

Electronic structure formed by Y_2O_3 -doping in lithium position assists improvement of charging-voltage for high-nickel cathodes

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 Check for updatesShijie Wang¹, Kang Liang¹, Hongshun Zhao¹, Min Wu¹, Junfeng He¹, Peng Wei¹, Zhengping Ding¹, Jianbin Li¹, Xiaobing Huang² & Yurong Ren¹✉

High-capacity power battery can be attained through the elevation of the cut-off voltage for $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$ high-nickel material. Nevertheless, unstable lattice oxygen would be released during the lithium deep extraction. To solve the above issues, the electronic structure is reconstructed by substituting Li^+ ions with Y^{3+} ions. The dopant within the Li layer could transfer electrons to the adjacent lattice oxygen. Subsequently, the accumulated electrons in the oxygen site are transferred to nickel of highly valence state under the action of the reduction coupling mechanism. The modified strategy suppresses the generation of oxygen defects by regulating the local electronic structure, but more importantly, it reduces the concentration of highly reactive Ni^{4+} species during the charging state, thus avoiding the evolution of an unexpected phase transition. Strengthening the coupling strength between the lithium layers and transition metal layers finally realizes the fast-charging performance improvement and the cycling stability enhancement under high voltage.

High safety and sustainability are needed for lithium-ion batteries (LIBs) to promote their practical application in the fields of power, energy storage, and consumption. Particularly, layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ ($x \geq 0.6$) with valuable attributes such as high capacity, high voltage, and environmental friendliness is a promising cathode for electric vehicles (EVs)¹. At present, in pursuit of higher specific capacity and lower costs, $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$ (NCM) has been produced on a large scale and appeared on the market. High nickel ternary material can achieve higher specific capacity by increasing the charging cut-off voltage to meet market demand for battery life. However, the poor structure and thermal stability of high-nickel materials, along with the increase in Ni concentration, lead to the degradation of electrochemical properties. Specifically, the high activity of Ni^{4+} could consume the electrolyte and form a thick and uneven cathode-electrolyte interface (CEI) film, increasing the diffusion resistance of the Li^+ ion. The inhomogeneous Li^+ ion distribution could accelerate the formation of intergranular cracks due to heterogeneous internal strain^{2,3}.

Significantly, the irreversible phase transition of H2-H3 also aggravates the intergranular microcracks under primary grain expansion and contraction⁴. Moreover, undesired losses of lattice oxygen are also caused by charging under the high cut-off voltage. The release of oxygen not only raises the risk of thermal runaway but also lowers the valence state of active nickel. This reduction in valence state may facilitate the migration of nickel ions to the octahedral site in the lithium layer, as both Ni^{2+} and Li^+ ions have similar ionic radii^{5,6}. TM segregation would initiate local phase transitions and block the diffusion channels of Li^+ ions⁷. Overall, transition metal ions and lattice oxygen exhibit complex coupling effects in thermal and high-charging-voltage fields due to their strong covalence. As is well known, lattice oxygen is the supporting framework in various layered oxide materials. Therefore, any modification measure cannot only focus on the irreversible behavior of transition metal ions.

In previous studies, the stability of transition metal ions and lattice oxygen in high-nickel materials has been improved by a cooperative

¹School of Materials Science and Engineering, Changzhou University, Changzhou, People's Republic of China. ²School of Chemistry and Materials Engineering, Hunan University of Arts and Science, Changde, People's Republic of China. ✉e-mail: ryrchem@cczu.edu.cn

strategy of lattice doping and surface coating^{8,9}. The common dopants include oxides, fluoride¹⁰, and hydrate¹¹. Taking Y_2O_3 as an example, to stabilize the layered structure, the substituted Y^{3+} ions at the transition metal sites provide stronger Y-O bond energy¹². Another benefit of doping Y^{3+} ions is the increase in initial nickel valence state, thus reducing the $\text{Li}^+/\text{Ni}^{2+}$ mixing¹³. In addition to being used as a dopant, Y_2O_3 can form an ultrathin coating that reduces interface impedance and prevents electrolyte erosion¹⁴. Similarly, other 4d transition metal elements show great potential. Nb substituted the transition metal position, and effectively inhibited oxygen release under the role of high dissociation energy in the Nb-O bond¹⁵. Considering the characteristics of high-valence metals, molybdenum atoms have become common dopants in the modified strategy of high-nickel materials¹⁶. It is worth noting that the Mo-substitution strategy could suppress the generation of microcracks by eliminating the local compositional inhomogeneity. Although these high-valence metals exploit their advantages to the full, their rarity limits the scale of industrial production. No matter what the dopant within the transition metal layer led to a decrease in electrochemically active components.

Recently, there has been a deep understanding of the improvement of surface structure by synthesizing functional coatings. For example, the $\text{LiF}\&\text{FeF}_3$ coating increases the formation energy of oxygen vacancy and slows down the release of lattice oxygen¹⁷. Moreover, the doping strategy of F⁻ or Cl⁻ at the O site have also been widely studied^{18,19}. Specifically, F⁻ ions can optimize the band structure of high nickel materials. Meanwhile, the presence of F⁻ ions promotes the formation of cationic ordered structures caused by the alternating occupation of lithium ions and transition metal ions¹⁰. However, introducing negative ions into the structure would decrease the valence state of nickel or increase the concentration of oxygen vacancy, which is not conducive to structural stability. At present, great efforts have been made to optimize the initial structure of the high nickel materials, but little attention has been paid to the effect of dopants on the structure change in deeply charged states.

To improve the stability of lattice oxygen and make full use of its reversible redox, we proposed an $\text{Y}^{3+}\text{-O}^{2-}\text{-Ni}^{4+}$ electron cloud coupling strategy to address this issue. It was worth mentioning that Y^{3+} ions can substitute for the Li^+ sites. The reconstructed electronic structure can promote the transfer of electrons to oxygen. Specifically, orbital hybridization can be formed between Y 3d and O 2p bands, which causes plenty of electrons to transfer from the dopant site to the adjacent oxygen site. And then, the accumulated electrons on the oxygen site were further transferred to the highly oxidizing Ni^{4+} at high voltage. The mechanism not only enhanced the redox reversibility of lattice oxygen, but also reduced the concentration of high-activity nickel. Ultimately, the improvement in the coordination environment of nickel effectively prevented the loss of oxygen and the irreversible behavior of transition metal ions. This work reveals the role of Y^{3+} in stabilizing surface structures and provides guidelines for the design of cathode materials with high specific energy.

Results

Characterizations of Y_2O_3 -modified strategy

Figure 1a shows the synthesis process of the Y_2O_3 -modified sample, and a schematic involving a double safeguard strategy resulting from $\text{Y}^{3+}\text{-O}^{2-}\text{-Ni}^{4+}$ electron cloud coupling. In Fig. 1b, all the diffraction peaks were indexed to the R-3m space group of the layered structure. In the magnified XRD pattern, it was noted that the diffraction peaks of (003) crystal plane were obviously shifted after introducing Y_2O_3 (Fig. 1c). Considering that Y^{3+} ions could enter the lattice, the XRD pattern by Rietveld refinement of NCM and NCM@Y-2 was studied (Fig. S1). The homologous analysis data are presented in Fig. S2. It is found that the c axis of NCM increases gradually with increasing Y_2O_3 concentration, which causes an increase in cell volume (Fig. S2a, b).

The increase in interlayer spacing has a certain effect on the improvement of lithium diffusion^{20,21}. Moreover, a ratio of c/a and $I_{(003)/(104)}$ reflected the ideality of the layered structure and the degree of cation mixing, and their values were usually higher than 4.93 and 1.2, respectively²². It is worth noting that all of the samples showed higher values of c/a and $I_{(003)/(104)}$ except for NCM (Fig. S2c, d). In Table S1, the degree of $\text{Li}^+/\text{Ni}^{2+}$ mixing in refined result for NCM@Y-2 sample was lower than additional Y-modified samples. The undesirable crystal structure caused by Y_2O_3 excess could have a negative impact on electrochemical performance, causing increase in $\text{Li}^+/\text{Ni}^{2+}$ mixing. According to the formula S1 and S2, the slab thickness of transition metal (S_{TM}) and the interslab space thickness of Li (I_{Li}) were calculated²³. As shown in Table S1, the value of I_{Li} changed obviously after the Y_2O_3 modification. The increased inter-slab space could shorten the thickness of the $[\text{MO}_6]$ octahedron ($M=\text{Mn/Co/Ni}$) and decrease the length of the M-O bond, thus improving the structural stability²⁴. X-ray photoelectron spectroscopy (XPS) analyses of Y 3d, O 1s, C 1s, and Ni 2p were carried out to detect the chemical valences of relevant elements of NCM and NCM@Y-2. In Fig. S3, the main peak at 284.8 eV was corresponded to the conductive carbon²⁵. Two other peaks at the binding energies of 288.4 and 289.8 eV were found, corresponding to the bonds of C=O and Li_2CO_3 ²⁶. The existence of lithium carbonate may seriously threaten cycling stability and safety properties. Contrasting the Li_2CO_3 concentrations of two samples, it was noted that the bare sample was slightly higher than the modified sample. As for O 1s spectra, only lattice oxygen (530.3 eV) was detected in NCM@Y-2, while more lithium carbonate (531.8 eV) was detected in the bare sample (Fig. S4)²⁷. In addition, Fig. S5 shows the oxidation state of Ni elements containing Ni^{3+} (binding energies of 855.8 and 873 eV) and Ni^{2+} (binding energies of 854.5 and 871.9 eV)²⁸. The increased concentration of Ni^{2+} in the bare sample might cause undesirable $\text{Li}^+/\text{Ni}^{2+}$ mixing²⁹. More importantly, the bonds of 157 and 159 eV were detected in NCM@Y-2, corresponding to Y 3d_{5/2} and Y 3d_{3/2}, respectively (Fig. S6)³⁰. By contrast, no oxidation state of Y element was detected in the bare sample, further revealing the presence of Y in NCM@Y-2.

