Layered \( \text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2 \) and \( \text{K}_2\text{Ti}_2\text{O}_4(\text{OH})_2 \) Nanoarrays for Na/Li-Ion Intercalation Systems: Effect of Ion Size

Jiale Xie\(^{a,b,c} \) Pingping Yang\(^{a,b} \) and Hong He\(^{a,b,z} \)

\(^{a}\) Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, People’s Republic of China
\(^{b}\) Chongqing Key Laboratory for Advanced Materials & Technologies of Clean Electrical Power Sources, Chongqing 400715, People’s Republic of China
\(^{c}\) Key Laboratory of Luminous and Real-Time Analytical Chemistry, Southwest University, Ministry of Education, Chongqing 400715, People’s Republic of China

Energy conversion and storage is a key issue in daily life and industry field. The urgent need of renewable and clean energy has attracted great attention in low-cost, safety and rechargeable battery with adequate voltage, capacity and rate capacity. Nowadays, Li ion battery (LIB) has conquered the portable electronic market, offering higher voltage, capacity and rate capacity with adequate voltage, capacity and rate capacity. However, the amount of storage on earth and higher cost to obtain Li has become a critical barrier to popularization and sustainable application in battery energy storage. Due to the wide availability and low-cost of sodium, Na ion battery (NIB) is a promising alternative to LIB in the future. But sodium has a lower reducing voltage (-2.71 V vs. SHE) and the gravimetric capacity is lower (1165 mAh g\(^{-1}\) vs. sodium, there is no dimensional change in layered materials. This work clearly demonstrates the influence of ion size in both electrode material and electrolyte. This provides convenience to study the effects of ion size in both electrode material and electrolyte. This work clearly demonstrates the influence of ion size in both electrode material and electrolyte.

Vertically oriented \( \text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2 \) (NTO) and \( \text{K}_2\text{Ti}_2\text{O}_4(\text{OH})_2 \) (KTO) nanoarrays on Ti foils are synthesized via one-step hydrothermal method. These titane-based layered materials with different cations are utilized to assemble binder-free LiNa- ion batteries (LIBs/NIBs). We experimentally find the ion size difference of K, Na and Li in electrode materials or/and electrolyte can dramatically influence the performances of LIBs/NIBs. NTO with larger volume of unit cell shows higher capacity in both NIBs (213 mAh g\(^{-1}\) at 165 mAh g\(^{-1}\) and LIBs (509 mAh g\(^{-1}\) vs. 288 mAh g\(^{-1}\)). That is, the ion size in host materials can significantly influence the intercalation/extraction of Na and Li ions. On the other hand, Na ions with larger size and atomic mass in the electrolyte show slower charge transfer (81.5-144.9 vs. 0.23 \( \mu \)s) and ion diffusion (7.52 \( \times 10^{-10} \) cm\(^2\) s\(^{-1}\) vs. 1.33 \( \times 10^{-9} \) cm\(^2\) s\(^{-1}\)) in Na\(_2\)Ti\(_2\)O\(_4\)(OH\(_2\)) based cells) than that of Li ions. This work clearly demonstrates the influence of ion size, which can clarify and provide fundamental information for fabricating high energy density and long-life batteries. In addition, it demonstrates that both Na\(_2\)Ti\(_6\)O\(_{13}\) (OH\(_2\)) and K\(_2\)Ti\(_6\)O\(_{13}\) (OH\(_2\)) can be used as anode materials with more than two ions storage, as for LIBs (4.6 for Na\(_2\)Ti\(_2\)O\(_4\)(OH\(_2\)) and 2.9 for K\(_2\)Ti\(_6\)O\(_{13}\)(OH\(_2\))), and NIBs (1.9 for Na\(_2\)Ti\(_2\)O\(_4\)(OH\(_2\)) and 1.7 for K\(_2\)Ti\(_6\)O\(_{13}\)(OH\(_2\)). Moreover, it is demonstrated that Li/Na ions are stored between the adjacent layered sheets in Na\(_2\)Ti\(_2\)O\(_4\)(OH\(_2\)) and K\(_2\)Ti\(_6\)O\(_{13}\)(OH\(_2\)).

