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Na1K1.66Ni2SbO6

K<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>

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# Na<sup>+</sup> Redistribution by Electrochemical Na<sup>+</sup>/K<sup>+</sup> Exchange in Layered Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub>

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mechanism occurring in layered  $Na_3Ni_2SbO_6$ . Structural characterizations using Xray diffraction and transmission electron microscopy uncover a remarkable and rich phase evolution as K is inserted in partially desodiated  $Na_xNi_2SbO_6$ . Rather than simple addition of K to the structure, we see significant Na rearrangement, with discrete Na phases traversing the full range of Na compositions, even though the overall Na content in the sample is not changed. At any given time as much as three distinct phases can be present in the sample, consistent with thermodynamic equilibrium rules. Using DFT computations we demonstrate that this remarkable phase behavior during ion exchange is due to the repulsion between Na<sup>+</sup> and K<sup>+</sup> which creates distinct phases of them. Our analysis should be applicable to other ion-exchange systems where the exchanged ions are not well miscible in the host structure.

# 1. INTRODUCTION

Ion exchange is a chemical process that involves the extraction of one mobile ion from a material and the insertion of another. It is part of the formation of various materials including clays, zeolites, hydrous oxides, and phosphates.<sup>1</sup> Ion-exchange reactions are also an important tool to produce metastable inorganic materials, unlike those prepared by direct chemical reactions at high temperature. This has for example been used to create novel nanomaterials.<sup>2</sup> New materials design for Li-ion batteries (LIBs) has frequently used Li<sup>+</sup>/Na<sup>+</sup> ion-exchange reactions to attain structural features of Na layered oxides not directly achievable via conventional synthesis methods for Li compounds. For example, Delmas et al. developed O2-type LiCoO<sub>2</sub> from P2-type Na<sub>0.7</sub>CoO<sub>2</sub>, even though O3-type  $LiCoO_2$  is the commonly observed structure.<sup>3</sup> Similarly, layered LiMnO<sub>2</sub> was first synthesized from  $\alpha$ -NaMnO<sub>2</sub> via Li<sup>+</sup>/Na<sup>+</sup> ion exchange by Armstrong et al. and Delmas et al.,<sup>4,5</sup> whereas an orthorhombic structure (space group Pmmn) is the stable form of LiMnO<sub>2</sub> under typical synthesis conditions.<sup>6–8</sup> Later, Paulsen and colleagues developed O2-type layered LiMnO<sub>2</sub>, which exhibits higher reversible capacity and better cycling stability than its O3-type analogue because the O2-type stacking remains unchanged during the de/lithiation process, whereas O3 structure converts to a spinel.<sup>9</sup> The ion-exchange approach to the development of new Li-layered oxides has also been applied to mixed transition metal systems.<sup>10-12</sup> Specifically, Kang et al. obtained LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> through Li<sup>+</sup>/Na<sup>+</sup> ion exchange from its Na analogue to reduce the amount of Li/Ni antisite disorder and improve the rate capability as compared to a solid-state prepared Li-Ni\_{0.5}Mn\_{0.5}O\_2.^{12}

O3/

01/P

?

Discharge (2) → (3)

Ni<sub>2</sub>SbO<sub>6</sub>

The microscopic theory of solid-state ion-exchange is not well developed. Historically, it has been described as a counterdiffusion of two ions in the solid state, driven by their concentration, or more precisely their chemical potential difference, in the solution,<sup>1</sup> implying some level of solid solution between the incoming and outgoing ion. Extensive characterization of Li<sup>+</sup>/Na<sup>+</sup> ion-exchange in compounds indicates a microscopically more complex picture. Several Xray diffraction (XRD) studies have confirmed the appearance two distinct phases (Li- and Na-rich phases) during Li<sup>+</sup>/Na<sup>+</sup> exchange in layered oxides.<sup>9,11,13,14</sup> The findings suggest that each alkali-ion layer is likely to be almost completely occupied by either Li or Na ions without mixing. Gwon et al. demonstrated that the Li<sup>+</sup>/Na<sup>+</sup> ion exchange occurs in two steps in layered NaNi0.5Mn0.5O2: (i) first, an intermediate phase in which Li and Na ions coexist in the same layer rapidly forms (<10 s) and (ii) a subsequent slow two-phase reaction  $(\sim 2 h)$  to form Li-rich LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> from the intermediate phase.<sup>13</sup> A very recent transmission electron microscopy (TEM) study by Xiao and colleagues revealed that Na-rich

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domains are segregated from Li layers in a particle if Na is electrochemically exchanged with Li in Li-Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>.<sup>14</sup> Similarly, Na-rich and Li-rich phase separation is observed in Li<sub>0.5</sub>CoO<sub>2</sub> during electrochemical Na insertion by electron back scatter diffraction.<sup>15</sup>

More recently, new energy storage materials for K-ion batteries (KIBs) have been developed by using Na<sup>+</sup>/K<sup>+</sup> ion exchange. As an example, P2-type K<sub>0.5</sub>CoO<sub>2</sub> was prepared from P2-Na<sub>0.84</sub>CoO<sub>2</sub> via electrochemical Na<sup>+</sup>/K<sup>+</sup> ion exchange by Baskar et al.<sup>16</sup> P3-type K<sub>x</sub>CrO<sub>2</sub> and K<sub>x</sub>Cr<sub>0.9</sub>Ru<sub>0.1</sub>O<sub>2</sub>, both cathodes which display good cycle life, have been derived from their Na analogues through ion exchange.<sup>17–19</sup> However, the microscopic mechanism for Na<sup>+</sup>/K<sup>+</sup> ion-exchange has been even less investigated than that of Li<sup>+</sup>/Na<sup>+</sup>. Somewhat surprisingly, using XRD, Na- and K-rich phases have been observed simultaneously during the ion exchange process<sup>17,19</sup> but with unidentified microstructure. In what may be a related problem, electrochemical Na<sup>+</sup>/K<sup>+</sup> ion exchange in layered oxides sometimes requires a very large number of chargedischarge cycles (>100) to complete, indicating either stubborn kinetics or a thermodynamic reason for one of the ions to remain in the structure.<sup>17–19</sup>

