

# High Nickel and No Cobalt—the Pursuit of Next-Generation Layered Oxide Cathodes

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## ABSTRACT

The prosperity of the electric vehicle industry is driving the research and development of lithium-ion batteries. As one of the core components in the entire battery system, cathode materials are currently facing major challenges in pushing higher capacity up to their theoretical limits and transitioning away from the unaffordable metals. To meet these requirements, the search for next-generation cathode materials has shifted to high-nickel and cobalt-free cathodes. In this review, we distinctly pointed out the shortcomings of cobalt in stabilizing layered structures, and systematically summarized the recent efforts to eliminate cobalt and achieve higher nickel content in layered

cathode materials. Finally, a reasonable prospect is put forward for further development of layered cathode materials and other promising candidates, which is likely to spur a wave of efforts toward developing high-performance and low-cost Li-ion batteries.

## Introduction

Cobalt (Co) has a long-term usage history in the development path of cathode materials in lithium-ion batteries (LIB), dating from the first commercialized  $\text{LiCoO}_2$  (LCO) in 1991 to recently sought-after nickel (Ni)-rich  $\text{Li}[\text{Ni}_x\text{Co}_y(\text{Mn or Al})_{1-x-y}]\text{O}_2$  ( $x \geq 0.5$ , NCM or NCA).<sup>1-5</sup> Although the proportion of Co in the cathode composition has been greatly reduced, it is still heavily used due to the extremely expansionary battery demands from the electric vehicle (EV) market.<sup>6-10</sup> In recent years, the price of Co has increased several times, driving up the cost of cathode raw materials.<sup>11-13</sup> Furthermore, Co is a resource-scarce element on earth and is mainly mined in a few African countries.<sup>14,15</sup> There have long been ethical and political dilemmas in its mining industry, which has resulted in an unreliable supply chain.<sup>16</sup> In the long run, this localized and limited material supply will inevitably lead to the unsustainable use of Co in batteries.<sup>17-20</sup> These objective facts and awkward situations are pushing a new trend of emerging low Co and Co-free materials as next-generation cathodes.

Admittedly, as one of the most successful applications of LIBs, the development of EVs has put forward ever-increasing performance requirements for the next-generation

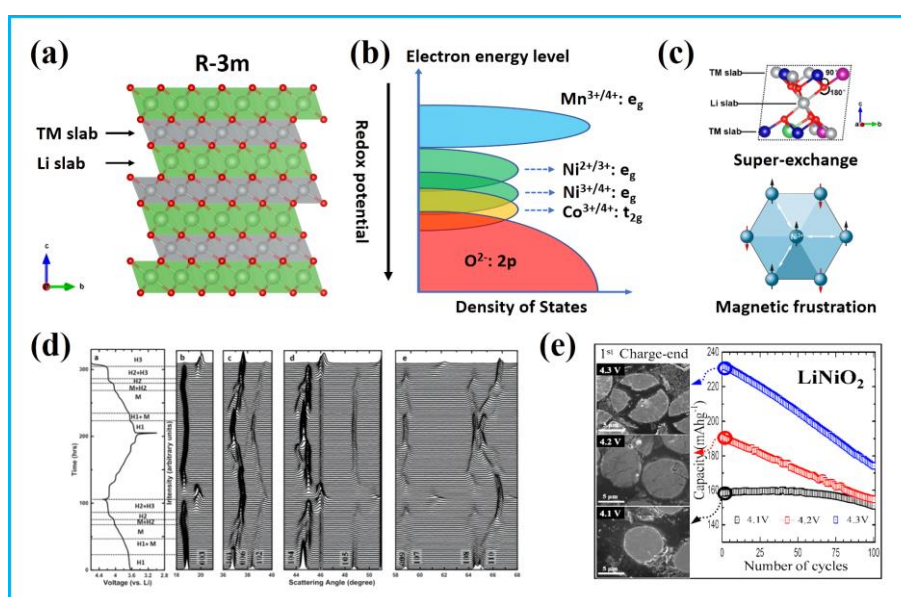
battery materials.<sup>22-25</sup> According to the roadmap published by the U.S. Department of Energy (DOE) and the U.S. Advanced Battery Consortium, automotive batteries need to reach an energy density of 300 Wh kg<sup>-1</sup> at cell level or 235 Wh kg<sup>-1</sup> at pack level by 2035.<sup>26</sup> Although the expectation is high, the current commercial LIBs yet only deliver 150-170 Wh kg<sup>-1</sup> at the pack level, which is the crux of mileage anxiety of EVs.<sup>27</sup> Since the cathode component pulls down the overall energy density of battery, there is an urgent need to further improve the cathode capacity. Among many cathode materials, Layered NCM has been considered as the most viable choice for high energy density batteries. It is well acknowledged that the Ni redox in NCM cathodes dominates the capacity contribution, and thus increasing Ni content (Ni > 0.8) has naturally been regarded as a straightforward strategy towards high energy density batteries.<sup>28-30</sup>