Experimental

Material preparation.—NTO was prepared by basic hydrothermal growth process of Ti foil in NaOH solution. Typically, a piece of Ti foil (2.5 \( \times 3.0 \) cm\(^2\)) was ultrasonically cleaned in water, ethanol and 4% HCl for 15 min each, and then placed against the wall of a 50 mL Teflon-lined stainless steel autoclave filled with 30 mL 1 M NaOH. After that, the sealed autoclave was kept inside in an electric oven at 220 °C for 24 h. After the hydrothermal reaction, Ti foil covered with NTO nanoarrays was washed with deionized water. Finally, the obtained NTO films were dried at 60 °C for 30 min. KTO was synthesized as same as above, except for using 1 M KOH solution.

Structural characterization.—Scanning electron microscope (SEM) equipment with energy dispersive spectrometer (EDS) and transmission electron microscope (TEM) experiments were performed on a JSM-6510LV and a JEM-2010 electron microscope, respectively. X-ray diffractometer (XRD) measurements were carried out on a XRD-7000 X-ray diffractometer using Cu K\(_\alpha\) radiation at 0.05° 2θ.
\[ \lambda = 1.54 \, \text{Å} \]

Nitrogen adsorption/desorption isotherms for surface area and pore analysis were measured at 77 K using a NOVA 1200e instrument. Thermal stability was examined with thermogravimetric analysis (TGA), Q50 in N\(_2\). To obtain the lattice constants, XRD and selected area electron diffraction (SAED) patterns are used to calculate lattice constants.

**Electrochemical measurement.**—Ti foils covered NTO on one side were cut into disc with tabling machine. Electrochemical tests were performed with 2035 coin cells with Na or Li metal as counter electrodes. The electrolyte was 1 M NaClO\(_4\) dissolved in a mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (1:1 by v.), and the separator was a microporous membrane (Celgard 2135). The cells were assembled in an argon-filled glove box. The galvanostatic charge-discharge tests were conducted at a voltage interval of 0.01-2.5 V with a Land System. Cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.05 mV s\(^{-1}\) using a CHI 660D electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were also conducted on CHI 660D in the frequency range of 0.01-10\(^5\) Hz at open circuit voltage. The measurement conditions of KTO were identical to NTO. For LIBs, the electrolyte is 1 M LiPF\(_6\) in a mixture of EC, diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1:1:1 by v.).

**Results and Discussion**

NTO and KTO have a layered structure (Fig. S1a) and belong to an orthorhombic system.\(^{28,29}\) The body-centered orthorhombic NTO (or KTO) consists of edge-sharing TiO\(_6\) octahedral that form corrugated layers, between which hydrated Na (or K) cations and protons (H\(^+\)) are located.\(^{30}\) The Na and K ions can be easily replaced with other elements by ion exchange reaction.\(^{22}\) The thermal stability of NTO was firstly characterized by thermogravimetric analysis under a nitrogen atmosphere. At 500 °C, only \(\sim 6\%\) mass loss is recorded due to dehydroxylation (Fig. S1b), which is consistent with similar layered titanate-based nanostructures, and is quite similar to that of mineral kassite (CaTi\(_2\)O\(_4\)(OH)\(_2\)).\(^{34–36}\) So it means the K may not be adequate as a counter ion for KTO. C. Kim et al. also observed the similar XRD peaks.\(^{33}\) After KOH-treated sample, the XRD pattern complies with the formula of K\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\), of which the phase is identical to Na\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\). This result is the same as that of mineral kassite (CaTi\(_2\)O\(_4\)(OH)\(_2\)).\(^{34–36}\) So it means the K may not be adequate. C. Kim et al. also observed the similar XRD peaks. After the Li or Na insertion, the asterisk peaks disappear, which means the inadequate K is supplied with Li or Na.

The morphological and structural characters of as-prepared NTO and KTO further characterized using TEM. Fig. 2a shows the uniform diameter distribution (\(\sim 79\) nm) of NTO nanowires, while it shows the large diameter distribution (around 20–125 nm) of KTO nanowires/nanobelts in Fig. 2d. Lattice resolution TEM images displayed in Figs. 2b and 2e further show that the lattice fringe perpendicular to the growth orientation of nanowire/nanobelt has an interplanar spacing of 0.193 nm (NTO) and 0.202 nm (KTO), corresponding to (020) facets respectively. Selected area electron diffraction patterns show single-crystalline patterns, indicating NTO and KTO nanocrystals are aligned with each other along growth orientation of [001] direction. Some crystal facets are also marked in Figs. 2c and 2f.

