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Na-doped LiNiO$_2$ layered cathode material for Li-ion batteries

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Na-doped LiNiO$_2$ layered cathode material
for Li-ion batteries

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Abstract

With growing needs for renewable energy storage systems, Li-ion batteries (LIBs) have become the most widely used as a power source for portable electronic devices such as mobile phones, laptops and Electric vehicles (EV). Most widely commercialized cathode material is LiCoO2 which has R-3m layered structure. Although it shows good structural stability, due to structural instability in high operating voltage (over 4.2V), its reversible capacity is limited to about 150mAh g\(^{-1}\) which does not undergo severe structural change. As increasing needs for high capacity battery materials, Nickel-rich cathode materials are promising candidates for alternatives to commercialized cathode materials. LiNiO\(_2\) is intensively studied for several decades because of its structural similarity and higher reversible capacity than LiCoO\(_2\).

Although LiNiO\(_2\) is able to perform high reversible capacity, reversibility of the material is critical problem which comes from cation mixing, transition metal dissolution, residual lithium on surface and phase transition during cycling. Those problems are closely related to instability of Ni\(^{3+}\) ion in octahedral site of R-3m structure. According to crystal field stabilization energy (CFSE), lone pair electron in \(e_g\) is unstable so Ni\(^{3+}\) ion is easily reduced into Ni\(^{2+}\) ion. This instability induces the non-stoichiometric structure which causes collapse of local structure. Transition metal, Ni\(^{2+}\) ion in transition metal layer, migrates into Li layer and this phenomenon is called cation mixing. Cation mixing causes decrease in rate capability during cycling. Migrated Ni ions easily make spinel and rock-salt structure on near-surface region of the particle which hinders Li ion diffusion. Furthermore, unstable Ni\(^{3+}\) ions on near-surface region which is easily attacked by H\(_2\)O or CO\(_2\) are reduced into Ni\(^{2+}\) and make LiOH or Li\(_2\)CO\(_3\) on surface. LiOH on the surface is transformed to Li\(_2\)CO\(_3\) accompanying the formation of H\(_2\)O. Water accelerates decomposition of LiPF\(_6\) and produces HF and LiF on the surface which is known as insulating layer.

There have been many tries to solve various problems of Ni-rich materials. One effective way to enhance the performance and stability of Ni-rich material is coating them with stable materials such as metal fluorides (AlF\(_3\), LaF\(_3\) and MgF\(_2\)), electrochemically inactive metal oxides (ZrO\(_2\), V\(_2\)O\(_5\), MgO) and metal phosphates (AlPO\(_4\), CoPO\(_4\)). These coating layers protect active materials by inhibiting direct contact with electrolyte, water or HF attack.

Substituting elements such as Co, Al, Ti, Ga, Mn, Y and Fe with Ni have effects on enhancing structure stability. In my research, I tried to enhance electrochemical property of LiNiO\(_2\) by substituting Li with Na ion. We confirmed that substitution of Na with Li enhanced cycle performance of LiNiO\(_2\). Substitution of Na with Li on LiNiO\(_2\) reduced cation mixing during electrochemical
cycling giving structural stability by Rietveld refinement. Also, it reduced nickel ion dissolution into electrolyte during cycling. Not only enhancing electrochemical property, storage characteristic is also enhanced by Na doping on LiNiO$_2$. 
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1. Introduction

1-1. Cathode materials for Li-ion batteries

With growing needs for renewable energy storage systems, Li-ion batteries (LIBs) have become the most widely used as a power source for portable electronic devices such as mobile phones, laptops and Electric vehicles (EV). Significant attention is focused on EV markets which seem to commercialized in near-future. With successful beginning of the Li-ion battery in 1991, which used LiCoO$_2$ and Graphite as cathode and anode materials, respectively, many researchers jumped into material design for Li-ion batteries. Over the past three decades, various types of cathode materials were developed such as layered oxides (LiMO$_2$, M=transition metal elements),\textsuperscript{3} spinel oxides (LiM$_2$O$_4$, M= Mn, Ni, Co and Fe)\textsuperscript{4} and olivine phosphates (LiMPO$_4$, M=transition metal elements).\textsuperscript{5} Each structural difference gives them show different electrochemical characteristics.