Eliminating Co and increasing Ni in layered NCM cathodes conform to the future demands of LIBs and have become the preferred development strategy of battery manufacturers.<sup>31</sup> LiNiO<sub>2</sub> (LNO) has thus re-emerged in the public consciousness as a promising starting material for Co-free cathodes, despite the fact that it was long overlooked due to numerous inherent issues such as off-stoichiometry, Li/Ni exchange, Ni<sup>3+</sup> instability, poor thermal stability, low coulombic efficiency, multiple phase transitions, and fast capacity fading upon cycling.<sup>32,33</sup> To alleviate these issues of LNO, foreign heteroatom doping, such as Co, Mg, Al, Mn, and others, has generally been considered a good option for stabilizing the layered structure and enhancing the electrochemical reversibility.<sup>34-36</sup> Besides, Co as the most successful substitution can

be incorporated into LNO at high enough levels. For the aim of eliminating Co, it is very necessary to clarify its roles in the Ni-rich cathodes.

Cathode materials has undergone a transition from low Ni, high Co compositions to high Ni, low Co and finally to Co free compositions in order to achieve higher energy and lower cost.<sup>37,38</sup> This requires a change in traditional mindset and by focusing on the problems caused by high Ni and Co deficiency. In this brief review, we start from LNO series and re-organize the recent development of Co-free high-Ni layered oxide materials. The mechanism of Co in layered NCM cathode is discussed in depth, and the recent achievements regarding stabilization of Co-lean cathodes are briefly summarized. In addition, a reasonable outlook for the further development of high capacity Co-free cathodes was also provided with a wish to spark the light on future innovations within the field.

## Fundamentals of LiNiO<sub>2</sub>



**Figure 1.** (a) Model of the layered structure with  $R-3m$  space group. (b) Band structure illustrations of the various redox couples. (c) Schematic diagram of super-exchange and magnetic frustration. Reprinted with permission from ref. 49. Copyright 2017, American Chemical Society; Reprinted with permission from ref. 50. Copyright 2020, The American Association for the Advancement of Science. (d) Charge/discharge curves of LNO and corresponding in-situ XRD data. Reprinted with permission from ref. 54. Copyright 2018, The Electrochemical Society. (e) Prominent crack generation of LNO after extended cycles. Reprinted with permission from ref. 59. Copyright 2017, American Chemical Society.

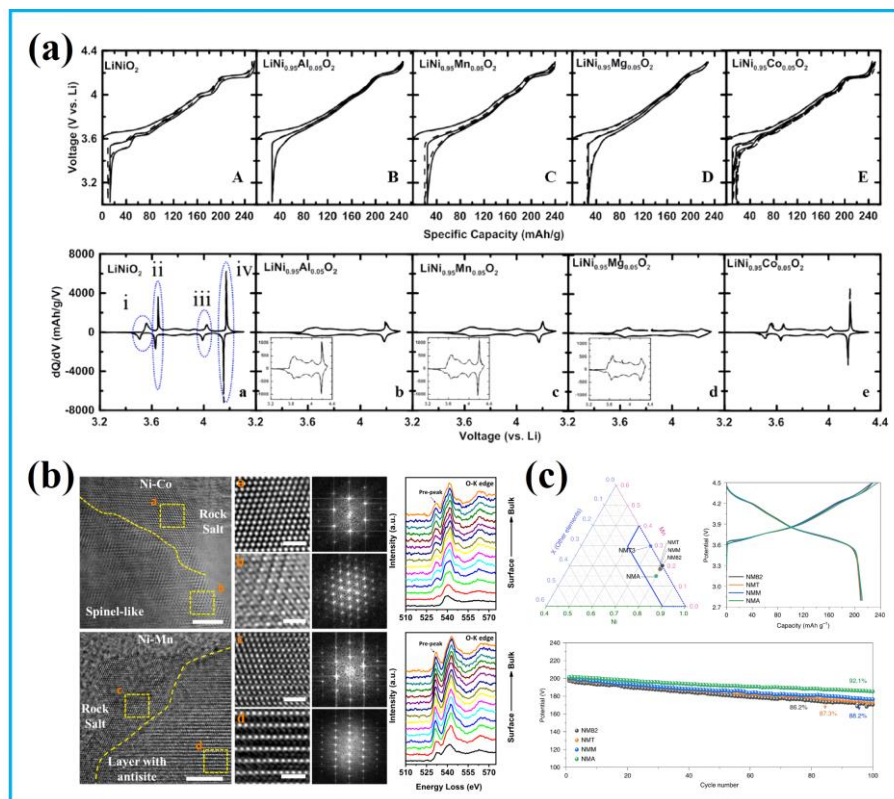
As the prototype material of Ni-rich layered cathodes, it is necessary to have a comprehensive understanding about LNO. LNO with the  $\alpha$ - $\text{NaFeO}_2$ -type hexagonal layered crystal structure ( $R-3m$  space group, Fig. 1a) was first reported in the 1950s, which is part of the solid solution obtained during simultaneous lithiation and oxidation of Ni.<sup>39</sup> In spite of the discovery of LNO was much earlier than LCO, its electrochemical applications started in the late 1980s.<sup>40</sup> As a cathode material in LIBs, LNO has the same high theoretical energy density as LCO due to the same layered structure, but with a lower average redox potential. In Fig. 1b, the  $e_g$  band of  $\text{Ni}^{3+/4+}$  just has a small orbital overlap with the 2p band of  $\text{O}^{2-}$ , indicating that LNO can achieve a higher degree of charge/discharge without the apparent release of oxygen from the lattice which is not the case in  $t_{2g}$  band of  $\text{Co}^{3+/4+}$ .<sup>41</sup> The reported LNO presented a capacity of over 220 mAh  $\text{g}^{-1}$  at the low upper voltage of 4.3 V versus  $\text{Li}^+/\text{Li}$ .<sup>42</sup> While the same condition, LCO only had a capacity of 150 mAh  $\text{g}^{-1}$ . However, LCO

