Structure and Interface Design Enable Stable Li-Rich Cathode
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ABSTRACT: Li-rich layered-oxide cathodes have the highest theoretical energy density among all the intercalated cathodes, which have attracted intense interests for high-energy Li-ion batteries. However, O3-structured layered-oxide cathodes suffer from a low initial Coulombic efficiency (CE), severe voltage fade, and poor cycling stability because of the continuous oxygen release, structural rearrangements due to irreversible transition-metal migration, and serious side reactions between the delithiated cathode and electrolyte. Herein, we report that these challenges are migrated by using a stable O2-structured Li1.2Ni0.13Co0.13Mn0.54−δO2−δ (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 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. Because cathode materials control the energy density of the LIBs, the rapid expansion of LIBs prompts the innovation for higher-energy and low-cost cathodes. Among the intercalation transition metal oxide cathodes, the lithium- and 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). The energy density of LMRCs is almost 2 times higher than that of the commercial cathodes of LiCoO₂ and LiFePO₄.

The LMRCs are composed of Li₂MnO₃ with a monoclinic structure of the C2/m space group and LiMO₂ (M = Mn, Ni, Co) with a trigonal structure of the R3m space group, consisting of a framework of CdI₂-type anionic MO₆²⁻ layers interleaved with Li⁺ ions. 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 (O²⁻). LMRCs have O3 or O2 structure. Previous investigations were mainly focused on O3-type LMRCs, in which the irreversible oxidation of O²⁻ occurs at high voltages (~4.4–4.8 V) with irreversible transition-metal migration into the Li layer, 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 Mn⁶⁺/Mn⁴⁺ and Co²⁺/Co³⁺, 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. 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, surface doping, surface coating, and materials blending, have
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,\textsuperscript{22−24} the substitution of TMs,\textsuperscript{25,26} and surface doping,\textsuperscript{27,28} 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\textsuperscript{29−32} and suppress the movements of transition metals within the Li layer.\textsuperscript{12} Therefore, the structural evolution from the layered to spinel phase in O2-type 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\textsubscript{1.25}Co\textsubscript{0.25}Mn\textsubscript{0.50}O\textsubscript{2})\textsuperscript{31} or Co-free (Li\textsubscript{1.19}Mn\textsubscript{0.73}Ni\textsubscript{0.08}O\textsubscript{2})\textsuperscript{12,29,30} cathodes. 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\textsubscript{0.8}Mn\textsubscript{0.1}Co\textsubscript{0.1}O\textsubscript{2} and LiNiO\textsubscript{2} cathodes.\textsuperscript{33−35} By combination of superstable O2-structured 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 layered-oxide cathode of Li\textsubscript{1.2}Ni\textsubscript{0.13}Co\textsubscript{0.13}Mn\textsubscript{0.54}O\textsubscript{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\textsubscript{6} 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\textsubscript{6}@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 O1-type Li12Ni0.13Co0.13Mn0.54O2 (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⁻¹) with little voltage decay, delivering an enhanced rate capability of 82.9 mAh g⁻¹ even at 50/3 C (1 C = 300 mA g⁻¹), 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 Li₁₂Ni₀.₁₃Co₀.₁₃Mn₀.₅₄O₂

The first-step precursor of Ni₀.₁₃Co₀.₁₃Mn₀.₅₄O₂ (NCM-CO₃) was prepared by a coprecipitation reaction. Figure 1A shows Rietveld refinement of the X-ray diffraction (XRD) pattern of NCM-CO₃ powder, which can be fitted to a space group of R3c. After that, the NCM-CO₃ was annealed with the mixture of Na₂CO₃ and Li₂CO₃ to prepare the second-step precursor of Na₃Li₄Ni₀.₁₃Co₀.₁₃Mn₀.₅₄O₄ (NCM-O₂) structure (Figure 1B). Then, the Li, Na-NCM-O was immersed into the molten salt mixture of LiNO₃/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 Li₂MnO₃ structure. As shown in Figure 1D, the NCM-CO₃ exhibits a spherical structure, with a diameter of ~2–4 μm. The inset of Figure 1D reveals that the NCM-CO₃ 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 μm with the sheet-like primary particles. In contrast, the particles of the O3-LR-NCM are irregular with a uniform diameter of ~1–5 μm (Figure S2A,C), and its primary particles possess irregular particle morphology with a diameter of ~100–300 nm.

