Microstructural control of new intercalation layered titanoniobates with large and reversible d-spacing for easy Na\textsuperscript{+} ion uptake

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Key issues for Na-ion batteries are the development of promising electrode materials with favorable sites for Na\textsuperscript{+} ion intercalation/deintercalation and an understanding of the reaction mechanisms due to its high activation energy and poor electrochemical reversibility. We first report a layered H\textsubscript{0.43}Ti\textsubscript{0.93}Nb\textsubscript{1.07}O\textsubscript{5} as a new anode material. This anode material is engineered to have dominant (200) and (020) planes with both a sufficiently large d-spacing of \(\sim\)8.3 Å and two-dimensional ionic channels for easy Na\textsuperscript{+} ion uptake, which leads to a small volume expansion of \(\sim\)0.6 Å along the c direction upon Na insertion (discharging) and the lowest energy barrier of 0.19 eV in the [020] plane among titanium oxide–based materials ever reported. The material intercalates and deintercalates reversibly 1.7 Na ions (\(\sim\)200 mAh g\textsuperscript{-1}) without a capacity fading in a potential window of 0.01 to 3.0 V versus Na/Na\textsuperscript{+}. Na insertion/deinsertion takes place through a solid-solution reaction without a phase separation, which prevents coherent strain or stress in the microstructure during cycling and ensures promising sodium storage properties. These findings demonstrate a great potential of H\textsubscript{0.43}Ti\textsubscript{0.93}Nb\textsubscript{1.07}O\textsubscript{5} as the anode, and our strategy can be applied to other layered metal oxides for promising sodium storage properties.

INTRODUCTION

Na-ion batteries (NIBs) have recently attracted growing attention for large-scale energy storage systems because of the fourth abundant element and the low cost of sodium (1, 2). In general, NIBs operate through the same mechanism as Li-ion batteries (LiBs) based on the shuttling of alkali ions between the cathode and the anode upon cycling (that is, the rocking chair or shuttlecock) (3). However, the Na\textsuperscript{+} ion has a larger cation radius and a heavier atomic weight (1.06 Å and 23 g mol\textsuperscript{-1}) than the Li\textsuperscript{+} ion (0.76 Å and 6.9 g mol\textsuperscript{-1}), which causes sluggish Na\textsuperscript{+} ion kinetics and a high potential barrier on intercalation into and deintercalation from active materials (4). A concentration variation of the Na\textsuperscript{+} ions in a microstructure of a host often accompanies the structural phase transition or phase separation that could cause coherent strain-stress and deteriorate electrochemical properties. Thus, the search for active materials with favorable sites for Na\textsuperscript{+} ion diffusion and an understanding of the reaction mechanisms, such as intercalation/deintercalation, conversion, and alloying, are important for the development of NIBs.

Transition metal oxides have been intensively studied as electrode materials, especially the intercalation/deintercalation mechanism (5–8). For the cathodes, layered Na\textsubscript{M}O\textsubscript{2} (M = 3d transition metals) compounds with alternating Na and M layers have proven to be promising, and the reaction mechanisms have been well established. It has been demonstrated that P2-type materials (\(x < 1\)) show better sodium storage properties than do O3-type materials because Na\textsuperscript{+} ions easily occupy larger trigonal prismatic sites in the P2 phase than smaller octahedral sites in the O3 phase. Moreover, the phase transition of the P2 phase to the others is relatively restricted, which leads to the negligible structural change (1, 9–11). In contrast, the studies for the anode materials have been less reported because of a lack of the promising transition metal compounds. Among them, titanium oxides have been proposed because of the lower redox potential of Ti\textsuperscript{3+/4+}. Layered Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}, \(n = 3\) members of the A\textsubscript{2}M\textsubscript{2n−1}O\textsubscript{4n+2} (A = Na, K and M = Ti, Nb, Ta) (12, 13) family, has the lowest reaction voltage (~0.3 V) versus Na/Na\textsuperscript{+} and uptakes 2 Na in the unit cell equivalent to the capacity of ~178 mAh g\textsuperscript{-1}. However, it shows a low initial coulombic efficiency of <50% and a continuous capacity fading during cycling. Although the reaction mechanism has not been fully understood, it is thought to be the two-phase reaction between Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} and Na\textsubscript{4}Ti\textsubscript{3}O\textsubscript{7} from the viewpoint of its plateau in the voltage profile (14–16). The spinel Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} with the “zero-strain” characteristic in LIB has also been explored. It shows an average reaction voltage of ~0.91 V and a reversible capacity of ~150 mAh g\textsuperscript{-1}. It was found that the reaction takes place through the unusual three-phase reaction of 2Li\textsubscript{2}Ti\textsubscript{3}O\textsubscript{12} + 6Na \(\leftrightarrow\) Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} + Na\textsubscript{8}Li\textsubscript{2}Ti\textsubscript{3}O\textsubscript{12}, which exhibits a quite large unit cell expansion of ~13%. For those multiphase reactions, the phase transformation inevitably develops, and interfaces between the different phases can deteriorate the Na\textsuperscript{+} ion diffusivity (17).

