

# Effect of Fluorination on Lithium Transport and Short-Range Order in Disordered-Rocksalt-Type Lithium-Ion Battery Cathodes

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Fluorine substitution is a critical enabler for improving the cycle life and energy density of disordered rocksalt (DRX) Li-ion battery cathode materials which offer prospects for high energy density cathodes, without the reliance on limited mineral resources. Due to the strong Li-F interaction, fluorine also is expected to modify the short-range cation order in these materials which is critical for Li-ion transport. In this work, density functional theory and Monte Carlo simulations are combined to investigate the impact of Li-F short-range ordering on the formation of Li percolation and diffusion in DRX materials. The modeling reveals that F substitution is always beneficial at sufficiently high concentrations and can, surprisingly, even facilitate percolation in compounds without Li excess, giving them the ability to incorporate more transition metal redox capacity and thereby higher energy density. It is found that for F levels below 15%, its effect can be beneficial or disadvantageous depending on the intrinsic short-range order in the unfluorinated oxide, while for high fluorination levels the effects are always beneficial. Using extensive simulations, a map is also presented showing the trade-off between transition-metal capacity, Li-transport, and synthetic accessibility, and two of the more extreme predictions are experimentally confirmed.

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# 1. Introduction

Over the past few decades, the application of lithium-ion batteries has expanded from portable devices to electric vehicles and grid storage. Commercialized cathodes for lithium-ion batteries are so far dominated by layered materials within the Li-Ni-Mn-Co-O composition space.<sup>[1-3]</sup> To further reduce cost and avoid over-reliance on geographically localized natural resources,<sup>[4]</sup> it would be beneficial to move away from Co based compositions toward lowercost metals such as Mn or Fe.<sup>[1,5]</sup> To this end, recent progress in cation-disordered cathode materials has widened the available chemistry space for materials design. In addition, Li excess disordered cathodes achieve very high capacity and energy density compared with typical layered materials, as demonstrated by several high-energydensity Co-free cathode materials.<sup>[6-8]</sup>

Disordered rocksalt (DRX) cathode materials have an "average" rocksalt-like

crystal structure, in which the cation sublattice is occupied by a mixture of cation species (Li and other metals) without longrange compositional order. These compounds can function as Li-intercalation cathodes despite their lack of long-range order because Li transport in DRX materials is facilitated by percolation of Li-rich local environments through which Li can easily migrate. One aspect of these materials that has been enormously beneficial to their energy density and cycling stability is their ability to incorporate fluorine.<sup>[9-11]</sup> Fluorine lowers the average cation valence enabling a higher fraction of the capacity to be derived from transition metal redox, rather than oxygen redox, which has been shown to be highly beneficial to cycle life of DRX compounds.<sup>[11,12]</sup> In addition, it may have stabilizing effects on the surface chemistry of these cathode materials as some highly fluorinated compositions can be charged to 5 V without any significant oxygen loss.<sup>[11]</sup>

In this work, we use first principles computations and Monte Carlo simulations to investigate the short-range order (SRO) and Li-percolation in seven of the most common DRX chemistries. We find that the fluorine indeed modifies the SRO, and therefore the cathode capacity, but its role is complex and its benefits on percolation is not simply linear with



fluorine content. Indeed, we observe that for typical Li-excess levels, Li-percolation deteriorates for low amounts of F substitution due to the Li-F gettering, especially in oxides that have good Li percolation properties when unfluorinated, but greatly improves for high levels of fluorine. Using extensive DFT-based Monte Carlo simulations we map the trade-off between electron capacity, Li-percolation, and synthetic accessibility to enable the rational optimization of fluorinated DRX materials that have both optimized metal redox capacity and kinetics. We experimentally verify these principles on two materials: In the Ni(II)-Ti-Mo system we show that fluorination significantly improves capacity even with only 5% of Li excess, a condition under which the pure oxide analogue would have poor capacity. In contrast, we show that in the Mn(II)-Nb system, which exhibits good Li transport in its pure oxide form, Li percolation is degraded at low fluorine concentrations.

## 2. Methods

In close-packed face-centered cubic (FCC) anion structures, the migration between adjacent octahedral sites occurs through a tetrahedral site. In DRX materials, it is the tetrahedral sites that do not face share with any transition metals (TM) (known as "0-TM sites") that allow for fast Li migration. These sites become percolating at a critical Li-excess concentration and thereby enable macroscopic Li transport. For a fully random cation arrangement, the critical Li-excess amount in  $\text{Li}_{1+x}M_{1-x}O_2$  compounds is  $x \approx 9\%$ ;<sup>[6,13]</sup> however, statistical SRO can enhance or diminish overall Li percolation depending on the nature of Li network.<sup>[14,15]</sup> Cation SRO is known to exist in DRX materials and varies significantly depending on the TM species present.<sup>[15]</sup> With the introduction of fluorine, the strong bonding preference between Li and F atoms induces additional SRO.<sup>[10,11,16]</sup> As suggested in previous work,<sup>[10,16]</sup> this interaction may give rise to a significant modification of the Li-ion transport upon F incorporation, but an in-depth understanding of the effect of fluorination on bulk Li transport is lacking.

To understand both the general and the compositiondependent SRO of fluorinated disordered rocksalt (F-DRX) materials, we employ two models. One is a simple qualitative model considering solely the pairwise attraction between Li and F, and it is applied to investigate the dominant effect of Li–F attraction on Li percolation. The other is a more complex quantitative cluster-expansion Hamiltonian model, parameterized from ab-initio calculations, that captures the interactions between all ions, and it is utilized to evaluate the specific chemistry dependence of the SRO in F-DRX.

