Heuristic solution for achieving long-term cycle stability for Ni-rich layered cathodes at full depth of discharge

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Abstract

The demand for energy sources with high energy densities continues to push the limits of Ni-rich layered oxides that are currently the most promising cathode materials in automobile batteries. Although most current research is focused on extending battery life using Ni-rich layered cathodes, long-term cycling stability using a full cell is yet to be demonstrated. Here, we introduce $Li[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2$ which exhibits 90% capacity retention after 2,000 cycles at full depth of discharge (DOD) with an energy density > 850 Wh kg^{-1}. In contrast, the currently most sought-after $Li[Ni_{0.90}Co_{0.09}Al_{0.01}]O_2$ cathode loses ~40% of its initial capacity within 500 cycles at full DOD. Cycling stability is achieved by radially aligned primary particles with [003] crystallographic texture that effectively dissipate the internal strain occurring in the deeply charged state, while the substitution of Ni^{3+} with higher valence ions induces ordered occupation of Ni ions in the Li slab and stabilizes the delithiated structure.

The CO_2 emissions of electric vehicles (EVs) are 30–40% lower than those of internal combustion engine vehicles over their entire lifecycle; thus, EVs not only reduce dependence on fossil fuels but are also integral in addressing climate change induced by greenhouse gas emissions[1]. However, the main barrier to the rapid large scale deployment of EVs is the existing battery technology, which is primarily based on Li-ion batteries (LIBs). Moreover, EVs have not gained significant attention owing to their limited driving range and the high cost of LIBs, which are largely dictated by their cathodes[2–4].

To overcome these limitations associated with LIB cathodes, Co in the layered $Li[Ni_xCo_y(Al\ or\ Mn)_{1-x-y}]O_2$ (NCA or NCM, respectively) oxide cathodes, which are the primary cathode materials for the current fleet of EVs, was replaced by Ni to increase the discharge capacity and reduce the cost of LIBs[5–9]. However, multiple phase transitions during delithiation, particularly in the deeply charged state, results in inherent instability, thereby rendering these Ni-rich layered oxide cathodes unsuitable for next-generation EVs. The compositions of Ni-rich NCA and NCM cathodes have been modified using various doping elements (Ti, Al, B, Nb, Zr, Mo, and W)[10–16] to increase their energy density without sacrificing cycling stability. Alternatively, the external surfaces and internal interparticle boundaries have been coated or infused with different materials (Al_2O_3, AlF_3, and Li_3PO_4)[17–19] to protect the active material from electrolyte attack and extend its cycle life. However, to date, the coating and doping of Ni-rich NCA and NCM cathodes have been marginal in producing the cycling stability necessary for EV application.

The general mechanism of capacity fading for Ni-rich layered cathodes involves the build-up of mechanical strain from the abrupt collapse of the layered structure during the phase transition in the deeply charged state, ensuing intergranular microcracking, which generates channels for electrolyte penetration, and accelerating structural deterioration[8,20–23]. Hence, solving the capacity fade problem essentially amounts to reducing the mechanical strain during the phase transition. To date, proposed Ni-rich NCM and NCA cathodes have been predominantly designed to provide chemical protection but have failed to provide an effective solution for the strain build-up. Since the phase transition in the deeply charged state generates highly anisotropic mechanical strain confined in the *c*-direction of the layered structure, radially oriented primary particles with crystallographic texturing can convert the non-uniform strain distribution arising from randomly oriented primary particles into to a uniformly distributed circumferential strain. The circumferential strain effectively suppresses local stress concentrations and enables individual primary particles to uniformly contract and expand during cycling, thereby minimizing local strain build-up and intergranular microcracking. Improvement in the cycling stability has been previously demonstrated in the compositionally graded NCM cathodes[24,25] and boron-doped $Li[Ni_{0.9}Co_{0.05}Mn_{0.05}]O_2$ cathodes[26]. Moreover, refining the particle size also deters microcracking as a network of interparticle boundaries deflects crack propagation and relieves strain energy[24,27,28]. Hence, in addition to chemical modification, tailoring the microstructure of Ni-rich layered cathodes could achieve the necessary cycling stability for EV applications. However, to date, there is yet to be a systematic study on determining the optimal microstructure without compromising discharge capacity partly because a large number of variables (dopants, doping concentration, and doping method) need to be considered. In this work, we introduced different dopants into a $Li[Ni_{0.91}Co_{0.09}]O_2$ (denoted as NC90) cathode to demonstrate that the microstructures of secondary particles can be significantly altered, depending on the tertiary doping element, with improved capacity retention and minimal loss of discharge capacity

