Mitigating the High-Charge Detrimental Phase Transformation in LiNiO\textsubscript{2} Using Doping Engineering

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ABSTRACT: Cobalt-free layered LiNiO\textsubscript{2} has gained increased interest due to the scarcity and high cost of cobalt. However, LiNiO\textsubscript{2} suffers from poor cycling stability, which is mainly due to oxygen loss and structural instability, especially when operating at high voltages. Herein, we present a doping strategy to mitigate the detrimental O3-to-O1 phase transformation in LiNiO\textsubscript{2} from first-principles calculations. Temperature−composition phase diagrams of pristine and doped Li\textsubscript{1-x}NiO\textsubscript{2} are obtained using a cluster-expansion and Monte Carlo simulation approach. We investigate the effects of dopant oxidation states, sizes, and concentrations on the dopant distribution in LiNi\textsubscript{1-y}M\textsubscript{y}O\textsubscript{2} (M = Sb, Ti, Si, Al, and Mg) as well as the phase transitions during delithiation. We find that introducing high-valence dopants with ionic radii similar to that of Ni\textsuperscript{3+} into LiNiO\textsubscript{2} stabilizes the O3-phase cathode bulk structure at high charge. Our results provide a general guidance on using doping engineering to realize Ni-rich, Co-free cathodes for lithium-ion batteries.

In the past decade, lithium-ion batteries (LIBs) have become the dominant power source for electric vehicles (EVs) and plug-in hybrid EVs (PHEVs) due to the dramatically reduced cost of an LIB pack from approximately US$1,200/kWh to approximately US$150/kWh in 2022.\textsuperscript{1} However, the projected increase of the EV market\textsuperscript{1,2} necessitates a re-evaluation of the metals used in the cathodes of LIBs, especially cobalt, which is not mined at the scale needed to sustain such growth. Indeed, the current cathode family of choice for the EV market, the layered oxide cathodes, i.e., Li\textsubscript{[Ni\textsubscript{1−y}−Co\textsubscript{y}−Al\textsubscript{z}]}O\textsubscript{2} (NCA) and Li\textsubscript{[Ni\textsubscript{1−y}−Co\textsubscript{y}−Mn\textsubscript{z}]}O\textsubscript{2} (NCM), has undergone a steep increase in the Ni content and a corresponding decrease in the Co content from, e.g., NCM111 (33% Ni, 33% Co) to today’s NCM622 (60% Ni, 20% Co) and NCM811 (80% Ni, 10% Co) compositions.\textsuperscript{3}

The ultimate end member of the NCA and NCM families is LiNiO\textsubscript{2}, which exhibits the highest theoretical capacity (275 mAh/g). However, the challenges that accompany its high specific capacity are substantially compromised cycling and thermal stability.\textsuperscript{4,5} During cycling, LiNiO\textsubscript{2} undergoes a series of phase transitions, whereof one, comprising of a shift from O3 to O1 oxygen stacking (sometimes denominated H2 to H3) at high potentials (V > 4.1 V), leads to extensive structural damages of the cathode particles and a rapid capacity fade.\textsuperscript{4,6} Figure 1 illustrates the change in oxygen stacking and the corresponding O3, O1, and O1-3 phases in LiNiO\textsubscript{2}. Specifically, at low Li content (less than 25% Li left),\textsuperscript{6,7} a two-phase region of O3+O1 emerges with heterogeneous Li

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distribution as the O1 phase is devoid of Li. Because of the Li depletion, the lattice contracts anisotropically and abruptly.\textsuperscript{6,7} Such lattice contraction is worsened by the presence of the O1 phase.\textsuperscript{8} Simultaneously, the formation of the O1 phase creates stacking faults in the layered structure because of the different oxygen stacking sequences (see Figure 1). Both these factors contribute to a strain-induced structural instability of the cathode, which typically manifests in the formation of microcracks.\textsuperscript{9} Recent studies also showed that the O1 phase could act as a nucleation site to (1) initialize cracking from the cathode particle surface and (2) provide diffusion pathways for oxygen loss, thereby promoting the irreversible transformation from the layered structure into a densified rocksalt structure.\textsuperscript{9,10} Therefore, to develop the next-generation Ni-rich layered cathodes, it is critical to suppress the O1 phase formation. While the structural instability can be avoided by simply limiting the upper cutoff voltage to 4.1 V, this remedy comes at the cost of a decreased specific capacity.\textsuperscript{11} Hence, it has been deemed a priority to develop Ni-rich, Co-free cathodes for next-generation EV batteries where the trade-off between specific capacity and cycling stability is mitigated.\textsuperscript{11}