Olivine phosphates show excellent structural stability which comes from strong bond between phosphorous and oxygen. Moreover, higher electron negativity of oxygen than phosphorous gives higher operating voltage than standard reduction potential. This phenomenon is called electron withdrawing. Although olivine phosphates show excellent structural stability, it is hard to be commercialized because it has poor electron conductivity and ionic conductivity which results in poor rate capability.\textsuperscript{6} Many researchers have tried to solve this problem by carbon coating or doping other metallic elements.

Spinel oxides have advantage in cheaper production costs compared with other cathodes materials. The most widely known spinel oxide material is LiMn$_2$O$_4$. Manganese is environmental friendly and cheap element due to its abundance. Also, its various oxidation states enable to perform high operating voltage. However, manganese dissolution in electrolyte during electrochemical performance is significant problem of manganese-spinel oxides which comes from instability of Mn$^{3+}$ in the structure. Mn$^{3+}$ is disproportionate into Mn$^{4+}$ and Mn$^{2+}$ which can be easily dissolved in electrolyte and makes lithium-blocking solid-electrolyte interface (SEI) on the surface of anode.\textsuperscript{7} There have been many researches to solve this problem by coating and doping other elements into the spinel structures.
Layered oxides can produce high capacity over 270mAhg$^{-1}$, theoretically. Cations locate in the octahedral sites while O$^{2-}$ anions building cubic-close packed (CCP) structure which coincides with Li$^+$ ions locate between MO$_2$ slabs which are arranged in [111] direction. M are transition metals and usually are solely or mixture of cobalt, nickel and manganese. The diffusion mechanisms of the layered oxides are usually called two-dimensional because Li$^+$ ions diffuse between MO$_2$ slabs. Diffusion path way enables layered oxides to show high rate capability which is related with power capability. Not only high rate capability but also high working voltage above 3.5V versus Li metal gives high energy density.

Figure 1. Expanding applications of Li ion batteries
Figure 2. Schematic structures of cathode materials for Li ion batteries

Dimensionality of the Li$^+$-ions transport

layered LiCoO$_2$ 2D
spinel LiMn$_2$O$_4$ 3D
olivine LiFePO$_4$ 1D
Figure 3. Crystal structure of LiCoO$_2$
1-2. Layered Oxides : LiCoO$_2$ and LiNiO$_2$

Among commercialized cathode materials, layered LiCoO$_2$ is the first-commercialized cathode material in 1991 by Sony. It has been widely used in LIB systems due to its excellent rate capability and high energy density. LiCoO$_2$ has iso-structure with α–NaFeO$_2$ (R-3m) which is consisted of consecutive alternating CoO$_2$ and Li$^+$ layers. Co$^{3+}$ and Li$^+$ residues in the 3a and 3b sites, respectively, which both are octahedrally coordinated, while O$^{2-}$ ions construct CCP lattice. Due to good stability of Co$^{3+}$ ions in the structure, LiCoO$_2$ can sustain $R$-$3m$ structure during cycling.

Although it has high theoretical capacity 274mAh g$^{-1}$, the practical capacity is limited to about 150mAh g$^{-1}$ because it undergoes phase transition from hexagonal to monoclinic phase around 4.1V versus Li metal.$^9$ With the increasing needs for high capacity cathode materials, replacing Co with Ni is approached. It enables using almost 80% reversible extraction of Li from host material which results in high practical capacity over 200mAh g$^{-1}$. Accompanied with this approaches, many LiNiO$_2$-based derivatives have been studied such as LiNi$_{1-x}$Al$_x$O$_2$, LiNi$_{1-y}$Co$_y$O$_2$, LiNi$_{1-a}$Co$_{1-b}$Mn$_{1-c}$O$_2$ as a doping method or coating electro-/chemically stable material on its surface.$^{10}$
Figure 4. First charging profile of a Li$_{1-x}$CoO$_2$ at the 0.01C rate from 3.5V to 5.2V vs Li/Li$^+$
1.3. **Drawbacks of LiNiO$_2$-based cathode materials**

