lvert\Delta\delta\rvert$(Ni^{2+})/ppm*
0 Ni in M1	291
1 Ni in M1	5057

nearest-neighbor Ni^{2+} lead to very broad signal

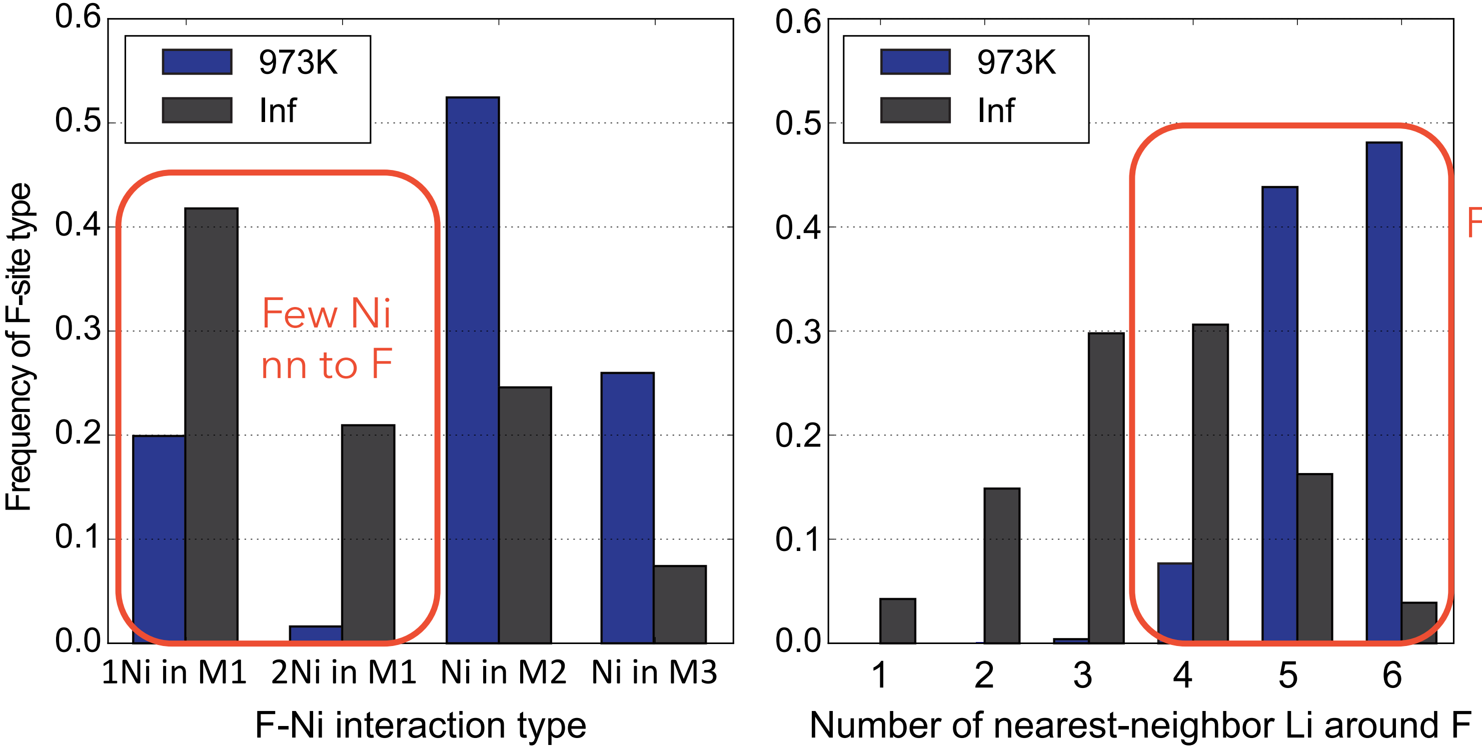
- F species directly bonded to paramagnetic Ni^{2+} are not observable experimentally.

* Average values obtained from hybrid DFT/HF calculations in CRYSTAL14 using B3LYP functional with 20% and 35% HF exchange.