The crystal structure of NTO and KTO films are characterized by XRD. The diffraction peaks of NaOH-treated films match well with orthorhombic Na\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\), which is identical to layered H\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\) (JCPDS, Card no. 47–0124). The observed diffraction peaks at 2\(\theta\) = 10.15°, 24.1°, 28.3°, 48.2° and 49.3°, correspond to the lattice planes (200), (110), (310), (020) and (220), respectively. The other peaks marked with square come from the Ti substrate.\(^{33}\) The lattice constants of NTO calculated from XRD are: \(a = 1.741\) nm and \(b = 0.377\) nm. For KOH-treated sample, the XRD pattern complies with the formula of K\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\), of which the phase is identical to Na\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\). This result is the same as what C. Kim et al. reported.\(^{33}\) The observed diffraction peaks of K\(_2\)Ti\(_2\)O\(_4\)(OH)\(_2\) at 2\(\theta\) = 10.63°, 24.1°, 28.4° and 47.7°, correspond to the lattice planes (200), (110), (310) and (020), respectively. The lattice constants of KTO calculated from XRD are: \(a = 1.663\) nm and \(b = 0.381\) nm. The difference of lattice constants between NTO and KTO can be attributed to the different radius and bond energy between Na and K ions. This provides the opportunity to investigate the effects of ion size. The asterisk marked peaks in Figs. 3a and 3b resemble a phase with crystal structure, and is quite similar to that of mineral hortsmithite (CaTi\(_2\)O\(_4\)(OH)\(_2\)).\(^{34–36}\) So it means the K may not be adequate. C. Kim et al. also observed the similar XRD peaks. After the Li or Na insertion, the asterisk peaks disappear, which means the inadequate K is supplied with Li or Na.

**Figure 1.** SEM images of as-prepared (a-d) and charge/discharged (e-h) films of NTO and KTO. The charge/discharged films of NTO and KTO are obtained from cycled NIBs (e, f) and LIBs (g, h).
Figure 2. TEM images of as-prepared NTO (a, b) and KTO (d, e). (c, f) SAED patterns of NTO and KTO, respectively.

Figure 3. (a, b) XRD patterns of NTO, KTO and the first full-intercalated NTO and KTO with Li (a) and Na (b) ions. (c) Nitrogen adsorption/desorption isotherms of NTO and KTO. (d) Pore diameter distribution curves of NTO and KTO.
After the first full discharge, the (200) and (020) peaks have visible movement. The magnified XRD patterns of (200) and (020) peaks are shown in supplementary Fig. S2. Based on this and TEM measurements, the lattice constants of as-prepared and intercalated NTO/KTO (Table I) can be obtained (see Table I note). As shown in Table I, lattice constant $a$ shows a larger shift than that of lattice constant $b$, e.g. 0.034 nm vs. 0.001 nm for NTO in LIBs. This can directly and powerfully demonstrate that the Li/Na ions are stored between the adjacent layered sheets in NTO and KTO. Element contents of various electrode materials are also illustrated in Table I, confirming the ion transfer of Li, Na and K during the first full discharge. The volume of NTO-based LIBs marked in Fig. 5a. But the three redox peaks of NTO-based LIBs are barely visible. During CV measurements, both one-dimensional nanoarrays are also collected and characterized by TEM. Figs. 4a and 4b show the first full-intercalated NTO with Na. The surface of NTO nanowire has some nanoparticles and ∼7.9 nm external layer which is distinct from the inside of nanowire. This should be attributed to the fact that the Na intercalation stimulates the volume expansion and the Na2O nanoparticles (SEI film) forms on the external layer. The similar case can be observed on the first full-intercalated KTO with Na (Figs. 4c and 4d). However, in LIBs, it has not been observed. This maybe a result of the smaller size of Li ions, but it also needs further investigation to reveal the inherent mechanism. After Na insertion, the variation value of the lattice distance of (020) plane is 0.151 nm and 0.155 nm for NTO and KTO, respectively. As for Li insertion process, the variation value of the interplanar spacing of (020) is 0.011 nm and 0.031 nm for NTO and KTO, respectively. This clearly and powerfully demonstrates Na with larger size will induce large volume expansion. And NTO with large volume of unit cell is favorable to Li/Na storage and has small volume expansion.