To further monitor the interface structure, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) were carried out. As shown in Fig. S7, the morphology of the secondary particles did not change with the addition of Y_2O_3 . Figure 1d shows the (003) crystal plane and a coating thickness of ~2 nm in NCM@Y-2. The TOF-SIMS result demonstrated that the element Y was distributed in the surface of secondary particle cross section (Fig. 1e). Meanwhile, as shown in Fig. S8, pure LiYO_2 could be obtained by adding the raw materials of Y_2O_3 and LiOH into the system under the same sintering environment, further demonstrating that Y^{3+} ions could be enriched on the particle surface and form a LiYO_2 coating. To ensure the presence of Y^{3+} ions in the bulk, a line scan test was performed from the outside to the inside of the particles in Fig. 1f. The strength of Y and O atoms was first increased before the strength of transition metal atoms was increased (Fig. 1g). The Y concentration gradually decreased until the depth of 400 nm. Due to the particle size of secondary particle were about 6 ~ 8 μm , the concentration of transition metals in the front position of line scan kept increasing. The above results demonstrated the existence of Y^{3+} both in the bulk and on the surface of secondary particles. To confirm that Y^{3+} occupies the lithium position, aberration corrected transmission electron microscopy was used. The ordered bright spot represents a transition metal atom in the high-angle annular dark-field (HAADF) mode (Fig. 1h)³¹. It is worth noting that a strong bright spot can be observed in the lithium layer of the Y-modified sample. Furthermore, the increase in layer spacing indicated that the Y atom occupies the 3a site for the lithium atom (Fig. 1i). The above result clearly verifies the reliability of the XRD refinement results.

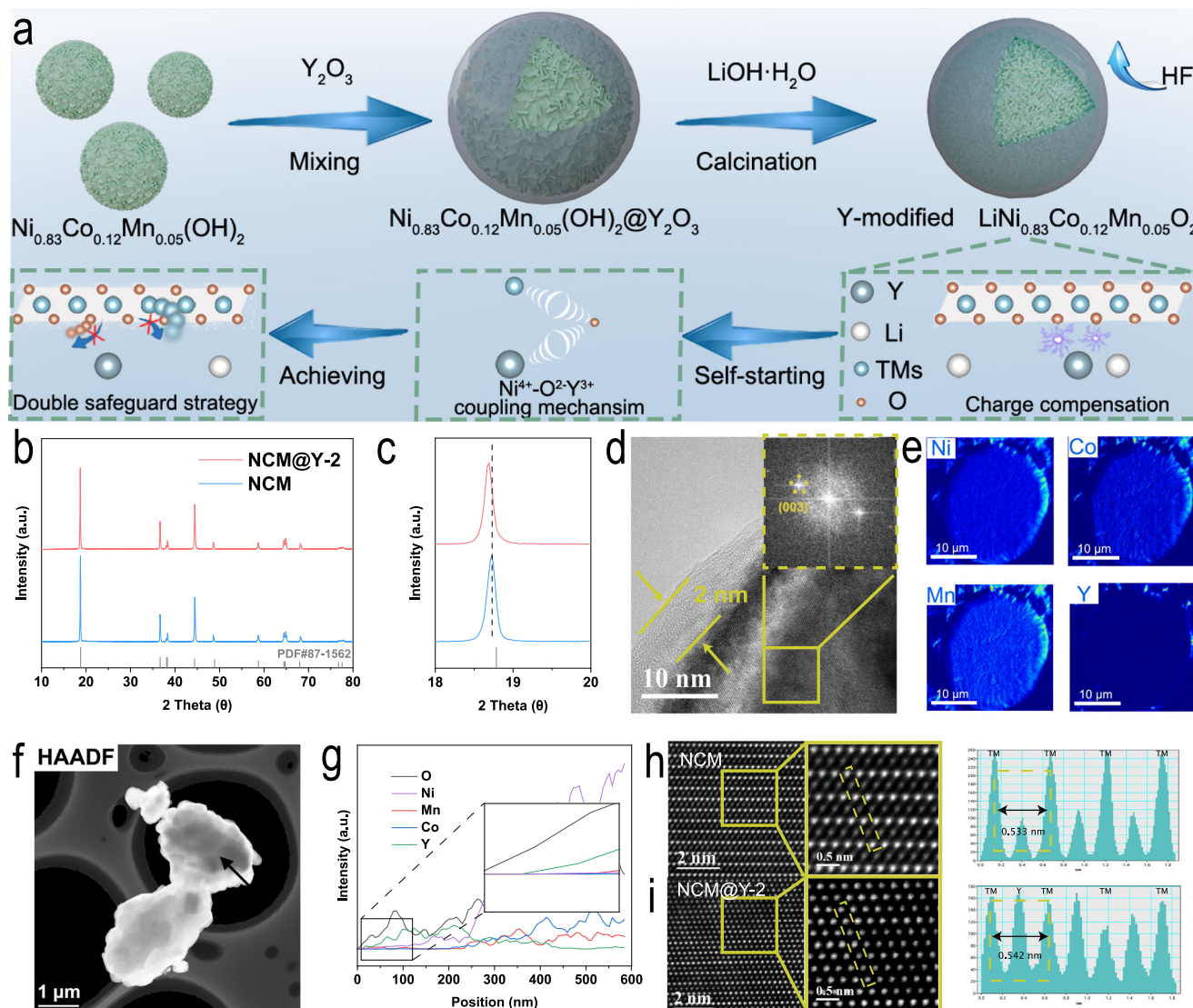


Fig. 1 | Physical characterizations of Y₂O₃-modified strategy. **a** Synthesis schematic and modification mechanism. **b, c** XRD pattern and selected range image of NCM and NCM@Y-2. **d** The high-resolution TEM of NCM@Y-2. **e** TOF-SIMS image of

cross section for NCM@Y-2. **f, g** TEM line scanning result for NCM@Y-2. STEM-HAADF image of **(h)** NCM and **(i)** NCM@Y-2 and their corresponding intensity plots.

Interlayer coupling mechanism

To reveal the effect of interlayer coupling mechanism for transition metal layer and Li layer, X-ray absorption near-edge structure (XANES) in NCM and NCM@Y-2 during the first cycle were collected. As shown in Fig. 2a, b, the Ni-edge position of both samples shifted to higher energy under a full-charging state, which means that the valence state of Ni was elevated³². Then, the Ni-edge position returned to low energy with the reduction of Ni during the discharge state due to the local electron exchange effect, indicating that Ni^{2+/3+} was involved in a redox reaction. Significantly, the energy difference of 1.41 eV for the NCM@Y-2 sample mean that the valence state of nickel was relatively small under the charging state. It was mainly because the plenty of electrons in high-charge-density YO₆ octahedron further transferred to the high activity of Ni⁴⁺. Therefore, the coupling of Y³⁺-O²⁻-Ni⁴⁺ electron cloud improved the coordination environment of nickel. Additionally, the Ni edge positions of the discharge state and the pristine state were well-overlapped in NCM@Y-2, demonstrating the surface oxygen was stable³³. Soft X-ray adsorption spectroscopy (sXAS) of O K-edge was employed to study the electronic structure changes of oxygen. Figure 2c, d show O K-edge spectra detected by TEY (total electron yield) mode. After being charged to 4.5 V, an abrupt

peak appeared at the photon energy of ~530.8 eV, which represents the redox reaction of O²⁻ ions being activated³⁴. In sharp contrast, the relating peak in Y-modified sample became stronger than that of the NCM, indicating more anions were oxidized to participate in charge transfer under overcharge conditions (Fig. 2d). Even if discharged to 2.75 V, the Y-modified sample still retained certain a reversibility of anions.

