

# Quaternary Layered Ni-Rich NCMA Cathode for Lithium-Ion Batteries

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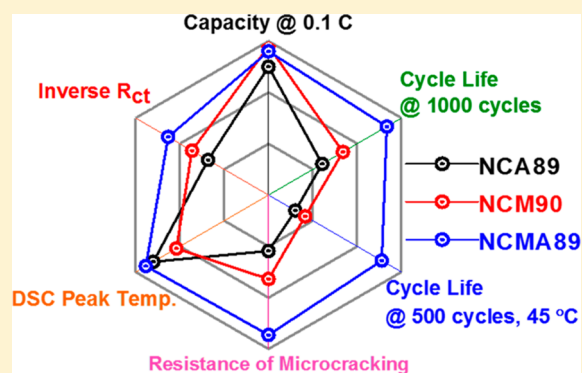
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## Supporting Information

**ABSTRACT:** Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>]O<sub>2</sub> (NCA) and Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>]O<sub>2</sub> (NCM) cathodes have been the archetypes of current high-energy-density cathodes for Li-ion batteries. A hybrid of NCA and NCM cathodes, a quaternary system consisting of Li[Ni<sub>0.89</sub>Co<sub>0.05</sub>Mn<sub>0.05</sub>Al<sub>0.01</sub>]O<sub>2</sub> (NCMA) was benchmarked against NCM and NCA with similar Ni contents. The quaternary NCMA cathode delivered a capacity of 228 mAh g<sup>-1</sup> and outperformed the benchmarking cathodes in long-term cycling stability (85% after 1000 cycles). The reduction in the volume change during deintercalation and the enhanced intrinsic mechanical strength confirmed by the single-particle compression test suppressed the microcrack nucleation and propagation. Microcrack suppression was important because microcracks serve as channels for electrolyte infiltration and lead to subsequent surface degradation of internal surfaces. The proposed NCMA cathode provides extra cycling stability, which is essential for electric vehicles, which require a long battery life and improves the thermal stability of the cathode, which contributes to a safer battery.



With the rapid development of electric vehicles (EVs) and large-scale energy storage systems, the demand for high-energy-density rechargeable batteries has grown dramatically, and the trend is expected to continue. Lithium-ion batteries (LIBs) have become the primary power source for EVs due to their high energy density, good rate capability, and long-term cycling performance. To satisfy the consumer-threshold driving range of 300 miles (480 km) per single charge,<sup>1,2</sup> extensive research for the development of high-capacity cathodes has been carried out in the past decades.<sup>3–10</sup> Among the cathodes developed to date, a series of layered Ni-rich lithium transition metal oxides, Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>]O<sub>2</sub> (NCA) or Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>]O<sub>2</sub> (NCM), are the most promising candidates because they provide high reversible capacity with a long cycle life and high operating potential of 3.6 V vs Li/Li<sup>+</sup>. To further increase the capacity of current NCM and NCA cathodes, the fraction of Ni in the cathodes has been progressively increased;<sup>11–13</sup> however, this approach is limited by the deterioration of capacity retention and thermal stability resulting from excessive Ni enrichment (above  $x = 0.6$  for NCM and 0.8 for NCA). One method for

