Asymmetric pathways for lithium extraction and recovery based on the two-phase equilibrium of layered oxides

Grant T. Hill[1], Raphael Stone[1], Yu Han[1], Jiadong Liu[1], Siqi Zou[1], Hua Zhou[2], Chong Liu[1,*]

1. Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, USA
2. Advanced Photon Source, Argonne National Laboratory, Lemont, IL 60439, USA
*Correspondence: chongliu@uchicago.edu

Abstract

Electrochemical intercalation offers a promising platform for Li^+ extraction. However, only limited types of electrode materials have been investigated. The challenge to broaden and tailor materials for electrochemical intercalation-based Li^+ extraction lies in the lack of understanding of material's response upon co-intercalation of multiple ions, therefore, paired process design to enable reversible Li^+ extraction and recovery. Here, we showcase the design of asymmetric ion pathways for Li^+ extraction and recovery for host material with complex Li^+ and Na^+ interaction using layered cobalt oxide as a model material, which could enable the large class of layered oxides for Li^+ extraction. The two-phase equilibrium of $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$ governs record high Li^+ selectivity when a high depth of intercalation is achieved (low vacancy level). We show that the relative rate between ion exchange and intercalation is critical to determine the ion pathways. The relationship can be quantitatively compared using the average pseudo ion exchange rate ($C_{pseudoIX}$) and the intercalation rate (C_{inter}). The ion pathways at the three regimes with $C_{pseudoIX} > C_{inter}$, $C_{pseudoIX} \sim C_{inter}$, and $C_{pseudoIX} < C_{inter}$ are constructed. By selecting the optimized ion pathway and particle size, we demonstrated 9.7×10^4 Li^+ selectivity with 99% purity Li^+ recovery from an initial 1:1000 Li: Na molar ratio solution using 115 mAh/g capacity with good reversibility.

Projected lithium supply will not meet half the expected demand by 2040 required by the renewable energy technology deployment for climate change mitigation goals[1]. Extracting Li^+ from unconventional sources is critical to overcoming the expected Li^+ supply shortage[2–4]. Even though feasible, Li^+ extraction from unconventional sources remains challenging due to competing ions such as Na^+ being 74 (Salton Sea, California) to 20,000 (seawater) times greater in abundance[3]. Electrochemically driven ion intercalation into the interstitial sites of electrode material is an attractive solution for Li^+ extraction by being environmentally friendly, highly Li^+ selective, and energy efficient[5–10]. The high Li^+ over Na^+ selectivity relies on the proper selection and tailoring of electrode materials to have preferable charge transfer and mass transport behaviors[6–9,11]. However, the development of tailored materials for Li^+ extraction is still a nascent field. This is because no mature Li^+ extraction system exists yet. The solution environments that the host electrode must go through repeatedly for extraction and recovery are largely undecided and host material dependent. Therefore, understanding and predicting host material response in complex solution environment is critical to define the working conditions and material challenges for Li^+ extraction and recovery, as well as to identify solutions for achieving high Li^+ selectivity, fast extraction, and durability that are required for technology deployment.

The layered transition metal oxides emerge as a new family of host materials for Li^+ extraction owing to their thermodynamic favorability of Li^+ to Na^+ and the ability to form heterostructures to stabilize Li^+ and Na^+ co-intercalation[7,12,13]. In particular, $Li_{1-v}CoO_2$ (v represents vacancy level) has been shown to undergo spontaneous, non-Faradaic ion exchange at room temperature in Na^+ containing aqueous electrolyte when 1-v < 0.94 to form phase equilibrium between $Na_{0.51}CoO_2$ and $Li_{0.94}CoO_2$[7]. This leads to $(NaLi)_{1-v}CoO_2$ heterostructures that have separations in the spatial distribution of alkali ions and cobalt valence states ($Co^{3+/4+}$), and variations of layer spacing throughout the particle. For $Na_{1-v}CoO_2$ parent material with 0.48<1-v<0.94, the phase equilibrium is between $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$. The slight difference in the Na phase could be due to particle property difference. When biphasic equilibrium occurs between $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$, it indicates that the mobile ions will be swinging between Na^+ and Li^+ with host vacancy level v changing between 0.06 and 0.52 (Fig. 1). The vacancy dependent composition indicates theoretically high Li^+ to Na^+ selectivity since the Li^+ contents increase as the vacancy level decreases during intercalation. Record high Li^+ to Na^+ selectivity (more than four orders of magnitude) has been validated for $(NaLi)_{1-v}CoO_2$ in our previous work[7,13]. However, the design of paired intercalation and recovery processes to enable reversible cycling has not been addressed. Fundamental understanding of how $(NaLi)_{1-v}CoO_2$ respond to (de)intercalation at different reaction rates in solutions with different concentrations and ratios of Li^+ and Na^+ is needed to design the system to finish the loop for Li^+ extraction and recovery.

In this work, using model layered cobalt oxide, we investigated the co-intercalation ion pathways and unveiled the importance of the relative kinetics of intercalation and ion exchange to Li^+ extraction capacity, selectivity, and reversibility. The two-phase equilibrium between $Li_{0.94}CoO_2$ and $Na_{0.48}CoO_2$ divided the materials space into Li-rich and Na-rich regions when out-of-equilibrium with v between 0.06 and 0.52 (Fig. 1a). To quantitatively compare the kinetics, we define an average ion exchange rate as $C_{pseudoIX}$ and divided the different intercalation behaviors into three regimes. Using both in situ and ex situ composition and structural characterization, we constructed the three different ion pathways that depends on the relationship between $C_{pseudoIX}$ and intercalation rate (C_{inter}). This relationship is predictive of the behavior when intercalating from

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$Li_{0.48}CoO_2$ as the extraction starting material. At $C_{pseudoIX} < C_{inter}$, the intercalation quickly brings the structure into the Na-rich out-of-equilibrium region with following intercalation resembling the Na^+ intercalation features. In this case, ion exchange is needed after intercalation to bring the structure back to equilibrium to restore the Li^+ content and if ion exchange cannot be completed, both Li^+ selectivity and recovered Li^+ purity will decrease. We also show that particle morphology is important and smaller particles can promote faster and more reversible ion exchange. At $C_{pseudoIX} > C_{inter}$, the intercalation will not push the structure out of the Li-rich region; therefore, a high depth of intercalation and high Li^+ selectivity can be achieved in a single step of intercalation without additional ion exchange. When $C_{pseudoIX}$ is close to C_{inter}, the ion pathway is a combination of the previous two with longer period of intercalation maintained in the Li-rich region; however, the structure still enters the Na-rich region at the end. Enabled by the understanding of the ion pathway, we designed the Li^+ extraction and recovery process and achieved 9.7×10^4 Li^+ selectivity during extraction from an initial 1:1000 Li: Na molar ratio solution and $\sim 99\%$ purity during Li^+ recovery with 115 mAh/g capacity. A good reversibility was also demonstrated with the optimized Li^+ extraction and recovery path.