Although LiNiO$_2$-based materials show high reversible capacity, they have various shortcomings which are closely related with instability of Ni$^{3+}$ ion. According to crystal field theory, electrons in 3d orbitals are split into $t_{2g}$ and $e_g$ which have different energy levels when octahedrally coordinated. According to Crystal Field Stabilization Energy (CFSE) of Ni ions, the relative energy levels of Ni$^{2+}$($t_{2g}^6e_g^2$), Ni$^{3+}$($t_{2g}^6e_g^1$) and Ni$^{4+}$($t_{2g}^6$), are $-12Dq$, $-18Dq+P$, $-24Dq+2P$, respectively. Assuming that the pairing energy ($P$) is relatively small, the most stable oxidation state of Ni ions is Ni$^{2+}$. Therefore, Ni ions in LiNiO$_2$-based materials tend to reduce from Ni$^{3+}$ into Ni$^{2+}$. Creation of Ni$^{2+}$ causes various problems such as cation mixing,$^{11}$ transition metal dissolution$^{12}$, residual lithium on surface$^{13}$ and phase transition on the near-surface region.$^{14}$

1.3.1 **Cation mixing**

Structural stability of Ni-rich cathode materials is related to the disordering between lithium sites (octahedral 3a site) and transition metal sites (octahedral 3b site). R-3m structure, which is a space group of general layered oxides, is a repeating of [oxygen-lithium-oxygen-transition metal] units in [001] direction. In a perfect crystal structure, Li and Ni ions locate in each site. However, Ni$^{3+}$ ions in octahedral sites are easily reduced to Ni$^{2+}$ due to its instability as described before. Ni$^{2+}$ ion has similar ionic radius (~0.69Å) with Li ion (~0.76Å). Due to this similarity, Ni$^{2+}$ ions in transition metal sites easily diffuse into Li ion predominant sites. Diffused Ni$^{2+}$ ions in Li predominant layer oxidized to Ni$^{3+}$ during delithiation. Due to smaller size of Ni$^{3+}$ than Ni$^{2+}$, interspacing between slabs decreases and hinders Li diffusion which leads to reduction of rate capability.$^{15}$

There have been reports about cation mixing occurs not only during the synthesis step but also during prolonged electrochemical cycling.$^{16}$ Due to structural instability, Ni-rich cathode materials undergo significant structural disorder. This cation mixing affects electrochemical performance of the materials.
Figure 5. Schematic view of cation mixed structure of LiNiO$_2$
1-3.2 Transition metal dissolution

Dissolution of transition metal into electrolyte during electrochemical cycling is a problem of transition metal oxide based cathode materials. Especially, for spinel manganese oxides, Mn\(^{2+}\) dissolution into electrolyte is serious problem for wider use. Due to chemical and structural instability of the spinel framework, Mn\(^{3+}\) is easily disproportionated into Mn\(^{2+}\) and Mn\(^{4+}\). Dissolved Mn\(^{2+}\) ions are reduced on surface of carbon based anodes and create compounds which hinders lithium diffusion because of the higher standard redox potential of Mn/Mn\(^{2+}\) (1.87V vs Li/Li\(^{+}\)) than that of the lithium intercalation into graphite (<0.3V vs Li/Li\(^{+}\)).

Similar to spinel manganese oxides, layered transition metal oxides have a similar problem. In case of LiCoO\(_2\) and LiNiO\(_2\), utilization of the material in high voltage results in severe dissolution of Co and Ni ion into electrolyte. The standard redox potentials of Ni/Ni\(^{2+}\) and Co/Co\(^{2+}\) are 2.80V and 2.77V versus Li/Li\(^{+}\), respectively.\(^{12}\) Especially, for Nickel rich oxides, Ni\(^{2+}\) is easily created which can be easily dissolved into electrolyte. Although Ni compounds deposited on anode surface do not causes other side reactions like Co and Mn based compounds do, Ni dissolution of Ni rich compounds still a problem because of loss of redox center and lithium hindering role.
Figure 6. Schematic view of the influence of transition metal addition in electrolyte on graphite anode during initial charge process
1-3.3 Storage Characteristics

