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Title

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Permalink

<https://escholarship.org/uc/item/9kj7p883>

Journal

Chem, 6(1)

ISSN

1925-6981

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Publication Date

2020

DOI

10.1016/j.chempr.2019.10.001

Peer reviewed

1 **Design principles for high-capacity Mn-based**
2 **cation-**

3 **disordered rocksalt cathodes**

4 **CHEMJOURNAL-D-19-00749**

5 **(Revised parts in the manuscript are highlighted in yellow)**

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1 Summary

- 2 Mn-based Li-excess cation-disordered rocksalt (DRX) oxyfluorides are promising candidates for
- 3 next-generation rechargeable battery cathodes owing to their large energy densities, earth-
- 4 abundance of Mn and potential for low cost. In this work, we synthesized and electrochemically
- 5 tested four representative compositions in the Li-Mn-O-F DRX chemical space with various Li
- 6 and F content. While all compositions tested achieve higher than 200 mAh g⁻¹
- 7 material with high Li-excess (1.3333 per formula unit, Li_xMn_{2-x}O_{2-y}F_y) and moderate fluorination
- 8 (0.3333 per formula unit) achieves 349 mAh g⁻¹ initial capacity and 1068 Wh
- 9 Higher fluorination (0.6667 per formula unit) at moderate Li-excess (1.25 per formula unit) can
- 10 activate Mn²⁺/Mn⁴⁺ redox and thereby balance capacity with cycle life,
- 11 Wh/kg) initial capacity (specific energy) with more than 85% retained after 30 cycles. We show
- 12 that the Li-site distribution (i.e., Li percolation properties) plays a more important role than the
- 13 metal-redox capacity in determining the initial capacity, whereas the metal-redox capacity is more
- 14 closely related to the cyclability of the materials. We apply these insights and generate a capacity
- 15 map of the Li-Mn-O-F chemical space, Li_xMn_{2-x}O_{2-y}F_y (1.167 ≤ x ≤ 1.333, 0 ≤ y ≤ 0.667), which
- 16 predicts both the accessible Li capacity and Mn-redox capacity. This map allows to design
- 17 compounds which balance high capacity with good cyclability.
- 18

19 **Keywords**

20 Cation-disordered rocksalt cathodes, Li-excess Mn-based oxyfluorides, short-range order, density

21 functional theory, Monte-Carlo simulation, Li percolation, fluorination

22

1 Introduction

- 2 The tremendous success and growth of Li-ion based energy storage in a broad range of
- 3 applications^{1,2} is likely to strain our natural resources³. Projected growth of Li-ion production
- 4 towards 1 TWh/year will require more than a million tons of Co/Ni combined, which constitutes
- 5 a very sizeable fraction of the annual production of these metals⁴. The recent development of Li-
- 6 excess cation-disordered rocksalt (DRX) cathodes^{5,6,7} is providing an avenue for the Li-ion battery
- 7 field to develop high energy density cathodes with more abundant and less expensive metals. In
- 8 these DRX compounds Li migrates through a percolating network of so called '0-TM' clusters in
- 9 which the absence of transition metals at the activated state enables facile migration^{5,6}. **Lifting the**
- 10 **restriction that cathode structures must be layered and remain layered during electrochemical**
- 11 **cycling has enabled the exploration of a much wider chemical space beyond the traditional Ni-Co-**
- 12 **Mn (NCM) space**^{5,8-17}. In addition, the ability to substitute some of the oxygen by fluorine in
- 13 locally Li-rich environments in DRX structures provides an extra handle to optimize performance
- 14 by introducing additional metal-redox capacity^{8,15,18} and improve cyclability^{13,18}.
- 15 Mn is a particularly promising redox active element for cathodes because of its low cost and natural
- 16 abundance. In addition, fully charged Mn-cathodes contain Mn⁴⁺ which is a stable valence state
- 17 thereby enhancing the thermal stability of cathode materials. The Mn³⁺/Mn⁴⁺ redox

couple is

- 18 active in LiMn_2O_4 spinel cathodes but can only be partially utilized because of the collective Jahn-
- 19 Teller distortion upon full reduction to Mn^{3+} ¹⁹. Recently, the highly F-substituted DRX
- 20 compounds $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$ and $\text{Li}_2\text{Mn}_{1/2}\text{Ti}_{1/2}\text{O}_2\text{F}$ were shown to have very high capacity with
- 21 two electron Mn^{2+} to Mn^{4+} oxidation⁸. Other high capacity Mn-compounds include $\text{Li}_4\text{Mn}_2\text{O}_5$,
- 22 which was argued to utilize a combination of $\text{Mn}^{3+}/\text{Mn}^{4+}$, O^{2-}/O^- , and $\text{Mn}^{4+}/\text{Mn}^{5+}$ redox, but
- 23 experiences severe capacity fading upon extended cycling¹⁰. In $\text{Li}_{1.9}\text{Mn}_{0.95}\text{O}_{2.05}\text{F}_{0.95}$, partial

1 fluorine substitution was applied to improve cyclability¹⁵. In another example, V⁴⁺ was applied as

2 a charge compensator in Li_{1.171}Mn_{0.343}V_{0.486}O_{1.8}F_{0.2} to obtain additional electron capacity from the

3 V⁴⁺/V⁵⁺ redox in addition to that provided by the Mn²⁺/Mn⁴⁺ redox¹⁴.

4 These initial results demonstrate that the Li-Mn-O-F chemical space may be particularly

5 important for finding high-capacity, low cost cathodes. Optimization of these materials is likely

6 to involve several tradeoffs: The Li-excess required for good transport in disordered rocksalts

7 reduces the transition metal electron capacity, necessitating oxygen redox to achieve high capacity.

8 Fluorine substitution on anion sites can negate this to some extent by lowering the average valence

9 requirement on the cations. At the same time, F incorporation is expected to change the Li

10 percolation network due to the large bonding preference between Li and F over Mn and F²⁰. In

11 this paper we systematically investigate the role of each compositional handle (Li excess, transition

12 metal redox capacity, and F-content) on the initial discharge capacity and cycle life within the

13 compositional space Li_xMn_{2-x}O_{2-y}F_y (1.167 ≤ x ≤ 1.333, 0 ≤ y ≤ 0.667). We use ab-initio

14 simulations to study how Li percolation is modified by short-range order (SRO), previously shown

15 to significantly affect the Li environments, their percolation, and ultimately the Li-transport of

16 DRX materials²¹⁻²⁴, and correlate it to measured electrochemical performance and spectroscopic

17 information.

18 We synthesize, characterize, model, and electrochemically test four well-chosen compositions

19 within the Li-Mn-O-F DRX chemical space with different Li content

and F content: 20 $\text{Li}_{1.3333}\text{Mn(III)}_{0.6667}\text{O}_{1.3333}\text{F}_{0.6667}$,

$\text{Li}_{1.3333}\text{Mn(III)}_{0.5}\text{Mn(IV)}_{0.1667}\text{O}_{1.5}\text{F}_{0.5}$, 21 $\text{Li}_{1.3333}\text{Mn(III)}_{0.3333}\text{Mn(IV)}_{0.3333}\text{O}_{1.6667}\text{F}_{0.3333}$,

and $\text{Li}_{1.25}\text{Mn(II)}_{0.1667}\text{Mn(III)}_{0.5833}\text{O}_{1.3333}\text{F}_{0.6667}$,

22 hereafter referred to as HLF67, HLF50, HLF33, LLF67, respectively, with 'HL' referring to 'high

23 lithium content' (1.3333 per f.u.), 'LL' referring to 'low lithium content' (1.25 per f.u.) and

1 numbers denoting the F content. For one group of samples, the lithium content is kept
the same

2 and the F content is gradually **decreased** from HLF67, HLF50 and HLF33, so that
progressively

3 less TM redox capacity is expected because of the incorporation of more Mn^{4+} ions in
the as-

4 synthesized material to maintain charge balance. For the other group, HLF67 and LLF67
are used

5 to contrast Li-capacity versus TM capacity. These samples have the same F content, but
Li-excess

6 is lowered in LLF67 in order to create more Mn^{2+} giving more transition metal (TM)
redox

7 capacity. **The redox behavior of these compounds is investigated combining
spectroscopic**

8 **methods and density functional theory (DFT) calculations, while SRO in the materials is
studied**

9 **using a combined DFT and Monte Carlo method.** Our investigations reveal that the
nature of the

10 Li network and its percolation properties play a more important role than the metal-
redox capacity

11 in determining the initial capacity of the compounds, whereas the metal-redox capacity
has a

12 greater effect on the capacity retention. We then apply these insights and expand our
computational

13 analysis to a larger compositional space within the Li-Mn-O-F chemistry and construct a
capacity

14 map to provide more practical guidance for experimental design.