Micro-scale structural characterization

Fig. 1 summarize the effect of doping NC90 with Mn, Al, B, Sb, and Ta on the cathode microstructure. The obtained microstructures varied from large equiaxed primary particles to fine needle-like particles, and the cycling stability also varied substantially, depending on the particular microstructure (See **Supplementary Fig. 1** and **supplementary Table 1** for other dopants). Among the different doping elements tested, Ta exhibits the highest cycling stability with an optimal concentration determined to be 1 mol% Ta. Above 1 mol%, the discharge capacity decreases substantially without any significant improvement in the cycling stability (**Supplementary Fig. 2** and **Supplementary Fig.3**). Ta introduced during the lithiation of the hydroxide precursor modifies the surface energy to generate the desired radial texture, as observed in B-doped NCM and NCA cathode[26,28]. Moreover, Ta addition hinders particle coarsening, thereby allowing optimal particle size refinement within the lithiation temperature window. To explicitly demonstrate the effect of Ta addition on the particle microstructure, the hydroxide precursor with and without Ta were lithiated at different temperatures. **Fig. 2a** depicts a series of cross-sectional images of NC90 cathodes lithiated at 730 - 850 °C. The width of the primary particle size increases considerably from 0.5 to 1.5 μm as the lithiation temperature increases from 730 to 850 °C. At 730 °C, the shape of the primary particles is approximately equiaxed and they tend to elongate at higher temperatures, likely owing to the dominance of the (003) facet. $Li[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2$ (denoted as NCTa90) cathode particles are significantly finer than those of NC90. The particle growth is nearly suppressed up to 790 °C and above 790 °C, exaggerated particle coarsening is observed (**Fig. 2b**). The primary particle widths of NC90 and NCTa90 cathodes plotted in **Fig. 2c**, clearly reveal the disparity in their particle size. There is also a large difference in the particle aspect ratio (particle length/width) (**Supplementary Fig. 3**). Regardless of the lithiation temperature, the aspect ratio of the primary particle for NC90 cathode remains at 1.4–1.5 due to the retention of their equiaxed shape. In contrast, the aspect ratio for NCTa90 cathode lithiated at 730 °C is 6.5, which reflects its elongated shape. The aspect ratio for NCTa90 cathode decreases below 2 only when lithiated at 790 °C, where exaggerated grain growth is observed. ASTAR, which maps the crystal orientation, was used to quantitatively assess the radial texture of NCTa90 cathode lithiated at different temperatures (**Fig. 2d,e**). When lithiated at 730 °C, a major portion of the primary particles is radially oriented with their longitudinal axes parallel to the *a*-direction (bright contrast in the figure denotes a stronger *a*-axis texture). Such radial orientation of the primary particles align the Li slabs to point outward from the particle centre, expediting Li migration. The mapping data indicate the gradual weakening of the crystallographic texture at higher lithiation temperatures (**Fig. 2d**). The spoke-like structure of NCTa90 is likely inherited from the hydroxide precursor (**Supplementary Fig. 4**). During lithiation, nano-sized metal hydroxide particles consolidate into a larger primary particle. Ta selectively lowers the (003) surface energy, thereby resulting in preferential (003) faceting. To theoretically verify the surface energy modification by Ta, the surface energies for (003) and (104) facets, which are surfaces with the lowest energy, were calculated using density functional theory. To reduce computational cost, Al- and Ta-doped $LiNiO_2$ (LNO) were modelled (**Supplementary Note 1**). The calculated surface energies, γ as a function of the chemical potential of Li ($\Delta\mu_{Li}$) are shown in **Supplementary Fig. 5**. The horizontal and sloping lines represent the computed $\gamma(\Delta\mu_{Li})$ for the non-polar stoichiometric LNO(104) and non-stoichiometric LNO(003) surfaces. For non-polar stoichiometric LNO(104) surfaces, where N_{Ni} is equal to N_{Li} (N = number of atoms), $\gamma(\Delta\mu_{Li})$ is constant and independent of $\Delta\mu_{Li}$. On the other hand, for non-stoichiometric Li-rich LNO(003) surfaces, where N_{Li} is larger than N_{Ni}, the calculated $\gamma(\Delta\mu_{Li})$ produces a negative slope. The calculation indicates that the value of $\gamma_{(003)}-\gamma_{(104)}$, which determines the relative contribution of (104) facet against that of (003) facet, for Ta-doped LNO is approximately 2 meV $Å^{-2}$ larger than that of Al-doped LNO. Further analysis shows that this is attributed to the larger orientation-dependent anisotropic (dopant-induced) strains for Ta-doped LNO. Doping-induced lattice strains in LNO are accompanied by changes in bond strengths in the host LNO system as bond lengths vary. Since a larger change in bond length would cost higher energy, a dopant that causes smaller dimensional changes in the unit cell would be energetically more favorable. Since Ta ions are larger than Al ones, larger lattice strains in LNO are obtained with Ta (**Supplementary Table 2**), and, therefore, values of γ are larger for the Ta-doped LNO than for the Al-doped LNO. Although dopant-induced lattice strains are larger in (104) than in (003) surfaces for both Ta- and Al-doped LNO, this increase is more significant for the Ta-doped LNO. Introducing ions with a larger ionic radius such as Ta tends to preferentially strain the (104) surface, thereby, increasing its surface energy. Thus, (003) facets are relatively more stable in the NCTa cathode than in the NCA cathode.

