

# Structure and Interface Design Enable Stable Li-Rich Cathode

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cathode and electrolyte. Herein, we report that these challenges are migrated by using a stable O2-structured Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>-O2 (O2-LR-NCM) and all-fluorinated electrolyte. The O2-LR-NCM can restrict the transition metals migrating into the Li layer, and the in situ formed fluorinated cathode-electrolyte interphase (CEI) on the surface of the O2-LR-NCM from the decomposition



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of all-fluorinated electrolyte during initial cycles effectively restrains the structure transition, suppresses the O2 release, and thereby safeguards the transition metal redox couples, enabling a highly reversible and stable oxygen redox reaction. O2-LR-NCM in all fluorinated electrolytes achieves a high initial CE of 99.82%, a cycling CE of >99.9%, a high reversible capacity of 278 mAh/g, and high capacity retention of 83.3% after 100 cycles. The synergic design of electrolyte and cathode structure represents a promising direction to stabilize high-energy cathodes.

#### INTRODUCTION

Li-ion batteries (LIBs) have been widely applied in multitudinous energy storage systems due to their remarkably high energy density, low self-discharge, and negligible memory effect.<sup>1</sup> Because cathode materials control the energy density of the LIBs,<sup>2</sup> the rapid expansion of LIBs prompts the innovation for higher-energy and low-cost cathodes.<sup>3</sup> Among the intercalation transition metal oxide cathodes, the lithiumand manganese-rich layered-oxide cathodes (LMRCs) received intensive research interest due to their high average discharge voltage (>3.5 V) and high specific capacities (>250 mAh  $g^{-1}$ ).<sup>4,5</sup> The energy density of LMRCs is almost 2 times higher than that of the commercial cathodes of LiCoO<sub>2</sub> and LiFePO<sub>4</sub>.

The LMRCs are composed of Li<sub>2</sub>MnO<sub>3</sub> with a monoclinic structure of the C2/m space group and LiMO<sub>2</sub> (M = Mn, Ni, Co) with a trigonal structure of the  $R\overline{3}m$  space group, consisting of a framework of CdI2-type anionic MO2<sup>-</sup> layers interleaved with Li<sup>+</sup> ions.<sup>6,7</sup> Compared to the traditional layered-oxide cathodes whose redox processes are solely dominated by transition metals (TMs), the LMRCs deliver much higher specific capacity beyond the theoretical values of typical layered-structure cathodes due to the participation of anionic redox (O<sup>2-</sup>).<sup>8,9</sup> LMRCs can have O3 or O2 structure. Previous investigations were mainly focused on O3-type LMRCs, in which the irreversible oxidation of O<sup>2-</sup> occurs at

high voltages (~4.4-4.8 V) with irreversible transition-metal migration into the Li layer,<sup>10-13</sup> leading to a low initial Coulombic efficiency (CE) and a potential decay in the charge/discharge cycles. In addition, oxygen gas will release from LMRCs due to the instability of the oxygen-oxygen dimers once charged to a high voltage of >4.4 V in the O3-type LMRCs. With the O2 gas release, redox couples with lower voltage, such as  $Mn^{3+}/Mn^{4+}$  and  $Co^{2+}/Co^{3+}$ , will be activated, directly resulting in the potential degradation. The oxygen loss in the lattice prompts the misalignment of Li and TMs and the layered to spinel structure evolution, leading to higher charge transfer resistance and severely capacity fading.<sup>14–16</sup> Moreover, the high cutoff voltage of the LMRCs induces continuous side reactions between the cathode and the electrolyte, further deteriorating the electrochemical performance of the cell. All of these issues seriously restrict their practical applications. Although vast efforts, including pretreating,<sup>17,18</sup> surface doping,<sup>19</sup> surface coating,<sup>20</sup> and materials blending,<sup>21</sup> have

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Figure 1. Structure and morphology characterization. X-ray diffraction patterns with Rietveld refinement of the precursor  $Ni_{0.13}Co_{0.13}Mn_{0.54}(CO_3)_{0.8}$  (A, NCM-CO<sub>3</sub>),  $Na_{5/6}Li_{1/4}(Ni_{0.13}Co_{0.13}Mn_{0.54})_{3/4}Ox$  (B, Li, Na-NCM-O), and O2-type  $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$  (C, O2-LR-NCM). SEM images of NCM-CO<sub>3</sub> (D) and O2-LR-NCM (E). TEM (F) and HRTEM (G) images of O2-LR-NCM. (H–K) Elemental mapping of Ni, Co, and Mn for O2-LR-NCM. XPS spectra of Ni 2p (L), Co 2p (M), Mn 2p (N), and O 1s (O) for O2-LR-NCM.

been conducted to improve the electrochemical performance of O3-type LMRCs, these strategies bring many inevitable negative effects, such as reduced specific capacity, poor cycling stability, and lowered average CEs in the prolonged cycling. In addition, the solutions for mitigating the structural evolution, which include the optimizing of the synthetic method and electrolyte,<sup>22–24</sup> the substitution of TMs,<sup>25,26</sup> and surface doping,<sup>27,28</sup> also bring some accompanied side reactions. The high cost and complex operation procedure in these strategies also limit the practical production.

As an isoform to O3-type LMRCs, the O2-type LMRCs with the oxygen layers stacking in the fashion of ABCBA have comparable capacities as O3-type LMRCs, which could suppress the formation of oxygen–oxygen dimers when charged to high voltages<sup>29–32</sup> and suppress the movements of transition metals within the Li layer.<sup>12</sup> Therefore, the structural evolution from the layered to spinel phase in O2type LMRCs is curbed during cycling, enabling a highly reversible lithiation/delithiation. Up to now, the research on O2-type LMRCs mainly focus on either Co-rich (Li<sub>1.25</sub>Co<sub>0.25</sub>-Mn<sub>0.50</sub>O<sub>2</sub>)<sup>31</sup> or Co-free (Li<sub>1.19</sub>Mn<sub>0.73</sub>Ni<sub>0.08</sub>O<sub>2</sub>) cathodes.<sup>12,29,30</sup> The Co-rich cathodes have a high cost, while the Co-free cathodes show fast energy decays. Therefore, the components optimizing with tri-transition metal oxides in O2-type LMRCs will provide a high performance with low cost. In addition, the recently reported all-fluorinated electrolytes brought another enlightenment to stabilize LMRCs. Our previous works have proved that such all-fluorinated electrolytes have a high oxidation stability of up to 5.6 V thanks to the in situ formed highly stable cathode–electrolyte interphase (CEI) on the cathode and robust SEI on the anodes, which enable excellent cycling stability for high-energy LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> and LiNiO<sub>2</sub> cathodes.<sup>33–35</sup> By combination of superstable O2structured LMRCs with all-fluorinated electrolyte, the in situ formation of the effective CEI on O2-type LMRCs should be able to accommodate the large volume change and severe side reactions on the LMRCs even at a high charging cutoff voltage, which provides a practical and promising strategy for constructing high-performance batteries.

