Lithium-Ion Batteries

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# Building the Stable Oxygen Framework in High-Ni Layered Oxide Cathode for High-Energy-Density Li-Ion Batteries

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High-Ni layered oxide cathodes hold a great promise for fabricating highenergy lithium-ion batteries. However, the oxygen evolution during cycling is a crucial factor in the structure deterioration, potential change, and capacity decay of cathodes, limiting the commercial application of high-Ni (Ni > 0.9) layered oxides in batteries. Herein, we demonstrate a feasible approach to enhance the stability of oxygen framework, through the surface oxygen immobilization with yttrium and bulk oxygen stabilization with aluminum in high-Ni layered oxides. As expected, benefiting from the oxygen-stabilized framework, the bulk structure deterioration, and interfacial parasitic reaction are mitigated obviously during battery operation, along with the improved thermal stability of cathode. Correspondingly, the as-prepared high-Ni oxide delivers high reversible capacity, impressive cycle ability, and low potential polarization upon cycling. Such significant improvement on the electrochemical performance is primarily attributed to the strong oxygen affinities of both yttrium at the surface layer and aluminum in the bulk, which synergistically stabilizes the oxygen framework of high-Ni oxide via raising the energy barrier for oxygen evolution. Therefore, building the stable oxygen framework is critical for enhancing the energy density output, cycle operation, and thermal stability of high-Ni oxide cathodes.

## 1. Introduction

The pursuit of high-energy storage devices to push the envelope of high-Ni (Ni>0.9) layered oxide cathodes, which are the most workable cathode materials due to their high specific capacity and low cost.<sup>[1]</sup> However, along with the increase in Ni content, the deterioration on both the bulk structure and interface of high-Ni layered oxide cathode during cycling is serious, accompanied simultaneously with the safety issue.<sup>[2]</sup> The routine composition regulation and surface coating are effective in improving the cycling stability of the conventional LiCoO<sub>2</sub> and ternary Li(Ni<sub>1-x</sub>Co<sub>x</sub>Mn<sub>y</sub>)O<sub>2</sub> (NCM) oxides,<sup>[3,4]</sup> however, which are unsatisfied for high-Ni (Ni > 0.9) layered oxides.

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It is noteworthy that the oxidation of nickel from +2 to +3 and then to +4 is primarily responsible for the capacity of conventional ternary NCM oxides with low Ni content, implying that the  $Ni^{2+/3+}$  and  $Ni^{3+/4+}$  redox couples contribute the majority of the charge compensation in delithiation process. However, when the Ni content is beyond 0.9, high-Ni layered oxides inherit the feature of their parent LiNiO2 compound, relying on only Ni<sup>3+/4+</sup> redox couple to provide the capacity. As compared to the  $\mathrm{Co}^{3+/\mathrm{\mathring{4}}+}$   $t_{2g}$  band, the overlap area of the Ni<sup>3+/4+</sup>  $e_{\sigma}$  band with the top of O 2p band is less (Figure S1), and the electron delocalization with Ni<sup>3+/4+</sup> is observed in high-Ni layered oxides in delithiation process.<sup>[5]</sup> Besides. increasing Ni content provides a good chance to oxidize the lattice oxygen and to weaken the oxygen-binding strength upon Ni<sup>3+</sup> oxidation, leading to the oxygen evolution.<sup>[6]</sup> Therefore, the oxygen evolution takes place unavoidably for high-Ni layered oxides at highly delithiated state. Correspondingly, the direct impact of oxygen evolution is the under coordination of transition metal cations, rendering the migration of

metal cations from the lattice and the consequent structure collapse from layered structure to spinel/rock-salt phase (**Figure 1**).<sup>[7,8]</sup> Another consequence of the oxygen evolution is the resultant oxygen radicals, which trigger the decomposition of electrolyte and the simultaneous formation of the cathode electrolyte interphase (CEI) layer on the cathode surface.<sup>[9,10]</sup> Both the structure deterioration and CEI accumulation raise the battery impedance, undermining the cycling stability of high-Ni layered oxide cathodes correspondingly.<sup>[11]</sup> In the meantime, the reaction between released oxygen and electrolyte generates heat and flammable gases, further triggering the thermal runaway of oxide cathodes.<sup>[12]</sup> Therefore, building the stable oxygen framework of high-Ni layer oxides is an irreplaceable way to develop long-lifespan and high-safety Liion batteries.