15

16 **Results**

17 **Structural characterization**

18 The four compounds were synthesized using a mechanochemical ball-milling
method (see
19 methodology). The X-ray diffraction (XRD) patterns shown in Figure 1a confirm that
all the
20 materials form a DRX structure with no observable impurity peaks. In addition, elemental
analysis
21 confirmed that the compositions of the materials are close to the target compositions, as
shown in
22 Table S1. The difference in lattice constants of the materials is consistent with the
degree of Mn
23 oxidation. The presence of more Mn⁴⁺ reduces the lattice constant from

1 to 4.1477 ± 0.0005 Å (HLF50) and 4.1184 ± 0.0005 Å (HLF33), whereas the introduction of large
2 Mn^{2+} ions increases the lattice constant to 4.2141 ± 0.0009 Å for LLF67,
3 Li content. The F to O ratio appears less significant in determining the lattice constant, consistent
4 with their small difference in ionic radius²⁵. Detailed refinements of the XRD
5 patterns are presented in Figure S1. Transmission electron microscopy (TEM) electron diffraction (ED)
6 patterns of the as-synthesized materials also show phase-pure DRX without observable impurities
7 (Figure 1b, S4). Nanosized small grains with different orientations pack closely together to form
8 a polycrystalline primary particle (Figure S4), the size of which is in the range of 100–200
9 nm for as-synthesized materials, as observed in the scanning electron microscopy (SEM) images
10 in Figure S2.

11 Although no LiF impurity phases were detected using XRD and TEM ED techniques, we called
12 on ^{19}F solid-state nuclear magnetic resonance spectroscopy (ssNMR) to further confirm that most
13 of the fluorine is incorporated within the bulk material rather than forming a separate LiF phase.

14 The ^{19}F NMR spectra collected on HLF67, HLF50 and LLF67 powders, as well as on LiF powder
15 and an empty rotor for reference, are presented in Figure 1c. While the small shoulder at
16 approximately -163 ppm originates from the probe background, we find that the ^{19}F NMR spectra
17 collected on the various cathode materials differ significantly from that of the LiF

reference. The

- 18 former spectra are composed of a number of broad, overlapping signals shifted away from the
- 19 resonance frequency of LiF at -204 ppm. As discussed in previous NMR studies on related
- 20 oxyfluoride materials ^{8,13,14,18,26}, these broad features arise from strong paramagnetic interactions
- 21 from short-range paramagnetic interactions between unpaired *d* electrons on Mn ions and the F
- 22 nucleus, which confirms the bulk incorporation of F into the disordered rocksalt phase.⁶ When F
- 23 is directly bonded to Mn ions, paramagnetic interactions are so strong that the resulting signals

1 are too broad to be detectable and are lost in the background noise. These invisible
paramagnetic
2 F sites prevent us from quantifying the fraction of F in LiF-like domains or particles in the
pristine
3 cathode samples, as evidenced by the sharp signal centered at -204 ppm and present
in all spectra.
4 Nevertheless, the present data indicate that the vast majority of the fluorine of the as-
synthesized
5 materials is incorporated into the particles. ^7Li NMR spectra are also presented in
Figure S3.
6 Supplementary Note 1 discusses the problem of attributing the ~ 0 ppm signal to either
impurities
7 or to the possible formation of diamagnetic Li-rich (Mn-poor) domains within the
disordered oxide
8 matrix. Finally, TEM energy dispersive spectroscopy (EDS) mapping images are shown in
Figure
9 1d and S4 and indicate a homogeneous distribution of F throughout the particles, which
further
10 confirms the bulk substitution of F.

11

12 **Electrochemical performance**

13 The electrochemical performance of the Li-Mn-O-F compounds was tested in
galvanostatic mode
14 at 20 mA g^{-1} and room temperature within different voltage windows ($1.5 - 4.6/4.8/5.0$
V). Figure
15 2a summarizes the first cycle discharge capacities, average voltage, and specific
energies for all of
16 the compounds. Figure 2b presents the voltage profiles of HLF67, HLF50, HLF33, and
LLF67 for
17 the first cycle between $1.5 - 4.8\text{V}$; the compounds exhibit discharge capacities (specific
energies)

- 18 of 259 mAh g⁻¹ (844 Wh kg⁻¹), 284 mAh g⁻¹ (909 Wh kg⁻¹), 336 mAh g⁻¹ (1059 Wh kg⁻¹), and
- 19 242 mAh g⁻¹ (771 Wh kg⁻¹), respectively. When cycling between 1.5 - 5.0V, their initial discharge
- 20 capacities (specific energies) increase to 290 mAh g⁻¹ (950 Wh kg⁻¹), 319 mAh g⁻¹ (1016 Wh
- 21 kg⁻¹), 349 mAh g⁻¹ (1068 Wh kg⁻¹), and 256 mAh g⁻¹ (822 Wh kg⁻¹), respectively, as shown in
- 22 Figure 2c.

1 Figure 2d-f present the representative voltage profiles for HLF67, HLF33 and
2 capacity retention, when cycling between 1.5 and 5.0 V. The red dashed lines
3 theoretical Mn-redox capacities in each compound. HLF67 exhibits an initial
4 energy) of 290 mAh g⁻¹ (950 Wh kg⁻¹) and good capacity retention (Figure
5 larger initial capacity (specific energy) of 349 mAh g⁻¹ (1068 Wh kg⁻¹) but
6 capacity retention compared to that of HLF67 (Figure 2e). LLF67 shows a
7 (specific energy) of 256 mAh g⁻¹ (822 Wh kg⁻¹) compared to HLF67 but
8 with less than 15% capacity fading over the first 30 cycles (Figure 2f). More
9 cycling results are presented in Figure S5.

10 In order to understand the relation between composition and
11 redox mechanism and local SRO in these compounds are carefully studied in
12 sections.

13

14 Redox mechanism

15 The redox mechanisms of the Li-Mn-O-F compounds were investigated using *ex-situ*
hard X-ray

16 absorption spectroscopy (XAS) and *ab-initio* calculations. The top panel of Figure 3a
shows the

17 Mn K-edge X-ray near-edge structure (XANES) of all four pristine compounds. The Mn K-
edge

18 energy increases in the order of LLF67 < HLF67 < HLF50 < HLF33. At the top of
charge, the

19 Mn³⁺ / Mn⁴⁺ redox process is almost complete in HLF50 and HLF33, while Mn ions in
HLF67 and

20 LLF67 are oxidized to a lesser extent, as shown in the lower panel of Figure 3a. This
finding is

21 consistent with the observation by Lee *et al.* that a large lattice constant and the
presence of more

22 Mn-F bonds create more overlap between Mn and O redox and can prevent Mn from being fully

1 oxidized to Mn⁴⁺.⁸ These interpretations are further supported by the Mn pre-edge
2 derivative
3 analysis, as presented in Figure S6 and Supplementary Note 2.
4 To compare the oxidation behavior of Mn in HLF67 and LLF67, we select five points at
5 different
6 states of charge in the first charge: the pristine state, and charged to 3.5 V, 4.2 V, 4.6V,
7 and 5.0 V,
8 respectively, as shown in Figure 3b. In general, similar redox behavior is observed for
9 the two
10 compounds: Mn oxidation dominates at low voltage, but at high voltage, the Mn K-edge
11 barely
12 shifts, indicating limited Mn redox. However, a small shift of the edge position to a lower
13 energy
14 at high voltage is observed in HLF67 but not in LLF67; this shift has been ascribed to the
15 partial
16 reduction of the TM (Mn in this case) due to oxygen oxidation²⁷. Partial reduction of Mn
17 at high
18 voltage is also observed in HLF50 and HLF33, as shown in Figure S7a and S7b, which
19 suggests
20 that the participation of oxygen redox processes in the overall charge compensation
21 mechanism is
22 more significant in HLF67, HLF50 and HLF33 than in LLF67.
23 To obtain further insight into the oxidation mechanisms in these cathode materials, we
24 used density
25 functional theory (DFT) to calculate the voltage curves and the evolution of Mn and O
26 oxidation
27 states upon delithiation. Figure 3c and 3d show the calculated redox mechanism for
28 HLF67 and
29 LLF67. It is clear that oxygen redox happens earlier in HLF67 than in LLF67 and
30 contributes more
31 to the overall capacity, consistent with the presence of more Li-excess in HLF67 to
32 facilitate

- 18 oxygen oxidation ²⁸. As a result, Mn partial reduction is observed in HLF67 at the top of charge
- 19 but not in LLF67. At the top of charge, Mn is less oxidized in LLF67 than in HLF67, which is
- 20 consistent with the XAS observations.
- 21 Combining the electrochemical performance and the redox center data establishes a clear
- 22 correlation between the charge compensation process and the capacity retention of the compounds:
- 23 with an increasing contribution of oxygen redox from LLF67 to HLF67, HLF50 and HLF33, the

1 capacity retention of the materials gradually decreases. Oxygen redox is
2 lead to less stable cycling compared to metal redox since it triggers
3 leaving behind a metal densified surface layer, which hinders Li transport.
4 effective way to lower the average cation oxidation states, enabling the
5 metal redox to improve the capacity retention. Consistently, the amount of
6 is reduced in the order of HLF33 > HLF50 > LLF67, as can be observed
7 electrochemical mass spectroscopy (DEMS) results (shown in Figure S8).