Figure 1. Schematic of possible paths for Li$^+$ extraction and recovery. a, CoO_2-$LiCoO_2$-$NaCoO_2$ phase diagram. The region of Li^+ extraction interest is the blue triangle, which is further highlighted in **b**. The grey regions are not favorable for Li^+ extraction due to kinetic barriers to ion exchange and material stability. The red region is area for transformation of Na phase that requires ion exchange after the current stops. **b,** Crystal structure illustration of the mixed $(NaLi)_{1-v}CoO_2$ (top), consisting of $Li_{0.94}CoO_2$ (right) and $Na_{0.48}CoO_2$ (left) phases, where blue triangles make up the CoO_2 layers, yellow circles are Na ions, and green circles are Li ions. **c**, Paths for Li^+ extraction and recovery. The green line is the path for Li^+ recovery in pure Li^+ solution as the material is deintercalated to the $Li_{0.48}CoO_2$ phase. The blue dashed lines are two hypothetical paths back to the $(NaLi)_{1-v}CoO_2$ material, which depends on the Li: Na ratio in the solution, intercalation kinetics, and the electrochemical working conditions.

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The possible paths for Li^+ extraction and recovery using model layered cobalt oxide are illustrated in Fig. 1. Fig. 1a shows the phase diagram of CoO_2-$LiCoO_2$-$NaCoO_2$ with the phase equilibrium between $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$ shown as the purple line. Regions out of equilibrium are shown in blue and red triangles as Li-rich and Na-rich regions for Li^+ and Na^+ dominated structures, respectively[13]. When the host composition is within either the blue or the red region, the host prefers to ion exchange with solution Na^+ (blue) or Li^+ (red), to reestablish the phase equilibrium. The composition is electrochemically controlled by modulating the vacancy and therefore the phase volume of the two phases that coexist in host material (Fig. 1b). Fig. 1c shows different hypothetical paths of Li^+ extraction and recovery considering the Faradaic Efficiency (FE) and purity of Li^+. FE describes the amount of Li^+ intercalated per e^- added. Based on the two-phase equilibrium between $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$, optimizing Li^+ extraction requires pushing the host to as close as $Li_{0.94}CoO_2$ at the end of the intercalation to minimize the content of Na^+ in the structure. If high depth of intercalation (1-v = 0.94) is not achieved, both the FE and purity of Li^+ will be sacrificed. Therefore, the kinetics of concurrent intercalation and ion exchange are critical to ensure that the depth of intercalation can be maximized, and two-phase equilibrium can be achieved. Moreover, there exist two extreme cases that needs to be understood in determining the extraction and recovery paths. The first case starts from $Na_{0.48}CoO_2$ and ends at $Li_{0.94}CoO_2$ which are both the equilibrium composition of the host at the given vacancy level. For this path, the FE can reach ~200% (46% charge capacity for 0.94 Li^+ composition), which is attractive from the energy perspective. The second one is for Li recovery to maximize Li^+ purity. This pathway requires the recovery to be done as delithiation in Li^+ solution from $Li_{0.94}CoO_2$ to $Li_{0.48}CoO_2$. To prioritize Li^+ selectivity and purity, it is ideal to use Li^+ solution for recovery which results in $Li_{0.48}CoO_2$ at the end of the recovery. However, $Li_{0.48}CoO_2$ could automatically convert to $Na_{0.48}CoO_2$ in the extraction condition (1:1000 Li: Na) by ion exchange. Therefore, it is unknown when starting from $Li_{0.48}CoO_2$, how the host structure will transform responding to the competitive intercalation and ion exchange and how to design the pathway of Li^+ extraction to enable a reversible loop to $Li_{0.94}CoO_2$.

Figure 2. Particle effect on Li$^+$ intercalation and ion exchange. **a–c,** The intercalation in 1:1000 Li: Na acetonitrile solution at C/10 rate with two different voltage cutoffs for $(NaLi)_{0.67}CoO_2$ formed by ion exchange with the different parent materials **a,** $Li_{0.67}CoO_2$ with insert SEM of $LiCoO_2$ and 10 μm scale bar, **b,** smaller $Li_{0.67}CoO_2$ with insert SEM of smaller $LiCoO_2$ and 500 nm scale bar, and **c,** $Na_{0.67}CoO_2$ with insert STEM of $Na_{0.67}CoO_2$ and 50 nm scale bar. The blue lines are for the -0.2 V cutoff and the red lines are for the 0.1 V cutoff (blue and red curves are different electrodes). The darker lines and arrows indicate intercalation, and the lighter lines and arrows indicate OCP. **d,** XRD spectra for parent $Na_{0.67}CoO_2$ (black), after ion exchange completion (blue), and after the pulse/ion exchange sequence (red, sequence in **f**). The black, blue, and red dashes indicate the peaks for $Na_{0.67}CoO_2$, $Na_{0.48}CoO_2$, and $Li_{0.94}CoO_2$, respectively. The * labels comes from the carbon cloth substrate. **e,** The OCP curves for $Na_{1-v}CoO_2$ with v = 0.50, 0.45, 0.33, and 0.28 while soaking in 1:1000 solution. **f,** The ion exchange (light red) and intercalation (dark red, at C/10) curves for the conversion of $Na_{0.67}CoO_2$ (parent material) to $Na_{0.08}Li_{0.86}CoO_2$ in Li: Na 1:1000 solution.

Particle morphology for optimizing Li extraction

First, to push the depth of intercalation to 1-v of 0.94 during Li$^+$ extraction and maintain two-phase equilibrium, the effect of particle size was investigated. It has been demonstrated that particle dimension is an important factor to determine the ion exchange kinetics of solid materials such as nanocrystals and clays[14–16]. We studied the ion exchange kinetics of three different layered cobalt oxides: commercial O3 $LiCoO_2$ (LCO), synthesized smaller O3 $LiCoO_2$ (sLCO), and synthesized P'3 $Na_{0.67}CoO_2$ (NCO). Their X-ray diffraction (XRD) patterns are shown in Supplementary Fig. 1. The LCO are single primary particles of irregular shapes with dimension of 11.1 ± 4.9 μm (Scanning electron microscopy (SEM), Fig. 2a). The sLCO and NCO are both platelet like particles. The sLCO has lateral size of 1.04 ± 0.24 μm and thickness of 420 ± 100 nm (Fig. 2b). The NCO has lateral size of 194 ± 66 nm and thickness of 96 ± 29 nm (Scanning transmission electron microscopy (STEM), Fig 2c). Particle sizes are summarized in Supplementary Table 1. The NCO are smaller due to their lower temperature requirement for solid state synthesis[17]. The larger (lateral) surface for the platelet type particles is the (001) surface, which has negligible alkali cation diffusion coefficient[18].