# 2.1. Pair-Interaction Hamiltonian for General Fluorinated Rocksalts

Experimental and computational studies have demonstrated that Li–F bonds are strongly preferred over M–F bonds<sup>[10,16]</sup> (M = other metal cation species) in F-DRX materials. Therefore, the Li–F interactions are considered net attractive

(negative energy contributions), whereas the M–F interactions are considered net repulsive (positive) as compared to the average interaction (see schematic in Figure S1, Supporting Information). Based on the observation of this general trend, we constructed a pairwise interaction model that is, within the scope of our application, transferable to any (transition) metal species.

In a lattice model for configurational order/disorder, a single effective interaction parameter can be defined that is the difference of the Li–F interaction energy  $E_{\text{Li}-F}$  and the M–F interaction energy  $E_{\text{M}-F}$  as

$$J = \frac{E_{\rm M-F} - E_{\rm Li-F}}{2}$$
(1)

Within this simple pair-interaction model, the energy of occupying an anion site i by F (rather than by O) is

$$E_i^{\rm F} = J \sum_{j=1}^{6} \sigma_j \quad \text{with} \quad \sigma_j = \begin{cases} 1 \text{ if site } j \text{ is a M site} \\ -1 \text{ if site } j \text{ is a Li site} \end{cases}$$
(2)

where the sum runs over the six neighboring cation sites *j*. Further details of the pair-interaction model are given in Section S1 in the Supporting Information.

For a given composition  $\text{Li}_x M_{2-x} O_{2-y} F_y$ , the energy of a fully random atomic ordering is  $\overline{E}_{\infty}^F(x) = 6(1-x)J$ , which only depends on the ratio of Li to TM in the composition and is precisely 0 for the stoichiometric composition with x = 1. The energy of each atomic configuration can be expressed in terms of the effective interaction parameter *J* such that the physics of the system described by the lattice model only depends on the ratio  $(k_BT)/J$ .

### 2.2. Cluster-Expansion Hamiltonian

A complete model for the configurational thermodynamics of F-DRX materials needs to account for the Li and transition metals distributions on the cation sublattice as well as the O/F arrangement on the anion sublattice. Such a system with coupled disorder on multiple sublattices can be well studied with the coupled cluster-expansion approach.<sup>[17]</sup> The cluster-expansion model has been demonstrated to be an effective method to capture long range order in intercalation cathodes<sup>[18]</sup> as well as SRO in DRX systems.<sup>[9,10,12]</sup> In a cluster expansion, the configurational energy dependence is captured by an expansion into different cluster functions, which can be formulated as<sup>[19]</sup>

$$E = \sum_{i,sp1} J_i^{sp1} \sigma_i^{sp1} + \sum_{i,j,sp1,sp2} J_{ij}^{sp1sp2} \sigma_i^{sp1} \sigma_j^{sp2} + \sum_{i,j,k,sp1,sp2,sp3} J_{ijk}^{sp1sp2sp3} \sigma_i^{sp1} \sigma_j^{sp2} \sigma_k^{sp3}$$
(3)

Here,  $\sigma_i^{sp}$  corresponds to the occupancy of a certain site(s) with a certain species sp and *J* refers to the effective cluster interactions (ECIs). In DRX materials, a cation site can be occupied by Li or two types of transition metals M and M'. The anion sites can be either O<sup>2–</sup> or F<sup>–</sup>.



For each system, pair interactions up to 7.1 Å, triplet interactions up to 4.0 Å, and quadruplet interactions up to 4.0 Å based on a rocksalt lattice with a cubic lattice parameter a = 3.0 Å were included in the cluster-expansion formulism. All interactions were taken with respect to a baseline electrostatic energy defined with respect to the formal charges of the ionic species, with a fitted dielectric constant. The ECIs were fitted to densityfunctional theory (DFT) energies of sampled structures using a L1-regularized least-squares regression approach,<sup>[20]</sup> with the regularization parameters selected to minimize cross-validation error.<sup>[20]</sup> Depending on the exact system, 600–800 DFT energies were required to reach a root-mean-squared error of less than 7 meV atom<sup>-1</sup> for all the cluster expansion models employed in our simulations. The minimized cross validation errors are converged to be less than 10 meV atom<sup>-1</sup> for all systems as well.

### 2.3. Monte Carlo Structural Sampling

Finite temperature configurations were sampled by canonical Monte Carlo (MC) using the Metropolis-Hastings algorithm.<sup>[21]</sup> With the pair-interaction model, canonical MC simulations were performed using a  $12 \times 10 \times 10$  rocksalt supercell containing a total of 2400 atoms. For each sampled composition and temperature, 480 000 MC steps were run for equilibration, followed by 24 000 000 production MC steps. During the production MC run, the structures after each 48 000 MC steps were stored for analysis, which yielded 500 MC structures. With the cluster-expansion Hamiltonian, an  $8 \times 9 \times 10$  supercell with 1440 atoms was used. For each sampled composition and temperature, the equilibration consisted of 2 000 000 MC steps, and the production consisted of 8 000 000 MC steps. A total of 1000 MC structures were sampled during the production run to guarantee good statistics for SRO and percolation analysis. In addition, MC simulations were also used to identify the phase separation temperatures of different Li-TM-O-F systems, as described in both the pair-interaction and clusterexpansion models (details in Sections S3 and S5 in Supporting Information).<sup>[9,10,22]</sup>

### 2.4. Li Percolation Analysis

Li transport occurs on the atomic scale as hops between two octahedral sites via a tetrahedral intermediate in the presence of a second Li vacancy.<sup>[3,23]</sup> A schematic illustration of this o-t-o divacancy mechanism is presented in Figure 1. As indicated in previous work, the cation disorder in DRX materials creates three types of Li migration channels that can be classified as 0-TM, 1-TM, or 2-TM channels depending on the number of TM ions that coordinate with the intermediate tetrahedral site.<sup>[13]</sup> Because of the electrostatic repulsion between the high-valent metal ion and migrating Li<sup>+</sup> ion,<sup>[23,24]</sup> the activation energy for diffusion through 0-TM channels is much lower than that for the other channels<sup>[6]</sup> (see Figure S2 in Supporting Information). A lower bound on the kinetically accessible Li capacity can be obtained by considering Li atoms only extractable when they are on cation sites connected to percolating 0-TM pathways.