9 Short-range order (SRO) analysis

10 The SRO in the Li-Mn-O-F compounds was investigated using a cluster expansion
Hamiltonian
11 parameterized by DFT total energy calculations. As the Li network significantly affects the
12 electrochemical performance of DRX compounds²³, we first evaluate the frequency of
tetrahedra
13 that are only occupied by Li ions (the 0-TM Li₄ tetrahedra) in the four compounds as
this is the
14 environment through which Li migrates. Figure 4a shows the fraction of tetrahedra that
are 0-TM
15 in the simulated Li-Mn-O-F compounds at 2573K as well as in the random limit (infinite
16 temperature). As calibrated in previous work²⁰ the temperature of 2573K was chosen as
a proxy
17 for the high energy conditions with which disorder is generated with ball milling in the
Li-Mn-
18 O-F chemical space but should not be taken as a particularly significant value. The
'Random limit'
19 cation configuration in the structure is one where the cations are distributed
20 over the cation lattice, only satisfying the concentration requirement. Such a

- 21 SRO and can be used as a reference. Comparing the 0-TM occurrence in HLF67, HLF50, and
- 22 HLF33, it is clear that fluorination generally leads to a higher number of tetrahedra being occupied
- 23 with Li4. This is consistent with the previously established idea that a F- anion in DRX materials

1 wants to maximize the Li content around it ^{20,21}. The Li-rich octahedra around F⁻ predispose the

2 tetrahedra with which they share three cations to be Li₄. The ability of F⁻ to create more Li₄

3 tetrahedra is clear when comparing LLF67 which has a larger fraction of them than HLF33, despite

4 containing less Li. However, good Li transport requires connectivity of these Li₄ tetrahedra and

5 this is where F seems to have the largest perturbing effect. Figure 4b presents the amount of Li

6 connected to the percolating network. Lowering the F content from HLF67 to HLF50, and HLF33,

7 increases the amount of percolating Li despite the fact that the fraction of Li₄ tetrahedra decreases.

8 These trends with F-content indicate that F modifies the connectivity of the Li₄ tetrahedra in a very

9 significant way. Li diffusion throughout the bulk materials only benefits from Li₄ tetrahedra that

10 create an efficient percolating network through the material. Highly localized Li clusters, for

11 example where one Li is shared by five O-TM tetrahedrons or more (as illustrated in Figure 4c),

12 will trap a lot of Li within small domains and prevent the formation of an extended network of O-

13 TM tetrahedra, thus reduce the 'efficiency' of O-TM connectivity. Figure 4d shows the fraction of

14 Li in Li₄ tetrahedra in all compounds, where the different Li environments are classified according

15 to the number of O-TM units around a central Li. Both "isolated" or highly shared Li ions are

16 detrimental for transport as they have limited contributions to the overall percolation. We can see

17 that in HLF67 and LLF67, a larger fraction of 0-TM Li is shared by more than five 0-TM
units,
18 whereas for HLF50 and HLF33, a larger fraction of the 0-TM Li is shared by two to four
0-TM
19 units, which is a more 'efficient' way to connect all the 0-TM tetrahedrons. The
influence of
20 different Mn valence states on the distribution of F is also investigated, but proven to
be less
21 important than the competition between Li-F and Mn-F, as discussed in Figure
S9 and
22 Supplementary Note 3. The correlation between discharge capacity changes and
the 0-TM

1 percolating Li fraction in Fig 4b shows that this percolation behavior, rather than just
2 simply the
3 amount of Li₄ tetrahedra, is the relevant factor that controls initial capacity.
4 Equipped with an enhanced understanding of the charge compensation process and Li-
5 transport
6 property in these Li-Mn-O-F compounds, we discuss in the next section the trade-offs
7 between
8 initial capacity and capacity retention, and rationalize some general design principles in
9 a practical
10 compositional space $\text{Li}_x\text{Mn}_{2-x}\text{O}_{2-y}\text{F}_y$ ($1.167 \leq x \leq 1.333$, $0 \leq y \leq 0.667$).

7 Discussion

8 Transition metal redox capacity and Li-site distribution

9 Figure 5a summarizes the theoretical Li/Mn capacities, accessible 0-TM capacities
10 predicted by
11 MC simulations, and experimental capacities obtained from the first charge/discharge
12 at 20 mA
13 g^{-1} within the voltage window of 1.5–4.8 V for the Li-Mn-O-F compounds. Although
14 both the
15 TM capacity and Li-site distribution can significantly affect the cycling performance of
16 Li-Mn-
17 O-F compounds, their effects appear in different manner. Comparing HLF67, HLF50, and
18 HLF33,
19 we observe that by increasing the amount of 0-TM percolating Li, the initial
20 charge/discharge
21 capacity of the compounds increases, even though the Mn-redox capacity decreases.
22 This trend is
23 further confirmed by the LLF67 compound which has the lowest theoretical Li capacity
24 and
25 highest Mn-redox capacity but delivers the lowest initial charge/discharge capacity.
26 These results

18 indicate that the initial capacity does not depend on the Mn-redox capacity but is more
related to

19 the Li percolation properties. However, the Mn capacity does strongly influence the
capacity decay

20 of the materials upon extended charge-discharge cycling. As observed in Figure 2 and
Figure S5,

21 the capacity retention improves in the order $\text{HLF33} < \text{HLF50} < \text{HLF67} < \text{LLF67}$,
consistent with

22 the increase of Mn redox capacity. To strengthen our hypothesis, we selected two
additional

23 compositions: DRX-Li₂MnO₃, which has more than 95% of its Li ions in the percolating
network,

1 based on our calculation, and $\text{Li}_{1.1667}\text{Mn(II)}_{0.3333}\text{Mn(III)}_{0.50}\text{F}_{0.6667}$ (denoted
as L167F67), with

2 a high theoretical Mn-redox capacity which matches its theoretical Li capacity. Both
materials

3 were synthesized using a similar mechanochemical ball-milling method described for
the other

4 samples. The voltage profiles (first cycle) and cyclability of both compounds together
with those

5 of the four previously studied compounds are presented in Figure 5b and 5c,
respectively. We can

6 see that DRX-Li₂MnO₃ exhibits the highest initial charge capacity but worst capacity
retention,

7 whereas L167F67F displays the opposite behavior, consistent with our analysis that Li
percolation

8 controls initial capacities while Mn redox content controls capacity retention.

9 Based on these insights, we generate in Figure 5d a capacity map for Li-Mn-O-F
compounds as

10 function of the Li excess content (x-axis) and fluorine content (y-axis). The color scale
gives the

11 calculated total amount of percolating Li per formula unit (f.u.) at each composition and
the solid

12 lines indicate the theoretical Mn-redox capacity. Ideally, a material would have high
amount of

13 percolating Li as well as high Mn-redox capacity, but the Fig.5d shows that there is
clearly a trade-

14 off between these two. Along the x-axis Li excess is increased at the cost of Mn-redox
capacity

15 leading to a higher fraction of percolating Li. This is expected to increase the initial
discharge

16 capacity but with rapid capacity fade. The percolation properties as a function of F
content with

17 fixed Li-excess behave in a more complicated manner. In general, upon increasing F

content at

- 18 fixed Li-excess, the fraction of percolating Li decreases initially but then increases. This trend
- 19 intuitively makes sense: when the fluorination level is low, the presence of F ions attracts Li around
- 20 them forming Li-rich clusters which do not percolate because their concentration - determined by
- 21 the F content- is not high enough for those Li-rich clusters to connect and percolate through the
- 22 sample. When the F content further increases, the Li-rich clusters around F connect together and
- 23 the overall percolation improves. **The Li-percolation properties as a function of F content are**

1 presented at five different Li-excess levels calculated from Monte Carlo
2 1.208, 1.25, 1.292, and 1.333 in $\text{Li}_x\text{Mn}_{2-x}\text{O}_{2-y}\text{F}_y$, as shown in Figure 5e. The
3 (marked in red) at which percolation starts to improve with F content
4 and for $x = 1.33$ the fraction of percolating Li actually decreases with F
5 range shown on the map. It is possible that a critical F content can be found
6 do not consider that range here due to the difficulty in synthesizing the very
7 materials. This map will be useful in guiding experimental design within the Li-Mn-O-F
space to
8 identify good candidates with both large 0-TM Li capacity and adequate Mn-redox
capacity, e.g.
9 those with metal redox capacity larger than 0.6 e^- per f.u. and percolating Li
10 0.7 per f.u. Considering the general presence of SRO^{23} and facile oxygen
11 materials, our general findings within the Li-Mn-O-F DRX chemical space are
12 valid in other DRX chemical spaces.