Atomic-level structural characterization

A detailed electron diffraction analysis of NCTa90 cathode reveals that Ta introduction also modifies the crystal structure of the primary particles. NCTa90 cathode lithiated at 730 °C contains a high degree of structural defects, including twin and cation mixing. These defects can be observed by extra diffraction spots appearing in the [100] zone selected area electron diffraction (SAED) pattern. These extra spots disappear at higher lithiation temperatures (**Fig. 3a – c**) such that the SAED pattern from the cathode lithiated at 790 °C match the calculated diffraction pattern (**Fig. 3d**). The magnified [100] zone SAED pattern from the NCTa90 cathode lithiated at 730 °C contains superlattice extra spots with additional spots from twinning overlaid on the fundamental [100] zone pattern (**Fig. 3e**). The extra spots (green) maintain a simple fractional relationship with the fundamental spots. The extra diffraction spots are indexed as (0½1) and (0½$\bar{2}$), suggesting the origin of these peaks from a superlattice structure rather than from a secondary phase. For the superlattice peaks, the most likely solution is the migration of Ni ion into the Li layer and their subsequent ordered-occupation of Li sites. The alternating occupation of Li sites by transition metal (TM) ions on every other row and the similarly ordered occupation of TM sites by Li ions creates a supercell with a unit cell dimension in the *a*–*b* plane that is twice as large as that of the normal layered structure (**Fig. 3f** and **Supplementary Fig. 6**). For direct observation of the supercell created by the alternating occupation of Li and TM ions, the structure needs to be viewed along the [100] direction. When the supercell is projected along the [100] direction, an alternating atomic contrast with a periodicity of $\sqrt{3}a$ is observed due to presence of TM ions in the alternating columns and rows. In a normal cell, the periodicity is $\frac{\sqrt{3}}{2}a$. The alternating contrast arising from the cation ordering with a periodicity of $\sqrt{3}a$ (0.5 nm) was verified from the high-angle annular dark-field scanning transmission electron microscope (STEM) image of the cation-ordered region (**Fig. 3g**). To establish statistical significance, the superlattice SAED pattern is consistently observed from multiple NCTa90 primary particles (**Supplementary Fig. 7**). The cation ordering observed at 730 °C is partially supported by the powder X-ray diffraction (XRD) data, which demonstrate a decrease in cation mixing (i.e., Ni occupation of Li sites) as the lithiation temperature increases (**Supplementary Fig. 8** and **Supplementary Table 3**) in agreement with the electron diffraction data. The observed cation ordering is not unique to NCTa90 cathode and is often found when a Ni-rich layered cathode is doped with ions with high oxidation states (e.g. Ta, Zr, Nb, W, Mo, and Sb) in **Supplementary Fig. 9**). Contrastingly, introducing Ti, Mg, and Ga does not produce this ordered phase. Thus, it is conjectured that the substitution of trivalent Ni^{3+} with ions with oxidation states higher than 3+ requires Ni^{2+} to maintain charge neutrality. This higher amount of Ni^{2+} promotes the migration of Ni ions into Li slabs. Theoretical calculation shows that there is little cost in energetics for the ordered occupation of TM ions in Li slabs compared to the normal layered structure [29]; however, only when TM ions randomly occupy Li slabs, Li migration is hindered by the presence of TM ions. The ordered state also lowers the delithiation energy, which is the energy required to remove a Li ion from the structure[29]. Considering the limited concentration of Ta, the ordered structure is, however, likely confined to surfaces and interparticle boundaries because Ta, introduced during lithiation of the hydroxide particles, segregates at surface and interparticle boundaries. It is likely that the interior primary particles retain the original layered structure because of the slow diffusion of Ta from the particle surface. The presence of the ordered structure on the surfaces and grain boundaries should be sufficient to stabilize the delithiated structure and protect the cathode from the electrolyte attack since all detrimental factors: microcracking, cathode/electrolyte reaction, and impurity layer formation occur along the exposed surfaces and grain boundaries. The modification of grain boundaries of Ni-rich layered cathodes using atomic layer deposition (ALD) also substantially improved their cycling stability[19]. Similarly ordered antisite defects were previously observed in Zr-doped $LiNiO_2$[29], and NCA/NCMA core-shell[30], where the ordered intermixing of Li and TM ions were attributed to the substantial improvement in the cycling stability. $Li[Ni_{0.5}Mn_{0.5}]O_2$, which also forms a $\sqrt{3}a_{Hex} \times \sqrt{3}a_{Hex} \times c_{Hex}$ superlattice through the ordering of Li and TM ions in the TM layer, has been observed to exhibit excellent cycling stability[31]. Enhanced capacity retention is also manifested in $Li[Ni_{0.90}Co_{0.09}W_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Mo_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Nb_{0.01}]O_2$, and $Li[Ni_{0.90}Co_{0.09}Sb_{0.01}]O_2$, which exhibit cation ordering identical to that of the NCTa90 cathode lithiated at 730 °C (**Supplementary Fig. 9**). The presence of TM ions in the Li slab is assumed to protect the collapse of the layered structure and maintain the structural scaffold in its highly delithiated state. Therefore, the desired particle microstructure (spoke-like structure with [100] crystallographic texture and particle size refinement) can be attained by lithiating the NCTa90 cathode at 730 °C, in addition to modifying the crystal structure which is demonstrated to be beneficial to the stabilization of the delithiated structure of Ni-rich layered cathodes.