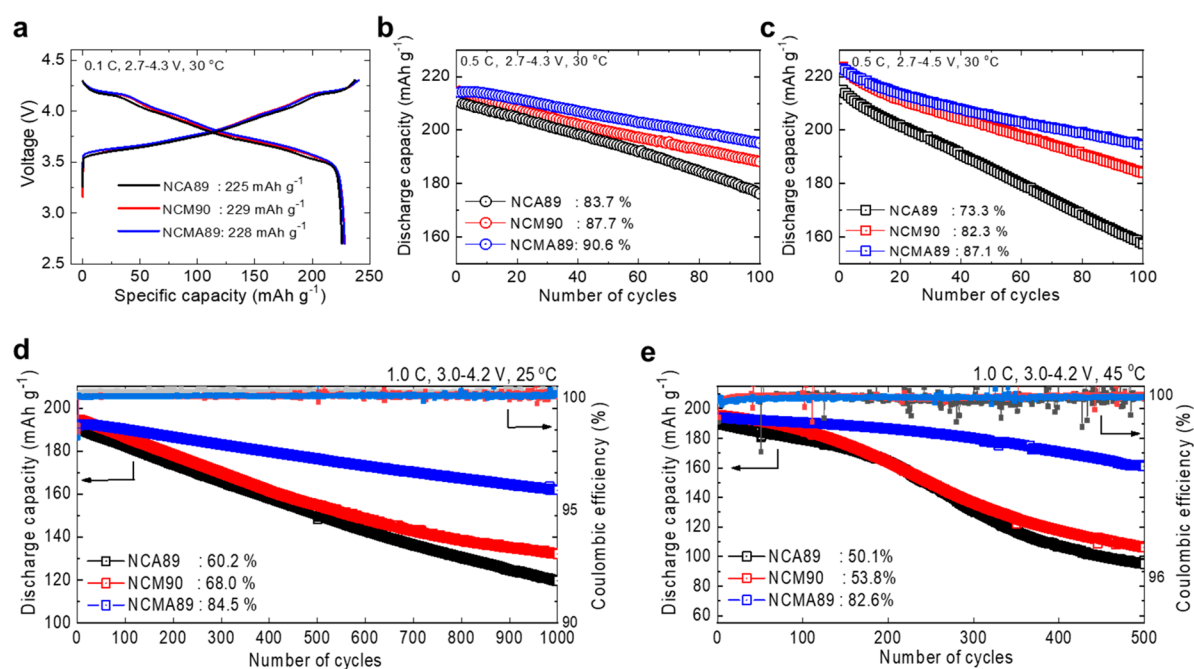
overcoming the obstacles posed by the Ni enrichment strategy is to dope alien metallic ions to pristine NCA or NCM cathodes to improve the structural stability and thus Li<sup>+</sup> intercalation stability.<sup>14–22</sup> Among the various doping metals, Al is the most widely used dopant because of its stabilizing role in the host layered structure. Moreover, it tends to improve the thermal stability owing to the stronger strength of Al–O bonds than those of Ni(Co, Mn)–O bonds.<sup>17–19,23</sup> However, the Al-doping content should be carefully considered because of its nonparticipation in the redox reaction. Therefore, the Al fraction has been limited to a relatively low concentration below 5 mol %. Recently, we demonstrated that Al-doping greatly extends battery life as the 2 mol % Al-doped gradient Li[Ni<sub>0.76</sub>Co<sub>0.09</sub>Mn<sub>0.15</sub>]O<sub>2</sub> cathode retained 95% of its initial capacity after 1000 cycles.<sup>23</sup>

Al-doping clearly improves the cycling stability of a Ni-rich NCM cathode but is accompanied by a concurrent capacity

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**Figure 1.** Comparison of electrochemical performance of the NCA89, NCM90, and NCMA89 cathodes: (a) first cycle voltage profiles for the three cathodes. All cells are cycled with a voltage range of 2.7–4.3 V at 0.1 C and 30 °C in a half-cell using Li metal as an anode. Cycling performance of the three cathodes tested with voltage ranges of (b) 2.7–4.3 and (c) 2.7–4.5 V at 0.5 C and 30 °C. Long-term cycling performance of the NCA89, NCM90, and NCMA89 cathodes using pouch full cells at 1.0 C and (d) 25 and (e) 45 °C with a voltage range of 3.0–4.2 V with mesocarbon microbead graphite as an anode.