As well known before, the basicity of LiNiO$_2$ and Ni rich oxides is much higher than that of LiCoO$_2$. The basicity is closely related to residual lithium compounds such as Li$_2$CO$_3$ and LiOH on the surface of active materials. X. J. Zhu et al. confirmed that Ni rich oxide (LiNi$_{0.85}$Co$_{0.163}$O$_2$) can react with CO$_2$ in atmosphere even at room temperature.\textsuperscript{17} Moshtev et al. also showed that LiNiO$_2$ can react with H$_2$O which can be interpreted as chemical delithiation without electron exchange reaction.\textsuperscript{18} Liu et al. investigated the origin of deterioration of LiNiO$_2$ during storage.\textsuperscript{13b} They confirmed that the electrochemical performance of LiNiO$_2$ can be reduced even with Ar atmosphere. This phenomenon is due to instability of Ni$^{3+}$ of LiNiO$_2$. Ni$^{3+}$ is easily reduced into Ni$^{2+}$ taking electron from oxygen in lattice and destabilized O$^-$ ions produces oxygen evolution. Moreover, activated O$^2$ ions produce not only oxygen evolution but also Li$_2$CO$_3$ or LiOH (so called residual lithium) when react with CO$_2$ or H$_2$O in atmosphere which accelerates creation of it. They also confirmed that reaction forming Li$_2$CO$_3$, NiO and O$_2$ is spontaneous reaction.\textsuperscript{13c} During this chemical reaction, Ni ions in bulk structure are affected by surface reaction. Storage characteristic is a one of key problems of utilizing Ni-rich and lithium nickel oxides.
Figure 7 Charge-discharge profile of LiNiO$_2$ after storage in air for various times in voltage range of from 2.7V to 4.3V versus Li/Li$^+$ at 18mA g$^{-1}$
1-3.4 Phase Transition on Near-Surface region

As we mentioned before, stability of near-surface region affects structural stability of Ni rich oxides. In a similar vein, phase transition on near-surface region also affects electrochemical performance of the materials. Not only during storage but also during electrochemical performance, phase transition occurs on near-surface region. According to Kang’s group, high-voltage cycling results in formation of rock-salt and spinel region in case of Li$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523).\textsuperscript{14b} This result shows different degradation behavior compared with Li$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111). The degradation mechanism of NCM111 material is known as formation of the O1 phase in highly delithiated state. They argue that this phenomenon is come from Li-Ni exchange (cation mixing) in the Ni rich oxides which inhibit sliding of slabs. So, for Ni rich oxides, phase transition of near-surface region is one of degradation cause of it.

Figure 8. (a) TEM image of LiNi$_{0.3}$Co$_{0.2}$O$_2$ cycled for only SEI formation cycle. (b) Schematic phase transition mechanisms of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ after cycle test
In my research

LiNiO₂ is a promising cathode material for Li ion batteries with its high reversible capacity. However, as we mentioned before, there are some problems that are critical for utilization. There have been many tries to enhance electrochemical performance of LiNiO₂ with doping. Many doping elements such as Al,₁⁹ Co,₁⁷ Ti,₂⁰ are located in transition metal layers. For example, in case of LiNi₁₋ₓAlₓO₂, Al ions locate in tetrahedral site while Ni ions and Li ions locate in octahedral sites. They hinder Li-Ni ion exchange by blocking diffusion way of it.
2. Experimental

2-1. Synthesis

Na-doped LiNiO$_2$ was made through solid-state method. LiOH·H$_2$O (sigma Aldrich, 98%), Ni(OH)$_2$ (Sigma Aldrich, 99%) and Na$_2$CO$_3$ (Sigma Aldrich) were used as precursors. 3% excess Li and Na precursors were used and the ratio of precursors were Li : Ni = 1.03 : 1 for LiNiO$_2$, Li : Na : Ni = 0.9785 : 0.0515 : 1 for Li$_{0.95}$Na$_{0.05}$NiO$_2$ and Li : Na : Ni = 0.927 : 0.103 : 1 for Li$_{0.9}$Na$_{0.1}$NiO$_2$. The precursors were ball-milled with Acetone for 2 hours. The ball-milled powders were dried and grounded for homogeneous mixture. Finally, the mixtures of powders were sintered at 700°C for 10h under O$_2$ flow.

2-2. Characterization

The structure of synthesized powders was characterized by a powder X-ray diffraction (XRD) system (Bruker D2-phaser) in the 2$\theta$ range of 10-80°. Rietveld refinement was done using TOPAS software. Scanning electron microscopy (SEM) images were collected for morphological analysis and Transmission electron microscopy (TEM) images were collected for phase transition on near-surface of the materials.