In this study, we demonstrate a complex phase sequence when Na<sup>+</sup> is electrochemically exchanged for K<sup>+</sup> in a layered transition metal oxide. Our model system is O3-type layered Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> (equivalently NaNi<sub>2/3</sub>Sb<sub>1/3</sub>O<sub>2</sub>), which has been studied as a high-voltage cathode for Na-ion batteries.<sup>20–22</sup> A conventional chemical ion-exchange process is driven by the concentration gradient between elements to be exchanged, and it is thus difficult to control the rate of the reaction. For example, ~80% of Na ions in layered  $NaNi_{0.5}Mn_{0.5}O_2$  are exchanged by Li ions within 10 s, whereas exchange of the remaining  $\sim$ 20% of Na takes >2 h.<sup>13</sup> In contrast, the rate of the electrochemical ion-exchange reaction can be largely regulated by a potentiostat in galvanostatic mode. To exchange Na<sup>+</sup> with K<sup>+</sup> electrochemically, Na is extracted from the material and K is subsequently inserted. This sequential process allows us to identify intermediate compounds during the exchange reaction using XRD and TEM, providing valuable information about the  $Na^+/K^+$  exchange mechanism. Furthermore, the large size and mass of Na and K ions enable them to be visualized by TEM and energy-dispersive X-ray spectroscopy (EDS), unlike the case for Li. Herein, we demonstrate for the first time the complex phase sequence this system goes through as Na and K are exchanged. We find that, at any given time, multiple wellformed phases are present, and that modifying the K content electrochemically does not only lead to changes in the Kcontaining phases but also induces phase transformation in the Na-rich phases, even though the overall Na content of the sample is not changed. These ion-exchange phase transformations seem to be fully reversible and satisfy the Gibbs phase rule at all times, suggesting a thermodynamic origin in nature.

First-principles calculations reveal that the large lattice size mismatch between Na<sup>+</sup> and K<sup>+</sup> drives phase separation between them which is responsible for the complex phase sequence. We suggest a quantitative phase diagram consistent with the phases observed during the ion exchange. We also observe that a certain amount of Na ions are unextractable even after repeated electrochemical Na<sup>+</sup>/K<sup>+</sup> ion-exchange processes, which may explain why completion of the ion exchange is difficult in some layered oxides.<sup>17–19</sup>

#### 2. EXPERIMENTAL SECTION

**2.1. Materials Synthesis.**  $Na_3Ni_2SbO_6$  was prepared by a solidstate method.  $Na_2CO_3$  (>99.5%, Sigma-Aldrich), NiO (99%, Alfa Aesar), and  $Sb_2O_3$  (>99.6%, Alfa Aesar) were homogeneously mixed using a planetary ball mill (Retsch PM200) at 300 rpm for 4 h. An excess amount of  $Na_2CO_3$  (10 at. %) was used to compensate for possible Na loss at high temperature. The mixture powder was pelletized and then sintered at 900 °C in air for 12 h. After natural aircooling to 200 °C, the samples were kept at this temperature to prevent contamination from moisture and transferred to an Ar-filled glovebox.

**2.2.** Ion Exchange and Electrochemical Measurements. Electrochemical methods were used to exchange Na<sup>+</sup> with K<sup>+</sup> in Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> (i.e., Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> was cycled in a K half-cell). Cathodes were prepared by mixing Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> (80 wt %), Super P carbon (Timcal, 10 wt %), and polytetrafluoroethylene binder (DuPont, 10 wt %) in an Ar-filled glovebox. Cathodes with a loading density of ~4.0 mg cm<sup>-2</sup> were assembled in a two-electrode configuration using a K-metal anode and glass fiber separator (Whatman, GF/F) in a 2032 coin cell. The electrolyte was custom-made using 0.7 M KPF<sub>6</sub> (Sigma-Aldrich) in anhydrous ethylene carbonate/diethyl carbonate (EC/DEC; 1:1 by volume, Sigma-Aldrich). Electrochemical tests were performed on a battery testing station (Arbin Instruments) at room temperature using galvanostatic or constant current–constant voltage (CCCV) modes.

**2.3. Materials Characterization.** The crystal structures of the obtained materials were analyzed using XRD (Rigaku Miniflex 600) with Cu K $\alpha$  radiation. In situ XRD was performed on a Bruker D8 Advance X-ray diffractometer using Mo K $\alpha$  radiation. A homemade in situ cell with a Be window was galvanostatically cycled at 3 mA g<sup>-1</sup> between 1.4 and 4.3 V using a Solartron 1287 potentiostat, and XRD patterns were collected from 4° to 30° 2 $\theta$  every 75 min at room temperature.

The particle morphology was verified using field-emission scanning electron microscopy (FE-SEM; Zeiss Gemini Ultra-55). Scanning transmission electron microscopy (STEM)/EDS was employed to identify the elemental distribution in the particle after the Na<sup>+</sup>/K<sup>+</sup> ion-exchange process. Powders of the active material were collected from the cathode film after cycling. After the film was sonicated in solvent to separate the mixtures of the active materials, binders, and carbon, a few drops of sonicated solvent were drop-casted on ultrathin carbon grids. TEM analysis was performed at 200 kV on a Titan X equipped with four EDS detectors at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL). STEM images were acquired in high-angle annular dark-field (HAADF) mode. Images and STEM/EDS were obtained after aligning the *c*-axis of the sample normal to the electron-beam direction.

Ex situ X-ray absorption spectroscopy (XAS) measurements were performed in transmission mode at room temperature at beamline 20-BM at the Advanced Photon Source at Argonne National Laboratory. The prepared XAS samples were sealed with polyimide tape (Kapton, DuPont) to prevent contamination from air exposure. The incident energy was selected using a Si(111) monochromator, and the beam intensity was reduced by 15% using a Rh-coated mirror to minimize high-order harmonics. Reference spectra of Ni and Sb were collected using pure Ni and Sb metal foils. The XAS data were analyzed using Athena software, and the spectral energies were calibrated by referencing the first inflection points in the spectra of Ni and Sb foils.

**2.4. Computation Methods.** Density functional theory (DFT) using a plane-wave basis as implemented in the Vienna ab initio simulation package (VASP) was applied to obtain energies of the different structures. Projector augmented wave potentials<sup>23</sup> with a kinetic energy cutoff of 520 eV were employed in all structural optimizations and total-energy calculations, and the exchange and correlation was described with the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE). A reciprocal space discretization of 25 K-points per Å<sup>-1</sup> was applied. The convergence



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Figure 1. (a) XRD pattern and (b) SEM image of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>

criteria were set to  $10^{-6}\ eV$  for electronic loops and 0.02  $eV/\text{\AA}$  for ionic loops.

