# Yttrium Surface Gradient Doping for Enhancing Structure and Thermal Stability of High-Ni Layered Oxide as Cathode for Li–Ion Batteries

Yang-Yang Wang, Ming-Yue Gao, Sheng Liu, Guo-Ran Li, and Xue-Ping Gao\*

Cite This: https://dx.doi.org/10.1021/acsami.0c21990			Read Online			
ACCESS	III Metrics & More		E Article Recommendations		Supporting Information	

**ABSTRACT:** The high-nickel layered oxides are potential candidate cathode materials of next-generation high energy lithium—ion batteries, in which higher nickel/lower cobalt strategy is effective for increasing specific capacity and reducing cost of cathode. Unfortunately, the fast decay of capacity/potential, and serious thermal concern are critical obstacles for the commercialization of high-nickel oxides due to structural instability. Herein, in order to improve the structure and thermal stability of high-nickel layered oxides, we demonstrate a feasible and simple strategy of the surface gradient doping with yttrium, without forming the hard interface between coating layer and bulk. As expected, after introducing yttrium, the surface gradient doping layer is formed tightly based on the oxidation induced segregation, leading to improved structure and thermal stability. Correspondingly, the good capacity retention and potential stability are obtained for the yttrium-doped sample, together with the superior thermal behavior. The excellent electrochemical performance of the yttrium-doped sample is primarily attributed to the strong



yttrium-oxygen bonding and stable oxygen framework on the surface layer. Therefore, the surface manipulating strategy with the surface gradient doping is feasible and effective for improving the structure and thermal stability, as well as the capacity/potential stability during cycling for the high-Ni layered oxides.

**KEYWORDS:** *Li*-*ion batteries, cathode, high-Ni oxides, cycle stability, thermal stability* 

# 1. INTRODUCTION

Lithium—ion batteries (LIBs), when talking about electric vehicles and off-peak grid energy storage, have drawn extensive attention as the most workable candidate due to their energy density.<sup>1</sup> Among all the intercalation cathode materials, high-Ni layered oxides are the most probable commercially available cathode materials with high specific capacity and low cost.<sup>2,3</sup> To further elevate the energy density of high-Ni layered oxide cathodes, increasing the Ni content, especially for Ni content over 90%, is considered to be a feasible technological approach to meet the need for higher specific capacity.

Despite the high efficiency in extracting more energy density, these cathode materials are confronted to poor cycling performance with increasing the Ni content in layered oxides. In particular, the capacity and potential decay of high-Ni layered oxide cathodes are mostly attributed to structural instability on the surface layer at the delithiated state, accompanied simultaneously with microsphere cracks and electrolyte consumption upon cycling.<sup>4,5</sup> The instability on the surface layer could further induce the bulk structure deterioration from layered structure into spinel and/or rock-salt phases, inherently leading to sluggish lithium ion kinetics, and thus bringing fast capacity fading, potential decay, and mechanical degradation.<sup>6</sup> In the meantime, the electrolyte

decomposition on the cathode/electrolyte interface, and oxygen evolution from the newly exposed surface on oxide microcracks can trigger thermal runaway of the battery.<sup>7</sup> Hence, the achievement of structural and thermal stability of high-Ni layered oxide cathodes is critical for developing high energy density LIBs.

The surface structure manipulating, such as coating, coreshell structure, and heterostructure, is proved to be effective for enhancing the cycling stability by reducing the interface parasitic reaction.<sup>8–10</sup> However, the structural mismatch on the hard interface between host sample and coating component causes unavoidable separation of coating layer and unstable protection of active materials upon long-term cycling.<sup>11</sup> In addition, the wet coating process may change the surface pH value or generate an impure phase. Foreign element doping, such as cation, anion, and dual-element doping, is

Received: December 11, 2020 Accepted: February 2, 2021





Figure 1. (a) Schematic working mechanism of high-Ni oxide with the yttrium surface gradient doping. (b) Element selection for dopant inclining to segregate onto the oxide surface, and to suppress the oxygen evolution based on two criteria (M-O bond energy and formation energy of metal oxides).

helpful for improving the electrochemical cycle stability of high-Ni layered oxide cathode by inhibiting phase transition;<sup>12–14</sup> however, the working mechanism of thermal stability is still under investigation.

It is well-known that the structure deterioration occurs initially on the surface, and then expands gradually into the bulk of high-Ni oxides during cycling.<sup>15</sup> Especially, the structure degradation is highly related to the oxygen release at the surface,<sup>16,17</sup> which is the driving force for the cation migration in the bulk. Furthermore, the oxygen release at the delithiated state could trigger the thermal instability of oxide cathode.<sup>18</sup> Therefore, strengthening the surface oxygen is the key issue to the structural and thermal stability of high-Ni oxide cathodes.

As a rare earth element, yttrium is a promising candidate of doping in layered oxide cathodes due to its high oxygen affinity. Previous studies indicate that yttrium prefers to occupy the lithium layer in the layered oxide due to similar ionic radius to Li<sup>+</sup> ( $r_{\text{Li}}^{+} = 0.76 \text{ Å}$ ,  $r_{Y}^{3+} = 0.89 \text{ Å}$ ).<sup>19–21</sup> Thus, yttrium cations could serve as pillar ions to stabilize the structure framework of the layered oxide upon lithium insertion/extraction. Importantly, yttrium possesses a strong bonding with oxygen to suppress the oxygen release at the delithiated state, beneficial to the thermal stability of high-Ni oxides.<sup>22</sup>

In this work, yttrium is elected as a doping element for the improvement of the structural and thermal stability of high-Ni oxide LiNi<sub>0.93</sub>Co<sub>0.07</sub>O<sub>2</sub> (termed as NC hereafter), based on the oxidation induced segregation of yttrium to the surface.<sup>23,24</sup> Different from the conventional surface coating with the obviously hard phase interface to foreign materials,<sup>25</sup> the continuous gradient distribution of yttrium in the surface doping layer could be formed without the separate phase interface (Figure 1), which would be more effective in facilitating fast lithium diffusion, preserving mechanical integrity, and suppressing transition metal (TM) dissolution. Correspondingly, the Y-doped high-Ni oxide Li-Ni<sub>0.91</sub>Co<sub>0.07</sub>Y<sub>0.02</sub>O<sub>2</sub> (termed as NCY hereafter) delivers excellent performance in terms of capacity retention and potential stability.

# 2. EXPERIMENTAL SECTION

**2.1. Sample Preparation.** The spherical  $Ni_{0.93}Co_{0.07}(OH)_2$  precursors were prepared by coprecipitation method using a continuously stirred tank reactor under  $N_2$  atmosphere. A 1 M mixed transition metal solution of  $NiSO_4.6H_2O$  and  $CoSO_4.7H_2O$  (molar ratio of Ni:Co is 93:7), and a 2 M base solution (NaOH and  $NH_3.H_2O$  with a molar ratio of NaOH:NH $_3.H_2O$  = 5:3) were separately pumped into the tank reactor. The pH (11.0), temperature



**Figure 2.** High-temperature in situ XRD patterns for the structural evolution from hydroxide precursor to oxide. (a) NC precursor with LiOH (\* is indexed to spinel structure), and (b) NCY precursor with LiOH (P: precursor, RS: rock-salt, L: layered). XRD patterns and Rietveld refinements of (c) NC and (d) NCY oxide powders.