2-3. Electrochemical Tests

To investigate electrochemical property, CR2032 cell was used. The cathode electrode were casted on aluminum foil after mixing 80% of the active materials with Super-P (Timcal Inc.) as conducting materials and poly(vinyl difluoride) (PVdF, KF1100, Kureha Chemical Industry) dissolved in n-methyl pyrrolidone (NMP) as binder. To assemble a cell, 1.3 M LiPF$_6$ in ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) solution (3:4:3 volume ratio) was used as electrolyte and Li metal as anode. A coin cell was assembled in argon filled glove box. Galvanostatic experiments were performed at 30 C, in voltage between 3.0 V and 4.4 V versus Li metal anode. In cycle test, 1 cycle of 0.1 C pre-cycle and 200 cycles of 0.5 C were performed. For ex-situ XRD tests, 50, 100, 150, 200 cycles were done then disassembled and electrodes were collected and attached to beryllium window to prevent exposure to air during x-ray diffraction measurement. To check transition metal dissolution at each cycle, cells were cycled upto 10, 20, 50, 100 cycles. After
cycling, cells were disassembled and electrodes were collected and washed with DMC for several times to ensure clearance of residual components on surface. After washing, electrodes were dipped into fresh electrolytes and stored at 60 °C for 2 weeks.

2-4. Storage tests

To confirm storage characteristics of prepared materials, synthesized materials were stored in decicator for 1 month. To investigate phase transition during storage, TEM analysis was done. Also, to investigate structural change, X-ray diffraction measurement and Rietveld refinement were done.
3. Result & Discussion

3-1. Synthesis & characterization of Na-doped LiNiO₂

Na-doped LiNiO₂ was synthesized by simple solid-state method. LiOH·H₂O (Sigma Aldrich) Ni(OH)₂ (Sigma Aldrich) and Na₂CO₃ (Sigma Aldrich) were used as source of lithium, nickel and sodium, respectively. Lithium and Sodium were weighed 3% excess molar ratio due to evaporation during high temperature reaction. Each source was wet-ball-milled for 2 hours with 300 rpm with acetone. After ball-milling, powder were dried in air for several hours and grounded in mortar to make homogenous mixture. Mixed powder was put into alumina crucible and calcined in tube furnace at 700 °C for 10 hours with O₂ flow. After calcination, powder was collected and grounded again in mortar to get fine powder.

Figure 9-(a) shows X-Ray Diffraction (XRD) patterns of samples varied with different sodium composition. LiMO₂ (M = Ni,Co,Mn) structure is indexed with R-3m space group. There is no signal of impurities and other phase except R-3m space group. As known before, aligned with (003) peak around 18°, (104) peak around 45° moves towards lower angle. According to bragg’s law (2d sin θ = nλ), as diffraction angle decreases, d-spacing increases in specific direction. In this case, d-spacing between (104) is slightly increases as sodium dopant is added. This may be due to larger ionic radius of sodium compared with lithium ions. To clarify the site occupancy of sodium ion, Rietveld refinement was done for each sample.

