Structure and electrochemical performance of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) as anode materials for lithium-ion battery

Wei Tao¹, Mao-Lian Xu¹, Yan-Rong Zhu^{1*}, Qianyu Zhang^{2*} and Ting-Feng Yi^{1*}

ABSTRACT A series of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) compounds as lithium storage materials were synthesized by a facile solid-state method. X-ray diffraction Rietveld refinement shows that the Bragg positions correspond to the $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$, indicating a successful preparation. The Na^+ ions doped $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ compounds have larger unit-cell volume than the pristine one because ionic radius of Na^+ ion is 55% larger than that of Li^+ ion. SEM shows that the $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0, 0.5$ and 1) powders show similar irregular shaped particles between 500 and 1000 nm. However, $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=1.5$ and 2) powders show similar rod-like shape. CV reveals that the passivating film is mainly formed during the first insertion process, and the solid electrolyte interface film on the surface of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) is formed below 0.7 V in the first cycle. Compared with other samples, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ exhibits higher reversible capacity, better rate capability and superior cyclability. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ delivers the delithiation capacities of 162.1 mA h g⁻¹ at 50 mA g⁻¹, 158.1 mA h g⁻¹ at 100 mA g⁻¹, 156.7 mA h g⁻¹ at 150 mA g⁻¹, 152.2 mA h g⁻¹ at 200 mA g⁻¹, 147.3 mA h g⁻¹ at 250 mA g⁻¹ and 142 mA h g⁻¹ at 300 mA g⁻¹, respectively. An interesting thing is that $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$ as anode also shows an acceptable electrochemical performance. All these improved electrochemical performances of $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ are attributed to the lowest polarization and the highest lithium ion diffusion coefficient among all samples. Hence, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ with excellent cycling performance, simple synthesis route and wide discharge voltage range can be a possible anode candidate for lithium-ion batteries.

Keywords: $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$, $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$, anode material, lithium-ion battery, delithiation capacity

INTRODUCTION

Lithium ion batteries (LIBs) have been considered as one

of the most promising electrochemical energy storage devices as environmentally-friendly energy because of their obvious advantages, such as high energy density and long cycle life. For commercial LIBs, carbonaceous material is often used as anode material. Unfortunately, the carbonaceous anodes cannot satisfy the urgent needs for electric vehicle (EV), hybrid electric vehicle (HEV) or plug-in hybrid electric vehicle (PHEV) due to the safety problem [1–3]. The main safety issue in carbonous anode for LIBs is the dendritic lithium growth on the anode surface at high rates because the conventional carbonous materials approach almost 0 V (*versus* Li/Li⁺) at the end of Li insertion [4]. Hence, developing new anode materials with excellent electrochemical performance and high safety is necessary. Among plenty of developed anode materials, titanate based materials have been regarded as promising candidates for LIBs because of their excellent cycle life and higher operating potential than carbonous materials [5–7]. Among them, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was viewed as one promising alternative to carbonous materials due to its small dimensional change during cycling and high insertion potential (1.55 V, *versus* Li/Li⁺) [8–10]. Despite the great significance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a famous lithium storage material, a new series of Ti-based compounds, $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ ($M = 2\text{Na}, \text{Sr}, \text{Ba}$), were proposed as host materials in LIBs [11–18]. Among them, only few researches on the electrochemical performance of $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ were reported. Solid-state reaction was the most common method to prepare electrode materials, and the physicochemical properties depend greatly on the synthesis conditions [19]. Belharouak *et al.* [20] firstly reported the electrochemical performance of $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ as lithium storage material prepared by a solid-state reaction method. $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ delivered a stable capacity of approximately 140 mA h g⁻¹