**Figure 1.** 0-TM diffusion channel and o-t-o mechanism. The hop from one octahedral Li site *i* to another octahedral site *j* via a tetrahedral intermediate state a) along the cubic (111) direction and b) in a perspective visualization. The tetrahedral intermediate of 0-TM channels is only coordinated by Li atoms (or vacancies once the Li sites have been vacated), as shown in panel (b). Fluorination replaces some of the oxygen atoms (red) with fluorine atoms (gray circles in (b)), which may affect the activation energy for Li hops.

In the present work, lattice-model percolation simulations were performed on MC structures sampled from both Hamiltonian types, as described above, to understand the correlation between the SRO and 0-TM percolation for different TM chemistries and fluorine concentrations. For each specific composition and temperature, the amount of percolating Li was determined by taking the average value of 500 MC structures sampled from the pair-interaction Hamiltonian or 1000 MC structures sampled from the cluster-expansion Hamiltonian.

### 2.5. First-Principles Density Functional Theory Calculations

First-principles DFT calculations were performed to obtain an accurate description of the structural energies and oxidation states of different cathode materials. All the calculations were performed using the projector-augmented wave (PAW) method<sup>[25]</sup> as implemented in the Vienna ab initio Simulation Package (VASP).<sup>[26]</sup> A rotationally averaged Hubbard U correction<sup>[27,28]</sup> was added to the PBE functional<sup>[29]</sup> to correct the self-interaction error in oxides containing Mn, Nb, Ni, and V. The U parameters were obtained from a previously reported calibration to oxide formation energies.<sup>[28]</sup> For all calculations, a reciprocal space discretization of 25 K-points per Å<sup>-1</sup> was applied, and the convergence criteria were set as 10<sup>-6</sup> eV for electronic loops and 0.02 eV Å-1 for ionic loops. All calculations were performed with spin-polarization and initialized in a ferromagnetic spin state. While stable short-ranged antiferromagnetic spin orderings are possible, the energy difference from the ferromagnetic state can be expected to be lower than 5-10 meV per O<sub>2</sub>.<sup>[30]</sup> Given that in a typical (F-)DRX system, the TM that carry spin are diluted by the Li excess and the d<sup>0</sup> charge compensator, the energy difference from magnetic ordering is much smaller than the energy differences of compositional ordering. Therefore, for the sake of computational efficiency we do not explicitly sample magnetic orderings in our calculations.

### 3. Results

To understand the impact of fluorine substitution on Li transport in DRX materials, we first evaluate the influence of Li–F



attraction and M–F repulsion on the fraction of Li within the 0-TM percolating network using the qualitative pair-interaction Hamiltonian. We then repeat this analysis for seven real DRX systems parametrized using cluster expansion Hamiltonians in order to take into account the effect of cation SRO. In both cases, we first identify the extent of the F-DRX phase in temperature and composition space to establish the thermodynamic bounds for F solubility. We then compute: a) the threshold Li composition at which 0-TM environments become percolating as the point at which macroscopic Li transport may be expected; and b), the fraction of Li connected to the percolating network as a lower bound on the kinetically accessible Li capacity.

### 3.1. Effect of Strong Li-F Attraction on 0-TM Percolation

The phase diagram using the qualitative pair-interaction model of Section 2.1 is shown in Figures S3 and S4 (Supporting Information) and defines the temperature and F-contents achievable. We chose 7.5% F substitution which was previously estimated to be the thermal F solubility limit at 1273 K in several DRX materials.<sup>[10,12,16,22]</sup> The percolation map in Figure 1 shows the predicted 0-TM capacity as function of temperature and Li-excess. The temperature in the percolation map is given in units of  $J/k_{\rm B}$ , where J and  $k_{\rm B}$  are the interaction parameter and Boltzmann's constant, respectively. The gray region indicates the temperature ranges in which phase separation into LiF and Li-TM oxide is predicted. The red region corresponds to nonpercolating conditions, and the thick black line indicates the percolation threshold. Within the percolating region of the map, the amount of Li per f.u. that can be accessed via percolating 0-TM diffusion channels is shown as shades of white to blue and with white contour lines (Figure 2).

At very high temperatures approaching 6  $J/k_{\rm B}$ , the Li–F and M–F interactions are overcome, and the atomic ordering becomes essentially random. Correspondingly, the percolation



**Figure 2.** 0-TM connected capacity in  $\text{Li}_x M_{2-x} O_{1.85} F_{0.15}$  with 7.5% fluorination. The 0-TM connected capacity is shown as accessible Li atoms per formula unit (f.u.). The thick black line represents the percolation threshold. Compositions within the red region are not 0-TM percolating. The gray region on the bottom is not accessible under equilibrium conditions as it is part of a miscibility gap in the phase diagram shown in Figure S3 (Supporting Information).

threshold approaches the value for fully disordered unfluorinated rocksalt materials of  $x_c \approx 1.09^{6.8}$ . The percolation threshold decreases significantly at lower temperatures, where the SRO is governed by the Li–F and M–F interactions. Below  $T = 1.5 J/k_B$ , the percolation threshold is as low as  $x_c \approx 0.96$ , i.e., no excess Li is required for percolation.

The same trend is also reflected in the amount of 0-TM accessible Li atoms per f.u. For example, at a total Li content of x = 1.05, the presence of 7.5% F at a temperature just above that of phase separation causes nearly 0.6 Li/f.u. to become accessible, whereas the same level of Li excess (5%) remains well below the percolation limit in fully random rocksalt oxides.