Figure 9-(c) and (d) shows Rietveld refinement result of pristine LiNiO₂ and Li₀.⁹₅Na₀.⁰₅NiO₂. For LiNiO₂, due to cation mixing, lithium and nickel ions exchange their site, so we assumed the composition of the material as [Li⁺Ni²⁺][Li⁺Ni³⁺]O₂. In case of bare LiNiO₂, Ni²⁺ ions migrated in Li layer about 0.26%. We think that this low value is possibly achieved, because of small particle size of precursor and abundant supply of oxygen during high temperature calcination. On the other hand, cation mixing of Na-doped sample was higher than that of bare one. Holzapfel et al. explained that reason of increased cation mixing by Na doping is large difference in ionic radius between Li (0.76Å) and Na ion (1.03Å). The structure of Li-dominant Na doped nickel oxide is R-3m which is isostructure with LiNiO₂. In this region, a small amount of Na ions in Li layer can induce lattice strain between slabs. Due to the strain, exchange of Li and Ni ion is facilitated. In result, Na doping on Li-dominant nickel oxide has higher degree of cation mixing. This affects electrochemical property of the material we will discuss later.
Figure 10 shows SEM images of Na-doped LiNiO$_2$ with different sodium composition. All particles were randomly shaped with several hundred nanometers to 1 micrometer size. There is no morphological difference with varied sodium composition from 0 to 10%. So there is no size effect of sodium doping in electrochemical property.
Figure 9. (a) X-ray diffraction (XRD) pattern of LiNiO$_2$ (LNO Bare), Li$_{0.95}$Na$_{0.05}$NiO$_2$ (Na 5%), Li$_{0.9}$Na$_{0.1}$NiO$_2$ (Na 10%) (b) (104) peak of R-3m structure. (c) and (d) show Rietveld refinement result for LiNiO$_2$ and Li$_{0.95}$Na$_{0.05}$NiO$_2$, respectively.
Figure 10. (a) Charge-Discharge curves of bare LiNiO$_2$ and Na-doped LiNiO$_2$ (b) Cycleability of LiNiO$_2$ and Li$_{0.95}$Na$_{0.05}$NiO$_2$

Figure 11. Scanning Electron Microscopy (SEM) images of (a) LiNiO$_2$ (b) Li$_{0.95}$Na$_{0.05}$NiO$_2$ (c) Li$_{0.9}$Na$_{0.1}$NiO$_2$
3-2 Effects on cation mixing during cycle

Figure 11-(a) shows voltage profile of 1st cycle of Na-doped LiNiO$_2$ materials. LiNiO$_2$ (LNO) shows the highest initial discharge capacity about 210 mA h g$^{-1}$. With increasing Na doping composition, initial discharge decreases. This phenomenon is closely related with cation mixing of the starting material. J.P. Peres et al. investigated the relationship between ratio of Ni ions in Li layer and initial discharge capacity of LiNiO$_2$. As Ni ions in Li layer increase, initial discharge capacity decreased and polarization increased. Ni ion in Li layer is oxidized during de-intercalation and shrinks Li layer. The shrinkage of Li layer hinders re-intercalation of Li during discharge process. For Na-doped LiNiO$_2$, increased cation mixing reduces initial discharge capacity and increase polarization during charge-discharge process. As a result, Na dopant over 10% shows severe polarization and reduced capacity. So, further analysis is about LiNiO$_2$ (LNO) and Li$_{0.95}$Na$_{0.05}$NiO$_2$ (LNO-Na5%).

Although Na-doped LNO has lower initial discharge capacity than bare one, it shows better cycleability than bare one. Figure 11-(b) shows cycleability of LNO and LNO-Na5%. The cycle retention of bare LNO is about 71% after 100 cycles. On the other hand, the cycle retention of LNO-Na5% is over 80% even after 100 cycles. To investigate structural effect of Na doping on cycle performance, ex-situ XRD and Rietveld refinement were done. Figure 12-(a) ~ (h) show results of Rietveld refinements for pristine, 50, 100, 150, 200 cycles for each samples and figure 13 shows degree of cation mixing after each cycles. Both sample showed increasing amount of cation mixing after cycling. However, LNO-Na5% increased 1.6% cation mixing while LNO increased 2.7% cation mixing after 200 cycles. This result means Na dopant in LiNiO$_2$ induce initial cation mixing but suppress cation mixing during cycle.
Figure 12. Rietveld refinement result of (a),(b) 50 cycles, (c),(d) 100 cycles, (e),(f) 150 cycles and (g),(h) 200 cycles for LiNiO\(_2\) and Li\(_{0.95}\)Na\(_{0.05}\)NiO\(_2\), respectively.
Figure 13. Degrees of cation mixing after 50, 100, 150, 200 cycles.
3-3. Effects on transition metal dissolution

Ni ion dissolution in electrolyte is also critical problem of LiNiO$_2$. Transition metal dissolution affects structural stability by expanding $c$-parameter. Each parameter of R-3m structure, $a$ and $c$ parameters, is closely related with bonding cation and anion. In case of LiNiO$_2$, Li-O and Ni-O bonding affects crystal structure. The dissolution of Ni ions can reduce bonding between Ni-O which can be result in expanding $c$-parameter. Figure 14 shows change of $c$-parameter during cycling for LiNiO$_2$ and Li$_{0.95}$Na$_{0.05}$NiO$_2$ cells. With increasing cycle number, $c$-parameter of both samples increase. However, Li$_{0.95}$Na$_{0.05}$NiO$_2$ shows smaller value than LiNiO$_2$ for increasing cycle number. This may due to different amount of dissolved Ni ions in electrolyte during cycling.