The non-Faradaic ion exchange kinetics were tested in a 1:1000 (1mM: 1M) Li: Na acetonitrile (ACN) solution. ACN was chosen due to the fast ion exchange kinetics for NCO that is measurable by the change in the open circuit potential (OCP) curve (Supplementary Fig. 2). This OCP curve changes resembles the charging curve of $Na_{0.67}CoO_2$ to $Na_{0.48}CoO_2$[13,19]. For comparing the different materials at the same starting state, both LCO and sLCO were deintercalated in pure Li$^+$ electrolyte to 33% vacancy to match the vacancy of NCO material and then soaked in 1M NaClO$_4$ ACN solution to reach two-phase equilibrium (Supplementary Fig. 3). For NCO particles, ion exchange to establish the two-phase equilibrium was allowed to occur in 1: 1000 Li: Na solution (Supplementary Fig. 2). The compositions after ion exchange were $Na_{0.32}Li_{0.35}CoO_2$ for LCO ($Li_{0.94}CoO_2$ and $Na_{0.51}CoO_2$ equilibrium), $Na_{0.27}Li_{0.40}CoO_2$ for sLCO parent ($Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$ equilibrium), and $Na_{0.27}Li_{0.40}CoO_2$ for NCO ($Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$ equilibrium), measured by XRD (Fig. 2d and Supplementary Fig. 3) and inductively coupled mass spectroscopy (ICP-MS) confirming two-phase equilibrium. The biphasic regime seems to consist of slight variations in the equilibrium, which may be related to variation between electrode properties[7,13].

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Ion exchanged LCO, sLCO, and NCO materials are then intercalated in the 1:1000 Li: Na solution to cutoff voltages of 0.1 V or -0.2 V vs Ag/Ag$^+$ and given sufficient time for ion exchange. The ion exchange OCP curves reveal substantial difference in the time to equilibrium. $Na_{0.32}Li_{0.35}CoO_2$ (from LCO) (Fig. 2a) could not ion exchange to reach OCP of ~ 0.45 V (two-phase equilibrium) after intercalation to both voltage cutoff of 0.1 and -0.2 V. The XRD spectra showed co-existence of a $Li_{0.94}CoO_2$ phase and a $Na_{0.67}CoO_2$ phase for the -0.2 V cutoff and a $(001)_{Na}$ phase peak between $Na_{0.67}CoO_2$ and $Na_{0.48}CoO_2$ for the 0.1 V cutoff indicating deviation from two-phase equilibrium (Supplementary Fig. 4). Both $Na_{0.27}Li_{0.40}CoO_2$ (from sLCO) and $Na_{0.27}Li_{0.40}CoO_2$ (from NCO) reached equilibrium with intercalation at a C/10 rate, which were shown by OCP curves and confirmed by ICP-MS and XRD (Fig. 2b–c and Supplementary Fig. 5–6). It is worth mentioning that the ion exchange process resembles pseudo $Na_{1-v}CoO_2$ charging, which can be enhanced to less than 2 hours by using a more dilute slurry with about half the mass loading for electrodes (Supplementary 7)[17,19]. Furthermore, the ion exchange for NCO retains faster rates (time to reach the final plateau) if the $Na_{1-v}CoO_2$ phase retains a high vacancy level (Fig. 2e and Supplementary Table 2). The rate becomes much slower when v < 0.33 after intercalation, which highlights the importance of Na phase vacancy, therefore cutoff voltage, on the ion exchange kinetics. From the SEM images of the three particle types after intercalation to -0.2 V, the smaller sLCO and NCO particles show no cracking unlike the larger LCO, which may be due to the increasing energy required for fracture with decreasing particle size (Supplementary Fig. 8)[20]. The smaller particle sizes can manage the larger stress from both the Li phase and Na phase separation in a single particle. The large mechanical stress in big particles could be a key hindrance to the ion exchange. Based on the ion exchange kinetics and particle fracture resilience, NCO particles were selected for further investigations and a cutoff voltage of -0.2 V were selected to ensure fast ion exchange to maintain two-phase equilibrium and large intercalation capacity.

To reach as close as $Li_{0.94}CoO_2$, the electrochemical intercalation and ion exchange processes can be repeated for NCO particles over a voltage window and then allowed to relax finally back to $Na_{0.48}CoO_2$ (Fig. 2f). The electrochemical curve shape was maintained for all intercalation pulses with a decreasing intercalation capacity with each subsequent pulse (Supplementary Fig. 9). The XRD reveals an almost complete transformation of the original $Na_{0.67}CoO_2$ to $Li_{0.94}CoO_2$ with only a small residual $(001)_{Na}$ peak at 1.13 Å^{-1} from the $Na_{0.48}CoO_2$ phase (Fig. 2d). The final composition $Na_{0.08}Li_{0.86}CoO_2$ contains an increased alkali ion content than expected (v=0.13) based on the intercalated capacity. Based on the equilibrium between $Li_{0.94}CoO_2$ and $Na_{0.48}CoO_2$, the final Na$^+$ content almost matches the expected 0.07 value; however, the Li$^+$ content is higher than the expected 0.80 value. This suggests that the additional capacity may come from additional intercalation via side reaction or Li salt precipitation but not carry over via non-specific adsorption, which would favor the higher concentration of Na$^+$. The recovery of this excess Li$^+$ will be discussed later.