#### 3. RESULTS

The XRD pattern of the as-synthesized Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> (Figure 1a) is consistent with the  $R\overline{3}m$  symmetry, which is consistent with previous results in the literature.<sup>20</sup> The background hump at 10–30° in the XRD pattern comes from the Kapton tape used to prevent contamination of the sample from air exposure. The SEM image in Figure 1b shows that the average particle size of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> is approximately 1  $\mu$ m.

To electrochemically exchange Na in Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> with K, we used Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> as the working electrode, 0.7 M KPF<sub>6</sub> in EC/DEC as the electrolyte, and K metal as the counter electrode. Figure 2a presents the voltage curve of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> as a function of specific capacity in a K half-cell. For the first charge, we used CCCV mode (5 mA g<sup>-1</sup> followed by a hold at 4.2 V for 5 h). After the voltage hold at 4.2 V for 5 h, the



**Figure 2.** (a) Electrochemical charge-discharge curves of  $Na_3Ni_2SbO_6$  (inset: cycling stability for first 15 cycles) in a K half-cell. (b) Electrochemical charge-discharge curves of  $Na_3Ni_2SbO_6$  in a Na half-cell.

current was relaxed to <6  $\mu$ A. Therefore, we assume that all mobile Na ions were extracted from the structure at the given potential (4.2 V vs K). The voltage profile (i.e., slope, shape, and steps) matches well with that for Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> in a Na halfcell,<sup>20–22</sup> indicating that the first charge process is indeed Na extraction. Note that the higher average charge voltage in Figure 2a relative to that in the literature can be attributed to the lower standard redox potential for the K metal anode than for Na.<sup>24</sup> The first charge capacity is 165 mAh g<sup>-1</sup>, which is equivalent to the extraction of ~2.5Na per formula unit assuming that all of the capacity originates from Na extraction. The possibility of side reactions such as electrolyte decomposition makes it likely that the amount of extracted Na is somewhat less.

The voltage curves of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> against K metal for the first five charge and discharge cycles after the Na extraction process are plotted in Figure 2a (black lines). The cell was cycled galvanostatically in the range of 1.5-4.2 V at 5 mA g<sup>-1</sup>. The first charge profile in Figure 2a differs significantly from the first discharge profile as well as from the subsequent charge and discharge profiles in terms of the overall voltage slope and the number of voltage steps. In addition, the subsequent charge and discharge profiles of Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub> in a K cell are different from those in a Na cell shown in Figure 2b. This finding strongly suggests that once Na is extracted in the first charge the structure hosts and releases K via subsequent discharge and recharge processes. Indeed, as explained in previous work<sup>25</sup> the increase in voltage slope after the first charge in Figure 2a is expected when large K ions are inserted into and extracted from the layered structure instead of Na. The first discharge capacity is 89 mAh  $g^{-1}$ , suggesting the nominal composition after the first discharge is Na<sub>0.5</sub>K<sub>1.37</sub>Ni<sub>2</sub>SbO<sub>6</sub>. The capacity retention of  $Na_{0.5}K_{\nu}Ni_{2}SbO_{6}$  at 5 mA g<sup>-1</sup> is shown in the inset of Figure 2a. The cathode maintains a capacity of ~60 mAh  $g^{-1}$  after the 15th cycle. The large irreversible capacity in the initial few cycles is likely due to the lack of stability of Kelectrolytes at high voltage. We also tested the rate capability of Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub> in a K cell. Figure S1 shows discharge profiles of  $Na_xNi_2SbO_6$  at different current rates from 10 mA g<sup>-1</sup> to 500 mA  $g^{-1}$ . A specific capacity of ~42 mAh  $g^{-1}$  is maintained at  $500 \text{ mA g}^{-1}$ 

To understand the mechanism of the electrochemical  $Na^+/K^+$  ion-exchange in  $Na_3Ni_2SbO_6$ , we traced the oxidation states of Ni and Sb. Figure 3 shows the X-ray absorption near-edge structure (XANES) of the Ni and Sb K-edges obtained from  $Na_3Ni_2SbO_6$  before and after electrochemical cycling against K metal. The Ni K-edge spectrum of pristine  $Na_3Ni_2SbO_6$  in Figure 3a overlaps with the  $Ni^{2+}$  edge from NiO (the dashed purple line marked as  $Ni^{2+}$ ), indicating the presence of  $Ni^{2+}$ .



Figure 3. (a) Ni K-edge and (b) Sb K-edge XANES spectra obtained from  $Na_3Ni_2SbO_6$ : pristine and after the first charge, first discharge, and second charge.



**Figure 4.** In situ XRD of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> in K-half cell (first cycle). (a) In situ XRD patterns combined with electrochemical charge–discharge profile of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>. (b) Magnified regions of the two-phase reaction between  $\alpha$  and  $\beta$  during discharge. (c) XRD peak intensity change at 6.37° (K-rich phase) and peak position change of Na-rich phases during K intercalation. (d) Magnified regions of two-phase reaction between  $\beta$  and  $\gamma$ .

After the first charge (desodiation), the absorption edge moves to higher energy, corresponding to Ni<sup>3+</sup> (reference: Na-Ni<sub>0.5</sub>Co<sub>0.5</sub>O<sub>2</sub>, dashed blue line marked as Ni<sup>3+</sup>).<sup>26</sup> This indicates that the nominal composition of the charged state is NaNi<sub>2</sub>SbO<sub>6</sub>. Ni<sup>3+</sup> is reduced after the first discharge (potassiation), but the absorption edge of Ni is positioned at slightly higher energy than Ni<sup>2+</sup>, indicating that the oxidation state of Ni is slightly higher than 2+ in the discharged state. This Ni<sup>2+δ</sup> is oxidized to Ni<sup>3+</sup> after the second charge (depotassiation) reversibly. These results indicate reversible Ni<sup>2+/3+</sup> redox in Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> upon ion exchange. In contrast, the Sb K-edge in Figure 3b remains unchanged upon charge and discharge, indicating that Sb does not participate in the redox reaction of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>.

