# Supporting Information

Structural regulation-induced Li-electron disentanglement for stabilized oxygen redox of Li-excess disordered rock-salt

cathode materials

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## Supplementary Note 1 Structure model generation:

The supercells used to assess oxygen redox activity were expanded from the refined cubic unit cell (2x2x2, 64 atoms in total) with the chemical formula of  $Li_{19}Ti_7Ni_6O_{32}$ (LTNO) and Li<sub>19</sub>Ti<sub>7</sub>Ni<sub>6</sub>O<sub>29</sub>F<sub>3</sub> (LTNOF). Recognizing the presence of short-range ordering (SRO) in DRX material, structures with randomly distributed atoms (Random) and those exhibiting SRO were both considered for each composition. Specifically, Random structures were generated using the special quasirandom structures (SQS) module within the ATAT package.<sup>[1,2]</sup> Specifically, fully disordered structures were constructed via a cluster-expansion-based Monte Carlo simulation, initiated with a rock-salt lattice with the target occupation. The objective function was constructed with pair interactions up to 7.1 Å, triplet interactions up to 4.5 Å, and quadruplet interactions up to 4.5 Å. For structures containing SRO, a combined approach using OCC-targeted Monte Carlo simulation and DFT calculations was adopted. This method aimed to recover the SRO features in DRX captured by neutron total scattering measurements, as detailed in our previous work.<sup>[3]</sup> To ensure statistical significance, three SRO and three Random structures were constructed for each composition (LTNO and LTNOF), respectively. Hence, statistical results in the main text are averaged from twelve DFT calculation results. Delithiated structures were obtained by enumerating all possible Li/vacancy configurations using the Pymatgen code, followed by Ewald electrostatic energy summation.<sup>[4]</sup> The 50 structures with the lowest Ewald energy were further screened using DFT static calculations. Changes in Bader charge and magnetization were obtained from the results of the fully lithiated  $(Li_{19})$  and highly delithiated  $(Li_4)$ structures.

### Supplementary Note 2 F-indued alterations at atomic-scale:

In the fluorinated DRX, i.e., LTNNOF, only Ni and O redox are taken into account, as the redox reaction seems to be not available at the F atom. Indeed, the calculated magnetic moments of F atoms remain almost unchanged upon delithiation, implying F is redox-inactive during charging (Fig. S10). Therefore, only the activity and numbers of oxygen clusters ( $OLi_xTM_{6-X}$ ) were studied by DFT and PDF+RMC. Regarding the Ni atoms, different coordination environments around Ni were not differentiated, thus Ni atoms bonded to F atoms have already been taken into account in our DFT calculations and statistical analysis of the RMC-fitted supercell.

As an anionic species, the F atom has a direct influence on the neighboring TM atoms but an indirect effect on its second-nearest oxygen atoms. The average magnetic moment changes upon delithiation are approximately ~0.75 in LTNO (Fig. S2) and ~0.78 in LTNOF (Fig. S3), suggesting that there is a greater contribution of Ni redox in LTNOF. More comprehensively, the effect of  $2^{nd}$  shell F atoms on center oxygen redox is studied. As compared in Fig. S11 and Fig. S12, for OLi<sub>5</sub>Ni oxygen clusters where the Ni atom has a valence state of +3 (Fig. S11(a)), the introduced F atom reduces the Ni atom to a +2 valence state (Fig. S11(b)). However, the reduction of the valence state of Ni within OLi<sub>5</sub>Ni (from Ni<sup>3+</sup> to Ni<sup>2+</sup>) slightly elevates the Li-O-Li energy level. For Ni atoms already in the +2 state (Fig. S12(a)), the incorporated F atom shows no obvious influence on its neighboring Ni atoms (still in the +2 state, Fig. S12(b)), thereby resulting in subtle changes in the second-nearest oxygen atom. It should be noted that all the DFT results are based on six LTNO and six LTNOF structural models, thereby incorporating all of these F-induced effects on the activity of oxygen atoms as reflected in Fig. 2a.

#### Supplementary Note 3 Statistical analysis:

The definition of a percolation network can differ subtly in previous publications, but the main idea remains clear.<sup>[5,6]</sup> Here we consider a Li transport network as a Li percolation network when it connects the supercell's periodic boundaries in any direction so that it spreads into an infinitely large network. The percolation network in a DRX supercell can be efficiently calculated using a union-find algorithm based on the disjoint-set data structure which has been explained in the Supporting Information of our previous work.<sup>[3,7]</sup> Once the lithium ions in the percolation network are identified, we scan every oxygen anion and TM cation in the supercell to find out those related to the percolating network. Here, an oxygen anion is considered percolation-related if any one of its six coordinated cations is a percolating lithium ion. Likewise, a TM cation is considered percolation-related if any one of its twelve coordinated cations is a percolating lithium ion.