Substantial efforts have put into strengthening the structure stability to improve the cycling stability of high-Ni oxides with a focus on the surface modification and element doping.<sup>[13,14]</sup> Previously, the surface modification with  $Al_2O_3^{[15]}$  and  $LiBO_2^{[16]}$  is effective to prevent the escape of oxygen from the particle surface. However, the structural mismatch between host material and coating layer leads inevitably to the separation of the hard interface, and failed protection on the active materials during long-term cycling.<sup>[17,18]</sup> Furthermore, doping with foreign element in the bulk is helpful to

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Figure 1. The schematic representation of oxygen evolution to degrade high-Ni cathode particles.

decrease the cation mixing and inhibit the migration of cations to a certain extent during cycling, improving the cycle stability of high-Ni oxides.<sup>[19]</sup> It seems that the struggling only on the cation mixing in high-Ni oxides is unsatisfied to avoid the structure collapse initiated originally from the surface cracks. Among the various doping elements, Al is one of the most promising candidates because of its role in making the lattice robust with strong Al-O bonds. Moreover, it is effective in improving the thermal stability of high-Ni oxides.<sup>[20]</sup> However, the Al doping in the bulk is insufficient to protect the vulnerable surface of oxide cathode. In addition, yttrium tends to enrich onto the oxide surface due to the oxidation-induced segregation, which is helpful to stabilize the interfacial structure owing to the strong Y-O bonds.<sup>[21]</sup> Intuitive bulk element substitution combing with surface stabilization strategies can overcome the challenges of material degradation of high-Ni oxides. Intrinsically, the oxygen diffusion and mobility from the core to the surface during cycling are the key reason for failure of high-Ni oxides.

In this sense, we herein propose a feasible strategy to build a stable oxygen framework in high-Ni layered oxide through immobilizing the surface oxygen with yttrium and stabilizing the bulk oxygen with aluminum. Differently from the conventional composition regulation and surface coating technologies, the stable oxygen framework can effectively constrain the migration of oxygen anions in the bulk and increase the energy barrier for oxygen evolution at the surface, which ensure the superior structural and interfacial stabilities of high-Ni layered oxide LiNi<sub>0.94</sub>. Co<sub>0.06</sub>O<sub>2</sub> (termed as NC hereafter). Consequently, the high-Ni layered oxide LiNi<sub>0.92</sub>Co<sub>0.06</sub>Al<sub>0.01</sub>Y<sub>0.01</sub>O<sub>2</sub> (termed as NCAY hereafter) exhibits exceptional electrochemical performance in terms of capacity and potential stabilities, together simultaneously with desired thermal behavior.

## 2. Results and Discussion

#### 2.1. Structural Analysis

The crystallographic structure and morphology of the as-prepared oxides are examined by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). As shown in Figure S2, both NC and NCAY have a rhombohedral layered structure ( $R\overline{3}m$  space group), without impurity phases. The Li/Ni cationic ordering in NCAY is improved obviously by increasing the intensity ratio from (003) to (104) planes. As confirmed by the Rietveld refinement results, NCAY displays a slightly lower cation mixing of 2.01%, which is helpful to the cycling stability of layered oxide cathodes. In the meantime, both samples exhibit spherical morphologies assembled with primary nanocrystallines. It is noteworthy that the grain size of NCAY is minor, resulting in the denser aggregation of microspheres and the smaller cavities within microspheres, which are beneficial to the mechanical integrity of oxide cathodes.<sup>[22]</sup> In addition, the chemical composition ratio of Ni:Co:Al:Y is estimated to be 0.9216:0.0595:0.0096:0.0093

for NCAY sample (Table S1), which agrees well with the designed composition.

It is well known that yttrium and aluminum have a strong bonding strength toward oxygen, which contributes to the inhibition of oxygen evolution (Figure 2a).<sup>[23,24]</sup> In particular, it is demonstrated by the large formation energy of yttrium oxide that yttrium inclines to segregate onto the surface, which inhibits the growth of primary nanocrystallines.<sup>[25]</sup> Energy dispersive spectra (EDS) mapping images confirm the enriched segregation of yttrium on the surface, together with the uniform distribution of aluminum throughout the particle, consistent with the line scan profiles (Figure 2b). Indeed, though the microstructure (including the lattice expansion and a series of edge dislocation) is changed by introducing yttrium onto the surface, NCAY still has a layered structure extending from the surface to the bulk without phase boundary, indicating the excellent structure integrity (Figure S3). The distribution of yttrium and aluminum in NCAY sample can be further proved by the X-ray photoelectron (XPS) depth analysis. As shown in Figure S4, the intensities of Ni and Co peaks increase, whereas the intensity of Y peak decreases with increasing the etching depth. Meanwhile, the intensity of Al peak shows a marginal change. The relative content of yttrium is decreased gradually from 15.2% to 0.9% with the etching depth reaching around 5.5 nm, accompanied by negligible change in aluminum content (Figure 2c). Therefore, yttrium is enriched onto the surface, and aluminum is dispersed across the bulk with strong bonding toward oxygen, synergistically building the stable oxygen framework in high-Ni oxide.