Herein, the O2-type lithium- and manganese-rich layeredoxide cathode of  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  (O2-LR-NCM) was synthesized by means of an ion exchange method. The lower content of cobalt and nickel in O2-LR-NCM effectively reduces the cost and scarcity issue and promises a good structural stability. Thanks to the in situ formed CEI layer within the all-fluorinated electrolyte (1.0 M LiPF<sub>6</sub> in a mixture of fluoroethylene carbonate (FEC), 3,3,3-fluoroethylmethyl carbonate (FEMC), and 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE) (2:6:2 by volume), with the additive of lithium difluoro(oxalato)borate (LiDFOB) (denoted as 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 for short)) and the extraordinarily stable O2 type structure, the O2-LR-NCM cathode delivers highly reversible anionic oxygen redox reactions with a high initial Coulombic efficiency (CE) of 99.82%, which is much higher than that (67.58%) of the conventional  $O_3$ -type  $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$  (O3-LR-NCM). The synergic effect of the in situ formed robust CEI and the superstructural stability of O2-LR-NCM renders an outstanding cycling stability with a capacity retention of 83.3% after 100 cycles (232.3 mAh g<sup>-1</sup>) with little voltage decay, delivering an enhanced rate capability of 82.9 mAh g<sup>-1</sup> even at 50/3 C (1 C = 300 mA g<sup>-1</sup>), much better than O3-LR-NCM in an all-fluorinated electrolyte and O2-LR-NCM in a commercial electrolyte, which represents a leap toward the commercialization of the Li-rich cathode batteries.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of Li<sub>1.2</sub>Ni<sub>0.13</sub>-Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub>. The first-step precursor of Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>- $(CO_3)_{0.8}$  (NCM-CO<sub>3</sub>) was prepared by a coprecipitation reaction. Figure 1A shows Rietveld refinement of the X-ray diffraction (XRD) pattern of NCM-CO<sub>3</sub> powder, which can be fitted to a space group of R3c. After that, the NCM-CO<sub>3</sub> was annealed with the mixture of Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> to prepare the second-step precursor of  $Na_{5/6}Li_{1/4}(Ni_{0.13}Co_{0.13}Mn_{0.54})_{3/4}$ - $O_{xy}$  (Li, Na-NCM-O), which can be indexed as P2-type Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> structure (Figure 1B). Then, the Li, Na-NCM-O was immersed into the molten salt mixture of LiNO<sub>3</sub>/LiCl (88:12, w/w) to conduct the ion-exchange process. The obtained product is O2-LR-NCM, and its Rietveld refinement of XRD pattern (Figure 1C) shows a Pawley fit to an O2-type Li<sub>2</sub>MnO<sub>3</sub>. For comparison, the conventional O3-LR-NCM was directly synthesized by annealing the mixture of NCM-CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>, which possesses an O3-type Li<sub>2</sub>MnO<sub>3</sub> structure (Figure S1). As shown in Figure 1D, the NCM-CO<sub>3</sub> exhibits a spherical structure, with a diameter of  $\sim 2-4 \ \mu m$ . The inset of Figure 1D reveals that the NCM-CO<sub>3</sub> spheres are composed of small primary particles with size of ~10 nm. After the annealing and ion-exchange process, the O2-LR-NCM (Figure 1E) inherits the spherical structure, but the diameter size grows to  $3-5 \ \mu m$  with the sheet-like primary particles. In contrast, the particles of the O3-LR-NCM are irregular with a uniform diameter of  $\sim 1-5 \ \mu m$  (Figure S2A,C), and its primary particles possess irregular particle morphology with a diameter of ~100-300 nm. The high-resolution transmission electron microscopy (HRTEM) images reveal that both the O2-LR-NCM (Figure 1G) and O3-LR-NCM (Figure S2D) deliver a typical interplanar distance of 0.47 nm, corresponding to the (003) plane of LiMO<sub>2</sub> ( $R\overline{3}m$ ) and the (001) plane of Li<sub>2</sub>MnO<sub>3</sub> (C2/m), in good agreement with the previous reports.<sup>36,37</sup> The energy-dispersive X-ray spectroscopy (EDS) elemental mapping results (Figure 1H-K and Figures S3-S5) reveal the elements of Ni, Co, and Mn are uniformly distributed in these materials and own an element ratio equal to the theoretical value.

The chemical environments of the Ni, Co, Mn, and O elements in O2-LR-NCM and O3-LR-NCM were analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 1L, the Ni 2p presents two spin—orbit lines, of which the Ni  $2p_{1/2}$  is located at ~872.4 eV with a satellite peak at about ~878.8 eV and the Ni  $2p_{3/2}$  is located at ~854.5 eV with a satellite peak at about ~860.9 eV, indicating the main valence state of the Ni cation is +2. The additional peak at ~856.2 eV is due to the some Ni<sup>3+</sup> cations in the sample. For the Co 2p (Figure 1M), the two peaks for the binding energy of Co  $2p_{1/2}$ .

(794.8 eV) and Co  $2p_{3/2}$  (780.0 eV) with two satellite peaks at ~803.3 and 788.5 eV can be ascribed to Co<sup>3+</sup>, while the two tiny peaks at 796.7 and 782.3 eV indicate the existence of a small amount Co<sup>2+</sup>. The Mn 2p spectrum (Figure 1N) at 655.1 eV (Mn  $2p_{1/2}$ ) and 644.2 eV (Mn  $2p_{3/2}$ ) can be fitted to the Mn<sup>4+</sup>. Two additional small peaks at ~653.7 and 642.1 eV indicate the coexistence of Mn<sup>3+</sup>. The O 1s spectrum (Figure 1O) delivers two typical peaks, in which the peak at 528.8 eV corresponds to the bonds between metal and oxygen and the other peak at 531.2 eV is related to oxygen species at the surface of the material. The XPS peaks of O3-LR-NCM in Figure S6 show analogous results with O2-LR-NCM and are consistent with the previous reports,<sup>37</sup> confirming the ideal chemical state of the elements in the as-prepared O2-LR-NCM and O3-LR-NCM.