Kinetic pathway for optimizing Li extraction from $Na_{0.48}CoO_2$ to $Li_{0.94}CoO_2$

It becomes clear that when the cutoff voltage is set for NCO particles, the intercalation C-rate is critical to determine the capacity per intercalation, the ion exchange time, the final depth of intercalation, and Li$^+$ selectivity. To understand the phase transformation during the repetitive intercalation and ion exchange, in situ synchrotron XRD was conducted during initial ion exchange

and (de)intercalation from starting particles of $Na_{0.67}CoO_2$. A 1:100 1 M Li:Na solution was used to avoid Li transport issues in the in situ cell. During the ion exchange (Fig. 3a), the $(001)_{Na}$ peak (1.14 Å^{-1}) and $(002)_{Na}$ peak (2.29 Å^{-1}) of the $Na_{0.67}CoO_2$ parent material is left shifting to lower Q values indicating the formation of Na phase with larger layer spacings and vacancy. At 0.0 V, a small peak at 1.32 Å^{-1} emerges that continually right shifts and grows in intensity until reaching 1.34 Å^{-1}. This indicates the formation of $Li_{0.94}CoO_2$ phase and suggests that it is facilitated by the formation of high vacancy Li phase. The appearance of the $(003)_{Li}$ peak is also coupled with abrupt emergence and increase in intensity of the Li phase peaks at ~0.05 V and decrease of the Na phase peaks that indicates a major change in the lattice to a predominant R-3m phase from the C2/m phase despite only a small amount of Li^+ present in the material. The $(001)_{Na}$ and $(002)_{Na}$ peaks continue to left shift until reaching the position of $Na_{0.48}CoO_2$ at 0.5 V. During the ion exchange process, the $(001)_{Na}$ peak intensity continues to diminish while the $(003)_{Li}$ peak intensity grows, and two-phase equilibrium was established. During the following intercalation, the electrochemical response resembles the $Na_{1-v}CoO_2$ discharging (Na^+ intercalation) behavior. The $(001)_{Na}$ and $(002)_{Na}$ peaks right shift while the Li phase peaks maintain their position. Additionally, the Li phase continues to grow in intensity while the Na phase decreases in intensity, which suggests that during the Na phase transformation, ion exchange with solution Li^+ occurs resulting in an increase of the volume fraction of Li phase. The $(003)_{Li}$ peak is the strongest at the end of intercalation (Supplementary Fig. 10).

The kinetics dependent ion pathways from $Na_{0.48}CoO_2$ to $Li_{0.94}CoO_2$ can be clearly explained using the CoO_2-$LiCoO_2$-$NaCoO_2$ phase diagram. As shown in Figure 3b red line i, when starting from any point on the $Na_{0.48}CoO_2$-$Li_{0.94}CoO_2$ equilibrium line (with point $Na_{0.48}CoO_2$ as the extreme case), if the intercalation C-rate is fast, the line showing the intercalation path quickly intersect with the $Na_{0.67}CoO_2$-$Li_{0.94}CoO_2$ co-existence line with limited cation content increase. In this case, Na^+ intercalation dominates, and it takes a long time for ion exchange with solution Li^+ to bring the structure back to the equilibrium line (horizontal path line). Also, it requires many cycles of intercalation and ion exchange to push the host to $Li_{0.94}CoO_2$. On the other hand, when the intercalation C-rate is slower (red line ii), the intercalation line tilts towards Li^+ intercalation and intersects with the $Na_{0.67}CoO_2$-$Li_{0.94}CoO_2$ co-existence line at lower vacancy level. Therefore, more Li^+ is intercalated, less ion exchange events are needed to bring the structure back to the equilibrium line, and less cycles of intercalation and ion exchange is needed. This trend points to the possibility that when the C-rate is extremely slow, the intercalation line could overlap with the $Na_{0.48}CoO_2$-$Li_{0.94}CoO_2$ equilibrium line and no ion exchange will be needed after intercalation. For $Na_{0.27}Li_{0.40}CoO_2$ (from $Na_{0.67}CoO_2$ via ion exchange) as the starting material, an electrochemical behavior was realized with a more slopped plateau at slow C-rates. The difference in voltage and shape of the plateau suggests different intercalation reaction path (possibly following $Li_{0.94}CoO_2$ and $Na_{0.48}CoO_2$ equilibrium) followed by Na phase transformation. (Supplementary Fig. 11).

Figure 3. Kinetics effect on Li⁺ extraction pathway. a, In situ XRD in the electrochemical flow cell of the initial ion exchange (black, OCP curve, 1:100 1M Li:NaClO₄ ACN) and

intercalation (red, C/10) with parent $Na_{0.67}CoO_2$ material. **b,** Schematic describing the electrochemical control over the three-phase equilibrium diagram. The purple line is the tie line between the $Na_{0.48}CoO_2$ and $Li_{0.94}CoO_2$ phases. The blue arrows follow the composition change for Li responsive phases and the red arrows follow the path for Na responsive phases. The horizontal red arrows are due to ion exchange after reaching the $Na_{0.67}CoO_2$ cutoff. Darker arrows are fast C-rates and lighter arrows are slow C-rates. The black arrow indicates the initial change in the Na composition with Regime 1 having the smallest Na^+ composition and Regime 3 having the highest Na^+ composition. **c,** Comparison of the Li^+ extraction regimes where Regimes 1, 2, and 3 are the light blue, dark blue, and red curves, respectively. **d,** The second intercalation (blue, C/10 1:100 1M Li:NaClO$_4$ ACN) and ion exchange (black, OCP curve). See Supplementary Fig. 20 for focused view of $(001)_{Na}$ peak evolution. **e** and **f,** STEM imaging (left) and Li K edge mapping with EELS (right) for **e** Regime 3 intercalation stopped at -0.2 V (v=0.2) and for **f** Regime 1 intercalation stopped on the plateau (v=0.3). The scale bars from left to right are 50 nm, 50 nm, 20 nm, and 20 nm.

Kinetic pathway for optimizing Li extraction from $Li_{0.48}CoO_2$ to $Li_{0.94}CoO_2$

After electrochemical intercalation and ion exchange, ideally $Li_{0.94}CoO_2$ will be delithiated to $Li_{0.48}CoO_2$ for high purity Li^+ recovery. The delithiation showed $Li_{1-v}CoO_2$ charging type curve (Supplementary Fig. 12)[21]. With no doubt, C-rate of the following extraction is still critical in determining the ion pathway from $Li_{0.48}CoO_2$ to $Li_{0.94}CoO_2$. We found that the intercalation behavior differs significantly at different rates, and it correlates with the relative rates of intercalation and ion exchange. Therefore, to be quantitative, we define $C_{pseudoIX}$ to characterize the average rate of the initial ion exchange starting from NCO so that $C_{pseudoIX} = (y_{initial} - y_{final})/\tau$, where $y_{initial}$ and y_{final} is the Na^+ content in Na_yCoO_2 phases before and after ion exchange, respectively (Supplementary Table 2). The y_{final} is determined by comparing the plateau voltage to $Na_{1-v}CoO_2$ charging curve[13]. The τ is the time of ion exchange between $y_{initial}$ and y_{final} (Supplementary Fig. 7). The kinetics of ion exchange is affected by many factors such as particle morphology, electrolyte transport, and especially particle packing and electrode porosity. A detailed investigation on these effects is beyond the scope of this work; however, the use of $C_{pseudoIX}$ offers a simplified metric to compare the ion exchange kinetics with intercalation kinetics, the applied C-rate (C_{inter}).