A notable feature of the NCTa90 cathode lithiated at 730 °C is the abundance of twin defects generated by the reflection of the fundamental diffraction spots about the (001) plane. (**Fig. 4a**). The accompanying high-resolution transmission electron microscope (TEM) image in **Fig. 4b** shows an example of the (001) twins observed in the primary particle at numerous places. Fourier transform (FT) of the twinned regions (marked as I and II) produces regular [100] zone diffraction patterns that are mirror images of each other. The FT of the large region (marked as III) contains the mirrored diffraction pattern overlaid a top the regular pattern, thereby confirming the presence of a twin defect. These twins with boundaries aligned along the longitudinal axis of the primary particles likely inhibit the consolidation of the primary particles of NCTa90 cathode during lithiation and limit the growth of primary particles in the lateral direction. Additionally, the activation energy for the Li migration across the twin boundaries is considerably greater than that along the twin boundaries[29]; thus, twin boundaries force Li ions to migrate along the radial direction, enhancing the Li migration rate.

Electrochemical performance and microcracking of NCTa90

The fundamental electrochemical performance of NCTa90 cathode lithiated at different temperatures was compared with that of the NCA90 cathode. NCA90 is a Ni-enriched version of the archetype of the layered cathode structure family. The initial charge–discharge curves (at 0.1 C and 30 °C) of NCA90 cathode lithiated at increasing temperatures indicate the progressive decrease in the discharge capacity from 225 mAh g^{-1} at 730 °C to 195 mAh g^{-1} at 850 °C and in the Coulombic efficiency of the first cycle from 94% to 85% (**Fig 5a** and **Supplementary Fig. 10**). Similarly, the NCTa90 cathode exhibits a decrease in the discharge capacity from 229 mAh g^{-1} at 730 °C to 203 mAh g^{-1} at 850 °C and in the first-cycle Coulombic efficiency from 96% to 89% (**Fig. 5b** and **Supplementary Fig. 10**). **Fig. 5c** plots the initial discharge capacity of the NCA90 and NCTa90 cathodes lithiated at different temperatures as a function of the primary particle width, revealing the clear correlation between the particle size and discharge capacity. Hence, the cathode microstructure has a large impact on Li migration as a large fraction of interparticle boundaries provides fast diffusion pathways and efficient transportation of Li ions from the particle interior to the surface. Superior cycling stability is observed for the NCTa90 cathode, except when the primary particles are excessively large at 850 °C. The NCA90 cathode can retain 75–80% of the initial capacity after 100 cycles regardless of the lithiation temperature, while NCTa90 cathodes lithiated below 800 °C maintain more than 95% of the initial capacity (**Fig. 5d,e**). The effect of Ta on the cycling stability is more pronounced with the increase in Ni content. Although both $Li[Ni_{0.95}Co_{0.04}Ta_{0.01}]O_2$ (NCTa95) and $Li[Ni_{0.95}Co_{0.04}Al_{0.01}]O_2$ (NCA95) cathodes deliver a similar initial discharge capacity of 237–239 mAh g^{-1} (at 0.1 C and 30 °C), the NCTa95 cathode cycled at 0.5 C retains 94% of the initial capacity but the NCA95 cathode only retains 81% after 100 cycles (**Fig. 5f**). The $Li[Ni_{1-x-y}Co_yTa_x]O_2$ cathode delivers a discharge capacity comparable to those of Ni-rich NCM or NCA cathodes while overcoming capacity fading, which hampers the practical application of Ni-enriched layered cathodes. The superior cycling stability of the NCTa90 cathode is substantiated by long-term cycling in full cells. NCA90 and NCTa90 cathodes lithiated at different temperatures were cycled in a pouch-type full cell with a graphite anode at 1.0 C (**Fig. 5g**). The discharge capacity of NCA90 cathode drops below 80% of the initial capacity only after 250 cycles, thereby rendering it unsuitable for EVs application. In contrast, regardless of the lithiation temperature, the NCTa90 cathode clearly outperforms the NCA90 cathode. Particularly, the NCTa90 cathode lithiated at 730 °C demonstrates outstanding cycling stability with a retention greater than 95% of the initial capacity, even after 1,000 cycles (90% for 2000 cycles). To the best of our knowledge, there are no NCM or NCA cathodes with Ni content greater than 0.9 at full depth of discharge (DOD) that have demonstrated such a high cycling stability. Current state-of-the-art NCA cathodes deployed in EVs limit their DOD to 60–80% to guarantee the required battery life. The NCTa90 cathode exhibits an outstanding cycling stability for 2,000 charge/discharge cycles, which is equivalent to a battery life of approximately 20 years for an EV subject to weekly full charging. The capacity retention of the NCTa90 cathode lithiated at 730 °C surpasses those of same cathodes lithiated at higher temperatures. The difference in the retained capacities becomes increasingly wider as the cycling progresses. The exceptionally stable cycling of NCTa90 cathode lithiated at 730 °C is attributed to the presence of the cation ordering, which stabilizes the delithiated structure of the cathode and improves the reversibility of the electrode reaction. Despite the repeated insertion and removal of Li ions, the cation ordering is preserved even after 2,000 cycles **(Fig. 6a)**.