Structure Impact on the Electrochemical Performance of  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  in 1.0 M LiPF<sub>6</sub>@ LiDFOB@F-262. The electrochemical properties of O2 and O3-LR-NCM at the first two cycles are compared in LillLR-NCM half-cells within a voltage range of 2.0–4.8 V in the electrolyte of 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. Figure 2A



**Figure 2.** Electrochemical charge–discharge comparison between O2-LR-NCM and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. The first and second galvanostatic charge–discharge curves of (A) O2-LR-NCM and (D) O3-LR-NCM at 2/3 C, (1 C = 300 mA g<sup>-1</sup>). The corresponding dQ/dV curves for the first (B, E) and second (C, F) cycle of O2-LR-NCM (B, C) and O3-LR-NCM (E, F).

reveals the first and second charge-discharge curves of O2-LR-NCM at 2/3 C (1 C = 300 mA g<sup>-1</sup>), and Figures 2B and 2C are their corresponding dQ/dV curves. The O2-LR-NCM cathode delivers a typical staircase-like first charge curve with a capacity of 278.8 mAh  $g^{-1}$ , in which the first plateau from the open-circuit voltage (OCV) to 4.46 V corresponds to the extraction of Li<sup>+</sup> from the layered LiMO<sub>2</sub> component, while the second plateau from 4.46 to 4.8 V is associated with further delithiation from the Li<sub>2</sub>MnO<sub>3</sub> component, accompanied by oxidation of  $O^{2-}$ . The O3-LR-NCM (Figure 2D-F) shows a similar staircase-like first charge curve, but its first charge capacity of O3-LR-NCM (313.8 mAh g<sup>-1</sup>) is much higher than O2-LR-NCM. Specifically, the O3-LR-NCM delivers a much higher capacity within the voltage of 4.46-4.8 V than O2-LR-NCM. In the following discharge process, although both O2-LR-NCM and O3-LR-NCM deliver typical S-shaped lithiation curves, the O2-LR-NCM cathode delivers a much higher discharge capacity (278.3 mAh g<sup>-1</sup>) than O3-LR-NCM (191.8 mAh  $g^{-1}$ ), corresponding to a much higher initial CE of O2-LR-NCM (99.82%) than that (61.12%) of O3-LR-NCM. Previous reports have proved that the low initial charge-

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**Figure 3.** Electrochemical performance of O2- and O3-LR-NCM. The galvanostatic charge–discharge curves and voltage fade comparison of O2-LR-NCM in commercial 1.0 M LiPF<sub>6</sub> in EC/DEC (volume ratio, 1:1) electrolytes (denoted as 1.0 M LiPF<sub>6</sub>@EC/DEC) (A, D), O3-LR-NCM (B, E), and O2-LR-NCM (C, F) in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 at 2/3 C. Therein, the 1st and 100th discharge capacity in (D, E, F) was normalized to 1. (G) Cycle performances of O2- and O3-LR-NCM at 2/3 C in two electrolytes. (H) Rate performances of O2- and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. (I) The corresponding charge/discharge curves of O2-LR-NCM at different rates from 1/5 to 50/3 C in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262.

discharge CE of O3-LR-NCM is mainly caused by the irreversible oxidation of  $O^{2-}$ , during which the  $O^{n-}$  (n < 2) is dimerized, and meanwhile some  $O_2$  is released.<sup>38-40</sup> In addition, the formed Li<sup>+</sup> and O<sup>2-</sup> vacancies are partially occupied by the transition metal cations, blocking the Li<sup>+</sup> insertion back.<sup>41</sup> Comparatively, the uniformly dispersed Li<sub>2</sub>MnO<sub>3</sub> superstructure in O2-LR-NCM can block the formation of oxygen-oxygen dimers, which suppresses the irreversible formation of O<sub>2</sub> and enables a higher initial CE. The cyclic voltammetry (CV) curves of O2-LR-NCM and O3-LR-NCM (Figure S7) deliver consistent results with their charge-discharge results, and the higher overlap of CV curves in the second and third cycles for O2-LR-NCM reveals a much better reversibility than O3-LR-NCM during charge-discharge cycles. The reaction kinetics of O2-LR-NCM and O3-LR-NCM at the first and sixth charge and discharge cycles was investigated by using the galvanostatic intermittent titration technique (GITT). As shown in Figure S8, the potential below  $\sim$ 4.46 V in the first charge process is attributed to the delithiation of Li<sub>2</sub>MnO<sub>3</sub>, while the potential plateau at potential of 4.46-4.8 V corresponds to the O-related redox reaction. The O2-LR-NCM delivers overpotentials of ~66 mV at ~4.4 V and 67-165 mV at 4.46-4.8 V, much lower than that of O3-LR-NCM (~99 and 99-215 mV) at the first charging process. Moreover, the overpotentials of O2-LR-NCM in the following charge-discharge process are also lower than that of O3-LR-NCM (Figure S9), revealing a better reaction kinetics of O2-LR-NCM than O3-LR-NCM.

**Electrolyte Impact on Electrochemical Performance** of O2- and O3-Structured  $Li_{1,2}Ni_{0,13}Co_{0,13}Mn_{0,54}O_2$ . The electrochemical performances of O2-LR-NCM and O3-LR-NCM electrodes are compared in all-fluorinated 1.0 M LiPF<sub>6</sub>@ LiDFOB@F-262 electrolyte and the commercial 1.0 M LiPF<sub>6</sub> in EC/DEC (volume ratio, 1:1) electrolytes (denoted as 1.0 M LiPF<sub>6</sub>@EC/DEC). As revealed in Figure 3A,D, the O2-LR-NCM cathode in 1.0 M LiPF<sub>6</sub>@EC/DEC delivers a comparable first discharge capacity (277.8 mAh  $g^{-1}$ ) with that in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (278.3 mAh g<sup>-1</sup>, Figure 3C). However, the reversible capacity of O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC decays fast and remains only 49.4%  $(137.3 \text{ mAh g}^{-1})$  of its initial capacity after 100 cycles, with a low average CE of only 95.4% (Figure 3G and Figure S10). Besides, the normalized first and 100th discharge curves (Figure 3D) reveal that the O2-LR-NCM cathode in 1.0 M LiPF<sub>6</sub>@EC/DEC exhibits a large voltage fade in the whole discharge profile after 100 cycles. Therefore, only change of LR-NCM structure from O3 to O2 cannot completely suppress the voltage decay of the O2-LR-NCM cathode, and formation of dense CEI in all-fluorinated electrolyte is also important to suppress the O2 release and to avoid side reactions between the O2-LR-NCM cathode and electrolyte. However, the O2 structure plays a more important role in suppressing voltage decay of LR-NCM than electrolytes. As demonstrated in Figure 3B,E, the O3-LR-NCM cathode still has severe voltage decay after 100 cycles in the 1.0 M LiPF<sub>6</sub>(a)LiDFOB@F-262 electrolyte. A significant concave at ~3.2 V is