The Fourier transformed extended X-ray absorption fine structure (EXAFS) has better sensitivity to the local coordination information of Ni-edge. From Fig. 2 e, f, the first peak observed in the range of 1-2 Å was related to the oxygen around the transition metal (Ni-O), while the second peak in the range of 2-3 Å was related to the bonds between the transition metal (Ni-TM)^{17,35}. The Ni-O bond length of the two samples in the final state of charging was obviously shortened, and the Ni-O bond length was recovered in the subsequent discharging reaction. However, comparing the amplitude and strength of Ni-O and Ni-TM bonds in the initial state and discharging state, the coincidence degree of the bare sample was obviously lower than that of the Y-modified sample. In general, the change was attributed to the movement of Ni³⁺O₆ octahedra due to the existence of Jahn-Teller active Ni³⁺ ions^{36,37}. The results show that the Y-modification strategy can effectively

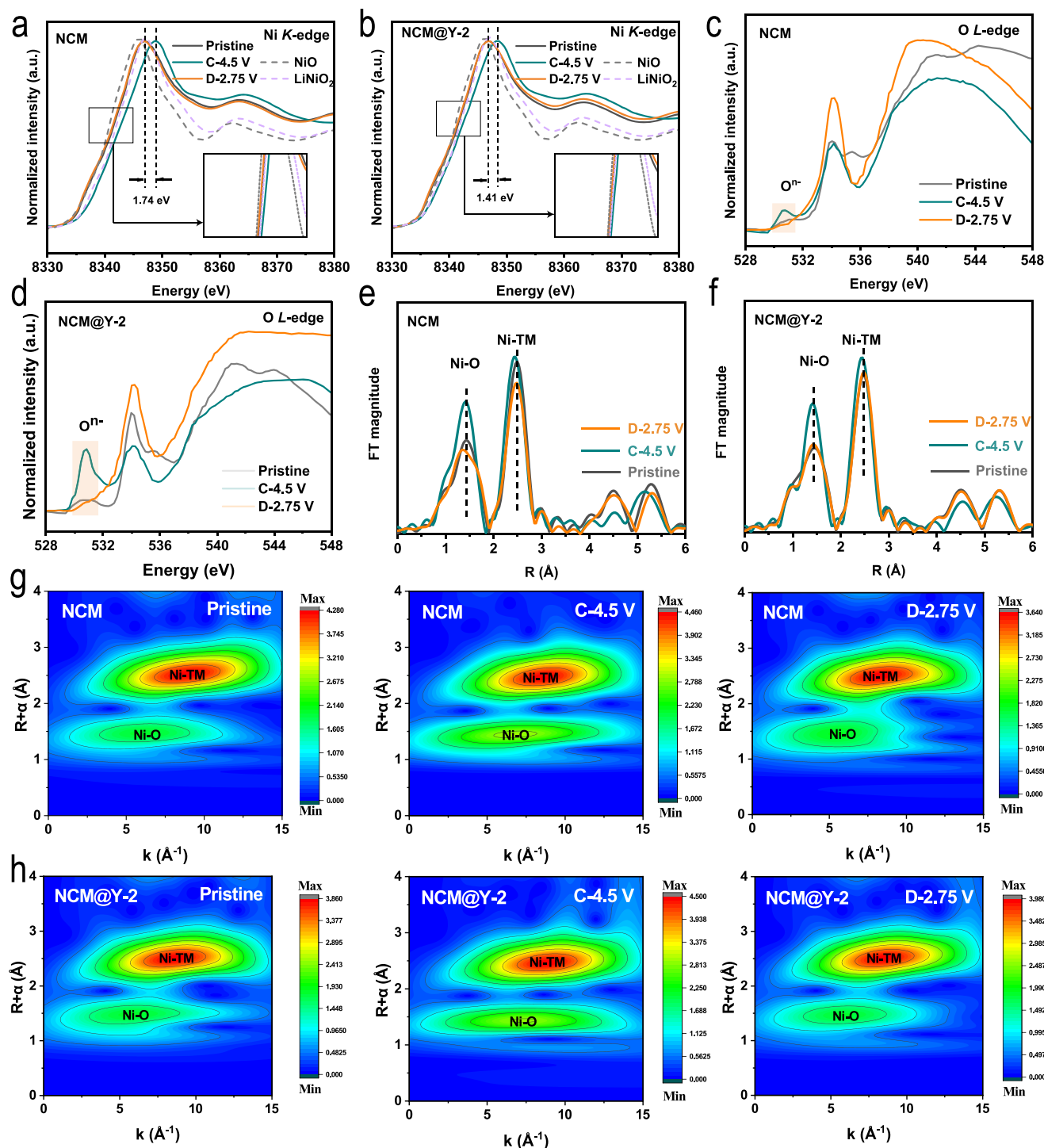


Fig. 2 | Interlayer coupling mechanism. Ex situ XANES spectra of Ni K-edge for (a) NCM and (b) NCM@Y-2 during the first cycle. Ex situ sXAS spectra of O K-edge for (c) NCM and (d) NCM@Y-2. Ex situ Ni K-edge EXAFS of (e) NCM and (f) NCM@Y-2

during the first cycle. Ni K-edge EXAFS WT images of (g) NCM and (h) NCM@Y-2 during the first cycle.

restrain transition metal migration caused by Jahn-Teller distortion and improve the cation order in transition metal layer. Similarly, for the wavelet transform (WT) of the k^3 -weighted EXAFS signal in NCM@Y-2, there was obviously no change in the intensity and position of Ni-O in pristine and discharge states when compared with the coordination environment in which the Ni of NCM was markedly different (Fig. 2g, h)^{17,38}. The results of EXAFS further confirmed that the coupling of Y^{3+} - O^{2-} - Ni^{4+} electron cloud enhanced the stability and reusability of Ni during the charge-discharge process.

Electrochemical characterization

To verify the enhanced lithium-ion diffusion kinetics after Y_2O_3 modification, the cycling tests under high cut-off voltage were performed on NCM and NCM@Y-2. Figures 3a and S9, shows that NCM@Y-2 delivered a high specific discharge capacity of 228 $mAh \cdot g^{-1}$ at 0.1C and a coulombic efficiency of 89.5%, while that of NCM had only a relatively specific discharge capacity of 221 $mAh \cdot g^{-1}$ and a coulombic efficiency of 91.3%. The improvement in specific capacity was attributed to the enhanced stability of the surface structure and the decrease in residual

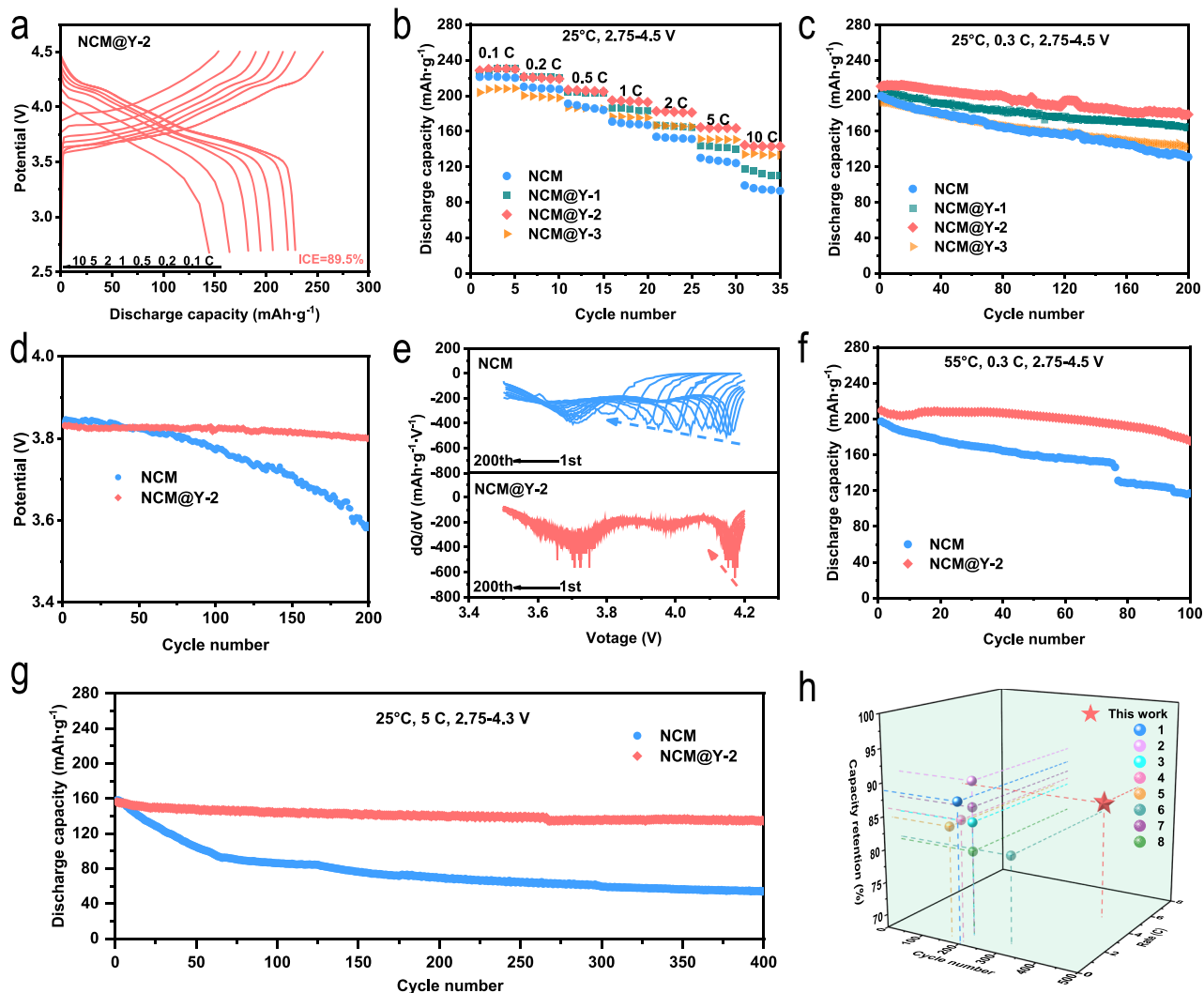


Fig. 3 | Electrochemical performance. **a** Charge-discharge profile of NCM@Y-2 under different rate. **b** Rate performance of NCM, NCM@Y-1, NCM@Y-2, NCM@Y-3. **c** Cycling performance of NCM, NCM@Y-1, NCM@Y-2, NCM@Y-3 under high-voltage of 4.5 V. **d** Voltage profile of NCM and NCM@Y-2. **e** calculated dQ/dV curves

during 200 cycles of NCM and NCM@Y-2. **f** Cycling stability test under the high-temperature. **g** Fast-charging performance of NCM and NCM@Y-2. **h** A literature survey of the cycle number, rate, and capacity retention for various half battery.