Clément, Kitchaev, Lee, Ceder, Short-range Order and Unusual Modes of Ni Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode, *Chem. Mater.*, **30**(19), 6945 (2018)

Determination of most favorable distribution of F sites from Monte Carlo simulations

- Two simulations* at 973 K (~synthesis temperature) and at 10^8 K (~statistical limit):



F substitutes O in 'Li-rich' FLi_6, FLi_5M, FLi_4M_2 sites

M=Ni, Ti, Mo

Short-range order minimizes number of high energy F-M bonds.

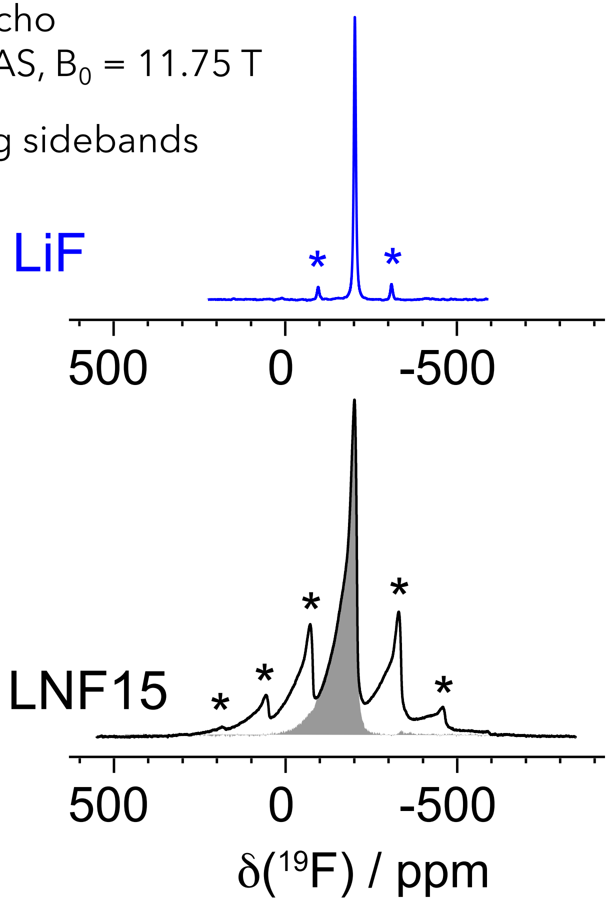
* Structure selection was performed using a cluster expansion Hamiltonian and DFT-computed interaction energies.

Clément, Kitchaev, Lee, Ceder, Short-range Order and Unusual Modes of Ni Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode, *Chem. Mater.*, **30**(19), 6945 (2018);

What type of F environments can NMR probe in the cathode?

^{19}F spin echo
60 kHz MAS, B_0 = 11.75 T

* spinning sidebands



LNF15: $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

What does ^{19}F NMR reveal about the nature of F environments in the DRX cathode?

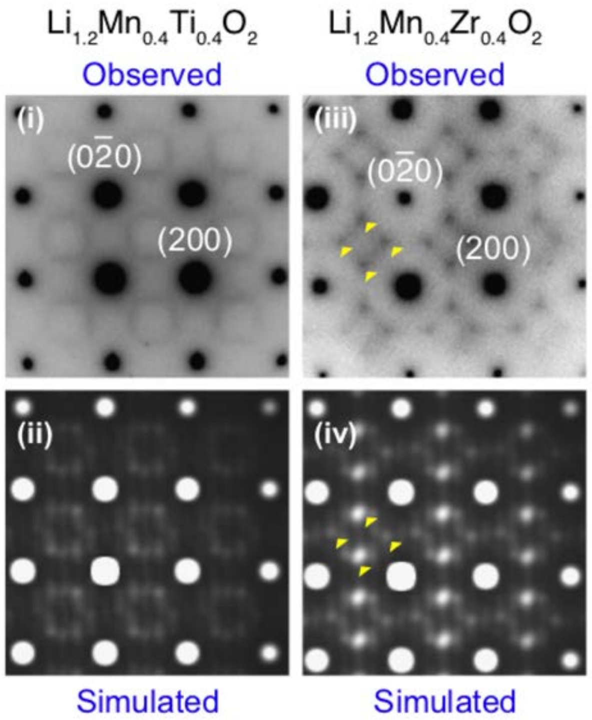
Paramagnetic NMR calculations
indicate that only F nuclei with no Ni nearest-neighbor can be observed with NMR.