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**Figure 4.** Evolution of the transition metal K-edge positions of O2-LR-NCM by ex situ X-ray absorption near-edge structure (XANES). (A) Ni, Co, and Mn XANES spectra of O2-LR-NCM at various charge and discharge states. Selection of the states is based on the dQ/dV curve in Figure 2. Reference spectra from all the three elements are also shown. The Ni<sup>IV</sup> reference spectrum is collected from a LiNi<sub>1/3</sub><sup>II</sup>Co<sub>1/3</sub><sup>III</sup>Mn<sub>1/3</sub><sup>IV</sup>O<sub>2</sub> cathode material charged to 5.2 V. (B) Evolution of redox couples in O2-LR-NCM during charging and discharging.

observed for the O3-LR-NCM cathode in the 100th discharge curve at Figure 3E, which is due to the continuous oxygen release and irreversible transition metal migration into Li layer. The O3-LR-NCM cathode in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 only remains a discharge capacity of 146.3 mAh g<sup>-1</sup> after 100 cycles, corresponding to a capacity retention of 76.3%.

O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (Figure 3C,F) delivers a much better electrochemical performance than O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. After 100 cycles (Figure 3C), the O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 retains a discharge capacity of 232.3 mAh g<sup>-1</sup>, corresponding to a capacity retention of 83.3%, which is much higher than that of O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. Besides, little voltage decay was observed for the O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (Figure 3F). All of these results demonstrate that the combination of the structurally stable O2-LR-NCM with high-voltage 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 electrolyte enables the O2-LR-NCM to achieve a superior electrochemical performance.

The rate performances of O2-LR-NCM and O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 were also investigated. As shown in Figure 3H, the O2-LR-NCM cathode delivers an capacity of 319.0, 291.2, 263.8, 229.0, 197.5, 155.2, and 82.9 mAh g<sup>-1</sup> at 1/5, 1/3, 2/3, 5/3, 10/3, 20/3, and 50/3 C, respectively, and well recovers to 262.6 mAh g<sup>-1</sup> after the current density reduces back to 2/3 C, with a high average CE of >99.9%. In contrast, the O3-LR-NCM cathode shows a much worse rate capability with the corresponding discharging

capacity of 229.5, 202.5, 175.9, 132.2, 93.0, 55.6, and 9.0 mAh  $g^{-1}$  at 1/5, 1/3, 2/3, 5/3, 10/3, 20/3, and 50/3 C, respectively, and recovers to only 173.7 mAh  $g^{-1}$  after the current density reduces back to 2/3 C (Figure S11). The corresponding charge–discharge curves in Figure 3I and Figures S12–S14 reveal the O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262, and O2-LR-NCM in LiPF<sub>6</sub>@EC/DEC shows more serious capacity and voltage decay than O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262.

Structural Evolution of LR-NCM Cathode during Charge-Discharge Cycles. The electrochemical performances of O2-LR-NCM cathodes are closely related to evolution of redox couples during the delithiation/lithiation process.<sup>1</sup> The redox couple evolution of O2-LR-NCM at different state of charges (as circled in Figure 2B) was characterized by using X-ray absorption near-edge structure (XANES) and is shown in Figure 4. By comparison with the reference spectra of Ni<sup>2+</sup> and Ni<sup>4+</sup>, Ni in the pristine state of O2-LR-NCM is divalent, Co is slightly more oxidized than trivalent, and Mn is tetravalent. The higher valence of Co may be due to the presence of lithium vacancy that is commonly found in LR-NCM.<sup>29</sup> As shown in Figure 4A, when the O2-LR-NCM cathode is delithiated from OCV to 4.46 V, the spectra of both Ni and Co shift to higher energy, indicating both Ni and Co are oxidized in the voltage region. In contrast, Mn spectra show no edge shift, suggesting its inertness (from OCV to 4.46 V). After 4.46 V, all transition metal XANES spectra show no shift at all, suggesting the redox couple is switched to oxygen anions, which is very similar to the case of O3-LR-NCM (Figure 4B).<sup>8</sup> From OCV to 4.46 V, Ni in the O2-LR-NCM

cathode is oxidized to a valence state that is lower than tetravalent as indicated by the comparison between 4.46 V Ni spectrum with Ni<sup>IV</sup> reference spectrum which is taken from a  $\text{LiNi}_{1/3}^{\text{II}}\text{Co}_{1/3}^{\text{III}}\text{Mn}_{1/3}^{\text{IV}}\text{O}_2$  cathode material charged to 5.2 V. Judging from the edge position, the highest Ni valence that reached during charging is around Ni<sup>3.5+</sup>. Because Ni<sup>IV</sup> is the root of thermal instability in cathode materials,<sup>42</sup> a lower valence suggests that O2-LR-NCM may have a better thermal stability than that of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. It is also interesting to note that Co spectra show rigid edge shift upon charging. During lithiation of O2-LR-NCM from 4.8 to 3.6 V, Ni spectra shift to lower energy while Co and Mn spectra are mostly unchanged, suggesting Ni redox is responsible for the capacity delivered in this region. However, the maximum deliverable capacity from Ni calculated by considering Ni content and number of electron transfer is limited and is significantly less than the full capacity of 120 mAh g<sup>-1</sup> from the 4.8-3.6 V voltage range. This suggests other element other than Ni is contributing to the capacity. Because Co and Mn are inert in this voltage range, it is very likely that oxygen anions contribute the capacity. Upon further lithiation from 3.6 to 3.0 V, all transition metals show no shift at all in XANES, indicating that redox couples center around oxygen anions. Below 3.0 V, Ni spectra do not change, but Co and Mn spectra obviously shift to lower energies, suggesting further reduction to contribute to the capacity. Based on these analyses, the map of redox couples can be concluded and is shown in Figure 4B. It is worth noting that the sequence of redox couples during charging is almost completely reversed during discharging. The minor switch of relative energy level of redox couples after charging which might be caused by oxygen vacancy and transition metal/lithium migration. However, the anion redox potential hysteresis in O2-LR-NCM is much smaller than that in a typical O3-LR-NCM cathode.<sup>43</sup> Therefore, the structure change of O2-LR-NCM is much more reversible than the O3-LR-NCM cathode.