One such proposed strategy is to introduce doping elements to develop non-standard cathode chemistries.\textsuperscript{5,11,12} In this context, LiNiO\textsubscript{2} provides a fertile chemical playground for compositional design of Ni-rich, Co-free cathode alternatives to the standard NCA and NCM chemistries. A range of dopants have been proposed to mitigate the O3-to-O1 phase transition and promote a more stable LiNiO\textsubscript{2} structure at high charge. Such dopants include W\textsubscript{13}, Nb,\textsuperscript{14} Ti,\textsuperscript{15} Mn,\textsuperscript{16} Ga,\textsuperscript{17} Al,\textsuperscript{18} Cu,\textsuperscript{19} and Mg.\textsuperscript{20} In addition, some of these dopants have been proposed to exhibit a stabilizing effect on other high-energy-density layered cathodes. For example, Levartovsky et al. reported that 1% W doping effectively suppresses the O3-to-O1 phase transition in LiNi\textsubscript{0.85}Co\textsubscript{0.1}Mn\textsubscript{0.05}O\textsubscript{2}.\textsuperscript{20} Similarly, Nayak et al. reported that 5% Al doping mitigates the layered-to-spinel phase transition and thereby improves the cycling performance of Li- and Mn-rich cathodes.\textsuperscript{21} Despite the enthusiasm for doping engineering in the design of Co-free cathodes, there is still a lack of understanding about the dopant role for LiNiO\textsubscript{2} or Ni-rich cathodes in general. In addition, since both dopant chemistry and concentration influence a variety of short-range as well as long-range materials properties, it is experimentally challenging to interpret and deconvolute their effects on the cycling and capacity retention. For example, Guilmar et al. reported that 10% Al doping in LiNi\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{2} is sufficient to suppress the phase transition and improve the cycling stability.\textsuperscript{22} Cao reported that 5% Al is the optimal doping concentration to achieve a uniform doping distribution and the best cycling performance compared to other Al doping concentrations and pristine LiNiO\textsubscript{2}.\textsuperscript{18} while Park et al. reported that 1% Al doping does not lead to a noticeable cycling performance improvement in LiNi\textsubscript{0.8}Mn\textsubscript{0.2}O\textsubscript{2}.\textsuperscript{12} On the other hand, modeling is a powerful tool to help identify the intrinsic impact of composition and doping engineering on electrochemical performance, avoiding effects of synthesis and cell processing. Indeed, numerous theoretical studies on doping engineering of LiNiO\textsubscript{2} have also been reported.\textsuperscript{3,23-25} For example, Yoshida et al. performed an \textit{ab initio} screening of dopant effects on lattice contraction in LiNi\textsubscript{1.75}Co\textsubscript{0.175}O\textsubscript{2} by calculating the layer spacing change in the O3 phase. In this work, Ni was substituted by various dopants and Nb was identified as a promising agent to minimize lattice contraction during cycling.\textsuperscript{26} Similarly, Kong et al. studied anion doping effects on the structural stability of LiNiO\textsubscript{2} by calculating lattice contractions and Ni migration in the O3 phase. They found Cl to be a promising dopant to reduce lattice contraction and that F may mitigate Ni migration.\textsuperscript{27} Recently, Mock et al. used lattice models to calculate the voltage profiles of pristine and Al-doped LiNiO\textsubscript{2} in the O3 phase. They reported that the two-phase plateau at low Li content (less than 25% Li left) in LiNiO\textsubscript{2} can be effectively suppressed with 10% Al-doping, which indicates a structural stabilization.\textsuperscript{28} However, to our best knowledge, there has been no systematic theoretical investigation of the doping effects on the phase evolution of LiNiO\textsubscript{2}, considering both O3 and O1 phases, as a function of dopant concentration. Indeed, experimental evidence shows that dopant concentration in Ni-rich cathodes can significantly impact batteries’ cycling performance\textsuperscript{13,14} and that dopant distribution behavior is specific to the chemistry of the dopant.\textsuperscript{13,15}