To examine the extent of microcracking, the cross-section images of NCA90 and NCTa90 cathodes lithiated at 730 °C were examined at different charge and discharge states (**Fig. 6b,c** and **Supplementary Fig. 11**). Even at 3.9 V, a wide microcrack from the NCA90 particle core is observed. This microcrack not only undermines the mechanical integrity of the particle but also opens channels for electrolyte penetration to the particle interior, making it susceptible to electrolyte attack[8,11,20–22]. At 4.3 V, microcracking becomes increasingly severe. Although these cracks close in the discharged state, the repetitive opening and closing of microcracks gradually builds up an impurity layer on the crack faces due to electrolyte attack, leading to capacity fading and eventually, catastrophic fracture. In contrast, the NCTa90 cathode barely develops any visible microcracks at 3.9 V. Fine microcracks observed at to 4.3 V are arrested before reaching the surface. **Fig. 6d** depicts the areal fraction of the microcracks as a function of the potential. This graphically illustrates the severity of the microcracking incurred by NCA90. Additionally, the two cathodes were mixed to ensure that they were subjected to identical electrode preparation and electrochemical testing. A cross-sectional image of the composite cathode at 4.3 V clearly demonstrates the mechanical stability of the NCTa90 cathode (**Fig. 6e** and **Supplementary Fig. 12**). To further emphasize that the origin of the microcracking suppression is the different microstructure, the dimensional changes of the unit cell for NCA90 and NCTa90 cathodes were monitored during charging (at 0.05 C) using in situ XRD measurements. The *c*- and *a*-axis lattice parameters were calculated as a function of the charge state (**Supplementary Fig. 13**). Both cathodes exhibit a similar dimensional change in the *c*-direction with an initial gradual expansion followed by abrupt contraction at approximately 4.0 V, corresponding to the onset of the H2 → H3 phase transition.

The normalized unit cell volume in **Fig. 6f** indicates the virtually identical lattice contraction for both cathodes. Therefore, the introduction of Ta has a minimal effect on the abrupt lattice contraction, which is the primary reason behind the severe microcracking in the fully charged NCA90 cathode[8,21,23]. Hence, the unique microstructure of NCTa90 cathode enables the dissipation of anisotropic mechanical strain and suppression of the microcrack formation and propagation.

Thermal stability

The structural stability of delithiated NCTa90 cathode was verified using in situ time-resolved (TR) XRD (30–400 °C) analysis of the partially delithiated cathodes ($Li_{0.1}[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2$). The contour plot in **Supplementary Fig. 14a** indicates the transformation of delithiated $Li_{0.1}[Ni_{0.90}Co_{0.09}Al_{0.01}]O_2$ from the $R\bar{3}m$ structure into a disordered spinel structure ($Fd\bar{3}m$) at 150 °C, as indicated by the weakening of the $(111)_L$ peak and sharp shifting of the $(104)_L$ and $(110)_L$ peaks. Subsequently, at 230 °C, the disordered spinel phase transforms into a fully cation-disordered rocksalt structure $Fm\bar{3}m$. The onset temperature of the $R\bar{3}m \rightarrow Fd\bar{3}m$ transformation for the $Li_{0.1}[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2$ cathode is considerably delayed to 190 °C while that of the $Fd\bar{3}m \rightarrow Fm\bar{3}m$ transformation is delayed to 310 °C. We believe that the ordered presence of Ni ions in Li slabs restricts its random migration into Li sites, thereby delaying the structural transformation into a cation-disordered state ($Fm\bar{3}m$). The chemical thermal stability of the NCTa90 cathode, which is essential for large-format batteries in EVs, is also improved. The thermal stability of the cathodes was characterized using differential scanning calorimetry (DSC) charged at 4.3 V in an electrolyte solution (**Supplementary Fig. 14b**).The charged NCA90 cathode produces a large exothermic peak at 191.8 °C with a total heat generation of 1753 J g^{-1}, whereas that of NCTa90 cathode appears at 201.3 °C with a total heat generation of 1055 J g^{-1}, which is considerably less than that of the NCA90 cathode.