eventually boomed the development of LIBs as a power source for portable devices, while LNO has been delayed in commercialization despite its high specific capacity.

In fact, perfect layered LNO is hard to achieve, and it is always accompanied by twin intricate disorders in the synthesis process, namely off stoichiometry and Li/Ni exchange.<sup>43-47</sup> The real formula of lithium nickelate should be denoted as  $\text{Li}_{1-z}\text{Ni}_{1+z}\text{O}_2$  ( $z > 0$ ). The off stoichiometry and Li/Ni exchange are generally considered to be caused by the following various reasons: (a) the loss of lithium from the host structure during high-temperature calcinations due to the high vapor pressure of lithium; (b) the inevitable presence of  $\text{Ni}^{2+}$  ions in the material resulting from the reduction of the  $\text{Ni}^{3+}$  ions at high temperatures; (c) Excess  $\text{Ni}^{2+}$  ions trend to reside in the lithium slab owing to the slight size difference between the  $\text{Li}^+$  (0.76 Å) and  $\text{Ni}^{2+}$  (0.69 Å) ions.<sup>48</sup> Besides, the recent reports also pointed out that the Li/Ni exchange is very likely to be controlled by super-exchange interaction and magnetic frustration (Fig. 1c).<sup>49-51</sup>  $\text{Ni}^{2+}$  ions in the lithium slab will block the diffusion path of  $\text{Li}^+$  ions, decreasing the rate performance and coulombic efficiency of materials. Currently, the modern synthesis method enables the optimization of the Li/Ni disorder within 1-2%, but this also creates great difficulties for reproducible synthesis and requires a lot of effort to carefully control the experimental conditions (oxygen, temperature and time).<sup>52,53</sup> Furthermore, as shown in Fig. 1d, X-ray diffraction (XRD) test indicates that LNO cathode undergoes multi-step phase transitions during  $\text{Li}^+$  ion intercalation and deintercalation ( $\text{H1} \rightarrow \text{M} \rightarrow \text{H2} \rightarrow \text{H3}$ , H: hexagonal phase, M: monoclinic phase).<sup>54,55</sup> Especially, the transition of  $\text{H2} \rightarrow \text{H3}$  at above 4.15 V will induce huge volume contraction owing to the formation of  $\text{Ni}^{4+}$

with smaller ionic radius, potentially resulting to the occurrence of crack.<sup>56,57</sup> Various degradation behaviors involving surface structure deterioration, oxygen release, and electrolyte decomposition will occur as the results of the undesirable side reactions when the highly oxidized Ni<sup>4+</sup> cations on the material surface contact with the organic electrolyte.<sup>58</sup> In addition, the generation of crack (Fig. 1e) will continue to expose fresh material surface to electrolyte, further exacerbating the breakdown of electrode.<sup>59</sup> In the face of the practical needs of EVs, stability is particularly important under the premise of meeting the energy density. Overall, the inferior structural stability is the main reason impeding the large-scale commercial applications of LNO.