In this study, we implement a first-principles, cluster-expansion and Monte Carlo approach to study LiNiO\textsubscript{2} doped with a series of dopant elements with varying valence states (Sb\textsuperscript{5+}, Ti\textsuperscript{4+}, Si\textsuperscript{4+}, Al\textsuperscript{3+}, and Mg\textsuperscript{2+}) to 1) obtain clarification on the direct role of the dopants as suppressants of the O1 phase at high charge and 2) provide general guidelines of dopant selection to improve the structural stability of Ni-rich and Co-free cathodes. We investigate the effects of dopant oxidation state, size, and concentration on dopant distribution in LiNi\textsubscript{1-y}M\textsubscript{y}O\textsubscript{2} (M = Sb, Ti, Si, Al, and Mg). We compare the phase stability of the O3, O1, and O1-3 phases as a function of Li concentration and temperature and calculate the phase diagrams of pristine and doped LiNiO\textsubscript{2}. The inclusion of the O1-3 phase corresponds to recent experimental reports of discrete O3 and O1 domains in charged Ni-rich cathodes.\textsuperscript{7,10} Combining our results with previously reported experimental studies, we recommend to introduce high-valence dopants with ionic radii similar to that of Ni\textsuperscript{3+} into Ni-rich and Co-free cathodes. This approach could potentially stabilize both surface and bulk structures of the cathode material.

### Pristine LiNiO\textsubscript{2}

To clearly illustrate the effects of dopants, we first reproduce the known phase behavior in pristine LiNiO\textsubscript{2} as a baseline. In Figure 2a, we plot the calculated composition—temperature phase diagram of Li\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{2}, which contains four single-phase regions separated by domains of two-phase regions. Thus, all phase transitions are first order, with a variety of intermediate ordered phases at \( x = 0.25, 0.5, \) and 0.75. For less than 75% delithiation (\( x < 0.75 \)) all Li\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{2} structures exhibit the O3 phase, which has been found to correlate with a stable bulk structure and cycling performance.\textsuperscript{4} Each two-phase region at \( x < 0.75 \) (hatched areas) is formed between two O3 structures with different Li ordering and concentration. Upon further delithiation (\( x > 0.75 \)), a two-phase region comprising the O3 and O1-3 phases emerges. The O1-3 phase exhibits O1 oxygen stacking which has been reported to promote cracking and oxygen loss.\textsuperscript{9,10} Therefore, the formation of O1 oxygen stacking indicates an emergent structural instability at \( x > 0.75 \), likely contributing to structural damage and deteriorated cycling stability.\textsuperscript{4} This is in excellent agreement with experimental observations, which reported that the maximum rechargeable capacity is 200 mAh/g with \( x = 0.75 \) in Li\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{2}.\textsuperscript{4} A two-phase region with large lattice contraction appears for \( x > 0.75 \).\textsuperscript{6} Yoon et al. reported detrimental phase transition and extensive structural damages after cycling LiNiO\textsubscript{2} particles above 4.2 V (\( x > 0.8 \)).\textsuperscript{6} Notably,
Figure 2a shows that the destructive O3+O1-3 two-phase region remains at high temperatures. Our calculated voltage profile of Li$_{1-x}$NiO$_2$ also agrees with the experimental one. Figure 2b illustrates the calculated voltage profiles of pristine LiNiO$_2$ at 300 and 900 K as a function of discharge capacity and composition. Each plateau corresponds to a two-phase region, whereas the single-phase regions are characterized by continuous changes in the cell voltage, which are reflected in the calculated phase diagram. For comparison, we also plot previously measured experimental and calculated voltage profiles of LiNiO$_2$ from Li et al.\textsuperscript{7} and Arroyo y de Dompablo et al.,\textsuperscript{31} respectively, in Figure 2b. Our calculated voltage overpredicts the experimental value by about 0.4 V, whereas Arroyo y de Dompablo et al. underpredicted the value by about 0.5 V, a difference that is attributed to the U value for the Ni 3d orbitals (the generalized gradient approximation (GGA) was used in ref 31). Nevertheless, our voltage profile correctly reflects the intercalation reaction mechanism during the charging of LiNiO$_2$, and the shape of the voltage curve qualitatively agrees with the experimental results, especially the voltage plateau at $x > 0.75$. Some minor variances are noted between the computed and experimental results for the phase behavior between 0 < $x < 0.75$. For example, we identify a two-phase region at 0.5 < $x < 0.75$, whereas it is reported at 0.6 < $x < 0.7$ in Li et al.’s study.\textsuperscript{7}