To overcome these obstacles, engineering microstructures, including lattice parameter, d-spacing, and planes with lower activation energies, which govern Na\textsuperscript{+} ion kinetics in active materials, can be powerful methodologies (18). In this respect, layered KTiNbO\textsubscript{5} (KTN) [\(n = 2\) members of the family A\textsubscript{2}M\textsubscript{2n−1}O\textsubscript{4n+2}] (19) is of great interest because of its unique structure with alternating K and M layers and a large d-spacing of ~0.94 nm, which can accommodate foreign species, including organic and inorganic species, into the layers. Moreover, potassium can be removed and exchanged for other cations, such as H\textsuperscript{+}, Li\textsuperscript{+}, and NH\textsubscript{4}\textsuperscript{+} (20–22). The appealing feature of those new compounds is that they almost retain their original structure and c parameter even after the cation exchange. In particular, HTiNbO\textsubscript{5} (HTNO) could provide the largest space and channels for Na\textsuperscript{+} ions because of the occupancy by protons with the smallest ionic radius of ~0.012 Å, which has motivated us to explore this compound as an anode material for NIBs.

Here, we first report the titanoniobate HTNO as the potential anode material for NIB. To promote sodium storage properties, we engineered a parent material, KTN, to allow it to have a dominant
(200) plane with a large d-spacing via an optimization of a calcination temperature. HTNO is further optimized by a partial removal of protons H⁺ to compensate more empty space and favorable ionic channels for Na⁺ ions while maintaining its original unit cell parameters. Various electrochemical characterizations, including charge/discharge, cycles, rates, and galvanostatic intermittent titration technique (GITT), are used to demonstrate the effect of engineering a dominant (200) plane on sodium storage property and the calculation of Na⁺ ion diffusion coefficient. Moreover, a reaction mechanism is investigated from direct experimental evidence using ex situ x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). Finally, to support experimental data, we used a density functional theory (DFT) calculation to theoretically assess the potential of HTNO with a favorable channel for Na⁺ ions as an anode material for NIBs.

RESULTS
Control on dominant planes of the starting material KTNO
Figure 1A shows unit cell structures of the parent compound KTNO. KTNO has a layered structure that consists of alternating 2 × 2 (Ti/Nb)O₆ edge-sharing octahedral and potassium layers, which have a direct effect on a and c parameters. As shown in the figure, (200) and (020) planes have an open frame with a large d-spacing of ~0.94 nm due to the intercalated potassium cations between the layers. Two-dimensional (2D) ionic channels can be obtained from KTNO after the removal of potassium cations, which could provide large reaction sites and enable high Na⁺ ion diffusivity, as shown in the bottom unit cells of (200), (020), and (101) planes. In contrast, the (002) plane is built with infinite blocks of (Ti/Nb)O₆ layers with a small d-spacing of ~0.32 nm, in which sluggish or limited Na⁺ ion diffusion is anticipated because of a lack of ionic channels through the (002) plane even if the potassium cations are removed. It should be noted that it is important to find out the favorable ionic channels from the crystallographic study, given that the main parameters governing the electrochemical performances are its crystal structure features, such as structure types, lattice parameters, and vacancies, according to LIBs (23).

KTNO is usually prepared by the solid-state reaction at the high calcination temperature over ~1100°C, which inevitably leads to the preferential crystalline growth to the (002) plane. To engineer microstructures of KTNO, including planes, sizes, and shapes, we used a solvothermal method to prepare amorphous K/Ti/Nb composite and then thoroughly optimized a calcination temperature as the bottom-up approach. Figure 1B shows XRD patterns of KTNO calcined at 500°, 700°, 900°, and 1100°C (KTNO-500/700/900/1100). Each peak, except for KTNO-500, was well indexed as the reference (International Centre for Diffraction Data (ICDD) card no. 54-1155). In particular, KTNO-700 has a dominant (200) plane compared to KTNO-900/1100. For a detailed structure analysis, Rietveld refinement was performed on KTNO-700 (fig. S1 and table S1). KTNO-700 has refined lattice parameters.
As shown in the graph, with an increase in the calcination temperatures, the intensity of the (002) peak was stronger and the (002) plane finally became the most dominant plane in KTNO-1100. This phenomenon was also observed by scanning electron microscopy (SEM) (fig. S2). Owing to their preferential growth, nanosized particles without a particular shape (KTNO-700) were transformed from microsized rods (KTNO-900) to microsized plates (KTNO-1100). As a result, the SEM and XRD studies demonstrate that the significant crystal growth and the change in dominant planes of KTNO develop at the temperature above ~700°C, and the control of calcination temperature is important to engineer the intrinsic properties, including size, geometry, and plane, of KTNO.