(50.5 °C), and stirring speed (600 rpm) were strictly controlled through the coprecipitation process. After washing, filtering, and drying, the as-obtained  $Ni_{0.93}Co_{0.07}(OH)_2$  powder was mixed with LiOH at 2% excess in molar ratio, and then calcined at 760 °C for 10h under flowing oxygen, to obtain LiNi<sub>0.93</sub>Co<sub>0.07</sub>O<sub>2</sub>.

To prepare LiNi<sub>0.91</sub>Co<sub>0.07</sub>Y<sub>0.02</sub>O<sub>2</sub>, stoichiometric amounts of YCl<sub>3</sub>· 6H<sub>2</sub>O and citric acid (molar ratio 1:2) were dissolved in deionized water, and then the desired amount of NH<sub>3</sub>·H<sub>2</sub>O was added to form solution with pH at 9. The yttrium solution and transition metal solution were simultaneously fed into the reactor at the same feed rate to obtain Ni<sub>0.91</sub>Co<sub>0.07</sub>Y<sub>0.02</sub>(OH)<sub>2</sub> precursor. Then, the mixture of precursor powder and LiOH (molar ratio of Li:(Ni+Co+Y) = 1.02:1) was calcined at 760 °C for 10 h under O<sub>2</sub> atmosphere.

2.2. Electrochemical Measurements. Active material, poly-(vinylidene) fluoride (PVDF), and Super P (weight ratio is 8:1:1) were radically mixed in N-methyl-2-pyrrolidone (NMP), followed by coasting slurry on Al substrate foil and drying at 110 °C overnight to obtain cathode. Then, the cathode was punched into discs with a diameter of 10 mm, and the corresponding loading mass of active material was  $2-3 \text{ mg cm}^{-2}$ . The 2032 coin cells were fabricated with as-prepared cathode, Li metal anode, electrolyte, and Celgard 2400 separator in Ar-filled glovebox. The electrolyte consists of 1 M LiPF<sub>6</sub> in ethyl carbonate and dimethyl carbonate (EC:DMC = 3:7 in volume). The coin cells measurements (galvanostatic charge/ discharge, rate, GITT, and open-circuit voltage tests) were performed on Land CT2001A battery test system at 25 °C, at 1C rate of 200 mA  $g^{-1}$ , and between 2.8-4.3 V. EIS measurements were carried out using Zahner IM6e in a frequency range from 100 kHz to 1mHz with a 5 mV potential perturbation. For GITT tests, all cells were activated at 20 mA g<sup>-1</sup> between 2.8-4.3 V for three cycles. And then, 10 min galvanostatic charge/discharge pulses (20 mA  $g^{-1}$ ) were applied to cells, followed by a 40 min relaxation period. The sequence was repeated until cell potential reached 4.5 and 2.8 V.

**2.3. Material Characterization.** X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was applied to assess the elements and chemical states. Depth analysis was measured by Ar ion etching for

20s and repeated three times. All spectra were calibrated referenced to C 1s line at 284.8 eV. X-ray diffraction was carried out to investigate crystalline phase and phase transition upon heating using Cu K $\alpha$  radiation utilizing Rigaku SmartLab together with high-temperature attachment. The morphology, surface lattice, and elemental mapping of sample were examined by SEM (JEOL-JSM7800F), TEM (TECNAI G2 F20), and EDS (Bruker Quantax 200), respectively. The thermal analyses were performed using DSC (NETZSCH 204F1) from 50 to 300 °C and TGA (Mettler Toledo) from 50 to 600 °C both at a scan rate of 5 °C min<sup>-1</sup> under Ar atmosphere. For cycled electrode characterizations, the cells were carefully disassembled, washed using DMC, and dried in Ar-filled glovebox.

## 3. RESULTS AND DISCUSSION

In order to characterize the crystallization of NC and NCY oxides in the synthesis process, the high-temperature in situ XRD patterns were collected from 40 to 760 °C. As shown in Figure 2a,b and Supporting Information (SI) Figure S1, XRD patterns display combining peaks of LiOH and hydroxide precursor at the beginning. With increasing the calcination temperature, XRD patterns for both samples remain almost unchanged. However, the peaks of hydroxide precursor, represented by (001), (100), and (101) peaks, vanish abruptly. In the meantime, two new (111) and (200) peaks associating with rock-salt structure appear at about 240 °C. It means that the rapid structure transition from quasi-layered hydroxide precursor ( $P\overline{3}m1$ ) to Li-free rock-salt structure ( $Fm\overline{3}m$ ) occurs due to dehydration of both NC and NCY precursors with increasing the calcination temperature. With further increasing the calcination temperature, the (111) and (200) peaks successively shift to higher angles together with the gradual disappearance of LiOH peak, indicating the complete insertion of Li-ions into the rock-salt structure. Compared with NC, the oxidation induced segregation of yttrium could occur for NCY



**Figure 3.** SEM images of (a) NC and (b) NCY microspheres. (c) The relative contents of Ni, Co, and Y as a function of etching depth based on XPS spectra for NCY. (d) EDS mappings with the line scan profile of NCY. (e) HRTEM images and (f) the inverse fast Fourier transform images near the surface of NC and NCY. The white arrows highlight the edge dislocations, and the white dash line indicates the dislocation line.

under oxygen environment during the calcination due to the high affinity of yttrium to oxygen. Specifically, for NC, the insertion of Li-ions into the structure takes place at above 250 °C, accompanied gradually with the appearance of the spinel structure. When the temperature reaches up to 760 °C, the spinel structure is finally transferred into Li-containing layered structure. However, a trace of spinel phase in NC sample is still observed before 760 °C. At the end of the calcination process, a trace of spinel peaks disappears quickly and the peaks related to layered structure become sharp, demonstrating the complete crystallization in the layered structure. In the case of NCY, the structure evolution is more convenient, and the Li-free rocksalt structure can be quickly converted to the layered structure from 240 to 760 °C, without a trace of spinel phase. In particular, the emergence of (003) peak as a typical layered structure feature can be detected at the temperature as low as 420 °C, indicating the facilitation of the initial nucleation for layered oxide and the improvement on cation ordering. Consequently, as shown in XRD patterns, the as-prepared NC and NCY oxides have a rhombohedral layered structure with no impurity phase (Figure 2c,d). In the LiMO<sub>2</sub> layered structure, Ni partially enters Li sites in the Li-layer, resulting in Li/Ni cation disordering.<sup>26</sup> Comparatively, NCY oxide exhibits a higher degree of Li/Ni cation ordering, evidenced by the intensity ratio of (003)/(104) peaks (2.04 for NCY, and 1.31 for NC). In the meantime, as indicated by the Rietveld refinements, the Ni content in the Li layer is decreased slightly from 2.34% to 1.87%, which could be beneficial to the cycle stability of the layered oxides. However, after doping with yttrium, a slight shift of (003) diffraction peak to lower angle is observed, accompanied by a mild enlargement in c-axis direction (SI Figure S2 and Table S1). It means that yttrium could be enriched onto the surface layer as demonstrated in the following figures, instead of doping in the bulk structure of high-Ni layered oxide.