### The anatomy of Co effectiveness in Ni-rich materials



**Figure 2.** (a) Voltage profiles and corresponding differential capacity plots ( $dQ/dV$ ) of  $\text{LiNi}_{1-n}\text{Mn}_n\text{O}_2$  ( $n = 0$  or  $0.05$ , and  $M = \text{Al, Mn, Mg, and Co}$ ). Reprinted with permission from ref. 61. Copyright 2019, The Electrochemical Society. (b) HRTEM and EELS characterizations of Ni-Co64 and Ni-Mn64. (c) Compositional phase plots, charge/discharge profiles, and cycling performance patterns of various Ni/Mn-based electrode materials. (b) and (c) Reprinted with permission from ref. 63. Copyright 2021, UChicago Argonne, LLC, Operator of Argonne National Laboratory under exclusive licence to Springer Nature Limited.

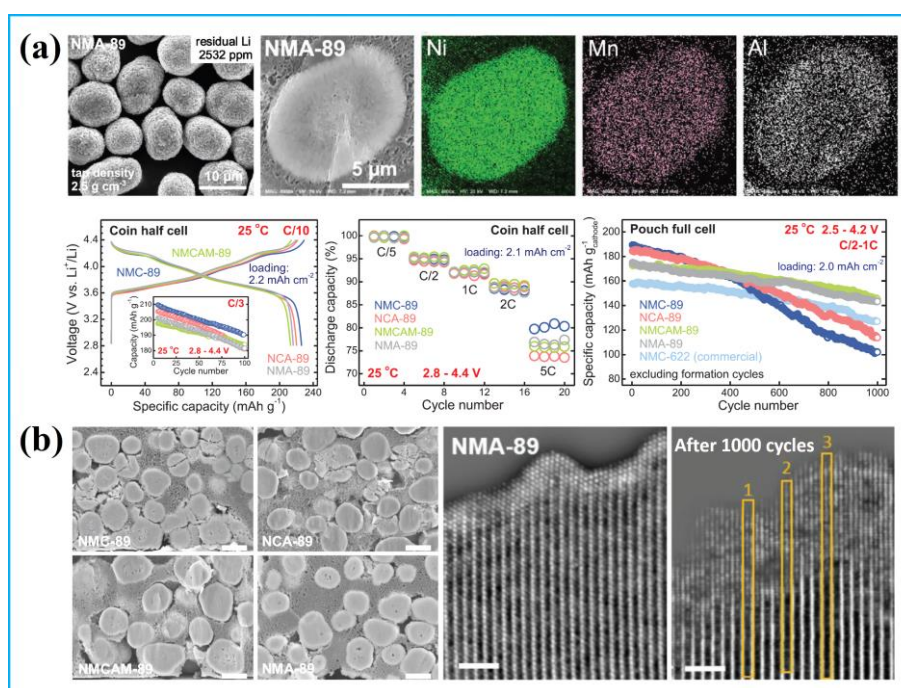
Over the years, many explorations have been carried out to improve the synthesis process of LNO and enhance its structure stability. Consequently, element substitution strategy is widely accepted to be an effective approach that can overcome the synthesis difficulties of LNO. In recent years, the prosperity of NCM and NCA in practical applications is a successful template, in which multiple elements work together to achieve a performance combination. It is not difficult to find that Co is a vital substituted element for Ni-based layered cathodes. According to the previously-mentioned magnetic frustration theory,  $\text{Co}^{3+}$  ions do not have a magnetic moment and can help relieve the magnetic frustration in the transition metal layer. Hence, they will largely inhibit Li/Ni disorder and enhance the reversible lithium de/intercalation, thereby improving the original electrochemical performance.<sup>60</sup>

However, Li et al. recently reported that the efficacy of Co in high-Ni layered oxides is not good as other dopants (such as Mg, Mn and Al).<sup>61</sup> Similar amounts of  $\text{Ni}^{2+}$

disorder can be obtained when the LNO is substituted with 5% Mg, Al and Co, implying that Co cannot achieve an extra reduction of cation mixing. Moreover, as shown in Fig. 2a, 5% Co substitution is not enough effective in suppressing the multiphase transition during the electrochemical process compared with Mg, Mn and Al. Actually, based on the cycling tests in this work, they also demonstrated that even 15% Co substitution used in commercial NCA material could not improve capacity retention compared with Co-free  $\text{LiNi}_{0.95}\text{Al}_{0.05}\text{O}_2$ . Another previous study indicated that when 30% Co is added into LNO, the electrode shows the smooth V vs. Q curves and could productively suppress the phase transition.<sup>62</sup> Nevertheless, Liu et al. found that the introduction of higher 40% Co still cannot prevent the fast structure degradation of cathode by the characterization of high-energy XRD and aberration-corrected high-resolution transmission electron microscopy (HRTEM).<sup>63</sup> They carefully investigated the physical properties and electrochemical performance of Ni-rich cathodes with 40% Mn and Co, respectively. As displayed in Fig. 2b, it is clear that the bulk structure of Ni-Co64 occurs severe cation mixing and has transformed into spinel-like structure after 100 cycles. Furthermore, the line-scan electron energy loss spectroscopy (EELS) shows the significant oxygen loss from surface through the interior of the material.<sup>64,65</sup> However, in the same case, Ni-Mn64 exhibits the stable electrochemical performance, despite the increase of some Li/Ni disorders and the loss of few capacity and rate capability. The HRTEM images show that the bulk area is remain layered structure, and the line-scan just exhibit the oxygen loss on the material surface. According to the obtained experimental results, Liu et al. reasonably presented the potential development route of