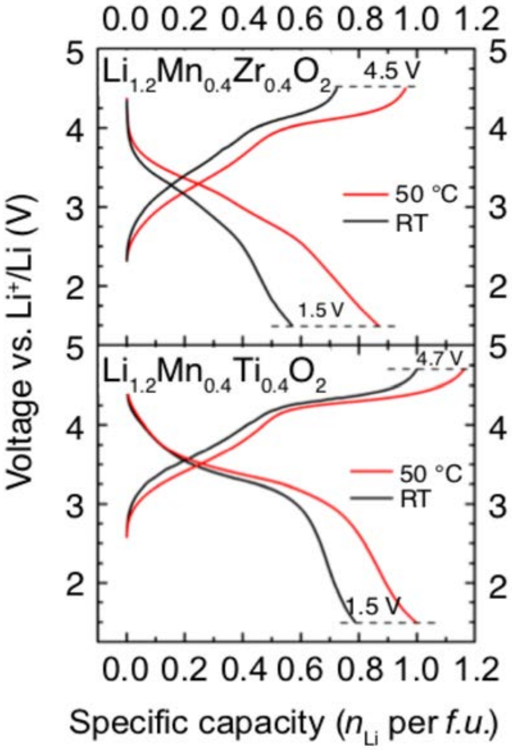
Monte Carlo simulations & DFT calculations
indicate that F substitution induces some short-range order, whereby most F are surrounded by 6 Li (~50%) and 5 Li (45%), and only 20% F are directly bonded to Ni.

Clément, Kitchaev, Lee, Ceder, Short-range Order and Unusual Modes of Ni Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode, *Chem. Mater.*, **30**(19), 6945 (2018);

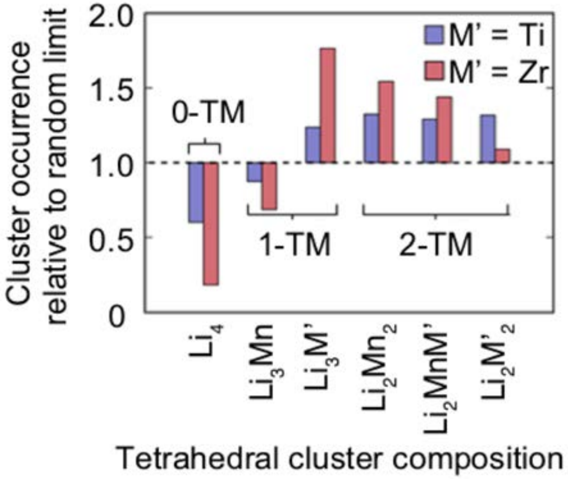
Short-range order is ubiquitous in DRX and affects Li^+ diffusion

- Comparative study of $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ and $Li_{1.2}Mn_{0.4}Zr_{0.4}O_2$ using electron diffraction and theoretical simulations indicates that nature of d^0 metal has a large influence on short-range order (SRO).





- SRO has a direct impact on proportion of 0-TM channels and on Li^+ percolation.



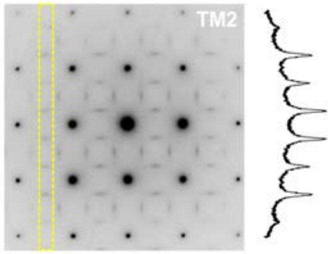
- At 50°C, LMZO delivers a reversible capacity of 0.87 Li per f.u., a 53% increase from that at room temperature. In contrast, the capacity of LMTO improves by only 27% to 1.0 Li per f.u., when cycled at 50 °C.

Ji, Urban, Kitchaev, Kwon, Artrith, Ophus, Huang, Cai, Shi, Kim, Kim, Ceder, Hidden structural and chemical order controls lithium transport in cation-disordered oxides for rechargeable batteries, *Nat. Commun.*, **10**(1), 592 (2019).