Note that these trends are based on the pair-interaction model that only considers Li–F and M–F interactions. In an actual material, additional SRO arising from cation–cation (Li–M, Li–Li, and M–M) interactions will be present to positively or negatively affect Li transport.<sup>[15]</sup> For some combinations of TMs, it is thus possible that small amounts of fluorination disturb the beneficial SRO already present in an unfluorinated material.<sup>[15]</sup> In the following section, we quantitatively investigate the effect of this interplay of interactions on the percolation properties of specific compounds.

### 3.2. Effect of Metal Short Range Order on 0-TM Percolation

To test the applicability of the trends seen in the pair-interaction model to real materials, we use the more elaborate cluster expansion model to compute the percolation properties of fluorinated variants of several common TM combinations seen in the DRX literature.<sup>[7,11,12,15,16,31]</sup> A typical general formula of a F-DRX material is  $\text{Li}_{2-x1-x2}M_{x1}M'_{x2}O_{2-\gamma}F_{\gamma}$ , where M is a redoxactive TM species and M' is a high-valent charge compensator. We focus on seven composition spaces, with three having M in the +3 oxidation state (Mn<sup>3+</sup>Ti<sup>4+</sup>, Mn<sup>3+</sup>Nb<sup>5+</sup>, and V<sup>3+</sup>Nb<sup>5+</sup>), and four with M in the +2 oxidation state (Ni<sup>2+</sup>Ti<sup>4+</sup>, Mn<sup>2+</sup>Ti<sup>4+</sup>, Ni<sup>2+</sup>Nb<sup>5+</sup>).

Using the cluster expansion model and MC simulations, we evaluate F solubility of the seven systems at different temperatures by computing the MO-Li<sub>a</sub>M'O<sub>b</sub>-LiF/LiMO<sub>2</sub>-Li<sub>a</sub>M'O<sub>b</sub>-LiF pseudo-ternary phase diagram for each M<sup>2+</sup>/M<sup>3+</sup> chemical space respectively. Within each space, we further focus on compositions with 20% Li excess  $(Li_{1,2}M_{x1}M'_{0,8-x1}O_{2-\nu}F_{\nu})$ , which is a typical Li excess composition reported for DRX compounds;<sup>[6,12,13,15]</sup> and annealing temperatures between 1273 and 1873 K. The lower range of this temperature range can be achieved with classic solid-state synthesis whereas the higher range has been previously suggested as a representative proxy for mechanochemical high-energy ball-milling synthesis respectively.<sup>[9,10,32]</sup> It should be noted that there is no known exact, quantitative mapping between mechanochemical highenergy ball-milling synthesis conditions and any thermodynamic state. However, we have previously established for a set of DRX materials that equilibrium solid-state behavior at an elevated temperature is a reasonable approximation to the states that can be achieved by mechanochemical processing.<sup>[9,10,32]</sup> The calculated F solubility limits for the seven compounds at three different temperatures are given in Table 1. The comparison between computed temperatures and experimental

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Table 1. Calculated solubility limits of  $Li_{1,2}M_{x1}M'_{0.8-x1}O_{2-\gamma}F_{\gamma}$  at three different temperatures.

Temperature	Mn <sup>2+</sup> Ti <sup>4+</sup>	Mn <sup>2+</sup> Nb <sup>5+</sup>	Ni <sup>2+</sup> Ti <sup>4+</sup>	Ni <sup>2+</sup> Nb <sup>5+</sup>	Mn <sup>3+</sup> Ti <sup>4+</sup>	Mn <sup>3+</sup> Nb <sup>5+</sup>	V <sup>3+</sup> Nb <sup>5+</sup>
1273 K	5.0%	15.9%	8.3%	20.1%	5.7%	6.8%	6.1%
1573 K	12.8%	21.4%	18.4%	24.2%	9.7%	11.3%	9.8%
1873 K	21.7%	25.7%	26.6%	27.7%	14.1%	18.9%	14.4%

conditions should be done with caution, as DFT calculations with only configurational entropy have a tendency to overpredict the temperatures at which disorder phenomena occur, implying that conditions in Table 1 may represent a slightly lower real temperature than the listed.<sup>[33]</sup>

Previous reports have established that most DRX systems can achieve at least 5% of fluorination by solid state synthesis,<sup>[9–12,16,22]</sup> a value that is within the solubility limits predicted by our calculations in Table 1. Therefore, we first evaluate the impact of 5% F-incorporation at 1273 K by comparing the 0-TM percolation in  $\text{Li}_{1.2}\text{M}_{x1}\text{M}'_{x2}\text{O}_{1.9}\text{F}_{0.1}$  and  $\text{Li}_{1.2}\text{M}_{x1}\text{M}'_{x2}\text{O}_{2}$  for the seven (M, M') pairs. As the Li-excess amount is kept constant, variation in F content is charge compensated by adjusting the M/M' amount. The results in **Figure 3**a show that fluorination slightly increases the amount of percolating Li in oxides, which have less than 25% of the Li accessible by percolation (Mn<sup>3+</sup>-Nb<sup>5+</sup>, V<sup>3+</sup>-Nb<sup>5+</sup>, and Mn<sup>2+</sup>-Nb<sup>5+</sup>). However, in systems exhibiting good Li-percolation (>25%) in the oxide, 5% F

substitution is detrimental ( $Mn^{3+}$ - $Ti^{4+}$ ,  $Ni^{2+}$ - $Ti^{4+}$ ,  $Ni^{2+}$ - $Nb^{5+}$ , and  $Mn^{2+}$ - $Ti^{4+}$ ) and reduces the amount of accessible Li.

To understand these findings, we track two features of the Li-metal short range order. First, we measure the cluster frequency of  $\text{Li}_4$  tetrahedra, the building block of the 0-TM percolating network, as the

ratio of the number of a specific cluster (e.g.,  $Li_4$ ) divided by the total number of tetrahedral clusters. Second, we classify the  $Li_4$  clusters depending on their connectivity with each other, as shown schematically in Figure 3c. We distinguish isolated  $Li_4$ , which are not connected with a percolating network; chained  $Li_4$ , which are percolating  $Li_4$  that corner-share with two neighboring  $Li_4$  and form chain-like motifs; and compacted  $Li_4$ , which are corner-sharing with more than two neighboring  $Li_4$ corresponding to locally Li-rich clusters. This feature captures how efficiently  $Li_4$  is connected with each other in forming a percolation network.