Three regimes with different reaction rates are defined (Fig. 3c). Regime 1 is defined as $C_{inter} < C_{pseudoIX}$ (i.e. C_{inter} = C/50 and $C_{pseudoIX}$ = C/12), and its key features are the largest intercalation capacity (1-v changes from 0.50 to 0.92), highest intercalation potential, and no Na^+ intercalation feature on the electrochemical curve. Regime 2 is defined as $C_{inter} \sim C_{pseudoIX}$, and its key features are smaller intercalation capacity, a more slopped plateau that occurs at a lower potential than Regime 1, which could describe the same reaction. For Regime 2, there is a clear transition to Na^+ intercalation behavior below 0.3 V which could be due to larger Na phase domains in Regime 2 than Regime 1. Finally, Regime 3 is defined as $C_{inter} > C_{pseudoIX}$, and its key features are a stretched Na^+ intercalation curve and the smallest capacity, which suggests the Na^+ intercalation dominates. The regimes were found to exist in different Li: Na molar ratio solutions (Supplementary Fig. 13–14). These regimes were found to be general not only to the NCO based particles but also for other synthesized $LiCoO_2$ over a range of sizes (Supplementary Fig. 15–18). It is extremely interesting to see that in Regime 1 single step of intercalation can achieve the

targeted depth of intercalation (v~ 0.06) with minimal ion exchange, which is confirmed by ICP-MS (Na$^+$ content decreases from 0.07 to 0.04 from -0.2 V to 0.1 V). To explain the significant differences among the three regimes, the reaction for the long plateau in Regime 1 needs to be identified and the reaction pathways for all regimes need to be unveiled.

Regime 2 intercalation process and phase evolution were observed using in situ synchrotron XRD (Fig. 3d). The sample was prepared by 1:1000 solution at C/50 intercalation outside the flow cell followed by deintercalation in Li$^+$ solution inside the flow cell (Supplementary Fig. 19). The in situ intercalation was carried out after switching solution to 1:100 Li: Na at C/10 starting from Li$_{1-v}$CoO$_2$. The electrochemical curve resembles the Regime 2 extraction process. The increased potential of the plateau could be due to higher shift in potential with 1:100 solution compared to 1:1000 solution (Supplementary Fig. 13). At the beginning of intercalation on the plateau at ~0.55 V, peaks of Li phase shift towards the Li$_{0.94}$CoO$_2$ phase positions and no Na phase was observed (Fig. 3d). As the (003)$_{Li}$ peak shifts to 1.32 Å^{-1} corresponding to the approximately the Li$_{0.66}$CoO$_2$ phase, Na$_{0.48}$CoO$_2$ phase emerged as indicated by the (001)$_{Na}$ peak (Supplementary Fig. 20). The emergence of Na phase could be due to either Na$^+$ intercalation or concurrent ion exchange. Once the Li phase finally transforms into the Li$_{0.94}$CoO$_2$ phase, the electrochemical curve transitions to a Na$_{1-v}$CoO$_2$ discharging type and the (001)$_{Na}$ peak began to right shift until the potential cutoff. The following second deintercalation showed the same behavior as the first deintercalation (Supplementary Fig. 21). High C-rates promote larger Na phases than low C-rates during this process indicated by the appearance of the Na phase peak with faster C-rates. (Supplementary Fig. 22–23). The in situ XRD provides critical information that the plateau ~0.55 V (~0.40 V in 1:1000 solution, Supplementary Fig. 13) is Li$^+$ intercalation. With only a slight ~50 mV difference between the two plateaus in Regime 1 and 2, the long plateau in Regime 1 could also correspond to Li$^+$ intercalation into Li phase.

To confirm this and resolve the ion pathway of Regime 1 in 1:1000 solution, electrode composition from starting Li$_{0.50}$CoO$_2$ was characterized in situ by measuring the change of solution ion concentration for Regime 1 intercalation. The electrode composition changed within the first minute of intercalation that the Na$^+$ composition increased from 0.02 to 0.11 and reached its maximum of 0.26 by the first change in the intercalation curve slop at ~0.60 V (Supplementary Fig. 24). A second electrode revealed the same trend but with less ion exchange. The variability in ion exchange may be due to differences in contact time without current (intercalation start time) as slow C-rates suppress ion exchange compared to no current (Supplementary Fig. 25). This composition change provides important information about the ion pathway. During the first minute, there is barely any increase of the total cation content in the host material, so that the Na$^+$ content increase should come from ion exchange. Based on our previous work, ion exchange prefers to establish equal potential phase equilibrium, therefore, for charge conservation, the vacancy level of Li phase will decrease, and a high vacancy Na phase (v>0.52) will be preferred to form[13]. This matches the fact that the Na$^+$ content kept increasing during intercalation from 0.8 V to 0.6 V. This first segment of the electrochemical curve resembles the transformation of Na$_{0.37}$CoO$_2$ to Na$_{0.48}$CoO$_2$[13]. The Na$^+$ composition decreased after passing 0.60 V and was 0.15 (first attempt) and 0.05 (second attempt) by the time the major plateau at 0.50 V was reached.

The evidence of the decrease of Na$^+$ content is critical for resolving the Regime 1 pathway. This indicates that even though at high vacancy level (0.52<v<0.06) Na$_{0.48}$CoO$_2$ is the preferred

phase based on the two-phase equilibrium, it is suppressed during intercalation in Regime 1. Moreover, the transformation of high vacancy Na phase (formed before intercalation started via ion exchange) to $Na_{0.48}CoO_2$ (0.8 V to 0.6 V) should prefer the formation of the equal potential $Li_{0.94}CoO_2$ phase based on the two-phase equilibrium. If so, ion exchange of solution Li^+ with Na phase could occur and result in the decrease of Na^+ content as the $Li_{0.94}CoO_2$ phase is formed while maintaining the existing high vacancy Li phase[13]. But the high Li^+ content phase ($Li_{0.94}CoO_2$) could disappear via merging with the existing Li phase. Therefore, the long plateau could be an equivalent Li^+ intercalation plateau with complicated Li^+ and Na^+ interactions involving high vacancy Na phase formation and transition to $Na_{0.48}CoO_2$ that then leads to $Li_{0.94}CoO_2$ phase formation and merging with existing Li phase. During this phase evolution, elastic forces are expected to be strongly influential[22,23]. In phase separating Li^+ electrodes, the C-rate can strongly influence the phase separation dynamics and resulting phase distribution[24–26]. Elastic forces begin to dominate the phase behavior and distribution at very slow C-rates as the characteristic time to reorganize the phase domains to minimize strain is faster than the characteristic times of the solid-state diffusion and charge transfer. Finally, this Regime 1 ion pathway can be achieved since high vacancy Li phase have available sites for Li^+ intercalation (exclusive site effects), and adequate time is given for Li^+ diffusion both from the solution and in the solid (Supplementary Fig. 26)[26–28]. For the commercial and synthesized $Li_{0.67}CoO_2$ without Na ion exchange before intercalation, the pure Li^+ intercalation plateau could be accessed. Since the starting LCO and sLCO have reduced vacancy level of 33%, therefore, slower ion exchange kinetics, Na phase formation was reduced before intercalation current started (Supplementary Fig. 27–28). This enabled Li^+ intercalation behavior followed by better post intercalation ion exchange kinetics.