13

14 Conclusion

15 In this work, we investigated Li-Mn-O-F DRX oxyfluorides which form a very
promising
16 chemical space to create high energy, resource-light cathodes. We systematically
studied four
17 representative compounds combining electrochemical tests, spectroscopy, and
modeling, and
18 demonstrated reversible capacities between 200 and 350 mAh g^{-1} . We found that
the Li-site
19 distribution plays a more important role in determining the initial capacity, whereas
the metal
20 redox capacity is more important for determining the cyclability of the material. This
intrinsic

- 21 tradeoff in DRX materials is related to the role of oxygen redox: increasing Li-excess leads to
- 22 better Li transport in DRXs, but results in a larger reliance on oxygen redox to achieve high
- 23 capacity, thus worse cyclability. Fluorination can compensate for this to some extent by enabling

- 1 more metal redox capacity, but its presence modifies the Li network in a significant way. A
- 2 capacity map, which includes both the Li percolation properties and Mn redox capacities, is
- 3 presented to provide further guidance for experimental design in this Li-Mn-O-F chemical space.

4

5 **Experimental procedures**

6 **Synthesis**

- 7 All Li-Mn-O-F compounds were synthesized by mechanochemical ball-milling. Li₂O (Alfa Aesar,
- 8 ACS, 99% min), MnO (Sigma-Aldrich, 99.99%), Mn₂O₃ (Alfa Aesar, 99%), MnO₂ (Alfa Aesar,
- 9 99.9%), and LiF (Alfa Aesar, 99.99%) were used as precursors. Precursors were stoichiometrically
- 10 mixed according to charge-balance with a Retsch PM 200 Planetary Ball Mill at a rate of 300 rpm
- 11 for 2 hours. The mixed precursors were then ball-milled at 500 rpm in Argon-filled stainless-steel
- 12 ball-mill jars, using a Retsch PM 200 Planetary Ball Mill. The duration of ball-mill synthesis for
- 13 HLF67, HLF50, HLF33, and LLF67 is 40 hours, and for L167F167 and Li₂MnO₃ is 55 hours. The
- 14 total amount of precursors was 1g. The grinding media were five 10mm (diameter) stainless balls
- 15 and ten 5mm (diameter) balls.

16 **Electrochemistry**

- 17 All cathode films were composed of active materials, SUPER C65 (Timcal), and

- 18 polytetrafluoroethylene (PTFE, DuPont, Teflon 8A) at a weight ratio of 70:20:10. To make the
- 19 cathode films, 280 mg active materials and 80 mg SUPER C65 were mixed and shaker-milled for
- 20 1 hour in argon atmosphere with SPEX 800M Mixer/Mill, and PTFE was later added and manually
- 21 mixed with the shaker-milled mixture for 40 minutes. The components were then rolled into thin
- 22 films inside the glovebox. Commercialized 1M LiPF₆ in ethylene carbonate (EC) and dimethyl
- 23 carbonate (DMC) solution (volume ratio 1:1) was used as electrolyte. Glass microfibers (Whatman)

1 were used as separator. FMC Li metal foil was used as anode. Coin cells were
assembled inside
2 the glovebox and tested on Arbin battery test instrument at room temperature. The
loading density
3 of the films was around 3 mg cm^{-2} based on active materials. The specific capacities
were then
4 calculated based on the weight of active materials (70%)
in the cathode films.
5 Potentiostatic intermittent titration technique (PITT) measurements were conducted on
the same
6 electrode for HLF67, HLF50, HLF33, and LLF67 to obtain quasi-equilibrium voltage
profiles. All
7 materials were charged from the open-circuit voltages to 4.8 V with a 0.01V step
interval, and the
8 voltage was held constant for 1 hour at each step.

9 **Characterization**

10 X-ray diffraction (XRD) patterns for the as-synthesized compounds were collected using a
Rigaku
11 MiniFlex diffractometer (Cu source) in a 2θ range of 5° - 85° . Rietveld refinement was
done with
12 PANalytical X'pert HighScore Plus software. Elemental analysis was performed by Luvak
Inc.
13 with direct current plasma emission spectroscopy (ASTM E 1079-12) for lithium,
manganese and
14 with an ion-selective electrode (ASTM D 1179-10) for fluorine. Scanning electron
microscopy
15 (SEM) images were collected using a Zeiss Gemini Ultra-55 Analytical Field Emission
SEM in
16 the Molecular Foundry at Lawrence Berkeley National Lab (LBNL). Scanning transmission
17 electron microscopy (STEM) / energy dispersive spectroscopy (EDS) measurements were

18 performed on a JEM-2010F microscope in the Molecular Foundry at LBNL. Neutron power
19 diffraction was measured at Nanoscale Ordered Materials Diffractometer (NOMAD) at the
20 Spallation Neutron Source at Oak Ridge National Laboratory. The neutron pair-
distribution
21 function (NPDF) refinement was performed using
22 **Solid-state nuclear magnetic resonance (NMR) spectroscopy**

1 ^{19}F and ^7Li NMR data on the as-synthesized HLF67, HLF50, and LLF67 powder samples
were
2 obtained at room temperature using a Bruker Avance 500 MHz (11.7 T) wide-bore
NMR
3 spectrometer, at Larmor frequencies of -470.7 MHz and -194.4 MHz, respectively. The
spectra
4 were acquired under 50 kHz magic angle spinning (MAS), using a 1.3 mm double-
resonance probe,
5 and chemical shifts were referenced against lithium fluoride powder (LiF , $\delta(^{19}\text{F}) = -204$
ppm and
6 $\delta(^7\text{Li}) = -1$ ppm).
7 Because the resonant frequency range of the ^{19}F nuclei in the as-synthesized HLF67,
HLF50, and
8 LLF67 cathodes is larger than the excitation bandwidth of the radio frequency (RF) pulse
used in
9 the NMR experiment, nine spin echo spectra were collected for each sample, with the
irradiation
10 frequency varied in steps of 250 ppm or 118 kHz from -1200 ppm to 800 ppm. The
individual sub-
11 spectra were processed using a zero-order phase correction so that the on-resonance
signal was in
12 the absorption mode. The four sub-spectra were then added to give an overall sum
spectrum with
13 no further phase correction required. This 'frequency stepping' ^{31,32}, 'spin echo
mapping' ³³, or
14 'VOCS' ³⁴ (variable offset cumulative spectrum) methodology provides a large excitation
15 bandwidth with uniform excitation of the broad ^{19}F signals. Individual ^{19}F spin echo
spectra were
16 collected using a 90° RF excitation pulse of $1.6 \mu\text{s}$ and a 180° RF pulse of $3.2 \mu\text{s}$ at 76.3 W
(or 156
17 kHz), with a recycle delay of 50 ms. For comparison, a spin echo spectrum was collected

on LiF

- 18 using similar RF pulses but a longer recycle delay of 14 s. A ^{19}F probe background spin echo
- 19 spectrum, acquired under the same conditions as the individual LMVF20 spin echo spectra but on
- 20 an empty rotor, revealed the presence of a low intensity background signal.
- 21 ^7Li spin echo spectra were collected on the HLF67, HLF50, and LLF67 cathode powders using a
- 22 90° RF pulse of $0.9\ \mu\text{s}$ and a 180° RF pulse of $1.8\ \mu\text{s}$ at 110 W and a recycle delay of 30 ms.

23 *Ex-situ* hard X-ray absorption spectroscopy (XAS)

1 The X-ray absorption near edge spectroscopy (XANES) of Mn K-edge was
acquired in
2 transmission mode at beamline 20-BM-B in Advanced Photon Source. The incident beam
energy
3 was selected using a Si (111) monochromator. The energy calibration was
performed by
4 simultaneously measuring the spectra of appropriate metal foil. Harmonic
rejection was
5 accomplished using a Rh-coated mirror. All the *ex-situ* samples are electrodes films,
composed of
6 active materials, SUPER C65 and PTFE with weight ratio of 70:20:10, and loading
density of 5
7 mg cm^{-2} (based on active materials). They were assembled as coin cells, charged to
designated
8 capacities, then disassembled and washed with DMC in glovebox (except for pristine
materials).
9 Additional spectra of reference standards were also measured to facilitate the
interpretation. The
10 raw data was normalized and calibrated using Athena software³⁵.