Ni/Mn-based electrode materials, such as  $\text{LiNi}_{0.79}\text{Mn}_{0.2}\text{Mg}_{0.01}\text{O}_2$  (NMM),  $\text{LiNi}_{0.79}\text{Mn}_{0.2}\text{Ti}_{0.01}\text{O}_2$  (NMT) and  $\text{LiNi}_{0.8}\text{Mn}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NMA). As shown in Fig. 2c, these all show high capacities of  $210 \text{ mAh g}^{-1}$  at a high voltage of 4.5 V and possess superior cyclic stability than Co-reliant Ni-rich cathodes. The latest studies have confirmed that Co is weak in stabilizing the layered structure of Ni-rich cathodes.

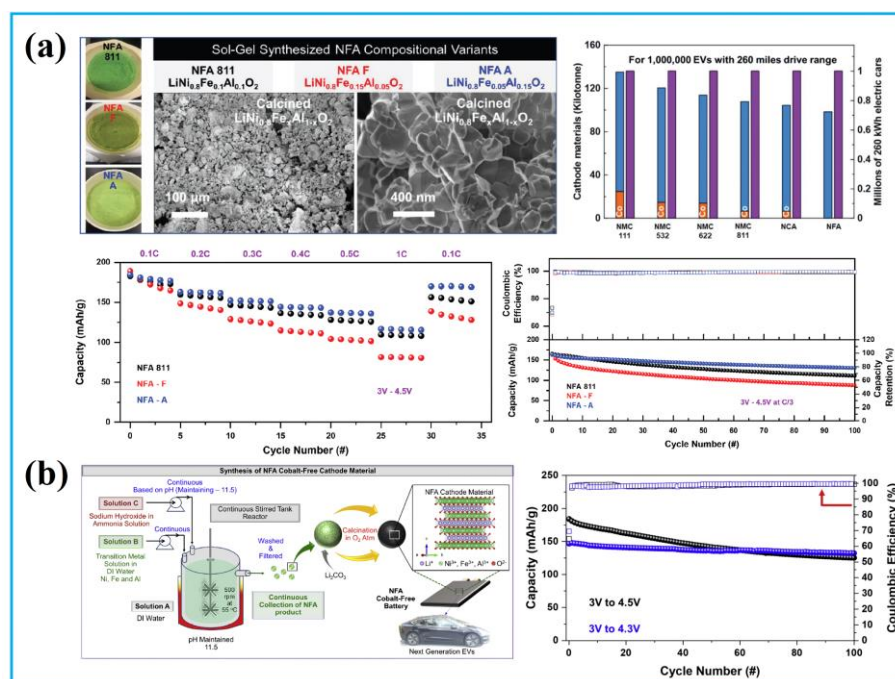
### Recently developed Co-free materials



**Figure 3.** (a) Cross-sectional SEM/EDX images and electrochemical performance of NMA-89. Adapted with permission from ref. 66. Copyright 2020, Wiley-VCH. (b) Cross-sectional SEM images and HTRTEM images of NMA-89 after 1000 cycles in pouch full cell. Adapted with permission from ref. 67. Copyright 2021, Wiley-VCH. The figure also shows the electrochemical performance and cross-sectional SEM images of some control samples.

