Elucidating the Effect of the Dopant Ionic Radius on the Structure and Electrochemical Performance of Ni-Rich Layered Oxides for Lithium-Ion Batteries

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ABSTRACT: The merits of Ni-rich layered oxide cathodes in specific capacity and material cost accelerate their practical applications in electric vehicles and grid energy storage. However, detrimental structural deterioration occurs inevitably during long-term cycling, leading to potential instability and capacity decay of the cathodes. In this work, we investigate the effect of the doped cation radius on the electrochemical performance and structural stability of Ni-rich cathode materials by doping with Mg and Ca ions in LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂. The results reveal that an increase in the doping ion radius can enlarge the interlayer spacing but lead to the collapse of the layered structure if the ion radius is too large, which undermines the cycling stability of the cathode material. Compared with the Ca-doped sample and the pristine material, Mg-doped LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ presents improved structural stability and superior thermal stability due to the pillar and glue roles of medium-sized Mg ions in the lithium layer. The results of this study suggest that a suitable ionic radius of the dopant is critical for stabilizing the structure and improving the electrochemical properties of Ni-rich layered oxide cathode materials.



KEYWORDS: Li-ion batteries, cathode, Ni-rich, doping, cation radius

1. INTRODUCTION

The high demands for energy density and cost concerns have been encouraging researchers to develop Ni-rich layered oxide cathode materials with a Ni content over 80% due to their high capacity.¹ An increase in the Ni content in layered oxides is effective for boosting energy density and reducing costs as compared with the conventional LiCoO2 and ternary $\text{LiNi}_{1-x-y}\text{Co}_{x}\text{Mn}_{y}\text{O}_{2}$ (NCM) oxides with a low Ni content.² However, when the Ni content increases, these cathode materials compromise the battery lifespan owing to the inherent structural and interfacial instabilities.³ For example, structural deterioration from the layered to densified structures, such as spinel and rock-salt structures, causes sluggish lithium transport and loss of active components, which undermine the electrochemical activity and the consequent cycling performance.^{4,5} The structural densification region can act as the nucleation site for incubation of intergranular and intragranular cracks, which make the electrolyte attack on the exposed fresh surface, thus intensifying interfacial parasitic reactions.⁶ It also has been found that this structural deterioration is inevitably accompanied by oxygen evolution. The released oxygen in the form of singlet oxygen inclines to decompose the electrolyte and renders the formation of the cathode-electrolyte interphase layer on the cathode surface.⁷ Strategies for limiting the impact of structural and interfacial degradations have been developed

over the decades, including surface modification, atomic substitution, and structural tailoring of Ni-rich layered oxide materials.^{8,9}

Cation doping is one of the most dominant approaches for enhancing the cycling performance of Ni-rich oxide cathodes, which can effectively suppress the phase transition and stabilize the lattice oxygen.¹⁰ Intensive previous studies have been implemented by selecting different cations, such as Na⁺, Mg²⁺, Al³⁺, Y³⁺, Zr⁴⁺, Nb⁵⁺, and Ta⁵⁺, which are all proven to be effective in improving the cycling stability.^{11,12} Our previous study also indicated that monovalent Na⁺ is effective in controlling the capacity and potential decline of Ni-rich oxide cathodes.¹³ However, the easy mobility of monovalent ions in oxide materials makes a compromise in retaining structural integrity upon long-term cycling. In particular, doping of Mg²⁺ is effective in suppressing the multiple phase transitions of Nirich oxides during delithiation.¹⁴ Mg²⁺ has a similar ionic radius (0.72 Å) to that of Li⁺ (0.76 Å), indicating that Mg²⁺

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Figure 1. (a) XRD patterns of NCM811 and Mg-, Ca-, and Mg/Ca-doped NCM811 samples and magnified (003) diffraction peaks on the right panel. (b) Variation of the (003) interlayer spacing after doping. (c) Schematic illustration of how Mg and Ca doping affects the interlayer spacing.

