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Layer spacing gradient $(NaLi)_{1-x}CoO_2$ for electrochemical Li extraction



The ion-exchange of Li_{1-x}CoO₂ with Na produces a core-shell (NaLi)_{1-x}CoO₂. The material consists of a Li-rich core and Na-rich shell that is connected by an intermediate phase. A layer spacing gradient exists in the material because of the small layer spacing of the Li phase and the large layer spacing of the Na phase. The Li phase restricts large layer spacing expansion and promotes Li intercalation over Na. During electrochemical insertion, (NaLi)_{1-x}CoO₂ achieved high Li selectivity in Na-rich aqueous solutions.

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Benchmark

First qualification/assessment of material properties and/or performance

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HIGHLIGHTS

 $(NaLi)_{1-x}CoO_2$ was synthesized by non-Faradaic ion-exchange of $Li_{1-x}CoO_2$ with Na

Li phase and Na phase are connected by an intermediate phase

The chemical compositions and spatial relation of the different phases is critical

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Layer spacing gradient $(NaLi)_{1-x}CoO_2$ for electrochemical Li extraction

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SUMMARY

Designing materials with high Li to Na selectivity is the key for direct extraction of Li from unconventional sources, such as seawater, without complex separations. However, material discovery is hindered by an insufficient understanding on how a material's composition and structure relate to Li selectivity during electrochemical co-intercalation. Here, we synthesized a core-shell structured $(NaLi)_{1-x}CoO_2$ with a core Li phase $(Li_{0.94}CoO_2)$, a shell Na phase (Na_{0.51}CoO₂), and a transition intermediate phase via Na ion-exchange of parent $Li_{1-x}CoO_2$. We reveal that the chemical compositions and spatial relation of these phases play critical roles in governing high Li to Na selectivity. The core Li phase restricts large layer spacing expansion and inhibits Na intercalation. The shell Na phase serves to maintain the electrode stability against further Na ion exchange. With the layer spacing gradient design, we achieved a high Li selectivity of 1.5×10^5 with a recovery of \sim 7.6:1 Li to Na from 1:20,000 initial ratio.

INTRODUCTION

The demand for lithium has grown tremendously over the past decades due to Li-ion battery development for electric vehicles, portable electronics, and stationary energy storage.^{1–3} The increasing lithium consumption has been projected to continue into the coming decades with a compound annual growth rate of 15%–30%, which poses a serious risk to the current supply chain in the near to mid-term future.^{4,5} Lithium from brines constitutes 66% of the world lithium resource, excluding oceans.⁶ This process relies on solar energy and arid climates for water evaporation over a period of 12–18 months, followed by multi-step chemical treatment and the precipitation of Li₂CO₃.⁶ These conditions limit the scaling up of lithium extraction from brines to meet long-term demands.^{7,8} Supply chain issues may be mitigated by mining other Li sources. Unconventional sources, including seawater, flowback water, and geothermal reservoirs, contain abundant Li. Currently, seawater is not an economically viable source due to the dilute lithium concentrations, 0.177 ppm.⁹ Efficient and environmentally friendly Li extraction methods enabling access to the 230 billion tons of lithium in seawater could sustain a practically infinite supply.

Methods for development of Li extraction have increased recently.^{10–12} In light of these developments, electrochemical extraction with Li-ion intercalation electrodes has demonstrated greater selectivity and recovery rates of lithium from brines relative to other methods, such as capacitive deionization and adsorption processes.¹³ The mechanism of intercalation could provide selectivity to Li due to the differences in intercalation potential between Li and Na ions in the host material, which partially depends on relative differences of Li-O versus Na-O bond strengths for a given a crystal structure. Selectivity also depends on phase stability and differences in ion

Progress and potential

Electrochemical extraction with insertion materials is a promising method to selectively extract lithium from Na-rich aqueous environments. However, the host structural evolution that accompanies the competitive cointercalation and the host structure-selectivity relationship is yet to be understood. Here, we designed a core-shell layered cobalt oxide, $(NaLi)_{1-x}CoO_2$, via non-Faradaic ion-exchange of the parent $Li_{1-x}CoO_2$ with Na ions for Li extraction. Using electrochemical intercalation, we perform successful Li extraction from 1:20,000 Li to Na solution to \sim 7.6:1 Li to Na, a Li selectivity of 1.5×10^5 over Na. We find the spatial relationship of the Li and Na in the core-shell structure plays an important role in achieving selective Li extraction as revealed by atomic resolution characterizations.

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migration barriers.¹⁴ Therefore, the efficiency of lithium extraction largely relies on the choice of electrode material. So far, electrodes investigated include olivine LiFePO₄,^{11,15} spinel λ -MnO₂,^{16,17} and layered LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NMC),¹⁸ which have mainly demonstrated Li selectivity in brine solutions (Table S1). All these previous works directly adopted conventional battery materials without tailoring the material structures and properties to the complex extraction from an aqueous environment. A fundamental understanding of the structure-selectivity relationship of the materials during competitive co-intercalation of both Li and Na is needed to improve the selectivity and stability of direct Li extraction from more dilute sources.