We employed in situ XRD to monitor the compound's structure during the electrochemical  $Na^+/K^+$  ion exchange.

Figure 4 presents in situ XRD patterns obtained from  $Na_3Ni_2SbO_6$  cycled in a K half-cell. The Na (x) content is estimated by normalizing the charge capacity to the theoretical capacity of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> (130 mAh g<sup>-1</sup>) upon 2 Na ions extraction because XANES in Figure 3a confirms the formation of NaNi<sub>2</sub>SbO<sub>6</sub> at the end of the charging. K (y) content is estimated by assuming that all of the capacity originates from K insertion. Upon Na extraction in the range 2.85 < x < 3 in  $Na_{x}Ni_{2}SbO_{6}$ , the host structure maintains the O3-type stacking as a single phase with  $(003)_{O3}$ ,  $(006)_{O3}$ ,  $(101)_{O3}$ ,  $(012)_{O3}$ , and  $(104)_{O3}$  peaks at 7.6°, 15.2°, 15.5°, 16.1°, and 18.4°, respectively. The strong peaks at 20.5° and 22.9° belong to the Al current collector and Be window from the in situ cell, respectively. The peak positions for the structure do not vary much in this region. At x = 2.85, two new peaks appear at  $7.2^{\circ}$ and 14.4°, and as desodiation proceeds, additional peaks at



Figure 5. In situ XRD patterns combined with electrochemical charge–discharge profile of  $NaK_yNi_2SbO_6$  (y = 1.66) in a K half-cell (second cycle for  $Na_3Ni_2SbO_6$ ).

 $16.0^{\circ}$  and  $16.5^{\circ}$  become evident. Note that a new peak also evolves at  ${\sim}20^\circ$  but overlaps with the Al peak. Overall, the set of these new peaks corresponds to the P3-type structure of  $Na_{1.5}Ni_2SbO_6^{20,22}$  and can be assigned as  $(003)_{P3}$ ,  $(006)_{P3}$ ,  $(101)_{P3}$ ,  $(012)_{P3}$ , and  $(015)_{P3}$ . Upon further charging, the O3 and P3 phases coexist for 1.78 < x < 2.85, indicating that Na extraction occurs via a two-phase reaction between O3-type Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> and P3-type Na<sub>1.5</sub>Ni<sub>2</sub>SbO<sub>6</sub>, consistent with the plateau at ~3.6 V in Figure 2a. For 1.58 < x < 1.78, the lowangle shifts of the  $(003)_{P3}$  and  $(006)_{P3}$  peaks indicate that Na is further extracted from the P3 structure. At x = 1.58, a new structure evolves with peaks at 7.0°, 14.1°, 16.0°, 17.4°, and 21.3°, which we assign to the  $(001)_{01}$ ,  $(002)_{01}$ ,  $(110)_{01}$ , (11- $1)_{O1}$ , and  $(11-2)_{O1}$  planes for an O1-type structure of  $Na_1Ni_2SbO_6$ .<sup>20,22</sup> The O1 and P3 phases coexist for 1.21 < x <1.58, corresponding to the second plateau at  $\sim$ 3.9 V in the voltage profile. The P3 phase disappears at x = 1.21, and Na is extracted from the O1 structure for 1.0 < x < 1.21. In summary, Na extraction from the Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> cathode in a K half-cell occurs via three solid-solution reactions and two twophase reactions, yielding the O3-P3-O1 phase sequence, which is identical to that in a Na half-cell reported in the literature.<sup>20,2</sup>

When the cell is discharged, we expect K to be inserted into the desodiated phase, leading to a nominal composition of NaK<sub>v</sub>Ni<sub>2</sub>SbO<sub>6</sub>. At the end of discharge (1.4 V), the composition assuming all current corresponded to K insertion is NaK<sub>1.66</sub>Ni<sub>2</sub>SbO<sub>6</sub>. Upon discharge, the O3-P3-O1 phase transitions observed upon Na-extraction appear to reverse but at different total alkali content: O1 for 0 < y < 0.057, P3 for 0.17 < y < 0.63, and O3 for 0.98 < y < 1.66, with two-phase reactions between these single-phase domains. However, additional peaks appear along the K-insertion trajectory: Potassiation in the 0.23 < y < 0.40 region shows additional peaks at 6.2°, 12.5°, and 17.2°, which do not belong to either the O1, P3, or O3 structure of  $Na_xNi_2SbO_6$ . The evolution of the new peak at around  $6.2^{\circ}$  is clearly shown in Figure 4b. Here, we denote this phase as  $\alpha$ . In the 0.40 < *y* < 0.52 region, another unidentified phase,  $\beta$ , appears with peaks at 6.35° 12.8°, and 19.1°. The simultaneous peak disappearance at  $6.2^{\circ}$ and peak evolution at 6.35°, shown in Figure 4b, indicate a two-phase reaction between  $\alpha$  and  $\beta$ . At y = 0.52, the peak

intensity of the  $\beta$  phase gradually increases for  $0.52 < \gamma < 1.03$ as shown in Figure 4c, whereas the peak positions barely changes suggesting growth of the  $\beta$  phase. The coexistence of the  $\beta$  phase and P3–Na phase is surprising. In addition, while the amount of  $\beta$  phase grows the peak position of the P3–Na phase shifts to higher angle and then converts to an O3-Na phase (Figure 4c). This observation suggests that the growth of the  $\beta$ -K phase upon K insertion increases the Na concentration (Na/TM ratio) of the remaining Na-rich phase. For a typical intercalation cathode with one mobile intercalant, the concentration and lattice parameter of each phase do not change in a two-phase reaction, as required by the Gibbs phase rule. However, NaK, Ni<sub>2</sub>SbO<sub>6</sub> has two mobile species (K and Na). We demonstrate later that K insertion does not change the total Na content of the cathode material. Nonetheless, K insertion can cause rearrangement of the Na ions, and the Gibbs phase rule now allows three-phase regions with the composition of each phase fixed, or two-phase regions in which the concentration of each phase varies as the two-phase region is traversed. When the K-content increases from 1.03 to 1.25 in the cathode material, the intensities of the  $\beta$  phase peaks at  $6.35^{\circ}$  and  $12.8^{\circ}$  decrease, and disappear at y = 1.25, but new peaks evolve at  $6.5^{\circ}$  and  $13.1^{\circ}$  (marked by the green circles). The asymmetric peak evolution at  $\sim 13^{\circ}$  that can be seen in the enlargement of Figure 4d indicates that the  $\beta$  phase transforms to another K-phase,  $\gamma$ . K intercalates into the  $\gamma$  phase via a solid-solution reaction for 1.25 < y < 1.66, as indicated by the 6.5° and 13.1° peak shifts to higher angle.