lithium³⁹. The reduction in coulombic efficiency of NCM@Y-2 could be related to lithium loss due to SEI film formation at high voltages. The three pairs of redox peaks containing phase transitions from hexagonal to monoclinic (H1-M), monoclinic to hexagonal (M-H2), and hexagonal to hexagonal (H2-H3) were observed in the cyclic voltammetry (CV) curves (Fig. S10)⁴⁰. The reversibility of NCM@Y-2 was higher than that of NCM after the initial charge/discharge, indicating that the structural stability of high-nickel material was improved after introducing Y₂O₃ in the system. In addition, a relatively small voltage difference of 0.156 eV in NCM@Y-2 proved reduced polarization with Y₂O₃ modification. Figure 3b shows the different discharge capabilities at various rates of 0.1, 0.2, 0.5, 1, 2, 5, and 10 C under the range of voltage from 2.75 V to 4.5 V of four samples. As for the NCM sample, the discharge specific capacity continued to decrease as the cycle number increased, especially at 10C, exhibiting only a lower discharge specific capacity of 99 mAh·g⁻¹. In comparison, the capacity decay in NCM@Y-2 was relatively slow and delivered a higher discharge specific capacity of 145 mAh·g⁻¹ at 10C. The improvement in rate performance was attributed to the avoidance of undesirable phase transitions in the bulk by Y³⁺-O²⁻-Ni⁴⁺ electron cloud coupling, and the construction of a fast migration channel for Li⁺ ions on the interface due to the LiYO₂ coating's stronger chemical bond with the particle surface.

Except for the remarkably improved rate performance, the cycling stability of NCM@Y-2 was also significantly enhanced. As shown in Fig. 3c, comparing the NCM@Y-2 to the NCM which has a reversible capacity of 200 mAh·g⁻¹ and a capacity retention of 65% after 200 cycles, the NCM@Y-2 showed a greater discharge capacity of 211 mAh·g⁻¹ and enhanced cycling stability of 86% capacity retention. Irreversible structural degradation usually results in voltage decay, especially at high voltages. As shown in Fig. 3d, NCM@Y-2 maintained a low voltage decay of 0.03 V compared to NCM, which revealed that Y³⁺ could stabilize the lattice oxygen and restrain the unfavorable transformation of the layered to spinel or rock salt phase in the surface structure. Besides, the dQ/dV curves were produced using the charge/discharge profiles from 1st to 200th (Fig. 3e). It was clear that the irreversibility of the redox peak was reduced in the NCM@Y-2, further demonstrating that Y₂O₃-modified material could improve structural stability. Especially at test environment of 55 °C, NCM@Y-2 could produce a highly reversible capacity of 210 mAh·g⁻¹ and enhance cycling stability with of 84% capacity retention after 100 cycles. Such well high-temperature performance demonstrated that the LiYO₂ coating not only resisted corrosion from the electrolyte but also provided thermal insulation. The advantage of the Y₂O₃-modification strategy was also shown in the cycling stability at 5 C of two samples.

The discharge specific capacity of 156 mAh g^{-1} in the NCM@Y-2 remained 135 mAh g^{-1} after 400 cycles (Fig. 3g). More importantly, the superiority of the Y_2O_3 -modified strategy in long-cycle performance was demonstrated. (Fig. 3h and Table S2). Moreover, the Y-modified sample as cathode was also assembled in the coin full-cell. It was worth that the results show that the Y-modified strategy had practical application value (Fig. S11).

The GITT test and the CV test with different scan rates were conducted to deeply investigate the effects of LiYO_2 coating and Y^{3+} doping on lithium-ion diffusion kinetics. Comparing the data on D_{Li} calculated by Formula S3, the NCM@Y-2 maintained a higher value of D_{Li} than the bare sample (Fig. S12)⁴¹. Similarly, the higher value of D_{Li} from CV testing in the Y_2O_3 modified sample was consistent with GITT results, further accounting for the enhanced lithium-ion diffusion kinetics by the Y_2O_3 modification strategy (Fig. S13 and Table S3). Moreover, the role of Y_2O_3 modification in NCM@Y-2 was also evaluated by electrochemical impedance spectroscopy (EIS). Two semi-circles of high /middle frequency and a straight line of low frequency were observed in the impedance patterns, corresponding to interfacial film resistance (R_f), charge-transfer resistance (R_{ct}), and Warburg impedance (W_o) (Fig. S14a)⁴². All impedance values were fitted by an equivalent circuit, and the results are shown in Fig. S14b. Significantly, the value of R_{ct} in NCM@Y-2 on the 1st and 100th cycles were lower than that of NCM, demonstrating that LiYO_2 coating effectively reduces the interface impedance. Moreover, the improved Li^+ ion diffusion coefficient in NCM@Y-2 was calculated by Formulas S5 and S6, consistent with the results of GITT and CV. (Fig. S14c, d).

Gas evolution process and phase transition

Considering the effect of Y^{3+} on the structure, differential electrochemical mass spectrometry (DEMS) was further used to investigate the gaseous reactants of NCM and NCM@Y-2. The oxidation of oxygen, while slightly increasing the energy density of high-nickel material, can exacerbate the irreversible loss of layered structures, such as the migration into the Li layer or dissolution at the interface of transition-metal ions. It was well known that electrolytes (e.g., EC species) undergo intense electrochemical oxidation at high potentials above 4.6 V, which drives the release of CO_2 ^{43,44}. As shown in Fig. 4a, a similar gas evolution trend of CO_2 in both samples at a voltage of 4.7 V was observed. For O_2 release, there was no oxygen evolved below the normal cutoff voltage (4.3 V). At the following voltage value of around 4.7 V, the emergence of oxygen was related to the $2p$ state of O as it approached the Fermi level under high voltage^{45,46}. The released oxygen from the lattice would promote the chemical oxidation of the electrolyte and generate more CO_2 ⁴⁷. It was precisely because of the gas evolution of oxygen in the bare sample that there was a difference in CO_2 concentration between the two samples. Thus, the smaller CO_2 peak value signifies that the Y_2O_3 -modified strategy can effectively anchor lattice oxygen to avoid structural degradation. Meanwhile, the result was also confirmed by the electron paramagnetic resonance (EPR) test (Fig. S15). Figure 4c, d shows the O K -edge and Ni L -edge spectra by testing soft X-ray absorption spectroscopy (sXAS). The pre-edge region (light-green rectangular), and the energies of $\sim 535 \text{ eV}$ (light-yellow rectangular) were detected in cycling-NCM and cycling-NCM@Y-2, corresponding to TM $3d$ -O $2p$ hybridized states and lithium carbonate, respectively^{48,49}. It was clear that a signal of relatively less lithium carbonate and more oxygen signal was observed in the NCM@Y-2. In Ni L -edge spectra, the surface of the cycling NCM sample contained more Ni^{2+} , which was not conducive to the stability of the layered structure⁵⁰. The XRD tests were performed for cycled samples (Fig. S16). As shown in Table S4, the lower degree of $\text{Li}^+/\text{Ni}^{2+}$ mixing in the cycled NCM@Y-2 proved that ordered structure was maintained effectively. In addition, the in-depth XPS test was used to detect the deeper chemical composition. The O 1s spectra exhibited two distinct peaks, which may be attributed to the presence of lattice oxygen and

the band associated with the dissolution of the electrolyte (C=O bond) (Fig. 4e, f)⁵¹. The fitting results show that the lattice oxygen concentration on the surface of the bare sample was relatively less than that of the Y_2O_3 -modified sample, and the growth rate was also kept at a low level. In the Ni $2p$ spectra, it was noted that the concentration difference on the surface of NCM between Ni^{2+} and Ni^{3+} was not obvious. The higher concentration of Ni^{3+} gradually appeared after etching into the bulk (Fig. 4g, h). As for NCM@Y-2, although the Ni^{2+} concentration on the surface was higher than that of NCM, the ratio of $\text{Ni}^{2+}/\text{Ni}^{3+}$ decreased more rapidly as the etching depth increased, revealing that the irreversible phase transition in the surface-to-bulk of second particles was inhibited under the charge supplement mechanism of Y^{3+} ions, thus improving the structure stability of high-nickel material.