Fig. 7 illustrates that tailoring the microstructure and crystal structure can resolve the rapid capacity fading, commonly exhibited by Ni-rich layered cathodes. Abrupt lattice contraction of randomly oriented primary particles (as in NCA90) creates a complex stress state, leading to crack nucleation and rapid capacity fading. Thick elongated primary particles with strong [003] texture (as in Li[$Ni_{0.89}Co_{0.09}Al_{0.01}B_{0.01}$]$O_2$ denoted as NCAB90) dissipates the strain energy and improves the cycling stability. The best long-term cycling is, however, achieved by NCW90 and NCTa90 cathodes with particle size refinement and cation ordering in addition to the radially oriented primary particles. Moreover, the NCTa90 cathode outperforms the NCW90 cathode in extended cycling, because the NCTa90 cathode possesses a stronger [003] texture.

Conclusions

The partial replacement of Ni with different elements in Li[$Ni_{0.90}Co_{0.09}M_{0.01}$]$O_2$ produced various particle microstructures, ranging from highly oriented needle-like columnar primary particles to randomly oriented equiaxed primary particles. NCTa90 cathode lithiated at 730 °C was found to possess an optimal microstructure, conducive to long-term cycling stability while providing a high capacity at 100% DOD. In addition, depending on the doping elements, replacing Ni^{3+} with TM ions with valence states higher than +3 induced the ordered occupation of TM ions in Li sites, thereby stabilizing the delithiated structure of the cathode. Hence, the optimal combination of micro- and atomic-level structures for producing the best overall electrochemical performance was achieved. The capacity and cycling performance exhibited by the NCTa90 cathode provides a viable solution to overcome inherent issues that limit the life of the Ni-rich layered cathode, thereby marking a step towards meeting the demands of next-generation EVs and achieving general electro-mobility.

Methods

Synthesis of spherical Ni-rich cathode particles

This section describes the synthesis of spherical NC90, NCMg90, NCA90, NCTi90, NCTa90, NCNb90, NCSb90, NCMo90, and NCW90 ($Li[Ni_{0.91}Co_{0.09}]O_2$, $Li[Ni_{0.90}Co_{0.09}Mg_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Al_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Ti_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Nb_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Sb_{0.01}]O_2$, $Li[Ni_{0.90}Co_{0.09}Mo_{0.01}]O_2$, and $Li[Ni_{0.90}Co_{0.09}W_{0.01}]O_2$, respectively). $[Ni_{0.91}Co_{0.09}](OH)_2$ precursor was synthesized by the co-precipitation method using an aqueous solution of 2.0 M $NiSO_4{\cdot}6H_2O$ (Samchun Chem., 98.5%, Republic of Korea), and $CoSO_4{\cdot}7H_2O$ (Daejung Chem., 98%, Republic of Korea) (Ni:Co = 91:9, in molar ratio) as the starting material. A homogeneously mixed solution was fed into a batch reactor (17 L) filled with a solution of deionized water, NH_4OH (aq) (Junsei Chemical Co., Ltd., Japan), and NaOH (aq) (Samchun Chemicals Co., Ltd., Republic of Korea), under a replenished N_2 atmosphere. Concurrently, 4 M NaOH (aq) (molar ratio of NaOH to TM = 2.0) and 10.5 M NH_4OH chelating agent (aq) (molar ratio of NH_4OH to TM = 1.2) were separately pumped into the reactor. The final precursor powder was obtained through rinsing, filtering, and vacuum-drying at 110 °C overnight. To obtain each cathode materials, the precursor, $[Ni_{0.91}Co_{0.09}](OH)_2$, was mixed with $LiOH{\cdot}H_2O$ (Sigma-Aldrich) and their corresponding chemical compounds (MgO, $Al(OH)_3{\cdot}3H_2O$, TiO_2, Ta_2O_5, Nb_2O_5, Sb_2O_3, MoO_3, and WO_3, respectively, all chemicals from Sigma-Aldrich) following the molar ratio of Li:M:(Ni+Co) = 1.01:x:1-x, where x = 0 for pure powder (without dopant) and 0.01 for others. The mixed powders with pure, Al, and Ta powders were calcined in a tube furnace (Lindberg, Thermofisher, USA) at various temperatures (730, 750, 770, 790, and 850 °C) for 10 h under an O_2 atmosphere (heating and cooling rate: 2 °C min^{-1}). The remaining mixture powders with Mg, Ti, Nb, Sb, Mo, and W, respectively were calcined at 730 °C for 10 h under an O_2 atmosphere.

Analytical approach

The chemical compositions of the prepared precursor and lithiated oxide were determined by inductively coupled plasma atomic emission spectroscopy (Optima 8300, PerkinElmer). XRD

(Empyrean, Panalytical) using Cu Kα radiation was used to confirm the crystal phases of the lithiated oxide powder. XRD data were obtained in the 2θ range of 10–110° with a 0.02° step size. The collected XRD spectra were analysed by applying the FullProf Rietveld refinement program. In situ XRD experiments were conducted using pouch-type half cells with Li metal as the anode (Empyrean, Panalytical). The assembled pouch-type cells were charged to a cut-off voltage of 4.3 V by applying a constant current of 0.05 C (9 mA g^{-1}). During the charging process, XRD patterns were recorded every 40 min using a detector (PIXcel 1D, PANalytical). The particle morphologies and structures of the powders were observed by scanning electron microscopy (SEM, Verios G4 UC, FEI) and transmission electron microscopy (Cs-corrected TEM with Cold FEG, JEM ARM200F JEOL Ltd. and Tecnai F20 G2, FEI). Cathode electrodes were cut using a cross-sectional polisher (CP, IB-19520CCP, JEOL). TEM samples were prepared using a focused ion beam (Helios NanoLab 600, FEI) and the precession diffraction analytical method was utilized for ASTAR (Crystal orientation mapping).