As shown in Figure 3a,b, both NC and NCY samples exhibit micrometer-spherical morphology with uniform distribution of secondary particles. Different from NC hydroxide precursor and oxide sample, both NCY hydroxide precursor and NCY oxide microsphere are assembled tightly with obviously smaller primary hydroxide or oxide grains (SI Figure S3). It means that the yttrium dopant has an obvious influence on the initial nucleation of hydroxide precursor and oxide grains, which could be impactful on the morphology and microstructure of final samples in the subsequent calcination. In the meantime, it is likely that yttrium tends to the surface segregation due to the strong formation energy of yttrium oxides (SI Table S2), which inhibits the further growth of primary grains during lithiation process.<sup>27,28</sup> In order to confirm the distribution of yttrium on the surface layer, X-ray photoelectron (XPS) depth profile analysis of NCY sample by Ar-ion etching is implemented. As shown in SI Figure S4a, the intensities of Ni and Co peaks are gradually increased; , however, the intensity of Y peak is progressively decreased with increasing etching depth. Specifically, the Y 3d<sub>5/2</sub> peak of NCY cathode is located at 156.4 eV, which is attributed to  $Y^{3+}$ . And the relative content of yttrium decreases gradually from 21% to 1% with increasing etching depth up to around 4.39 nm (Figure 3c), demonstrating a continuous gradient distribution of yttrium from the surface toward the bulk.

The gradient distribution of Ni, Co, and Y near the surface region can be further observed on mapping scan images in Energy dispersive spectra (EDS) (Figure 3d). The Ni and Co elements are evenly dispersed across the microsphere particle, while the yttrium element is clearly enriched on the surface layer, consistent well with the line scan profile analysis. This segregation phenomenon of yttrium is also reported in YSZ ceramic or metal oxides.<sup>29,30</sup> Although the yttrium surface segregation is demonstrated here; however, there is no hard interface or phase boundary on the surface doping layer of NCY oxide as shown from HRTEM image (Figure 3e),

www.acsami.org



Figure 4. (a) The charge/discharge curves of NC and NCY cathodes at 0.1C rate. (b) dQ/dV profiles of two cathodes derived from the charge/discharge curves. (c) Long-term cycling performance at 1C rate. (d) The charge/discharge midpoint potential evolution of two cathodes upon cycling. (e) The discharge capacities of two cathodes obtained at various C-rates. (f) The open-circuit potential evolution of two cathodes during resting for 50 h at 25 °C.

indicating the good surface structure integrity. Of course, the microstructure changes arisen from yttrium doping are still observed, including the lattice expansion and defects on the surface layer. In the case of NCY, the interplanar spacing of 0.475 nm, indexed to the (003) plane, is slightly wider than that in NC due to the large ion radius of yttrium. In addition, the slightly decreased signal of lattice lithium bonding at 53 eV is shown in Li 1s core level of NCY (SI Figure S4b), due to the surface yttrium doping in lithium layer,<sup>31</sup> leading to a mild lattice expansion and a trace of defects on the surface layer. Typically, for NCY oxide, a few lattice distortions (stacking fault, consisted of a series of edge dislocation) coexist with crystalline lattices at the surface layer as shown in inverse fast Fourier transform (IFFT) image (Figure 3f), due to the slight altering of the local environment by doping large yttrium ions. Such lattice distortions with fixing large yttrium ions in lithium layer could act as a protective screen, blocking the structure deterioration from the surface into the bulk during long cycling.<sup>32</sup> It means that the surface gradient doping with yttrium may contribute to the structure integrity and the consequent electrochemical stability during cycling.

The surface gradient doping shows a good advantage for improving the electrochemical performance of high-Ni layered oxide cathodes between 2.8 and 4.3 V. As shown in Figure 4a, both NC and NCY cathodes show the similar charge/discharge curves and Coulombic efficiency. In particular, NCY cathode delivers a high initial discharge capacity of 224.6 mAh g<sup>-1</sup> at 0.1C rate, which is almost identical to that (225.8 mAh g<sup>-1</sup>) of NC cathode. It means that the gradient doping layer does not harm the key electrochemical properties of high-Ni layered oxides. Meanwhile, it is noted that the discharge capacity of high-Ni (>0.9) oxide cathodes exceeds 220 mAh g<sup>-1</sup>, demonstrating the good advantage of high capacity and good lithium utilization as compared with conventional Li-Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) cathodes.

curves that two electrodes display a multiplateau feature during Li deintercalation and intercalation. In particular, NC cathode exhibits an extra plateau at about 3.5 V during discharge process, indicating that NC cathode may suffer from serious irreversible phase transition during lithium insertion/extraction. Furthermore, this multiplateau feature can be more sensitively analyzed by dQ/dV profiles. As shown in Figure 4b, both electrodes undergo the multistep phase transitions in the cathodic and anodic processes,<sup>35</sup> corresponding to the multiplateau feature in the charge/discharge curves. Comparatively, the anodic/cathodic peaks on the NCY electrode are likely passivated, especially for H2  $\rightarrow$  H3 phase transition peak, indicating the suppressed phase transition to a certain extent by the surface gradient doping with yttrium. The stabilizing effect of the gradient doping layer on the structure transition can be also confirmed by cyclic voltammograms (SI Figure S5).

Due to the stabilization by the surface gradient doping with yttrium, the superior cycling life is obtained for NCY cathode (Figure 4c). In comparison with the low capacity retention of 56% of NC cathode, NCY cathode can retain 77.4% of the initial capacity at 1 C rate after 300 cycles. It means that the surface gradient doping is helpful to maintain the structure integrity of high-Ni layered oxides during long cycling based on the capacity evaluation and well-preserved peaks upon cycling (SI Figure S6). Actually, the potential evolution is much more sensitive to the structure deterioration of layered oxide cathodes during cycling.<sup>36</sup> As shown in Figure 4d, the discharge potential decay and charge/discharge polarization are notable for NC cathode. Specifically, after 300 cycles, the midpoint potential difference in the charge/discharge curves is only 0.14 V for NCY cathode, almost a half value of NC cathode (0.29 V). It is further confirmed that the serious polarizarion of high-Ni layered oxide during cycling can be depressed remarkably by the surface gradient doping with yttrium. Moreover, both NC and NCY cathodes show a good

www.acsami.org



Figure 5. Potential profile and the corresponding ex situ XRD pattern evolution of (a,b) NC cathode and (c,d) NCY cathode. (e) The corresponding evolution of lattice parameters (a, c, and V) obtained from XRD data.

and similair high rate discharge capability from 1C to 5C rate (Figure 4e), implying that the high rate performance of oxide cathode can not be undermined by the yttrium doping. In addition, the self-discharge performance with severe potential drop during storage is also a common index for evaluating the stability of cathodes, which is usually attributed to the parasitic reaction on the interface between cathode and electrolyte. Satisfactorily, at both room temperature (Figure 4f) and elevated temperature (SI Figure S7), NCY displays a relatively stable potential evolution during resting after charging, demonstrating that the surface gradient doping is also effective for mitigating the parasitic reaction on the interface of high-Ni oxide cathode.