In the typical layered oxides, the gliding of oxygen layers is inevitable due to the electrostatic repulsion of adjacent oxygen layers, resulting in the reversible  $H1 \leftrightarrow H2 \leftrightarrow H3$  phase transition upon lithiation and delithiation.<sup>[26]</sup> To evaluate the impact of oxygen evolution on the phase transition in high-Ni oxide, in situ XRD measurement is carried out during the initial charging process. As shown in Figure 3a and b, both NC and NCAY samples display a similar structural behavior due to the removal of lithium below 4.1 V, namely the evolution of H1 to H2 phase. However, in distinct contrast to the two-phase coexistence for NC cathode, NCAY cathode exhibits a single-phase transition upon further charging to 4.5 V, corresponding to the H2 to H3 phase transition. Such phenomenon is related to the slight gliding of oxygen layers to block the H2↔H3 phase transition,<sup>[27]</sup> leading to the single-phase transition pathway in NCAY cathode. Meanwhile, the (003) peak shifts to lower angle and then to higher angle, correlating to the expansion and contraction of the c-axis. The (110) peak moves consecutively to higher



Figure 2. a) Illustration of NCAY oxide with surface-segregated yttrium and bulk-introduced aluminum deriving from two criteria of M-O bond energy and oxide formation energy. b) Elemental images with the area mapping and line scan profile of NCAY. c) The relative elemental content based on quantitative XPS analysis for NCAY.

angle upon the delithiation (Figure S5), representing the continuous shrinkage in the a/b-axis.<sup>[28]</sup> Comparatively with NC sample, the peak displacement of (003) peak in NCAY is slightly smaller at the charge cutoff potential of 4.5 V, meaning the suppressed H2 $\leftrightarrow$ H3 phase transition. Accordingly, the maximum contraction in the c-axis lattice for NCAY is only 5.79%, in contrast to the larger contraction (6.54%) of c-axis lattice for NC cathode (Figure 3c).

In fact, the lattice stress between H2 and H3 phases, and non-uniform contraction on c-axis would cause microcracks within close-packed microspheres.<sup>[29]</sup> To survey the internal microcracks, the cross-sectional SEM images of NC and NCAY are examined at different charge and discharge states during the initial cycle. As compared in Figure 3d, microcracks appear obviously in a NC microsphere initiated from the particle center after charging to 4.3 V, corresponding to the completion of H2 to H3 phase transition.<sup>[30]</sup> Even worse, these microcracks become quite severe traversing the entire particle when the cathode was further charged to 4.5 V. Although such microcracks gradually close back after discharging to 4.1 V, the repeated opening and closing of microcracks in NC cathode render the penetration of electrolyte into the particle interior, which accelerates the structural degradation and ultimate pulverization of oxide microspheres.<sup>[31]</sup> Eventually, NC microspheres are completely destroyed to leave many loose primary crystallites after long cycling (Figure S6). In contrast, for NCAY sample, only a trace of microcracks can be observed during charge and discharge process, especially, near the particle core at a charge state of 4.5 V. Given the approximate contraction of unit cell volume for both cathodes (Figure 3e), the suppression of microcracks is attributed mainly to the moderated local stress by oxygen-stabilized framework of NCAY cathode, which inhibits the anisotropic mechanical strain build-up. Besides intergranular microcracks, intragranular microcracks are also examined in both cathodes after charging to 4.5 V.<sup>[32]</sup> As shown in the high-resolution transmission electron microscopy (HRTEM) image in Figure 3f and g, the hairline intragranular microcracks are developed in the ab plane of NC cathode, as marked by white arrows, which is caused mainly by a greater degree of lattice mismatch between H2 and H3 phases. However, no obvious intragranular microcracks are observed in NCAY cathode, indicating that the internal stress produced by H2 $\leftrightarrow$ H3 phase transition can be accommodated by the oxygen-stabilized framework.