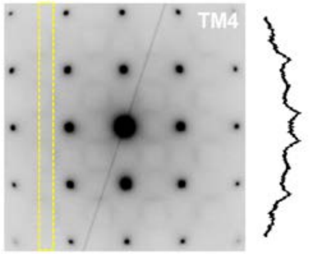
High entropy as a strategy to reduce short-range order

- Large configurational entropy of multi-principal element compounds is expected to results in a uniform distribution of TM species in the lattice and reduced short-range order.

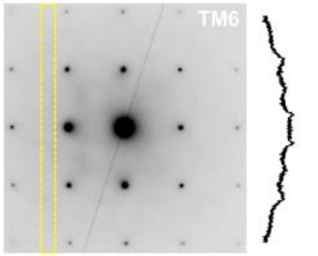
TM mixing reduces short-range order.



TM2: $Li_{1.3}Mn(III)_{0.4}Ti_{0.3}O_{1.7}F_{0.3}$

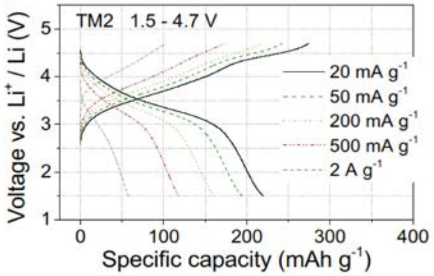


TM4:
$Li_{1.3}Mn(II)_{0.2}Mn(III)_{0.2}Ti_{0.1}$
$Nb_{0.2}O_{1.7}F_{0.3}$

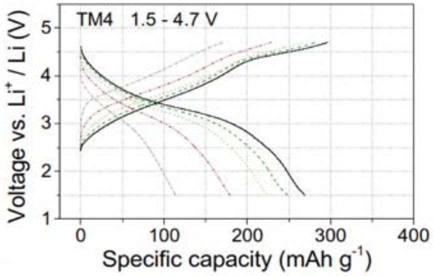


TM6:
$Li_{1.3}Mn(II)_{0.1}Co(II)_{0.1}Mn(III)_{0.1}$
$Cr(III)_{0.1}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$

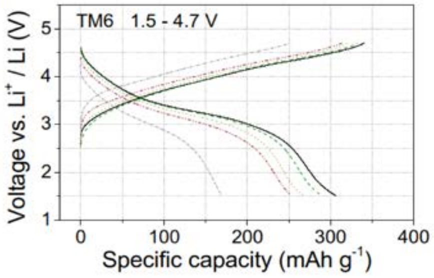
TM mixing results in improvements in energy density in rate capability.



- 704 Wh/kg
- 58 mAh/g at 2 A/g rate

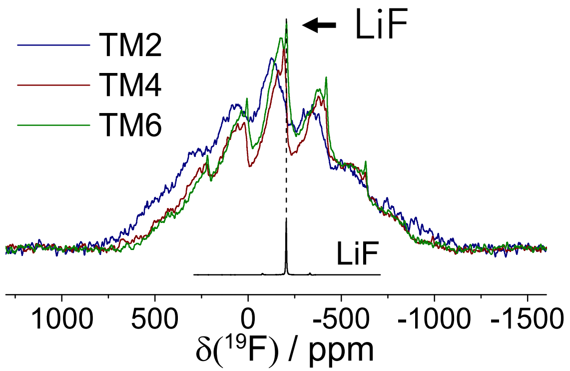


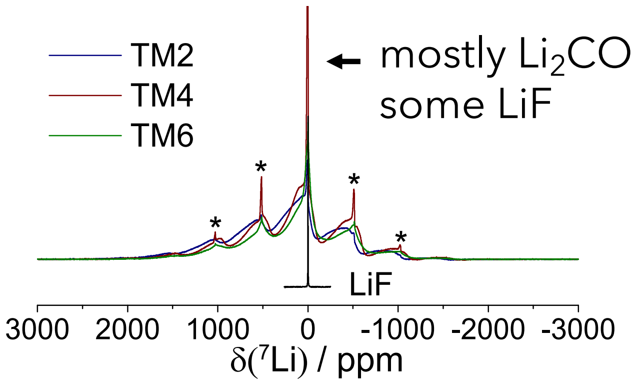
- 849 Wh/kg
- 110 mAh/g at 2 A/g rate



- 955 Wh/kg
- 170 mAh/g at 2 A/g rate (7 minute (dis)charge)

NMR indicates good incorporation of F in bulk DRX structure. Spectra still too broad to identify details of SRO.