It should be emphasized that the peak positions of  $(003)_{O3}$ observed when NaK<sub>1.66</sub>Ni<sub>2</sub>SbO<sub>6</sub> is fully discharged are identical to those of Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>. The peak positions of  $(003)_{P3}$  of NaK<sub>0.63</sub>Ni<sub>2</sub>SbO<sub>6</sub> are also identical to those observed when Na<sub>1.5</sub>Ni<sub>2</sub>SbO<sub>6</sub>, forms during charge. This finding suggests strongly that, during discharge with K, a set of pure Na phases form and that no K is present in these Na-phases. Because of its large size, mixing of K into the Na layers of Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub> compounds would increase the Na slab spacing in a significant way and thus modify the XRD peak position, in contrast to what we observe. Rather, new phases with a very different *c*lattice parameter that can accommodate large K ions may occur, separated from Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub>. This explains the appearance of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases upon potassiation, which we refer to as K-rich phases. In contrast, the O3, P3, and O1 phases are denoted as Na-rich phases.

We attribute the  $\alpha$ ,  $\beta$ , and  $\gamma$  as K-rich phases because their *c*lattice parameter is larger than those of the Na phases consistent with the larger ionic radius of K.<sup>27,28</sup> Indeed, the first two peaks of the  $\alpha$  and  $\beta$  phases in Figures 4, which arise from diffraction of the (00*l*) planes, are positioned at lower  $2\theta$ angles than those of the O1- and P3-type Na phases. Similarly, the  $\gamma$  phase has a larger *c*-lattice parameter than the O3-type Na phase. Furthermore, these *c*-lattice parameters for  $\alpha$ ,  $\beta$ , and  $\gamma$  are similar to those obtained from typical K-layered oxides.<sup>27,29</sup> We further argue that the stacking of the K-rich  $\gamma$  phase is likely to be P3-type as large K ions tend to occupy prismatic sites over octahedral sites at intermediate potassiation (nominally, 1.7 out of 3 K sites) $^{27,29-31}$  and the similar compound K<sub>1.5</sub>Ni<sub>1.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> is also P3-type.<sup>32</sup> In summary, the collective observations from the in situ XRD analysis and the data in the literature leads us to conclude that K-rich ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) and Na-rich (O3, P3, O1) phases coexist in the cathode upon discharge of NaK<sub>v</sub>Ni<sub>2</sub>SbO<sub>6</sub> in a K-cell. This coexistence is shown to the left of the diffraction panel in Figure 4a, with the domains of the Na-rich phases as green bars and the concentrations that bound the distinct K-phases in pink. Because we cannot directly refine the composition of the coexisting phases, we estimated the compositions and ratio of Na-rich and K-rich phases in the structure from the Na and K concentration in the composite, estimated from XANES and discharge capacity  $(NaK_{1.66}Ni_2SbO_6)$ , and the composition of Na-rich phase  $(Na_3Ni_2SbO_6)$  in the discharged state by XRD. From this estimate, the discharged product is approximately 1/  $3Na_3Ni_2SbO_6 + 2/3 K_{2.5}Ni_2SbO_6$ .

To investigate whether the complex coexistence of K and Na-rich phases is a temporary phenomenon we also investigate the structural changes during the second cycle. Figure 5 shows the in situ XRD patterns of NaK<sub>1.66</sub>Ni<sub>2</sub>SbO<sub>6</sub> taken during the second charge and discharge in a K half-cell. The peak shifts at  $6.5^{\circ}$  and  $13^{\circ}$  upon K extraction and insertion confirm the reversibility of the  $\gamma - \beta - \alpha$  phase transition. The  $\gamma$  phase is present for 1.43 < y < 1.66. The  $\gamma$ -to- $\beta$  two-phase transition occurs in the 1.31 < y < 1.54 region. Upon further charging, the  $\beta$  phase is retained in the 0.74 < y < 1.31 region until it transforms to the  $\alpha$  phase via the two-phase reaction in the 0.64 < y < 0.74 region. The  $\alpha$  phase is then stable to the end of charging (y = 0.43). While qualitatively these phase boundaries are similar to what is observed in the first discharge the phase domains have generally shifted to higher K-content. While it is possible that this shift is real, it is also possible that some error is present due to our association of all current with K<sup>+</sup> insertion or removal, not allowing for parasitic reactions. Surprisingly, we found that the Na-rich phases continue to coexist with the K-phases  $(\alpha,\beta,\gamma)$  and even undergo phase transitions during charging even though no Na is removed from the cathode. The O3(Na) phase undergoes a phase transition to the P3(Na)phase in the 0.74 < y < 1.25 region (a two-phase reaction). P3(Na) exists in the range of 0.43 < y < 0.74. Comparing this evolution with the in situ XRD result for the first cycle shown in Figure 4 indicates that both the K and Na phase transitions are reversible upon charge and discharge. The O1 phase is not observed at the end of the second charge as the in situ cell could not reach the voltage at which the O1 phase forms upon charging because of relatively large polarization. Thus, we conducted ex situ XRD experiments as shown in Figure S2. In the first cycle, the ex situ XRD clearly confirms the formation

of the O1 formed similar to what is observed in the in situ experiment. At the end of the second charge, we observed much reduced intensity and broadening of (00*l*) peaks while the other peaks are well preserved. This may be attributable to Na and K mixing in the same layer at the top of charge.