Here, we demonstrate that a new material, from the layered cobalt oxide family, can achieve highly selective Li extraction through structural design. The selection of the layered cobalt oxide family is due to the large difference in stabilization energy between Li and Na, which shows a preference for Li intercalation, and the rich knowledge of its structural information during both Li and Na intercalation.¹⁴ Even though it has been successful in Li-ion batteries,¹⁹ layered cobalt oxide has never been investigated for the electrochemical extraction of Li. We discovered for the first time that, when immerged into a Na dominating water solution without any applied current, $Li_{1-x}CoO_2$ particles, with x above a threshold value, transfer into a core-shell structure with most of the core of Li_{0.94}CoO₂, a shell of Na_{0.51}CoO₂, and an intermediate phase connecting the two. The chemical compositions and spatial distribution of these phases in the $(NaLi)_{1-x}CoO_2$ is significant in governing a high Li selectivity with stable co-intercalation. The shell Na phase and the intermediate phase serve as a sink for further intercalation. The existence and connection of the core Li phase to the shell restricts layer expansion and promotes high selectivity toward Li. The Na_{0.51}CoO₂ shell also prevents further Na ion-exchange and maintains the stability of the electrode. During intercalation and deintercalation, the ratio of the Li phase/ Na phase oscillates dynamically, which increases during intercalation and decreases during deintercalation, which indicates that Li dominates the charge transfer in the electrode. The $(NaLi)_{1-x}CoO_2$ electrode can extract Li selectively for a range of combined solutions of Li and Na, with a Li to Na mol ratio of 1:100 to 1:20,000. In the lowest Li concentration solution (Li:Na of 1:20,000), we achieved a recovery solution with a Li to Na mol ratio of \sim 7.6:1 in a single electrochemical extraction, which is equivalent to a high Li selectivity of 1.5×10^5 .

RESULTS AND DISCUSSION

Li/Na ion-exchange with parent $Li_{1-x}CoO_2$

Electrochemical extraction of Li works by extracting (electrochemical intercalation) Li from a dilute Li solution and then recovering (electrochemical deintercalation) Li in a fresh solution (schematics shown in Figure S1). The aqueous cycling stability of pure LiCoO₂ (LCO) is good between 0.6 and 0.72 V versus Ag/AgCl, as shown in Figure S2. The stable cycling verified that LCO can be cycled in aqueous solution when an oxygen evolution reaction (OER) and a hydrogen evolution reaction (HER) are avoided.^{20,21} For electrochemical extraction with layered cobalt oxide, vacancies are first created using an initial delithiation of parent LCO. An aqueous 1 M Na⁺ solution instead of Li⁺ was used as the electrolyte. From X-ray diffraction (XRD) analysis, the (003)_{LCO-r} Bragg peak of the pristine LCO (R3m) shifts from 1.344 to 1.342 Å⁻¹ after delithiation at a rate of 0.6 C for 1 h in Na⁺ solution (Figure S3; Notes S1 and S2). This phase transformation is far from the expected Li_{0.70}CoO₂.²² New peaks appear, with the most notable being at 1.128 Å⁻¹. The peaks match well for a combination of rhombohedral Li_{0.94}CoO₂ (R3m) and monoclinic Na_{0.51}CoO₂ (C2/m). The characteristic peak at 1.128 Å⁻¹ is (003)_{NCO-m}.

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the $(003)_{NCO-m}$ peak than the $(003)_{LCO-r}$ indicates an expansion of the layer spacing due to the intercalation of the Na⁺ (102 pm) relative to the smaller Li⁺ (76 pm), as well as a higher vacancy percentage and increased electrostatic repulsion.

Once vacancies are formed, the Na/Li exchange occurs quickly without applied current, as characterized by in situ XRD during initial delithiation (Figure S4; Note S3). To maintain the charge neutrality, Na in the solution exchanges with Li in the structure and leaves the material with the same vacancy percentage as $(NaLi)_{1-x}CoO_2$ $((NL)_{1-x}CO)$. Alkali metal exchange processes allow the creation of electrode materials with metastable structures and mixed compositions of Li and Na.²³⁻²⁷ These materials are formed by the (electro)chemical oxidation of the parent material to extract the original alkali ions, followed by an (electro)chemical reduction to insert new alkali ions. The ion-exchange of layered cobalt oxides has been performed; however, spontaneous ion-exchange with Li partially exchanged with Na after oxidation has not been reported. For this process to be understood, the dependence of the Na/Li exchange on the vacancy percentage was investigated, and the equilibrium of the same Li phase and Na phase was observed. $Li_{1-x}CoO_2$ at different vacancy percentage x was generated using 1 M Li⁺ solution. Figure 1A shows the shifting (003)_{LCO-r} peak of LCO from delithiation due to the increased vacancy composition. Next, the samples were soaked in a 1 M Na⁺ solution overnight for cation exchange. As shown in Figure 1B, the $(003)_{NLCO-r}$ peak of $Li_{1-x}CoO_2$, with vacancies of $x \ge 0.06$, shifts to 1.342 Å⁻¹ and allows the emergence of the (003)_{NCO-m} peak at 1.128 $Å^{-1}$. The expected threshold should be greater than 6% of vacancy so that enough vacancy composition is available for both phases. The emergence of a Na phase at the 6% vacancy sample could be due to the heterogeneity, as demonstrated by the (003)_{LCO-r} peak splitting shown in Figure 1A. The (003)_{NCO-m}/(003)_{LCO-} $_{\rm r}$ intensity ratio increases with the vacancy percentage, with 0.104 at 6% vacancy and 1.093 at 30% vacancy, indicating a growing Na phase at higher vacancy percentage. The key material changes are summarized in Figure 1C. The illustration highlights the formation of the (NL)_{1-x}CO from $Li_{1-x}CO_2$ transforming into a combination of $Li_{0.94}CoO_2$ with a contracted layer spacing and $Na_{0.51}CoO_2$ with an expanded layer spacing and distorted lattice compared with the rhombohedral $Li_{1-x}CoO_2$.