Doped Li$_{1-x}$Ni$_1-M_xO_2$, $M = $ Sb, Ti, Si, Al, and Mg. For each dopant case, we investigate the dopant spatial distribution in LiNi$_{1-x}$M$_x$O$_2$. Figure 3 illustrates the dopant distribution behaviors for Sb, Ti, Si, Al, and Mg in O3 LiNi$_{0.95}$M$_{0.05}$O$_2$ host structures (each has 46,080 atoms). We find that Sb and Ti tend to aggregate while Si, Al, and Mg distribute randomly in LiNi$_{1-x}$M$_x$O$_2$. To quantitatively differentiate the dopant distribution behavior, we calculate the dopant–dopant coordination numbers from the radial distribution functions, see Figure 3. The aggregating dopants, Sb and Ti, exhibit rapidly rising coordination numbers, as a function of dopant–dopant distance, as compared to those of Si, Al, and Mg. It should be noted that the dopant distribution is similar at other doping concentrations (see Figure S5) and in 1,440-atom structures that are used in the grand canonical Monte Carlo (GCMC) simulations.

In Figure 4a–c, we plot the temperature–composition phase diagrams for Sb-, Ti-, Si-, Al-, and Mg-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$. The phase diagrams clearly show the single-phase regions and two-phase regions in Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ structures. Neither the O1 nor the O3-1 phase appears in the phase diagram of Sb- or Ti-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ but one exists in the phase diagram of Si-, Al-, or Mg-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ after 75% delithiation. For less than 75% delithiation ($x < 0.75$), the single-phase and two-phase regions in Sb-, Ti-, Al-, or Mg-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ are similar to those in pristine Li$_{1-x}$NiO$_2$ and are all in O3 host structures, without the presence of the O1 phase. On the other hand, Li$_{1-x}$Ni$_{0.95}$Si$_{0.05}$O$_2$ structures exhibit a wide solid solution region for $x < 0.5$. Upon further delithiation ($x > 0.75$), all Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ structures exhibit a two-phase region. Interestingly, the two-phase region in Sb- or Ti-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$ is formed between two O3 structures with different Li orderings, which indicates that Sb and Ti can effectively stabilize the O3 host structure during the entire delithiation procedure. On the other hand, in Si-, Al-, or Mg-doped Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$, a two-phase region comprising O3+O1-3 or O3+O1 phase appears, which indicates the existence of the O1 oxygen stacking that contributes to the structural vulnerability. In Figure 4f–j, we plot the calculated voltage profiles at 300 and 900 K as a function of discharge capacity and composition for Li$_{1-x}$Ni$_{0.95}$M$_{0.05}$O$_2$. The predicted voltage profiles all exhibit pronounced steps and plateaus which correspond to the intermediate single-phase and two-phase regions in the phase diagrams. In addition, we explore