prefers to occupy the lithium layer, acting as a pillar ion to limit the interslab collapse at the delithiated state. Ca^{2+} (0.99 Å) has similar properties as Mg²⁺ in terms of the electronic structure and oxidation state in its compounds, except for the ionic radius.¹⁵ Doping of Ca²⁺ also contributes to the improvement of the cycling stability of Ni-rich oxide cathodes. 16,17 Moreover, both Mg^{2+} and Ca^{2+} in bivalence lead to the evolution of the electronic structure associated with Ni oxidation from Ni²⁺ to Ni³⁺ during the synthesis process, which facilitates Li/Ni ordering and the consequent lithium diffusivity.¹⁸ Indeed, it is unclear whether the incorporated Ca²⁺ occupied the lithium sites or the transition metal sites. According to density functional theory calculations, the substitution of transition metal with low-valence cations such as Ca²⁺ would generate structural strain owing to the significant difference in the ionic radii.¹⁹ Also, doping of large cations in transition metal sites increases defect formation energy, whereas doping in lithium sites has a modest influence on the defect formation energy, implying that the substation of Li with large dopants is thermodynamically more stable.²⁰ Therefore, it is believed that dopants with large ionic radii are inclined to substitute into the lithium layer, whereas small doping ions prefer to occupy the transition metal layer because of the similarity in the ionic radii.²¹ Some large dopants occupying Li sites can expand the Li-ion diffusion pathway and increase the rate capability.²² However, the effect of the radius of the doping cations on the electrochemical performance of layered cathodes remains implicit and needs investigation.

In this work, we chose Mg and Ca cations as proof-ofconcept dopants into one of the most prevalent Ni-rich layered oxide cathodes, $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811). Doping of Mg²⁺ can improve the electrochemical performance of the NCM811 cathode in terms of capacity and potential stability due to the decent radius of Mg²⁺, whereas doping of large Ca²⁺ shows inferior performance but is still better than the pristine material. The correlation between the dopant ionic radius and the electrochemical properties was illustrated. This work elucidates that it is crucial to pick out the doping elements with an appropriate ionic radius for tuning the structural and electrochemical behaviors of Ni-rich layered oxide materials.

2. EXPERIMENTAL SECTION

2.1Preparation and Characterization. The quasi-spherical LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ was prepared via the co-precipitation process. In brief, 1 M transition metal aqueous solution including NiSO₄•6H₂O, CoSO₄•7H₂O, and MnSO₄•H₂O (molar ratio of Ni/Co/Mn = 8:1:1) and 2 M base solution including NaOH and $NH_3 \bullet H_2O$ (molar ratio of NaOH/NH₃ $\bullet H_2O = 5:3$) were separately pumped into the co-precipitation reactor. The pH was controlled at 11.0 with the temperature at 50 °C, stirring speed at 600 rpm, and a nitrogen atmosphere to acquire the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ precursor after 48 h. To obtain $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ and $LiOH \bullet H_2O$ (molar ratio 1:1.03) were thoroughly mixed and calcined at 480 °C for 6 h and then at 800 °C for 12 h under oxygen flow. For the preparation of Mg-, Ca-, and Mg/Ca-doped LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ and LiOH•H₂O (molar ratio 1:1.03) were intermixed with magnesium acetate (3.0 mol %), calcium acetate (3.0 mol %), and magnesium acetate (1.5 mol %) and calcium acetate (1.5 mol %), respectively, followed by calcining at 480 °C for 6 h and then at 800 °C for 12 h under an oxygen atmosphere.

The crystal structure and lattice parameters of the samples were determined using X-ray diffraction (XRD, Smart Lab). The morphology and the structural integrity of powders and electrodes were determined using a scanning electron microscope (JEOL-7800F). To explicitly compare the crack of cycled particles, the electrodes were annealed under air at 500 °C for 3 h to get rid of the conductive carbon and binder before scanning electron microscopy (SEM) observation. The elemental composition and chemical state were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). To investigate the structural stability of the delithiated samples, high-temperature XRD patterns were collected from 40 to 500 °C at a heating rate of 5 °C min⁻¹ and in the scan range (2θ) of $17-20^{\circ}$ at a rate of 1° min⁻¹. The XRD patterns were



Figure 2. (003) diffraction peaks in high-temperature in situ XRD patterns and the corresponding interlayer spacing expansion ratios at various temperatures for the samples of (a) NCM811 and (b) Mg-, (c) Ca-, and (d) Mg/Ca-doped NCM811.

measured at a temperature step of 10 $^{\circ}\mathrm{C}$ with each temperature held for 3 min before data collection.