The results in Figure 3b show a complex change in shortrange order when fluorine is introduced. In all cases except for Ni<sup>2+</sup>-Ti<sup>4+</sup>, fluorination leads to a small increase in Li<sub>4</sub> content, which is consistent with the fact that F attracts Li and form Li rich environments (Figure S5, Supporting Information). However, this trend by itself does not explain the observed change in Li percolation. Figure 3b also shows that in most systems



**Figure 3.** 0-TM percolation and short-range configurational analysis on seven DRX systems with 1.2 Li per f.u. at 1273 K. a) Amount of 0-TM percolating Li with or without 5% fluorination for seven compounds. b) Absolute change in the frequency of total Li<sub>4</sub>, isolated Li<sub>4</sub> and chained Li<sub>4</sub> cluster upon 5% O to F substitution. The cluster frequency in oxide ( $f_{Oxide}$ ) and F-DRX (f) are calculated by taking the total amount of tetrahedral clusters as the baseline and the difference between them is plotted for visualization. c) Atomic configurations of the first neighboring cation shell for a cation, with examples of isolated, chained and compacted Li<sub>4</sub> distribution.

the increase in total Li<sub>4</sub> is accompanied by a significant increase in isolated Li<sub>4</sub>, so much so that in  $Mn^{2+}$ -Ti<sup>4+</sup>, Ni<sup>2+</sup>-Nb<sup>5+</sup>, and  $Mn^{3+}$ -Ti<sup>4+</sup>, the fraction of Li in the percolating network actually decreases. This overall trend of Li percolation is also consistent with the evolution of the chained Li<sub>4</sub> configuration. As the chained Li<sub>4</sub> fraction tracks the environments that bridge two Li rich domains, these units are critical at low F to form percolating channels. In the Ni<sup>2+</sup>-Ti<sup>4+</sup>, Mn<sup>2+</sup>-Ti<sup>4+</sup>, and Ni<sup>2+</sup>-Nb<sup>5+</sup> systems these chained Li<sub>4</sub> configurations decrease with fluorination, consistent with the poorer percolation.

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We also investigate the effect of fluorine content on the percolation behavior. Our calculations indicate that among the seven chemical spaces, equilibrium fluorination beyond 5% is only likely to be possible for the M2+-containing compositions, though higher fluorine amounts may be achievable with nonequilibrium synthesis. For this group of M<sup>2+</sup> compounds, we keep the overall composition at  $Li_{1,2}M_{x1}M'_{0,8-x1}O_{2-\nu}F_{\nu}$  and extend the analysis to a higher temperature of 1873 K as a proxy for ball-milling synthetic conditions at which fluorine substitution of up to 30% can be achieved for all four systems as indicated in Table 1. Figure 4 shows the fraction of Li accessible by percolation in the M2+ systems under these conditions Figure 4a. We also plot the evolution of isolated Li<sub>4</sub> as a function of fluorination amount in Figure 4b. Note that while chained Li<sub>4</sub> is an effective descriptor comparing DRX oxide and F-DRX with 5% fluorine as shown in Figure 3, we did not use it here since we are comparing compounds over a wide range of F concentration. As opposed to compounds with small amounts of F or no F, heavily fluorinated compound always have a large fraction of Li in Li-rich domains due to Li-F clustering, such that chained-Li units no longer make up a significant fraction of the percolating network and thus are not effective descriptors of the percolating Li fraction across different F contents.

For all four systems, the 0-TM percolating Li amount initially decreases as F is added to the system, consistent with the data in Figure 3, but then increases at high F content. When

the fluorination level is sufficiently high (>20%), the 0-TM percolating Li amount approaches and even surpasses the random limit. Given the fact that most of the oxides have percolating Li fraction below that of the random limit,<sup>[15]</sup> this result suggests a transition from "less percolating" SRO to "more percolating" SRO with heavy fluorination. Meanwhile, the minimum in the amount of percolating Li correlates well with the evolution of isolated Li<sub>4</sub> as shown in Figure 4b. While initially the amount of isolated Li increases, at the highest F-levels there are almost no isolated Li4 clusters, indicating that most Li is in the percolating clusters. These results indicate that lower amounts of fluorination (<10%) can deteriorate percolation in these specific systems as the redistribution of cations leads to segregation of Li4 into local domains. It also indicates that the increasing amount of Li4 unit that origins from Li-F attraction (Figure S7, Supporting Information) does not guarantee good Li percolation. We stress however that these findings are confined to the M2+-containing materials and to an evaluation of percolation. Fluorination in all cases seems to improve cyclability<sup>[11,12]</sup> and reduce oxygen loss. In addition, there is very little change in percolation behavior of the M<sup>3+</sup> compounds with small amounts of fluorination.

### 3.3. Predicted Percolation Maps for Rational Design of F-DRX

We have established that changing the F content in a fluorinated DRX may profoundly change the preferred SRO in the material and thereby, accessible Li capacity. We now evaluate the percolating Li fraction while varying the total Li and F content independently so as to establish a map of the kinetically accessible Li across the entire region of the pseudo-ternary phase diagram. As mentioned earlier, in order to reach higher fluorine content, high energy ball milling is often used. There is currently no theory or guiding principle that can predict what is made under ball milling conditions, but as in previous



Figure 4. 0-TM percolation analysis and short-range order parameters for four types of  $Li_{1,2}$  compounds obtained at 1873 K. a) 0-TM percolating Li, and b) amount of Li in isolated  $Li_4$  as a function of F content.