Core-shell phase separation of Li phase and Na phase

Since the spatial distribution of these phases would impact further intercalation, and therefore the selectivity of the electrode, the (NL)_{0.7}CO was characterized to atomic resolution. Individual particles were thinned using a focused ion beam (FIB)/scanning electron microscope (SEM) for imaging using scanning transmission electron microscopy (STEM). Elemental characterization was achieved with energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). The first area of interest was near the side of the particle at the electrode and electrolyte interface where the Na/Li exchange occurs. Pt was deposited on the outer surface of the particle before sample thinning, and its position labeled the electrode and electrolyte interface. Selected area diffraction patterns confirmed the STEM image view along the [110] zone axis (Figure S5). The STEM high-angle angular dark field (HAADF) image in Figure 2A shows four distinct regions by contrast. First, the bottom of the image consists of the protective Pt coating from the particle thinning procedure. Second, above the Pt region, there exists a darker contrast region that would have previously been the electrode and electrolyte interface. Third, a lighter-contrast region makes up the core of the particle. Fourth, a significant number of streaks run parallel to each other within the core region (clearly visible in Figure S6A). The particle surface was confirmed by the EDS data to be Na rich, with thicknesses varying between 10 and 25 nm (Figure 2B). Significant numbers of streaks were also confirmed to be Na, traveling through the core via the 2D planes and diffusing

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Figure 1. Phase transformation of delithiated $Li_{1-x}CoO_2$ into $(NaLi)_{1-x}CoO_2$

(A) XRD patterns of the (003)_{LCO-r} peak of Li_{1-x}CoO₂ after delithiation in aqueous 1 M LiCl at a rate of 0.6 C, where x = 0, 0.025, 0.06, 0.10, 0.20, or 0.30 from the bottom to the top spectrum, respectively. Each spectrum is a new electrode sample.

(B) XRD patterns of $(NaLi)_{1-x}CoO_2$ after soaking the delithiated $Li_{1-x}CoO_2$ in aqueous 1 M NaCl for 16 h. Each spectrum is from the same electrode from (A) directly to its left. The dashed lines indicate the positions of the $(003)_{NCO-m}$ peak and the $(003)_{LCO-r}$ peak.

(C) Crystal structure illustrations of the $Li_{0.70}CoO_2$ transforming into a combination of $Na_{0.51}CoO_2$ and $Li_{0.94}CoO_2$. Note that the Li phase and Na phase have differing alkali concentrations. The blue octahedrals represent CoO_6 units, green spheres represent Li^+ , and yellow spheres represent Na^+ .

across the Co layers (Figure S6B). As expected, the EDS data show that Co and O are present. The center of the particle accommodates a small content of Na in the form of Na phase streaks; the Na phase and Li phase remain separated. The small phase content of Na indicates that the Li phase dominates the core of the (NL)_{0.7}CO.

The core-shell structure of $(NL)_{0.7}CO$ was confirmed by a second sample thinned at the center of the particle at the terminating CoO_2 plane. The STEM HAADF images in Figure 2C show three of the four distinct regions in Figure 2A that are confirmed by EDS to be Pt coating, Na shell, and Li core (Figure S7). The surface thickness of the Na phase varies by 35–45 nm. The atomically sharp boundary (Figure S8) in contrast marks the Na phase transition to the Li phase set by a CoO_2 layer. From both STEM



Figure 2. Characterization of the shell Na phase and core Li phase in (NL)_{0.7}CO

(A) STEM high-angle angular dark field (HAADF) image of the (NL)_{0.7}CO particle cut near the electrode/electrolyte interface. Dashed lines separate Pt coating, Na phase, and Li phase domains. The insert illustrates the micron-sized (NL)_{0.7}CO particle, where the yellow section of the box is the region of interest for imaging and the gray section is the Pt coating.

(B) STEM HAADF image and its corresponding EDS elemental mapping (Na, Co, O, Pt).

(C) STEM HAADF image of an $(NL)_{0.7}$ CO particle near the center of the terminated CoO₂ surface. The insert illustrates the region of imaging (highlighted in the box).

(D–F) STEM low-angle annular dark field images of a core with a Na streak (D) and the shell (E) with labeled layers for its corresponding Li-EELS spectra (F). The gray box indicates region of interest.

(G) High-resolution STEM HAADF image of the core with a Na streak. Layer spacings are marked with arrows.

(H) Layer spacing highlighted with colored dashed lines. Blue indicates 4.64 Å (Li phase), green indicates 4.92–5.02 Å (intermediate phase), and red indicates 5.60 Å (Na phase).

(I) Schematic showing the ion-exchange process and the resulting core-shell $(NL)_{1-x}CO$ particle with a Na phase shell (red) and a Li phase core (blue), connected by the intermediate phase (green).

samples, the Na phase constitutes the particle surface indicating a core-shell structure with Li phase as the core.

The compositions of the observed Li and Na regions were further determined. EDS provides evidence that, despite coexisting in the same particle, the Li phase does

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not contain Na. However, Li might exist in the Na phase or in an additional phase. The Li presence was probed with EELS both in the core near the Na phase streaks (Figure 2D) and in the shell (Figure 2E). The EELS spectra in Figure 2F show the superposition of the Li-K and Co-M_{2.3} edges in the low-loss region.²⁸ The spectra reveal three distinct sets of data that are grouped based on overall intensity and the onset edge slope between 59.1 and 61.9 eV. The overall intensity will be larger when Li and Co are present due to the superposition of their signals, and the onset slope will be steeper for a larger Li composition due to those energies being more characteristic of the Li-K edge. The first set (a-c), contains the spectra with the largest overall intensity and the largest onset edge slope, indicating the highest Li composition. Layers (a-c) have a 4.61 Å layer spacing that corresponds well with the expected $Li_{0.94}CoO_2$ layer spacing from XRD (4.62 Å). The second set (f-h) contains the spectra with a lower overall intensity and a flatter onset edge slope, indicating a decrease in the composition of Li. Layers (f-h) have a 4.92 Å layer spacing, indicating an intermediate layer spacing relative to the expected Li_{0.94}CoO₂ and Na_{0.51}-CoO₂ phase layer spacings. The third set (d, e, i, and j) contains the spectra with smallest overall intensity and smallest onset edge slope. Layers (e and d) have a 5.33 Å layer spacing, and layers (i and j) from the shell have a 5.45 Å layer spacing, which correspond well with $Na_{0.51}CoO_2$ phase layer spacing (5.57 Å), indicating minimal presence of Li. The Li phase, Na phase, and their transition was further characterized with high-resolution STEM. Figures 2G and S9A ([110] zone axis) displays a clear image of the planes of Co atoms. Transition across the cobalt oxide layers was accomplished using an intermediate phase with a spacing of 4.92-5.05 Å from the Na phase (5.60 Å) to the Li phase (4.64 Å). The existence of multiple phases in a single layer leads to nonuniformities in layer spacing; particularly in the intermediate phase (Figures 2H and S9B). These nonuniformities are caused by strain from the Li phases and Na phases separated in the same plane and the complexities of the strain fields in a single multiphase particle. With the STEM characterization, we summarize that the (NL)_{0.7}CO structure displays a Na phase (Na_{0.51}CoO₂) at the particle surface, a Li core ($Li_{0.94}CoO_2$) with a discrete Na phase, and an intermediate phase for the transition (Figure 2I). The Li_{0.94}CoO₂ and Na_{0.51}CoO₂ phases are exclusive to Li and Na ions, respectively.