2.2Electrochemical Measurement. To implement electrochemical tests, the cathode slurry was obtained by blending the active powder, super P, and polyvinylidene fluoride with 8:1:1 weight ratio in N-methylpyrrolidinone. The cathodes were fabricated by casting the as-prepared slurry on an Al foil, followed by drying in a 110 °C oven for 10 h and then being punched into 10 mm discs with a loading mass of \sim 3 mg cm⁻². Electrochemical tests were performed using 2032-type half-cells with a lithium foil anode and 1 M LiPF₆ salt dissolved in an ethylene carbonate-dimethyl carbonate mixture (3:7 in volume) solution. The charge/discharge tests were conducted at 0.1 and 1 C rates (1 C = 200 mA g^{-1}) between 2.8 and 4.3 V at 25 °C. The cyclic voltammetry (CV) curves were measured using an electrochemical workstation (LK2010) at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) were collected using an electrochemical workstation (Zennium Pro) in the frequency range of 100 kHz-10 mHz after the electrode was charged to 4.3 V.

3. RESULTS AND DISCUSSION

All the as-prepared oxide samples show spherical morphologies and have an average particle size of $\approx 5 \,\mu m$ as determined from the SEM images (Supporting Information Figure S1), so the doping processes have no visible impact on the morphology. Energy dispersive spectra (EDS, Supporting Information Figure S2) present the doped Mg and Ca evenly distributed along with the transition metal elements Ni, Co, and Mn. Moreover, all samples can be indexed to the hexagonal layer structure with a $R\overline{3}m$ space group, and no impurity phases can be detected, as shown in Figure 1a. The results of XRD analysis together with elemental mappings verify that Mg and Ca dopants are uniformly dispersed throughout the oxide particles, and the doping process does not affect the crystallographic structure of the oxide. However, the subtle difference in XRD patterns still can be observed in the enlarged view (Figure 1a, right). The typical (003) diffraction peaks of Mg-doped NCM811 and Ca-doped NCM811 shift to the opposite directions relative to those of the pristine NCM811

sample. This observation is due to the difference in the radius of doping cations. Specifically, the occupation of Mg ions with smaller radii in the Li layer causes a slight contraction of the (003) interlayer spacing and the associated *c* lattice parameter (Figure 1b). By contrast, the introduction of Ca ions with larger radii into the Li layer leads to an increase in the (003) interlayer spacing by 0.25% from 4.757 Å in NCM811 to 4.769 Å in Ca-doped NCM811, as evidenced by the (003) peak shifting to a lower angle. The previous study has indicated that the expansion of interlayer spacing would facilitate lithium diffusion.²³ Co-doping of Mg and Ca (1.5 mol % for each) is also investigated, illustrating that co-doping can expand the interlayer spacing of the (003) plane, but the extent of increase is lower than that by Ca doping. As shown in Figure 1c, the effect of Mg and Ca doping on the interlayer spacing is schematically illustrated. Moreover, the c/a ratio and the intensity ratio of (003)/(104) peaks of the samples are obtained from the XRD patterns and summarized (Supporting Information Table S1), demonstrating that Mg-doped NCM811 has the highest degree of Li⁺/Ni²⁺ cation ordering. Similar results can be also confirmed by comparing the XPS spectra of the samples (Supporting Information Figure S3) because Mg-doped NCM811 displays the lowest amount of Ni²⁺ in the XPS spectra. Specifically, all Ni 2p spectra consist of two dominant peaks, $2p_{3/2}$ at about 854.6 eV and $2p_{1/2}$ at about 872.3 eV, which are accompanied by two weak shake-up satellite peaks. The most intense Ni 2p_{3/2} peak shifts from the low binding energy of 854.6 eV to a higher binding energy of 855.1 eV after Mg²⁺ doping, indicating that more Ni²⁺ in Mgdoped NCM811 is oxidized to Ni³⁺ to maintain the balance of valence states. By quantification of XPS spectra, Mg-doped NCM811 has the maximum ratio of Ni³⁺ with a value of 58.2%, indicating the minimum $\mathrm{Li}^{\scriptscriptstyle +}/\mathrm{Ni}^{2+}$ cation mixing among these cathode materials. For the Ni-rich layered oxides, a high degree of Li⁺/Ni²⁺ cation ordering facilitates high structural stability of the oxide cathodes.