#### 2.2. Interfacial Analysis

The microcracks and pulverization of oxide microspheres could facilitate the corrosion on the exposed fresh surface by electrolyte, resulting in the continuous accumulation of CEI layer on the cathode surface.<sup>[33]</sup> As shown in Figure S7, an amorphous CEI layer can be observed on the surface of both the cycled cathodes. Evi-

dently, the thickness of the CEI layer on NC surface is thicker than that on NCAY surface. Based on XPS analyses, the CEI layer is composed mainly of organic species derived from the decomposition of carbonate solvents,<sup>[34]</sup> including C=O and C-O bonds, and inorganic species deriving from LiPF<sub>6</sub> salt decomposition,<sup>[35]</sup> including LiF and LiPF<sub>x</sub>O<sub>y</sub> (Figure 4a). Specifically, the relative intensity of both organic and inorganic species for the cycled NC cathode is larger, indicating severe parasitic reactions between electrolyte and oxygen released from the high-Ni oxide particles. In particular, the intensities of LiF and  $LiPF_xO_y$  are high, whereas the signal from lattice oxygen disappears almost, indicating the formation of a thick CEI layer covered on the cycled NC surface. Quantitative analysis of XPS results reveals that the CEI layer dominates the cycled NC cathode surface, in which the organic species are the major components, such as C=O and C-O bonds (Figure S8). As regards the ingredient of the CEI layer on the NCAY surface, more active material species are still detected, indicating the thinning of the CEI layer. All these results demonstrate that NCAY with the high oxygen-stabilized framework is capable to resist electrolyte corrosion, assuring the thermal and cycling stability of high-Ni oxide.

In order to intuitively investigate the CEI layer deposited on the cycled NC and NCAY surface, time-of-flight secondary ion mass spectrometry (TOF-SIMS) is carried out to inspect the difference in the surface chemistry. Figure 4b and c depict the distribution of main components with increasing sputtering time, including organic species represented by  $C_2HO^-$  and  $C_2H_3O^-$  fragments, inorganic



**Figure 3.** Potential profile and the corresponding *in situ* XRD pattern evolution of a) NC and b) NCAY cathodes. c) The evolution of c-axis lattice parameter. d) Cross-sectional SEM images of NC and NCAY cathodes at different charge and discharge states during the initial cycle. The scale bars are 1 µm. e) Comparison of unit cell volume of NC and NCAY cathodes. f) High-resolution TEM image of charged NC together with the degree of lattice mismatch, and g) high-resolution TEM image of NCAY cathode charged to 4.5 V.

species represented by POF2-, and active mass dissolution product of NiF-. Specifically, for both NC and NCAY cathodes, the intensities of organic species reach their peak values earlier than inorganic species. It indicates that the distribution of principal components through CEI layer is non-uniform, and the outer layer of CEI is consisted mainly of organic species. This result is also supported by the chemical mappings of corresponding fragments. Meanwhile, as the sputtering time goes on, the signals of organic species decline quickly in NCAY cathode, further confirming a thinner CEI layer on the surface. In the combination of XPS and TOF-SIMS analyses, the architecture of CEI layer on the particle surface of high-Ni oxide cathode upon cycling is proposed (Figure 4d). Herein, NCAY cathode possesses a stable oxygen framework enabling the alleviation of microcracks and subsequent electrolyte decomposition during cycling. In fact, after the formation of microcracks and the accumulation of CEI layer, the rapid capacity fading happens for NC cathode, accompanied simultaneously with the increase in chargetransfer resistance, dissolution of active components, and degradation of bulk structure (Figure S9).

#### 2.3. Thermal Analysis

The safety hazard of high-Ni oxide cathodes is another critical concern for their large-scale application, which is directly ascribed to the release of oxygen at high delithiated state.<sup>[36,37]</sup> To evaluate the impact of the oxygen-stabilized framework on the thermal stability, the thermal decomposition of both cathodes is monitored by hightemperature X-ray diffraction heating from 40 to 500 °C (Figure \$10). With a focus on the (003) reflection, a distinct comparison is observed on the phase transition temperature (Figure 5a and b). This phase transition from layered structure to spinel phase is initiated by the oxygen evolution from the lattice due to the thermal instability.<sup>[38]</sup> Obviously, the onset temperature for NCAY cathode is considerably delayed as compared to NC cathode, reflecting a strong bonding between metal cations and oxygen anions within oxygen-stabilized framework. Additionally, the shifting of  $(003)_{H3}$ peak toward lower angle for NC cathode discloses the weak interaction between adjacent oxygen layers, evidenced by the enlargement of interlayer spacing with the increased temperature.