Li et al. (Fig. 3a) systematically investigated the electrochemical application of  $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Al}_y\text{O}_2$  as a Co-free high-Ni cathode, in which Mn and Al work together to stabilize the structure but with a slight difference.<sup>66</sup> Mn can be mixed into Ni-based layered oxides up to 33-50 mol% without structural reconstruction into a spinel phase, whereas the amount of Al used is typically limited to  $\leq 5-6$  mol% to avoid secondary phases. Furthermore, this is also very dependent on the preparation method. When 5-6 mol% Al is added, the co-precipitation method can achieve good dispersion and uniformity of each component. In contrast, the conventional post-processing solid-phase mixing method will still appear impure to cause rapid performance degradation. On the other hand,  $\text{Mn}^{4+}$  induces more Li/Ni mixing while  $\text{Al}^{3+}$  reduces it, so the synthesized  $\text{LiNi}_{0.883}\text{Mn}_{0.056}\text{Al}_{0.061}\text{O}_2$  (NMA-89) shows an excellent *R-3m*-phase layered structure and does not have much higher Li/Ni mixing than the Co-bearing materials. The electrochemical results reveal that NMA-89 has a capacity of 216 mAh  $\text{g}^{-1}$  at 4.4 V and capacity retentions on par with NCM-89 and NCA-89 up to 2C rate. The benign rate capability benefits from the suppression of Li/Ni mixing by  $\text{Al}^{3+}$ . Furthermore, after the prolonged charge/discharge tests of 1000 cycles in pouch full cell, the NMA-89 shows the better cyclic stability than NCM-89 and NCA-89, demonstrating that Mn and Al are a superior combination. Lee et al. (Fig. 3b) further analyzed the cyclic stabilization mechanism of NMA-89 in depth.<sup>67</sup> It is found that the stable performance is mainly attributed to the inhibition of  $\text{H2} \rightarrow \text{H3}$  phase transition by Mn and Al synergistically. Hence, the NMA-89 does not show a noticeable crack in the particles after 1000 cycles at 4.2 V in the pouch full cell. The HRTEM images also

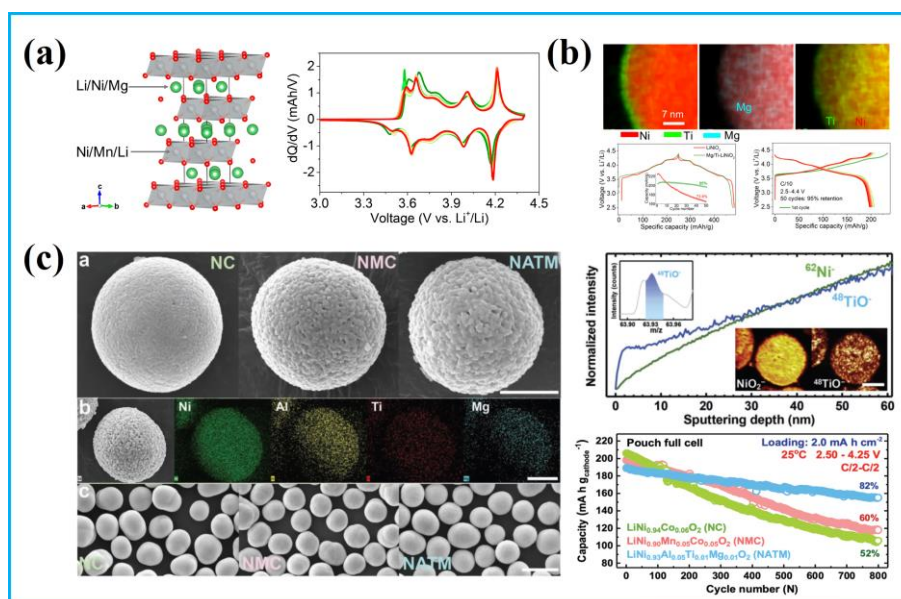
display that the material remains layered in bulk and just a thicker rock salt phase on the surface. These results are exciting that NMA is promising as a new class of Co-free layered oxide material to defeat conventional NCM and NCA.



**Figure 4.** (a) Sol-gel synthesis and electrochemical comparison of NFA. Adapted with permission from ref. 68. Copyright 2020, Wiley-VCH. (b) Large scale co-precipitation synthesis and electrochemical comparison of NFA. Adapted with permission from ref. 69. Copyright 2020, Elsevier.

Iron (Fe) is a common and cheap element, and Muralidharan et al. (Fig. 4a) tried to validate the feasibility of Fe substitution and achieve “zero” Co in the cathode.<sup>68</sup> They estimate that this initiative can save hundreds to thousands of tons of Co each year. They designed the  $\text{LiNi}_x\text{Fe}_y\text{Al}_z\text{O}_2$  ( $x + y + z = 1$ ,  $x=0.8$ , NFA) with various Fe/Al ratios to study the effect of Fe substitution. The authors focused on the issue of Li/Ni mixing