¹ School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China

² School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China

* Corresponding authors (emails: zhuyrong@163.com (Zhu YR); zhangqy@dgut.edu.cn (Zhang Q); tfyhit@163.com (Yi TF))

for at least 40 cycles with an operating potential of around 1.4 V, suggesting its potential as high safety anode material. Unfortunately, $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ also approximate insulator, and then exhibits poor electrochemical properties due to the low electronic conductivity and small lithium-ion diffusion coefficient. To solve these problems mentioned above, many approaches were used to improve the electrochemical performance of $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$. One of the most effective method is to dope $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ with heterogeneous ions, such as the Li or Ti-site substitution by Ag^+ [21], Pb^{2+} [22], La^{3+} [23], Al^{3+} [21], etc. In our previous work, we found that Na doping can improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode in Li site because the large ionic radius of Na^+ can expand the migration channel of Li^+ [24]. In addition, Na^+ doping can be considered as an effective way to enhance the electrochemical properties of LiFePO_4 [25] and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [26] cathode material. To our knowledge, doping the $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ with sodium ion has not been reported until now. As we know, sodium is abundant in the earth and less expensive than the most of transition metals and lithium metal [27], so Na doped $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ is expected to be an anode material with lower cost than other transition metals substituted one.

It is generally known that safety of LIBs is the key in the realistic applications as power battery. This is why the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode is often discharged to 1 V (vs. Li^+/Li). However, LIB full battery usually undergoes a risk of explosion for possible inner short circuit due to the drastic operational fault conditions, such as over-charge [28]. The internal short induces an enormous heat instantaneously and locally to cause thermal runaway. The over-discharge (lithiation) of the anode material in half cell corresponds to the over-charge of full battery. Hence, the structural stability (related to safety) of the anode material in half cell at extremely low potential condition becomes very important. Hence, the electrochemical performance of the anode material in half cell deserves serious considerations. In addition, the high-energy density can be obtained with high capacity. Therefore, it is necessary to investigate the over-discharge behaviors (lithiation) down to 0 V of

$\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) anode materials considering the safety and energy density in half cell. The same strategy can also be applied to study relevant Ti-based materials, which opens a way for the evaluation and optimization of this kind of anode materials in the future. With this consideration, Na-doped $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) compounds were prepared by a solid-state method, and the electrochemical performances were investigated in half cells.

EXPERIMENTAL

Material preparation

Pristine $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ and Na-doped $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0.5, 1, 1.5$ and 2) were synthesized by a solid-state reaction, and the preparation process is illustrated in Fig. 1. Anatase TiO_2 (AR, 99.0%), BaCO_3 (AR, 99.0%), Li_2CO_3 (AR, $\geq 99.0\%$), and Na_2CO_3 (AR, 99.5%), used as raw materials, were mixed by ball milling for 4 h in an acetone slurry, followed by drying at 80°C for 12 h. The obtained mixture was pretreated at 600°C for 4 h, and then calcined at 950°C for 10 h in air to obtain the final products. Excessive Li (3 wt.%) was provided to compensate for the volatilization of Li during synthesis.

Material and electrochemical characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku instrument with Cu K α radiation. The particle morphologies of the samples were examined using a scanning electron microscope (SEM, SU8000). CR2025 coin-type cells were used to perform electrochemical characterizations. The working electrodes comprise active material (80 wt.%), carbon black conductive additive (10 wt.%) and polyvinylidene difluoride binder (10 wt.%). The average loading of active material is about 1.8 mg cm^{-2} . Metal lithium and Celgard 2300 porous membrane were used as counter electrodes and separator, respectively. The electrolyte solution was 1 mol L^{-1} LiPF_6 /ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1:1:1 by volume). Cyclic voltammetry (CV)

Figure 1 Schematic of the preparation process of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) powders.

test was carried out on a CHI 1000C electrochemical work station in a voltage range between 0 and 3 V (*versus* Li/Li⁺), and the scanning rate is 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was measured by a PAR-STAT4000 electrochemical work station over a frequency range from 0.01 to 10 kHz, and the potentiostatic signal amplitude is 5 mV. Charge-discharge performance of the cell was characterized galvanostatically on a Land 2000T (Wuhan, China) tester at different rates between 0 and 3 V (*versus* Li/Li⁺).