Figure 3. Comparison of (a) initial charge/discharge profiles at 0.1 C rate and (b) CV of NCM811 and Mg-, Ca-, and Mg/Ca-doped NCM811 electrodes at 0.1 mV s⁻¹.

The ionic radius of the dopant has a significant impact on the slab height of layered oxides and the corresponding adhesion capability between layers.²⁴ The high-temperature in situ XRD patterns were collected to examine the correlation of interlayer spacing and separation capability of layered oxides. Particular attention is paid to the (003) diffraction peak, which represents the lithium ion transport layer.²⁵ As shown in Figure 2, the diffraction peaks of all samples shift to smaller angles along with the temperature increase, indicating the gradual separation of close-packed layers due to the increase in the repulsive interaction. To estimate the expansion ratio, we calculate the interlayer spacing of the (003) crystal plane. Although the interlayer spacing is slightly contracted, the expansion ratio of 0.32% for Mg-doped NCM811 is significantly lower than that for pristine NCM811 (0.61%). This result suggests that doped Mg acts as not only pillar ions to mitigate the collapse upon high delithiation but also glue ions to bond the adjacent layers, thus significantly contributing to the structural stability. Comparatively, the expansion ratio of interlayer spacing for Ca-doped NCM811 is up to 0.85%, indicating that overenlarged interlayer spacing induced by Ca doping destabilizes the layered structure. Also, the expansion of interlayer spacing for Mg/Ca-doped NCM811 also undermines the toughness of the layered structure. Since the structural degradation of cathode materials is directly related to the transition metal migration,²⁶ the overincrease in interlayer spacing would decrease the migration barriers of transition metal, thus accelerating the structural deterioration from layered to spinel and eventually rock-salt structures.^{27,28}

To correlate the interlayer spacing and the electrochemical properties, the initial charging/discharging measurements were performed at 0.1 C rate between 2.8 and 4.3 V. As shown in Figure 3a, the initial discharge capacities are near values of 183.9 mA h g^{-1} for NCM811, 184.9 mA h g^{-1} for Mg-doped NCM811, 184.7 mA h g^{-1} for Ca-doped NCM811, and 188.1 mA h g^{-1} for Mg/Ca-doped NCM811. Meanwhile, the initial Coulombic inefficiency that is defined as the difference

between Coulombic efficiency and 100% of each doped sample is lower than that of NCM811, implying an improved electrochemical activity and a higher lithium utilization. In particular, Ca-doped NCM811 shows the lowest Coulombic inefficiency with a value of 13.1%, suggesting that Li⁺ can be extracted more easily from the lithium layer. In fact, the decrease in Coulombic inefficiency can be largely attributed to the expansion of interlayer spacing of the (003) crystal plane.²⁵ However, the increase in the interlayer spacing releases the intermediate tetrahedral space, causing a decrease in the diffusion barriers of transition metal ions and thereby facilitating structural reconstruction.³⁰ Therefore, Mg doping is helpful in improving the Coulombic efficiency, while also ensuring the structural stability of NCM811 due to the pillar and glue effects of Mg²⁺ during the lithium insertion and extraction process.

To further investigate the effect of the interlayer spacing change induced by different dopants on electrochemical activity, CV measurements were performed, and the kinetics of the four oxide electrodes was assessed. As shown in Figure 3b, all four electrodes display three pairs of redox peaks, which correspond to the phase transitions from hexagonal (H1) to monoclinic (M), to hexagonal (H2), and then to hexagonal (H3) phases during the anodic process.³¹ In particular, the CV curve of Mg-doped NCM811 maintains a similar shape to that of the pristine NCM811, suggesting that Mg doping has no impact on the electrochemical reaction of NCM811. As for the Ca-doped NCM811, the CV curve shows a much higher initial peak current of 0.86 A g^{-1} as compared to that of NCM811 (0.29 A g^{-1}) , and this peak is significantly shifted to a high potential, indicating that the large interlayer spacing helps improve the diffusion kinetics of lithium in the oxide materials, but the Ohmic impedance increases because of the surface passivation. For this reason, Mg/Ca-doped NCM811 still reveals a subtle potential polarization upon the initial delithiation process. The delithiation kinetics were further investigated using galvanostatic intermittent titration techni-