Therefore, the differences of the intercalation behavior in Regime 1, 2, and 3 is due to the limit of Li^+ mass transfer of both solution and solid diffusion. For Regime 3, large quantities of Na^+ will be inserted into the host structure due to both ion exchange and electrochemical intercalation, which squeeze the Li phase and force the quick formation of $Li_{0.94}CoO_2$ and $Na_{0.48}CoO_2$ phase equilibrium which end up on the equilibrium line (Supplementary Fig. 29). After that, the process will be similar to that from $Na_{0.48}CoO_2$ to $Li_{0.94}CoO_2$ as described above (a transition to red path lines on the phase diagram). The intercalation curve looks like Na^+ discharge, and ion exchange is needed after each intercalation step to drive the host back to two-phase equilibrium. The ion pathway of Regime 2 is the combination of Regime 1 and Regime 3 that at the beginning during the plateau of ~0.45 V, Li^+ intercalation is dominate. From ~ 0.3 V, two-phase equilibrium was established and the host switch to Na^+ intercalation and requires ion exchange to increase the Li^+ content in the structure. This switch in intercalation behavior could be caused by solid diffusion limitation that the emergent $Li_{0.94}CoO_2$ cannot merge with the original Li phase fast enough and the original Li phase was consumed by ion exchange with solution Na^+. Additionally, the higher currents in Regime 2 than Regime 1 promotes more Na phase growth during the beginning of the intercalation process (Supplementary Fig. 30). The three types of ion pathways can also be clearly explained on the CoO_2-$LiCoO_2$-$NaCoO_2$ phase diagram as shown using the blue lines (Fig. 3b).

The Li and Na phase element distribution was characterized on a single particle level for Regimes 1 and 3 (Supplementary Fig. 31–34). For Regime 3, the particle selected was intercalated to $(NaLi)_{0.80}CoO_2$. The electrode was pulled out of the solution immediately without ion exchange. The scanning transmission electron microscopy (STEM) images with electron energy-loss

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spectroscopy (EELS) mapping of the Li K edge reveals nonuniformity for Regime 3 (Fig. 3e and Supplementary Fig. 32). Furthermore, the energy dispersive X-ray spectroscopy (EDS) signal was used to quantify the Na^+ content in each of the particle which confirms the large particle to particle heterogeneity again. Phase separation heterogeneity has been well characterized for insertion materials from the single particle level to the electrode level[22,25,29–32]. The effects of particle characteristics and processing conditions can affect the phase separation morphology and ability of phase domains to coarsen during intercalation[24,33,34]. For Regime 3, the heterogeneity could be caused by the fast intercalation rate. The sample selected in Regime 1 was in the middle of the plateau at v=0.3 (Fig. 3f and Supplementary Fig. 33). Based on our assignment of ion pathway in Regime 1, the particle should have minimal level of Na^+ content with uniform Li^+ distribution. Based on the EELS and EDS mapping, this is true for some of the particles, but not for all. There is still large heterogeneity existed for the Na^+ content and elemental distribution. But this could be caused by the ion exchange after the current stops as mentioned in the ex situ XRD characterization, which cannot be avoided for ex situ samples.

Demonstration of reversible Li extraction and recovery

For Li^+ extraction, operating in Regime 1 ($C_{inter} < C_{pseudoIX}$) offers the highest capacity in a single intercalation pass and requires minimal ion exchange (Fig. 4) The Li^+ extraction results for Regime 2 ($C_{inter} \sim C_{pseudoIX}$) and Regime 3 ($C_{inter} > C_{pseudoIX}$) are summarized in Supplementary Fig. 35–38. The main findings are that Regime 3 requires multiple pulses to increase the capacity and approach high Li^+ selectivity; both Regime 2 and Regime 3 require ion exchange after intercalation, which begins to degrade the $C_{pseudoIX}$ rate with each extraction sequence. Therefore, even though operating at Regimes 2 and 3 can lead to reasonably good depth of intercalation and they have faster C_{inter} rates, the total time to the final depth of intercalation to ensure a good Li selectivity is longer than Regime 1 due to their long ion exchange time. Therefore, Regime 1 is selected as a better condition for Li^+ extraction. Moreover, it is worth mentioning that autointeraction was observed for the Li^+ extraction process that results in increased Li^+ content than predicted by the electrochemical capacity (FE>100%). A spontaneous side reaction involving the $(LiNa)_{1-v}CoO_2$ was observed which allows for the reduction of the Co^{4+} that promotes Li^+ intercalation (Supplementary Fig. 39–42). In the most extreme cases, $Li_{0.48}CoO_2$, formed via delithiation in 1 M $NaClO_4$ solution, can transform into $Li_{0.90}Na_{0.05}CoO_2$ without any use of electricity over 90 hours. The reactivity of the ion exchanged sample could be related to the high strain at the interface[35]. Additionally, this excess Li^+ can be electrochemically recovered by using a voltage cutoff instead of a time cutoff during the recovery step in the pure Li^+ solution.

Figure 4. NCO Li$^+$ extraction regimes and performance. **a,** The capacity change after multiple Li$^+$ extraction sequences. The black, blue, and red curves correspond to the first, second, and third Li extraction sequences, respectively. The light colors are the deintercalation at 1C in 0.1 M LiClO$_4$ ACN and the dark colors are the intercalation at C/50 in 1:1000 1M Li: NaClO$_4$ ACN. The deintercalation curves are shifted to the right as indicated by the dotted lines and listed values based on the amount of excess Li$^+$ recovered to reach 50% vacancy. **b,** The resulting OCP curves after intercalation for the 2nd and 3rd intercalation. **c,** The resulting composition change from ICP-MS measurements. The black dots and lines reveal the expected total alkali ion composition based on electrochemical (de)intercalation processes. The red, blue, and grey bars are Na$^+$, Li$^+$, and vacancy composition, respectively.