11 **Differential electrochemical mass spectrometer (DEMS) measurement**

12 The custom-built DEMS, cell geometry, and instrument operation is described in previous
13 publications³⁶⁻³⁸. The electrochemical cells used with the DEMS device were prepared
in glove
14 box using modified Swagelok design and the cathode film is composed of active
materials, carbon
15 black and PTFE with weight ratio of 70:20:10, and loading density of $\sim 10 \text{ mg cm}^{-2}$
(based on
16 active materials). The electrolyte, separators, and anodes used were identical to those
used for the
17 coin cell tests in this study. The assembled cells were charged at 20 mA g^{-1} under a

static head of

18 positive argon pressure (around 1.2 bar) at room temperature after being appropriately attached to

19 the DEMS.

20 **Computational methods**

21 A combination of density functional theory (DFT) calculations together with cluster expansion

22 Monte Carlo simulations as described in previous reports^{14,39} has been applied to understand the

23 energetics, short range order and Li percolation in LiF-MnO-LiMnO₂-Li₂MnO₃ compositional

1 space. Using the DFT energy of 1019 structures, a cluster expansion for cation
occupancy in the

2 rocksalt structure consisting of pair interactions up to 7.1 Å, triplet interactions up to
4.0 Å, and

3 quadruplet interactions up to 4.0 Å was fitted. The effective cluster interactions and
dielectric

4 constant were obtained from a L1-regularized least squares regression⁴⁰, with the
regularization

5 parameters chosen to minimize cross-validation error⁴⁰. By this procedure, an root-
mean-squared

6 error below 7 meV/atom has been obtained.

7 The DFT calculations have been performed with the Vienna ab-initio simulation package
(VASP)⁴¹

8 and the projector-augmented wave (PAW) method⁴². For each of the structural
optimization

9 calculation, a reciprocal space discretization of 25 Å is applied, and the convergence
criteria are

10 set as 10^{-6} eV for electronic loops and 0.02 eV/Å for ionic loops. The PBE exchange-
correlation

11 functional with the rotationally-averaged Hubbard U correction⁴³ has been applied for
obtaining

12 more accurate DFT energetics, the U parameters are chosen from a previously reported
calibration

13 to oxide formation energies⁴⁴ (3.9 eV for Mn).

14 Short range order and percolation information was obtained from canonical Monte Carlo
sampling

15 of fully lithiated structure using the Metropolis-Hastings algorithm^{45,46}. To guarantee
good

16 statistics percolation analysis and short-range order for each composition and
temperature are

17 averaged over 500 structures with each consist of 6×6×8 supercells with 576 atoms.

- 18 To evaluate the voltage curve and redox mechanism, all possible Li-Vacancy ordering in small
- 19 supercells are enumerated with energies calculated by the SCAN meta-GGA exchange correlation
- 20 functional⁴⁷ which provides a more accurate ranking of structural energetics^{48,49}. With energetics
- 21 evaluated by SCAN, the delithated cluster expansion is then fitted as an offset from a baseline of
- 22 formal charge electrostatics. The various oxidation states of Mn and O were treated as different
- 23 species and were identified according from the magnetic moment on these species in the SCAN

1 calculations. The final root-mean-square error of this cluster expansion is less than 5
meV/atom.
2 With this cluster expansion, the most stable Li-Vacancy ordering at each delithiation
stage has
3 been fully optimized using DFT for constructing the voltage curve. The pymatgen code ⁵⁰
has been
4 utilized for all the structure analysis and post-processing.

5

6 **Supplementary information**

7 Supplemental information can be found with the article online at XXXX.

8

9 **Acknowledgements**

10 This work was supported by the Umicore Specialty Oxides and Chemicals the Assistant
Secretary
11 for Energy Efficiency and Renewable Energy, Vehicle Technologies Office, of the U.S.
12 Department of Energy under Contract No. DEAC02-05CH11231, under the Advanced
Battery
13 Materials Research (BMR) Program. Work at the Molecular Foundry was supported by the
Office
14 of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under
contract No.
15 DE-AC02-05CH11231. The NMR experimental work reported here made use of the shared
16 facilities of the UCSB MRSEC (NSF DMR 1720256), a member of the Material Research
17 Facilities Network. This research used resources of the Advanced Photon Source, an
Office of
18 Science User Facility operated for the U.S. Department of Energy (DOE) Office of
Science by
19 Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-
AC02-

- 20 06CH11357. This research used resources at the Spallation Neutron Source, a DOE Office of
- 21 Science User Facility operated by the Oak Ridge National Laboratory. The computational analysis
- 22 was performed using computational resources sponsored by the Department of Energy's Office of
- 23 Energy Efficiency and Renewable Energy and located at the National Renewable Energy

1 Laboratory, computational resources provided by Extreme Science and Engineering
Discovery
2 Environment (XSEDE), which was supported by National Science Foundation grant
number
3 ACI1053575, as well as the National Energy Research Scientific Computing Center
(NERSC), a
4 DOE Office of Science User Facility supported by the Office of Science and the U.S.
Department
5 of Energy under Contract No. DE-AC02-05CH11231. The authors thank Dr. Hyunchul Kim
and
6 Dr. Nongnuch Artrith for helpful discussion. The authors thank Mr. Jingyang Wang for the
help of
7 XAS measurement. The authors thank Dr. Jue Liu for the help of neutron diffraction
measurement.

8

9 **Author contributions**

10 Z.L. planned the project with G.C.; Z.L. designed, synthesized, characterized (XRD) and
11 electrochemically tested the proposed compounds with the help from Z.C., H.J. and H.K.;
B.O.
12 performed Monte Carlo and DFT calculations and analyzed the data with the help from
D.A.K.;

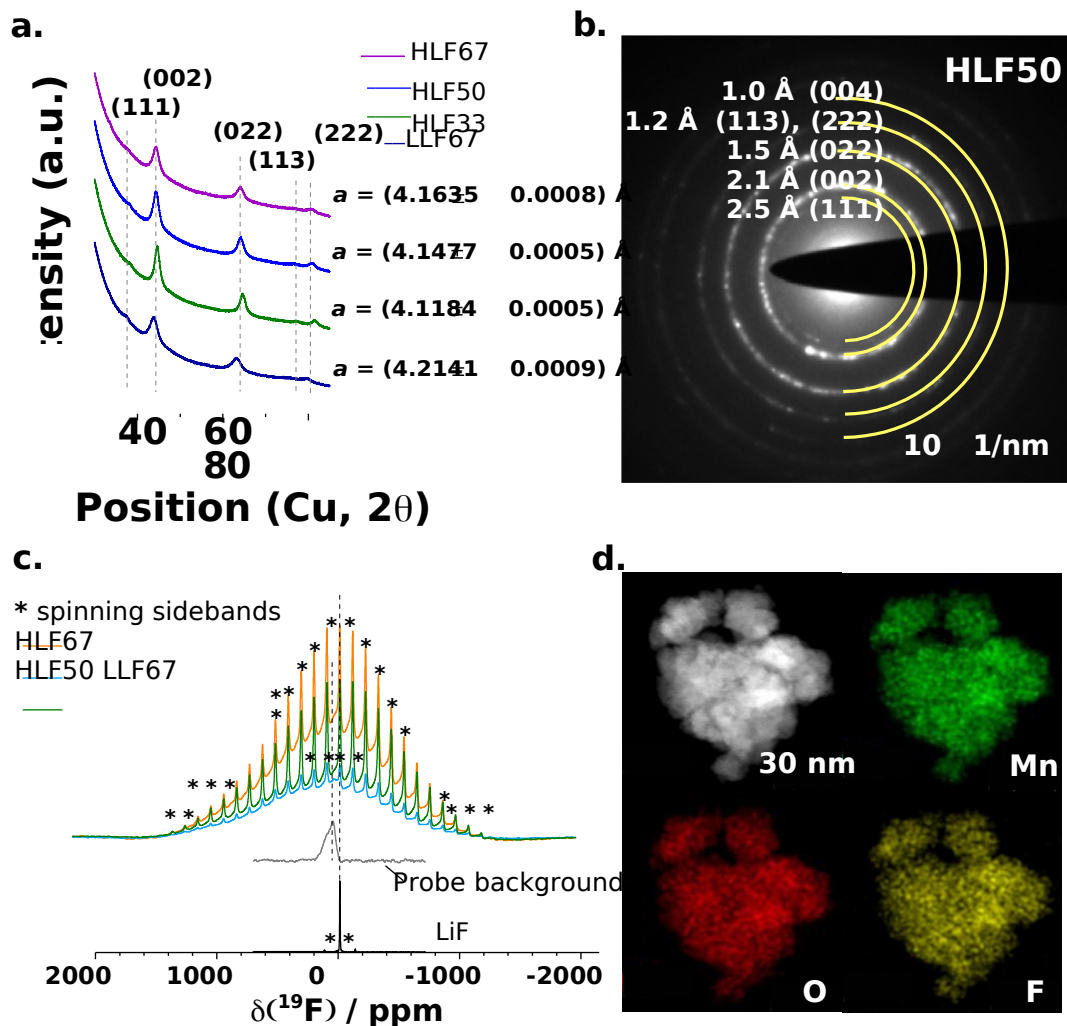
13 R.J.C. acquired and analyzed the NMR data; Z.L. acquired and analyzed the XAS data
with the
14 help from M.B. and J. H.; D.K. acquired and analyzed TEM data; J.K.P. acquired and
analyzed
15 DEMS data with input from B.D.M.; Y.T. performed SEM. The manuscript was written by
Z.L.
16 and was revised by R.J.C., D.A.K., H.J. and G.C. with the help of the other authors. All
authors
17 contributed to discussions.