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**Figure 5.** Percolation maps from cluster-expansion MC simulations for a)  $Mn^{2+}Ti^{4+}$ , b)  $Ni^{2+}Ti^{4+}$ , c)  $Mn^{2+}Nb^{5+}$ , and d)  $Ni^{2+}Nb^{5+}$ . The color map indicates the fraction of Li per formula unit that is percolating at a given composition and the solid lines indicate the theoretical  $Mn^{2+}/Mn^{4+}$  or  $Ni^{2+}/Ni^{4+}$  electron capacity. The red dashed line indicates the Li = 1.2 isopleth. e) Compositional boundaries when 0.6 Li/f.u. is percolating. The critical composition that percolates (Li\_{1.0}Ni\_{0.64}Ti\_{0.36}O\_{1.72}F\_{0.28}) is marked by a white star symbol in panel (a) noted as "critical composition." Meanwhile, two sets of heavily fluorinated compositions reported in the literature<sup>[11]</sup> are indicated by a white star in panels (b,d), respectively.

work we use an "equivalent" high temperature of 1873 K at which we equilibrate the four materials with the metal couples  $Mn^{2+}Ti^{4+}$ ,  $Ni^{2+}Ti^{4+}$ ,  $Mn^{2+}Nb^{5+}$ , and  $Ni^{2+}Nb^{5+}$ . The resulting percolation maps are shown in **Figure 5**. In the percolation maps, the amount of percolating Li per f.u. is indicated by the color. Using the computed phase diagram in Figure S6 (Supporting Information) for the four  $M^{2+}$ -containing systems, compositions that are beyond the computed F solubility limit are overlaid with a dark gray shade. Solid black contour lines indicate the theoretical TM redox capacities.

All four percolation maps have similar shapes and exhibit similar trends: a high fluorination level always improves Li percolation, while a minimum in percolating Li with respect to fluorine content exists at low fluorination level. The improved percolation seen in the high-F limit is consistent with the general behavior predicted by the pair-interaction model (Figure 2 and Figure S8, Supporting Information). Even though Li<sub>1.09</sub> is the threshold Li amount for 0-TM percolation in systems with random cation arrangement, the cluster-expansion simulations predict that no Li excess is required to achieve 0-TM percolation in the Ni<sup>2+</sup>Ti<sup>4+</sup> system if a sufficient amount of fluorination (>14%) can be realized. The corresponding critical composition of Li<sub>1.0</sub>Ni<sub>0.64</sub>Ti<sub>0.36</sub>O<sub>1.72</sub>F<sub>0.28</sub> is marked with a white star in Figure 5a. For Li contents between Li<sub>1.15</sub>-Li<sub>1.25</sub>, small amounts of fluorination (<15%) do not always lead to better 0-TM percolation. To give an example, the Li = 1.2 isopleth line investigated in the



previous section is indicated by a red dashed line in Figure 5a–d. The color evolution along this Li amount isopleth indicates the evolution of the percolating Li fraction. Increasing the F content from 0 does not result in a monotonic increase of the amount of 0-TM percolating Li until higher amounts of fluorination ( $\gamma > 0.15$ ) are reached. This behavior is consistently observed for Li-contents up to the limit of 1.33 shown in the figure.

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In addition to the general trends that apply to all systems, one system-specific trend can be observed in Figure 5e: The two Ni<sup>2+</sup>-based systems need less Li excess to achieve good 0-TM percolation than the Mn<sup>2+</sup>-based systems, especially at low Li-excess (x < 1.1). This makes Ni<sup>2+</sup> system of interest to achieve high Li capacity, but needs to be weighed against the issue that in Ni systems electron capacity limitations may dominate because the Ni<sup>4+</sup> valence state is typically difficult to access in DRX materials due to its overlap with the oxygen states.<sup>[16,22]</sup> Furthermore, the choice of high-valent TM species also appears to have an impact on percolation, although no definitive trends emerge: when paired with Ni<sup>2+</sup>, Ti<sup>4+</sup> requires less fluorination to reach a percolating amount of 0.6 Li/f.u at moderate Li excess content (x < 1.2) than the Nb<sup>5+</sup> analogue, while the opposite is true for Mn<sup>2+</sup>.

# 4. Experimental Validation of the Theoretical Predictions

Although the influence of fluorine substitution on SRO is complex, our ab initio modeling results demonstrate several important and verifiable facts. First, F substitution is beneficial for percolation in any DRX oxide that has poor 0-TM percolation due to either an insufficient Li amount or unfavorable cation SRO.<sup>[12,15]</sup> This insight can be used to improve Li transport in DRX oxides with poor 0-TM percolation. Second, for those DRX oxides that already have good 0-TM percolation, a small amount of F (<10%) can be detrimental to Li accessibility, which is only recovered if more F (>15%) is incorporated. To test these trends directly, we designed two experiments: 1) To test the improvement of percolation with fluorination, we designed a DRX system with low Li excess so that the 0-TM percolation in the unfluorinated oxide would be poor; 2) To test whether small amounts of fluorination could be detrimental to Li kinetics, we designed a DRX system with large Li excess so that the 0-TM percolation in the unfluorinated oxide would be good.

In the first experiment, an oxide  $\text{Li}_{1.05}\text{Ni}_{0.458}\text{Ti}_{0.458}\text{Mo}_{0.033}\text{O}_2$  (LNO) and a lightly fluorinated analogue  $\text{Li}_{1.05}\text{Ni}_{0.533}\text{Ti}_{0.383}$   $\text{Mo}_{0.033}\text{O}_{1.85}\text{F}_{0.15}$  (LNF15) were synthesized using a traditional solid-state method. Given that 5% Li excess is well below the percolation threshold of 9%, fluorination is expected to improve the kinetically accessible capacity.<sup>[6,13]</sup> The resulting X-ray diffraction (XRD) patterns are presented in **Figure 6a** and can be indexed in the rocksalt structure (space group *Fm-3m*), suggesting that phase-pure DRX materials are obtained. The electrochemical performance of the two materials is shown in Figure 6b. Consistent with our prediction, fluorination enhances the amount of extractable Li and increases the capacity from around 0.7 Li/f.u. for LNO to around 0.8 Li/f.u. for LNF15. This finding confirms that light fluorination improves Li percolation in otherwise poor-performing systems.