Figure 4. (a) Charge/discharge profiles of NCM811 and Mg-, Ca-, and Mg/Ca-doped NCM811 at 1 C rate from 3rd to 400th cycles (IS: interlayer spacing). (b) dQ/dV profiles of NCM811 and Mg-, Ca-, and Mg/Ca-doped NCM811 deriving from the charge/discharge profiles. (c) Impedance spectral evolution measured at the 4.3 V charged state after the 1st and 200th cycles.

ques during the initial charging process (Supporting Information Figure S4a). Comparatively, the steady-state condition can be easily reached for Ca-doped NCM811 during relaxation of the potential (Supporting Information Figure S4b), indicating a higher delithiation kinetics compared with NCM811 and Mg-doped NCM811.³² Therefore, the calculated $D_{\rm Li}$ of Ca-doped NCM811 is higher than that of the other three electrodes (Supporting Information Figure S4c). In addition, the steady-state time-consuming $D_{\rm Li}$ for NCM811 and Mg-doped NCM811 electrodes is almost identical, suggesting their similar lithium deintercalation capability. Of course, the delithiation kinetics of the Mg/Ca-doped NCM811 electrode compromises as compared to that of the Ca-doped NCM811 electrode because of the introduction of small Mg ions.

Fast lithium attrition would induce a nonuniform delithiation between oxide particles, leading to reaction heterogeneity and associated structural deterioration.³³ As shown in Figure 4a, charge/discharge tests were carried out to evaluate the structural integrity during long cycling for all four samples. Apparently, NCM811 exhibits severe-deformed plateaus after 400 cycles, implying that pristine NCM811 suffers from serious potential polarization and irreversible structural change upon cycling. For Mg-doped NCM811, however, the initially observed plateaus are well preserved over cycling, indicating superior structural stability as compared with the pristine sample. Also, it can be seen that the plateau preservation of Ca-doped NCM811 and Mg/Ca-doped NCM811 is inferior to that of Mg-doped NCM811 after 400 cycles. This result confirms that a kinetically fast process to some extent can lead to detrimental structural degradation, especially as the cycling progresses and at high rates. In addition, the charge/discharge profile of Mg-doped NCM811 has a subtle Ohmic drop at the initial stage of discharge,

demonstrating a fast ion flow through the electrode.³⁴ More specifically, the Ohmic resistance for Mg-doped NCM811 is only 137.5 Ω after 400 cycles (Supporting Information Figure S5), almost a quarter of the value of the NCM811 electrode (546 Ω), which further confirms the superior structural and mechanical stabilities after Mg doping.

To further compare the structural stability of four samples, dQ/dV curves were obtained by differentiating the charge/ discharge curves. As shown in Figure 4b, all electrodes undergo multiple phase transitions during cathodic and anodic processes. The anodic/cathodic peaks for NCM811 display a noticeable reduction in intensity, especially for the H2 \leftrightarrow H3 phase transition peak, whereas the same redox peaks remain relatively stable for the Mg-doped NCM811 electrode. The preserved redox peaks for Mg-doped NCM811 upon cycling can be an indication of structural reversibility,³⁵ which is attributed to the tough layered structure arising from the pillar and glue effects of Mg ions. Indeed, the intensity of the H2 \leftrightarrow H3 phase transition peak is closely related to the reversibility of the original layered structure, which can act as a sensitive indicator for structural deterioration.³⁶ However, Ca doping is incapable of blocking the deterioration of reversibility of the structure during cycling, which is evidenced by the gradually weakened peaks for Ca-doped NCM811 and Mg/Ca-doped NCM811.