#### Electrochemical Performance

Figure 2 reveals the first and second charge–discharge curves of O2-LR-NCM at 2/3 C (1 C = 300 mA g⁻¹) 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 4.46 to 4.8 V corresponds to the extraction of Li⁺ from the layered LiMO₂ component, while the second plateau from 4.46 to 4.8 V is associated with further delithiation from the Li₂MnO₃ component, accompanied by oxidation of O₂⁻. 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 4.46 to 4.8 V is associated with further delithiation from the Li₂MnO₃ component, accompanied by oxidation of O₂⁻. 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 4.46 to 4.8 V is associated with further delithiation from the Li₂MnO₃ component, accompanied by oxidation of O₂⁻.
discharge CE of O3-LR-NCM is mainly caused by the irreversible oxidation of O\(^{2-}\), during which the O\(_n\(^{2-}\)\((n<2)\) is dimerized, and meanwhile some O\(_2\) is released.\(^{38-40}\) In addition, the formed Li\(^+\) and O\(_2\)\(^{-}\) vacancies are partially occupied by the transition metal cations, blocking the Li\(^+\) insertion back.\(^{41}\) Comparatively, the uniformly dispersed Li\(_2\)MnO\(_3\) superstructure in O2-LR-NCM can block the formation of oxygen-oxygen dimers, which suppresses the irreversible formation of O\(_2\) 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 (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 ~4.46 V in the first charge process is attributed to the delithiation of Li\(_2\)MnO\(_3\), 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\(_6@\)LiDFOB@F-262 electrolyte and the commercial 1.0 M LiPF\(_6\) in EC/DEC (volume ratio, 1:1) electrolytes (denoted as 1.0 M LiPF\(_6@\)EC/DEC). As revealed in Figure 3A, D, the O2-LR-NCM cathode in 1.0 M LiPF\(_6@\)EC/DEC delivers a comparable first discharge capacity (277.8 mAh g\(^{-1}\)) with that in 1.0 M LiPF\(_6@\)LiDFOB@F-262 (278.3 mAh g\(^{-1}\), Figure 3C). However, the reversible capacity of O2-LR-NCM in 1.0 M LiPF\(_6@\)EC/DEC decays fast and remains only 49.4% (137.3 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\(_6@\)EC/DEC exhibits a large voltage fade in the whole discharge profile after 100 cycles. Therefore, only change of LR-NCMs 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\(_6@\)LiDFOB@F-262 electrolyte. A significant concave at ~3.2 V is presented.
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 in 1.0 M LiPF$_6$@LiDFOB@F-262 only remains a discharge capacity of 146.3 mAh g$^{-1}$ after 100 cycles, corresponding to a capacity retention of 76.3%.

O2-LR-NCM in 1.0 M LiPF$_6$@LiDFOB@F-262 (Figure 3C,F) delivers a much better electrochemical performance than O2-LR-NCM in 1.0 M LiPF$_6$@EC/DEC and O3-LR-NCM in 1.0 M LiPF$_6$@LiDFOB@F-262. After 100 cycles (Figure 3C), the O2-LR-NCM in 1.0 M LiPF$_6$@LiDFOB@F-262 retains a discharge capacity of 232.3 mAh g$^{-1}$, corresponding to a capacity retention of 83.3%, which is much higher than that of O2-LR-NCM in 1.0 M LiPF$_6$@EC/DEC and O3-LR-NCM in 1.0 M LiPF$_6$@LiDFOB@F-262. Besides, little voltage decay was observed for the O2-LR-NCM in 1.0 M LiPF$_6$@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$_6$@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$_6$@LiDFOB@F-262 were also investigated. As shown in Figure 3H, the O2-LR-NCM cathode delivers an 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$_6$@LiDFOB@F-262, and O2-LR-NCM in LiPF$_6$@EC/DEC shows more serious capacity and voltage decay than O2-LR-NCM in 1.0 M LiPF$_6$@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.$^{11}$ 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$^{2+}$ and Ni$^{4+}$, 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.$^{29}$ 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 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).$^8$ 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 NiIV reference spectrum which is taken from a LiNi1/3Co1/3Mn1/3O2 cathode material charged to 5.2 V. Judging from the edge position, the highest Ni valence that reached during charging is around Ni3.5+. Because NiIV is the root of thermal instability in cathode materials, a lower valence suggests that O2-LR-NCM may have a better thermal stability than that of LiNi1/3Co1/3Mn1/3O2. 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\(^{-1}\) 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. 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 and O2-LR-NCM cathodes after 100th cycles in 1.0 M LiPF\(_6\)@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\(_6\), LiDFOB, and the fluorinated solvent in 1.0 M LiPF\(_6\)@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\(_6\)@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 LiPF\(_6\)@LiDFOB@F-262. Although the cycled O2-LR-NCM in 1.0 M LiPF\(_6\)@EC/
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 LiPF6@EC/DEC possesses much less LiF content than O2-LR-NCM in 1.0 M LiPF6@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 O2 into superoxides or peroxides.33 The LiF-enriched CEI can effectively block the electron leakage44 and protect the electrolyte from being 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, leading to the continuous electrolyte oxidation at high voltage, increased interphase resistance, and severe capacity fading.