Figure 6. Structural and electrochemical characterization of fluorinated and unfluorinated compounds. a) XRD patterns of as-synthesized LNO and LNF15 prepared by solid-state synthesis. b) First-cycle voltage profiles of LNO and LNF15 within a voltage window of 1.5–4.5 V. c) XRD patterns of as-synthesized LMNO, LMNF10, and LMNF30 prepared by solid-state synthesis. d) First-cycle voltage profiles of LMNO, LMNF10, and LNF30 within a voltage window of 1.5–4.5 V.



To check whether a small amount of F substitution (5%) harms the overall Li percolation when Li percolation is already good in the unfluorinated oxide, but can be recovered by further increasing F content,  $Li_{1.3}Mn_{0.267}Nb_{0.433}O_2$  (LMNO),  $Li_{1.3}Mn_{0.3}$  Nb<sub>0.4</sub>O<sub>1.9</sub>F<sub>0.1</sub> (LMNF10), and  $Li_{1.3}Mn_{0.367}Nb_{0.333}O_{1.7}F_{0.3}$  (LMNF30) were synthesized using a traditional solid-state method. The XRD patterns shown in Figure 6c indicate that pure phases are obtained for all three compounds. The electrochemical performance in Figure 6d shows that 5% fluorination reduces the amount of extractable Li with respect to the oxide. But as the fluorination level further increases from 5% to 15%, the observed capacity again increases, confirming that the extractable Li amount of fluorination.

It is worth mentioning that both experiments only utilize first cycle capacity to demonstrate that F indeed changes the SRO in the materials. The precise amount of reversibly extractable Li depends on the experimental conditions and various materials properties. However, in previous published work,<sup>[14,15,32,34]</sup> comprehensive experiments were conducted and demonstrate that SRO is indeed the limiting factor for the first cycle capacity of DRX. Meanwhile, given that our theoretical predictions are fully consistent with what we see in experiments, we believe that it is reliable to correlate the initial capacity with change of SRO and other factors would not influence such trend.

## 5. Discussion

Using a combination of a qualitative pair-interaction model and a quantitative first-principle based composition-specific clusterexpansion model, we have deconvoluted the impact of fluorination on Li transport in DRX materials. The percolation of 0-TM migration channels in fluorinated DRX is governed by a complex interplay between strong Li–F attraction and cation shortrange order.

In all conditions we studied the Li-F attraction enhances the formation of Li-rich environments, which leads to an increased 0-TM channel concentration. A large amount of fluorine substitution (>15%) therefore generally improves 0-TM percolation, as predicted by both the pair-interaction model and the cluster-expansion model. At low F concentration, the impact of fluorination is strongly composition- and chemistry- dependent. When the origin of poor Li transport in the unfluorinated oxide is cation SRO that disfavors 0-TM percolation, fluorination enhances Li transport by disrupting these local configurations and promoting the formation of connected Li-rich environments. The formation of these environments is so favorable that even in compounds with insufficient Li excess for percolation in the random limit (x < 1.09 per f.u.) fluorination can introduce enough favorable SRO to enable 0-TM percolation. We have validated this effect in the Ni<sup>2+</sup>Ti<sup>4+</sup> system and expect that it may be observed in other systems with reasonable fluorine solubility.

On the other hand, if the cation SRO in the pure oxide already exhibits good 0-TM Li percolation,<sup>[6,13]</sup> the Li redistribution caused by small amounts of fluorine substitution can be detrimental to 0-TM percolation as it may interrupt the existing connections between local Li-rich domains. To be more specific, while the substituted F atoms always strongly attract Li, resulting in the formation of  $Li_6F$  and  $Li_5MF$  clusters for all compositions,

the mechanism by which they disrupt the metal SRO depends on the valence of the transition metal. As argued in previous studies.<sup>[15,35]</sup> the nature of the Li/TM distribution in oxides is governed by both cation ionic radius and local charge neutrality. Ideal percolation is achieved when Li ions "segregate" together onto a tetrahedron (enhancing the number of Li<sub>4</sub> environments) with the transition metal (M) and charge compensator (M') occupying other tetrahedra. While Li and the M' cations are respectively always below and above the average cation valence required, the transition metal M can be either above or below. Local charge neutrality will create a preference for a low-valent cation to have higher valent cations as neighbors. For example, in M2+-containing DRX oxides, combinations of Li and the M2+ can never create local neutrality as the average anion charge is -2, but M<sup>2+</sup> cations can be nearest neighbors to each other as they maintain local charge neutrality. This potential for "segregation" of M2+ ions on tetrahedra, also creates more Li4 tetrahedra, explaining why M2+-containing DRX generally have better percolation than M<sup>3+</sup>-based compounds. In the latter systems, the ability of Li<sup>+</sup> and M<sup>3+</sup> to create charge neutrality on a tetrahedron tends to favor such tetrahedra, removing them from contributing to the percolation which requires Li<sub>4</sub> tetrahedra, as indicated in our previous work.<sup>[15]</sup> The introduction of F will gradually change the local charge balance by lowing the average charge states of anion sites, which in turn will alter the degree of Li/TM mixing on tetrahedra. While mixtures of M<sup>2+</sup> and Li<sup>+</sup> can never compensate the negative charge of O<sup>2-</sup> they can achieve local neutrality when the average anion charge is sufficiently lowered by fluorine introduction. This will lead to more mixed (Li, M) tetrahedra and poorer percolation. These insights, together with our simulation results, indicate that care must be taken when fluorinating DRX oxide cathodes with good 0-TM percolation, such as Li<sub>1.2</sub>Mn<sub>0.4</sub>Ti<sub>0.4</sub>O<sub>2</sub> or Li<sub>1.2</sub>Ni<sub>0.2</sub>Ti<sub>0.6</sub>O<sub>2</sub>, as fluorination at the level of 5-10% does not improve Li transport. However, there can be other reasons to fluorinate material. such as improving cycling stability.<sup>[12]</sup>