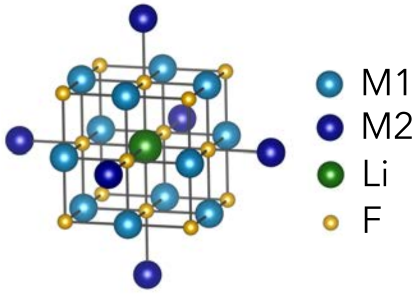


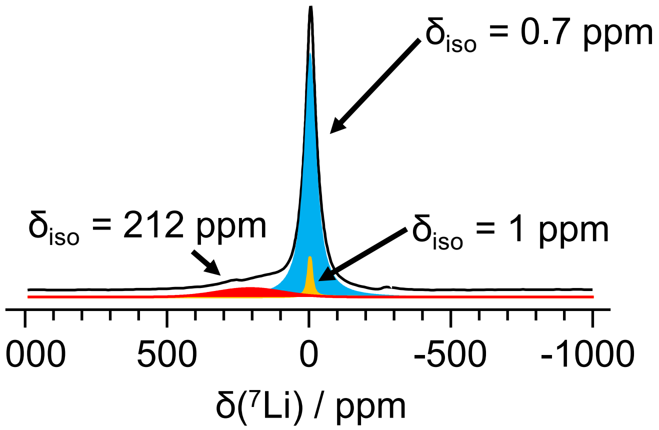
← mostly Li_2CO_3, some LiF

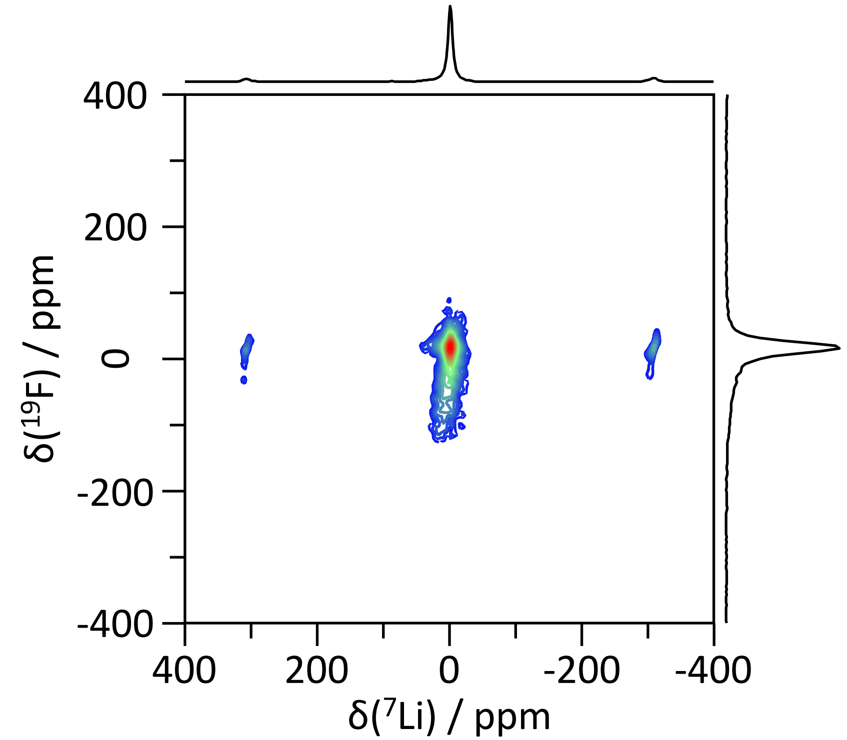
Lun, Ouyang, Kwon, Ha, Foley, Huang, Cai, Kim, Balasubramanian, Sun, Huang, Tian, Kim, McCloskey, Yang, Clément, Ji, Ceder, Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries, *Nat. Mater.*, in press.