The microstructures of KTNO samples were characterized by schemes in Fig. 1C and TEM in Fig. 1D. KTNO-700 is a nanoparticle in the range of 50 to 100 nm. Rod-shaped KTNO-900 has a length of ~600 nm and a width of ~200 nm. KTNO-1100 shows a rectangular plate shape. KTNO-700 has a dominant (200) plane with a lamellar structure and a large interlayer distance of ~0.94 nm. For KTNO-900/1100, the same (002) lattice fringe of 0.32 nm was observed (Fig. 1E). Figure 1F shows the selected-area electron diffraction (SAED) patterns projected along the [100] direction for KTNO-700 and the [001] direction for KTNO-900/1100, which confirms their high crystalline phases and an orthorhombic unit cell with $\alpha = \beta = \gamma = 90^\circ$. For a compositional analysis of the KTNO after calcination, inductively coupled plasma optical emission spectroscopy (ICP-OES) was used. It revealed that the as-prepared sample is a nonstoichiometric $K_{0.90}Ti_{0.93}Nb_{1.07}O_5$ compound. According to previous reports (24, 25), $K_1-xTi_{1-x}Nb_{1+x}O$ has the same crystalline structure but slightly different lattice constants within the range of $0 \leq x < 0.3$, which agrees with our experimental results.

### Characterization of a topotactic reaction of $H_{0.85}Ti_{0.93}Nb_{1.07}O_5$

Layered HT$K_{1-x}Ti_{1-x}Nb_{1+x}O_5$ was prepared from the parent structure $K_{0.90}Ti_{0.93}Nb_{1.07}O_5$ via the simple cation exchange method (26, 27). Considering that the HTNO should act as a negative material in this experiment, it uptakes Na$^+$ ions into its unit cell at the beginning of discharging (Na insertion). In this regard, it is favorable to remove the occupied K$^+$ ions between (Ti/Nb)O$_6$ layers and compensate more reaction sites for Na$^+$ ions. Figure 2A shows SEM images of KTNO-700 particles before and after the cation exchange. The particle size of both KTNO and HTNO is ~100 nm, and there are no significant changes in the shape and size between them. To investigate the cation exchange rate, the amount of K$^+$ ions in the HTNO sample was examined by ICP-OES. The ratio of K to Ti to Nb was 0.05:0.93:1.07, which indicates that almost 95% of K ions were exchanged for H ions (hereafter designated as $H_{0.85}Ti_{0.93}Nb_{1.07}O_5$).

Although the $H_{0.85}Ti_{0.93}Nb_{1.07}O_5$ nanoparticles provide favorable intercalation sites for Na$^+$ ions through 2D ionic channels, it is better to eliminate protons in $H_{0.85}Ti_{0.93}Nb_{1.07}O_5$ to minimize the repulsion forces due to proton presence. For a compositional analysis of the HTNO after calcination, inductively coupled plasma optical emission spectroscopy (ICP-OES) was used. It revealed that the as-prepared sample is a nonstoichiometric $K_{0.90}Ti_{0.93}Nb_{1.07}O_5$ compound. According to previous reports (24, 25), $K_1-xTi_{1-x}Nb_{1+x}O$ has the same crystalline structure but slightly different lattice constants within the range of $0 \leq x < 0.3$, which agrees with our experimental results.
force between H\(^+\) and Na\(^+\) ions and prevent any side reaction with the electrolyte. We determined defect formation energy developed by proton elimination using DFT calculation (fig. S3). The calculated defect formation energy with a charge \(q\) \(\Delta E_f(q)\), as a function of the Fermi level, can be calculated using the following equation (28)

\[
\Delta E_f(q) = E[D^0] + \mu_i - E^0 + q(E_v + \Delta V + \varepsilon_f)
\]  

(1)

The oxygen and nitrogen chemical potentials at a given temperature, \(T\), and partial pressure, \(P\), were expressed using the ideal gas approximation (29)

\[
\mu_O(T, P_{O_2}) = \frac{1}{2} \beta_{O_2}(T, P^*) + k_B T \ln \left( \frac{P_{O_2}}{P} \right)
\]  

(2)

\[
\mu_H(T, P_{H_2}) = \frac{1}{2} \beta_{H_2}(T, P^*) + k_B T \ln \left( \frac{P_{H_2}}{P} \right)
\]  

(3)

The formation energy of single H vacancy is found to be negative with dominant charge state \(q = -1\). Hence, the nonstoichiometric form of HTNO is assumed to be thermally stable. From a charge viewpoint, there might be unpaired electrons and dangling bonds created by hydrogen evolution. In addition, the calculation confirms that Nb substitution for Ti near the defects can also occur, which will contribute to a charge neutrality of H\(_{0.85}\)Ti\(_{0.97}\)Nb\(_{1.07}\)O\(_5\) without a significant change in the oxidation states of Ti\(^{4+}\) and Nb\(^{5+}\). In contrast, removing all the H atoms in HTNO costs large energy (>4 eV per H atom), which can result in an unstable unit cell structure. In this regard, the elimination of H atoms inevitably causes changes in the unit cell structure and formula of HTNO (the so-called topotactic reaction).