18

19 Declaration of interests

20 The authors declare no competing interests.

21



1

2 **Figure 1 | Structural characterization of the as-synthesized Li-Mn-O-F**
compounds. a. XRD

3 **patterns and refined lattice constants of the as-synthesized materials. b.** Electron
diffraction pattern

4 of as-synthesized HLF50. **c.** ^{19}F frequency-stepping spectra obtained for the as-
synthesized HLF67,

5 HLF50, LLF67 powders by summing over nine spin echo sub-spectra acquired at
different

6 excitation frequencies. The spectra are scaled according to the amount of sample in the
rotor. For

7 comparison, ^{19}F spin echo spectra collected on LiF powder and on an empty rotor (to
measure the

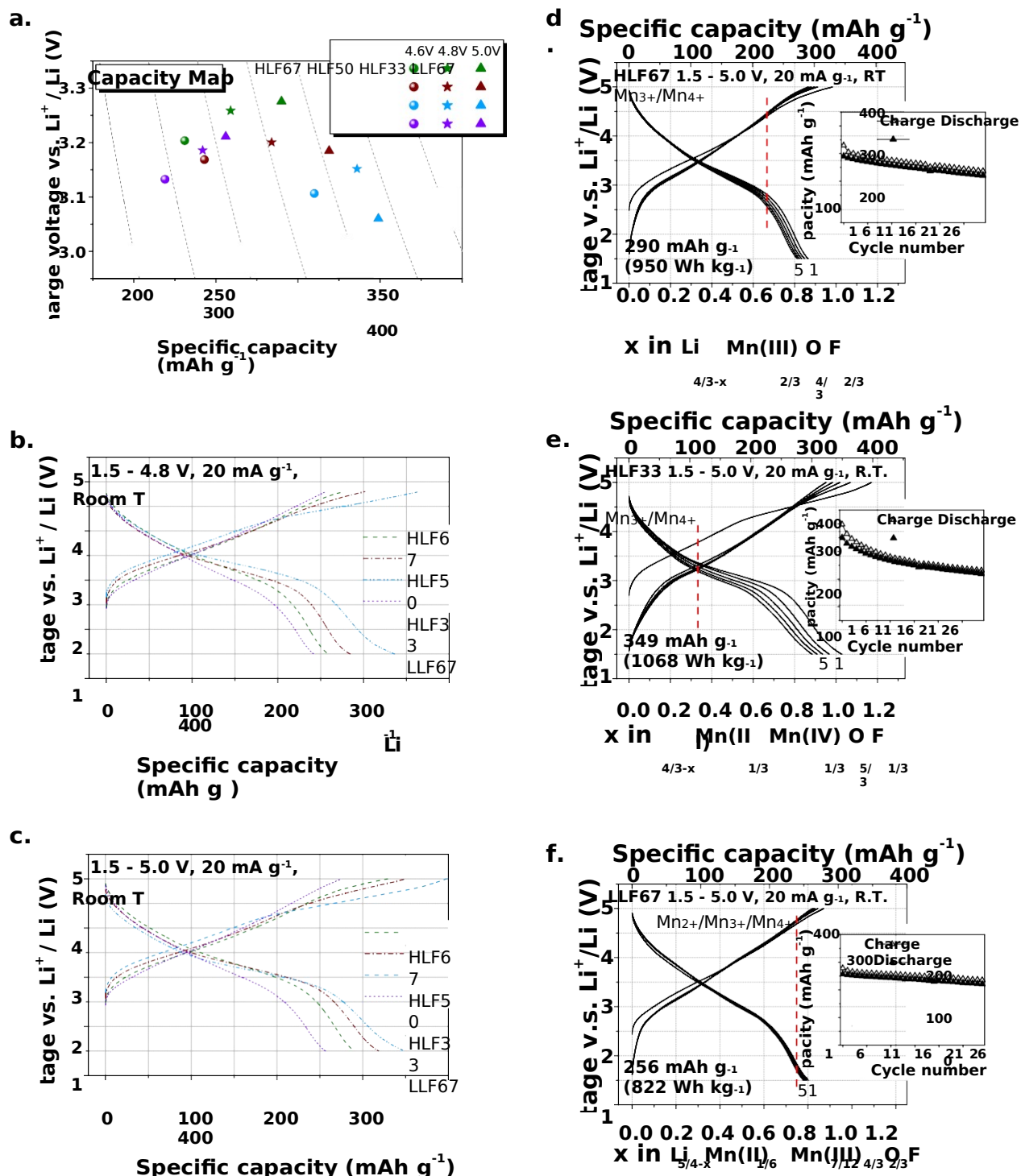
8 probe background signal) are overlaid. The shoulder observed to the left of the most
intense peak

9 in the spectra, at ca. -163 ppm, is ascribed to the probe background signal. Spinning