Figure 15-(a) shows 19 F-NMR data of electrolyte of LNO and LNO$_{Na5\%}$ for 50 and 100 cycles, respectively. Peak around -190 ppm means NiF or NiFHF like compound. Figure 14-(b) shows amount of Ni ions in electrolyte. Although the dissolution of Ni ions into electrolyte is not perfectly inhibited, Na doped sample showed lower concentration of Ni ions in electrolyte than bare sample. This also means dissolution of Ni ion dissolution is suppressed by enhanced structural stability by Na doping.
Figure 14. plot of c-lattice parameter during cycling.

Figure 15. (a) 19F-NMR analysis and (b) amount of Ni ions in electrolyte measured by ICP-MS analysis of electrolyte stored in 60 °C for 2 weeks with electrode cycled for each cycles.
3-4. Origin of structural stability

During charge-discharge process and intensive cycling, c-lattice parameter of R-3m structure continuously repeats increasing and decreasing. After cycling, c-parameter increases and this means reduced bonding between cations and oxygen ions. Diffusion in Li-dominating Li$_{1-x}$Na$_x$NiO$_2$, Na diffusion may not be easy. Ceder’s group investigated diffusion barrier difference of LiMO$_2$ and NaMO$_2$ ($M = \text{Co, Ni, Mn}$). In their research, lower activation barrier for di-vacancy diffusion of Na ion than Li ion in host MO$_2$ structure. It says that lower barrier for di-vacancy diffusion is affected by larger d-spacing of layered NaMO$_2$ than LiMO$_2$ which has been shown to affect closely diffusion of alkali metals. In Li-dominant Li$_{1-x}$Na$_x$NiO$_2$ structure, Na ions cannot effectively diffuse due to small d-spacing. Therefore, residual Na ion in host material after delithiation process due to slow kinetics still bond with oxygen which acts as pillaring agent.

He et al. and Li et al. investigated pillaring effect of Na and K ions in layered structure. Migration of transition metal is closely related with creation of tri-vacancy site in Li layer during discharge process. As shown in Figure 15, Transition metal such as Mn ion surrounded by tri-vacancy site is unstable. So transition metal ion migrates into tetrahedral site in Li layer which facilitates creation of spinel or rock salt phase. However, pillaring agents in Li layer suppress creation of tri-vacancy site which leads to suppression migration of transition metal during discharge process. In order to cation mixing in LiNiO$_2$ occur, the migration of Ni is mandatory. To migrate from transition metal layer to Li layer, Ni ions pass through tetrahedral site between slabs. If pillaring agent hindered creation of tri-vacancy site of Li layer, Ni ions are hard to pass through tetrahedral site due to its ionic radius and electrostatic repulsion. Therefore, pillaring effect can hinder cation mixing during cycling.
Figure 16. Schematic diagrams of the phase evolution routes for (a) potassium-free and (b) potassium-doped insertion oxides. It was built on O3 layered model with unrealistic radii ratios. Vertexes of the octahedrons are oxygen atoms. V1, V2 and V3 stand for vacancies in lithium layer; Vt stands for tetrahedral vacancy and Vo for octahedral vacancy.
3-5. Effects on storage characteristics