Further insights into short-range from NMR spectroscopy

- By carefully choosing our composition we can identify various ^{7}Li environments in DRX cathodes.
- First principles NMR calculations to assign resonances.
- Monitor evolution of population of ^{7}Li sites across a series of samples to determine SRO.
- 2D correlation NMR experiments to obtain information on Li-F proximities.



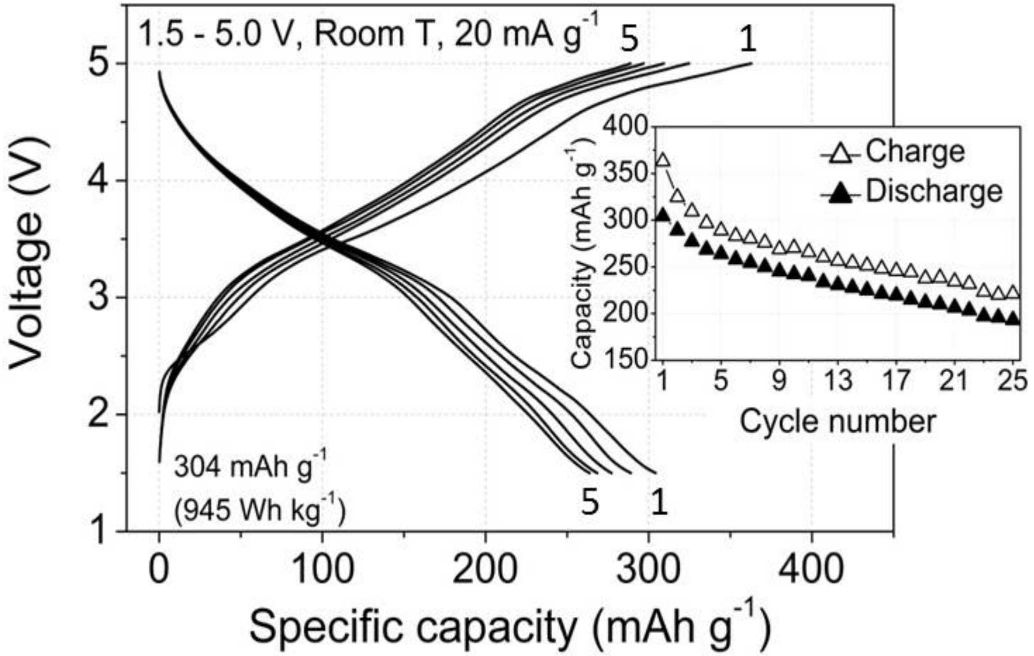




unpublished results

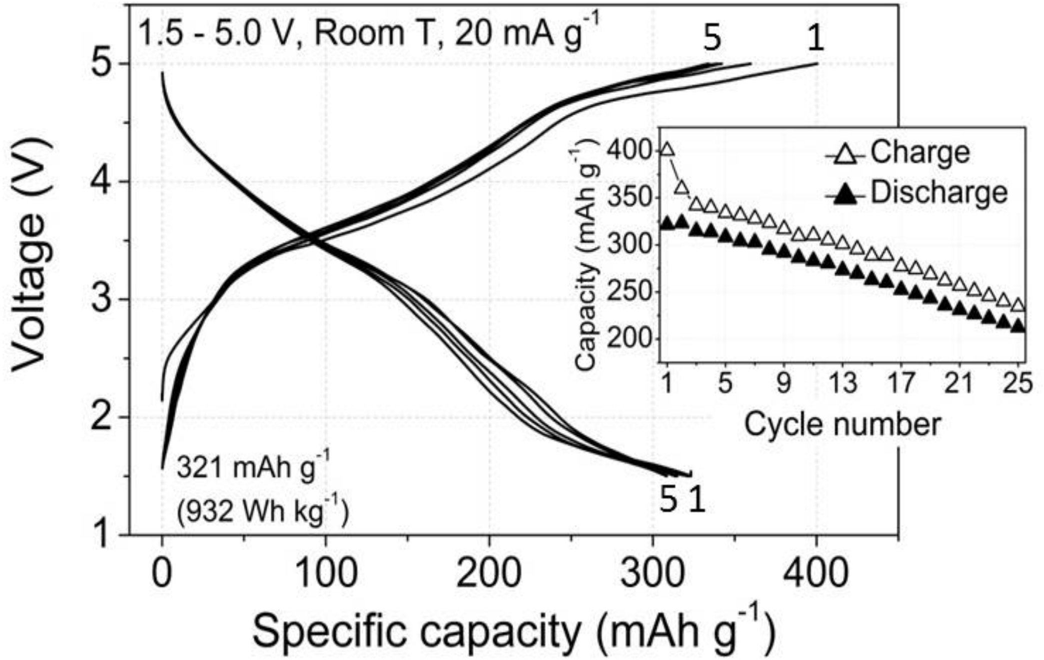
First demonstration of high energy cathodes based on $Mn^{2+/4+}$ redox chemistry