To understand the large difference in cycle stability between O3-LR-NCM and O2-LR-NCM cathodes, structure changes of O3-LR-NCM and O2-LR-NCM cathodes after 100th cycles were analyzed by using XANES spectra (Figure 5). For O3-LR-NCM, all transition metal XANES spectra, especially those of Co and Mn, show an obvious shift to lower energy when O3-LR-NCM is charged-discharged from the 1st cycle to the 100th cycle, suggesting their continues reduction during charge-discharge cycles. Such a result is consistent with the previous report on O3-type lithium-rich layered materials.<sup>11</sup> However, all transition metal XANES spectra of O2-LR-NCM virtually show no shift from the 1st cycle to the 100th cycle. Only Mn spectra show some slight shift. This suggests that transition metal valences in O2-LR-NCM are stable and the redox couples are well maintained during cycling, differing from the case of O3-LR-NCM in which transition metals are significantly reduced and new redox couples (with lower voltage) are activated during cycling. The higher stability of O2-LR-NCM than O3-LR-NCM in all-fluorinated electrolytes is attributed to the different oxygen packing between O2-LR-NCM and O3-LR-NCM and formation of LiF CEI on electrode surface, restricting the transition metal to migrate into Li layer and preventing the side reaction between electrolyte and LR-NCM cathodes.

**CEI on O2-LR-NCM Surface in All-Fluorinated Electrolytes.** As stated early, the CEI formed from all-fluorinated electrolyte also plays an important role in electrochemical



**Figure 5.** Comparison of XANES spectra change during cycling for O3-LR-NCM and O2-LR-NCM. In all figures, the blue and the red spectra correspond to the 1st and the 100th cycle, respectively.

performance of O2-LR-NCM cathode. The CEI compositions on O2-LR-NCM cathode after 100 cycles in 1.0 M LiPF<sub>6</sub>@ LiDFOB@F-262 electrolytes were analyzed by using TEM with EDS and XPS (Figure 6) techniques. As shown in Figure 6A,B, a CEI layer with a thickness of ~3–5 nm is uniformly coated on the O2-LR-NCM cathode after charging/discharging in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 electrolytes for 100 cycles. In sharp contrast, a nonuniform CEI is observed on the surface of cycled O2-LR-NCM cathode in 1.0 M LiPF<sub>6</sub>@EC/ DEC (Figure 6C,D). The energy-dispersive X-ray spectroscopy (EDS) line scan (inset of Figure 6A,C) along the blue line reveals the CEI on a cycled O2-LR-NCM cathode in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 has a higher F content than that of O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC.

The CEI components of cycled O2-LR-NCM in 1.0 M LiPF6@LiDFOB@F-262 and 1.0 M LiPF6@EC/DEC were further investigated by using X-ray photoelectron spectroscopy (XPS). As shown in Figure 6E, two F 1s peaks are detected in cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262, which correspond to a Li-F bond (LiF) at 685.2 eV and a C-F bond at 687.8 eV, respectively. Therein, the LiF is formed from the decomposition of LiPF<sub>6</sub>, LiDFOB, and the fluorinated solvent in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262, and the C-F bond is attributed to the C-F containing species in the CEI and poly(vinylidene fluoride) (PVDF). The much stronger LiF peak than C-F bond in the CEI indicates that the LiF content in the CEI was much higher than C-F species, implying a good sealing and protective effect of the in situ formed CEI layer for the cathode of cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@ LiDFOB@F-262. Besides, the time-of-flight secondary ion mass spectrometry (ToF-SIMS, Figure S15) characterization confirms the strong fluorine signal at the surface of cycled O2-LR-NCM in 1.0 M LiPF6@LiDFOB@F-262 electrolytes. Although the cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/



**Figure 6.** Surface analyses performed on cycled O2-LR-NCM in the electrolyte of 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 and 1.0 M LiPF<sub>6</sub>@EC/DEC. High-resolution transmission electron microscopy (HRTEM) images of cycled O2 in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (A, B) and 1.0 M LiPF<sub>6</sub>@EC/DEC (C, D). Inset of (A, C): the EDS line scan along the section of blue line. Characterization of the CEI components by XPS on cycled O2 in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (E–H) and 1.0 M LiPF<sub>6</sub>@EC/DEC (I–L).

DEC (Figure 6I) also owns the typical Li–F bond (685.2 eV) and C–F bond (687.9 eV), the LiF peak is much weaker than that of the C-F bond, indicating that the CEI of cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>-EC/DEC possesses much less LiF content than O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. As is well-known, the formation of the CEI is a complicated process relating to the dissolution of the transition metals in the cathode, the corrosion by HF or other H-included groups in electrolytes, and the oxidation of O<sup>2-</sup> into superoxides or peroxides.<sup>33</sup> The LiF-enriched CEI can effectively block the electron leakage44 and protect the electrolyte from been excessively oxidized. However, the CEI formed in 1.0 M LiPF6@EC/DEC electrolytes has less LiF content and is nonuniformly distributed on the O2-LR-NCM electrode surface, which cannot effectively protect the cathode surface, leading to the continuous electrolyte oxidation at high voltage, increased interphase resistance, and severe capacity fading.

The C 1s in CEI on cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>(@LiDFOB(@F-262 (Figure 6G) and 1.0 M LiPF<sub>6</sub>(@EC/DEC (Figure 6K) show the typical peaks at ~293.1, ~290.5, ~288.5, ~285.7, and ~284.1 eV, corresponding to the C–C/C–H, C– O, C=O, LiCO<sub>3</sub>, and C–F bonds in the CEI, agree well with previous reports.<sup>33,45</sup> Besides, the O 1s including O=C–O, C–O, and Li<sub>2</sub>O revealed by the typical peaks at ~534.1, ~532.5, and ~529.6 eV are also observed in Figure 6F,J. The detected high contents of the Li<sub>2</sub>O and Li<sub>2</sub>CO<sub>3</sub> are in good agreement with the previous reports.<sup>46–48</sup> The Li<sub>2</sub>O content in the CEI that was formed in 1.0 M LiPF<sub>6</sub>(@LiDFOB(@F-262 is lower than in the conventional carbonate electrolyte, indicating the CEI layer in 1.0 M LiPF<sub>6</sub>(@LiDFOB(@F-262 electrolyte is more compact and efficiently suppresses the side reactions between the delithiated cathode and electrolyte. The peaks at 191.6 eV correspond to the B–O bond from the decomposition of LiDFOB, and peaks at 193.7 eV belong to the remaining LiDFOB salt (Figure 6H), indicating that the LiDFOB participates in the formation of the CEI layers in the 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262. However, no B 1s (Figure 6L) was detected in the CEI of cycled O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@EC/DEC. The presence of B-containing species can effectively control the size and shape of the LiF in the CEI, modify its surface to prevent the agglomeration of LiF particles,<sup>49</sup> and further enhance the compaction and uniformity of the CEI. With the protection of such a robust and uniform LiF-enriched CEI, the catalytic activity of the O2-LR-NCM surface for oxidation of 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 was effectively deactivated, ensuring a superior cycling stability of O2-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262.