The topotactic reaction of the HTNO compound was investigated and optimized by TEM, TGA (thermogravimetric analysis), and XRD in terms of post-annealing temperatures. Figure 2B shows the TGA curve of H\(_{0.85}\)Ti\(_{0.97}\)Nb\(_{1.07}\)O\(_5\) in the range of 25° to 900°C. The total weight loss is ~5.5 wt % from the initial sample, which is mostly due to the removal of H\(^+\) (~4.5 wt % in total). There are two significant slopes at ~300° and 450°C and a plateau above ~700°C. Rebbah et al. proposed the change in atomic compositions of HTiMo\(_5\) (M = Nb and Ta) during the annealing process in air as follows (20)

\[
2\text{HTiNbO}_5 \rightarrow \text{H}_2\text{O} + \text{Ti}_2\text{Nb}_2\text{O}_9 \text{(at } \sim 330°C\} \quad (4)
\]

\[
\text{Ti}_2\text{Nb}_2\text{O}_9 \rightarrow \text{TiNb}_2\text{O}_7 + \text{TiO}_2 \text{(at } \sim 750°C\} \quad (5)
\]

The removal of proton proceeds in the range of 25° to 330°C. On the basis of the chemical equations, the post-annealing temperatures of 300°C (II), 450°C (III), and 700°C (IV) were chosen. On the basis of Eq. 1 and the thermogravimetric curve, a ~4.5 wt % weight loss is ascribed to the total removal of 0.85 hydrogen in H\(_{0.85-x}\)Ti\(_{0.93}\)Nb\(_{1.07}\)O\(_5\) in the temperature range of 25° to 400°C. In this regard, the weight loss in the range of 25° to 300°C is approximately 2.3 wt %, which is converted to a removal of 0.43 hydrogen. Therefore, the x value of 0.42 is given to the HTNO-300 sample (designated as H\(_{0.42}\)Ti\(_{0.93}\)Nb\(_{1.07}\)O\(_5\)). Figure 2C shows XRD patterns of the dried HTNO sample at 100°C (HTNO-100) and the post-annealed HTNO samples (HTNO-300/450/700). HTNO-300 has almost the same peak positions despite the partial removal of H\(^+\) (H\(_{0.42}\)Ti\(_{0.93}\)Nb\(_{1.07}\)O\(_5\)). In contrast, HTNO-450/700 show (002) peak shifts to higher angles of ~11.9° and 17.5° (black arrows), which indicates a decrease in the c parameter. It should be noted that all those titanoniobates maintain the layered structures and channels of (200)- and/or (020)-derived planes due to the gliding of (Ti/Nb)O\(_5\) layers only.
through $a$ and $c$ directions and the slight unit cell changes (fig. S4) (30, 31). Figure 2 (D to G) shows inverse fast Fourier transform (FFT) images and their corresponding line profiles to visualize the change of d-spacing ($c$ lattice constant). All the samples exhibit well-defined parallel layers composed of (Ti/Nb)O$_6$ octahedra. As temperatures increase, the number of stacking layers increases from 6 to 9, whereas the interlayer distances decrease to ~0.85, ~0.83, ~0.74, and 0.53 nm.

To thoroughly monitor the lattice parameter changes, Rietveld refinement experiments were carried out on each sample, as shown in Fig. 3, and refined lattice parameters were summarized in table S2. The crystallographic information demonstrates the same $c$ parameter decrease. In addition, we demonstrated that the HTNO-700 sample is a composite of TiNb$_2$O$_7$ and rutile TiO$_2$, which agrees with the previous theory proposed by Rebbah et al. (20). However, there is a discrepancy in the weight ratio between the two phases. The theoretical ratio calculated from their molecular weights is 81:19. According to the refined value, the weight ratio of TiNb$_2$O$_7$ and rutile TiO$_2$ is 63.3:36.6, which deviated from the theoretical ratio. This might be due to the slight lower calcination temperature that is not sufficient for the crystallization and the separation of two phases. Further studies are needed to clarify this point in future work. Atomic coordinates and site occupancies of all the samples after the refinement were also listed in tables S3 to S6.