RESULTS AND DISCUSSION

Fig. 2 shows that the XRD patterns of all the as-prepared BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) compounds. It can be found that all peak signals of the samples correspond to the orthorhombic structure BaLi₂Ti₆O₁₄ phase with *Cmca* space group [29], indicating that Na doping does not change the structure. No impurity peak is observed in the XRD pattern of all samples, indicating a successful substitution by Na ion in BaLi₂Ti₆O₁₄. These results are confirmed by the XRD Rietveld refinement profiles of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) compounds as shown in Fig. 3. It is clearly seen that the Bragg positions correspond to the BaLi₂Ti₆O₁₄, indicating a successful preparation. However, according to the refinement results, it can be found that the Na⁺ doped BaLi₂Ti₆O₁₄ compounds have larger unit-cell volume than the pristine one because ionic radius of Na⁺ ion is 55% larger than that of Li⁺ ion, and an obvious shift of diffraction peaks for BaNa₂Ti₆O₁₄ can be found.

SEM was used to study the surface morphology and elemental composition of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) compounds. Fig. 4 shows the SEM images of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) compounds. It can be found that BaLi_{2-x}Na_xTi₆O₁₄ (x = 0, 0.5 and 1) powders show similar irregular shaped

Figure 2 XRD patterns of BaLi_{2-x}Na_xTi₆O₁₄ (x = 0.0, 0.5, 1.0, 1.5, 2.0) powders.

particles between 500 and 1000 nm. However, BaLi_{2-x}Na_xTi₆O₁₄ (x = 1.5 and 2) powders show similar rod-like shape, indicating that there is a different morphology between BaLi₂Ti₆O₁₄ and BaNa₂Ti₆O₁₄ prepared by the same method, suggesting the successful fabrication of Li-site doping by Na in the structure of BaLi_{2-x}Na_xTi₆O₁₄. In addition, the energy dispersive spectrometer (EDS) mapping results of BaLi_{2-x}Na_xTi₆O₁₄ (x = 1.5) compound also prove the existence of Na, Ba, Ti and O elements in the BaLi_{0.5}Na_{1.5}Ti₆O₁₄ powder as shown in Fig. 5. EDS results supply a strong evidence about the uniform element distribution of Na, Ba, Ti and O elements in BaLi_{0.5}Na_{1.5}Ti₆O₁₄, suggesting the successful doping by Na in the structure.

To get clear on the nature of the redox behavior, the CV tests of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) compounds were carried out. Fig. 6 exhibits the initial three CV cycles of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) half cells between 0 and 3.0 V at 0.1 mV s⁻¹. In the first cycle, two redox peaks during cycling can be found in the BaLi_{2-x}Na_xTi₆O₁₄ (x = 0 and 0.5). The first discharge (lithium intercalation process) process evolves with two reduction peaks at 1.24 and 1.51 V, which are related to the step-by-step formation of BaLi_{2-x}Ti₆O₁₄ from the BaLi₂Ti₆O₁₄ phase. According to previous reports [29,30], lithium ions occupy 8f, 4a, 4b and 8c sites in turn during the lithium intercalation process, which correspond to the voltage plateau (or slope) at 1.54 V (8f), 1.36 V (4a, 4b) and 0.50–1.2 V (8c), respectively. Then, the process is reversed in charge (lithium deintercalation) with two oxidation peaks at a potential value of 1.13 and 1.35 V, corresponding to the removal of Li⁺ ion from the lithiated BaLi_{2-x}Ti₆O₁₄. However, the redox peaks located at 1.13/1.24 V gradually disappear in the BaLi_{2-x}Na_xTi₆O₁₄ (0.5 ≤ x ≤ 1.5). These results reveal that Na doping affects the redox behavior of the half-cells. These two pairs of redox peaks of BaLi₂Ti₆O₁₄ correspond to a two-step reversible intercalation reaction above 1 V between Ti³⁺ and Ti⁴⁺ ions, but BaLi_{2-x}Na_xTi₆O₁₄ (x = 1 and 1.5) only has a pair of redox peaks corresponding to a one-step reversible intercalation reaction above 1 V between Ti³⁺ and Ti⁴⁺ ions. Two pairs of redox peaks also can be found in BaNa₂Ti₆O₁₄, but the potential shifts to 1.10/0.92 V and 1.55/1.69 V, respectively. This result indicates that the BaNa₂Ti₆O₁₄ has higher voltage plateau than the BaLi₂Ti₆O₁₄. In comparison with the first and second CV curves of all samples, it is clear that the passivating film is mainly formed during the first insertion process, and the solid electrolyte interface (SEI) film of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) was formed below 0.7 V in the first cycle [31,32]. Like Li₄Ti₅O₁₂ [32,33], it is therefore reasonable to infer that BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) is a SEI film free material cycled between 1.0 and 3.0 V.