As we mentioned before, due to instability of Ni$^{3+}$, LiNiO$_2$ is thermodynamically unstable state. Therefore, deterioration of active material occurs during storage. Figure 17-(a) and (b) show electrochemical performances of LNO and LNO$_{Na5%}$ materials after 1 month storage in air. Reversible capacity of bare LNO decreased about 14% after 1 month storage for both 0.1C and 0.5C C-rates while LNO$_{Na5%}$ decreased about 7%. The origin of deterioration of LiNiO$_2$ was investigated by several groups. Liu et al. investigated reaction mechanism of deterioration of LiNiO$_2$ during storage.$^{13b}$ Unstable Ni$^{3+}$ ion in lattice is reduced to Ni$^{2+}$ taking electron from lattice O$^{2-}$. Activated O$^-$ ions create O$^2$ evolution and reduced Ni$^{2+}$ ion form NiO phase. This reaction is facilitated on surface where CO$_2$ and H$_2$O which help forming Li$_2$CO$_3$ and LiOH can easily contact. TEM analysis was done to check phase transition on near-surface region. Figure 18 to 21 show TEM images of LNO and LNO$_{Na5%}$ before and after storage. About 1.72 nm of NiO region was detected on bare LNO and 0.51 nm for LNO$_{Na5%}$ powders. After 3 weeks storage, NiO region in LNO increased to 2.72 nm thickness while that of LNO$_{Na5%}$ sustained similar thickness (0.81 nm). Larger area of NiO phase in LNO than LNO$_{Na5%}$ sample may be due to contamination by CO$_2$ or H$_2$O during sample preparation. This can be a proof of better chemical stability of Na-doped LiNiO$_2$ than bare LiNiO$_2$. Na doping effectively suppressed creation of NiO phase on near-surface region during storage. Not only for near-surface region, Na dopants can influence whole bulk structure. To clarify effect of Na doping during storage, Rietveld refinement was done. Figure 22 shows Rietveld refinement result after 1 month storage of LNO and LNO$_{Na5%}$ powders. Cation mixing during storage 1 month of bare sample increased from 0.26% to 3.8% while that of Na-doped sample increased from 0.9% to 1.9%. This means that Na ions in Na-doped sample hindered cation migration during storage. In other words, Na-doped sample is more thermodynamically stable than bare sample. To compare thermodynamic stability of both samples, fresh powders were stored in Ar filled glove box where O$_2$ and H$_2$O concentration is sustained under 0.5 ppm so that effect of reaction on surface is negligible. Figure 23 shows XRD pattern and Rietveld refinement data of LiNiO$_2$ and Li$_{0.95}$Na$_{0.05}$NiO$_2$ after storage in Ar atmosphere for 2 weeks. Na-doped sample has lower cation mixing than bare sample. This means Na doped sample is more thermodynamically stable than un-doped sample.
Figure 17. Cycling performance of fresh and 1 month stored sample of (a) LiNiO$_2$ and (b) Li$_{0.95}$Na$_{0.05}$NiO$_2$
Figure 18. (a) TEM image of near-surface region of LiNiO₂ before storage (b) FFT-pattern of rock salt phase very-near-surface region (c) FFT-pattern of R-3m in bulk.
Figure 19. (a) TEM image of near-surface region of LiNiO$_2$ after 3 weeks storage (b) FFT-pattern of rock salt phase very-near-surface region (c) FFT-pattern of R-3m in bulk.
Figure 20. (a) TEM image of near-surface region of Li$_{0.95}$Na$_{0.05}$NiO$_2$ before storage (b) FFT-pattern of rock salt phase very-near-surface region (c) FFT-pattern of R-3m in bulk.
Figure 21. (a) TEM image of near-surface region of Li_{0.95}Na_{0.05}NiO after 3 weeks storage (b) FFT-pattern of rock salt phase very-near-surface region (c) FFT-pattern of R-3m in bulk.
Figure 22 Rietveld refinement result of 1 month stored powders of (a) LiNiO$_2$ and (b) Li$_{0.95}$Na$_{0.05}$NiO$_2$
Figure 23. Plot of cation mixing after storage in Ar-filled glove box for LiNiO$_2$ and Li$_{0.95}$Na$_{0.05}$NiO$_2$. 

LNO

LNO$_{\text{Na5\%}}$
4. Conclusion

Na-doped LiNiO$_2$ was synthesized to investigate pillaring effect of Na ions in Li layer. Na-doped LiNiO$_2$ showed enhanced cycleability with reduced cation mixing during cycling and transition metal dissolution. This is due to slower kinetic of Na ion than Li ion so that Na ions can act as pillaring agent during electrochemical performance. Not only enhancing electrochemical performance but also enhanced storage characteristic was observed. Phase transition on near-surface region and cation mixing during storage is reduced by Na doping. Doping elements which have slower kinetic than Li ions can be a possible solution for suppress degradation of LiNiO$_2$. 
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