Table I. Element contents and lattice constant parameters of various electrode materials.*

| Sample   | Na/at% | K/at% | Ti/at% | O/at% | $a_{XRD}$/nm | $b_{XRD}$/nm | $c_{TEM}$/nm |
|----------|--------|-------|--------|-------|--------------|--------------|--------------|
| NTO      | 10.03  | -     | 28.50  | 61.47 | 1.741        | 0.377        | 0.330        |
| NTO-Li   | 1.76   | -     | 28.35  | 69.90 | 1.707        | 0.378        | -            |
| NTO-Na   | 10.53  | -     | 28.04  | 61.43 | 1.769        | 0.377        | -            |
| KTO      | -      | 7.40  | 32.12  | 60.48 | 1.663        | 0.381        | 0.316        |
| KTO-Li   | -      | 4.79  | 24.12  | 71.08 | 1.691        | 0.380        | -            |
| KTO-Na   | 4.85   | 4.88  | 28.89  | 61.38 | 1.778        | 0.381        | -            |

*Note: ‘at%’ refers to the atomic ratio in the sample. ‘$a_{XRD}$’ refers to the lattice constant $a$ obtained from XRD characterizations. ‘$c_{TEM}$’ refers to the lattice constant $c$ obtained from TEM characterizations. The samples of NTO-Li, NTO-Na, KTO-Li and KTO-Na are collected from the first full discharged batteries.

Figure 4. TEM images of the first full discharged NTO with Na (a, b) and Li (e, f). TEM images of the first full discharged KTO with Na (c, d) and Li (g, h).
cathodic curves show great decay between first and second cycles (e.g. from \(-0.5 \text{ A g}^{-1}\) to \(-0.25 \text{ A g}^{-1}\)), suggesting the formation of the SEI films. On first and second cycles, the redox peaks overlap so they could not be well defined. Some peaks such as peak II or/and peak III only existed during the first cycle, indirectly suggesting them are from the side reaction. NTO-based LIBs show higher intensity of oxidation peak I, indicating more Li ions can be efficiently extracted from NTO. NTO shows more anodic redox peak potential (1.48 V) than that of KTO (1.1 V). The difference is consistent with the fact that the reducing voltage of potassium is lower than that of sodium.

The redox reactions of MTO (M = Na or K) in Li intercalation system can be illustrated as,

\[
\text{M}_2\text{Ti}_2\text{O}_4(\text{OH})_2 + x\text{Li}^+ + xe^- = \text{Li}_x\text{M}_2\gamma\text{Ti}_2\text{O}_4(\text{OH})_2 + y\text{M} \quad [1]
\]

In Fig. 5b, for NIBs, two broader redox peaks can be observed. Among the first three cycles, all the intensity of redox peaks decrease gradually. But the magnitude of this decrease is not large as LIBs and the side reaction is not significant. Moreover, NTO-based NIBs show higher intensity of oxidation peak I, indicating more Na ions can be inserted into NTO. NTO shows more anodic redox peak potential (1.48 V) than that of KTO (1.1 V). The difference is consistent with the fact that the reducing voltage of potassium is lower than that of sodium.

The redox reactions of NTO (M = Na or K) in Li intercalation system can be illustrated as,

\[
\text{M}_2\text{Ti}_2\text{O}_4(\text{OH})_2 + x\text{Na}^+ + xe^- = \text{Na}_x\text{M}_2\gamma\text{Ti}_2\text{O}_4(\text{OH})_2 \quad [2]
\]

Figs. 5c and 5d show the first three charge/discharge curves of NTO- and KTO- based NIBs/LIBs. Assuming that there is one electron redox reaction between Ti\(^{4+}\) and Ti\(^{3+}\) (one Na ion storage), the theoretical capacity of NTO and KTO is 111.8 mA h g\(^{-1}\) and 98.6 mA h g\(^{-1}\), respectively. In Figs. 5c and 5d, the first discharge capacity is 1379 mA h g\(^{-1}\) (NTO) and 701 mA h g\(^{-1}\) (KTO) for LIBs, and 472 mA h g\(^{-1}\) (NTO) and 503 mA h g\(^{-1}\) (KTO) for NIBs at 10 mA g\(^{-1}\). These much larger capacities of the first cycle are mainly attributed to the formation of SEI films. For the reversible discharge curves (the third cycle), the number of Na insertion is 1.9 (NTO) and 1.7 (KTO). And the number of Li insertion is 4.6 (NTO) and 2.9 (KTO). Thus, Li ions can be stored easily in NTO and more Li ions can be inserted into the crystal lattice than Na ions.