To further validate the kinetic behavior of Li ions originated from the surface doping layer, galvanostatic intermittent titration techniques (GITT) are conducted to acquire diffusion coefficient  $(D_{Li})$  after activation for three cycles (SI Figure S8). In the discharge process, the reaction resistance and calculated  $D_{\rm Li}$  from SI eq S1 are almost identical for both NC and NCY electrodes, corresponding to their similar high-rate capability. In the charge process, the calculated  $D_{Li}$  of NCY electrode is slightly higher than that of NC electrode, due to the pillar effect of large yttrium ions in the lithium layer. Therefore, the surface gradient doping with moderate yttrium is a feasible strategy to improve the stability of high-Ni layered oxides, based on the capacity, midpoint potential, self-discharge, and diffusion feature. Of course, excessive doping with heavy and large yttrium could sacrifice the electrochemical capacity of high-Ni layered oxide cathode (SI Figure S9).

The structure evolution of NC and NCY cathodes during extraction of Li-ions is examined by ex situ XRD measurement. As depicted in Figure 5, both samples exhibit a similar structural behavior, namely phase evolution from H1 to H2 and then finally to H3 phase in the charge process (extraction

of Li-ions). Specifically, the shift of (003) peak reflects the expansion/contraction of the *c*-axis, and the shift of (101) peak represents the change of lattice parameters along the a/baxis.<sup>37</sup> For both cathodes, the (101) peaks shift consecutively to higher angle in the charge process due to the oxidation of transition-metal ions and extraction of Li-ions, implying a continuous shrinkage of a/b lattice parameters. The terminal of peak displacement is in close proximity for both cathodes at the charge cutoff potential, demonstrating a comparable change of a/b lattice parameters for NC and NCY cathodes. However, the lattice distortion along *c*-axis undergoes a distinct evolution route as evidenced by (003) peak change. In the charge process before 4.2 V, the (003) peak of both cathodes moves gradually toward lower  $2\theta$  degree due to the electrostatic repulsion of adjacent oxygen layers, corresponding to the phase transition from H1 to H2 and the expansion of the *c*-axis. Upon further charging up to 4.5 V, the (003) peak of NCY cathode shifts smoothly from H2 phase to H3 phase. While, for NC cathode, the two-phase coexistence is clearly observed: the new  $(003)_{H3}$  peak appears at higher angle, the original  $(003)_{H2}$  peak is not yet entirely vanished, leading to the large gap between H2 and H3 phases. Furthermore, during the discharging process, this two-phase coexistence is also observed to be reversible for NC cathode (SI Figure S10), indicating severe internal stress between H2 and H3 phases.

The changes of lattice parameters calculated from XRD patterns are plotted in Figure 5e. With the extraction of Lions, both NC and NCY cathodes show an approximate shrinkage of 2.39% and 2.35% on the *a*-axis, respectively. The *c*-axis lattice parameter is increased progressively during the phase transition from H1 to H2. With the further extraction of Li-ions, the abrupt contraction on the *c*-axis lattice parameter is observed due to the phase transition from H2 to H3 in both cathodes. However, the maximum change on the *c*-axis lattice

# **ACS Applied Materials & Interfaces**

www.acsami.org



Figure 6. SEM images of (a) NC and (b) NCY electrodes upon cycling.



Figure 7. Nyquist plots of (a) NC and (b) NCY electrodes at the charged state before and after cycling. (c) Ni and Co concentrations dissolved in electrolyte for cathodes upon cycling. (d) HRTEM and corresponding FFT images of NC and NCY after 300 cycles. (e) XRD patterns of NC and NCY cathodes after 300 cycles.

parameter for NCY cathode is only 4.53%, which is increased up to 4.92% for NC cathode. Therefore, the total contraction of the unit cell volume of NCY cathode is mitigated as compared with NC cathode when charged to 4.5 V. Herein, the continuous phase tansformation or structure evolution during extraction/insertion of Li—ions are benificial to ensure the structure integrity, while the jumping phase transition is harmful to the stability of high-Ni layered oxide cathode. Therefore, in terms of microstructure change, the surface gradient doping is helpful to suppress the serious phase transition and expansion/shrinkage of lattice parameters of high-Ni layered oxides in the charge/discharge processes. Usually, such serious microstructure degradations in the bulk structure could extend to the surface with the consequent microcracks and particle pulverization after extensive cycling.<sup>38</sup> To survey the mechanical integrity of oxide microspheres, SEM images of NC and NCY cathodes are examined after long-term cycling. As shown in Figure 6, both samples show varied morphologies with microcracks inside a microsphere due to anisotropic strain after repeated charge/discharge cycling. For NC cathode, the close-packed microspheres suffer from drastic pulverization after long cycling. Eventually, NC microspheres are almost disintegrated into cauliflower-like particles after 300 cycles. In contrast, although a few microcracks can be observed on the microsphere surface,



Figure 8. Contour plots of high-temperature in situ XRD patterns of (a) NC and (b) NCY cathodes charged at 4.3 V. (R: rhombohedral, S: spinel, RS: rock-salt) (c) Scheme of the phase transitions of NC and NCY during thermal decomposition. (d) DSC profile of cathodes charged at 4.3 V.

however, NCY cathode still shows the integrated microsphere morphology after long cycling, suggesting that the surface gradient doping can stabilize the mechanical integrity of oxide microspheres during cycling due to the restrained phase transition from H2 to H3. Furthermore, the microcracks and pulverization of oxide microspheres provide more extra pathways for electrolyte penetration, leading to a serious corrosion on the interior fresh surface by electrolyte, as well as the structure deterioration, and increase of internal resistance.<sup>39</sup> Herein, NCY cathode presents a relatively good integrity on microstructure and morphology during long cycling, consistent with its good electrochemical performance. The electrochemical impedance spectra (EIS) further confirm the slight increase of the interfacial charge-transfer resistance for NCY cathode during cycling. As shown in Figure 7a,b, Nyquist plots of both cathodes show similar shapes, consisted of a slope line in the low frequency region, two semicircles in the high and medium frequency regions. Here, the surface film resistance  $(R_f)$  and charge-transfer resistance  $(R_{ct})$  can be simulated from two semicircles, respectively, and diffusion impedance  $(W_{o})$  is calculated from the slope line.<sup>40</sup> The corresponding fitting data (SI Table S3, and Figure S11) reveal that both  $R_{ct}$  and  $R_{f}$  for NCY cathode are lower than those for the NC cathode after 300 cycles, indicating the high surface electrochemical activity during cycling due to the effective surface protection by the gradient doping layer. In addition, the diffusion impedance of NCY cathode is 326.5  $\Omega$  after 300 cycles, nearly a third of that (938.8  $\Omega$ ) of NC cathode,

indicating a good transport of Li–ions within the lattice even after long-term cycling for NCY cathode.