The percolation maps provided in Figure 5 are useful tools for the rational optimization of F-DRX materials in a certain compositional space. Several tradeoffs are quantified in Figure 4: the TM-redox capacity decreases with increasing Liexcess. Lower TM-redox capacity requires a larger contribution of oxygen redox which tends to lead to poorer cycle life.<sup>[12,36]</sup> On the other hand, Li transport improves as the amount of 0-TM percolating Li increases with the Li excess, which has been shown to increase the first cycle capacity. An optimized working DRX cathode composition should thus be a balance between these two opposing trends. As seen in the percolation maps of Figure 5, fluorination offers a tuning handle to improve the compromise between TM-content and Li-percolation, as highly fluorinated compounds with low Li excess may still have good 0-TM percolation properties. This is the region of the percolation maps where most of the Li is kinetically accessible, while remaining in the composition region where one would not expect an overreliance on oxygen redox. However, this highly fluorinated composition space is restricted by the F solubility limit, requiring specialized synthesis techniques such as high temperature synthesis and mechanochemical methods.<sup>[9-11]</sup> Hence, some research in understanding the fluorine solubility in rocksalt materials and how it can be manipulated through



metastable synthesis routes would be highly beneficial to the development of stable, high capacity DRX materials.

Alternatively, more than 30% Li excess guarantees good 0-TM percolation regardless of fluorination (right side of the percolation maps). In this region of the percolation maps, however, the greatest challenge is the reliance on oxygen redox to achieve high capacity. This limitation can be addressed by sufficient fluorination to lower the average TM valence state, as the F solubility in this high Li-excess region is also generally high. Some compositions in this region, published<sup>[11]</sup> in the literature and marked in the maps in Figure 5 as white stars, indeed show high performance with good cycling stability.<sup>[11]</sup>

### 6. Conclusions

We have computationally and experimentally demonstrated that fluorination can dramatically alter the Li transport properties of disordered rocksalt cathodes. Depending on the DRX metal chemistry and Li-excess, low F substitution levels (<10%) may induce poor connectivity of Li migration channels and result in a decrease in kinetically accessible Li and observed capacity. At high enough levels of F substitution, the accessible capacity can always be increased from the baseline oxide, even though for high Li-excess compositions this fluorination level may be hard to reach. To facilitate the rational design of F-substituted DRX materials with optimal capacity and Li transport properties, we introduced percolation maps that combine the phase stability, Li kinetics, and electron capacity.

# 7. Experimental Section

The first group of materials that are demonstrated in Figure 6a,b are synthesized with Li<sub>2</sub>CO<sub>3</sub> (Alfa Aesar, ACS, 99% min), NiCO<sub>3</sub> (Alfa Aesar, 98%), TiO<sub>2</sub> (Anatase, Alfa Aesar, 99.9%), MoO<sub>2</sub> (Alfa Aesar, 99%), and LiF (Alfa Aesar, 99.99%) as precursors. All the precursors were stoichiometrically mixed (except for adding 5% more Li<sub>2</sub>CO<sub>3</sub> and 4% more NiCO<sub>3</sub> to compensate for their possible loss during synthesis) with a Retsch PM 200 planetary ball mill at a rate of 300 rpm for 4 h. The precursors were then pelletized and sintered at 750 °C in air for 3 h, followed by quenching in air. The pellets were then transferred to a glovebox and ground into powders.

The second group of materials that are demonstrated in Figure 6c,d are synthesized with  $Li_2CO_3$  (Alfa Aesar, ACS, 99% min), MnO (Sigma-Aldrich, 99.99%), Nb<sub>2</sub>O<sub>5</sub> (Alfa Aesar, 99.9%), and LiF (Alfa Aesar, 99.99%) as precursors. All the precursors were stoichiometrically mixed (except for adding 8% more  $Li_2CO_3$  to compensate for possible loss during synthesis) with a Retsch PM 200 planetary ball mill at a rate of 300 rpm for 4 h. Pelletized LMNO and LMNF10 were sintered at 1000 °C in argon for 6 h, and LMNF30 was sintered at 1050 °C in argon for 6 h. The sintered pellets were then transferred to a glovebox and ground into powders.

To make the cathode films, composed of active materials, SUPER C65 (Timcal), and polytetrafluoroethylene (PTFE, DuPont, Teflon 8A) at a weight ratio of 70:20:10, 280 mg active materials and 80 mg SUPER C65 were mixed and shaker-milled for 30 min in argon atmosphere with SPEX 800M Mixer/Mill, and PTFE was later added and manually mixed with the shaker-milled mixture for 40 min. The components were then rolled into thin films inside the glovebox. Commercialized 1  $\mbox{MiPF}_6$  in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (volume ratio 1:1) was used as electrolyte. Glass microfibers (Whatman) were used as separator. FMC Li metal foil was used as

anode. Coin cells were assembled inside the glovebox and tested on Arbin battery test instrument at room temperature. The loading density of the films was around 5 mg cm<sup>-2</sup> based on active materials. The specific capacities were then calculated based on the weight of active materials (70%) in the cathode films. X-ray diffraction patterns for the as-synthesized compounds were collected using a Rigaku MiniFlex diffractometer (Cu source) in a  $2\theta$  range of  $20^\circ$ -85°. Rietveld refinement was done with PANalytical X'pert HighScore Plus software. Results of the elemental analyses were also performed to confirm the composition of both groups of compounds as shown in Table S1 (Supporting Information).

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# Keywords

cluster expansion, lithium batteries, percolation theory, short-range order, transition metal oxides

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