The rate performance of NTO- and KTO- based LIBs/NIBs is summarized in Figs. 5e and 5f. The cells were cycled at six current densities of 10, 20, 50, 100, 200 and 500 mA g\(^{-1}\) in a voltage window of 0.01-2.5 V. As expected, in both LIBs and NIBs, the discharge capacity decreases as the current density increase. Upon decreasing the current density from 500 mA g\(^{-1}\) to 100 mA g\(^{-1}\), in LIBs, 223 mA h g\(^{-1}\) (NTO) and 200 mA h g\(^{-1}\) (KTO) are obtained, which are about 95.1% and 94.8% capacity retentions, respectively. In NIBs, when the current changed from 500 mA g\(^{-1}\) to 100 mA g\(^{-1}\), 110 mA h g\(^{-1}\) (NTO) and 68 mA h g\(^{-1}\) (KTO) are obtained, which are about 99.3% and 100% capacity retentions, respectively. These results indicate that both LIBs and NIBs have an acceptable rate performance. Comparing NTO with KTO, NTO-based cells possess higher capacities, which is in agreement with the CV curves in Figs. 5a and 5b. At 100 mA g\(^{-1}\), the ratio of NTO capacity to KTO capacity is 2.98 in LIBs, while the ratio is 1.63 in NIBs. Compared with NIBs, LIBs show superior capacity at all current densities. In addition, the Coulombic efficiencies during the rate performance tests are shown in Fig. S3. LIBs have higher efficiencies, even KTO-based LIBs exhibit more than 100% efficiency. This may be due to more quantity of electricity contributed by some K ions in KTO crystal extraction. The
long-term cycling stability is shown in Fig. S4. To quantitatively reveal the stability, the ratio of the 500th cycle capacity to the 5th cycle capacity is calculated. For LIBs, 32.48% and 49.28% are obtained for KTO and NTO, respectively. While 38.46% and 22.48% are obtained in NIBs for KTO and NTO, respectively. Moreover, NTO shows around 100% Coulombic efficiency, while KTO shows less than 100% and more than 100% efficiencies in NIBs and LIBs, respectively. More than 100% efficiency achieved by KTO-based LIBs is agreement with the results in rate performance measurements, suggesting this is repeatable and reliable.

Since the results from the CV curves hint at a diffusion limited response, further investigations were carried out using electrochemical impedance spectroscopy (EIS). EIS is a non-destructive technique to study the electrode kinetics of electrode materials.38 Figs. 6a–6c presents the Nyquist plots of NTO- and KTO-based LIBs/NIBs at open circuit voltage. To distinguish various phenomena taking place in an electrode at different time scales, an equivalent circuit for these cells was used to fit the Nyquist plots, as shown in Fig. 6d. In this circuit, $R_e$ represents the equivalent series resistance. $R_{(sf+ct)}$ depicts the SEI film (sf) and charge transfer resistance (ct). $R_b$ is the bulk (b) resistance. The constant phase elements $CPE_{(sf+ct)}$ is due to the SEI film and double layer (dl) capacitance, whereas $CPE_b$ refers to bulk capacitance. In addition, $W_s$ and $C_{int}$ represent the Warburg impedance and intercalation capacitance. Detailed discussion of this equivalent circuit can be found in the references.38–41 The extracted impedance parameters are listed in Table II. Compared with LIBs, NIBs exhibit larger $R_e$, $R_{(sf+ct)}$ and $W_s$, indicating a larger resistance of electrolyte in NIBs, a slower charge transfer in NIBs, and a slower ion diffusion in NIBs. These results demonstrate, in electrolyte, the Li/Na ions can significantly influence the electrode processes due to the radius and atomic mass differences. For fresh cells, the values of $R_b$ in both cells deliver similar results, demonstrating the NTO- and KTO-covered Ti foils possess almost the same conductivity. But KTO-based cells exhibit higher resistance of $R_{(sf+ct)}$, demonstrating the lower