To clarify whether the Na that is extracted in the first cycle can be reinserted upon discharge we performed a series of experiments where we first charge the cell in a Na-electrolyte and then wash the cathode and discharge it in a fresh K-cell. This excludes the possibility of Na reinsertion from the electrolyte or anode. As shown in Figure 6a, the discharge profile with the intermediate washing step is virtually identical to that obtained without washing, but they are different from the discharge profile in a Na cell, confirming that the extracted



**Figure 6.** Discharge profiles and XRD pattern of  $Na_xK_yNi_2SbO_6$ . (a) Discharge profiles of  $Na_xK_yNi_2SbO_6$  under various conditions (green: discharged in a K half-cell after charging in a Na half-cell with intermediate washing to remove Na ions from the electrolyte; brown: the electrode is charged and discharged in a K half-cell without the intermediate washing process; black: the electrode is charged and discharged in a Na half-cell without the intermediate washing process.) (b) XRD pattern of  $Na_xK_yNi_2SbO_6$  upon discharge in a K half-cell after charging in a Na half-cell with intermediate washing to remove Na ions from the electrolyte. (c) XRD patterns of discharged  $Na_xK_yNi_2SbO_6$  electrodes under various conditions: (i) discharged  $Na_xK_yNi_2SbO_6$  after the first cycle in a K half-cell (black line) and (ii) discharged  $Na_xK_yNi_2SbO_6$  after the fifth cycle with intermediate electrode washing at the end of each charge cycle (green line).



**Figure 7.** EDS mapping and HR-TEM image of  $Na_xK_yNi_2SbO_6$  after cycling. (a–g) STEM–EDS mapping [(a) Na/K, (b) Na, (c) K, (d) image, (e) O, (f) Sb, and (g) Ni], (h) HR-TEM image of the highlighted spot in panel a. Intensity profiles of (i) K-rich and (j) Na-rich phases. (k and l) STEM–EDS mapping results for a different particle.

Na ions that remain in the electrolyte after the first charge do not participate in the discharge process. Figure 6b presents the XRD pattern obtained from the washed sample after K insertion. We identify a two-phase mixture of an O3typeNa<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> and a P3-type K<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub>. Crystallographic information for the latter was obtained from the Inorganic Crystal Structure Database allowing for adjustment of the *c*lattice parameters to align the (00*l*) peak position to our results. This finding proves that a Na-rich phase can form without Na reinsertion, as similarly observed in the Na<sup>+</sup>/K<sup>+</sup> ion exchange reaction of NaCrO<sub>2</sub>.<sup>17</sup>

We also examined how the number of repeated potassiation charge/discharge cycles affects the structure and phase composition of  $Na_xK_yNi_2SbO_6$ . Figure 6c presents an ex situ XRD pattern of  $Na_xK_yNi_2SbO_6$  after the fifth discharge. At the end of each charge cycle, the cell was disassembled to rinse the  $Na_xK_yNi_2SbO_6$  and then reassembled using a fresh electrolyte (0.7 M KPF<sub>6</sub> in EC/DEC) and a fresh K metal anode to

ensure that no resodiation occurred. The positions and relative intensity ratios of the diffraction peaks for Na<sub>x</sub>K<sub>y</sub>Ni<sub>2</sub>SbO<sub>6</sub> after the fifth discharge are identical to those after the first discharge. If Na ions are progressively extracted from the material during each charge process, the XRD pattern after the fifth cycle should show a reduced amount of the Na-rich phase. Our findings suggest that Na ions remaining after the first charge are not extractable, consistent with other findings in the literature.<sup>17–19</sup> Therefore, a plausible mechanism for the Na-rich phase formation observed by XRD is redistribution of residual Na in the material, rather than reinsertion.

The coexistence of the distinct Na- and K-rich phases in discharged  $Na_xK_yNi_2SbO_6$  can be directly demonstrated by STEM/EDS mapping. Figure 7a-g shows STEM/EDS images obtained from  $Na_xK_yNi_2SbO_6$  at the first discharge. In Figure 7a-c, the Na- and K-rich domains are clearly separated and distinguishable. As the *a*-axis of the crystal is aligned with the electron-beam direction, the Na-rich domains lie along the



**Figure 8.** K–Na site energy calculation in  $Na_xK_yNi_2SbO_6$ . (a) Schematic illustration of K–Na mixing in  $Na_{3-x}K_xNi_2SbO_6$ . (b) K–Na site energy difference in  $Na_3Ni_2SbO_6$  structure as a function of fraction of K occupancy in "layer 1". The remainder of the sites in layer 1 are occupied by Na. For example, 60% K occupancy indicates 60% K and 40% Na in layer 1. (Blue: K–Na site energy difference between layer 1 and layer 2; olive: K–Na site energy difference between layer 1 and other layer.) (c) Slab space change of 1st layer and other layers as a function of K occupancy in the layer 1.

direction perpendicular to the *c*-axis, i.e., in the *ab*-plane of the layered structure. The other elements (oxygen, antimony, and nickel) are uniformly distributed in the particle, as observed in Figure 7d-g. Figure 7h presents an HR-TEM image obtained from the area where the Na- and K-rich domains coexist. We see that the Na-rich domain with a slab spacing of  $\sim$ 5.3 Å is separated from the K-rich domains with a slab spacing of  $\sim 6.3$ Å (Figure 7i,j). This feature was observed throughout the sample. The STEM-EDS images in Figure 7k,l also show the phase separation between the two phases, with a small K-rich domain sandwiched between large Na-rich phases. It is likely that Na ions are redistributed inside the particle rather than travel to other particles because the former is faster. We believe this is the first direct observation of the stacking of Na- and Krich phases along the *c*-axis in a particle resulting from  $Na^+/K^+$ ion exchange in layered oxides. We investigated the morphology of Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub> after Na<sup>+</sup>/K<sup>+</sup> exchange. Figure S3 shows the SEM images of Na, Ni, SbO<sub>6</sub> before and after electrochemical Na<sup>+</sup>/K<sup>+</sup> exchange reactions. While the overall particle size and shape do not change after the Na<sup>+</sup>/K<sup>+</sup> exchange, some cracks are observed in the particle. The cracks might come from large lattice mismatch between K- and Nainserted regions.