**Sodium storage property of $H_{0.43}Ti_{0.93}Nb_{1.07}O_5$ and its derivatives**

Theoretical capacities were first determined on the basis of their total atomic weights and possible three redox couples of Ti$^{4+/3+}$, Nb$^{5+/4+}$, and Nb$^{4+/3+}$ using the same concept of TiNb$_2$O$_7$ as an anode material for LIB (32–35). The calculated capacities are 360 mAh g$^{-1}$ (HTNO-100/300), 362 mAh g$^{-1}$ (HTNO-450), and 378 mAh g$^{-1}$ (HTNO-700). All the electrochemical properties were then characterized in a potential window of 0.01 to 3.0 V versus Na/Na$^+$ at room temperature. First, the sodium storage property of KTNO-700 and HTNO-100 was evaluated to clarify the effect of the cation exchange of K$^+$ for H$^+$ and the obtained 2D channels for Na$^+$ ions (fig. S5A). KTNO-700 exhibits almost half the capacity of HTNO-100 after the cation exchange, which confirms that the removal of K$^+$ ions gives much larger reaction sites for Na$^+$ ions upon charging/discharging. Second, the electrochemical properties of HTNO samples prepared from KTNO-700/900/1100 were characterized (fig. S5B). Three electrodes show discharge/charge capacities of 213/201, 205/145, and 174/129 mAh g$^{-1}$. Coulombic efficiencies were 94, 71, and 74%. Noticeably, the property of Na deinsertion (charging) is significantly different between samples, in contrast to the property of the Na insertion (discharging) even at a slow rate of 0.1 C. Hence, the improvements in not only the capacity but also the efficiency of HTNO-100 prepared from KTNO-700 could be due to the size reduction as well as the dominant (200) and (020) planes capable of favorable Na$^+$ ion diffusion channels. Third, the effects of the removal of protons and d-spacing changes were investigated to optimize the electrochemical performances (Fig. 4A). HTNO-100/300/450/700 electrodes delivered charge capacities (Na deinsertion) of 201, 228, 187, and 135 mAh g$^{-1}$ with high coulombic efficiencies of 94, 97, 95, and 90%, respectively. Figure 4B shows a cycle performance and coulombic efficiencies over 150 cycles at a high rate (1 C). Capacity retentions were 87% (153 mAh g$^{-1}$), 91% (174 mAh g$^{-1}$), 83% (102 mAh g$^{-1}$), and 71%...
(67 mAh g⁻¹) for the HTNO-100, HTNO-300, HTNO-450, and HTNO-700 electrodes, respectively. Figure 4C shows the rate capability at various current densities (0.2 to 10 C). Although HTNO-100 shows a remarkable property, the capacity retention of HTNO-300 was better than that of HTNO-100 over the whole current densities. Particularly, the retention of HTNO-300 is ~43% (98 mAh g⁻¹) at an extremely high rate (10 C). Another rate capability was tested in HTNO-300 by fixing the discharge rate at 0.1 C (Na insertion) and changing the charge rate from 0.2 to 20 C (Na deinsertion). A high capacity retention of ~77% (152 mAh g⁻¹) was obtained even at 20 C, as shown in Fig. 4D. To the best of our knowledge, with these outstanding performances, HTNO-300 exceeds the titanium oxide materials previously reported, in terms of coulombic efficiency, discharge capacity, and rate capability (table S7) (14, 15, 17, 36–42). It should be noted that the improvements on the coulombic efficiency and rate capability could be assigned not only to favorable microstructures of HTNO but also to the use of an ether-based electrolyte, diethylene glycol dimethyl ether. It has been recently demonstrated that the ether-based electrolytes have relatively higher anodic stability than carbonate-based electrolytes, resulting in the negligible solid electrolyte interface (SEI) layer formation and improved electrochemical properties of graphite through the intercalation/deintercalation reaction (43, 44). This agrees with the TEM observation in the HTNO sample after one cycle. No noticeable SEI layer was found on the surface of the HTNO particle (fig. S6). Hence, the introduction of the ether-based electrolytes can provide one route to improved sodium storage properties of transition metal oxides that particularly experience the intercalation/deintercalation reaction.

To determine the Na⁺ diffusivity of HTNO-300, we used GITT. A transient voltage profile was obtained by applying a constant current density of ~360 mA g⁻¹ on the anode for 30 min and switching off for 1 hour (rest time), as shown in Fig. 4E. The Na⁺ diffusion coefficient (DNa) was calculated by using Eq. 6 based on Fick’s second law

\[ D_{Na} = \frac{4}{\pi \tau} \left( \frac{m_3 V_m}{M_1 A} \right)^2 \left( \frac{\Delta E_n}{\Delta E_T} \right)^2 \]

Figure 4F shows the overall LA of four samples during charging. The average sodium diffusion coefficient (DNa) of HTNO-300 is ~2.6 × 10⁻¹² cm² s⁻¹.