| Samples                  | $R_e$ / $\Omega$ | $R_{(sf+ct)}$ / $\Omega$ | $CPE_{(sf+ct)}$ / F | $CPE_{(sf+ct)}$-P | $R_b$ / $\Omega$ | $CPE_b$ / F | $CPE_b$-P | $W_s$ / $\Omega$ | $C_{int}$ / F |
|--------------------------|------------------|---------------------------|---------------------|-------------------|-----------------|--------------|------------|----------------|--------------|
| NTO-Li As-prepared       | 2.44             | 41.30                     | 2.55E-5             | 0.79              | 31.42           | 1.88E-2      | 0.75       | 470.7          | 0.54         |
| NTO-Li After cycled      | 3.13             | 43.22                     | 4.91E-5             | 0.85              | 597.7           | 5.77E-3      | 0.60       | 254.3           | 0.13         |
| KTO-Li As-prepared       | 1.86             | 78.53                     | 1.88E-5             | 0.79              | 24.26           | 4.00E-2      | 0.69       | 697.4           | 0.44         |
| KTO-Li After cycled      | 4.83             | 43.25                     | 2.92E-5             | 0.78              | 37.63           | 8.89E-2      | 0.58       | 659.8           | 0.03         |
| NTO-Na As-prepared       | 37.16            | 60.47                     | 6.65E-6             | 0.87              | 37.88           | 1.84E-3      | 0.90       | 945.1           | 1.57         |
| NTO-Na After cycled      | 98.55            | 343.50                    | 2.00E-5             | 0.86              | 63.91           | 1.72E-4      | 0.48       | 579.3           | 0.17         |
| KTO-Na As-prepared       | 17.16            | 141.20                    | 1.28E-5             | 0.84              | 22.13           | 1.44E-2      | 0.98       | 653.8           | 0.04         |
| KTO-Na After cycled      | 31.10            | 319.20                    | 1.72E-5             | 0.90              | 66.37           | 7.19E-5      | 0.76       | 4339            | 0.14         |
describes an ideal capacitor while the case $C_{PEb-P}$ a pure resistor. The reason for the decreased $R_{(sf)}$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $A$ is the area of the electrode surface, $F$ is the Faraday’s constant (96,500 C mol$^{-1}$) and $C$ is the molar concentration of Li/Na ions. For LIBs, the $D$ is $1.33 \times 10^{-9}$ cm$^2$ s$^{-1}$ of as-prepared NTO cell, 1.32 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of cycled NTO cell, 1.34 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of as-prepared KTO cell, and 1.34 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of as-prepared KTO cell. For NIBs, the $D$ is 7.33 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of as-prepared NTO cell, 1.27 $\times 10^{-9}$ cm$^2$ s$^{-1}$ of cycled NTO cell, 1.36 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of as-prepared KTO cell, and 1.80 $\times 10^{-10}$ cm$^2$ s$^{-1}$ of as-prepared KTO cell. NIB-based cells show larger $D$ than that of KTO-based cells, directly demonstrating the large unit cell of NTO is beneficial to the Li/Na ions diffusion. Comparing LIBs to NIBs, LIBs cells have larger $D$ than that of NIBs cells, indicating the smaller and low-weight Li ions has superior diffusion ability. As expected, the as-prepared LIBs have larger $D$ than cycled. However, the cycled NIBs show larger $D$ than as-prepared. This might be due to the relative larger Na ions induced more volumetric expansion and opened diffusion pathway.