By operating in Regime 1, the vacancy can approach 0.06 so that most of the capacity is used for Li$^+$ extraction (Fig. 4a). By using the extended deintercalation to a voltage cutoff, additional Li$^+$ is recovered from the Li$^+$ intercalated from the autointercalation reaction and not the applied C-rate. The OCP curve quickly changes to a positive potential after intercalation and does not become more sluggish with additional Li$^+$ recovery sequences since minimal to no ion exchange is needed (Fig. 4b). The Na$^+$ composition does not change anymore after the first extraction sequence and that less than 5% available sites hold Na$^+$ in the structure. Therefore, we can achieve 99% Li$^+$ purity on the 3rd extraction sequence with FE of 120% during intercalation (Fig. 4c). The extraction sequence has increasing purity after each extraction sequence approaching levels appropriate for battery grade precursors (Supplementary Table 3). Therefore, a Li$^+$ recovery can be achieved with 99% purity while using ~40% of the theoretical capacity of the (NaLi)$_{1-v}$CoO$_2$ material without large variability in the post intercalation equilibrium kinetics or large loss of capacity between extraction sequences.

In conclusion, we revealed the complicated and intriguing Li$^+$ and Na$^+$ co-intercalation and ion exchange behavior in layered oxides. The two-phase equilibrium between Li$_{0.94}$CoO$_2$ and Na$_{0.48}$CoO$_2$ can be harnessed to guide the understanding of the ion (de)intercalation pathways. We unveiled that the relative kinetics of intercalation and ion exchange is crucial to determine the Li$^+$ extraction capacity, selectivity, and reversibility. We define an average ion exchange rate $C_{pseudoIX}$ to quantitatively compare the kinetics and divided the different intercalation behaviors into three regimes with $C_{pseudoIX} > C_{inter}$ (Regime 1), $C_{pseudoIX} \sim C_{inter}$ (Regime 2), and $C_{pseudoIX} < C_{inter}$ (Regime 3). The ion pathways for different regimes are constructed and illustrated clearly using the phase diagram of CoO$_2$-LiCoO$_2$-NaCoO$_2$ by correlating the electrochemical response with in situ XRD and composition data. In regime 1 when $C_{pseudoIX} > C_{inter}$, high vacancy Li phases are maintained, and the ion pathway can be kept for Li$^+$ intercalation to achieve the largest intercalation capacity and high Li selectivity without the assistance of ion exchange. By choosing the right particle running in Regime 1, the layered cobalt oxide demonstrated a 9.7×10^4 Li$^+$ selectivity and produced recovery solution with 99% Li$^+$ purity using 115 mAh/g capacity per recovery sequence with good reversibility. Interestingly, (LiNa)$_{1-v}$CoO$_2$ can benefit from an autointercalation phenomenon that favored Li$^+$ over Na$^+$ to enable FE > 100%. Our results show promise to enable the large class of layered oxides for Li$^+$ extraction to solve the Li supply chain concerns.

Methods

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Sample preparation

LiCoO$_2$ (LCO) was purchased from MTI corporation. The smaller LiCoO$_2$ (sLCO) was synthesized by a standard solid-state method [36]. Li$_2$CO$_3$ and Co$_3$O$_4$ (Alfa, 99.7%) were mixed in a stoichiometric ratio of Li: Co = 1: 1 with 5% weight excess Li$_2$CO$_3$ in a SPEX 8000M Mixer higher energy ball mill with steel container and balls for 30 min. The powder was pressed into pellets and sintered at 1000 °C for 10 hr. The product was ground again and sintered at 900 °C for 10 hr. Na$_{0.67}$CoO$_2$ was synthesized by a standard solid-state method[17]. Na$_2$O$_2$ (Alfa, 95%) and Co$_3$O$_4$ (Alfa, 99.7%) were transferred in a stoichiometric ratio of Na: Co = 0.68: 1 with 5% weight excess Na$_2$O$_2$ into a stainless-steel container with balls while in an Ar glovebox. The powders were mixed for 30 mins in the high energy ball mill. The powder was formed into pellets in the Ar glovebox and then sintered in air at 535 °C for 16 h. The pellet was moved back into the glovebox after cooling down to 300 °C. Electrodes were prepared by casting a slurry of active material, Super P carbon black (MTI), and polyvinylidene fluoride (PVDF, MTI) with a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone (Sigma-Aldrich). The slurry is made with 1:5 weight ratio of active material:NMP. The electrode slurry was drop casted on a ~ 0.8 cm^2 geometrical surface of a 1 cm x 5 cm rectangular carbon cloth (ELAT-H, Fuel Cell Etc, 406 μm in thickness, 80% porosity) current collector and dried on a hotplate at 100 °C overnight. The mass loading of active material ranged from 0.64–2.40 mg per electrode. The differences of the dense NCO and dilute NCO were the drop casting method. Dense NCO electrodes were prepared by drop casting the slurry using a 1 mL pipette and the dilute NCO electrodes were prepared by drop casting the slurry using a 3 mL pipette. The geometry of the pipette tips is different in diameter and tapering angle, which may play a key role in the slurry deposition.

The additional synthesis for LiCoO$_2$ materials listed in Supplementary Fig. 15 (a)–(f) were synthesized according to the literature. LCO(a) was prepared using a molten salt synthesis of KCl with CoO: LiOH·H$_2$O:KCl mol ratio 1:1:4 at 850°C for 8 hrs[37]; LCO(b) was prepared by mixing Co oxalate precursor with 5% weight excess LiOH·H$_2$O in Agate mortar followed by calcination at 500 °C and 900 °C. The Co oxalate precursor was prepared by precipitation method by slowly adding stoichiometric equivalent of H$_2$C$_2$O$_4$·2H$_2$O in ethanol to 0.2 M Co(CH$_3$COO)$_2$ in ethanol. The recovered Co oxalate precursor was centrifuged and washed three in water and twice in ethanol[38]. LCO(c) was prepared using a molten salt synthesis of KCl with CoO: LiOH·H$_2$O:KCl mol ratio 1:1:1mol ratio 1:1 at 850°C for 8 hrs[37]; LCO(d) was prepared by mixing Li$_2$CoO$_3$ and Co$_3$O$_4$ (Alfa, 99.7%) in Agate mortar followed by sintering at 1000 °C and 900 °C[36]; LCO(e) was prepared using a molten salt synthesis of KNO$_3$ with CoO:LiOH·H$_2$O:KNO$_3$ mol ratio 1:1:3 at 800 °C for 8 hr[39]; and LCO(f) was prepared by high energy ball milling LCO (MTI) for 1 hr in steel container with steel balls followed by 10 hr sintering at 550 °C. A heating rate of 5 °C/min was used for all sintering.