Usually, such H2 \leftrightarrow H3 phase transition is accompanied by the abrupt lattice contraction and expansion and the consequent microcracks and particle pulverization after longterm cycling.^{37,38} To correlate the structural reversibility with the mechanical integrity sustained by each cathode during cycling, the morphologies of cycled electrodes were examined using SEM. As shown in Supporting Information Figure S6, the NCM811 microspheres suffer from numerous microcracks and drastic pulverization after long cycling. In contrast,



Figure 5. (a) Cycling performance of different cathodes at 1 C rate. (b) Discharge capacities at different C rates. (c) Comparison of the charge/ discharge midpoint potentials upon cycling.

although a few microspheres are partially cracked, the Mgdoped NCM811 electrode still maintains the spherical morphology after cycling, demonstrating that Mg doping can stabilize the mechanical integrity of oxide materials due to the improved structural reversibility. The mechanical integrities of Ca-doped NCM811 and Mg/Ca-doped NCM811 are better than those of pristine NCM811 but inferior to those of Mgdoped NCM811.

Furthermore, the microcracks and pulverization allow electrolyte penetration onto the interior fresh surface, resulting in the deterioration of the surface structure and the increase in internal resistance.³⁹ The electrochemical impedance spectra were implemented to evaluate the extent of the surface degradation for all electrodes. As shown in Figure 4c and Supporting Information Table S2, all four electrodes demonstrate similar shapes with surface film resistance (R_s) in the high-frequency region, charge-transfer resistance (R_{ct}) in the medium-frequency region, and diffusion impedance (W_0) in the low-frequency region.⁴⁰ The R_s for the doped electrodes is lower than that for the NCM811 electrode before and after cycling, indicating high interfacial stability after Mg or/and Ca doping. Instead, the R_{ct} for the NCM811 cathode is increased significantly after cycling, while that for the Mg-doped NCM811 cathode exhibits a smaller growth, increasing only by 109 Ω after 200 cycles. This result indicates that microcrack suppression during cycling minimizes electrolyte infiltration, protects the intergranular boundary from electrolyte attack, and eventually inhibits the impedance increase. In addition, the W_{0} for Ca-doped NCM811 shows the minimum value among all four tested electrodes before and even after cycling, indicating a remarkable transport of Li⁺ within the lattice of the Ca-doped NCM811 cathode.

The effect of the dopant ionic radius is evident in the capacity retention of these four cathodes. When cycled at 1 C

rate, the Mg-doped NCM811 cathode retains 91.7% of the initial capacity after activation at 0.1 C rate, whereas the NCM811 cathode retains only 63.4% after 400 cycles (Figure 5a and Supporting Information Table S3). The superior capacity retention of the Mg-doped NCM811 cathode is manifestly demonstrated that tailoring the dopant radius and the associate interlayer spacing can alleviate the rapid capacity fading that plagues Ni-rich layered oxide cathodes. Moreover, Ca doping slightly enhances the cycling stability of Ca-doped NCM811 with a capacity retention of 81.1%. In the meantime, Mg-doped NCM811 exhibits a discharge capacity of up to 138.3 mA h g⁻¹ even at the high discharge current density of 10 C rate, much higher than that of NCM811 (Figure 5b). The improved rate capability after Mg doping can be attributed to the high structural stability as discussed above. However, the large interlayer spacing for Ca-doped NCM811 and Mg/Cadoped NCM811 facilitates the irreversible structural transition, resulting in the inferiority in the discharge capacity under high current density in comparison with Mg-doped NCM811. This result demonstrates that Ca2+ with a large ionic radius is not comparable to Mg²⁺ in impeding the migration of transition metal ions toward the lithium layer.

Since potential evolution is a sensitive indicator of the structural deterioration for Ni-rich oxide cathodes during cycling,^{41,42} we compare the charge/discharge potential polarization to show the potential fading of the electrodes. As shown in Figure 5c, the potential fading for NCM811 is the most prominent as cycling proceeds. Specifically, the 400-cycle discharge potential decrease and the discrepancy between charge and discharge midpoint potentials are 0.17 and 0.32 V for NCM811, respectively, whereas they are 0.04 and 0.12 V for Mg-doped NCM811. Apparently, the potential decay for Mg-doped NCM811 is effectively suppressed due to the improvement of structural integrity. As for Ca-doped NCM811



Figure 6. Contour plots of the time-resolved XRD patterns in the selected 2θ range of (a) NMC811, (b) Mg-doped NCM811, and (c) Ca-doped NCM811 electrodes charged at 4.3 V.

and Mg/Ca-doped NCM811, structural deterioration is still observable, as evidenced by the discharge potential drop and polarization increase.