**Conclusions**

In summary, we synthesized layered Na$_2$Ti$_2$O$_4$(OH)$_2$ and K$_2$Ti$_2$O$_4$(OH)$_2$ nanoarray films directly on Ti foil substrates via one-step hydrothermal method. Li/Na ions are stored between the adjacent layered sheets in Na$_2$Ti$_2$O$_4$(OH)$_2$ and K$_2$Ti$_2$O$_4$(OH)$_2$, which is demonstrated by XRD characterizations. Based on these two layered materials, the effects of ion size were investigated in LIBs and NIBs cells. Na$_2$Ti$_2$O$_4$(OH)$_2$ with larger volume of unit cell shows 1.76 times and 1.29 times higher capacity in both LIBs and NIBs than that of K$_2$Ti$_2$O$_4$(OH)$_2$ based cells, respectively. That is, the ion size in host materials can significantly influence the intercalation/extraction process of Na and Li ions. On the other hand, Li ions with smaller size and atomic mass in the electrolyte show 1.81 times and 5.53 times faster ion diffusion than that of Na ions in LIBs and NIBs, respectively. The charge transfer of LIBs is 0.23 $\mu$s, which is significant faster than that of NIBs (81.5-144.9 $\mu$s). In addition, both Na$_2$Ti$_2$O$_4$(OH)$_2$ and K$_2$Ti$_2$O$_4$(OH)$_2$ can be used as anode materials with around two ions storage for LIBs (4.6 for Na$_2$Ti$_2$O$_4$(OH)$_2$ and 2.9 for K$_2$Ti$_2$O$_4$(OH)$_2$) and NIBs (1.9 for Na$_2$Ti$_2$O$_4$(OH)$_2$ and 1.7 for K$_2$Ti$_2$O$_4$(OH)$_2$), but the long-term stability should be further improved. This work has clarified how the performance of NIBs/LIBs is affected by the ion size in electrode materials or/and electrolyte.

**Acknowledgments**

This work is financially supported by Fundamental Research Funds for the Central Universities under XDJK2016C005 and XDJK2015C061, China Postdoctoral Science Foundation under 2015M582495, Program for the Youth Talent in Science and Technology of Chongqing (cstc2014kjrc-qnrc50006).

**References**

1. V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez, and T. Rajo, *Energy Environ. Sci.*, 5, 5884 (2012).
2. J. M. Tarascon and M. Armand, *Nature*, 414, 359 (2001).
3. B. L. Ellis, W. R. M. Makahnouk, Y. Makimura, K. Toghill, and L. F. Nazar, *Nat Mater*, 6, 749 (2007).
4. M. D. Slater, D. Kim, E. Lee, and C. S. Johnson, *Adv. Funct. Mater.*, 23, 947 (2013).
5. G. E. Pascal and M. Fouletier, *Solid State Ionics*, 28, 1172 (1988).
6. M. M. Doeff, Y. P. Ma, S. J. Visco, and L. C. Dejonghe, *J Electrochem Soc*, **140**, L169 (1993).
7. S. W. Kim, D. H. Seo, X. H. Ma, G. Ceder, and K. Kang, *Adv Energy Mater*, **2**, 710 (2012).
8. H. Xiong, M. D. Slater, M. Balasubramanian, C. S. Johnson, and T. Rajh, *J Phys Chem Lett*, **2**, 2560 (2011).
9. J. P. Huang, B. X. Lei, H. Y. Chen, D. B. Kuang, and C. Y. Su, *Energ Environ Sci*, **5**, 5750 (2012).
10. M. Sugita, M. Tsuji, and M. Abe, *Bulletin of the Chemical Society of Japan*, **63**, 1978 (1990).
11. Y. Zhang, L. Guo, and S. Yang, *Nanoscale*, **7**, 14618 (2015).
12. J. L. Xie, C. X. Guo, and C. M. Li, *Energ Environ Sci*, **7**, 2559 (2014).
13. M. V. Reddy, R. Jose, T. H. Teng, B. V. R. Chowdari, and S. Ramakrishna, *Electrochimica Acta*, **55**, 3109 (2010).
14. L. Xin, Y. Liu, B. Li, X. Zhou, H. Shen, W. Zhao, and C. Liang, *Sci Rep*, **4**, 4479 (2014).
15. M. Sugita, M. Tsuji, and M. Abe, *Bulletin of the Chemical Society of Japan*, **63**, 1978 (1990).
16. T. Sasaki, M. Watanabe, Y. Komatsu, and Y. Fujiki, *Inorganic Chemistry*, **24**, 2265 (1985).
17. J. Y. Liao, B. X. Lei, H. Y. Chen, D. B. Kuang, and C. Y. Su, *Energ Environ Sci*, **5**, 5750 (2012).
18. M. Shirpour, J. Cabana, and M. Doeff, *Chem Commun*, **49**, 7451 (2013).
19. Z. H. Bi, M. P. Paranthaman, P. A. Menchhofer, R. R. Dehoff, C. A. Bridges, M. F. Chi, B. K. Guo, X. G. Sun, and S. Dai, *J Power Sources*, **222**, 461 (2013).
20. Y. Cui, X. Zhao, and R. Guo, *Electrochimica Acta*, **55**, 922 (2010).