The serious corrosion by electrolyte on the interior fresh surface in cracked oxide microspheres can be identified by monitoring the dissolution of transition metal elements of high-Ni oxide cathodes during cycling.41 Indeed, benefited from the good mechanical integrity of microspheres, much low dissolution of Ni and Co elements in electrolyte is observed for NCY cathode after various cycling (Figure 7c). It is further confirmed that the surface gradient doping layer can effectively depress the dissolution and loss of active elements in cathode from electrolyte attack. With the formation of microcracks and dissolution of transition metal elements, the structure integrity at the surface is destroyed inevitably after cycling.<sup>42</sup> As shown in Figure 7d, the disordered domains and stacking faults can be found in the cycled NC cathode. More specifically, the rocksalt phase is detected at the surface region, indicating severe structure deterioration from layered structure to rock-salt phase. In sharp contrast, for the cycled NCY cathode, the layered structure is well conserved at the surface region without serious structure damage. It means that the surface gradient doping layer is effective to protect the surface structure against the corrosion of electrolyte. Meanwhile, the gradient distribution of yttrium on the surface layer is preserved after cycling evidenced by the EDS mappings (SI Figure S12), demonstrating the superior structure stability of NCY. Furthermore, the structure degradation could be spread from the surface into the bulk upon cycling. XRD patterns of

www.acsami.org



Figure 9. (a) TEM images of NC and NCY cathodes after 300 cycles. (b) C 1s, O 1s, F 1s, and P 2p XPS spectra of CEI on NC (top) and NCY (down) surface after 300 cycles. (c) The surface concentration of C, O, F, and P elements from XPS spectra.

cycled electrodes are described in Figure 7e. After 300 cycles, both NC and NCY cathodes preserve the rhombohedral layered structure at the bulk level. However, the peak intensity ratio of (003) to (104) planes of cathodes is decreased moderately after 300 cycles, especially for NCY (from 1.987 to 1.413), indicating a low Li/Ni cation mixing (SI Figure S13 and Table S4). Furthermore, the increase (0.049) in c/a ratio for NCY cathode after 300 cycles is slight, demonstrating weak active lithium loss within NCY lattice after long-term cycling.<sup>43</sup> Based on the evaluation of the Li/Ni cation mixing and active lithium loss, evidently, NCY cathode possesses a superior advantage on both the surface morphology and bulk microstructure integrity.

The thermal stability of high-Ni layered oxide cathodes is an another key concern for LIBs commercialization.<sup>44,45</sup> To probe the effect of surface doping layer on the thermal stability of pristine material, high-temperature X-ray diffraction is used to evaluate the phase transition during thermal decomposition. As shown in Figure 8a,b, XRD patterns of both samples at room temperature can be indexed to rhombohedral phase  $(R\bar{3}m)$ .<sup>46,47</sup> In the case of NC cathode, the complete structure transform from  $R\bar{3}m$  phase to spinel  $(Fd\bar{3}m)$  phase is observed at about 200 °C, and spinel phase is further converted to the rock-salt  $(Fm\bar{3}m)$  phase at above 300 °C. In contrast, NCY cathode displays a different structure transition upon heating. First, at about 210 °C, the  $R\bar{3}m$  phase and  $Fd\bar{3}m$  phase coexist still without achieving a complete structure transition. When the temperature is increased to above 310 °C, the  $R\bar{3}m$  phase

disappears, however, the coexistence of  $Fd\overline{3}m$  and  $Fm\overline{3}m$ phases is shown until 500 °C in NCY cathode, as summarized in Figure 8c. It is well-known that the phase transition is closely related to the oxygen release from the lattice.<sup>48</sup> Consequently, the surface gradient doping of yttrium with strong oxygen bonding is beneficial to suppress the oxygen evolution and subsequent phase transition. The suppression of the oxygen evolution in NCY cathode during heating can be further confirmed from thermogravimetric analysis (SI Figure S14) with less mass loss and higher onset temperature.

Usually, the thermal instability of cathode is evaluated based on the heat release and oxygen evolution. In particular, the released oxygen with high activity from the lattice can react with flammable electrolyte to trigger the thermal runaway.<sup>49</sup> Differential scanning calorimetry (DSC) analysis is an efficient technique to detect thermal stability of cathode at the delithiated state. Clearly, as compared with NC cathode (Figure 8d), NCY cathode presents a good thermal stability with high exothermal peak (228.3 °C) and low heat release (341.2 J g<sup>-1</sup>). Such thermoanalysis results further support the improved thermal stability of NCY cathode by the surface gradient doping with yttrium.

The consequence of interfacial parasitic reactions is to form a passivation cathode electrolyte interface (CEI) layer, undermining the electrochemical performance of cathodes directly.<sup>50</sup> As shown in Figure 9a, CEI layers are observed clearly on the surface of both cathodes after 300 cycles due to the corrosion and decomposition of electrolyte on the cracked

particles. The CEI thickness on the cycled NC particle is about 69 nm, obviously larger than that (13 nm) on the cycled NCY particle. As presented in XPS spectra (Figure 9b), such CEI layers are consisted mainly of  $Li_2CO_3$ , LiF, and  $LiPF_xO_y$  by the decomposition of electrolyte during long cycling.<sup>51</sup> Specifically, the C 1s spectra is regarded as the representative of CEI, originating from the decomposition of carbonate solvents, including C-C/C-H bonds, C-O bonds, and Li<sub>2</sub>CO<sub>3</sub>. Herein, C-O bonds and Li<sub>2</sub>CO<sub>3</sub> are related to the organic and inorganic species in CEI, respectively. Clearly, the relative intensity of Li<sub>2</sub>CO<sub>3</sub> for NC cathode is much larger, indicating more inorganic species formed due to the electrolyte decomposition. These inorganic species can be identified as a signal of surface passivation, inhibiting lithium transfer and increasing cell impedance. In contract, the intensity of C-O bonds for NCY cathode is higher, indicating that the organic species is the essential component of CEI. Such organic species can be considered as fast lithium ion conductor facilitating lithium transport. Therefore, the surface gradient layer is effective in inhibiting electrolyte decomposition to form inorganic species. Comparatively, such fluorine and phosphorus signals from decomposition products of LiPF<sub>6</sub> are weaker on the cycled NCY cathode (Figure 9c). Additionally, the higher O content on the cycled NCY cathode is attributed to the strong metal-oxygen bonding after yttrium doping.<sup>52</sup> It implies that the surface gradient doping with yttrium is helpful to depress the growth of CEI layer during cycling due to the corrosion and decomposition of electrolyte on the cracked particles with more fresh surface.

Indeed, the high-Ni oxides present a good advantage of high electrochemical capapcity of over 225 mAh g<sup>-1</sup>, which is highly important for fabricating high energy LIBs. However, during long cycling, the high-Ni oxides suffer from serious structural deterioration, including the structure transforming from layered phase into spinel/rock-salt structure, originated from the surface toward the bulk. In particular, the serious microcracks, high dissolution of key components, and thicker CEI layer on the surface are observed for high-Ni oxide microspheres after 300 cycles, leading to the fast capacity and potential decay. After doping with yttrium, the surface gradient doping layer is formed due to the oxidation induced segregation of yttrium to the surface. Correspondingly, the great improvement of structural and thermal stability of high-Ni layered oxides can be achieved by the yttrium surface gradient doping, accompanied by moderate microcracks, low dissolution of key components, and thin CEI layer on the surface. As expected, the as-prepared NCY cathode shows the excellent electrochemical performance, with both good capacity retention and potential stability. In addition, the good thermal stability is also obtained for NCY cathode due to the high oxygen affinity of yttrium. Therefore, stabilizing the surface based on the gradient doping is s feasible strategy to stabilize the bulk structure, thermal stability, and subsequent electrochemical performance of high-Ni oxide cathode during cycling.