Li selectivity in mixed Li and Na solutions

Next, we investigated the selectivity of core-shell (NL)_{0.7}CO material to Li. A Na⁺ electrolyte (1 M) spiked with different concentrations of Li⁺ was used for the tests. The (NL)_{0.7}CO electrode was cycled 20 times before the final intercalation (extraction). The 20-times cycling was to establish an equilibrium state between the electrode and the solution to avoid recovery of structural Li from the original (NL)_{0.7}CO. Then the electrode was moved to a fresh solution (see the Experimental procedures) for recovery, followed by inductively coupled plasma-mass spectroscopy (ICP-MS) measurement of Li and Na concentrations. As shown in Figure 3A, (NL)_{0.7}CO demonstrated high recoverability of Li⁺ in these solutions by electrochemical extraction at a rate of 0.6 C. The recovery was consistently high from solutions containing Li to Na ratios of 1:100, 1:1,000, 1:5,000, 1:10,000, and 1:20,000, with recovered mol ratios of Li to (Li + Na) of 89.5% \pm 0.6%, 92.7% \pm 2.2%, 89.3% \pm 3.0%, 87.9% \pm 1.1%, and 88.4% \pm 0.5%, respectively, corresponding to Li to Na ratios of \sim 8.5:1, 12.8:1, 8.3:1, 7.2:1, and 7.6:1 in the recovery solution. The accuracy of ICP-MS measurement of selectivity was confirmed by high agreement between the measured cations and the expected values from the electrochemical extraction reported as percentages of ions measured/ions deintercalated all within 7% of each other (Figure 3B). The ratios were most likely below 100% due to adsorption of deintercalated cations onto the electrode. The $(NL)_{1-x}CO$

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(A and B) Performance results for deintercalation into recovery solution after cycling in various concentrations (M) of Li⁺ with 1 M Na⁺, denoted by Li to Na ratios of 1:100, 1:1,000, 1:5,000, 1:10,000, and 1:20,000. The recovered Li/(Li + Na) (A) is the ratio moles of Li⁺ to the total moles of Li⁺ and Na⁺ in the recovery solution. The efficiency of the recovery process (B) compares the total mols of measured cations (Li⁺, Na⁺) via ICP-MS over the expected total mols via Coulomb counting. All data represented as mean \pm standard deviation.

(C and D) Performance results for various rates of C over the same state of charge range. The cycled solutions were: Li:Na 1:1,000 (green) and Li:Na 1:20,000 (yellow). Recovery (C) and efficiency (D) are reported the same as in parts (A) and (B), respectively.

electrodes reach Li selectivity factors (Figure S10A) as high as 1.5×10^5 in the 1:20,000 solution, a similar ratio to seawater. These results show promise for high Li recoverability from real seawater using the (NL)_{1-x}CO electrode compared with other electrode materials (Table S1).

The electrochemical extraction rates varied for solutions with Li to Na ratios of 1:1,000 and 1:20,000. These rates were important because they are related to the productivity of the mining method for Li. No strong dependence of the Li recoverability on the rate over the same state of charge was observed. For rates between 0.12 C and 1.20 C, 90.4% \pm 0.6%, 93.8% \pm 2.2%, 92.7% \pm 2.2%, and 95.4% \pm 0.6% Li to (Li + Na) mol ratios were measured for 1:1,000 Li to Na and 92.7% \pm 1.2%, 84.7% \pm 1.3%, and 88.4% \pm 0.5% were measured for 1:20,000 Li to (Li + Na), as shown in Figures 3C and 3D. The increased overpotential from faster rates increases the probability of OER, which prevented the measurement in the 1:20,000 solution at a rate of 1.2 C. The electrochemical extraction rate can be adjusted without a Li selectivity trade-off (Figure S10B). Therefore, extraction can be accomplished at higher rates as long as the overpotential is not high enough to cause OER. In addition, the high selectivity is retained in seawater-like concentrations of 0.49 M 1:20,000 Li:Na at a rate of 0.60 C (Figure S10C). These results reveal the efficient capability of layer gradient spacing (NaLi)_{1-x}CoO_{2 for} extracting Li from seawater.



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Figure 4. Phase and composition changes upon cycling in aqueous solution with a Li to Na ratio of 1:1,000 for Li⁺ recovery

(A) Constant current intercalation (red) and deintercalation (blue) at a rate of 0.6 C in the Li^+ spiked solution. The x in $(NaLi)_{1-x}CoO_2$ ranges between 0.195 and 0.300.

(B) The Li⁺ (blue) and Na⁺ (red) ratios measured after dissolving the cathodes for the following stages: pristine LiCoO₂ (LCO), initial (NL)_{1-x}CO (Delith), 1st intercalation (1st int), and deintercalation (1st deint), 2nd intercalation (2nd int), 19th deintercalation (19th deint), and 20th intercalation (20th int), and deintercalation (20th deint) after cycling in the 1:1,000 solution. (C) XRD spectra for sample (NaLi)_{1-x}CoO₂ at end of the intercalation, x = 0.195 (red), and deintercalation, x = 0.300 (blue) at different cycles.

(D) Detailed view of the $(003)_{NCO-m}$, $(003)_{LCO-r}$, and intermediate peaks from the XRD spectrum. A more detailed view of (D) is available in Figure S13.