$Li_2Mn_{2/3}Nb_{1/3}O_2F$



Theoretical $Mn^{2+/4+}$ capacity: 270 mAh/g
2 Li extracted = 405 mAh/g

$Li_2Mn_{1/2}Ti_{1/2}O_2F$

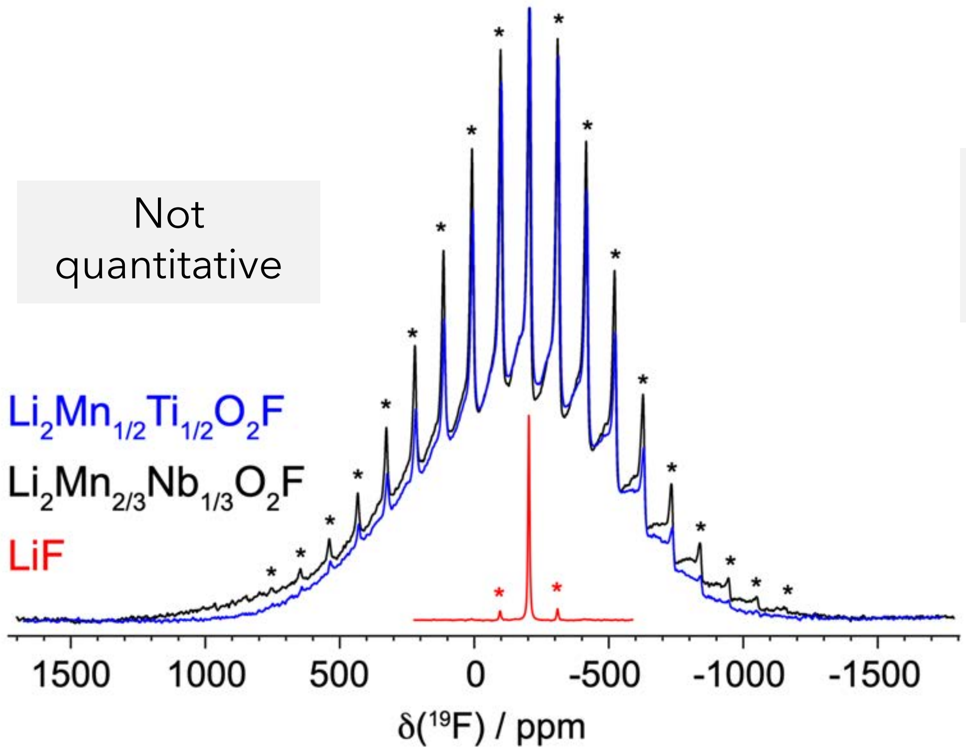


Theoretical capacity: $Mn^{2+/4+}$ = 230 mAh/g
2 Li extracted = 460 mAh/g

Lee, Kitchaev, Kwon, Lee, Papp, Liu, Lun, Clément, Shi, McCloskey, Guo, Balasubramanian, Ceder, Reversible Mn^{2+}/Mn^{4+} double redox in lithium-excess cathode materials, *Nature* **556** (7700), 185 (2018)