# 4. CONCLUSIONS

In summary, in order to stabilize the bulk structure and achieve the desired electrochemical performance of high-Ni layered oxide cathode, we propose a feasible strategy of the yttrium surface gradient doping based on the oxidation induced segregation. As demonstrated, the surface doping layer can be constructed by the yttrium gradient distribution with sturdy oxygen bonding in high-Ni layered oxide, LiNi093C0007O2. With the formation of the yttrium surface gradient doping layer, the electrochemical capacity and high rate capability of cathode are not undermined, which are essential requirements for high energy cathode materials. Importantly, the electrochemical cycling stability based on the capacity and midpoint potential can be greatly improved by the surface gradient doping with yttrium. Such electrochemical stability on capacity and potential is highly related to the structure stability of high-Ni oxide cathode during cycling. Intrinsically, the yttrium surface gradient doping is effective to depress the serious structure deterioration originated from the surface toward the bulk during cycling, which is usually accompanied by the microcracks of oxide microspheres, dissolution of key components, and growth of thick CEI layer on the particle surface. In addition, the simultaneously produced consequence of the yttrium surface gradient doping is to dramatically improve the thermal stability of high-Ni oxide cathode. As distinct from the common surface coating with the obviously hard phase interface to guest materials, this surface gradient doping provides an elastic surface modification strategy for improving the performance of high energy density cathode materials of LIBs.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c21990.

Schematic figure; lattice parameters; formation energy; SEM images; XPS spectra; CV curves; charge–discharge curves and dQ/dV profiles; XRD patterns of cathodes during discharge process; EDS mappings of cycled NCY, TG, and DTG curves; and the comparison of capacity retention and thermal stability (PDF)

## AUTHOR INFORMATION

### **Corresponding Author**

Xue-Ping Gao – Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China; orcid.org/0000-0001-7305-7567; Email: xpgao@nankai.edu.cn

# Authors

- Yang-Yang Wang Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China
- Ming-Yue Gao Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China
- Sheng Liu Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China; orcid.org/0000-0001-5933-1101
- Guo-Ran Li Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China; orcid.org/0000-0002-6380-5725

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c21990

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work is supported by the National Key Research and Development Program (2016YFB0100500) and the Fundamental Research Funds for the Central Universities of China. This work is also supported by the Ph.D. Candidate Research Innovation Fund of NKU School of Materials Science and Engineering.

## REFERENCES

(1) Li, W.; Erickson, E. M.; Manthiram, A. High-Nickel Layered Oxide Cathodes for Lithium-Based Automotive Batteries. *Nat. Energy* **2020**, *5*, 26–34.

(2) Kim, T.; Song, W.; Son, D. Y.; Ono, L. K.; Qi, Y. Lithium-Ion Batteries: Outlook on Present, Future, and Hybridized Technologies. *J. Mater. Chem. A* **2019**, *7*, 2942–2964.

(3) Gao, X. P.; Yang, H. X. Multi-Electron Reaction Materials for High Energy Density Batteries. *Energy Environ. Sci.* 2010, 3, 174–189.
(4) Xia, Y.; Zheng, J. M.; Wang, C. M.; Gu, M. Designing Principle for Ni-Rich Cathode Materials with High Energy Density for Practical Applications. *Nano Energy* 2018, 49, 434–452.

(5) Park, K. J.; Hwang, J. Y.; Ryu, H. H.; Maglia, F.; Kim, S. J.; Lamp, P.; Yoon, C. S.; Sun, Y. K. Degradation Mechanism of Ni-Enriched NCA Cathode for Lithium Batteries: Are Microcracks Really Critical? ACS Energy Lett. **2019**, *4*, 1394–1400.

(6) Kasnatscheew, J.; Röser, S.; Börner, M.; Winter, M. Do Increased Ni Contents in LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) Electrodes Decrease Structural and Thermal Stability of Li Ion Batteries? A Thorough Look by Consideration of the Li<sup>+</sup> Extraction Ratio. *ACS Appl. Energy Mater.* **2019**, *2*, 7733–7737.

(7) Wang, Y. Y.; Sun, Y. Y.; Liu, S.; Li, G. R.; Gao, X. P. Na-Doped  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  with Excellent Stability of Both Capacity and Potential as Cathode Materials for Li-Ion Batteries. *ACS Appl. Energy Mater.* **2018**, *1*, 3881–3889.

(8) Yuan, K.; Li, N.; Ning, R. Q.; Shen, C.; Hu, N.; Bai, M. H.; Zhang, K.; Tian, Z. Y.; Shao, L.; Hu, Z. W.; Xu, X.; Yu, T.; Xie, K. Y. Stabilizing Surface Chemical and Structural Ni-Rich Cathode via a Non-Destructive Surface Reinforcement Strategy. *Nano Energy* **2020**, 78, 105239.

(9) Xu, G. L.; Liu, Q.; Lau, K. K. S.; Liu, Y.; Liu, X.; Gao, H.; Zhou, X.; Zhuang, M.; Ren, Y.; Li, J.; Shao, M.; Ouyang, M.; Pan, F.; Chen, Z.; Amine, K.; Chen, G. H. Building Ultraconformal Protective Layers on Both Secondary and Primary Particles of Layered Lithium Transition Metal Oxide Cathodes. *Nat. Energy* **2019**, *4*, 484–494.

(10) Chen, Z.; Kim, G. T.; Bresser, D.; Diemant, T.; Asenbauer, J.; Jeong, S.; Copley, M.; Behm, R. J.; Lin, J.; Shen, Z.; Passerini, S.  $MnPO_4$ -Coated Li( $Ni_{0.4}Co_{0.2}Mn_{0.4})O_2$  for Lithium(-Ion) Batteries with Outstanding Cycling Stability and Enhanced Lithiation Kinetics. *Adv. Energy Mater.* **2018**, *8*, 1801573.

(11) Liu, S.; Liu, Z. P.; Shen, X.; Li, W. H.; Gao, Y. R.; Banis, M. N.; Li, M.; Chen, K.; Zhu, L.; Yu, R. C.; Wang, Z. X.; Sun, X. L.; Lu, G.; Kong, Q. Y.; Bai, X. D.; Chen, L. Q. Surface Doping to Enhance Structural Integrity and Performance of Li-Rich Layered Oxide. *Adv. Energy Mater.* **2018**, *8*, 1802105.

(12) Sun, Y. Y.; Liu, S.; Hou, Y. K.; Li, G. R.; Gao, X. P. In-situ Surface Modification to Stabilize Ni-Rich Layered Oxide Cathode with Functional Electrolyte. J. Power Sources **2019**, 410–411, 115– 123.