Electrochemical test

To fabricate the cathodes the synthesized powders were mixed with a conducting agent, carbon black (Alfa Aeser, USA), and poly(vinylidene fluoride) (Solef 5130, Solvay) at a ratio of 90:5.5:4.5 by wt% in *N*-methyl-2-pyrrolidone by a Thinky mixer (ARE310, Thinky Corp., Japan). The slurry was coated on the Al foil (UACJ Corp., Japan) of the current collector with an active material loading level of 4–5 mg cm^{-2}, vacuum dried, and roll-pressed. The electrolyte was 1.2 M $LiPF_6$ in ethylene carbonate–ethyl methyl carbonate (EC:EMC, 3:7 by vol%) with 2 wt% vinylene carbonate (VC) (Panax Etec Co., Ltd., Republic of Korea). Preliminary half-cell tests were performed with 2032 coin-type cells (Hohsen Corp., Japan) using Li metal (Honjo Metal Co., Ltd., Japan) as the anode and polypropylene/polyethylene/polypropylene(PP/PE/PP) (Celgard 2320, Celgard LLC, USA) as the separator. The cells were charged and discharged by applying constant current and voltage and densities of 90 and 9 mA g^{-1}, respectively, at 0.5 C and 30 °C. Long-term cycle life tests were performed in a laminated pouch-type full cell (55 mAh). For the fabrication of the full cell positive electrodes, synthesized powders were mixed with carbon black and poly(vinylidene fluoride) (PVdF) (94:3:3 by wt.%) in N-methylpyrrolidone. The obtained slurry was coated with an Al foil with an active material loading level of 9-10 mg cm^{-2}. Commercial graphite (artificial graphite) (Posco Chemical, Republic of Korea) was used as the anode. The size of the cathode and anode for the pouch cells were 3×5 cm and 3.1×5.1 cm, respectively. Based on areal capacity, the N/P ratio for the full-cell was in the range of 1.15–1.20. The full cells were charged and discharged between 3.0 and 4.2 V by applying a constant 1 C current (55 mA corresponding to 200 mA g^{-1}) at 25 °C.

Thermal stability measurements

For thermal stability measurement, 2032 coin-type half-cells were charged at a constant voltage of 4.3 V versus Li metal and dis-assembled to recover the cathodes in an Ar-filled glove box. The electrodes were washed with dimethyl carbonate to remove the remaining electrolyte solution on its surface. The cathode materials for these measurements were separated from the cycled and washed composite electrodes. A stainless-steel-sealed pan with Au-plated Cu seals was used to accommodate 7–8 mg samples with 100 μL of fresh electrolyte (1.2 M $LiPF_6$ in EC:EMC= 3:7 by vol% with 2 wt% VC). The measurements were performed using DSC 214 polyma (Netzsch, Germany) at a temperature scan rate of 5 °C min^{-1}. TR-XRD data were collected using a high-resolution XRD (SmartLab, Rigaku). Meanwhile, 10 mg of the delithiated cathode was placed on a crucible under vacuum conditions. XRD patterns were collected every 10 min for each temperature scan and heated from 30 to 400 °C for 24 h at a heating rate of approximately 5 °C min^{-1} maintained for 30 min.

Data availability

All the data generated or analysed during this study are included in this published article and its Supplementary Information files. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Acknowledgements

This work was mainly supported by the Global Frontier R&D Program (NRF-2013M3A6B1078875) at the Center for Hybrid Interface Materials of the Ministry of Science, ICT & Future Planning. Additionally, this work was also supported by the Human Resources Development program (No. 20184010201720) of the Korea Institute of Energy Technology Evaluation and Planning funded by the Ministry of Trade, Industry and Energy of the Korean government. J. Liu would like to thank University of Washington for supporting his effort on this manuscript.

Author contributions

U.H. Kim and Y.K. Sun conceived and designed the research. U.H. Kim, G.T. Park, B.K. Son, and G.W. Nam performed the experiments and characterization of materials. U.H. Kim, C.S. Yoon, and Y.K. Sun analysed the data. L.-Y. Kuo, P. Kaghazchi performed the theoretical calculations. U.H. Kim, C.S. Yoon, J. Liu, and Y.K. contributed to the discussion of the results. C.S. Yoon and Y.K. Sun wrote the manuscript. All the authors commented and revised the manuscript.

Competing interests

The authors declare no competing interests.