Figure 3. Dopant–dopant coordination numbers as a function of dopant–dopant distance in LiNi$_{0.95}$M$_{0.05}$O$_2$ (M = Sb, Ti, Si, Al, and Mg) along with dopant distributions in LiNi$_{0.95}$M$_{0.05}$O$_2$. Each structure has 46,080 atoms. Only Ni and dopant sites are shown, and the size of the dopant is enlarged to show the dopant distribution behavior. A dopant–dopant bond is added when the bond distance is less than 5.5 Å.
the doping concentration effect on the phase stability of Si-, Al-, and Mg-doped structures by increasing the doping concentration to 10%. In Figure S1, we plot the phase diagrams and voltage profiles of Si-, Al-, and Mg-doped Li$_{1-x}$Ni$_{0.9}$M$_{0.1}$O$_2$. It can be seen that, with a 10% dopant concentration, the O1 phase is prevented in Al- or Mg-doped Li$_{1-x}$Ni$_{0.9}$M$_{0.1}$O$_2$ phase diagram and the O3 host structure is stabilized during the entire delithiation process. On the other hand, the O3+O1-3 two-phase region still persists in Li$_{1-x}$Ni$_{0.9}$Si$_{0.1}$O$_2$ after 75% delithiation. The 10% Al-doping requirement agrees nicely with a previous theoretical study. Experimentally, it has been shown that a 5% Al or Mg dopant concentration decreases the intensity of the O3-to-O1 phase transition in LiNiO$_2$; however, this phase transition virtually disappears with a 10% Al or Mg dopant.

In addition, it should be noted that the inclusion of Al$^{3+}$ or Mg$^{2+}$ leads to a direct reduction in available Ni$^{3+}$ redox capability due to charge compensation. During Li deintercalation, Ni$^{3+}$ sites are oxidized to Ni$^{4+}$, and charging beyond the Ni$^{3+}$ redox capability typically results in oxygen redox, which is associated with oxygen release and structural damages. Therefore, for Li$_{1-x}$Ni$_{0.9}$Al$_{0.1}$O$_2$, the delithiation should be limited to 90% ($x \leq 0.9$, 255 mAh/g) and 80% delithiation ($x \leq 0.8$, 227 mAh/g) for Li$_{1-x}$Ni$_{0.9}$Mg$_{0.1}$O$_2$. A similar recommendation has also been reported in a previous experimental study.

Overall, we predict that Sb and Ti favor dopant aggregation in LiNi$_{1-x}$M$_x$O$_2$ bulk structure and stabilize the O3 host structure during the delithiation process. We find that the dopant-enriched aggregates have a beneficial effect in suppressing the formation of the O1 phase, therefore enhancing the structural stability of the cathode. Interestingly, using dopant aggregates to enhance the mechanical strength of the layered cathode and suppress cracking has also been reported in Mg-doped Na$_{0.05}$Ni$_{0.55}$Mn$_{0.4}$O$_2$. On the other hand, Si, Al, and Mg tend to distribute homogeneously throughout the cathode particles. The use of Al or Mg requires a higher doping concentration to effectively prevent the formation of the O1 phase, and Si is ineffective in stabilizing the O3 host structure, even with a higher doping concentration. The benefit of a higher doping concentration has also been experimentally confirmed in Al-doped LiNiO$_2$, where a sufficient amount of Al doping (≥5%) is needed to reduce the detrimental effect of the O3-to-O1 phase transition.