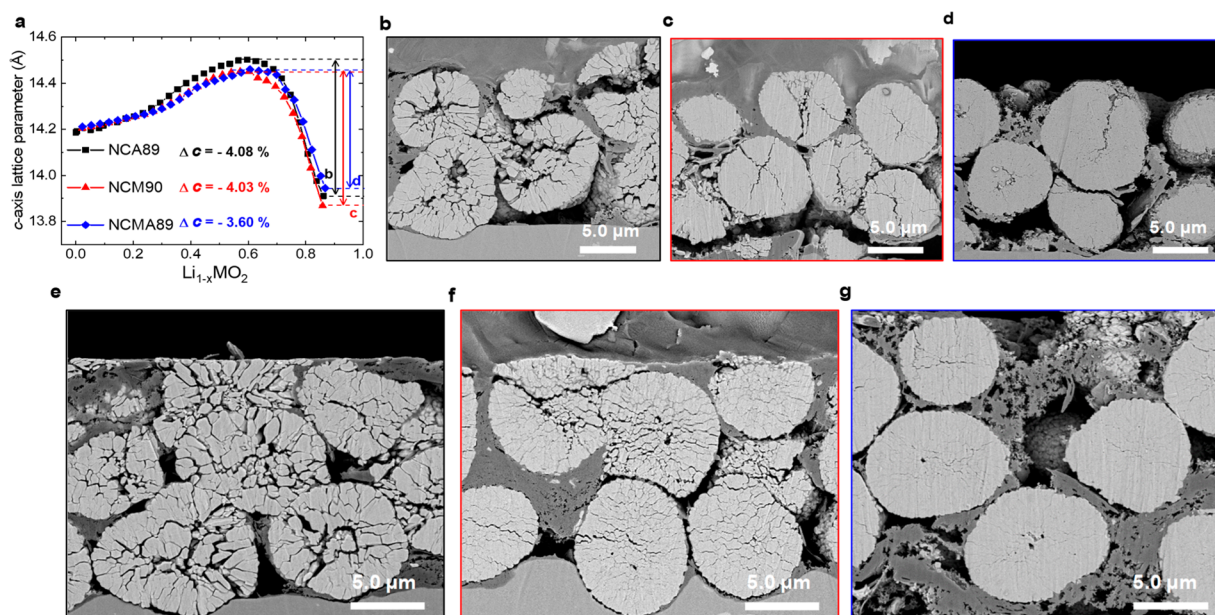
loss when introduced in excess (Figure S1). Here, we report a hybrid NCM and NCA cathode  $\text{Li}[\text{Ni}_{0.89}\text{Co}_{0.05}\text{Mn}_{0.05}\text{Al}_{0.01}]\text{O}_2$  (hereafter referred to as NCMA89) that provides an optimal combination of capacity and cycle life among cathodes with different Al content and whose performance surpasses that of the NCA and NCM cathodes with similar Ni contents. A comparative study of structural and electrochemical properties of  $\text{Li}[\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$  (NCM90),  $\text{Li}[\text{Ni}_{0.885}\text{Co}_{0.100}\text{Al}_{0.015}]\text{O}_2$  (NCA89), and NCMA89 is carried out by investigating bulk and surface structural degradation before and after long-term cycling.

Scanning electron microscopy (SEM) images of the NCA89, NCM90, and NCMA89 cathode particles show that the synthesized cathodes have spherical morphology with an average particle diameter of 10  $\mu\text{m}$  (Figure S2a). There is no essential difference in the size and shape of particles among the three cathodes, implying that particle morphology is an unlikely factor affecting the electrochemical performance of the cathodes. X-ray diffraction (XRD) patterns of the NCA89, NCM90, and NCMA89 cathodes in Figure S2b are indexed to an  $\alpha\text{-NaFeO}_2$  structure with  $R\bar{3}m$  space group, and no impurity phases were observed. Both  $a$ - and  $c$ -axis parameters for the tested cathodes in Table S1 were similar in magnitude.

Figure 1a shows the initial charge–discharge curves of the three cathodes cycled between 2.7 and 4.3 V at 0.1 C (18  $\text{mA g}^{-1}$ ) at 30 °C in 2032 coin-type half-cells. NCM90 delivers a high initial discharge capacity of 229  $\text{mAh g}^{-1}$ . In comparison, the NCMA89 cathode exhibits a slightly reduced capacity of 228  $\text{mAh g}^{-1}$  due to the addition of inactive Al, while the NCA89 cathode produces a yet lower capacity of 225  $\text{mAh g}^{-1}$ . Interestingly, the NCMA89 cathode, as shown in Figure 1b, exhibits a substantial improvement in capacity retention at 90.6% after 100 cycles compared to the NCA and NCM cathodes, although the Al-doping level was limited to a mere 1

mol %. The NCM90 and NCA89 cathodes exhibit capacity retentions of 87.7 and 83.7%, respectively, during the same cycling period. Increasing the upper cutoff voltage to 4.5 V further substantiates enhancement of the cycling stability by the addition of Al to NCM90 as NCMA89, NCM90, and NCA89 maintain 87.1, 82.3, and 73.3% of their respective initial capacities after 100 cycles at 0.5 C (Figure 1c). Moreover, the NCM90 cathode apparently exhibits better Li intercalation stability than the NCA89 cathode when charged to 4.3 and 4.5 V. The improved cycling stability is emphasized during long-term cycling of the cathodes in aluminum pouch-type full cells using a graphite anode. As shown in Figure 1d, the full cell with the NCMA89 cathode exhibits outstanding capacity retention of 84.5% after 1000 cycles, while NCM90 and NCA89 cathodes retain only 68.0 and 60.2% of their respective initial capacities, respectively. The cycling stability of the NCMA89 cathode at an elevated temperature (45 °C) is much better than that of the NCM90 and NCA89 cathodes (Figure 1e). After 500 cycles, 82.6% of the initial capacity of NCMA89 is retained, while that of the NCM90 and NCA89 cathodes is limited to 53.8 and 50.1%, respectively.