Fig. 1 | Correlation between primary particle morphology and electrochemical performance. a. STEM image of a cross-sectional cathode particle and the corresponding schematic of the primary particles. (Li[$Ni_{0.90}Co_{0.05}Mn_{0.05}$]$O_2$, Li[$Ni_{0.895}Co_{0.09}B_{0.015}$]$O_2$, Li[$Ni_{0.90}Co_{0.09}Al_{0.01}$]$O_2$, Li[$Ni_{0.90}Co_{0.09}W_{0.01}$]$O_2$ denoted as NCM90, NCB90, NCA90, and NCW90, respectively) **b.** Cycling performance of NCM90, NCB90, NCA90, and NCW90 cathodes in the voltage range of 2.7–4.3 V at 30 °C in half-cells using Li-metal as the anode. **c**. Cathode level energy density versus capacity retention for NCM90, NCB90, NCA90, and NCW90 cathodes.

Fig. 2 | Morphology and orientation of primary particles as a function of the dopant and calcination temperature. Cross-sectional SEM images of **a.** NC90 and **b.** NCTa90 cathodes, lithiated at different temperatures. The error bars represent the standard deviation calculated over 100 particles for each cathode. **c.** Primary particle width for NC90 and NCTa90 cathodes lithiated at different temperatures **d.** Estimated percentage of primary particles with *a*–*b* planes pointed in the radial direction for NCTa90 (see text for detailed explanation). **e.** ASTAR images of NCTa90 cathodes, highlighting the tendency of the *a*–*b* planes of primary particles to point to the radial direction as the lithiation temperature is lowered.

Fig. 3 | (Li/TM) ordered structure observed in the NCTa90 cathode lithiated at 730 °C. [100] zone SAED pattern from a primary particle from NCTa90 cathodes lithiated at **a.** 730, **b.** 750, and **c.** 790 °C. **d.** Calculated [100] zone diffraction pattern. **e.** Magnified [100] zone diffraction pattern of NCTa90 cathode lithiated at 730 °C, containing superlattice peaks from the cation ordered structure (diffraction spots marked in green) and twin peaks (diffraction spots marked in blue). **f.** Schematic image of Li/TM cation-ordered structure viewed along the [001] direction. **g.** High-angle annular dark-field (HAADF) TEM image of NCTa90 cathode lithiated at 730 °C with contrast line scan along the [010] direction of the cation-ordered (Li/TM) structure, demonstrating the alternate occupation of Li and TM atoms.

Fig. 4 | Twin defect structure observed in the NCTa90 cathode lithiated at 730 °C. a. Diffraction pattern corresponding to twin defect in the [100] zone SAED pattern from NCTa90 cathode lithiated at 730 °C with a schematic representation of the atomic arrangement of the twin defect. **b.** High-resolution TEM image with Fourier transform of marked regions (I, II, and III) of NCTa90 cathode lithiated at 730 °C, verifying the presence of the twin.

Fig. 5 | Electrochemical performances of NCA90 and NCTa90 cathodes lithiated at different temperatures. Initial charge and discharge curves at 0.1 C and 30 ºC during cycling between 2.7 and 4.3 V for **a.** NCA90 and **b.** NCTa90 cathodes. **c.** Plot of the first initial discharge capacity for NCA90 and NCTa90 cathodes as a function of the primary particle width. Cycling performance (at 0.5 C) of **d.** NCA90 and **e.** NCTa90 cathodes lithiated at different temperatures. **f.** Cycling performance (at 0.5 C) with the initial charge and discharge curves in the inset for NCA95 and NCTa95 cathodes. **g.** Long-term cycling stability in full cells using graphite as the anode for NCA90 and NCTa90 cathodes lithiated at different temperatures.

Fig. 6 | Structural and mechanical stability of NCTa90 cathode verified by structure characterization. a. SAED pattern and high-resolution TEM image of NCTa90 cathode lithiated at 730 °C after 2,000 cycles with Fourier transform of the marked regions, verifying the presence of cation ordering after 2,000 cycles. The extra spots in the SAED pattern (yellow arrow), corresponding to a superlattice identical to those observed in the as-prepared state. **b.** and **c.** Cross-sectional SEM images of NCA90 and NCTa90 cathodes at different charge/discharge state during the first cycle. **d.** Area fraction of microcracks corresponding to b) and c) for NCA90 and NCTa90 cathodes. The bars represent the statistical distribution of values found for the area fraction of microcrack at different charge/discharge state. **e.** Cross-sectional SEM images of the composite cathode composed of 1:1 mixture of NCA90 and NCTa90 cathodes, charged to 4.3 V to highlight the different extent of microcracking when subjected to identical electrochemical conditions. **f.** Comparison of the normalized unit cell volume for NCA90 and NCTa90 cathodes as a function of cell voltage.

Fig. 7 | Mechanisms that enable superior cycling stability of NCTa90 cathode in comparison with other metal-doped NC cathodes. Comparison of the electrochemical performances of randomly oriented primary particles (NCA90), radially aligned primary particles (NCAB90), and ordered structure (NCTa90, NCW90) in a pouch-type full cell for 2,000 cycles.