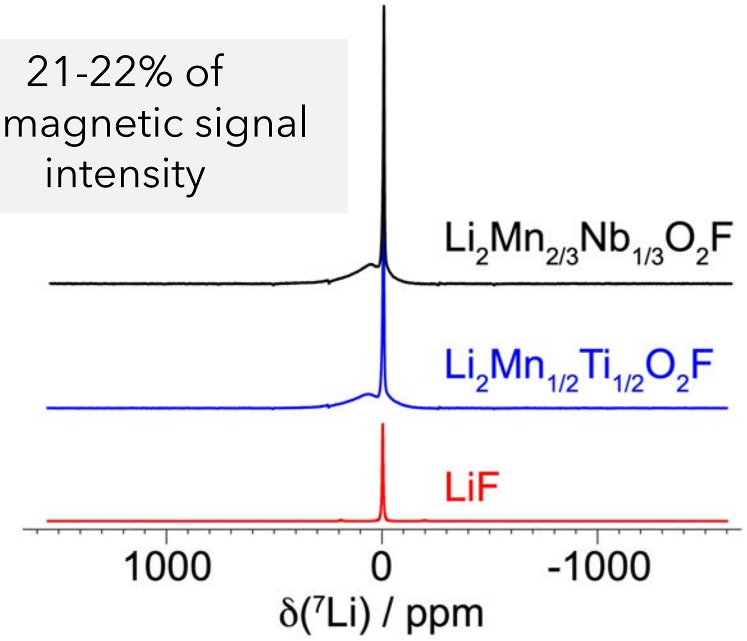
Impact of limited F solubility on the electrochemical performance

Sharp signal at this position (-204 ppm) indicates presence of LiF-like F sites



Not quantitative

Sharp signal at this position (0 ppm) indicates presence of diamagnetic Li sites (LiF, Li_2CO_3)



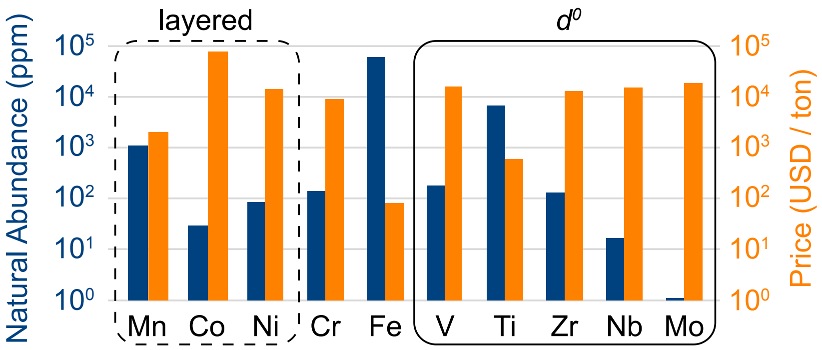
21-22% of diamagnetic signal intensity

- Residual LiF likely prevents side-reactions with the electrolyte at high voltage.

Lee, Kitchaev, Kwon, Lee, Papp, Liu, Lun, Clément, Shi, McCloskey, Guo, Balasubramanian, Ceder, Reversible Mn^{2+}/Mn^{4+} double redox in lithium-excess cathode materials, *Nature* **556** (7700), 185 (2018)

Summary

- DRX cathodes are promising Co-free alternatives to layered transition metal oxide cathode, achieving up to 1000 Wh/kg of energy density.



- Bulk F substitution for O can be achieved, resulting in more stable electrochemical cycling and higher average redox potentials.
- Short-range order depends on the nature of the d^0 species, as well as on F substitution, and can be reduced by increasing the configurational entropy of DRX cathodes.
- In turn, rate performance and energy density are improved in high entropy DRX cathodes.
- Unanswered questions: What is the optimal (and achievable) F substitution level? What are the major degradation pathways of DRX cathodes? How can we improve their long-term cyclability?

Acknowledgements


Clément group @ UC Santa Barbara

- Clément group: Raynald Giovine, Emily Foley, Howie Nguyen, Yuefan Ji.
- Collaborators: Zhengyan Lun, Daniil Kitchaev, Jinhyuk Lee, Huiwen Ji, Gerbrand Ceder and Ceder Group.

NSF DMR 1720256

National Science Foundation
MRSEC
Materials Research Science and Engineering Centers

MRL-MRSEC spectroscopy Facility & Dr. Jerry Hu.

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