Figure 3 XRD Rietveld refinement results of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) (a) $x=0$, (b) $x=0.5$, (c) $x=1$, (d) $x=1.5$, (e) $x=2$ and (f) refinement model.

Moreover, all curves show a broad peak with envelope feature at low potentials at each cycle, revealing a formation of amorphous phase during discharge to 0 V [34]. Similar electrochemical behavior can be found in other Ti-based anodes, such as $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ [13,35], $\text{PbLi}_2\text{Ti}_6\text{O}_{14}$ [17], $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ [16], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [34], $\text{Li}_5\text{Cr}_7\text{Ti}_6\text{O}_{25}$ [36] and $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ [37]. The 2nd and 3th CV curves are quite similar to the first cycle, indicating the good reversibility of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) compounds [38]. In addition, the 2nd and 3th CV curves are nearly overlap, and reveals good reversibility, excellent cyclability, super kinetics and

high cyclic efficiency for lithium ions insertion/extraction at the electrodes [37].

To evaluate the effect of Na ions doping on the capacity of $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$, the charge-discharge tests of all samples were carried out at a current density of 50 mA g^{-1} between 0 and 3 V. Fig. 7a–c shows the typical 1st, 25th and 50th charge-discharge curves of the $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) half cells. In the discharge (lithiation) process, an obvious plateau at about 1.4 V, an obscure plateau at about 1.2 V, an unstable plateau at about 0.8 V and an inclined curve below 0.7 V can be found in the discharge curve of BaLi_2 -

Figure 4 SEM images of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0.0, 0.5, 1.0, 1.5, 2.0$) samples. (a, b) $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$, (c, d) $\text{BaLi}_{1.5}\text{Na}_{0.5}\text{Ti}_6\text{O}_{14}$, (e, f) $\text{BaLi}_{1.0}\text{Na}_{1.0}\text{Ti}_6\text{O}_{14}$, (g, h) $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ and (i, j) $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$.

Ti_6O_{14} , respectively. However, an obvious plateau at about 1.6 V, an obscure plateau at about 1.2 V and an inclined curve below 1 V can be found in the discharge curve of $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$, respectively. The plateau at about 1.4 V gradually disappears in the $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0.5 \leq x \leq 1.5$) corresponding to a one-step reversible intercalation reaction above 1 V between Ti^{3+} and Ti^{4+} ions, which is associated with the CV results. In the charge (delithiation) process of $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$, a short charge plateau at about 1.2 V and obvious plateau at about 1.5 V can be found.

Figure 5 Elemental mapping images of $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$: (a) Ba element, (b) Na element, (c) Ti element and (d) O element.

Figure 6 CV curves of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$): (a) $x=0$, (b) $x=0.5$, (c) $x=1$, (d) $x=1.5$ and (e) $x=2$.

However, only an obvious plateau at about 1.6 V can be found in the charge curve of $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$. Only a short charge plateau at about 1.2 V can be found in the $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0.5 \leq x \leq 1$). When almost all the lithium ions are extracted from the electrode, the working potential rises quickly to 3.0 V. As shown in Table S1 in Supplementary information (SI), the initial delithiation capacities of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0, 0.05, 0.1, 0.15$ and 0.2) are 163.0, 193.0, 175.4, 163.7 and 146.4 mA h g^{-1} , respectively. This result shows that appropriate Na doping improves the delithiation capacity of $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$. It is obvious that there

is a high irreversible capacity loss between the lithiation and delithiation cycles. The high irreversible capacity loss may be mainly attributed to some side reactions for SEI formation composed of organic lithium alkylcarbonates, the lithium adsorption in the conductive additive carbon black and irreversible electrochemical decomposition of the electrolyte [32,39–41]. As shown in Fig. 7b, c, it can be found that the potential difference between the delithiation and lithiation plateaus of all samples is obviously different after 25 and 50 cycles, revealing a different polarization for all electrodes. Clearly, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$