Structure and interface stability

To assess the effect of Y_2O_3 -modification on phase transition, in-situ XRD analysis was performed during the first charge-discharge process. Figure 5a shows that the (003) peak first migrated to a small angle as the charge reaction progressed (voltage below 4.2 V). This was mainly because Li^+ extracted from the lithium layer caused increased repulsion in the oxygen layer^{11,52}. As the voltage exceeded 4.2 V, the shift of the (003) peak toward a higher 2θ was observed due to the transfer of electrons from the lattice oxygen to the highly oxidized nickel, and the resulting sharp contraction of the transition metal layer spacing occurred³⁸. In Figs. S17 and 5b, a higher peak shift (1.31°), maximum contraction in the c -axis lattice (5.4%), and a larger lattice volume change (8%) were observed in the NCM, which led to particle breakage and a rapid decrease in capacity under severe stress accumulation⁵³. As for NCM@Y-2, in addition to reducing the charge depletion of oxygen anions, the modified strategy also alleviated the large electrostatic repulsion interaction due to the decrease in the concentration of highly reactive Ni^{4+} species. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was utilized in study the distribution of surface species of NCM and NCM@Y-2 after 200 cycles (Fig. 5c, d). The organic fragments from CH_2^+ represented the decomposition of carbonate solvents. LiO^+ and LiF^- fragments derives from Li_2O and LiF precipitates from decomposition of lithium salts⁵⁴. A NiF_3^- fragment was identified in relation to the product from the reaction of transition metal with HF on the surface⁵⁵. In general, the half-strength of fragment normalization could evaluate the thickness of CEI film⁵⁶. By contrast, the thickness was obviously reduced in the Y-modified sample. To prove the superiority of the Y_2O_3 -modified strategy, TEM tests were performed on the two electrodes after long-term cycle. The thickness of CEI film was distinctly different between the cycled electrodes at the different cycle numbers (Fig. S18). Moreover, low by-product concentration in Y-modified sample from 3D reconstruction and chemical images demonstrated that the cathode-interface degradation reactions induced by interface corrosion were effectively alleviated. The significant differences in the concentration of all species further support that view (Figs. S19, S20).

In the SEM images after long-term cycling, it was clear that the second particle in the NCM sample contained an irreversible crack. In contrast, the second particles in NCM@Y-2 were intact, intuitively manifesting the positive effect on Y_2O_3 modification (Fig. S21). A transmission electron microscopy test after cycling the battery was further conducted to verify the effect of NCM@Y-2. In Fig. 5f, the thick rock salt phase (Fm-3m) in NCM could be visualized in the internal structure, while the structural damage of NCM@Y-2 after cycling was relatively weak (Fig. 5g). Moreover, the transition-metal concentration of the cycling samples is also shown in Fig. S22, where the difference in content was significant. It was concluded that the interlayer coupling between lithium layer and transition metal layer induced by Y_2O_3 modification improved the structural stability.

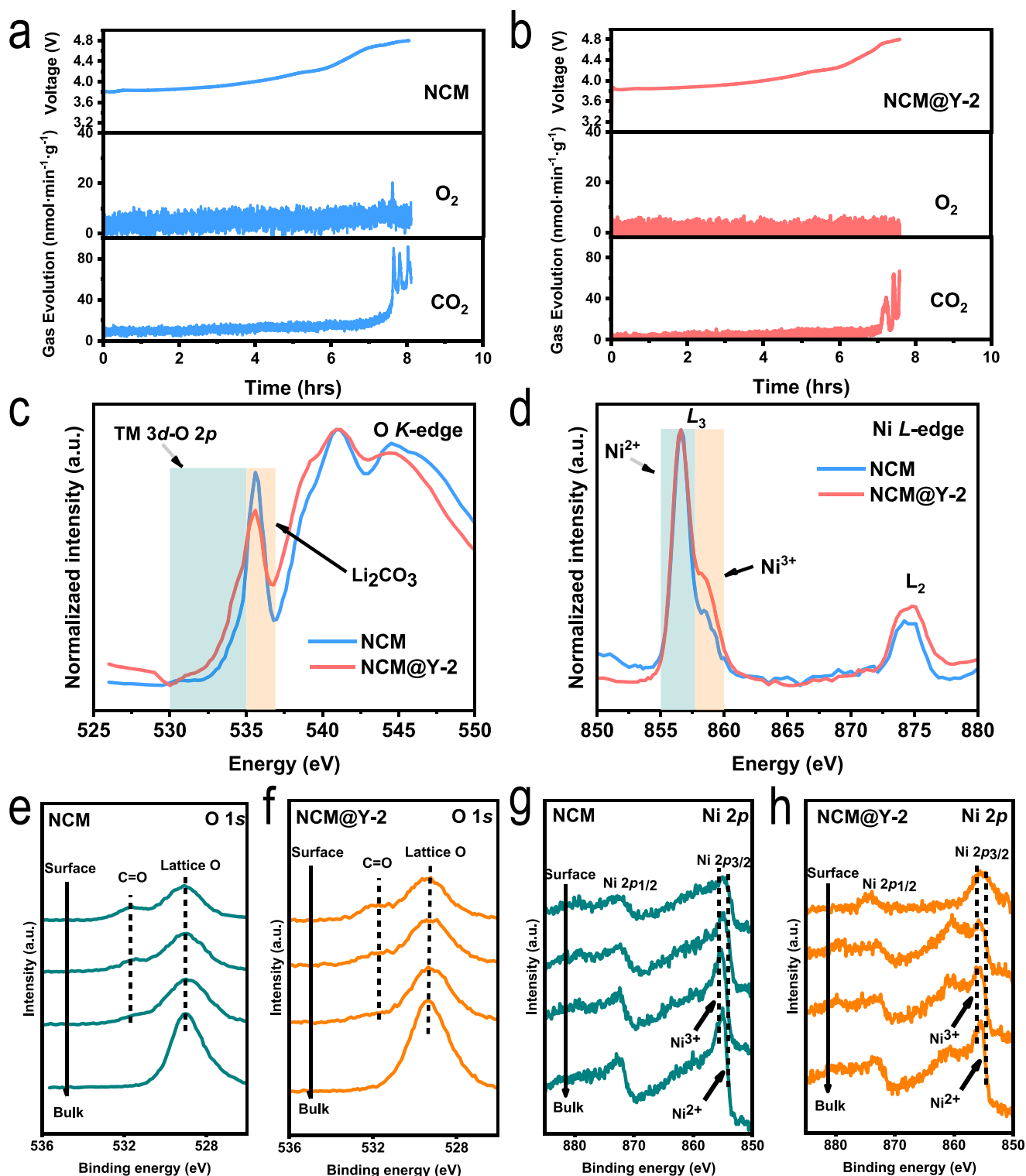


Fig. 4 | Gas evolution and phase transition investigation. O₂ and CO₂ gas evolution during the first three cycles from (a) NCM and (b) NCM@Y-2. c O K-edge and (d) Ni L-edge of XAS spectra after cycling of NCM and NCM@Y-2. High-resolution O

1s spectra from surface to bulk of (e) NCM and (f) NCM@Y-2. High-resolution Ni 2p spectra of (g) NCM and (h) NCM@Y-2.

Meanwhile, the LiYO₂ coating effectively protected the surface of secondary particles and avoided interface corrosion by electrolyte infiltrated into the primary particle gap. In terms of thermal failure, the results of differential scanning calorimetry (DSC) on NCM@Y-2 were consistent with high-temperature performance. Specifically, after introducing Y₂O₃, an onset temperature was increased from 234 to 238 °C, and heat production was decreased by 74% (Fig. S23).