caused by high Ni content, hence neutron diffraction was conducted and demonstrated minimal ( $\approx 4\%$ ) Li/Ni antisite defects in all the samples. Besides, the acquired operando Mössbauer spectroscopy indicated that half of the trivalent Fe will take part in the redox reaction during charging/discharging process. All the prepared samples show the similar discharge capacities around  $200 \text{ mAh g}^{-1}$  at C/20 between 3 and 4.5 V. Nonetheless, the rate and cyclic performance have obvious differences. Among them, the  $\text{LiNi}_{0.8}\text{Fe}_{0.05}\text{Al}_{0.15}\text{O}_2$  presents the best rate retention and cyclic stability. This work proves the potential of  $\text{LiNi}_x\text{Fe}_y\text{Al}_z\text{O}_2$  as a Co-free high-Ni cathode. However, the optimal substitution amount of Fe is only 5%, and the author did not propose a detailed stabilization mechanism of Fe. To certify the practical applications of  $\text{LiNi}_x\text{Fe}_y\text{Al}_z\text{O}_2$ , Muralidharan et al. (Fig. 4b) further explore its co-precipitation synthesis in large industrial scale Continuous Stirred Tank Reactors (CSTR).<sup>69</sup> The pH of  $\sim 11.5$  was selected to facilitate the co-precipitation of three kinds of transition metal ions. As a result, conventional spherical secondary particles with a size of around  $10 \mu\text{m}$  were obtained, and they also exhibited similar electrochemical performance with the one prepared by the sol-gel method.



**Figure 5.** (a) The crystal model and dQ/dV curves of Mg/Mn dual-doped LNO. Reprinted with permission from ref. 70. Copyright 2020, American Chemical Society. (b) The element distribution and electrochemical performance of Mg/Ti dual-doped LNO. Reprinted with permission from ref. 72. Copyright 2019, American Chemical Society. (c) Morphological, electrochemical, and TOF-SIMS characterizations of NC, NCM, NATM, and their corresponding graphite anodes. Adapted with permission from ref. 75. Copyright 2021, Wiley-VCH.

Recently, Mu et al. (Fig. 5a) reported the Mg/Mn dual-doped LNO as a new no-Co cathode material, in which Mg and Mn respectively reside in the Li slab and Ni slab to steady the layered structure.<sup>70</sup> To achieve a high capacity, a composite of 96% Ni content with a 2% doping amounts of both Mg and Mn is prepared. The discharge capacity of Mg/Mn-LNO exhibited a 216 mAh g<sup>-1</sup> at C/10 within 2.5-4.4 V and maintained a 76% capacity retention after 350 cycles at C/2 (22 °C). However, X-ray absorption spectroscopy (XAS) results uncovered the irreversible reduction of Ni

starting from the very first cycle. For ultrahigh Ni content in the Mg/Mn-doped LNO, it still has a significant Ni reduction on the surface, and the reduction depth can be extended up to 50 nm. During the accumulation of cycles, this severe surface degradation can lead to metal migration and more cation mixing. At the same time, the reduced Ni is easily dissolved in the electrolyte and deposited on the anode. Hence, there is a large space to improve for this sample.

Titanium (Ti) is also a promising substitution element that tends to inhibit the transition metal dissolution. Several studies reported that Ti dopant is mainly enriched on the particle surface, and its concentration spreads gradually in a gradient to the interior of the particle.<sup>71</sup> This is due to the slow kinetics of Ti diffusion in the LNO or LCO during high-temperature calcination. It is precisely because of this, the surface-enriched Ti distribution can passivate the surface and improve the chemical stability, effectively mitigating the pernicious side reactions between the active material and electrolyte. Mu et al. (Fig. 5b) also surveyed the electrochemical applications of Mg/Ti dual-doped LNO in detail.<sup>72</sup> The material delivers a capacity of 208 mAh g<sup>-1</sup> at C/10 within 2.5-4.4 V, slightly below the baseline LNO (225 mAh g<sup>-1</sup>). But its rate performance and cyclic stability both have an obvious improvement. In addition, synchrotron X-ray fluorescence microscopy (XFM) discloses that the corresponding lithium anode collected from the Mg/Ti-LNO cell after 50 cycles shows nearly 10 times lower Ni concentration than that collected from the LNO cell, indicating a great inhibition for the transition metal dissolution.

Manganese (Mn) is often regarded as the culprit responsible for the transition metal dissolution.<sup>73,74</sup> Lately, Cui et al. (Fig. 5c) developed a Co and Mn-free ultrahigh-Ni  $\text{LiNi}_{0.93}\text{Al}_{0.05}\text{Ti}_{0.01}\text{Mg}_{0.01}\text{O}_2$  (NATM) cathode used for LIBs.<sup>75</sup> As previously mentioned, Al likes to occupy the Ni site, Mg likes to occupy the Li site, and Ti likes to enrich on the surface. This combination is expected to form all-round protection of the material. The reported degree of Li/Ni cation mixing only has 2.4%. In a coin half-cell configuration with Li-metal anode, NATM show a high capacity of  $221 \text{ mAh g}^{-1}$  at C/10 within 2.8-4.4 V. Furthermore, in a pouch full cell configuration with graphite anode, NATM exhibited an outstanding capacity retention (82%) over 800 deep cycles. Surface ecology of the cathode and anode by TOF-SIMS characterization indicated that NATM significantly inhibited active material dissolution, and the paired graphite anode displays an ultrathin ( $\approx 8 \text{ nm}$ ), monolayer anode-electrolyte interphase architecture after extensive cycling. The parasitic cathode to anode transition metal crossover is drastically reduced for NATM cells, which is proposed to benefit from the well-designed Mn-free composition and a Ti-enriched cathode surface. Besides, differential scanning calorimetry (DSC) also demonstrate the better thermal stability of NATM than NC and NCM.