### Characterization of a reaction mechanism of H₅O₃TiO₂.₇₉Nb₂.₃₁O₅

An electrochemical reaction mechanism of HTNO was investigated by ex situ XRD analysis (Fig. 5). It revealed that Na insertion and deinsertion take place through a solid-solution reaction and/or a pseudo-capacitive reaction instead of the phase separation evidenced not only by the continuous peak shifts without evolution of new peaks but also the voltage profile with a smooth slope and no plateau (Fig. 3A), which is observed in active materials such as rutile TiO₂, layered Li₄Ti₅O₁₂, and Li₂TiS₂ for the solid-solution reaction (45–47) and in titania nanotubes (nt-TiO₂) for the pseudocapacitive reaction (48, 49). HTNO exhibits a reversible lattice constant change along the c direction during cycling (8.4 Å (pristine) → 9.0 Å (Na insertion) → 8.6 Å (Na deinsertion)). It is worth noting that a great advantage of using active materials that experience the insertion/deinsertion mechanism such as HTNO is that they can prevent large volume changes upon cycling, which is observed in materials that undergo conversion or alloying reactions.

For further characterization of the Na⁺ reaction mechanism, TEM, STEM, STEM-EELS (electron energy-loss spectroscopy), and DFT calculations were used. Figure 6A shows an HRTEM image of (NaₓH₀.₄₃)Ti₀.₉₃Nb₁.₀₇O₅ after discharging to 0.01 V versus Na/Na⁺. It retains its lamellar structure without a structural collapse. Moreover, a STEM image and an energy-dispersive x-ray spectroscopy (EDX) map in Fig. 6B confirm that Na⁺ ions (blue) were distributed in the space between the (Ti/Nb)₆ layers, not in the whole area, which strongly supports the solid-solution reaction mechanism as shown in Fig. 6C.

The DFT calculation was carried out to obtain the diffusion energy barrier of Na⁺ ions in TiNbO₅ crystal and explain why the control of the dominant plane with favorable ionic channels is important. As shown in Fig. 6D, the simulation was performed specifically in the [010] direction, which is assumed to be one of the most open channels of the HTNO host for Na⁺ ions. The energy barrier of Na atoms in bulk TiNbO₅ is determined to be ~0.19 eV, which is much smaller than ~0.91 eV of Na⁺ ions in Li₄Ti₅O₁₂ (previously reported as the promising oxide material) (17) and ~0.4 eV of Na⁺ ion diffusion in the Na layer of Na₀.₆₆Li₀.₃₄Ti₀.₇₈O₅ (the lowest value ever reported) (39). Therefore, the simulation result supports the fact that our material is an excellent Na⁺ ion conductor with energetically favorable Na⁺ ion channels.

EELS core-loss spectra of Na K-edge, Nb M₄,5-edge, and Ti L₃-edge were determined before and after charging to investigate a change of oxidation states. As shown in Fig. 6E, no edge was observed in pristine HTNO. After sodiation, Na K-edge associated to 1s electrons is characterized by an edge with onset potential at ~1080 eV, which is a direct evidence of Na⁺ intercalation (50). Figure 6F shows Ti ELNES (energy-loss near-edge structure) spectra related to the electron transitions from Ti 2p to Ti 3d levels in the molecular orbitals. Before sodiation, the L₁₃-edge is split into peaks labeled as a, a’, and b, and the L₂₋₃-edge into peaks labeled as c and d. After sodiation, a’ in the L₁₋₃-edge almost disappears, and two white lines become broader and less distinct. In addition, the onset potentials of two edges shift to the lower energy (L₃: 460.5 → 460.3 eV and L₂₋₃: 466.3 → 465.8 eV). This is due to a decrease in oxidation state of Ti⁴⁺ to Ti³⁺ (51). It is worth noting that the Ti ELNES spectrum after charging is almost identical to the Magnéli phase Ti₃O₅ or TiₓO₅ (52). The ratios of Ti⁴⁺ to Ti³⁺ in two phases are 1:1 and 1:2, respectively, which confirms the partial reduction of Ti in (NaₓH₀.₄₃)Ti₀.₉₃Nb₁.₀₇O₅. Nb ELNES spectra were obtained as shown in Fig. 6G. The Nb M₄,5 edges represent the electron transition from Nb 3d levels to unoccupied Nb 4f and 5p levels. Nb ELNES spectra...
also show the same trend as that of titanium in the shift of the $M_{5,4}$ edges to the lower energy position after sodiation, which is attributed to the decrease in the oxidation state of Nb$^{5+}$ (53). Bach et al. (53) performed the EELS investigation of Nb$_2$O$_5$ (+5), NbO$_2$ (+4), and NbO (+2). In comparison with Nb ELNES spectra in the reference, the delayed maximum shape after sodiation is similar to that of NbO$_2$ (+4), which is an evidence for the reduction of niobium. Because the variations of the valance states of Ti and Nb transition metals have a direct effect on the degree of distortion of (Ti/Nb)O$_6$, it is deduced from the EELS spectra that an electron transfer from Na metal to HTNO was estimated from the variation of the valance states of Ti and Nb. It is in the range of 1.5 to 1.7 e$^-$, which is converted to a capacity of 180 to 204 mAh g$^{-1}$ and agrees with the capacity obtained from the electrochemical performance. Finally, (Na$_{1-x}$H$_{0.43}$)Ti$_{0.93}$Nb$_{1.07}$O$_5$ can be labeled as Na$^{+}$ ions that occupy the sites between the (Ti/Nb)O$_6$ layers. The resultant was washed with ethanol and centrifuged at 1000 rpm for 10 min three times. The precipitation was