Theoretical calculations

To verify the above Y₂O₃-modification mechanism, density functional theory (DFT) was carried out. All calculations were performed on the (104) stable crystal plane in NCM. Based on the optimized structure of the bare sample and LiYO₂ coated NCM (Fig. 6a), the projected density of states (PDOS) was calculated to investigate the effect of LiYO₂ coating. From Fig. S24a, more electronic states in LiYO₂ coated NCM

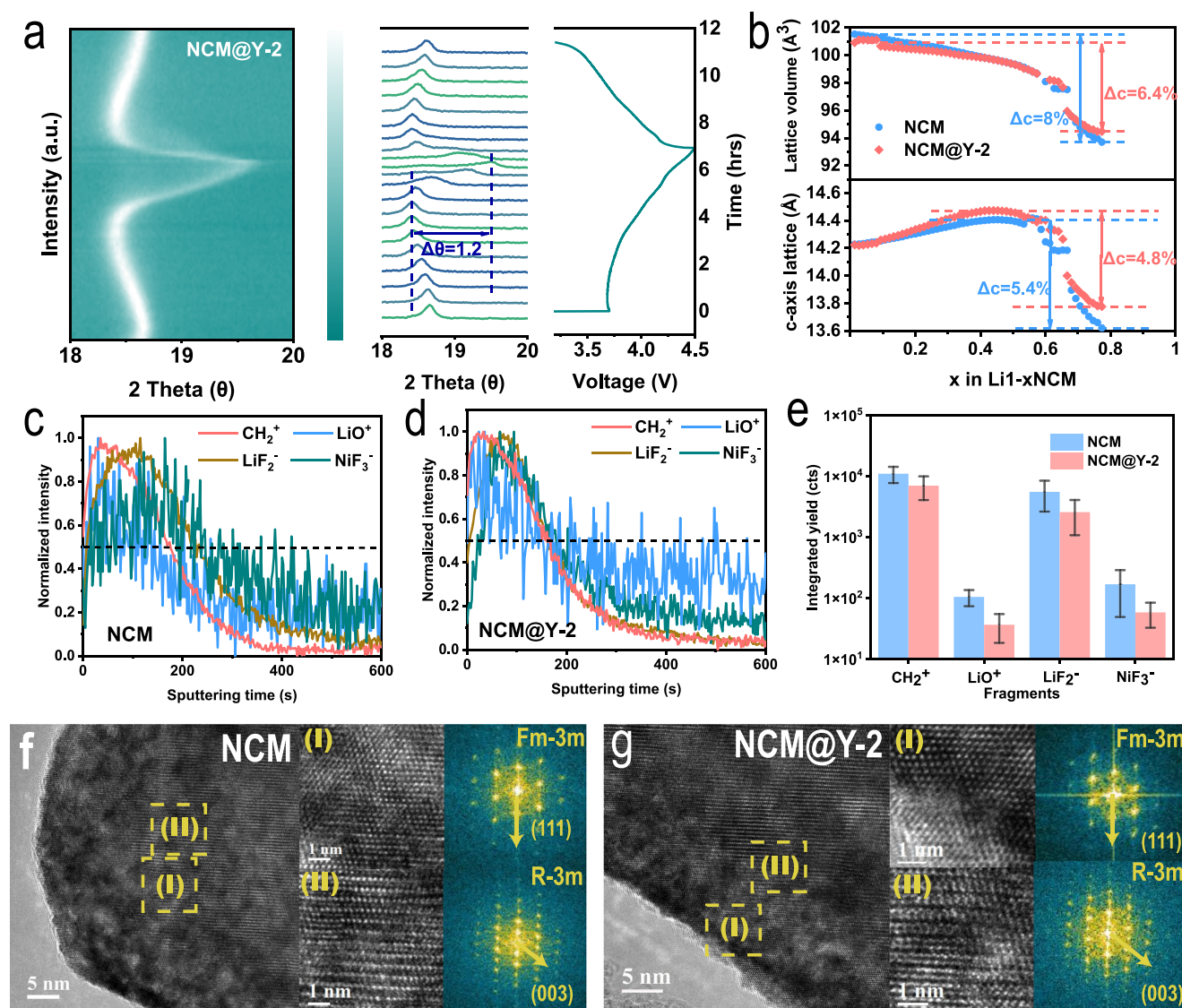


Fig. 5 | Surface structural degradation analysis. Operando XRD patterns of (a) NCM@Y-2. b Lattice parameters (c axis and volume) as functions of voltage during the initial charge process for the NCM and NCM@Y-2 electrodes at charge cut-off

voltages of 4.5 V. The depth profiles curve of (c) NCM and (d) NCM@Y-2. e Integrated yield of different species in both samples. High-resolution TEM image and selected area image for cycled (f) NCM and (g) NCM@Y-2 electrode.

were clearly observed, which indicated that the conductive path of the NCM widens after coating LiYO₂. In addition, the result was further confirmed by the enlarged picture of the position of the Fermi levels (Fig. S24b). Thus, LiYO₂ coated NCM would provide better rate performance under the influence of enhanced conductivity. In previous research, the loss of lattice oxygen was strongly correlated with transition metal ion transfer and led to structural changes⁵⁷. Subsequently, the possible substitution sites doped in Y³⁺ were considered by calculating the formation energy and are shown in Fig. S25. The calculated results show that the formation energies in positions Ni, Co, Mn, and Li were -3.3734, -5.9129, -3.7818, and -7.5786, respectively (Fig. 6a). Notably, the lowest formation energy of Y³⁺ in Li position demonstrated that Y³⁺ was most likely to replace Li position.

In addition to being the pillar ion to support the lithium layer after lithium was extracted, Y³⁺ also had multi-electron properties (vs. Li⁺). The local electronic structure was studied by using valence charge density difference (VCDD) and Bader charge analysis. Figure 6b, c show the electron cloud changes near the Li position, and the Y position that replaced Li, respectively. The adjacent oxygen atoms around the Y position were observed to accept more charge. In addition, the charge

transfer in NCM and Y³⁺-doped NCM is illustrated in Fig. 6d. Obviously, the increase in the charge number of labeled oxygen further proved that the dopant anchors the lattice oxygen by transferring more charge to the adjacent oxygen. As is well known, calculated DOS was a vital tool to distinguish the different orbital hybridization and d-orbital splitting in the crystal field. The integral overlap of the Y 3d and O 2p bands indicated that there is certain interaction (Fig. 6f). From Fig. 6e, g, the Ni 3d band approached the O 2p band after half the lithium ions were removed. Meanwhile, the Ni 3d band near the center of the O 2p band increased with the decrease in lithium concentration, indicating enhanced covalence between Ni and O. In general, there was a redistribution of covalency-induced charge in Ni and O because of the Ni 3d-O 2p hybrid state, which resulted in the instability of lattice oxygen⁵⁸. However, for the Y doped sample, the overlapping integral area in the Ni 3d and O 2p bands was relatively small during the delithiation process. In addition, Ni 3d orbital splitting was utilized to investigate specific valence states of Ni, and the results are shown in Fig. 6i-l. The Ni⁴⁺ oxidation state was observed near the Fermi level in the two samples under the charging state (Fig. 6k, l). It was found that the Y doped NCM was dominated by a large amount of Ni³⁺ and a small

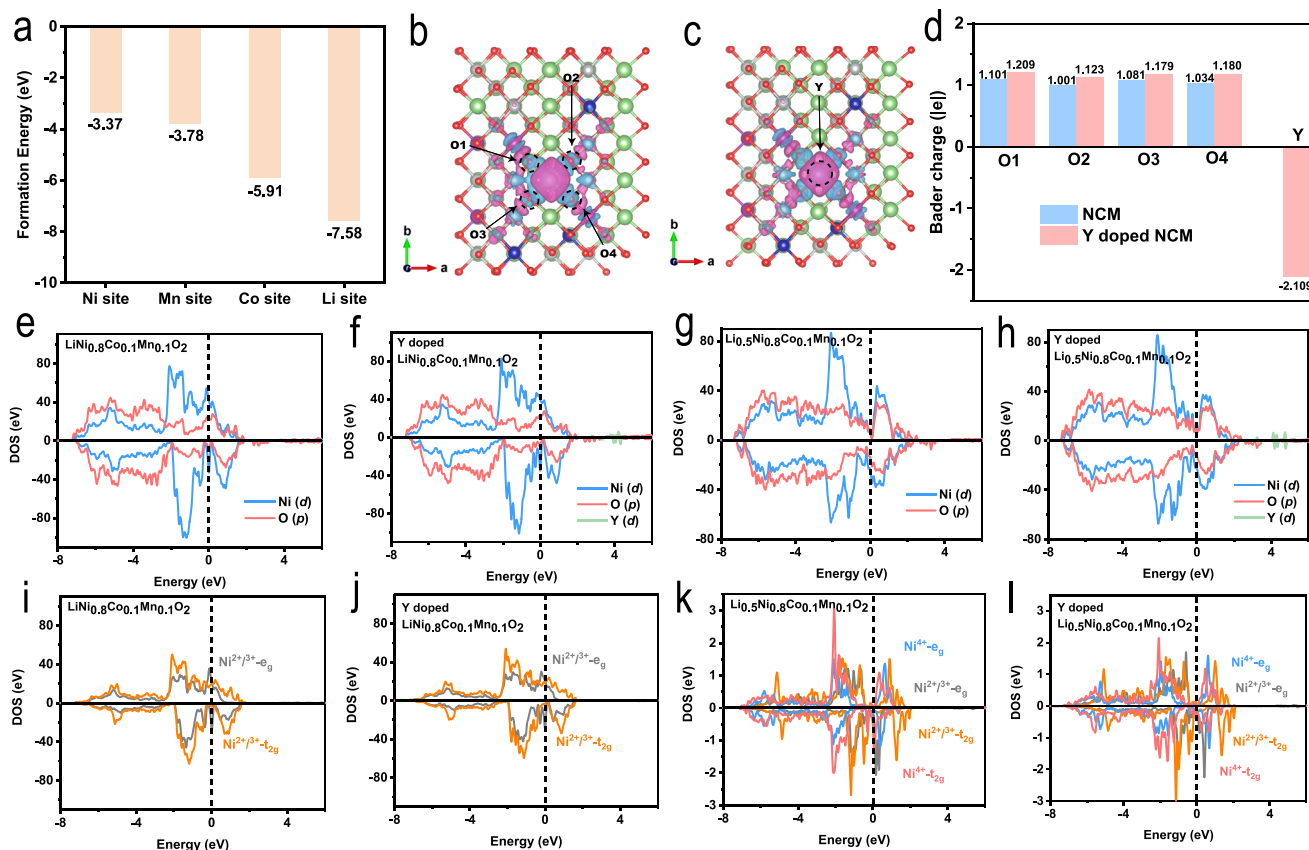


Fig. 6 | Density functional theory calculations. **a** Calculated formation energies for Y cation doped at the different substitution sites in NCM. VCDD of **(b)** NCM and **(c)** Y doped NCM. **d** Charge transfer number for different atoms of NCM and