Characterization during co-intercalation

To understand and confirm the high selectivity using (NL)_{0.7}CO, a series of structure and composition analyses were conducted during 20 cycles in a 1:1,000 solution. In the potential curve (Figure 4A), the first intercalation from states of charges x =(0.300–0.195) for (NaLi)_{1-x}CoO₂ reveals a departure from LCO cycling behavior in a pure Li⁺ electrolyte. The (NaLi)_{1-x}CoO₂ potential curves have a greater range and more slope changes than LiCoO₂ cycling in a pure Li⁺ electrolyte due to both phase transformations and a lower half cell potential from a dilute Li⁺ concentration. The potential reaches a similar voltage to Na_{0.51}CoO₂ in a Na-ion battery (~0.1 V versus Ag/ AgCl)²⁹ at the end of intercalation, but overall remains at a higher voltage, possibly due to the co-existence of a Li_{0.94}CoO₂ phase and the Li ion being the major charge carrier ions. The intercalation curves following the 1st intercalation indicate a permanent change in the structure as they have shifted to higher potentials and are now characterized by two, new, shallower slopes, 0.195 $\leq x \leq$ 0.245 and 0.245 $\leq x \leq$ 0.287. As the number of cycles increases, the hysteresis of the intercalation/deintercalation curve decreases, which corresponds to a decrease in the kinetic polarization and



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free energy barrier representing the interfacial energy and coherency strain energy in a single, multiphase particle.³⁰ The electrochemical curve shows a good reversibility for the material. To reveal the change of the $(NL)_{1-x}CO$ chemical composition during cycling, parallel samples were sacrificed at different intercalation/deintercalation cycles and the electrodes were dissolved for ICP-MS measurement.

In Figure 4B, the LCO transformed into $Li_{0.50}Na_{0.20}CoO_2$ after the initial deintercalation. The Li content is higher than that predicted using phase equilibrium between $Li_{0.94}CoO_2$ and $Na_{0.51}CoO_2$ for the initial deintercalated (NaLi)_{0.7}CoO_2. This is due to the formation of the intermediate phase (shown in Figures 2G–2I), which has a high Li content. Over the 20 cycles, the Li to Na ratio in the material was ~7:3, with an oscillating pattern. Comparing samples in close time series, the Li content was observed to increase upon intercalation and decrease upon deintercalation (Figure 4B). This trend confirms that Li constitutes most of the charge transfer from the Li⁺-spiked solutions. Li is most likely not intercalated directly into the $Li_{0.94}CoO_2$ phase due to the increase in the migration barrier at low vacancy compositions.³¹ Even at a low rate of C, the capacity cannot be fully used in a 1:1,000 aqueous solution for a (NL)_{1-x}CO when x = 0.06 or x = 0.04 (Figure S11). As expected, the Na phase does not form in the low vacancy state.

Moreover, synchrotron XRD confirms the oscillating pattern of material change during cycling. The spectra in Figure 4C show changes in the relative intensities of the Na phase and Li phase peaks; notably the $(003)_{NCO-m}$ and $(003)_{LCO-r}$ peaks (Figure 4D). The $(003)_{NCO-m}/(003)_{LCO-r}$ ratio remains decreasing during each intercalation until the $(003)_{NCO-m}$ peak almost completely disappears by the 20^{th} intercalation, but continues to partially reverse after deintercalation, when more vacancies are formed. The Na phase has an apparent change in the c-lattice parameter with each intercalation and deintercalation. The $(003)_{NCO-m}$ peak shifts to the same higher Q value (1.137 Å⁻¹) during intercalation; thus indicating a decrease in the c-lattice parameter and a compression of the Na phase layers; potentially due to Na intercalation as well as the increased Li intercalation squeezing the Na to a lower vacancy phase.^{26,27,32} Upon deintercalation, the $(003)_{NCO-m}$ peak shifts back to its original position (1.127 Å⁻¹) and the Na phase layers expand again.

The shell Na phase maintains a Na composition, despite a dynamic phase volume, that stabilizes the structure by limiting further ion-exchange between Li in the $(NL)_{1-x}CO$ and Na in the solution. Concurrently, the $(003)_{LCO-r}$ peak remains in the same position and shows no signs of a change in layer spacing. This is consistent, and small layer spacing of the core Li phase prevents Na intercalation. For a $L_{1-x}CO$ material, there is no stabilizing Na phase shell to form the electrode-electrolyte interface. When $L_{0.7}CO$ is used for intercalation in the 1:1,000 solution, the Na ion-exchange and intercalation leads to a decrease in the Li composition of the electrode and a significant increase of the composition of Na (Figure S12). The differences in the 1st intercalation curve are due to differences in the initial material and ongoing Li/Na ion-exchange in the $L_{1-x}CO$ material. This reveals that the Li phase alone will not provide high selectivity during co-intercalation.

Interestingly, a new peak appears that varies between 1.255 and 1.267 Å⁻¹ for every intercalation step (Figure 4D, and with better resolution in Figure S13) and then disappears again upon each deintercalation. This peak has a low intensity and has no accompanying peaks; thus providing little information for phase determination. This peak corresponds to a 4.93 to 5.02 Å d-spacing, which matches well with the intermediate layer spacing regions from the core-shell (NL)_{0.7}CO STEM images.

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The peak growth implies an increasing volume of the intermediate phase and its increased significance in a particle. During the cycling, the preferred Li intercalation may enable the conversion of the Na phase into the intermediate phase, which then precipitates out the Li phase. Because the intermediate phase has a layer spacing well below the 5.57 Å Na phase layer spacing, the energy barrier for layer expansion limits Na intercalation into the intermediate phase. The structural evolution leads to dominant intermediate phase has the important role of storing extracted Li and limiting the large Na ion because of its small layer spacing. Similar trends were observed in the intercalation/deintercalation curve and XRD spectrum (Figure S14) for the 1:20,000 solution; thus supporting the same phase transformations in varying Li⁺ concentrations.