## Conclusions and outlooks

In summary, element doping and substitution strategies are facile and effective ways to push the development of Co-free high energy cathodes. In view of the issues originating from high Ni content, especially the fast capacity decay, numerous cheap and common

elements have been validated to stabilize performance, though at the expense of capacity. In addition, elemental substitution was found to be effective in strengthening the chemical stability of the material, but it seems to provide only limited improvement in mechanical stability. Currently, it is gradually realized that crack propagation and mechanical failure are the main reasons for the decay of high-Ni materials at high voltages.<sup>76</sup> Simple element doping may be powerless to cater this situation, and other feasible measures are urgently needed to remedy it. Composition design strategies, such as concentration gradient cathodes, have been proven to alleviate the uneven strain of the particles, which can effectively suppress chemo-mechanical degradation of high-Ni cathode materials.<sup>77,78</sup> Besides, a recent morphology design strategy that replaces the traditional concept of secondary particles with micron-sized single crystal particles to enhance the mechanical integrity has also attracted widespread attentions.<sup>79-82</sup> Although these strategies have shown their effectiveness in performance improvement, it remains premature to promote them in the electric vehicle industries before solving the cost concerns.

In recent years, several alternative Co-free cathodes have included Li-rich Mn-based materials (LMR), high-voltage spinel and disordered rock-salt cathodes. Some of them exhibit excellent performance in the lab-scale experimental stage, but they are still far from commercialization.

Li-rich Mn-based materials, which is composed of a layered rhombohedral  $\text{LiTMO}_2$  (TM = Ni, Co, Mn) component and a monoclinic  $\text{Li}_2\text{MnO}_3$  component, have a high

specific capacity ( $> 250 \text{ mAh g}^{-1}$ ).<sup>83</sup> Compared to the conventional layered oxide cathodes, its higher capacity stems from the activation of the  $\text{Li}_2\text{MnO}_3$  component with partially reversible oxygen redox above 4.5 V, which has brought some fatal drawbacks. Voltage decay and voltage hysteresis are the most critical limitations in the commercial application of LMR cathode and yet to be completely resolved, though much effort has been made.<sup>84</sup>

High-voltage spinel,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has a high operating voltage of 4.7 V vs.  $\text{Li}/\text{Li}^+$  and fast three-dimensional  $\text{Li}^+$  ion diffusion, leading to a significant increase in energy density as well as power density.<sup>85-87</sup> However, this high working voltage also brings a heavy burden to the entire battery system. Even if the cathode can tolerate such a high voltage, the carbonate-based electrolytes and other cell components will be severely decomposed at this point. Hence, a specialized electrolyte that is stable under high voltage is required for effective implementation, complicating the battery preparation process.

Disordered rock salt is a new type of high energy density cathode material.<sup>88,89</sup> Unlike conventional layered oxide materials that mainly rely on specialized transition metal elements (Ni, Mn and Co), it has a large compositional flexibility and can incorporate multiple transition metal species.<sup>90</sup> Traditionally, rock salt structure is considered electrochemically inactive due to the absence of available  $\text{Li}^+$  ion diffusion channels. However, recent findings indicate that a lithium excess of more than 10% can form a permeable network of 0-TM channels in disorder rock salt for low-barrier  $\text{Li}^+$

ion diffusion. Disordered rock salt does not undergo a structural transition during the electrochemical process because its own structure is already a large degree of cationic disorder. But, the observed short-range order and oxygen loss still can degrade Li<sup>+</sup> ion transport, resulting in a substantial capacity fading. At present, the viable approach is to use high-valent metal or fluorine substitution to stabilize the disordered structure.<sup>91,92</sup>

Generally, eliminating expensive elements like Co is critical for sustainable energy materials but developing low-cost cathode without compromising electrochemical performance is still a challenge. At present, Ni-rich layered oxide cathodes remain the preferred choice for Co-less and Co-free cathodes since they are more reliable and accessible than other alternatives. However, as the theoretical capacity limit is approached, improvement space left for Ni-rich cathodes is gradually shrinking. In the long run, it can be predicted that the invention of new electrode materials and the development of sustainable recycling methods for key components will open up new paths for future electrochemical energy storage.

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