NCM@Y-2. DOS of Ni and O in **e** NCM, **f** Y doped NCM, **g** NCM with delithiation, and **h** Y doped NCM with delithiation. Projected DOSs Ni at different state of **i** NCM, **j** Y doped NCM, **k** NCM with delithiation, and **l** Y doped NCM with delithiation.

contribution of Ni^{4+} , while the NCM was the opposite. Indeed, Y^{3+} was not only used to stabilize the lattice oxygen. The electrons accumulated at the oxygen sites were transferred to the nickel in a high-valence state under restore coupling, which led to a decrease in nickel activity in the charging process.

Discussion

In summary, the Y_2O_3 -modification strategy can optimize the surface structure and enhance interface stability of high-nickel materials by inhibiting oxygen loss and transition metal ion transfer at high voltage. Based on the characterization results of XRD, STEM-HAADF, and DFT, it is demonstrated that Y^{3+} substitutes Li^+ and becomes an electron donor in the lithium layer. The characterization of XAS and DFT further proves that the mechanism of $\text{Y}^{3+}\text{-O}^{2-}\text{-Ni}^{4+}$ electron cloud coupling improves structural stability by stabilizing the lattice oxygen and reducing highly active nickel. Therefore, compared with the bare sample, the rate performance, cycle stability, and particularly high temperature performance of the modified sample show significant enhancement at high cut-off voltage.

Methods

Material and method

Firstly, $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$ was provided by CNGR Advanced Material Co., Ltd. Then the anhydrous ethanol dispersion of Y_2O_3 was prepared. 4 g of $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$ was added to the above solution and stirred until the ethanol evaporated. Finally, to obtain Y^{3+} modified $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$, dried $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2\text{-Y}_2\text{O}_3$ were mixed with excess LiOH (99.99%, Aladdin) and calcined at 480 and 780 °C for 4 and 15 h, respectively. Herein, the as-prepared samples were named NCM@Y-1, NCM@Y-2, and NCM@Y-3,

corresponding to the addition of Y_2O_3 at 1, 1.5, and 2% wt in the system. In comparison, no precursor mixed with Y_2O_3 anhydrous ethanol was named NCM.

Physical characterization

The elemental oxidation state was examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi+) with an Al $K\alpha$ rays ($h\nu = 1486.6$ eV) as the excitation source. The crystal structure and lattice parameter for all samples were analyzed by powder X-ray diffraction (XRD, D8-ADVANCE) employing Cu $K\alpha$ radiation at a scanning rate of 12°-min^{-1} . In-situ XRD patterns were acquired to survey the phase change of samples during the first cycle. The surface morphology and coating thickness of all samples were visualized by scanning electron microscopy (SEM, ZEISS Sigma 300) and transmission electron microscopy (TEM, FEI Talos F200X G2). The contents of transition metal elements were captured by ICP-OES (Thermo Fisher iCAP PRO). The thermal stability was analyzed with the differential scanning calorimeter (DSC, PerkinElmer STA 8000) test, equipped with a temperature range of 30 °C to 300 °C under the Ar atmosphere. The Ni K -edge was performed at the beamline of SSRF (Shanghai). The O K -edge and Ni L -edge were characterized by the beamlines MCD-A and MCD-B (Soochow Beamline for Energy Materials) at national synchrotron radiation laboratory (NSRL, Hefei). The gas evolution was employed by differential electrochemical mass spectrometry (DEMS). The loss of lattice oxygen was investigated by an electron paramagnetic resonance (EPR) test (Bruker EMX PLUS).

Electrochemical measurement

The half-cells were made by slurry containing 80% wt active material, 10% wt Super P, 10% wt PVDF, and appropriate NMP and then drying at

105 °C. Dred circular electrodes with an area density of 2.5 mg·cm⁻² and Li disks were employed as cathodes and anodes to assemble CR2032 coin cells, respectively. For coin full-cell, the area density of the cathode increases to 3.5 mg·cm⁻², and the Li disk was replaced by natural graphite. Among them, the graphite anode used was pre activated for 5 cycles to obtain. Electrolyte was dominated by 1 M LiPF₆ dissolved in EC/EMC (3:7 by volume). Battery testing system (CT-4008T) was employed to test the rate and cycling performance at 2.75–4.3/4.5 V under the room-temperature. Electrochemical workstation (CHI 604e) was carried out to record the data of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

DFT calculation

The Vienna ab initio simulation package (Vasp) was utilized to perform spin-polarized density functional theory calculations within on-site Coulomb interaction (DFT + U). The d-orbital electrons of Ni, Co, and Mn ions were characterized by the U value (6.7, 4.91, and 4.64 eV) and the same J value (0 eV).

The projector-augmented wave (PAW) approach was used to signify core-valence interactions. The exchange-correlation function was obtained by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The plane wave basis expansion's energy cutoff was set to 500 eV. Optimized structures were obtained by minimizing the forces on each ion using the conjugate gradient algorithm where the value was 0.02 eV/Å. Then, the cutoff convergence energy in self-consistent calculations was 10⁻⁵ eV.

The (104) surface of the layered LiNiO₂ was simulated by a supercell that contained 50 Li, 50 Ni, and 1000 atoms, with two surfaces separated by a 15 Å vacuum layer. Mn&Co-doped LiNiO₂ (104) surface was obtained by randomly replacing Ni atoms in LiNiO₂ (104) surface (Mn:Co:Ni atom ratio 1:1:8). The structural models used for the calculations are shown in the following paragraphs.

Data availability

The data that support the findings detailed in this study are available in the article and its Supplementary Information or from the corresponding authors on request. Source data are provided with this paper.