Although the cycled O3-LR-NCM in 1.0 M LiPF<sub>6</sub>(@) LiDFOB@F-262 also has a uniform CEI layer (Figure S16B) and delivers high LiF content and typical B-containing species in its CEI layer (Figure S17D), the intrinsic O3 structure instability still leads to a poor cycling performance. In addition, a large number of pores are revealed (cycled by a red dashed line in Figure S16A) in the interior of the cycled O3-LR-NCM in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262, which is caused by the irreversible oxygen losses, in accordance with the previous reports.<sup>11</sup> In sharp contrast, no pores are observed in the interior of cycled O2-LR-NCM cathodes in 1.0 M LiPF<sub>6</sub>@LiDFOB@F-262 (Figure 6A), further confirming its high effectiveness in suppressing the O<sub>2</sub> release.

# CONCLUSION

In conclusion, an O2-type Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> (O2-LR-NCM) cathode with low Co and rich Mn was synthesized through a coprecipitation followed by an ion exchange and annealing process. Different from the O3-LR-NCM cathode, the formation of oxygen-oxygen dimers in O2-LR-NCM was critically suppressed, and the structural evolution from layered to spinel structure was effectively curbed in the O2-LR-NMC. The in situ formed robust fluorinated CEI in the all-fluorinated electrolyte (1.0 M LiPF<sub>6</sub>@LiDFOB@F-262) critically prevents the side reactions between the delithiated O2-LR-NMC cathode and electrolyte and further restrains the structure transition by suppressing the O<sub>2</sub> release. Therefore, a highly stable oxygen redox reaction with little voltage fade was achieved. The O2-LR-NCM in 1.0 M LiPF6@LiDFOB@F-262 achieves a much higher initial Coulombic efficiency of 99.82%, a high discharge specific capacity of 278.3 mAh g<sup>-1</sup>, and an excellent cycling stability with a capacity retention of 83.3%  $(232.3 \text{ mAh g}^{-1})$  of the original discharge capacity after 100 cycles, much better than that of O2-LR-NCM cycled in commercial electrolyte (1.0 M LiPF<sub>6</sub>@EC/DEC) (49.4%, 137.3 mAh  $g^{-1}$ ) and the O3-LR-NCM cycled in 1.0 M LiPF<sub>6</sub>@ LiDFOB@F-262 electrolyte (76.3%, 146.3 mAh  $g^{-1}$ ). The integration of the O2-type Li, Mn-rich cathode with the allfluorinated electrolyte provides an efficient avenue for constructing next-generation LIBs with high energy density.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02302.

Synthetic details and full characterization, electrochemical experiments, and supporting figures (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Larcher, D.; Tarascon, J.-M. Towards Greener and More Sustainable Batteries for Electrical Energy Storage. *Nat. Chem.* **2015**, *7* (1), 19.

(2) Choi, J. W.; Aurbach, D. Promise and Reality of Post-Lithium-Ion Batteries with High Energy Densities. *Nat. Rev. Mater.* **2016**, *1* (4), 16013.

(3) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334* (6058), 928–935.

(4) Kalyani, P.; Chitra, S.; Mohan, T.; Gopukumar, S. Lithium Metal Rechargeable Cells Using  $Li_2MnO_3$  as the Positive Electrode. *J. Power Sources* **1999**, *80* (1–2), 103–106.

(5) Lu, Z.; MacNeil, D.; Dahn, J. Layered Cathode Materials  $Li[Ni_{x}Li_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_{2}$  for Lithium-Ion Batteries. *Electrochem. Solid-State Lett.* **2001**, *4* (11), A191–A194.

(6) Nayak, P. K.; Erickson, E. M.; Schipper, F.; Penki, T. R.; Munichandraiah, N.; Adelhelm, P.; Sclar, H.; Amalraj, F.; Markovsky, B.; Aurbach, D. Review on Challenges and Recent Advances in the Electrochemical Performance of High Capacity Li-and Mn-Rich Cathode Materials for Li-ion Batteries. *Adv. Energy Mater.* **2018**, *8* (8), 1702397.

(7) Zheng, J.; Myeong, S.; Cho, W.; Yan, P.; Xiao, J.; Wang, C.; Cho, J.; Zhang, J. G. Li-and Mn-Rich Cathode Materials: Challenges to Commercialization. *Adv. Energy Mater.* **2017**, 7 (6), 1601284.

(8) Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y.-S.; Edstrom, K.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Charge-Compensation in 3d-Transition-Metal-Oxide Intercalation Cathodes Through the Generation of Localized Electron Holes on Oxygen. *Nat. Chem.* **2016**, *8* (7), 684.

(9) Assat, G.; Tarascon, J.-M. Fundamental Understanding and Practical Challenges of Anionic Redox Activity in Li-Ion Batteries. *Nat. Energy* **2018**, *3* (5), 373.

(10) Yan, P.; Zheng, J.; Tang, Z.-K.; Devaraj, A.; Chen, G.; Amine, K.; Zhang, J.-G.; Liu, L.-M.; Wang, C. Injection of Oxygen Vacancies in the Bulk Lattice of Layered Cathodes. *Nat. Nanotechnol.* **2019**, *14* (6), 602.

(11) Hu, E.; Yu, X.; Lin, R.; Bi, X.; Lu, J.; Bak, S.; Nam, K.-W.; Xin, H. L.; Jaye, C.; Fischer, D. A.; Amine, K.; Yang, X.-Q. Evolution of Redox Couples in Li-and Mn-rich Cathode Materials and Mitigation of Voltage Fade by Reducing Oxygen Release. *Nat. Energy* **2018**, 3 (8), 690.

(12) Eum, D.; Kim, B.; Kim, S. J.; Park, H.; Wu, J.; Cho, S.-P.; Yoon, G.; Lee, M. H.; Jung, S.-K.; Yang, W.; et al. Voltage Decay and Redox Asymmetry Mitigation by Reversible Cation Migration in Lithium-Rich Layered Oxide Electrodes. *Nat. Mater.* **2020**, *19* (4), 1–9.