Figure 6. Surface analyses performed on cycled O2-LR-NCM in the electrolyte of 1.0 M LiPF6@LiDFOB@F-262 and 1.0 M LiPF6@EC/DEC. High-resolution transmission electron microscopy (HRTEM) images of cycled O2 in 1.0 M LiPF6@LiDFOB@F-262 (A, B) and 1.0 M LiPF6@ 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 LiPF6@LiDFOB@F-262 (E–H) and 1.0 M LiPF6@EC/DEC (I–L).

The C 1s in CEI on cycled O2-LR-NCM in 1.0 M LiPF6@LiDFOB@F-262 (Figure 6G) and 1.0 M LiPF6@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, Li2CO3, and C−F bonds in the CEI, agree well with previous reports.33,45 Besides, the O 1s including O=C−O, C−O, and Li2O 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 Li2O and Li2CO3 are in good agreement with the previous reports.46−48 The Li2O content in the CEI that was formed in 1.0 M LiPF6@LiDFOB@F-262 is lower than in the conventional carbonate electrolyte, indicating the CEI layer in 1.0 M LiPF6@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 LiPF6@LiDFOB@F-262. However, no B 1s (Figure 6L) was detected in the CEI of cycled O2-LR-NCM in 1.0 M LiPF6@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,49 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 LiPF6@LiDFOB@F-262 was effectively deactivated, ensuring a superior cycling stability of O2-LR-NCM in 1.0 M LiPF6@LiDFOB@F-262.

Although the cycled O3-LR-NCM in 1.0 M LiPF6@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 LiPF6@LiDFOB@F-262, which is caused by the irreversible oxygen losses, in accordance with the previous reports.11 In sharp contrast, no pores are observed in the interior of cycled O2-LR-NCM cathodes in 1.0 M LiPF6@LiDFOB@F-262 (Figure 6A), further confirming its high effectiveness in suppressing the O2 release.
CONCLUSION

In conclusion, an O2-type Li$_{x}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_{2}$ (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$_6$@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$_2$ release. Therefore, a highly stable oxygen redox reaction with little voltage fade was achieved. The O2-LR-NMC in 1.0 M LiPF$_6$@LiDFOB@F-262 achieves a much higher initial Coulombic efficiency of 99.82%, a high discharge specific capacity of 278.3 mAh g$^{-1}$, and an excellent cycling stability with a capacity retention of 83.3% (232.3 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$_6$@EC/DEC) (49.4%, 137.3 mAh g$^{-1}$) and the O3-LR-NCM cycled in 1.0 M LiPF$_6$@LiDFOB@F-262 electrolyte (76.3%, 146.3 mAh g$^{-1}$). The integration of the O2-type Li, Mn-rich cathode with the all-fluorinated 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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REFERENCES


(17) Kang, S.-H.; Johnson, C.; Vaughey, J.; Amine, K.; Thackeray, M. The Effects of Acid Treatment on the Electrochemical Properties of 0.5Li2MnO3•0.5Li[Ni0.4Mn0.3Co0.3]O2 Electrodes in Lithium Cells. J. Electrochem. Soc. 2006, 153 (6), A1186–A1192.


(20) Wu, Y.; Manthiram, A. High Capacity, Surface-Modified Layered Li[Li0.64(Ni0.54Co0.13Mn0.33)O2] 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 Li[Li0.64(Ni0.54Co0.13Mn0.33)O2] 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 Li1.2Ni0.15Mn0.55Co0.1O2 Cathodes. J. Electrochem. Soc. 2015, 162 (4), A596–A602.


(26) Park, J.-H.; Lim, J.; Yoon, J.; Park, K.-S.; Gim, J.; Song, J.; Park, H.; Im, D.; Park, M.; Ahn, D.; Pak, Y.; Kim, J. The Effects of Mo Doping on 0.3Li4Ti5O12•0.7Li[Ni0.2Mn0.5Co0.3]O2 Cathode Material. Dalton T. 2012, 41 (10), 3053–3059.

(27) Zheng, J.; Li, J.; Zhang, Z.; Guo, X.; Yang, Y. The Effects of TiO2 Coating on the Electrochemical Performance of Li[Ni0.2Mn0.5Co0.3]O2-Based Lithium-Ion Battery. Solid State Ionics 2008, 179 (27–32), 1794–1799.


(29) de Boisse, B. M.; Jiang, J.; Okubo, M.; Yamada, A. Cobalt-Free Li0.2Ni0.5Mn0.3O2 Layered Oxides. J. Electrochem. Soc. 2018, 165 (16), A3630–A3633.

Cathode Li[Ni0.2Li0.2Mn0.6]O2. J. Am. Chem. Soc. 2006, 128 (26), 8694–8698.