**DISCUSSION**

In summary, layered H$_{0.43}$Ti$_{0.93}$Nb$_{1.07}$O$_5$ was applied to an anode material for NIBs for the first time. The parent compound KTNO was designed to have a dominant (200) plane for 2D ionic channels by the solvothermal method and with controlled calcination temperature. HTNO has an optimized interlayerspace of ~8.3 Å and favorable 2D ionic channels to Na$^+$ ions after cation exchange and the partial removal of H$^+$ ions through the optimized post-annealing process. The HTNO electrode shows a reversible capacity of ~220 mAh g$^{-1}$, a stable cycle performance of ~91% capacity retention over 150 cycles, and a high rate capability of ~43% capacity retention at 5 C. The DFT calculation confirmed the lowest diffusion energy barrier of 0.19 eV for Na$^+$ ions in the [010] direction due to the favorable open channels for Na$^+$ ion transfer. It was also demonstrated that the reaction of HTNO takes place through the solid-solution mechanism and accompanies a small lattice change of ~0.6 Å along the c direction upon charging, rather than the phase separation, which might release strain upon reaction and enable stable cycle performance. Our design strategy opens a new avenue to the development of the promising anode material by engineering microstructures, such as lattice constants, planes, and d-space, for easy uptake of Na$^+$ ions and can be applied to new layered transition metal oxides for NIBs in the future.

**MATERIALS AND METHODS**

**Synthesis**

KTNO nanoparticles were prepared by the solvothermal method. In detail, 0.1 ml of diethylentriamine (99% Sigma-Aldrich) was dissolved in 40 ml of isopropyl alcohol. After magnetic stirring for 5 min, 0.56 g of potassium acetate (American Chemical Society reagent, ≥99.0%; Sigma-Aldrich), 0.35 ml of titanium (IV) isopropoxide (≥99.0%, Sigma-Aldrich), and 0.3 ml of niobium (V) ethoxide (99.95% trace metal basis, Sigma-Aldrich) were added in the solution. The mixture was magnetically stirred for 12 hours. Then, it was transferred to an 80-ml Teflon-lined stainless steel autoclave and kept in an oven at 200°C for 12 hours. After the reaction was over, a yellowish precipitation was obtained. The resultant was washed with ethanol and centrifuged at 1000 rpm for 10 min three times. The precipitation was

![Fig. 6. Characterization of Na$^+$ ion insertion mechanism of H$_{0.43}$Ti$_{0.93}$Nb$_{1.07}$O$_5$.](http://advances.sciencemag.org/)
dispersed in a mixture of ethanol and deionized water by tip sonication and dried in an oven at 80°C until the liquid was totally evaporated. The obtained powder was thoroughly ground using a mortar and pestle and calcined at 700/900/1100°C in air for 5 hours (at a heating rate of 5°C min⁻¹) in a tube furnace to obtainKTNO nanoparticles/rods/plates. For KTNO nanoparticles, the obtained powders were dispersed in deionized water by tip sonication. Then, only the supernatant was transferred and dried to obtain very fine KTNO nanoparticles without agglomeration. HTNO nanoparticles/rods/plates were prepared by cation exchange of H⁺ ions for K⁺ ions in as-prepared KTNO. In a typical synthetic way, 0.5 g of KTNO particles was immersed in 5 N hydrochloric acid solution for 48 hours at room temperature. After the cation exchange reaction, the powder was washed with distilled water and centrifuged until the supernatant was neutralized at pH 7. Then, the powder was dried in an oven at 110°C.