To study the effect of the  $\text{H}_2 \leftrightarrow \text{H}_3$  phase transition,  $dQ/dV$  profiles were obtained by numerically differentiating the charge–discharge curves (Figure S3a,b). All three Ni-rich cathodes undergo multiphase transitions during  $\text{Li}^+$  removal and insertion. The intensity changes of the redox peaks at  $\sim 4.2$  V corresponding to the  $\text{H}_2 \leftrightarrow \text{H}_3$  phase transition during cycling correlate well with the relative cycling stability of the three cathodes. For both NCA89 and NCM90 cathodes, the deteriorating reversibility of the redox peak is clearly observed as the  $\text{H}_2 \leftrightarrow \text{H}_3$  peak intensity gradually decreases during cycling, whereas that of the NCMA89 cathode remains nearly unchanged during the same cycling period. The relative reversibility of the  $\text{H}_2 \rightarrow \text{H}_3$  phase transition can be better

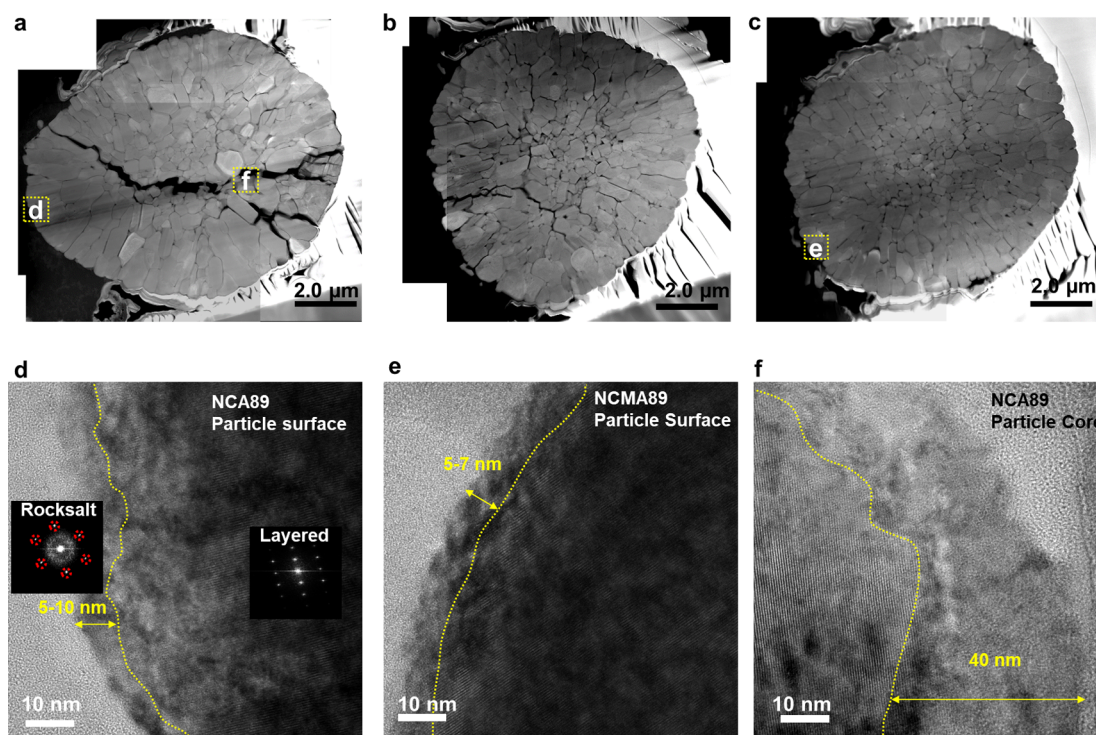


**Figure 2.** (a) *c*-axis lattice parameters of the NCA89, NCM90, and NCMA89 cathodes as a function of the extracted lithium. Cross-sectional SEM images of the fully charged cathodes at first cycle ( $\text{Li}_{1-x}\text{MO}_2$ ,  $x = 0.88$ ): (b) NCA89, (c) NCM90, and (d) NCMA89. Cross-sectional SEM images of the fully discharged cathodes after 1000 cycles: (e) NCA89, (f) NCM90, and (g) NCMA89.