Generally, the thermal stability of cathode materials is evaluated by differential scanning calorimetry (DSC) analysis to detect the exothermic peak and heat release.<sup>[39]</sup> As shown in Figure 5c and d, the peaks observed at about 110 °C and 220 °C in the delithiated state are attributed to the decomposition of CEI layer and cathode decomposition with releasing oxygen, respectively.<sup>[40]</sup> Clearly, compared with NC cathode, the exothermic peak related to the CEI layer decomposition for NCAY cathode is much weak, indicating the thinning of the CEI layer, which is consistent well with XPS and TOF-SIMS results. Furthermore, the peak corresponding to the cathode decomposition is delayed (223.1 °C) for NCAY cathode, accompanied by a lower heat release (383.1 J g<sup>-1</sup>).

This indicates that the thermal stability can be effectively improved owing to the oxygen-stabilized framework on NCAY cathode.

#### 2.4. Electrochemical Performance

Due to the stabilizing effect of oxygen-stabilized framework on the bulk structure and interface of high-Ni oxide cathode, the superior electrochemical performance can be obtained between 2.8 and 4.3 V. As shown in **Figure 6**a, both NC and NCAY cathodes deliver a large discharge capacity of ~220 mAh g<sup>-1</sup> at 0.1C rate, indicating high lithium



Figure 4. a) XPS C 1s, O 1s, F 1s, and P 2p spectra of the CEI layer on NC (left) and NCAY (right) cathodes surface after 100 cycles. Normalized depth profiling of several secondary ion fragments on b) NC and c) NCAY cathodes surface after 100 cycles by sputtering via TOF-SIMS and the chemical mappings of corresponding fragments. d) Schematic illustration of CEI layer evolution at the surface of high-Ni layered oxide cathodes.



**Figure 5.** Contour plots of high-temperature XRD patterns of a) NC and b) NCAY cathodes charged at 4.3 V. c) DSC analysis of cathodes charged at 4.3 V. d) Comparison of thermal behavior and phase transition temperature between NC and NCAY.

utilization as compared with the prevailing cathodes (LiNi0.8- ${\rm Co}_{0.1}{\rm Mn}_{0.1}{\rm O}_2$  (NCM811) and  ${\rm LiNi}_{0.8}{\rm Co}_{0.15}{\rm Al}_{0.05}{\rm O}_2$  (NCA)). The charge/discharge curves of both cathodes are featured with multiplateaus during Li deintercalation and intercalation. NC cathode even exhibits an extra plateau at about 3.5 V during lithiation process, which is correlated with the structural transition from monoclinic phase to hexagonal phase at the very end of the intercalation process.<sup>[41]</sup> Furthermore, the multi-plateau feature can be more identified through dQ/dV analysis.<sup>[42]</sup> As shown in Figure 6b, both cathodes undergo a series of phase transitions in the cathodic and anodic processes. Comparatively, the anodic/cathodic peaks assigned to H2↔H3 phase transition are weak for NCAY cathode, indicating the suppressed phase transition due to the oxygen-stabilized framework, in agreement with the in situ XRD result. The passivation of the phase transition can be a good indicator of stable structure during charge and discharge process,<sup>[43]</sup> avoiding the detrimental  $H2 \rightarrow H3$  phase transition of NC cathode. Eventually, the charge/discharge profile of NC cathode becomes deformed because of severe structural collapse after long cycling at 1C rate (Figure 6c), whereas NCAY cathode exhibits well-preserved curve shape benefited from the oxygen-stabilized framework.

The cycling performance of NC and NCAY cathodes is compared in Figure 6d. Clearly, NCAY cathode delivers an impressive cyclability with a large discharge capacity of 161.2 mAh  $g^{-1}$ , corresponding to a high-capacity retention of 80.24% after 500 cycles at 1C rate. However, NC cathode only retains 54.66% of the initial discharge capacity after cycling, due to the structural degradation and interfacial parasitic reactions. In the meantime, the high and stable average Coulombic efficiency of NCAY is another indicator for the improved reversibility (Figure S11). In addition, the single element doped samples (NCY and NCA) show better performance on the cycle stability than bare NC, but still uncompetitive to NCAY (Figure S12a). Indeed, the potential change can act as a sensitive fingerprint of the structural evolution of high-Ni layered oxide cathodes during cycling.<sup>[44]</sup> As shown in Figure 6e, the decay of the discharge midpoint potential of NC cathode is more severe, ultimately leading to the overpotential increased by 0.22 V after cycling. In contrast, the over-potential of NCAY cathode increases only by 0.14 V, indicating that the oxygen-stabilized framework is beneficial to suppress the structural evolution of high-Ni oxides during cycling. Meanwhile, both NC and NCAY deliver similar discharge capacities from 0.1C to 10C rate (Figure S12b), implying that the rate capabilities of cathode material are not undermined by the stable oxygen framework.