One of the high-priority criteria for a cathode used in an electric vehicle is its safety property,⁴³ which can be evaluated by the thermal stability of the oxide materials.⁴⁴ Here, the thermal stability of the Ni-rich cathodes is investigated using high-temperature XRD, which is an effective technique to probe the bulk structural change during thermal decomposition.⁴⁵ As shown in Figure 6, with increasing the temperature, the Mg-doped NCM811 material experiences (003) peak disappearance at 250 °C, which is higher than 200 °C for NCM811 and 190 °C for Ca-doped NCM811. These observations show that Mg doping contributes to thermal stability, whereas Ca doping produces an adverse effect on the thermal stability of Ni-rich cathodes. The reason is that Mg²⁺ doping in the oxide cathode plays not only a pillar role but also a glue role, thus suppressing phase transition and improving the associated thermal stability. Ca2+ doping expands the interslab but decreases the energy barrier of transition metal ion migration from their original sites to the lithium sites, thus deteriorating the structural and thermal stabilities. Hence, Mg doping of a Ni-rich oxide cathode not only extends the lifespan of the associated battery but also enhances battery safety. Moreover, in comparison with the obvious (003) peak shift to a lower angle for delithiated NCM811 and Ca-doped NCM811 cathodes, there is almost no shift in the (003) diffraction peak for delithiated Mg-doped NCM811, further indicating that the enlargement of interlayer spacing of the (003) plane is also suppressed upon heating, as agreed well with the high-temperature XRD result of pristine Mg-doped NCM811.

According to the abovementioned investigations, it is definitive to corroborate the relationship between the dopant ionic radius and cathode properties of Ni-rich layered oxides. As shown in Figure 7, the overall performance comparison of the NCM811, Mg-doped NCM811, and Ca-doped NCM811 is depicted in a radar summary chart. Because both Mg and Ca ions occupying Li sites act as pillar ions, the doping of Mg and Ca can improve the cyclability of NCM811. However, differences in structural properties and electrochemical behaviors between the doped Ni-rich oxide materials still rise due to the different ionic radii of Mg, Ca, and Li ions, which obviously affect the electrochemical performance of the cathodes, especially during long cycling. Mg ions with adequate ionic radii are expected to provide pillar and glue effects, which strengthen the structural toughness upon lithium insertion/



Figure 7. Radar summary chart displaying the comparison of NCM811, Mg-doped NCM811, and Ca-doped NCM811 materials.

extraction and in turn optimize the thermal behavior. Ca ions have larger ionic radii as compared with Li ions, and thus, their presence in the lithium layer can expand the interplanar spacing and enhance the kinetic property. However, if the ionic radius of the dopant is remarkably different from that of the host cation, such a dopant would introduce structural deformity around the dopant, which facilitates the transition from layered to spinel/rock-salt structures. Due to the strain penalty associated with the large size difference between Ca and Li ions, the stabilization effect of Ca doping on the cycling performance is less effective than that of Mg doping.

4. CONCLUSIONS

In summary, we elucidate the effect of the ionic radius of doping elements on the structural and electrochemical properties of Ni-rich layered oxide cathodes. The results reveal that the structural integrity and cycling stability strongly depend on the microstructure (interlayer spacing) and the kinetic properties (Li⁺ diffusivity), which are affected by the doped cations with different ionic radii. We find that Mg dopants with a small radius can reduce the interlayer spacing and improve the stabilization of the layered structure, thereby contributing to excellent capacity and potential stabilities and superior thermal stability, whereas Ca doping with a large ionic radius is effective for extracting Li⁺ from the host but malignant to structural stability. Intrinsically, the doped Mg ions in the lithium layer serve as glue ions at the partially delithiated state

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and then act as pillar ions at the highly delithiated state, suppressing the drastic collapse of the interlayer and maintaining the mechanical integrity during lithiation delithiation. This investigation substantiates the close correlation between the ionic radius of the dopant and the electrochemical performance of Ni-rich cathodes and is expected to pave the way for elemental substitution and composition optimization for high-energy density lithium-ion batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c17991.

SEM image and the corresponding EDS elemental mapping, EDS results, lattice parameters, XPS spectra of Ni 2p, GITT results, Ohmic resistance, SEM images of cycled electrodes, and impedance data (PDF)

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Notes

The authors declare no competing financial interest.

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