seen in Figure S3c,d, which illustrates the normalized integrated peak intensity against the cycle number. The superior structural stability of the NCMA89 cathode is pronouncedly advertised when cycled at 4.5 V as the H2  $\rightarrow$  H3 peaks for NCA89 and NCM90 cathodes decay at a much faster rate in comparison to that for the NCMA89 cathode (Figure S3b,d). To explicitly demonstrate the deleterious effect of the H2  $\rightarrow$  H3 phase transition, which causes highly anisotropic strain in the deeply charged state, a series of in situ XRD experiments were performed while charging the three cathodes from 3.0 to 4.5 V at a constant current density of 36 mA g<sup>-1</sup>. The lattice parameters estimated from the XRD data are plotted as a function of the state of charge in Figures 2a and S4. As equal amounts of Li ions are extracted from each cathode, the *a*-axis parameter continuously decreases. The magnitude of the overall lattice parameter reduction,  $\Delta a$ , is 2.1–2.2% for the three cathodes (Figure S4). However, in the *c*-direction, the lattice parameter gradually increases and then contracts sharply at the onset of the H2  $\rightarrow$  H3 phase transition. This abrupt contraction in the *c*-direction, which amounts to  $\sim 4\%$ , undermines the mechanical integrity of the secondary particle. The mechanical strain triggered by this phase transition is further aggravated by its anisotropy because the contraction in the *a*-direction is limited to  $\sim 0.5\%$  while the unit cell concurrently contracts by 4% in the *c*-direction during the phase transition. Hence, the extent of the *c*-axis contraction during the H2  $\rightarrow$  H3 phase transition critically determines the magnitude and the distribution of the local internal strain.  $\Delta c$  for the NCMA89 cathode was considerably lower than that of the NCA89 and NCM90 cathodes (Figure 2a). The effect of the reduced strain for the NCMA89 cathode is manifested by reduced or lack of microcracks in the secondary particles of the NCMA89 cathode in its deeply charged state ( $x = 0.88$ ), whereas visible microcracks were observed in the cross-sectional images even in the first charge state for the other two cathodes (Figure 2b–d). In the case of the NCA89 cathode, the microcracks that nearly fractured the secondary

particles were observed at  $x = 0.88$ , which is in agreement with the noticeably faster capacity fading observed when the cathode cycled at 4.5 V (Figure 2b). The cross-sectional images of both 1000 cycled NCA89 and NCM90 cathode particles fractured along the interparticle boundaries, exhibited almost pulverizing the cathode particles (Figure 2e,f), whereas the NCMA89 secondary particles remained mostly free of any microcracks (in the discharged state) even after performing 1000 cycles (Figure 2g). The cross-sectional SEM images of the cycled cathodes suggest that the introduction of a minute amount of Al together with Mn not only reduces the magnitude of the anisotropic strain of the NCMA89 cathode in the deep charge state but also appears to increase the interparticle boundary strength, which is plausible because Al–O bonds provide strong bonding.<sup>13,24,25</sup> To directly verify the enhancement of the fracture toughness of the NCMA cathode, the fracture strength of a single particle from each cathode was measured using a microcompression tester. Shown in Figure S5, the NCMA89 particle withstood a force of 22.9 mN, which amounts to a particle strength of 185.7 MPa. In comparison, the failure load of the NCA89 particle was limited to only a 12.9 mN force (particle strength of 125.5 MPa), while the NCM90 particle had a slightly larger particle strength (force of 14.0 mN and particle strength of 137.2 MPa) than that of NCA89. It appears that the simultaneous presence of both Al and Mn ions in the NCMA89 cathode improves the mechanical stability, as evidenced by the microcompression test and the microcracking extent. The particle strength data also correlate well with the long-term cycling behavior of the three cathodes, and the Mn–Al-doping toughens the boundaries among primary particles to retard microcrack formation during the deleterious phase transition.<sup>26,27</sup>

The mechanical stability of the NCMA89 cathode (i.e., retardation of the microcrack nucleation and propagation) brings an additional benefit because the microcracks serve as channels for electrolyte infiltration into the particle interior. The infiltrated electrolyte attacks the internal exposed surface