(13) Li, S.; Lee, S.-J.; Wang, X.; Yang, W.; Huang, H.; Swetz, D. S.; Doriese, W. B.; O'Neil, G. C.; Ullom, J. N.; Titus, C. J.; et al. Surface-to-Bulk Redox Coupling Through Thermally Driven Li Redistribution in Li-and Mn-rich Layered Cathode Materials. *J. Am. Chem. Soc.* **2019**, *141* (30), 12079–12086.

(14) Mohanty, D.; Sefat, A. S.; Li, J.; Meisner, R. A.; Rondinone, A. J.; Payzant, E. A.; Abraham, D. P.; Wood, D. L., III; Daniel, C. Correlating Cation Ordering and Voltage Fade in a Lithium-Manganese-Rich Lithium-Ion Battery Cathode Oxide: A Joint Magnetic Susceptibility and TEM Study. *Phys. Chem. Chem. Phys.* **2013**, *15* (44), 19496–19509.

(15) Gu, M.; Belharouak, I.; Zheng, J.; Wu, H.; Xiao, J.; Genc, A.; Amine, K.; Thevuthasan, S.; Baer, D. R.; Zhang, J.-G.; Browning, N. D.; Liu, J.; Wang, C. Formation of the Spinel Phase in the Layered Composite Cathode Used in Li-Ion Batteries. *ACS Nano* **2013**, *7* (1), 760–767.

(16) Boulineau, A.; Simonin, L.; Colin, J.-F.; Bourbon, C.; Patoux, S. First Evidence of Manganese–Nickel Segregation and Densification Upon Cycling in Li-rich Layered Oxides for Lithium Batteries. *Nano Lett.* **2013**, *13* (8), 3857–3863.

(17) Kang, S.-H.; Johnson, C.; Vaughey, J.; Amine, K.; Thackeray, M. The Effects of Acid Treatment on the Electrochemical Properties of  $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$  Electrodes in Lithium Cells. J. Electrochem. Soc. **2006**, 153 (6), A1186–A1192.

(18) Yu, D. Y. W.; Yanagida, K.; Nakamura, H. Surface Modification of Li-Excess Mn-Based Cathode Materials. *J. Electrochem. Soc.* **2010**, *157* (11), A1177–A1182.

(19) Qing, R. P.; Shi, J. L.; Xiao, D. D.; Zhang, X. D.; Yin, Y. X.; Zhai, Y. B.; Gu, L.; Guo, Y. G. Enhancing the Kinetics of Li-Rich Cathode Materials through the Pinning Effects of Gradient Surface Na<sup>+</sup> Doping. *Adv. Energy Mater.* **2016**, *6* (6), 1501914.

(20) Wu, Y.; Manthiram, A. High Capacity, Surface-Modified Layered Li  $[Li_{(1-x)/3}Mn_{(2-x)/3}Ni_{x/3}Co_{x/3}]O_2$  Cathodes with Low Irreversible Capacity Loss. *Electrochem. Solid-State Lett.* **2006**, 9 (5), A221–A224.

(21) Gao, J.; Manthiram, A. Eliminating the Irreversible Capacity Loss of High Capacity Layered  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  Cathode by Blending with Other Lithium Insertion Hosts. *J. Power Sources* **2009**, 191 (2), 644–647.

(22) Nayak, P. K.; Grinblat, J.; Levi, M.; Aurbach, D. Understanding the Effect of Lithium Bis(oxalato) Borate (LiBOB) on the Structural and Electrochemical Aging of Li and Mn Rich High Capacity  $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$  Cathodes. J. Electrochem. Soc. **2015**, 162 (4), A596–A602.

(23) Zheng, J.; Gu, M.; Genc, A.; Xiao, J.; Xu, P.; Chen, X.; Zhu, Z.; Zhao, W.; Pullan, L.; Wang, C.; Zhang, J.-G. Mitigating Voltage Fade in Cathode Materials by Improving the Atomic Level Uniformity of Elemental Distribution. *Nano Lett.* **2014**, *14* (5), 2628–2635.

(24) Liu, P.; Zhang, H.; He, W.; Xiong, T.; Cheng, Y.; Xie, Q.; Ma, Y.; Zheng, H.; Wang, L.; Zhu, Z.-Z.; Peng, Y.; Mai, L.; Peng, D.-L. Lithium Deficiencies Engineering in Li-rich Layered Oxide  $Li_{1.098}Mn_{0.533}Ni_{0.113}Co_{0.138}O_2$  for High-Stability Cathode. J. Am. Chem. Soc. **2019**, 141 (27), 10876–10882.

(25) Nayak, P. K.; Grinblat, J.; Levi, M.; Levi, E.; Kim, S.; Choi, J. W.; Aurbach, D. Al Doping for Mitigating the Capacity Fading and Voltage Decay of Layered Li and Mn-Rich Cathodes for Li-Ion Batteries. *Adv. Energy Mater.* **2016**, *6* (8), 1502398.

(26) Park, J.-H.; Lim, J.; Yoon, J.; Park, K.-S.; Gim, J.; Song, J.; Park, H.; Im, D.; Park, M.; Ahn, D.; Paik, Y.; Kim, J. The Effects of Mo Doping on  $0.3Li[Li_{0.33}Mn_{0.67}]O_2 \cdot 0.7Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$  Cathode Material. *Dalton T.* **2012**, *41* (10), 3053–3059.

(27) Zheng, J.; Li, J.; Zhang, Z.; Guo, X.; Yang, Y. The Effects of  $TiO_2$  Coating on the Electrochemical Performance of Li- $[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$  Cathode Material for Lithium-Ion Battery. Solid State Ionics **2008**, 179 (27–32), 1794–1799.

(28) Bettge, M.; Li, Y.; Sankaran, B.; Rago, N. D.; Spila, T.; Haasch, R. T.; Petrov, I.; Abraham, D. P. Improving High-Capacity  $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ -Based Lithium-Ion Cells by Modifiying the Positive Electrode with Alumina. *J. Power Sources* **2013**, 233, 346–357.

(29) de Boisse, B. M.; Jang, J.; Okubo, M.; Yamada, A. Cobalt-Free O2-Type Lithium-Rich Layered Oxides. *J. Electrochem. Soc.* **2018**, *165* (16), A3630–A3633.

(30) Yabuuchi, N.; Hara, R.; Kajiyama, M.; Kubota, K.; Ishigaki, T.; Hoshikawa, A.; Komaba, S. New O2/P2-Type Li-Excess Layered Manganese Oxides as Promising Multi-Functional Electrode Materials for Rechargeable Li/Na Batteries. *Adv. Energy Mater.* **2014**, *4* (13), 1301453.