#### Supplementary Note 4 Redox contribution breakdown:

To quantify the influence of SRO on redox reactions in DRX, we conducted a breakdown of the total redox contribution. Firstly, the total redox activity equates to the total number of lithium atoms that can be extracted, namely the size of the lithium percolation network. Next, we calculated the redox contributions from percolationrelated TM (Ni) and O atoms. This evaluation involves determining the number of redox centers and the charge transfer number per center. For instance, the charge transfer of different types of oxygen atoms was calculated using DFT calculations (Fig. 2a). The number of percolation-related oxygen atoms (i.e., oxygen atoms bonded to percolating lithium atoms) was obtained by counting throughout the RMC-derived supercells (Fig. 2b and c). Similarly, the redox contribution of percolation-related Ni atoms was determined. Five independent RMC fittings were conducted to ensure statistical significance. Finally, the difference between the total redox activity and the sum of contributions from percolation-related Ni and O ions was defined as the contribution outside the percolation network. Our current method may be subject to systematic errors due to distinct calculation results from different theoretical approaches. Previous studies suggest differences in the absolute values of calculated oxidation states, yet consistent evolution trends upon delithiation.<sup>[8]</sup> Importantly, considering that the redox activity of each atom is closely related to its bonding environment, only one set of charge transfer numbers was used for LTNNO and LTNNOF supercells (both SRO and Random). This implies that differences in redox contribution stem solely from changes in the numbers of each type of redox center, i.e., SRO. Consequently, the redox contribution value is more meaningful in relative terms than in absolute terms.



**Fig. S1** Schematic depicting the workflow combining RMC modeling and DFT calculations to investigate oxygen redox reactions in DRX cathode materials. DFT was utilized to assess the activity of various oxygen environments in DRX, while RMC modeling of neutron total scattering patterns facilitated the experimental identification of the realistic structure of DRX within a supercell containing 64000 atoms.



**Fig. S2** The evolution of net magnetization in (a) Ni ions, and (b) O ions of  $Li_{19}Ti_7Ni_6O_{32}$  during delithiation. The decrease in the magnetic moment of Ni corresponds to the oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup>/Ni<sup>4+</sup>. The deviation of the magnetic moment of O from zero indicates the oxidation of oxygen atoms. These results suggest that charge compensation is achieved through a combined process of TM and oxygen redox in LTNO.



Fig. S3 The evolution of net magnetization in (a) Ni ions, and (b) O ions of  $Li_{19}Ti_7Ni_6O_{29}F_3$  during delithiation. These results suggest that charge compensation is achieved through a combined process of TM and oxygen redox in LTNOF.



Fig. S4 The evolution of Bader charge of Ni and O ions in (a)  $Li_{19}Ti_7Ni_6O_{32}$ , and (b)  $Li_{19}Ti_7Ni_6O_{29}F_3$  during delithiation.



**Fig. S5** The calculated pDOS of Ni 3d orbitals and O 2p orbitals in LTNOF at different states of charge: (a)  $\text{Li}_{1.1875}$ , (b)  $\text{Li}_{0.875}$ , (c)  $\text{Li}_{0.5625}$ , and (d)  $\text{Li}_{0.25}$ . The increased unoccupied states of Ni eg and O 2p orbitals during delithiation are consistent with the concurrent involvement of transition metal (TM) and oxygen redox.



**Fig. S6** Diverse oxygen environments and the calculated electronic structure. The pDOS of the O 2p orbital for oxygen atoms with coordination environments of (a)  $OLi_5Ni$ , (b)  $OLi_5Ti$ , (c)  $OLi_4Ni_2$ , and (d)  $OLi_4Ti_2$  are shown. In each case, the pDOS differentiates between the Li-O-Li state and the Li-O-TM/TM-O-TM state, as shown in (e)-(h). The corresponding local structures of these oxygen environments are displayed on the right side.