**Figure 3.** Mosaic scanning TEM images of the cycled cathodes after 100 cycles: (a) NCA89, (b) NCM90, and (c) NCMA89. High-resolution TEM images of surface primary particles: (d) NCA89 and (e) NCMA89 cathodes after 100 cycles. The high-resolution TEM images in (d,e) correspond to the regions marked by yellow boxes in (a,c). Fourier transforms of the marked regions by numerals are shown in (d) as insets. (f) High-resolution TEM image of a primary particle in the core region of the cycled NCA89 cathode marked by a yellow box in (a).

and increases the cathode's impedance through the continuous accumulation of a passivating NiO-like impurity layer on the particle surfaces.<sup>28,29</sup> Electrochemical impedance spectroscopy (EIS) was used to measure the impedance at the charged state. The impedance growth anticipated from the cycling data was clearly observed for the three cathodes (Figure S6a–c). The three cathodes exhibit a similar surface film resistance, which hardly changes during the entire cycling duration. Meanwhile the charge transfer resistance ( $R_{ct}$ ) of the NCA89 cathode increases from 6.3 to 55  $\Omega$  after 100 cycles, whereas the NCMA89 cathode has a relatively stable  $R_{ct}$  value at 33  $\Omega$  after same cycling period (Figure S6d). The  $R_{ct}$  values from EIS data verify that the electrolyte infiltration into the particle interior is substantially reduced in the NCMA89 cathode because the three cathodes have a similar particle diameter and the damage of the external particle surface is likely identical in extent for the three cathodes. The relative electrolyte damage was also confirmed using TEM analysis of the cycled cathodes. The dark-field STEM image of the cycled NCA89 cathode shows a major crack traversing the entire particle and nearly fracturing the secondary particle into two halves (Figure 3a). Although several cracks in the cycled NCM90 cathode reached the particle surface and expedited the electrolyte infiltration (Figure 3b), the secondary particle remained mechanically intact. In turn, no visible cracks were observed in the NCMA89 cathode, attesting to its superior mechanical stability (Figure 3c). While assessing the surface structure degradation using high-resolution TEM (HR-TEM), a typical NiO-like surface layer that increases the charge transfer resistance was observed on the surface of the cycled NCA89 cathode, as shown in Figure 3d. Local Fourier transform images of the cycled cathode show that the surface rocksalt layer was confined to a

thickness of 5–10 nm. Figure 3e shows the surface damaged layer of the cycled NCMA89 cathode whose thickness was 5–7 nm, demonstrating that the extent of the impedance-increasing surface damage was roughly the same for the three cathodes. However, the HR-TEM image of an interior grain along the microcrack in the NCA89 and NCM90 cathodes reveals that the rocksalt layer was substantially thicker (NCA89: ~40 nm; NCM90: ~25 nm) in Figures 3f and S7 compared to that found on the surface grain (5–10 nm). It appears that the exposed interior surfaces on the interior primary particles are relatively more susceptible to the electrolyte attack. Once the microcracks originating in the particle core extend to the external surface during charging (Li removal phase) and thereby allow electrolyte infiltration, crack faces are exposed to electrolyte attack. These internal surfaces are more vulnerable to electrolyte attack compared to the external surfaces as Li migration out of the particle core likely leaves the particle interior in a Li-deficient state, which is thermodynamically unstable and predisposed to phase transformation to the rocksalt state.<sup>30</sup> The TEM analysis in agreement with the EIS result, i.e., the  $R_{ct}$  buildup observed in the NCA89 cathode, mostly stems from the degradation of the interior surface exposed to the electrolyte through the microcracks. Thus, the retardation of microcrack formation in the NCMA89 cathode reinforces not only the mechanical integrity of the secondary particles in the Ni-rich layered cathodes but also the chemical stability against electrolyte attack by preventing infiltration of the electrolyte into the particle interior.

Recently, it was proposed that oxygen release from the lattice during deintercalation promotes transition metal dissolution and destabilizes the crystal structure of the layered