Conclusions

The $(NL)_{1-x}CO$ material enabled the highly selective electrochemical extraction of Li from solutions with initial Li to Na ratios of 1:100 and 1:20,000. The solution with a Li to Na ratio of 1:20,000 was concentrated to a Li to Na ratio of ~7.6:1, emphasizing the potential to successfully extract Li from real seawater. This high selectivity was made possible by the transformation of the parent Li_{1-x}CoO₂ into the core-shell (NL)_{0.7}CO. The key components of this electrode are the shell Na phase, core Li phase, and the intermediate phase. Upon cycling in the dilute Li solutions, the phases transform into an intermediate phase plus a Li phase dominant structure at lower states of charge and a higher Na phase plus Li phase structure at higher states of charge. This complex phase relationship enables high Li extraction by storing Li in the intermediate phase and particle stability by having a core-shell mixed cation composition. These insights showcase the importance of understanding the phase transformation behavior due to cation co-intercalation as well as reveal the opportunities in developing new electrode materials.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the Lead contact, Chong Liu (chongliu@uchicago.edu).

Materials availability

This study did not generate new unique reagents.

Date and code availability

This study did not generate or analyze datasets or codes.

Electrode preparation

The LiCoO₂ (LCO, MTI Corporation) electrodes were prepared by casting a slurry of Li-CoO₂, Super P carbon black, and polyvinylidene fluoride with a mass ratio of 80:10:10, in *N*-methyl-2-pyrrolidone. The electrode slurry was drop casted on a 1.25 × 1 cm² geometrical surface of a carbon cloth (ELAT-H, FuelCellEtc) current collector of 5 × 1 cm² and dried on a hotplate at 100°C overnight. The other end of the carbon cloth was connected to a Pt clamp. The active material mass loadings ranged between 7 and 12 mg cm⁻². NaFePO₄ counter electrodes were made with the same slurry compositions above by first galvanostatically delithiating LiFePO₄ (LFP, MTI Corporation) in an aqueous 1 M NaCl solution at a C/2 rate until reaching a 0.5 V versus Ag/AgCl voltage cutoff and then sodiated in a new, aqueous 1 M NaCl solution at a C/60 rate until reaching a -0.6 V versus Ag/AgCl voltage cutoff. Carbon felt (Alfa Aesar) disks (0.9525 cm

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diameter × 3.18 mm thickness) were connected to a Ti wire and coated with the electrode slurry and dried on a hotplate at 100°C. The active material mass loading ranged between 60 and 70 mg cm⁻². For the delithiation and sodiation, an Ag|AgCl|KCl (4.0 M) reference electrode and a graphite rod counter electrode were used in a three-neck round-bottomed flask with 60 mL of solution. N₂ was continuously bubbled into the solution to displace dissolved O₂. All electrochemical operations were performed on a BioLogic VMP3 workstation. The sodiated NaFePO₄ (NFP) counter electrodes were paired with the delithiated (NaLi)_{1-x}CoO₂ electrode for galvanostatically cycling in 600 mL of synthetic brine/seawater solutions. The synthetic brine/seawater contained varying amounts of LiCl (10 mM, 1 mM, 200 μ M, 100 μ M, and 50 μ M) in an aqueous 1 M Na⁺ (Cl⁻, OH⁻) solution (pH 11.5).

Electrochemical tests

The initial delithiation of LCO was done in a three-neck round-bottomed flask with an Ag|AgCl|KCl (4.0 M) reference electrode, a graphite rod counter electrode, and 60 mL of electrolyte solution. The aqueous electrolyte solutions consisted of either 1 M LiCl (pH 7) or 1 M Na⁺ (Cl⁻, OH⁻) (pH 11.5). For the samples delithiated in 1 M LiCl in Figure 1, the LCO electrodes were galvanostatically delithiated at a rate of 0.6 C for various times. The delithiated electrodes were rinsed with deionized (DI) water and dried under vacuum at 60°C for 1 h. The samples were then characterized using XRD, as shown in Figure 1A. These samples were then soaked in an aqueous 1 M Na+ (Cl⁻, OH⁻) solution (pH 11.5) for 16 h. The electrodes were then characterized using XRD, as shown in Figure 1B.

For all other electrochemical tests, samples were prepared by delithiating LCO electrodes in an aqueous 1 M Na⁺ (Cl⁻, OH⁻) solution (pH 11.5) to create the (NaLi)_{1-x}CoO₂ $((NL)_{1-x}CO)$ electrodes. Then, they were rinsed in three different 60 mL 10 μ M KOH (aq.) solutions for 30 min with continuous N_2 bubbling to remove excess adsorbed cations. For the sample for STEM (Figure 2), the (NL) $_{1-x}$ CO electrode was washed with DI water, vacuumed dried at 60°C for 1 h, and then stored in an Ar glovebox. For the recovery measurements (Figure 3), the (NL)_{0.7}CO samples were rinsed with DI water and transferred into 600 mL of the synthetic brine/seawater solution. The NFP replaced the graphite rod as the counter electrode. The electrode was cycled for varying C rates over the same 19.5%–30% state of charge range for 20 cycles, followed by a final intercalation to 19.5% state of charge. The sample was then rinsed in three separate 60 mL 10 μ M KOH (aq.) solutions for 30 min with continuous N₂ bubbling to remove excess adsorbed cations. The electrode was then moved to 60 mL 30 mM K⁺ (Cl⁻, OH⁻) solution (pH 11.5) with a graphite counter electrode and bubbling N₂. The electrode was deintercalated at the same rate as the cycling of the sample to 30% state of charge and then the recovery solution was analyzed using ICP-MS.

For the cycled electrode composition and XRD data (Figure 4), the cycling was stopped at 19.5% SOC for intercalation and 30% SOC for deintercalation for a given cycle as labeled. The dissolved samples were rinsed with flowing DI water to remove excess adsorbed cations from the solution. The working electrodes were then placed in aqua regia acid for 72 h. The acid samples were diluted and then analyzed via ICP-MS. The samples for synchrotron radiation XRD were rinsed in DI water, dried under vacuum 60°C for 1 h, and then covered in Kapton tape.