### 4. DISCUSSION

The data in Figure 4–6 indicates that rearrangement of residual Na ions in the material may lead to the formation of Na-rich phases upon potassiation. To further investigate this phase separation in  $Na_{3-x}K_xNi_2SbO_6$ , we use density functional theory to calculate the variations of site energies for Na upon K intercalation in O3– $Na_{3-x}K_xNi_2SbO_6$ . A 2 × 1 × 7 supercell of  $Na_{3-x}K_xNi_2SbO_6$  is used and a representative structure is shown in Figure 8a. We model K-intercalation in a single layer denoted as layer 1. The layers above and below the layer 1 are defined as layers 2. Layers further away from layer 1 are referred to as other layers. Layers "2" and "others" are fully occupied by Na. Layer 1 is fully occupied as well but with

mixed Na and K occupancy. Figure 8b shows the difference in Na site energy in layer 2 (blue color) or layer "other" (olive) and layer 1. In all cases the site energy difference is negative indicating that Na prefers the pure layer "2" or "other" over coexistence with K in layer 1. This is the case for all fractions of K in layer 1.

These finding suggest that Na does not want to mix with K in layer 1. The lower value of  $E_{\text{site}}^{\text{Other}} - E_{\text{site}}^{\text{layer1}}$  compared to  $E_{\text{site}}^{\text{layer2}} - E_{\text{site}}^{\text{layer1}}$  suggests that Na also wants to move away from K along the c-axis, strongly suggesting that separate phases will form. Figure 8c shows how the slab spacing of layer 1 and other layers change as a function of K occupancy in layer 1. The slab spacing of layer 1 gradually increases from ~5.6 Å when layer 1 is occupied with Na to ~6.4 Å as the K occupancy increases to 100%. In contrast, the slab spacing of the other layers is independent of the K content in layer 1, as similarly reported for Li<sub>r</sub>Na<sub>v</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>, where Na ion intercalation does not affect the adjacent Li slab spacing.<sup>14</sup> We reason from Figure 8c that the increasing slab spacing of layer 1 upon K insertion increases the Na site energies in that layer, which explains why Na prefers to segregate into other layers further away from the K intercalated layer (layer 1) as seen in Figure 8b. While the computed  $Na_{3-x}K_xNi_2SbO_6$  compound is at slightly higher alkali content than the experimentally discharged state (2.66 alkali ions) we believe that its results qualitatively show that Na and K ions do not prefer to mix in the same layer.

We also performed site energy calculations in the P3-type structure of  $Na_{1.5}Ni_2SbO_6$  with 66.7% Na replaced by K in layer 1 (Figure S4) to confirm that K and Na ions do not prefer to mix in the prismatic sites of the same layer. In this calculation we used a Na deficient composition  $(Na_{1.5}Ni_2SbO_6)$ , which has P3-type oxygen stacking. From the calculations it is clear that the Na site energy from Na layers that are far away from the substituted layer (layer 1) is still lower than that in layer 1 where Na and K ions are mixed. However, it is also worth noting that the site energy difference

is smaller compared with the case of  $Na_3Ni_2SbO_6$  indicating that the effective repulsion between  $Na^+$  and  $K^+$  in the same layer decreases with decreasing concentration. This observation is consistent with the repulsion being driven by elastic effects. At high states of charge it may therefore become possible for the remaining  $Na^+$  and  $K^+$  to mix in a layer, which would be consistent with the peak broadening observed in the diffraction pattern in Figure S2.

By combining the findings from the in situ XRD and DFT computations we can now rationalize the phase behavior of  $Na_xK_yNi_2SbO_6$  when it subjected to K insertion. In Figure 9 we



Figure 9. Experimentally derived ternary phase diagram for the desodiation and potassiation of K–Na–Ni<sub>2</sub>SbO<sub>6</sub>. The dashed line represents the potassiation, *y*, in NaK<sub>y</sub>Ni<sub>2</sub>SbO<sub>6</sub>. Along binary axes (Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> to Ni<sub>2</sub>SbO<sub>6</sub>; Ni<sub>2</sub>SbO<sub>6</sub> to K<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub>, single phases and two-phase reactions are solid bars and hatched bars, respectively. Colors denote different phases indexed by XRD: O3 (yellow), P3 (blue), O1 (red),  $\alpha$  (purple),  $\beta$  (orange), and  $\gamma$  (green). Across the ternary phase diagram, colored areas are single-phase regions corresponding to the phase as colored on the respective binary axis, areas with thin black lines represent two-phase regions, gray areas are three-phase regions.

show a qualitative ternary phase diagram constructed to be consistent with the phase evolution observed by in situ XRD. In this phase diagram single phases are shown as colored regions: O3 (yellow), P3 (blue), O1 (red),  $\alpha$  (purple),  $\beta$ (orange), and  $\gamma$  (green). Two-phase regions are hatched with the hatch lines representing the tie lines which connect the compositions of the two phases in equilibrium. Finally, threephase equilibria are indicated by the light gray triangles and consist of a linear combination of three phases with fixed composition. In general, tie lines in two-phase regions span either two Na-only, two K-only, or a Na-only and K-only phase consistent with our DFT finding that Na and K do not prefer to mix in the same compound. A small amount of solubility is drawn in each single phase, though this solubility is not accurately determined. The first charge from point 1 to point 2 follows the desodiation process from Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> to NaNi<sub>2</sub>SbO<sub>6</sub>. In O1-NaNi<sub>2</sub>SbO<sub>6</sub>, the remaining Na ions are likely distributed evenly over all the layers in the O1 structure.<sup>20–22</sup>

The first discharge from point 2 to point 3 involves potassium insertion into NaNi<sub>2</sub>SbO<sub>6</sub>, to form NaK<sub>1.66</sub>Ni<sub>2</sub>SbO<sub>6</sub>. Tracking this potassium insertion across the phase diagram now shows the reason for the remarkable phase evolution observed. Increasing the K concentration starting from O1 makes the system enter the three-phase region O1–P3- $\alpha$ . As

the inserted K requires regions that are free of Na ions, Na becomes more concentrated in other regions driving the Na domains into the O1-P3 phase region. In this three-phase region the system takes up K by increasing the fraction of  $\alpha$ phase and reducing the amount of O1 phase ultimately bringing the material into two-phase coexistence between P3 and  $\alpha$ . At this point, increasing the K content leads to a firstorder transformation from  $\alpha$  to  $\beta$  (P3 +  $\alpha$  +  $\beta$ ). Once this transformation is complete P3 transforms to O3 to concentrate the Na even further in the material pushing the system into what appears to be a small two-phase region between O3 and  $\beta$ . The P3  $\rightarrow$  O3 transformation enables the volume fraction of  $\beta$  to increase thereby accommodating more K. Finally, the system enters another three-phase region by transforming  $\beta$  to  $\gamma_{i}$  and ultimately loses all  $\beta$  to end in a two-phase region between O3 and  $\gamma$ .