(13) Mu, L.; Zhang, R.; Kan, W. H.; Zhang, Y.; Li, L.; Kuai, C.; Zydlewski, B.; Rahman, M. M.; Sun, C. J.; Sainio, S.; Avdeev, M.; Nordlund, D.; Xin, H. L.; Lin, F. Dopant Distribution in Co-Free High-Energy Layered Cathode Materials. *Chem. Mater.* **2019**, *31*, 9769–9776.

(14) Yang, H.; Wu, H. H.; Ge, M.; Li, L.; Yuan, Y.; Yao, Q.; Chen, J.; Xia, L.; Zheng, J.; Chen, Z.; Duan, J.; Kisslinger, K.; Zeng, X. C.; Lee, W. K.; Zhang, Q.; Lu, J. Simultaneously Dual Modification of Ni-Rich Layered Oxide Cathode for High-Energy Lithium-Ion Batteries. *Adv. Funct. Mater.* **2019**, *29*, 1808825. (15) Li, N.; Sallis, S.; Papp, J. K.; McCloskey, B. D.; Yang, W. L.; Tong, W. Correlating the Phase Evolution and Anionic Redox in Co-Free Ni-Rich Layered Oxide Cathodes. *Nano Energy* **2020**, *78*, 105365.

www.acsami.org

(16) Das, H.; Urban, A.; Huang, W.; Ceder, G. First-Principles Simulation of the (Li-Ni-Vacancy)O Phase Diagram and Its Relevance for the Surface Phases in Ni-Rich Li-Ion Cathode Materials. *Chem. Mater.* **2017**, *29*, 7840–7851.

(17) Kong, F.; Liang, C.; Wang, L.; Zheng, Y.; Perananthan, S.; Longo, R. C.; Ferraris, J. P.; Kim, M.; Cho, K. Kinetic Stability of Bulk LiNiO<sub>2</sub> and Surface Degradation by Oxygen Evolution in LiNiO<sub>2</sub>-Based Cathode Materials. *Adv. Energy Mater.* **2019**, *9*, 1802586.

(18) Asl, S. S.; Lu, J.; Amine, K.; Yassar, R. S. Oxygen Release Degradation in Li-Ion Battery Cathode Materials: Mechanisms and Mitigating Approaches. *Adv. Energy Mater.* **2019**, *9*, 1900551.

(19) Zhang, M. L.; Zhao, H. Y.; Tan, M.; Liu, J. T.; Hu, Y. Z.; Liu, S. S.; Shu, X. H.; Li, H.; Ran, Q. W.; Cai, J. J.; Liu, X. Q. Yttrium Modified Ni-Rich  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  with Enhanced Electrochemical Performance as High Energy Density Cathode Material at 4.5 V High Voltage. J. Alloys Compd. 2019, 774, 82–92.

(20) Zhao, X.; Liang, G.; Liu, H.; Liu, Y. Improved Conductivity and Electrochemical Properties of  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  Materials via Yttrium Doping. RSC Adv. **2018**, *8*, 4142–4152.

(21) Kang, S.; Qin, H.; Fang, Y.; Li, X.; Wang, Y. Preparation and Electrochemical Performance of Yttrium-doped Li-[Li<sub>0.20</sub>Mn<sub>0.534</sub>Ni<sub>0.133</sub>Co<sub>0.133</sub>]O<sub>2</sub> as Cathode Material for Lithium-Ion Batteries. *Electrochim. Acta* **2014**, *144*, 22–30.

(22) Huang, Y.; Cao, S.; Xie, X.; Wu, C.; Jamil, S.; Zhao, Q.; Chang, B.; Wang, Y.; Wang, X. Y. Improving the Structure and Cycling Stability of Ni-Rich Layered Cathodes by Dual Modification of Yttrium Doping and Surface Coating. *ACS Appl. Mater. Interfaces* **2020**, *12*, 19483–19494.

(23) Wang, X. G. Yttrium Segregation and Surface Phases of Yttria-Stabilized Zirconia (111) Surface. *Surf. Sci.* **2008**, *602*, L5–L9.

(24) Bučevac, D.; Kosmač, T.; Kocjan, A. The Influence of Yttrium-Segregation-Dependent Phase Partitioning and Residual Stresses on the Aging and Fracture Behaviour of 3Y-TZP Ceramics. *Acta Biomater.* **2017**, *62*, 306–316.

(25) Croy, J. R.; O'Hanlon, D. C.; Asl, S. S.; Murphy, M.; Mane, A.; Lee, C. W.; Trask, S. E.; Yassar, R. S.; Balasubramanian, M. Insights on the Stabilization of Nickel-Rich Cathode Surfaces: Evidence of Inherent Instabilities in the Presence of Conformal Coatings. *Chem. Mater.* **2019**, *31*, 3891–3899.

(26) Lin, Q. Y.; Guan, W. H.; Zhou, J. B.; Meng, J.; Huang, W.; Chen, T.; Gao, Q.; Wei, X.; Zeng, Y. W.; Li, J. X.; Zhang, Z. Ni-Li Anti-Site Defect Induced Intragranular Cracking in Ni-Rich Layer-Structured Cathode. *Nano Energy* **2020**, *76*, 105021.

(27) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1*, 011002.

(28) Singh, A. K.; Zhou, L.; Shinde, A.; Suram, S. K.; Montoya, J. H.; Winston, D.; Gregoire, J. M.; Persson, K. A. Electrochemical Stability of Metastable Materials. *Chem. Mater.* **2017**, *29*, 10159–10167.

(29) González-Romeroa, R. L.; Meléndezbc, J. J. Yttrium Segregation and Oxygen Diffusion along High-Symmetry Grain Boundaries in YSZ. J. Alloys Compd. **2015**, 622, 708–713.

(30) Wang, Q. L.; Lian, G.; Dickey, E. C. Grain Boundary Segregation in Yttrium-Doped Polycrystalline TiO<sub>2</sub>. *Acta Mater.* **2004**, *52*, 809–820.

(31) Sun, H.; Cao, Z.; Wang, T.; Lin, R.; Li, Y.; Liu, X.; Zhang, L.; Lin, F.; Huang, Y.; Luo, W. Enabling High Rate Performance of Ni-Rich Layered Oxide Cathode by Uniform Titanium Doping. *Mater. Today Energy* **2019**, *13*, 145–151.

(32) Zhang, H. Z.; Qiao, Q. Q.; Li, G. R.; Gao, X. P. PO<sub>4</sub><sup>3-</sup> Polyanion-Doping for Stabilizing Li-Rich Layered Oxides as Cathode Materials for Advanced Lithium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 7454–7460. (33) Wu, F.; Liu, N.; Chen, L.; Su, Y. F.; Tan, G. Q.; Bao, L. Y.; Zhang, Q. Y.; Lu, Y.; Wang, J.; Chen, S.; Tan, J. Improving the Reversibility of the H2-H3 Phase Transitions for Layered Ni-Rich Oxide Cathode towards Retarded Structural Transition and Enhanced Cycle Stability. *Nano Energy* **2019**, *59*, 50–57.