XRD characterization

The XRD images in Figure 1 were measured using a Bruker D8 Discover GADDS with a Vantec-2000 2D detector at a frame range of 20° (2 θ) for 10 min/frame at a

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monochromatic X-ray incident beam of 0.15406 nm. All XRD spectrum intensities were scaled to the same range. The XRD synchrotron radiation for most of the samples was measured at beamline 11-BM of the Advanced Photon Source at Argonne National Laboratory using ultrahigh-resolution powder XRD with a monochromatic X-ray incident beam of 0.457884 Å. All XRD spectrum intensities were scaled to the same range. Samples labeled Delith, 1st int, 1st deint, 20th int, and 20th deint in Figures 4C and 4D were measured at beamline 11-ID-C of the Advanced Photon Source at Argonne National Laboratory with a monochromatic X-ray incident beam of 0.1173 Å. The 2D diffraction patterns were obtained in the transmission geometry using a PerkinElmer large area detector placed downstream at 1.5 m away from the sample. All XRD spectrum intensities were scaled to the same range. For an equalfooting comparison between XRD data obtained at both the 11-BM and 11-ID-C beamlines, an instrumental resolution function for the setup used at 11-ID-C was convoluted into the data from beamline 11-BM (e.g., peak smearing).

In situ synchrotron radiation XRD integrated with electrochemical control was done at beamline 12-ID-D of the Advanced Photon Source at the Argonne National Laboratory. In the experiment, a monochromatic X-ray incident beam with a wavelength of $\lambda = 0.6199$ A was introduced into a custom-designed electrochemical sample cell adopted for in situ measurements. The sample cell frame and all components were made of strong corrosion-resistant polymer Kel-F. LCO, on a carbon cloth electrode with 12.48 mg cm⁻² of active material, was placed within the central position of the *in* situ electrochemical cell between two sealed Kapton windows, with a gap of between 0.5 and 1 mm, which permits the electrolyte to be purged through the active LCO/carbon cloth layer. The 2D synchrotron radiation XRD diffraction patterns were collected using a Detrics Pilatus 100K photon counting area detector (pixel size 172 \times 172 μ m), which was located at about 150 mm after the sample position. The original 2D diffraction patterns were processed and integrated using FIT2D software to obtain plots of diffraction intensity versus Q (scattering vector). In the course of in situ experiments, fresh 1 M Na $^+$ (Cl $^-$, OH $^-$) solution (pH 11.5) was continuously pumped through the sealed sample cell to maintain a thin liquid film at a flow rate of 5 mL/min using a programmed NE-300 syringe pump. At the same time, galvanostatic delithiation was recorded using a Gamry Reference 600 potentiostat at a rate of 1.2 C for 33 min using an Ag/AgCl reference electrode and NaFePO₄ coated on a graphite counter electrode.

ICP-MS characterization

The recovery and dissolved sample compositions were diluted in a 3% HNO₃ matrix and measured using either Thermo iCAP Q ICP-MS or Thermo iCAP RQ ICP-MS.

SEM/FIB sample preparation

The $(NL)_{1-x}CO$ electrode sample for transmission electron microscope was prepared using a focus ion beam (FEI Helios NanoLab). The samples were prepared via the standard lift-out procedure, which includes coating the surface with a protective 1.2 μ m thick Pt layer to avoid Ga beam damage. The sample was attached to a Cu half grid and thinned to 70 nm using 30 and 5 kV Ga ion beams. A final sample cleaning was performed using a 2 kV Ga ion beam to remove any surface damage.

STEM characterization

STEM images were acquired using JEOL ARM 200F equipped with a cold field emission source. HAADF images were acquired at 200 kV with a less than 0.8 Å spatial resolution. The HAADF detector angle was 90–270 mrad to give Z contrast images. The low-angle annular dark-field detector angle ranged between 40 and 120 mrad.



EELS spectra were acquired using a Gatan GIF Continuum ER with a dwell time of 0.03 s per pixel. EDS spectra imaging was acquired using an Oxford X-Max 100TLE windowless SDD detector with a dwell time of 6.14 ms.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.matt. 2021.02.005.

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AUTHOR CONTRIBUTIONS

C.L. initiated the project. C.L. and G.T.H. conceived the idea and experiment design. G.T.H. conducted the experiments and analyzed the data. F.S. assisted in STEM imaging and elemental characterization with EELS and EDS. H.Z. assisted with synchrotron radiation XRD characterization. Y.H. assisted with data analysis. C.L. and G.T.H. wrote the manuscript, and all authors were involved in revising it.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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REFERENCES

- 1. Chu, S., Cui, Y., and Liu, N. (2017). The path towards sustainable energy. Nat. Mater. *16*, 16–22.
- Dunn, B., Kamath, H., and Tarascon, J.-M. (2011). Electrical energy storage for the grid: a battery of choices. Science 334, 928–935.
- 3. Armand, M., and Tarascon, J.-M. (2008). Building better batteries. Nature 451, 652–657.
- 4. Crabtree, G. (2019). The coming electric vehicle transformation. Science 366, 422–424.
- Ding, Y., Cano, Z.P., Yu, A., Lu, J., and Chen, Z. (2019). Automotive Li-ion batteries: current status and future perspectives. Electrochem. Energ. Rev. 2, 1–28.
- 6. Gruber, P.W., Medina, P.A., Keoleian, G.A., Kesler, S.E., Everson, M.P., and Wallington, T.J.

(2011). Global lithium availability: a constraint for electric vehicles? J. Ind. Ecol. *15*, 760–775.