Counter electrodes were prepared by dipping carbon felt in a slurry of 8:1:1 LiFePO$_4$ (MTI):Super P: PVDF in NMP solvent and drying at 100 °C overnight similar to previous work[7]. The mass loading of LiFePO$_4$ was about 80 mg per electrode. For layered oxide intercalation experiments, the LiFePO$_4$ was used as counter to maintain close to 1:1000 1M Li:Na ratio in the solution. For layered oxide deintercalation experiments, the counter was first prepared by the deintercalation of LiFePO$_4$ in 1 M LiCl (aq) solution at C/5 (based on 160 mAh/g theoretical capacity) to 0.4 V vs Ag/AgCl to make FePO$_4$.

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Electrochemistry

Electrochemical experiments were performed in a three-neck round-bottom flask using a Biologic VMP-3 potentiostat. The working electrodes were the active material on carbon cloth held by a Pt clamp, the counter electrode was the $LiFePO_4/FePO_4$ electrodes on carbon felt held by Ti wire, and the reference electrode was commercial non-aqueous Ag/Ag^+ reference electrode (CH Instrument Inc.) consisting of silver nitrate and tetrabutylammonium perchlorate in acetonitrile. N_2 was bubbled into the flask to displace dissolved O_2 and H_2O. The open circuit potential and intercalation experiments were done in 80 mL 1 mM $LiClO_4$ and 1M $NaClO_4$ acetonitrile solutions with a stir bar mixing the solution. The salts were stored in an Ar filled glovebox. The deintercalation experiments were done in 40 mL of 0.1 M $LiClO_4$ acetonitrile solution. LCO and sLCO soaking experiments were done in 40 mL of 1 M $NaClO_4$ acetonitrile solution after deintercalation in 0.1 M $LiClO_4$ acetonitrile solution. The electrodes were rinsed three times in pure acetonitrile when switching solutions to remove residual Na and Li salts. C-rates and expected changes in the capacity after (de)intercalation were defined based on theoretical capacities of 252.028 mAh/g for $Na_{0.67}CoO_2$ materials and 273.838 mAh/g for $LiCoO_2$.

X-ray diffraction

Synchrotron XRD measurements were conducted at the 13-BM-C (X-ray wavelength 0.4335 Å) and 33-BM-C (X-ray wavelength 0.6199 Å) beamlines of the Advanced Photon Source (APS) at Argonne National Laboratory and 11-3 (X-ray wavelength 0.9763 Å) beamline of the Stanford Synchrotron Radiation Lightsource (SLAC)[40]. In situ experiments were performed by the transmission of a monochromatic X-ray incident beam through a custom designed electrochemical flow cell. The cell was identical to that used by Zhang et al[41]. The sample cell frame and all components were made of corrosion-resistant polymer Kel-F. The carbon cloth electrode was placed within the central position of the cell between two sealed Kapton windows. The cell body can hold roughly 5 mL solution around the center to make sure the electrode is always in contact with the solution. This solution was continuously refreshed by a peristaltic pump operating at 10 RPM. The reference electrode was the same commercial, non-aqueous Ag/Ag^+ described above and the counter electrode was Pt wire. The electrochemical measurements were performed with a Biologic SP-50 potentiostat. All synchrotron XRD measurements were performed at 13-BM-C (APS) except for Supplementary Fig. 22 and 23 were performed at 33-BM-C (APS) and Supplementary Fig. 25 at 11-3 (SLAC) using the same setup. Ex situ samples were covered in Kapton film and transported in a vacuum sealed containers to protect samples from ambient conditions. Pristine powder samples (Supplementary Fig. 1 and 15) were collected by using a Rigaku MiniFlex 600 with a Cu Kα source. The tube voltage and the current used were 40 kV and 15 mA, and the step size was 0.02° step width and a 10°/min speed. Carbon cloth electrode samples measured using in house XRD were performed with a Rigaku SmartLab multipurpose diffractometer, using Cu Kα radiation. The tube voltage and the current used were 40 kV and 40 mA, and the step size was 0.02° step width and a 3°/min speed.

Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained on a Zeiss Merlin scanning electron microscope using a 20 kV accelerating voltage and 300 pA. Particle sizes were determined by measuring diameter and thickness using imageJ[42]. At least 10 particles were used for each average and standard deviation.

Scanning transmission electron microscopy (STEM)

STEM images were acquired using JEOL ARM 200F equipped with a cold field emission source at 200 kV. HAADF detector able was 90–270 mrad and the LAADF detector angle ranged between 30 and 120 mrad. EELS spectra were acquired using a Gatan GIF Continuum ER with a dwell time of 0.03 s per pixel. The Li K signal was assigned between 60.3 eV to 62.8 eV for mapping. EDS spectra imaging was acquired using an Oxford X-Max 100TLE windowless SDD detector with a dwell time of 6.14 ms.

Inductively coupled plasma - mass spectrometry (ICP-MS)

Compositions were measured using a Thermo iCAP RQ ICP-MS with a 3% HNO3 (aq) diluting matrix. All electrodes were dissolved in 8 mL of aqua regia after rinsing at least 6 times with at least 10 mL of pure acetonitrile. The Li concentration measurements were performed by diluting the sampled acetonitrile solution 100 times (Supplementary 24). The selectivity is calculated by $[\Delta Li/\Delta Na]/[Li_{initial}/Na_{initial}]$ where the change in Li^+ and Na^+ composition between intercalation and deintercalation states in the electrode is called ΔLi and ΔNa, respectively. $Li_{initial}$ and $Na_{initial}$ refer to the initial Li^+ and Na^+ composition in the solution.

Data availability
The authors declare that all relevant data are included in the paper and Supplementary Information files and are available from the corresponding author upon reasonable request.

Author contributions

G.T.H and C.L. conceived the idea and designed the experiments. G.T.H. performed all the experimental work and analyzed the experimental data. R.S. assisted with electrochemical experiments and synthesis. Y.H. performed the STEM imaging. Y.H., J.L., and S.Z. helped with synchrotron XRD and analysis. H.Z. helped with synchrotron XRD measurements. C.L. supervised the work. G.T.H. and C.L. wrote the manuscript and all the authors revised the manuscript.

Competing interests
The authors declare no competing interests.

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