#### 2.5. Oxygen Evolution

Considering the strong interaction between electrolyte and oxygen released from cathode, the leakage current testing is conducted to evaluate

the surface reactivity of cathode charged to 4.5 V during holding at 60 °C.<sup>[45]</sup> As shown in Figure 7a, the leakage current values of NCAY cathode are lower than those of NC cathode before and after cycling, indicating that the chemical reactivity toward electrolyte is reduced obviously for NCAY cathode. Such high chemical reactivity could result in the accumulation of oxygen radicals in electrolyte, further oxidizing the electrolyte.<sup>[46]</sup> It is confirmed from electron paramagnetic resonance (EPR) that the intensities of signal from electrolyte are higher when NC is charged to 4.3 and 4.5 V (Figure 7b), indicating more oxygen radicals produced into electrolyte. After the escape of oxygen radicals from the crystal lattice, the atomic ratio of O to Ni reduces inevitably, which can be a sensitive indicator to evaluate the oxygen evolution.<sup>[47]</sup> Based on XPS (reflecting the O/Ni ratio of the surface) and EDS (reflecting the O/Ni ratio of the bulk) results (corresponding quantitative analysis is shown in Figure S13), the O/Ni atomic ratio reduces dramatically for NC cathode after cycling, especially at the surface region, meaning massive oxygen evolution during the structural deterioration (Figure 7c). However, the O/Ni atomic ratio of cycled NCAY cathode is higher than that of NC cathode, further corroborating the stability of oxygen framework. To substantiate the oxygen stability on the surface and bulk, the oxygen vacancy formation energy at the site adjacent to Ni, Al, and Y atoms is calculated. As shown in Figure 7d, obviously, the oxygen vacancy formation energies at the site adjacent to Al and Y are as high as 3.25 and 3.34 eV, respectively, whereas that adjacent to Ni is only 0.84 eV. It indicates that the oxygen evolution becomes energetically unfavorable in NCAY cathode, because of the increased energy barrier of the oxygen vacancy formation adjacent to yttrium and aluminum. With the above information, a comparison of the effect of the oxygen evolution on cathode degradation is schematically summarized in Figure 7e. Introducing yttrium onto the surface layer and aluminum into the bulk is beneficial for the structure stability and inhibition of oxygen



**Figure 6.** a) The charge/discharge curves of NC and NCAY cathodes at 0.1C rate. b) dQ/dV profiles of two cathodes derived from the charge/discharge curves. c) The charge/discharge curves of NC and NCAY cathodes at 1C rate. d) Long-term cycling performance at 1C rate. e) The discharge mid-point potential and overpotential (the difference between charge/discharge mid-point potential) of two cathodes upon cycling.

evolution, due to the increased energy barrier for oxygen release, thus consequently mitigating the electrolyte decomposition and improving the thermal stability.

#### 2.6. Stabilization Principle

The oxygen evolution is the key factor of structural and interfacial degradation and safety threating of high-Ni layered oxide cathodes. Intrinsically, oxygen on the surface is unstable, which is more favorable to release from the lattice upon delithiation. The application of oxygen-scavenging electrolyte additive,<sup>[48]</sup> non-flammable electrolyte, and ethylene carbonate-free electrolyte is a prospective solution to suppress the reaction activity with oxygen radicals.<sup>[49-52]</sup> Comparatively speaking, the surface coating with oxygen blocking layers is an effective way to stabilize high-Ni oxide cathodes in the practical application. However, such surface coating layer is easy to split away off from host materials due to the microcracks and pulverization of cathode during cycling, losing the protective function on active materials.<sup>[53]</sup> Therefore, to realize the application of high-capacity cathodes in Li-ion batteries, it is necessary to introduce active elements with strong oxygen bonding capability onto the surface and into the bulk of high-Ni layered oxides. The strategy of stabilizing high-Ni oxide cathodes is to build the stable oxygen framework, in which the surface modification and component adjusting could be taken into consideration simultaneously. According to the results above, the stable oxygen framework is feasible on stabilizing high-Ni oxide cathodes, as confirmed by the excellent stability on the capacity and mid-point potential.