sidebands of

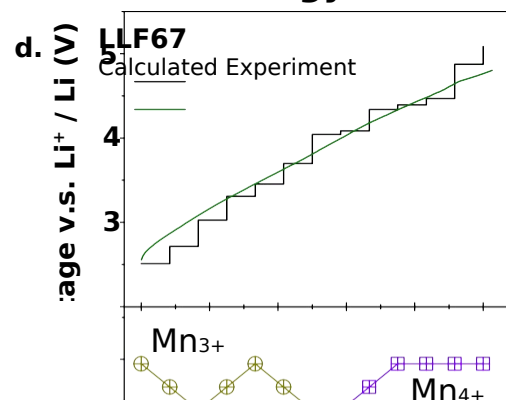
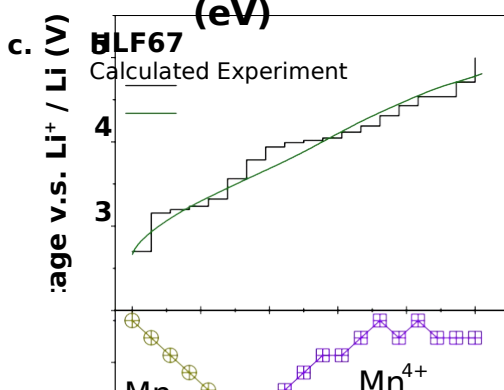
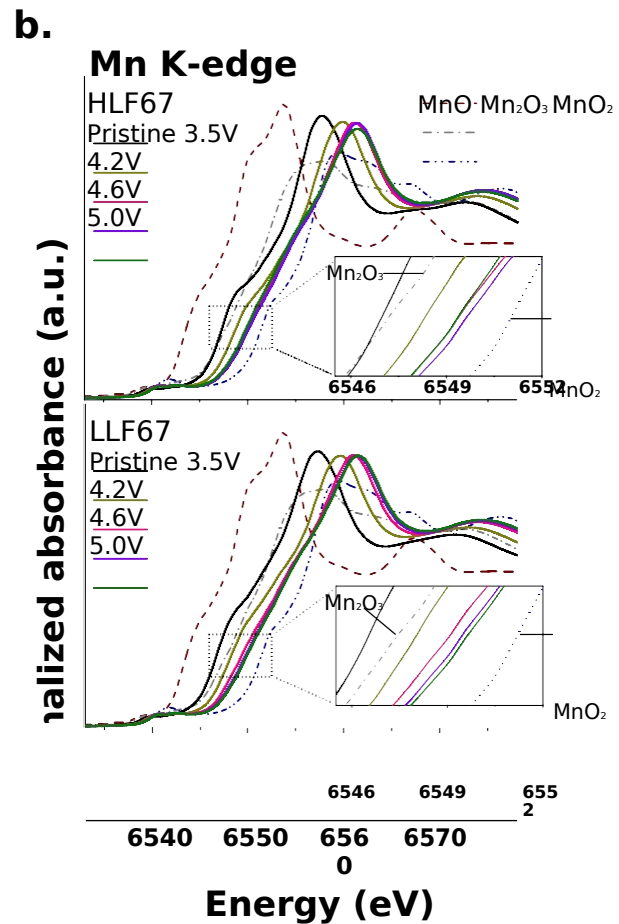
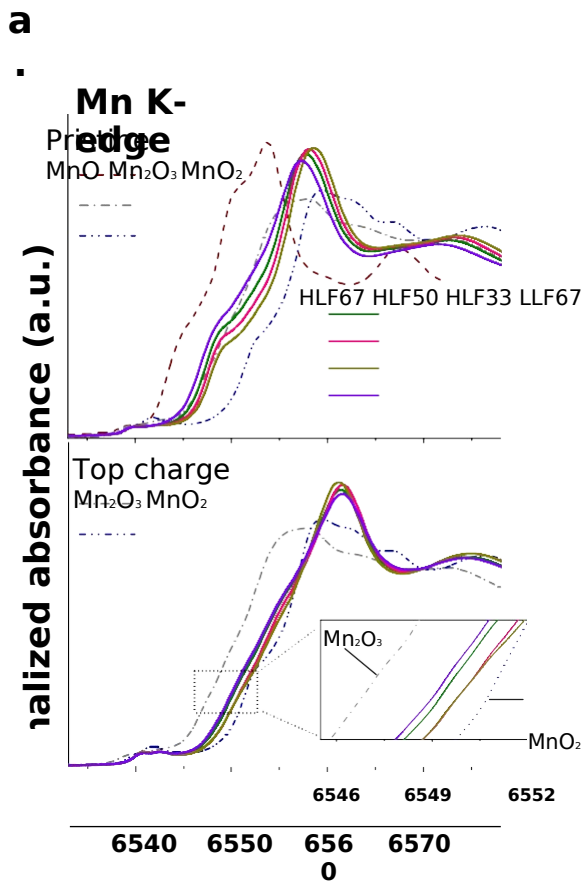
10 the sharp, diamagnetic signals are indicated with asterisks. **d.** TEM/EDS mapping of the elemental

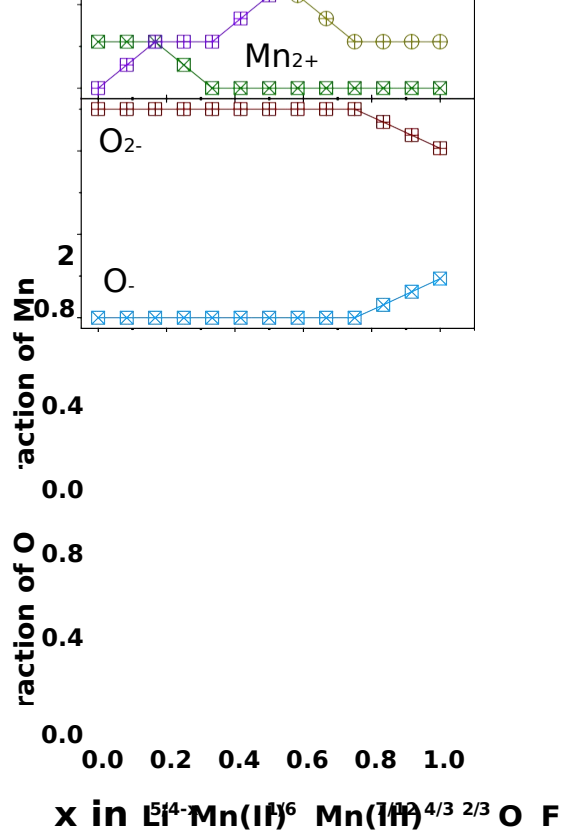
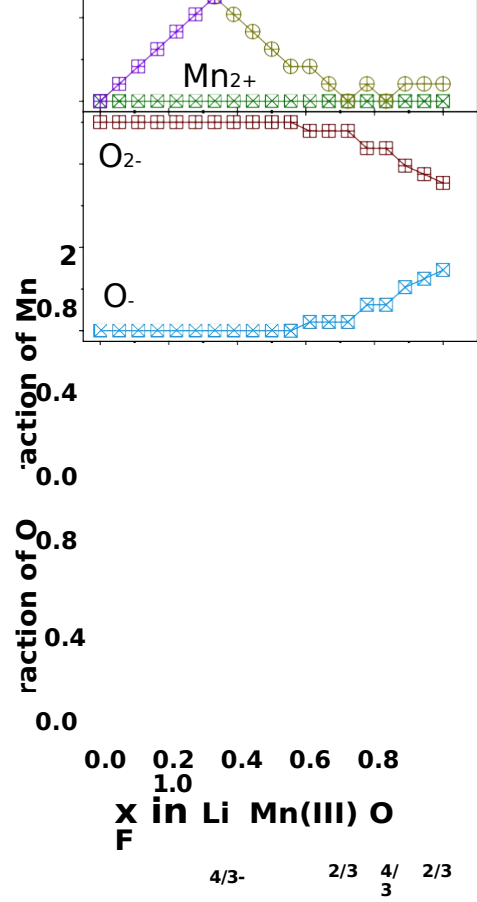
11 distribution in a particle cluster of as-synthesized HLF50.



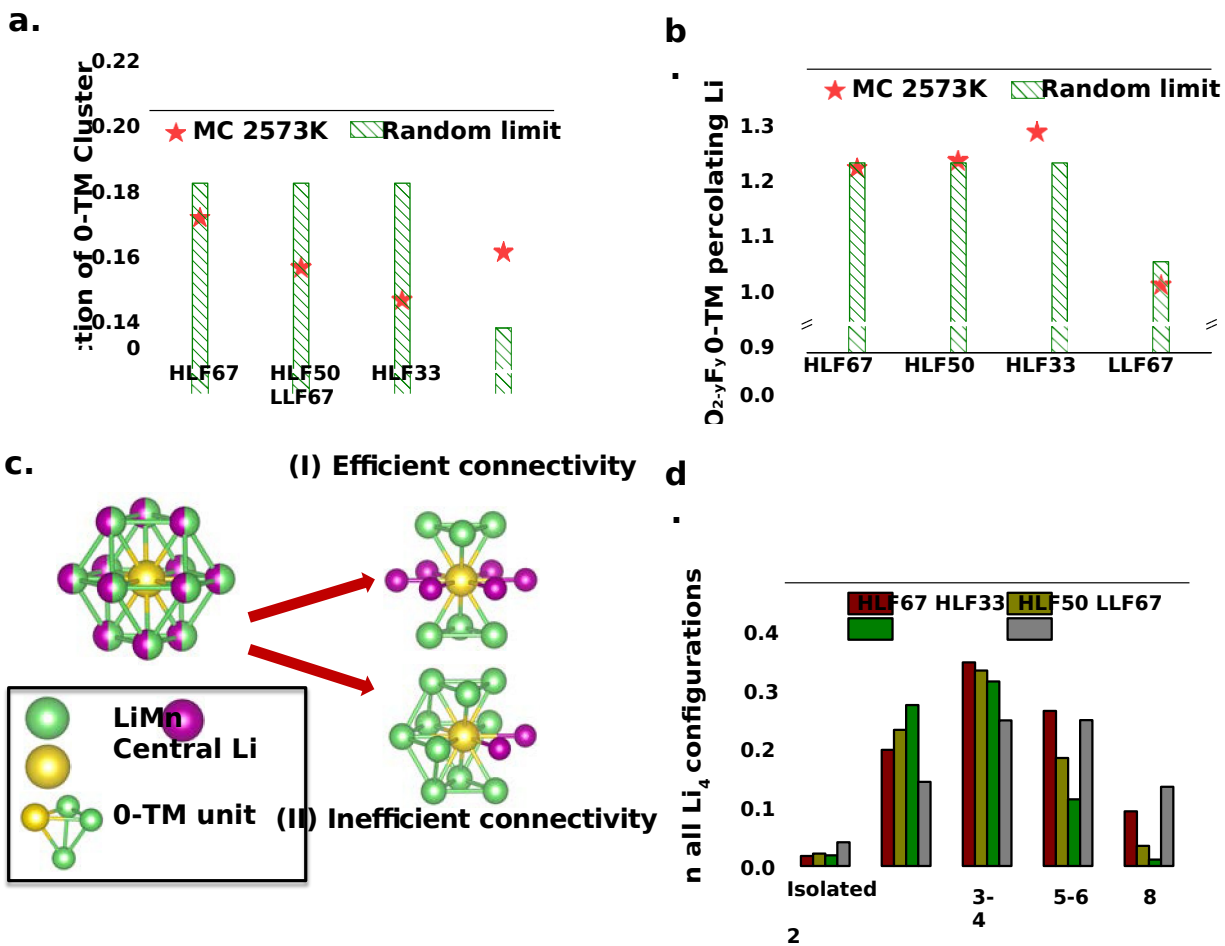
1
2 **Figure 2** | Electrochemical performance of Li-Mn-O-F compounds. a. Capacity map showing