The tendency toward different dopant distributions is reflected in the effective cluster interaction (ECI) values from the fitted cluster-expansion models. In Figure S2, we plot the estimated ECI values of two-site dopant–dopant clusters as a function of pair distance. We observe that both Sb and Ti exhibit negative ECI values, which gradually become less negative with dopant–dopant pair distance and indicate attractive dopant–dopant pair interactions. The Ti–Ti and Sb–Sb ECIs reflect the aggregation behavior of Sb and Ti in LiNi$_{1-x}$M$_x$O$_2$ bulk structure. Conversely, Si–Si, Al–Al, and Mg–Mg exhibit positive ECI values, especially when the two dopants occupy nearest-neighbor sites, which indicate repulsive dopant–dopant pair interactions. As a result, the repulsive dopant–dopant interactions favor a uniform dopant distribution in Si-, Al-, or Mg-doped LiNi$_{1-x}$M$_x$O$_2$. The details of our cluster-expansion settings of pristine and doped LiNiO$_2$ can be found in Table S1. The tendency toward dopant aggregation is likely attributable to a combination of electrostatic and size effects. For example, the Sb$^{5+}$–Sb$^{5+}$ pair interaction is expected to be less electrostatically favorable than the Sb$^{5+}$–Ni$^{3+}$ pair; however, the overall attractive Sb–Sb pair interactions imply that the electrostatic effect does not dominate the dopant aggregation behavior. On the other hand, the dopants exhibit different ionic sizes (see Table S2), which induce different amounts of local strain in the bulk of LiNiO$_2$, especially if the dopants aggregate. Indeed, the ionic radii of Sb$^{5+}$, Ti$^{4+}$, and Al$^{3+}$ are similar to that of Ni$^{3+}$, whereas Si$^{4+}$ is much smaller than Ni$^{3+}$, and Mg$^{2+}$ is significantly larger than Ni$^{3+}$. Figure S3 shows that the octahedron formed by Sb, Al, or Mg exhibits a larger octahedral volume difference between the dopant and Ni as compared to the Sb or Ti octahedron. As a result, an energy penalty is associated with any aggregate of Si, Al, or Mg, which favors a more random dopant distribution of Si, Al, or Mg. Except for Al$^{3+}$, a large size difference between the dopant and Ni$^{3+}$ corresponds to a large volume difference of local octahedrons formed by dopant and Ni. More dopants with ionic radii similar to that of Ni$^{3+}$, such as W$^{6+}$, Nb$^{5+}$, Ta$^{5+}$, and Mo$^{6+}$, are recommended for exploration. Nonetheless, recent experimental studies also reported a homogeneous dopant distribution in Mg-doped Ni-rich oxides and Al-doped Li- and Mn-rich oxides. Both...
dopants have been found to improve the cathode bulk stability at a highly delithiated state. Our recent study of Sb-doped LiNiO\textsubscript{2} found that Sb tends to aggregate toward the cathode surface with a hierarchical Sb distribution.\textsuperscript{3} The surface enrichment of Sb can effectively mitigate the oxygen-loss-induced surface densification and therefore improve the cycling performance. In this study, we further demonstrate that Sb improves the structural stability of LiNiO\textsubscript{2} by preventing the onset of the O1 phase at high charge. Such combined surface and bulk stabilization effects from the dopants have also been reported in Ti\textsuperscript{3+}, Ta\textsuperscript{5+}, W\textsuperscript{5+}, or Mo-doped\textsuperscript{18} Ni-rich cathodes and in Nb-doped\textsuperscript{49} Li-rich disordered rocksalt oxide. Interestingly, these dopants all exhibit a hierarchical distribution with an aggregation at the cathode surface.

Combining our current study and the previous reports, we propose materials design principles governing dopant selection for Ni-rich oxide cathodes. High-valence dopants with ionic radii similar to that of Ni\textsuperscript{3+} tend to exhibit a hierarchical distribution with an aggregation at the cathode surface and, therefore, may stabilize both the surface and bulk of Ni-rich oxide cathodes and improve the cycling performance. A recent study by Park et al.\textsuperscript{12} reported that doping high-valence ions delays and suppresses the O3-to-O1 phase transition in LiNi\textsubscript{0.8}Mn\textsubscript{0.2}O\textsubscript{2} cathode, therefore dissipating the deleterious strain-induced microcracks and enhancing the cycling stability. Despite the excellent agreements with the experimental results, it should be noted that the structural models used in this study are simplified compared with those observed in experiments:

1. We assume no Li--Ni cation mixing in as-synthesized pristine or doped LiNiO\textsubscript{2}. On the other hand, regardless of the synthesis method, LiNiO\textsubscript{2} is usually found to be Li-deficient and Ni\textsuperscript{3+}-excessive, which yields an overall Li\textsubscript{1.0+x}Ni\textsubscript{1-x}O\textsubscript{2} composition with the smallest departure from stoichiometry at \( z = 0.015 \sim 0.02 \).\textsuperscript{40,41} With an extra \( z \) Ni\textsuperscript{2+} in the Li-layer, due to the similar sizes of Li\textsuperscript{+} and Ni\textsuperscript{2+}. The degree of Li--Ni cation mixing could be further increased with introducing doping elements, especially high-valence dopants, as the charge balance is achieved by generating more Ni\textsuperscript{2+} ions.\textsuperscript{12}