#### 3. Conclusions

In summary, the effect of oxygen evolution on the structural deterioration of high-Ni layered oxide is investigated in detail. It is demonstrated that the oxygen release is the key factor for the microcracks and surface passivation of high-Ni layered oxide cathode, leading to a rapid cycling fading on the capacity and potential. In order to build the stable oxygen framework and obtain the desirable electrochemical performance, we introduce active elements (yttrium and aluminum) with strong oxygen bonding capability onto the surface and into the bulk of high-Ni layered oxides. Benefited from the oxygen-stabilized framework on the surface and in the bulk, the excellent capacity retention and low potential polarization are achieved, together with the good thermal stability. Intrinsically, the oxygen-stabilized framework can effectively accommodate the internal stress resulted from the phase transition during cycling, which usually triggers the microcracks of oxide microspheres and dissolution of active elements. Additionally, the suppressed oxygen release from the oxygen-stabilized framework mitigates the electrolyte decomposition and the consequent thermal decomposition of high-Ni layered oxide cathode. Therefore, building the stable oxygen framework is a feasible strategy in stabilizing high-Ni oxide cathodes for high-energy-density Li-ion batteries.

### 4. Experimental Section

Materials Preparation: LiNi $_{0.94}$ Co $_{0.06}$ O<sub>2</sub> and LiNi $_{0.92}$ Co $_{0.06}$ Al $_{0.01}$ Y $_{0.01}$ O<sub>2</sub> were prepared via the co-precipitation method. Briefly, the transition metal



**Figure 7.** a) Leakage current of cathodes charged to 4.5 V during holding at 60  $^{\circ}$ C after 1st and 100th cycles. b) EPR signals from electrolyte with DMPO added when charging NC and NCAY cathodes to 4.3 V and 4.5 V after activation for 3 cycles. c) The O and Ni atomic ratio at the surface (based on XPS analysis) and bulk (based on EDS analysis) regions of NC and NCAY cathodes before and after 100 cycles. d) The vacancy formation energy of oxygen adjacent to Ni, Al, and Y atoms. e) Schematic summarizing the consequence of the oxygen evolution at delithiated state and the stable oxygen framework after introducing Al and Y.

solution (1.0 M NiSO<sub>4</sub>·6H<sub>2</sub>O and CoSO<sub>4</sub>·7H<sub>2</sub>O in a 94:6 molar ratio) and base solution (5.0 M NaOH and 3.0 M NH<sub>4</sub>OH) were separately pumped into the batch reactor (5 L) under strictly controlled conditions, that is, pH at 11.2, the temperature at 55 °C, stirring speed at 600 rpm, and N<sub>2</sub> atmosphere. The hydroxide precursors were filtered, washed, and dried at 100 °C overnight. To obtain LiNi<sub>0.94</sub>Co<sub>0.06</sub>O<sub>2</sub>, the precursor was mixed thoroughly with LiOH·H<sub>2</sub>O (molar ratio of Li:(Ni + Co) = 1.02:1) and then calcined at 680 °C for 10 h under O<sub>2</sub> flow.

For the oxygen-stabilized oxide LiNi<sub>0.92</sub>Co<sub>0.06</sub>Al<sub>0.01</sub>Y<sub>0.01</sub>O<sub>2</sub>, the transition metal solution (1.0 M NiSO<sub>4</sub>·6H<sub>2</sub>O and CoSO<sub>4</sub>·7H<sub>2</sub>O in a 92:6 molar ratio), introducing solution (1.0 M YCl<sub>3</sub>•6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O in a 1:1 molar ratio dissolved in 2.0 M citric acid solution followed by regulating pH to 9.0 with NH<sub>3</sub>·7H<sub>2</sub>O, Ni:Co: Al:Y = 92:6:1:1 in molar ratio), and base solution (5.0 M NaOH and 3.0 M NH<sub>4</sub>OH) were separately pumped into the batch reactor under N<sub>2</sub> atmosphere. Other parameters and procedures were the same as above. The obtained

precursor was blended with LiOH·H<sub>2</sub>O thoroughly in a molar ratio of Li: (Ni + Co + AI + Y) = 1.02:1 and calcined at 700 °C for 10 h under following  $O_2$  to obtain the product of oxygen-stabilized oxide LiNi<sub>0.92</sub>Co<sub>0.06</sub>Al<sub>0.01</sub>Y<sub>0.01</sub>O<sub>2</sub>.