(31) Zuo, Y.; Li, B.; Jiang, N.; Chu, W.; Zhang, H.; Zou, R.; Xia, D. A High-Capacity O2-Type Li-Rich Cathode Material with a Single-Layer Li<sub>2</sub>MnO<sub>3</sub> Superstructure. *Adv. Mater.* **2018**, *30* (16), 1707255. (32) Delmas, C.; Braconnier, J.-J.; Hagenmuller, P. A New Variety of LiCoO<sub>2</sub> with an Unusual Oxygen Packing Obtained by Exchange Reaction. *Mater. Res. Bull.* **1982**, *17* (1), 117–123.

(33) Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Zheng, J.; Yang, C.; Liou, S.-C.; Amine, K.; Xu, K.; Wang, C. Non-Flammable Electrolyte Enables Li-Metal Batteries With Aggressive Cathode Chemistries. *Nat. Nanotechnol.* **2018**, *13* (8), 715–722.

(34) Deng, T.; Fan, X.; Cao, L.; Chen, J.; Hou, S.; Ji, X.; Chen, L.; Li, S.; Zhou, X.; Hu, E.; Su, D.; Yang, X.-Q.; Wang, C. Designing In-Situ-Formed Interphases Enables Highly Reversible Cobalt-Free LiNiO<sub>2</sub> Cathode for Li-ion and Li-metal Batteries. *Joule* 2019, 3 (10), 2550–2564.

(35) Fan, X.; Ji, X.; Han, F.; Yue, J.; Chen, J.; Chen, L.; Deng, T.; Jiang, J.; Wang, C. Fluorinated Solid Electrolyte Interphase Enables Highly Reversible Solid-State Li Metal Battery. *Sci. Adv.* **2018**, *4* (12), eaau9245.

(36) Mohanty, D.; Kalnaus, S.; Meisner, R. A.; Rhodes, K. J.; Li, J.; Payzant, E. A.; Wood, D. L., III; Daniel, C. Structural Transformation of a Lithium-rich  $\text{Li}_{1.2}\text{Co}_{0.1}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{O}_2$  Cathode During High Voltage Cycling Resolved by In Situ X-ray Diffraction. *J. Power Sources* **2013**, 229, 239–248.

(37) Li, H.; Wei, X.; Yang, P.; Ren, Y.; Wang, S.; Xing, Y.; Zhang, S. Uniform Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> Hollow Microspheres with Improved Electrochemical Performance by a Facile Solvothermal Method for Lithium Ion Batteries. *Electrochim. Acta* **2018**, *261*, 86–95.

(38) Chen, H.; Islam, M. S. Lithium Extraction Mechanism in Li-Rich Li<sub>2</sub>MnO<sub>3</sub> Involving Oxygen Hole Formation and Dimerization. *Chem. Mater.* **2016**, *28* (18), 6656–6663.

(39) Saubanère, M.; McCalla, E.; Tarascon, J.-M.; Doublet, M.-L. The Intriguing Question of Anionic Redox in High-Energy Density Cathodes for Li-Ion Batteries. *Energy Environ. Sci.* **2016**, *9* (3), 984– 991.

(40) Nishimoto, S.; Katukuri, V. M.; Yushankhai, V.; Stoll, H.; Rößler, U. K.; Hozoi, L.; Rousochatzakis, I.; Van Den Brink, J. Strongly Frustrated Triangular Spin Lattice Emerging from Triplet Dimer Formation in Honeycomb Li<sub>2</sub>IrO<sub>3</sub>. *Nat. Commun.* **2016**, *7*, 10273.

(41) Armstrong, A. R.; Holzapfel, M.; Novák, P.; Johnson, C. S.; Kang, S.-H.; Thackeray, M. M.; Bruce, P. G. Demonstrating Oxygen Loss and Associated Structural Reorganization in the Lithium Battery

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Cathode Li $[Ni_{0.2}Li_{0.2}Mn_{0.6}]O_2$ . J. Am. Chem. Soc. 2006, 128 (26), 8694–8698.

(42) Hu, E.; Bak, S.-M.; Liu, J.; Yu, X.; Zhou, Y.; Ehrlich, S. N.; Yang, X.-Q.; Nam, K.-W. Oxygen-Release-Related Thermal Stability and Decomposition Pathways of  $\text{Li}_x \text{Ni}_{0.5} \text{Mn}_{1.5} \text{O}_4$  Cathode Materials. *Chem. Mater.* **2014**, *26* (2), 1108–1118.

(43) Gent, W. E.; Lim, K.; Liang, Y.; Li, Q.; Barnes, T.; Ahn, S.-J.; Stone, K. H.; McIntire, M.; Hong, J.; Song, J. H.; et al. Coupling between Oxygen Redox and Cation Migration Explains Unusual Electrochemistry in Lithium-Rich Layered Oxides. *Nat. Commun.* **2017**, 8 (1), 2091.

(44) Lu, Y.; Tu, Z.; Archer, L. A. Stable Lithium Electrodeposition in Liquid and Nanoporous Solid Electrolytes. *Nat. Mater.* **2014**, *13* (10), 961–969.

(45) Chen, L.; Fan, X.; Hu, E.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Li, J.; Su, D.; Yang, X.; Wang, C. Achieving High Energy Density through Increasing the Output Voltage: A Highly Reversible 5.3 V Battery. *Chem.* **2019**, 5 (4), 896–912.

(46) Qian, Y.; Niehoff, P.; Börner, M.; Grützke, M.; Mönnighoff, X.; Behrends, P.; Nowak, S.; Winter, M.; Schappacher, F. M. Influence of Electrolyte Additives on the Cathode Electrolyte Interphase(CEI) Formation on  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  in Falf Cells with Li Metal Counter Electrode. J. Power Sources **2016**, 329 (15), 31–40.

(47) Baggetto, L.; Dudney, N. J.; Veith, G. M. Surface Chemistry of Metal Oxide Coated Lithium Manganese Nickel Oxide Thin Film Cathodes Studied by XPS. *Electrochim. Acta* **2013**, *90* (15), 135–147.

(48) Li, W.; Dolocan, A.; Oh, P.; Celio, H.; Park, S.; Cho, J.; Manthiram, A. Dynamic Behaviour of Interphases and Its Implication on High-Energy-Density Cathode Materials in Lithium-Ion Batteries. *Nat. Commun.* **2017**, *8*, 14589.

(49) Jurng, S.; Brown, Z. L.; Kim, J.; Lucht, B. L. Effect of Electrolyte on the Nanostructure of the Solid Electrolyte Interphase (SEI) and Performance of Lithium Metal Anodes. *Energy Environ. Sci.* **2018**, *11* (9), 2600–2608.