(34) Sun, Y. Y.; Wang, Y. Y.; Li, G. R.; Liu, S.; Gao, X. P. Metalophilic Gel Polymer Electrolyte for in Situ Tailoring Cathode/ Electrolyte Interface of High-Nickel Oxide Cathodes in Quasi-Solid-State Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 14830– 14839.

(35) Song, S. H.; Cho, M.; Park, I.; Yoo, J. G.; Ko, K. T.; Hong, J.; Kim, J.; Jung, S. K.; Avdeev, M.; Ji, S.; Lee, S.; Bang, J.; Kim, H. High-Voltage-Driven Surface Structuring and Electrochemical Stabilization of Ni-Rich Layered Cathode Materials for Li Rechargeable Batteries. *Adv. Energy Mater.* **2020**, *10*, 2000521.

(36) Wang, T.; Ren, K. L.; Xiao, W.; Dong, W. H.; Qiao, H. L.; Duan, A. R.; Pan, H. Y.; Yang, Y.; Wang, H. L. Tuning the Li/Ni Disorder of the NMC811 Cathode by Thermally Driven Competition between Lattice Ordering and Structure Decomposition. *J. Phys. Chem. C* 2020, 124, 5600–5607.

(37) Goonetilleke, D.; Sharma, N.; Pang, W. K.; Peterson, V. K.; Petibon, R.; Li, J.; Dahn, J. R. Structural Evolution and High-Voltage Structural Stability of  $Li(Ni_xMn_yCo_z)O_2$  Electrodes. *Chem. Mater.* **2019**, *31*, 376–386.

(38) Fan, X. M.; Hu, G. R.; Zhang, B.; Ou, X.; Zhang, J. F.; Zhao, W. G.; Jia, H. P.; Zou, L. F.; Li, P.; Yang, Y. Crack-Free Single-Crystalline Ni-Rich Layered NCM Cathode Enable Superior Cycling Performance of Lithium-Ion Batteries. *Nano Energy* **2020**, *70*, 104450.

(39) Liang, L. W.; Zhang, W. H.; Zhao, F.; Denis, D. K.; Zaman, F.; Hou, L. R.; Yuan, C. Z. Surface/Interface Structure Degradation of Ni-Rich Layered Oxide Cathodes toward Lithium-Ion Batteries: Fundamental Mechanisms and Remedying Strategies. *Adv. Mater. Interfaces* **2020**, *7*, 1901749.

(40) Muralidharan, N.; Essehli, R.; Hermann, R. P.; Amin, R.; Jafta, C.; Zhang, J.; Liu, J.; Du, Z.; Meyer III, H. M.; Self, E.; Nanda, J.; Belharouak, I. Lithium Iron Aluminum Nickelate, LiNi<sub>x</sub>Fe<sub>y</sub>Al<sub>z</sub>O<sub>2</sub>— New Sustainable Cathodes for Next-Generation Cobalt-Free Li-Ion Batteries. *Adv. Mater.* **2020**, *32*, 2002960.

(41) Xiao, B.; Sun, X. Surface and Subsurface Reactions of Lithium Transition Metal Oxide Cathode Materials: An Overview of the Fundamental Origins and Remedying Approaches. *Adv. Energy Mater.* **2018**, *8*, 1802057.

(42) Liang, L. W.; Sun, X.; Wu, C.; Hou, L. R.; Sun, J. F.; Zhang, X. G.; Yuan, C. Z. Nasicon-Type Surface Functional Modification in Core-Shell  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_{2}$   $(\text{NaTi}_2(\text{PO}_4)_3)$  Cathode Enhances Its High-Voltage Cycling Stability and Rate Capacity toward Li-Ion Batteries. ACS Appl. Mater. Interfaces **2018**, 10, 5498–5510.

(43) Buchberger, I.; Seidlmayer, S.; Pokharel, A.; Piana, M.; Hattendorff, J.; Kudejova, P.; Gilles, R.; Gasteiger, H. A. Aging Analysis of Graphite/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> Cells Using XRD, PGAA, and AC Impedance. *J. Electrochem. Soc.* **2015**, *162*, A2737–A2746.

(44) Noh, H. J.; Youn, S.; Yoon, C. S.; Sun, Y. K. Comparison of the Structural and Electrochemical Properties of Layered Li[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]-O<sub>2</sub> (x = 1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) Cathode Material for Lithium-Ion Batteries. *J. Power Sources* **2013**, 233, 121–130.

(45) Hou, Y. K.; Pan, G. L.; Sun, Y. Y.; Gao, X. P. Li-Rich Layered Oxide Microspheres Prepared by the Biomineralization as High-Rate and Cycling-Stable Cathode for Li-Ion Batteries. *ACS Appl. Energy Mater.* **2018**, *1*, 5703–5711.

(46) Lee, M. J.; Noh, M.; Park, M. H.; Jo, M.; Kim, H.; Nam, H.; Cho, J. The Role of Nanoscale-Range Vanadium Treatment in  $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$  Cathode Materials for Li-Ion Batteries at Elevated Temperatures. *J. Mater. Chem. A* **2015**, *3*, 13453–13460.

(47) Jo, E.; Park, J. H.; Park, J.; Hwang, J.; Chung, K. Y.; Nam, K. W.; Kim, S. M.; Chang, W. Different Thermal Degradation Mechanisms: Role of Aluminum in Ni-Rich Layered Cathode Materials. *Nano Energy* **2020**, *78*, 105367.

(48) Li, W.; Li, M.; Hu, Y.; Lu, J.; Lushington, A.; Li, R.; Wu, T.; Sham, T. K.; Sun, X. L. Synchrotron-Based X-ray Absorption Fine Structures, X-ray Diffraction, and X-ray Microscopy Techniques Applied in the Study of Lithium Secondary Batteries. *Small Methods* **2018**, *2*, 1700341.

(49) Rinkel, B. L. D.; Hall, D. S.; Temprano, I.; Grey, C. P. Electrolyte Oxidation Pathways in Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2020**, *142*, 15058–15074.

(50) Sari, H. M. K.; Li, X. F. Controllable Cathode-Electrolyte Interface of  $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$  for Lithium Ion Batteries: A Review. *Adv. Energy Mater.* **2019**, *9*, 1901597.

(51) Chen, J.; Zhu, L.; Jia, D.; Jiang, X.; Wu, Y.; Hao, Q.; Xia, X.; Ouyang, Y.; Peng, L.; Tang, W.; Liu, T. LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> Cathodes Exhibiting Improved Capacity Retention and Thermal Stability due to a Lithium Iron Phosphate Coating. *Electrochim. Acta* **2019**, *312*, 179–187.

(52) Qiu, L.; Xiang, W.; Tian, W.; Xu, C. L.; Li, Y. C.; Wu, Z. G.; Chen, T. R.; Jia, K.; Wang, D.; He, F. R.; Guo, X. D. Polyanion and Cation Co-Doping Stabilized Ni-Rich Ni-Co-Al Material as Cathode with Enhanced Electrochemical Performance for Li-Ion Battery. *Nano Energy* **2019**, *63*, 103818.