Materials Characterization: The morphology and the cross-sectional image were collected by focused ion beam scanning electron microscopy (FIB-SEM, ZEISS Crossbeam340/550). The fine structure and elemental mapping were examined by TEM (TECNAI G2 F20) and EDS (Bruker Quantax 200), respectively. The quantitative EDS microanalysis in TEM provides the mass fraction of O and Ni present in the bulk of samples due to the high energy of X-ray generation (KeV). As a surface analysis technique with weak energy (eV) and thin depth (1–5 nm), X-ray photoelectron spectra (XPS, ESCALAB 250Xi) were carried out to determine the elements and chemical states. For the surface O/Ni ratios of cycled electrode, Ni 2p and O 1s XPS spectra were measured after Ar ion etching

for 50s to get the rid of the blanket of CEI layer. The relative atomic concentration of O and Ni is calculated through their peak intensities given by:

$$\frac{\eta_{\rm O}}{\eta_{\rm Ni}} = \frac{I_{\rm O}/S_{\rm O}}{I_{\rm Ni}/S_{\rm Ni}}$$

where  $\eta_0$  and  $\eta_{Ni}$  are the relative content of O and Ni, respectively, I is the peak area, and S is the sensitivity factor of element. The sensitivity factors of O and Ni are 0.91 and 4.83, respectively. The TOF-SIMS analysis is performed to study the surface structure with 1 keV Cs^+ ion beam sputtering at the 100  $\times$  100  $\mu m^2$  analysis area for 1000 s. The X-ray diffraction (XRD) patterns were collected using a Rigaku Smart Lab XRD instrument (Cu Ka) equipped with high-temperature attachment and in situ cell test system. The crystalline structure data were collected in a  $2\theta$  range of  $10-80^{\circ}$  with a scan step of  $0.02^{\circ}$ . Rietveld refinement was performed using the GSAS software. The high-temperature XRD patterns were collected from 40 to 500 °C at a scan rate of 5 °C min<sup>-1</sup> and in the 2 $\theta$  range of 10-50°. The *in situ* XRD patterns were collected in the  $2\theta$  range of 17-21°, and  $56-72^{\circ}$  with a scan step of  $0.02^{\circ}$ , and the cells were being charged at 0.1C from open-circuit potential to 4.5 V. For DSC measurements, the charged (4.3 V) electrodes were dissembled at glove box, washed with DMC solvent, dried, and then sealed into stainless steel high-pressure capsules. The DSC profiles were collected from 50  $^{\circ}$ C to 300  $^{\circ}$ C at a scan rate of 5  $^{\circ}$ C min<sup>-1</sup> under Ar atmosphere. The electron paramagnetic resonance (EPR) spectra were collected using Bruker EMXplus from the electrolyte added 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to trap the oxygen radicals.

Electrochemical Test: The electrode was fabricated by blending the active particle, super P, and polyvinylidene fluoride in weight ratio of 8:1:1 in N-methyl pyrrolidinone to form cathode slurry. The slurry was coated on aluminum foil and then dried in 110 °C chamber for 12 h to obtain cathode. Electrochemical testing was conducted using a 2032 coin-type half-cell in which Li metal, Celgard 2400, and 1.0 M LiPF6 dissolved in ethyl carbonate and dimethyl carbonate (EC: DMC = 3:7 in volume) act as anode, separator, and electrolyte, respectively. The charge/discharge tests were conducted using Land CT2001A between 2.8 and 4.3 V at desired rates (1C = 200 mA g<sup>-1</sup>) at 25 °C. ElS measurements were performed using Zahner IM6e in a frequency range from 100 KHz to 1 MHz with a 5 mV potential perturbation after charged to 4.3 V. The leakage current testing was conducted using Keysight BT2191A measurement after cell charged to 4.5 V at 0.1C.

Theoretical Calculations: The first-principles calculations were conducted using the Vienna *ab initio* simulation package (VASP) with projector augmented-wave (PAW) method to describe the interactions between ion cores and valence electrons. The Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used for the exchange and correlation functionals. The Kohn-Sham equations were expanded in a plane-wave basis set with a cutoff energy of 400 eV. The Brillouin zone sampling was performed using a 3 × 3 × 1 Monkhorst-Pack *k*-point grid. To compare the activity of oxygen, the stoichiometric clean and Al/Y stabilized LiNiO<sub>2</sub> (104) surfaces were used, with a vacuum layer of 15 Å to avoid virtual interaction. The formation energy ( $\Delta E_o$ ) of oxygen vacancy ( $V_o$ ) was calculated by the following equation:  $\Delta Eo = E_{V_o} + \frac{1}{2}E_{O_2} - E_0$ , where  $E_{V_0}$  is the total energy of (104) surface with one oxygen vacancy per supercell,  $E_{O_2}$  is the energy of the gas phase O<sub>2</sub> molecule, and  $E_0$  is the energy of the supercell without oxygen vacancy.

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## **Conflict of Interest**

The authors declare no conflict of interest.

# **Supporting Information**

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

### **Keywords**

Li-ion batteries, cathode, high-Ni oxide, oxygen evolution, structure stability

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