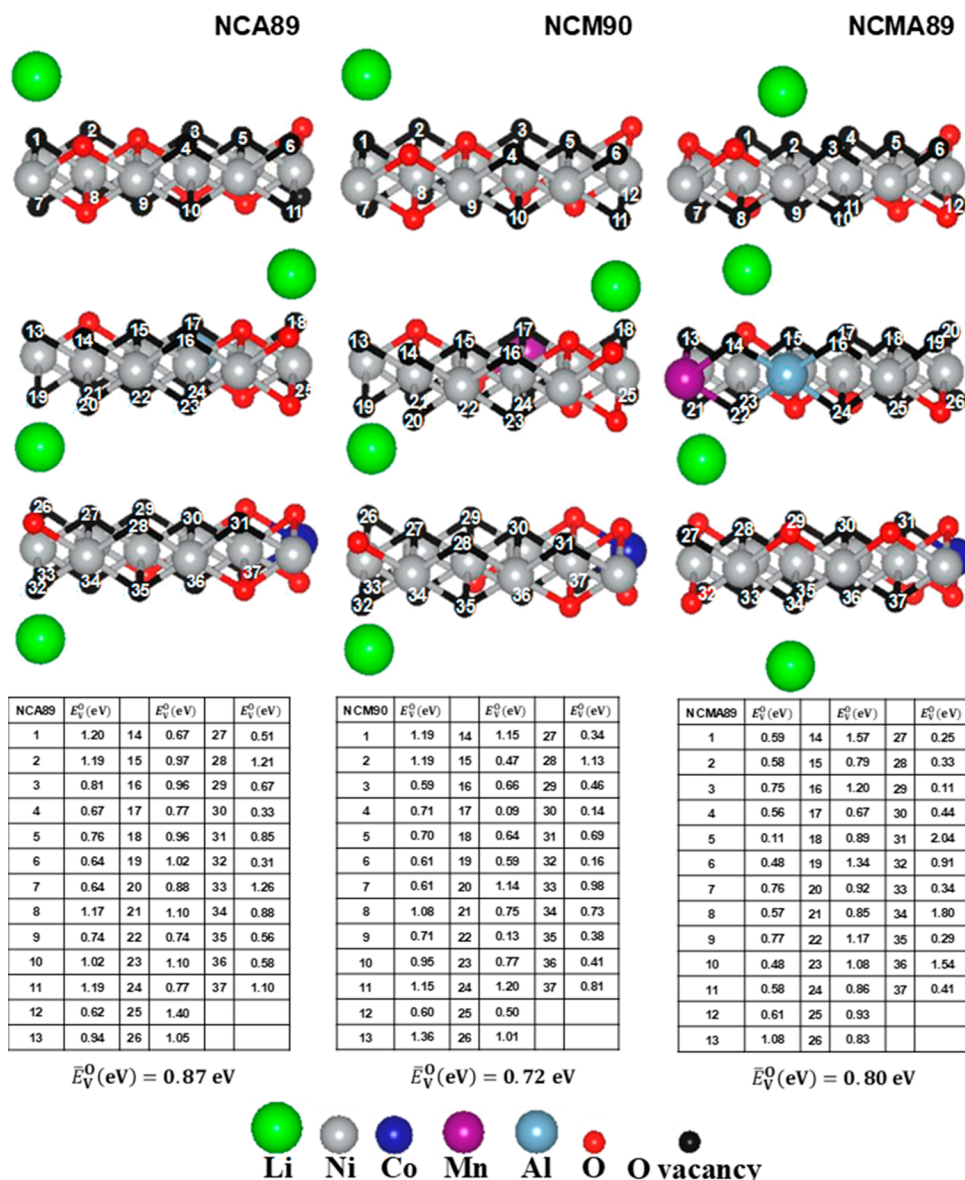
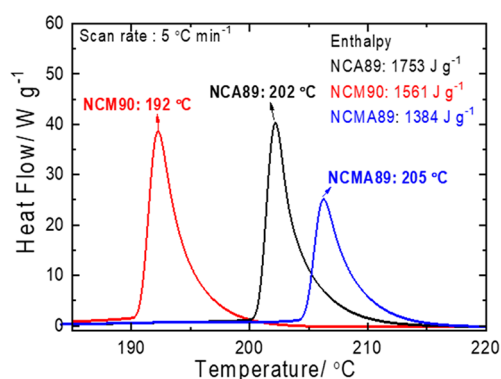


Figure 4. Side views of atomic structures and calculated oxygen vacancy formation energy:  $E_V^0$  for the labeled oxygen sites and average vacancy formation energies and  $\bar{E}_V^0$  for the NCA89, NCM90, and NCMA89 cathodes with 89% of Li ions removed from the lattice.