References

- Guo, F., Xie, Y. & Zhang, Y. Low-temperature strategy to synthesize single-crystal LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ with enhanced cycling performances as cathode material for lithium-ion batteries. *Nano Res.* **15**, 2052–2059 (2021).
- Biasi, L. et al. Chemical, structural, and electronic aspects of formation and degradation behavior on different length scales of Ni-Rich NCM and Li-Rich HE-NCM cathode materials in Li-Ion batteries. *Adv. Mater.* **31**, 1900985 (2019).
- Ni, L. et al. Crack-free single-crystalline Co-free Ni-rich LiNi_{0.95}Mn_{0.05}O₂ layered cathode. *eScience* **2**, 116–124 (2022).
- Ni, L. et al. Challenges and strategies towards single-crystalline Ni-Rich layered cathodes. *Adv. Energy Mater.* **12**, 2201510 (2022).
- Zheng, W. et al. Understanding voltage hysteresis and decay during anionic redox reaction in layered transition metal oxide cathodes: a critical review. *Nano Res.* **16**, 3766–3780 (2023).
- Huang, Y. et al. Suppress moisture sensitivity of Ni-rich cathode materials by bioinspired self-assembly hydrophobic layer. *Chem. Eng. J.* **477**, 146850 (2023).
- Han, D. et al. Review—revealing the intercrystalline cracking mechanism of NCM and some regulating strategies. *J. Electrochem. Soc.* **169**, 040512 (2022).
- Ko, G. B. et al. Doping strategies for enhancing the performance of lithium nickel manganese cobalt oxide cathode materials in lithium-ion batteries. *Energy Storage Mater.* **60**, 102840 (2023).
- Zhang, C. et al. Towards rational design of high performance Ni-rich layered oxide cathodes: the interplay of borate-doping and excess lithium. *J. Power Sources* **431**, 40–47 (2019).
- Kim, U.-H. et al. Cation ordered Ni-rich layered cathode for ultra-long battery life. *Energy Environ. Sci.* **14**, 1573–1583 (2021).
- Dai, Z. et al. In situ construction of gradient oxygen release buffer and interface cation self-accelerator stabilizing high-voltage ni-rich cathode. *Adv. Funct. Mater.* **32**, 2206428 (2022).
- Shin, J.-W. et al. Yttrium-doped and conductive polymer-coated high Nickel layered cathode material with enhanced structural stability. *J. Electrochem. Sci. Technol.* **12**, 272–278 (2021).
- He, R. et al. Y₂O₃ modification on nickel-rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ with improved electrochemical performance in lithium-ion batteries. *J. Rare Earths* **40**, 309–317 (2022).
- Dai, S. et al. Ultrathin-Y₂O₃-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ as cathode materials for Li-ion batteries: synthesis, performance and reversibility. *Ceram. Int.* **45**, 674–680 (2019).
- Xin, F. et al. What is the role of Nb in Nickel-rich layered oxide cathodes for lithium-ion batteries? *ACS Energy Lett.* **6**, 1377–1382 (2021).
- Park, G.-T. et al. Introducing high-valence elements into cobalt-free layered cathodes for practical lithium-ion batteries. *Nat. Energy* **7**, 946–954 (2022).
- Chu, Y. et al. Thermodynamically stable dual-modified LiF&FeF₃ layer empowering Ni-rich cathodes with superior cyclabilities. *Adv. Mater.* **35**, 2212308 (2023).
- Yu, Y. et al. Enhanced cycling of Ni-rich positive electrodes by fluorine modification. *J. Electrochem. Soc.* **168**, 060538 (2021).
- Chen, Z. et al. Facile preparation of carbon-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with enhanced stability and rate capability for lithium-ion batteries. *J. Alloy Compd* **780**, 643–652 (2019).
- Yang, G. et al. Li-rich channels as the material gene for facile lithium diffusion in halide solid electrolytes. *eScience* **2**, 79–86 (2022).
- Huang, Y.-D. et al. Enhancing structure and cycling stability of Ni-rich layered oxide cathodes at elevated temperatures via dual-function surface modification. *J. Energy Chem.* **75**, 301–309 (2022).
- Gao, D. et al. Atomic horizons interpretation on enhancing electrochemical performance of Ni-Rich NCM Cathode via W doping: dual improvements in electronic and ionic conductivities from DFT calculations and experimental confirmation. *Small* **19**, 2205122 (2022).
- Guilmard, M. Effects of aluminum on the structural and electrochemical properties of LiNiO₂. *J. Power Sources* **115**, 305–314 (2003).
- Zhang, D. et al. Effect of Ti ion doping on electrochemical performance of Ni-rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode material. *Electrochim. Acta* **328**, 135086 (2019).
- Zhang, X. Y. et al. Building a stabilized structure from surface to bulk of Ni-rich cathode for enhanced electrochemical performance. *Energy Storage Mater.* **47**, 87–97 (2022).
- Zuo, L. L. et al. Highly thermal conductive separator with in-built phosphorus stabilizer for superior Ni-Rich cathode based lithium metal batteries. *Adv. Energy Mater.* **11**, 2003285 (2020).
- Guo, Y. et al. Rejuvenating LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode directly from battery scraps. *eScience* **3**, 100091 (2023).
- Qin, Z. Y. et al. A ternary molten salt approach for direct regeneration of LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode. *Small* **18**, 2106719–2106728 (2022).
- Zhang, C. et al. Regulating oxygen covalent electron localization to enhance anionic redox reversibility of lithium-rich layered oxide cathodes. *Energy Storage Mater.* **46**, 512–522 (2022).
- Huang, Y. et al. Improving the structure and cycling stability of Ni-rich layered cathodes by dual modification of Yttrium doping and

- surface coating. *ACS Appl Mater. Interfaces* **12**, 19483–19494 (2020).
31. Lauro, S. N., Burrow, J. N. & Mullins, C. B. Restructuring the lithium-ion battery: a perspective on electrode architectures. *eScience* **3**, 100152 (2023).
 32. Li, N. et al. Lowering sodium-storage lattice strains of layered oxide cathodes by pushing charge transfer on anions. *Energy Environ. Mater.* **7**, e12671 (2024).
 33. Cheng, C. et al. Anionic redox activities boosted by aluminum doping in layered sodium-ion battery electrode. *Small Methods* **6**, 2101524 (2022).
 34. Wang, E. et al. Al/Ti synergistic doping enhanced cycle stability of Li-rich layered oxides. *Adv. Funct. Mater.* **32**, 2201744 (2022).
 35. Lou, S. et al. Insights into interfacial effect and local lithium-ion transport in polycrystalline cathodes of solid-state batteries. *Nat. Commun.* **11**, 5700 (2020).
 36. Zhao, C. et al. Suppressing strain propagation in ultrahigh-Ni cathodes during fast charging via epitaxial entropy-assisted coating. *Nat. Energy* **9**, 345–356 (2024).
 37. Liu, Z. et al. Regulating electron distribution of P2-type layered oxide cathodes for practical sodium-ion batteries. *Mater. Today* **68**, 22–33 (2023).
 38. Zhang, Q. et al. Tungsten boride stabilized single-crystal $\text{LiNi}_{0.83}\text{Co}_{0.07}\text{Mn}_{0.1}\text{O}_2$ cathode for high energy density lithium-ion batteries: performance and mechanisms. *Adv. Funct. Mater.* **33**, 2301336 (2023).
 39. Kim, Y. et al. Unraveling the intricacies of residual lithium in high-Ni cathodes for lithium-ion batteries. *ACS Energy Lett.* **6**, 941–948 (2021).
 40. Li, J. et al. An effective doping strategy to improve the cyclic stability and rate capability of Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode. *Chem. Eng. J.* **402**, 126195 (2020).
 41. Jiang, W. et al. Achieving high structure and voltage stability in cobalt-free Li-rich layered oxide cathodes via selective dual-cation doping. *Energy Storage Mater.* **32**, 37–45 (2020).
 42. Liang, Y. et al. Heuristic design of cathode hybrid coating for power-limited sulfide-based all-solid-state lithium batteries. *Adv. Energy Mater.* **12**, 2201555 (2022).
 43. Jung, R. et al. Oxygen release and its effect on the cycling stability of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) cathode materials for Li-ion batteries. *J. Electrochem Soc.* **164**, A1361–A1377 (2017).
 44. Wang, H. et al. $\text{CO}_{(2)}$ and $\text{O}_{(2)}$ evolution at high voltage cathode materials of Li-ion batteries: a differential electrochemical mass spectrometry study. *Anal. Chem.* **86**, 6197–6201 (2014).
 45. Shi, C. G. et al. Investigation and suppression of oxygen release by $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode under overcharge conditions. *Adv. Energy Mater.* **12**, 2200569–2200579 (2022).
 46. Kim, S. et al. In situ gas analysis by differential electrochemical mass spectrometry for advanced rechargeable batteries: a review. *Adv. Energy Mater.* **13**, 2301983 (2023).
 47. Luo, K. et al. Charge-compensation in 3d-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* **8**, 684–691 (2016).
 48. Wang, L. et al. Electrochemical restoration of battery materials guided by synchrotron radiation technology for sustainable lithium-ion batteries. *Small Methods* **7**, 2201658 (2023).
 49. Kim, J. et al. Critical factors to understanding the electrochemical performance of all-solid-state batteries: solid interfaces and non-zero lattice strain. *Small* **19**, 2304269 (2023).
 50. Xu, Z. et al. Restraining the octahedron collapse in lithium and manganese rich NCM cathode toward suppressing structure transformation. *Adv. Energy Mater.* **12**, 2201323 (2022).
 51. Shen, Y. B. et al. Stabilization of high-voltage layered oxide cathode by utilizing residual lithium to form NASICON-type nanoscale functional coating. *Nao Res.* **16**, 5973–5982 (2023).
 52. Sun, Z. et al. Unveiling intrinsic potassium storage behaviors of hierarchical nano Bi@N-doped carbon nanocages framework via in situ characterizations. *Angew. Chem. Int. Ed.* **60**, 7180–7187 (2021).
 53. Zhou, Y. et al. Relieving stress concentration through anion–cation codoping toward highly stable Nickel-Rich cathode. *ACS Nano* **17**, 20621–20633 (2023).
 54. Zhao, W. et al. Assessing long-term cycling stability of single-crystal versus polycrystalline Nickel-Rich NCM in pouch cells with 6 mAh cm^{-2} Electrodes. *Small* **18**, 2107357 (2022).
 55. Jin, B., Cui, Z. & Manthiram, A. In situ interweaved binder framework mitigating the structural and interphasial degradations of High-nickel cathodes in lithium-ion batteries. *Angew. Chem. Int. Ed.* **62**, e202301241 (2023).
 56. Lee, S. et al. In-depth analysis of the degradation mechanisms of High-Nickel, low/no-cobalt layered oxide cathodes for lithium-ion batteries. *Adv. Energy Mater.* **11**, 2100858 (2021).
 57. Tan, Z. et al. Enabling superior cycling stability of $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ with controllable internal strain. *Adv. Funct. Mater.* **33**, 2215123 (2023).
 58. Shen, Y. et al. A universal multifunctional rare earth oxide coating to stabilize high-voltage lithium layered oxide cathodes. *Energy Storage Mater.* **56**, 155–164 (2023).

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Author contributions

Shijie Wang conceived the experiment and carried out data analysis. Kang Liang and Hongshun Zhao conducted the SEM and TEM experiments and related data analysis. Min Wu and Junfeng He carried out the hard-XAS and soft-XAS experiments. Peng Wei and Xiaobing Huang operated the in-situ XRD and DEMS measurements. Zhengping Ding performed FIB-TEM and TOF-SIMS experiments. Jianbin Li conducted theoretical calculation. Yurong Ren supervised all aspects of the research. All the authors discussed and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Yurong Ren.

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