Characterizations

The size and morphology of as-prepared KTNO and HTNO particles were studied using field-emission SEM (JEOL, JSM7060F), field-emission TEM (FEI, Titan 80-300), STEM-EDX, and EELS. In detail, a low-magnification TEM study was carried out at an operation voltage of 300 kV, and high-magnification TEM, STEM, and STEM-EELS studies were performed at a lower operation voltage of 80 kV to protect the samples from damage during the observation. X-ray powder diffraction patterns were obtained with an XRD analyzer (Rigaku, D/MAX RINT-2000). The tests were performed in the range of 5° to 70° at a scan rate of 3.0°/min under the continuous scan mode and using a CuKα x-ray source. To obtain ex situ XRD patterns, 2025-type coin cells were assembled and cycled at different cutoff voltages (charge to 1.0/0.8/0.6/0.4/0.2/0.01 V and discharge to 0.4/1.0/1.2/1.8/2.3/3.0 V). After cycling, the cells were disassembled to take out the electrodes. The samples were immersed in diethyl ethylene carbonate (Sigma-Aldrich, anhydrous, ≥99%) solution to remove any residual electrolyte and by-product. The electrodes were peeled off from the copper current collector using a polyimide (Kapton) tape and sealed to prevent them from contact with air and moisture. All experiments for the sample preparation were carried out in an Ar-filled glove box. Ex situ XRD patterns were collected at a slower scan rate of 0.5°/min. To determine the amount of potassium, titanium, and niobium in KTNO and HTNO composites, ICP-OES was used. To investigate the topotactic reaction of the HTNO particles coupled with XRD analysis, the thermal weight change of the sample was examined by thermogravimetry and with a differential thermal analyzer (SDT Q600, Auto-DSCQ20 system). All the unit cell structures for KTNO and HTNO were drawn by the 3D visualization program for structural models (VESTA 3).

Electrochemical measurement

For the evaluation of electrochemical performances, working electrodes were prepared by making slurry. In a typical procedure, KTNO and HTNO particles as active materials, acetylene black as a conducting agent, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 were put in a 20-ml vial and thoroughly mixed using a Thinky mixer at a high rotation speed of 2000 rpm for 3 min. As-prepared slurry was cast on a copper foil (T = ~18 μm) using a doctor blade. A mass loading level of the electrodes was set at ~0.5 mg/cm². The electrode was dried in an oven at 110°C for 20 min. Before the cell assembly, all the electrodes were dried in a vacuum oven at 120°C for 5 hours to remove residual moisture in the electrodes. For half-cell tests, 2032-type coin cells, which consist of the electrodes with KTNO and HTNO particles, acetylene black, PVDF as a working electrode, sodium foil as a counter electrode, 1.0 M Na₂SO₄·CF₃ in diethylene glycol dimethyl ether (diglyme) as an electrolyte, and a polypropylene film as a separator, were assembled. For electrochemical evaluation, all the cells were aged for at least 12 hours and tested using a battery cycle tester (TOSCAT 3000, Toyo System). Impedance spectra were gained using an impedance analyzer (PARSTAT 2273, Princeton Applied Research).

GITT measurement

The GITT was used to calculate Na⁺ ion diffusivity coefficients of HTNO nanoparticles with different values of d-spacing. Internal resistances of each sample were obtained from the gap between the quasi-open-circuit voltage (60-min rest) and the closed-circuit voltage (30-min current application) in each transient step at 0.1 C.

DFT calculation

DFT calculations were performed using the generalized gradient approximation, with Perdew-Burke-Ernzerhof parameterization (54, 55). We used the Vienna ab initio simulation package (VASP) program (56). Khon-Sham orbitals were expanded with a cutoff energy of 400.0 eV, and 2 × 2 × 2 equally spaced k-point grids (57) were used for the Brillouin zone sampling for the supercell with 168 atoms (Ti₂₃Nb₂O₆₃). To calculate the diffusion energy barrier of Na atoms in TiNbO₅ crystal, we used the “drag method,” which is the most intuitive method to obtain the diffusion energy barrier of single atoms.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/10/e1700509/DC1

fig. S1. HR-XRD patterns of as-prepared KTNO calcined at 700°C.
fig. S2. SEM observation of as-prepared KTNO particles.
fig. S3. DFT calculation for defect chemistry of HTiNbO₅.
fig. S4. Change in unit cell structures through a and c directions as a function of post-annealing temperatures.
fig. S5. Sodium storage properties.
fig. S6. Ex situ TEM observation.
table S1. Rietveld lattice parameters of KTNO calcined at 700°C.
table S2. Refined unit cell parameters and R values of HTNO and its derivatives.
table S3. Refined atomic coordinates and site occupancies of HTNO-450.
table S4. Refined atomic coordinates and site occupancies of HTNO-100.
table S5. Refined atomic coordinates and site occupancies of HTNO-300.
table S6. Refined atomic coordinates and site occupancies of HTNO-450.
table S7. Electrochemical performances of titanium-based oxide materials as negative electrodes for NIBs by virtue of the insertion/deinsertion mechanism.

REFERENCES AND NOTES

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Microstructural control of new intercalation layered titanoniobates with large and reversible d-spacing for easy Na\(^+\) ion uptake

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