cathodes.<sup>31,32</sup> Density functional theory (DFT) calculations were employed to calculate the lithium and oxygen vacancy energies of the three cathodes in order to elucidate the Al-doping effect on the intrinsic structural stability of the three cathodes. To compute the average values of Li vacancy formation energies ( $\bar{E}_V^{\text{Li}}$ ), we considered fully lithiated NCA89, NCM90, and NCMA89 cathodes. Li vacancy energies of the cathodes were calculated for 16 different vacancy sites (alphabet marking) shown in Figure S8 and Table S2. The respective average Li vacancy formation energies for the NCA89, NCM90, and NCMA89 cathodes were 3.96, 3.94, and 3.97 eV. These nearly identical Li vacancy energies suggest that the energy required for Li intercalation/deintercalation for the three cathodes is nearly equal for the three cathodes because of their similar compositions, which is in agreement with the fact that the initial discharge capacities delivered by the three cathodes were almost the same. The difference in the structural stability is, however, clearly observed in the O vacancy energy calculated with 89% of Li atoms removed from each lattice.

The respective O vacancy energies for the three cathodes in the delithiated state were calculated for 37 different O sites, as shown in Figure 4, and the O vacancy energies are also listed in the accompanying tables. The average O vacancy energies were 0.87, 0.72, and 0.80 eV for the NCA89, NCM90, and NCMA89, respectively, indicating that the oxygen atoms are least likely released from the NCA89 cathode, as conjectured from the strong binding energy of Al–O bonds. The density functional calculation provides a strong basis for confirming the relative high structural stability of the NCA89 cathodes, in general, compared to the NCM90 cathodes. Incidentally, the O vacancy energy for the NCMA89 cathode is an average of the vacancy energies of the NCA89 and NCM90 cathodes so that the NCMA89 cathode partially benefits from the improved structural stability in the delithiated state by having Al ions in its lattice.

Thermal stability of a cathode is also important to battery safety. As seen in the differential scanning calorimetry (DSC) data in Figure 5, the peak temperature of the exothermic



**Figure 5.** DSC profiles for the NCA89, NCM90, and NCMA89 cathodes measured in their second charged state ( $\text{Li}_{0.3}\text{MO}_2$ ) in the presence of 1.2 M  $\text{LiPF}_6$ , EC:EMC = 3:7 by vol % with 2 wt % VC.

reaction for the NCA89 cathode was 202 °C, with heat generation of  $1753 \text{ J g}^{-1}$ , while the NCM90 cathode exhibited a peak temperature of 192 °C and heat generation of  $1561 \text{ J g}^{-1}$ . In comparison, NCMA89 demonstrates improved thermal stability with its exothermic peak temperature at 205 °C and heat generation of  $1384 \text{ J g}^{-1}$ . The improved thermal property of the NCMA89 cathode is ascribed to the decreased amount of microcracks, which reduces the amount of the infiltrated electrolyte. The DSC result confirms that the NCMA89 cathode is structurally stable due to the synergetic effect of Al and Mn ions stabilizing the layered structure and delaying the thermally induced phase transitions.

We have demonstrated that a hybrid of Ni-rich NCA and NCM cathodes, a quaternary system consisting of  $\text{Li}[\text{Ni}_{0.89}\text{Co}_{0.05}\text{Mn}_{0.05}\text{Al}_{0.01}]\text{O}_2$ , is capable of outperforming both NCA89 and NCM90 with similar Ni contents in terms of cycling and thermal stabilities. In situ XRD analysis shows that the Al-doping effect is rather subtle as the volume contraction/expansion during the H2  $\leftrightarrow$  H3 phase transition is slightly reduced by Al-doping of the NCM cathode. This reduction in volume change, however, together with the enhanced intrinsic mechanical strength directly confirmed by the single-particle compression test, is sufficient to suppress microcrack nucleation and propagation. It was shown that the microcrack suppression observed in the NCMA89 cathode was the key to ensure its long-term cycling stability as microcracks serve as channels for electrolyte infiltration and lead to subsequent surface degradation of internal surfaces. The proposed Ni-enriched NCMA cathode provides extra cycling stability, which is essential in the case of EVs that require a long battery life (>500 cycles). The structural stability gained by Al-doping also improved the thermal stability of the cathode, which contributes to a safer battery.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsenergylett.8b02499](https://doi.org/10.1021/acsenergylett.8b02499).

Experimental methods, electrochemical performance data, lithiated oxide SEM image, XRD patterns, lattice parameters of cathodes, Nyquist plots as a function of cycles, microcompression tests, TEM image of the cycled cathode, and simulation data for the formation energy (PDF)

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### Notes

The authors declare no competing financial interest.

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