Remarkably, the system obeys the Gibbs phase rule at all times. Even though both the pure Na and pure K system display two-phase regions when their alkali concentration is changed, the combined ternary system never traverses a twophase region on the Na and K side at the same time, as such a four-phase equilibrium would violate the Gibbs phase rule. Instead, whenever two Na-rich phases are present, only a single K-rich phase is present and vice versa, as can be observed in Figure 5. Hence, most of the time three phases are in equilibrium in this mixed-alkali system, either two Na phases and one K phase or two K phases and one Na phase.

The rearrangement of the Na ions in the material upon potassiation requires mobility of the Na-ion and a transport path from one layer to another. It is unlikely that Na penetrates the close-packed Ni<sub>2</sub>SbO<sub>6</sub> layers (i.e., migrates perpendicular to the layers). One plausible mechanism of Na redistribution in the layered structure is via solvent-assisted surface-ion diffusion, which was recently demonstrated in LiFePO<sub>4</sub> by Li and colleagues.<sup>33</sup> According to their work, organic solvent molecules in electrolytes effectively promote the surface-ion diffusion occurring at LiFePO<sub>4</sub>, rendering it a three-dimensional Li-ion conductor. Similarly, Na ions in Na<sub>x</sub>Ni<sub>2</sub>SbO<sub>6</sub> may move from one layer to another via solvent-assisted surface diffusion. Another possibility is temporary solvation of Na<sup>+</sup> followed by desolvation and reinsertion.

Recently, Xiao et al. studied Li<sup>+</sup>/Na<sup>+</sup> ion exchange in layered LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub><sup>14</sup> and observed the segregation of Liand Na-rich phases upon sodiation in delithiated  $Li_x Ni_{1/3} Mn_{1/3} Co_{1/3} O_2$ , similar to our findings in  $Na_xK_vNi_2SbO_6$ . However, they argued that the phase separation is attributable to inhomogeneous delithiation and that Na ions intercalate in the Li vacancies without affecting the Li ions; they also did not consider that Li ions could move from one layer to another upon Na intercalation. Our results indicate that there may be a straightforward thermodynamic explanation for these observations. Like K and Na, Li and Na do not like to mix in a single alkali layer, which will qualitatively lead to phase similar to the one shown in Figure 9. Hence, when a partially delithiated compound is sodiated, it is likely that Li-rich phases form and update their concentration as Na is inserted. However, as typically less phase transformations take place in lithium layered oxides, these Li concentration changes may only be observable from a shift in their peak positions.

Exchange of alkali ions is quite common, either in ionexchange reactions<sup>4,5,12,13,34–36</sup> or when charged cathodes with remaining alkali are cycled with a different alkali.<sup>14–17,37,38</sup> Our observations and explanations indicate that results in these systems may be more complex to interpret than previously acknowledged. For example, Gwon et al. observed unidentified phases during the electrochemical Na<sup>+</sup>/Li<sup>+</sup> exchange in Na<sub>0.29</sub>Li<sub>0.53</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>.<sup>13</sup> Those phases are neither Li<sub>x</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> nor Na<sub>x</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>.

Finally, the interaction between a remaining and inserted alkali may also provide design benefits for cathodes. In the mixed alkali system investigated in this paper the voltage is not just the traditional insertion chemical potential<sup>39</sup> but also needs to account for the concentration of the remaining alkali ions in the cathode. This concentration (in our case Na) comes at an energy cost, which increases the energy of the discharged product and lowers the potential. In addition the presence of an alkali ion that redistributes when the electroactive alkali is removed may be used to prevent a structure from reaching a complete state of charge and thereby prevent oxygen loss<sup>40</sup> or a sudden drop in alkali mobility.<sup>41,42</sup>

#### 5. SUMMARY

In this work, we rigorously investigated the electrochemical  $Na^+/K^+$  ion exchange mechanism in  $Na_3Ni_2SbO_6$ . We found that K ion insertion into the desodiated Na, Ni<sub>2</sub>SbO<sub>6</sub> leads to the phase separation between K- and Na-rich phases. The phase separation of the K- and Na-rich phases does not originate from simultaneous K and Na intercalation from the electrolyte. Instead, K insertion into Na<sub>2</sub>K<sub>2</sub>Ni<sub>2</sub>SbO<sub>6</sub> requires areas that are free of Na, thereby pushing the remaining Na ions into higher concentration domains. This thermodynamic coupling creates phase transition between Na-only phases, even though the Na concentration of the sample does not change. Interestingly, because of this phenomenon three phases are usually present for the desodiation and potassiation of Na<sub>x</sub>K<sub>v</sub>Ni<sub>2</sub>SbO<sub>6</sub>: "one K-rich and two Na-rich phases" or "two K-rich and one-Na-rich phase", consistent with the Gibbs phase rule for the ternary Na-K-host system. Our theoretical study demonstrates that the root cause of the phase separation is the large lattice mismatch along the *c*-axis between the two phases (K-rich and Na-rich phases). Our observations have implications for other exchange systems and indicate that results in "ion-exchange" reactions may be more complex to interpret than previously understood. We also observed that a certain amount of Na ions are not extractable from the Na<sub>3</sub>Ni<sub>2</sub>SbO<sub>6</sub> structure even after repeated electrochemical  $Na^+/K^+$  ion-exchange processes, which could explain why completion of the ion exchange is difficult in some layered oxide compounds.

# ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01152.

Rate capability of  $Na_xNi_2SbO_6$  in a K half-cell; ex situ XRD patterns of  $Na_xK_yNi_2SbO_6$  after the 1st and 2nd charge; SEM images of  $Na_xNi_2SbO_6$  before and after electrochemical  $Na^+/K^+$  exchange reactions; the atomic configuration of  $Na_{1.5-x}K_xNi_2SbO_6$  and the K–Na site energy difference in the  $Na_{1.5-x}K_xNi_2SbO_6$  structure when K occupancy at layer 1 is 66.7% (PDF)

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#### Notes

The authors declare no competing financial interest.

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