- 3 initial discharge capacities and energy densities of Li-Mn-O-F compounds at different voltage windows.
- 4 windows. First cycle voltage profiles of Li-Mn-O-F compounds within the voltage windows of **b**.
- 5 1.5 - 4.8V and **c**. 1.5 - 5.0V at a rate of 20 mA g⁻¹ and room temperature. Representative profiles and capacity retention of **d. HLF67**; **e. HLF33**; **f. LLF67** within the voltage window of 1.5 - 5.0V at 20 mA g⁻¹ and room temperature. The red dashed lines indicate the theoretical Mn-redox capacities. The initial oxidation states of Mn in the as-synthesized materials can be found from the bottom x-axis.

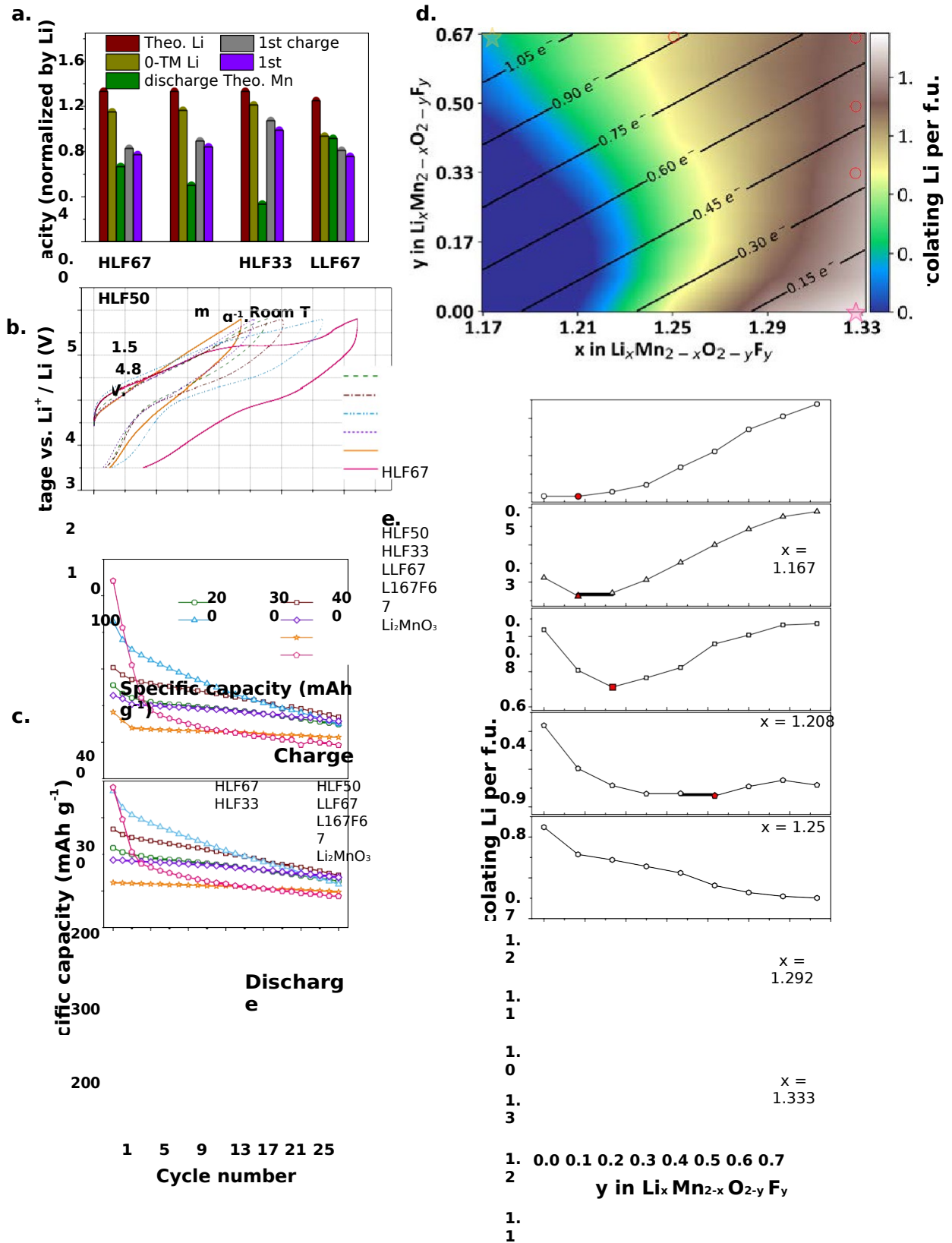




1 **Figure 3 | Redox mechanism of Li-Mn-O-F compounds. a.** Mn K-edge XANES spectra of all
 2 compounds at the pristine state and top charge in the first cycle. **b.** Mn K-edge XANES spectra of
 3 HLF67 and LLF67 at different states of charge in the initial cycle. Computed voltage
 4 profiles and evolution of Mn and O oxidation states calculated from DFT, denoting the dominant
 5 capacity source at each state of delithiation for **c.** HLF67 and **d.** LLF67. The experimental
 6 profiles overlaid in the figures of each compound are the quasi-equilibrium voltage
 7 obtained from potentiostatic intermittent titration technique (PITT) measurements when
 8 from open circuit voltage to 4.8 V.
 9
 10



2 **Figure 4 | SRO analysis of Li-Mn-O-F compounds.** **a.** Fraction of 0-TM tetrahedral
clusters in
3 Li-Mn-O-F compounds obtained from the simulated MC structures at 2573K and random
limit
4 (infinite temperature). **b.** Amount of 0-TM-connected Li (percolating Li) per formula
unit and
5 comparison with random limits in Li-Mn-O-F compounds. **c.** Illustration of representative
local
6 bonding configurations around a central Li (highlighted in yellow), with green spheres
and purple
7 spheres referring to Li and Mn ions respectively. Configuration (I) presents an
'efficient' Li
8 connectivity with the central Li shared by two 0-TM units; configuration (II)
presents an
9 'inefficient' way to create an extended percolation network, where five 0-TM units are
highly
10 localized. **d.** Distribution of different bonding environments around all the Li that are
presented in
11 0-TM tetrahedrons: the x-axis represents the number of 0-TM units one Li is shared by.



1

2 **Figure 5 | Design analysis for Li-Mn-O-F compounds.** a. Comparison of the theoretical Li/Mn-

- 3 redox capacities, accessible 0-TM capacities predicted by Monte Carlo simulations, and
- 4 experimental capacities obtained from the first charge/discharge at 20 mA g⁻¹ and room
- 5 temperature within the voltage window of 1.5-4.8V for HLF67, HLF50, HLF33, LLF67.
- 6 Experimental first cycle **b.** voltage profiles and **c.** cyclability for all the Li-Mn-O-F compounds
- 7 at 20 mA g⁻¹ and room temperature within a voltage window of 1.5-4.8V. **d.** Design map within
- 8 the Li-Mn-O-F DRX space. The color scale maps the total amount of percolating Li per formula

- 1 unit (f.u.) through 0-TM percolation network at each composition, obtained from Monte Carlo
- 2 simulations at 2573K. The solid lines and numbers in the map indicate the theoretical Mn-redox capacity. The red circles mark the compositions that are studied in previous sections. The pink and
- 3 yellow stars mark the composition with the highest amount of 0-TM Li (DRX-Li₂MnO₃) and the
- 4 highest Mn-redox capacity (L167F67, Li_{1.1667}Mn(II)_{0.3333}Mn(III)_{0.501.3333}F_{0.6667}) in the map,
- 5 respectively. e. Li percolation analyses in Li_xMn_{2-x}O_{2-y}F_y as a function of F (y values) at various
- 6 Li-excess levels (x values). The critical F contents (local minimum) are highlighted in red.

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