2. We assume no interlayer or intralayer dopant migration during cycling such that the dopant positions are fixed at the NiO\textsubscript{2} layers during GCMC simulations. However, Mg dopants have been reported in both the Li layer and the transition metal layer.\textsuperscript{15,42} Additionally, the presence of dopants in the Li layer may act as pillaring ions at delithiated states at high voltages, reducing the large anisotropic lattice distortion and enhancing structural stability.\textsuperscript{42} In Figure S4, we plot the calculated unit cell volumes as a function of Li concentration for pristine Li\textsubscript{1-x}NiO\textsubscript{2} and Li\textsubscript{1-x}Ni\textsubscript{1-y}M\textsubscript{y}O\textsubscript{2} at 300 K. We observe a large lattice contraction beyond 75% delithiation, associated with NiO\textsubscript{2} appearance, across all the considered cathode chemistries. The lattice contraction is only marginally improved with Sb and Ti doping.

3. The impact of oxygen evolution on the phase transition at a high charge state is not considered. Recently, Park et al.\textsuperscript{43} reported that the O3-to-O1 phase transition in LiNiO\textsubscript{2} is more severe in the surface region of the cathode than in the bulk region, due to a higher concentration of oxygen vacancies near the surface. Wang et al.\textsuperscript{8--10} also demonstrated that the O1 phase is more vulnerable to oxygen loss as compared to the O3 phase. The oxygen loss lowers the energy barrier of Ni migration into the Li layer, thereby facilitating a transformation from the layered structure into a densified rocksalt structure and compromising reversibility of the O3-to-O1 transition.

In summary, using a first-principles, cluster-expansion and Monte Carlo approach, we have obtained temperature-composition phase diagrams for pristine and Sb-, Ti-, Si-, Al-, and Mg-doped LiNiO\textsubscript{2}. We find, in agreement with experiments, that in pristine LiNiO\textsubscript{2} the structural instability appears after 75% delithiation due to the formation of the O1 oxygen stacking in the structure. The O3-to-O1 phase transition is found to be effectively prevented in Sb- or Ti-doped LiNiO\textsubscript{2}, even with a small dopant concentration, i.e., less than 5%. On the other hand, we find that a higher dopant concentration of Al or Mg is necessary, i.e., at least 10%, to prevent the O3-to-O1 phase transition. We also find that Si doping is ineffective in stabilizing the O3 phase. Interestingly, Sb and Ti tend to aggregate in LiNiO\textsubscript{2} due to an attractive dopant--dopant interaction, whereas Si, Al, and Mg exhibit a uniform distribution behavior. Such dopant-enriched aggregates are shown to effectively prevent the O1 phase formation and stabilize the O3 host structure during the delithiation process, which has experimentally been shown to correlate with improved cycling performance. Overall, we attribute the factors modulating the suppression of the O3-to-O1 phase transition to a combination of dopant aggregation and concentration. For the concentrations examined here (2.5% to 10%), a dopant aggregate of Si, Al, or Mg in LiNiO\textsubscript{2} is found to be thermodynamically unfavorable, partially due to local strain effects. Dopant aggregates with Sb or Ti are found to beneficially prevent the formation of the O1 phase, while a higher concentration of homogeneously distributed Al or Mg is needed to achieve the same effect. However, while a higher concentration (10%) of Al or Mg can stabilize the O3 phase, we note that a higher dopant concentration also lowers the discharge capacity, as redox-active Ni is replaced with a redox-inactive dopant. Based on these results, we propose to introduce high-valence dopants with ionic radii similar to that of Ni\textsuperscript{3+} into the Ni-rich oxide cathodes to stabilize the cathode bulk structure. These dopants include W\textsuperscript{6+}, Mo\textsuperscript{5+}, V\textsuperscript{5+}, Nb\textsuperscript{5+}, Ta\textsuperscript{5+}, Sb\textsuperscript{5+}, Ti\textsuperscript{5+}, Mn\textsuperscript{4+}, and Ge\textsuperscript{4+}. In addition, the dopants may aggregate at the cathode surface and form a hierarchical distribution that could stabilize both the surface and bulk of the cathode particles. The derived materials design principles not only provide guidance on doping engineering of Ni-rich, Co-free cathodes but also shed light on stabilizing the bulk structure of all high-energy-density cathodes.
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