**Fig. S7** Diverse oxygen environments and the calculated electronic structure. The pDOS of (a) O  $2p_y$  orbital along the Li-O-Li direction of oxygen atoms with OLi<sub>6</sub> configuration. (b) O  $2p_x$  orbital along the Li-O-Li direction of oxygen atoms with OLi<sub>5</sub>Ni and OLi<sub>5</sub>Ti configuration. (c) O  $2p_z$  orbital along the Li-O-Li direction of oxygen atoms with OLi<sub>4</sub>Ni<sub>2</sub> and OLi<sub>4</sub>Ti<sub>2</sub> configuration. (d) O  $2p_x$  and  $2p_z$  orbital of oxygen atoms with OLi<sub>3</sub>Ni<sub>3</sub> configuration, O  $2p_y$  orbital of oxygen atoms with OLi<sub>3</sub>Ti<sub>3</sub> configuration. The corresponding local structures of the oxygen environments are displayed on the right side.



**Fig. S8** Calculated overall O 2p pDOS, with the right panel displaying the isosurface plot of charge density around oxygen atoms within specific  $OLi_xTM_{6-x}$  clusters, in the energy range of (a) -1.0 to 0 eV, (b) -1.5 to 0 eV, (c) -2 to 0 eV.



**Fig. S9** Calculated pDOS of the oxygen atom with the configuration of (a)  $OLi_4TiNi$  and (b) $OLi_4Ti_2$  at the pristine state and charged state, respectively. The distinct redox activity is evident from the evolution of the unoccupied states following lithium extraction.



Fig. S10 The evolution of net magnetization in O and F ions of  $Li_{19}Ti_7Ni_6O_{29}F_3$  during delithiation.



Fig. S11 Calculated pDOS of Ni and O ions in the  $OLi_5Ni$  configuration, where the Ni atoms reside in a coordination environment of (a)  $NiO_6$  and (b)  $NiO_5F$ 



Fig. S12 Calculated pDOS of Ni and O ions in the  $OLi_4$ TiNi configuration, where the Ni atoms reside in a coordination environment of (a) NiO<sub>6</sub> and (b) NiO<sub>5</sub>F



**Fig. S13** Schematic illustrations of (a) Percolation network and percolation-related Ni atoms, and (b) Percolation network and percolation-related oxygen atoms in the RMC-derived LTNNO supercells. The percolating lithium atoms are depicted in grey.



**Fig. S14** Structural model of LTNO for DFT calculation, where the Ti-rich domain is enlarged, and the lithium atom of interest is octahedrally coordinated. Here, for clarity, only the hole densities in the enlarged Ti-rich domain are presented in Fig.3 of the main text.



**Fig. S15** Calculated pDOS and its evolution during charging of Ti 3d, Ni 3d, and O2p orbitals of LTNO. Upon extracting the octahedrally coordinated lithium, new unoccupied states immediately emerge above the Fermi level in both the Ni 3d and O 2p pDOS, while no noticeable changes are observed in the Ti 3d pDOS after delithiation. The DOS evolution is consistent with the calculated hole density, where a newly emerged hole state can be observed around the Ni atom upon delithiation.



**Fig. S16** (a) Schematic representation of the oxygen octahedral clusters  $(OLi_xTM_{6-X})$  and the definition of cluster charge. (b) Cluster charge for different types of  $OLi_xTM_{6-X}$  at the pristine and charged states. (c) Charge transfer of different types of clusters upon delithiation. Charge evolution was monitored by calculating the charge of the oxygen cluster, defined as the average Bader charge of the oxygen octahedron for each coordination environment ( $OLi_xTM_{6-X}$ ). Statistical results of cluster charge at the pristine and charged states, along with the value of charge transfer, are depicted in Fig. S11(b) and (c). As anticipated, the cluster charge of  $OLi_4Ti_2$  and  $OLi_3Ni_3$  is nearly zero at the pristine state, indicating local charge neutrality. With the inclusion of more lithium or TM atoms in other types of oxygen environments, the cluster becomes negatively or positively charged. Consequently, the charge of the system is intricately balanced among different types of clusters on a broader scale, rather than within the single oxygen cluster as observed in layered oxide cathode materials.



Fig. S17 XRD pattern measured for as-synthesized LTNNO-ND sample.



**Fig. S18** Conceptualization of DRX materials with the general formula  $Li_{1+X}TM_yTM''_{1-x-y}O_2$ , illustrating four types of oxygen clusters with distinct capacities to conduct  $Li^+$  and electrons, enabling the independent manipulation of the  $Li^+$  and electron percolation networks in DRX.

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