- 7. Kushnir, D., and Sandén, B.A. (2012). The time dimension and lithium resource constraints for electric vehicles. Resour. Pol. *37*, 93–103.
- Flexer, V., Baspineiro, C.F., and Galli, C.I. (2018). Lithium recovery from brines: a vital raw material for green energies with a potential environmental impact in its mining and processing. Sci. Total Environ. 639, 1188–1204.
- Diallo, M.S., Kotte, M.R., and Cho, M. (2015). Mining critical metals and elements from seawater: opportunities and challenges. Environ. Sci. Technol. 49, 9390–9399.
- Razmjou, A., Asadnia, M., Hosseini, E., Korayem, A.H., and Chen, V. (2019). Design principles of ion selective nanostructured

membranes for the extraction of lithium ions. Nat. Commun. 10, 5793.

- Liu, C., Li, Y., Lin, D., Hsu, P.-C., Liu, B., Yan, G., Wu, T., Cui, Y., and Chu, S. (2020). Lithium extraction from seawater through pulsed electrochemical intercalation. Joule 4, 1459– 1469.
- Yang, S., Zhang, F., Ding, H., He, P., and Zhou, H. (2018). Lithium metal extraction from seawater. Joule 2, 1648–1651.
- Battistel, A., Palagonia, M.S., Brogioli, D., Mantia, F.L., and Trócoli, R. Electrochemical methods for lithium recovery: a comprehensive and critical review. Adv. Mater. 32, 1905440.
- Ong, S.P., Chevrier, V.L., Hautier, G., Jain, A., Moore, C., Kim, S., Ma, X., and Ceder, G. (2011). Voltage, stability and diffusion barrier



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differences between sodium-ion and lithiumion intercalation materials. Energy Environ. Sci. *4*, 3680.

- Pasta, M., Battistel, A., and La Mantia, F. (2012). Batteries for lithium recovery from brines. Energy Environ. Sci. 5, 9487.
- Kanoh, H., Ooi, K., Miyai, Y., and Katoh, S. (1991). Selective electroinsertion of lithium ions into a platinum/λ-manganese dioxide electrode in the aqueous phase. Langmuir 7, 1841–1842.
- Trócoli, R., Erinmwingbovo, C., and LaMantia, F. (2017). Optimized lithium recovery from brines by using an electrochemical ionpumping process based on λ-MnO₂ and nickel hexacyanoferrate. ChemElectroChem 4, 143–149.
- Lawagon, C.P., Nisola, G.M., Cuevas, R.A.I., Kim, H., Lee, S.-P., and Chung, W.-J. (2018). Li_{1-x}Ni_{0.33}Co_{1/3}Mn_{1/3}O₂/Ag for electrochemical lithium recovery from brine. Chem. Eng. J. 348, 1000–1011.
- Mizushima, K., Jones, P., Wiseman, P., and Goodenough, J. (1981). Li_xCoO₂ (0<x≰1): a new cathode material for batteries of high energy density. Solid State Ionics 3–4, 171–174.
- Ruffo, R., Wessells, C., Huggins, R.A., and Cui, Y. (2009). Electrochemical behavior of LiCoO₂

as aqueous lithium-ion battery electrodes. Electrochem. Commun. 11, 247–249.

- Luo, J.-Y., Cui, W.-J., He, P., and Xia, Y.-Y. (2010). Raising the cycling stability of aqueous lithium-ion batteries by eliminating oxygen in the electrolyte. Nat. Chem. 2, 760–765.
- Reimers, J.N., and Dahn, J.R. (1992). Electrochemical and in situ X-ray diffraction studies of lithium intercalation in Li_xCoO₂. J. Electrochem. Soc. 139, 2091.
- Mendiboure, A., Delmas, C., and Hagenmuller, P. (1984). New layered structure obtained by electrochemical deintercalation of the metastable LiCoO₂ (O2) variety. Mater. Res. Bull. 19, 1383–1392.
- Berthelot, R., Carlier, D., Pollet, M., Doumerc, J.-P., and Delmas, C. (2009). Synthesis and investigations on an O4-LiCoO₂ polytype. Electrochem. Solid State Lett. 12, A207.
- Paulsen, J.M., Larcher, D., and Dahn, J.R. (2000). O2 structure Li_{2/3}Ni_{1/3}Mn_{2/3}O₂: a new layered cathode material for rechargeable lithium batteries III. Ion exchange. J. Electrochem. Soc. 147, 2862.
- Heubner, C., Matthey, B., Lein, T., Wolke, F., Liebmann, T., Lämmel, C., Schneider, M., Herrmann, M., and Michaelis, A. (2020). Insights into the electrochemical Li/Na-exchange in

layered LiCoO₂ cathode material. Energy Storage Mater. 27, 377–386.

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- Xiao, B., Wang, K., Xu, G., Song, J., Chen, Z., Amine, K., Reed, D., Sui, M., Sprenkle, V., Ren, Y., et al. (2019). Revealing the atomic origin of heterogeneous Li-ion diffusion by probing Na. Adv. Mater. 31, 1805889.
- Kikkawa, J., Mizoguchi, T., Arai, M., Nagai, T., and Kimoto, K. (2018). Identifying lithium K edge anisotropy in LiCoO₂. Phys. Rev. B 98, 075103.
- Berthelot, R., Carlier, D., and Delmas, C. (2011). Electrochemical investigation of the P2– Na_xCoO₂ phase diagram. Nat. Mater. 10, 74–80.
- Van der Ven, A., Garikipati, K., Kim, S., and Wagemaker, M. (2009). The role of coherency strains on phase stability in Li_xFePO₄: needle crystallites minimize coherency strain and overpotential. J. Electrochem. Soc. 156, A949.
- Van der Ven, A., and Ceder, G. (2001). Lithium diffusion mechanisms in layered intercalation compounds. J. Power Sources 97–98, 529–531.
- Kim, H., Kwon, D.-H., Kim, J.C., Ouyang, B., Kim, H., Yang, J., and Ceder, G. (2020). Na⁺ redistribution by electrochemical Na⁺/K⁺ exchange in layered Na_xNi₂SbO₆. Chem. Mater. 32, 4312–4323.