Figure 7 The (a) 1st, (b) 25th, (c) 50th charge-discharge curves and (d) corresponding cycling properties of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0.0, 0.5, 1.0, 1.5, 2.0$) samples at the current density of 50 mA g^{-1} .

shows a smaller potential difference than other $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ compounds, indicating an excellent reversibility and lower polarization. In addition, the $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ anode shows a lower delithiation plateau voltage than those of other $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ compounds and the reported $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which may be beneficial to improve the energy density of the LIBs used in full battery as anode.

Cycling performance of the $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) half cells between 0 and 3 V at a current density of 50 mA g^{-1} is given in Fig. 7d. Although $\text{BaLi}_{1.5}\text{Na}_{0.5}\text{Ti}_6\text{O}_{14}$ shows the highest initial delithiation capacity, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ exhibits the highest delithiation capacity after 25 cycles among all samples as shown in Fig. 7d and Table S1. After 50 cycles, the delithiation capacities of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0, 0.5, 1, 1.5$ and 2) are $140.8, 140.4, 117.1, 163.9$ and $123.6 \text{ mA h g}^{-1}$, respectively. The corresponding capacity retentions are $86.4\%, 72.8\%, 70.8\%, 100\%$, and 84.4% , respectively. Obviously, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ anode shows the highest delithiation capacity and capacity retention after 50 cycles among all samples.

Fig. 8 shows the rate capabilities of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) at various current densities between 0.0 and 3.0 V.

Figure 8 Rate properties of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0.0, 0.5, 1.0, 1.5, 2.0$) half cells at different current densities.

It can be found that $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ delivers the delithiation capacities of $162.1 \text{ mA h g}^{-1}$ at 50 mA g^{-1} , $158.1 \text{ mA h g}^{-1}$ at 100 mA g^{-1} , $156.7 \text{ mA h g}^{-1}$ at 150 mA g^{-1} , $152.2 \text{ mA h g}^{-1}$ at 200 mA g^{-1} , $147.3 \text{ mA h g}^{-1}$ at 250 mA g^{-1} and 142 mA h g^{-1} at 300 mA g^{-1} , respectively. It is also shown that the delithiation capacity of $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$

Figure 9 (a) Nyquist plots, (b) curve chart of the real part of impedance (Z_{re}) plotted against $\omega^{-1/2}$ at low-frequency region and (c) lithium-ion diffusion coefficient for $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) after 50 cycles at 300 mA g^{-1} .

delivers at 300 mA g^{-1} is corresponding to 87.6% of that obtained at 50 mA g^{-1} . For a comparison, the reversible delithiation capacities of other half cells obvious decrease with the increase of current density. For example, $\text{BaLi}_{1.5}\text{Na}_{0.5}\text{Ti}_6\text{O}_{14}$ exhibits the delithiation capacity of $189.1 \text{ mA h g}^{-1}$ at 50 mA g^{-1} , but the delithiation capacity is only $130.2 \text{ mA h g}^{-1}$ at 300 mA g^{-1} , which corresponds to 68.9% of the delithiation capacity at 50 mA g^{-1} . It is particularly worth mentioning here that the introduction of Na^+ ion in the $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ structure can reduce the theoretical capacity because the molar mass of Na is larger than Li element. In spite of this, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ obviously shows a greater rate performance than other samples.

To explore the effect of Na doping on the kinetic performance, the charged state EIS was measured. Fig. 9a shows the charged state EIS curves of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) after 50 cycles at current density of 300 mA g^{-1} between 0 and 3.0 V. The lithium-ion diffusion coefficient (D_{Li}) was calculated based on the above EIS data. The D_{Li} can be calculated from the plots in the low-frequency region, which represents the diffusion ability of lithium-ion in the bulk of electrode material. The diffusion coefficient values by EIS can be calculated according to the following

equation [29,42–44]:

$$Z_{re} = R_{ct} + R_s + \sigma \omega^{-1/2}, \quad (1)$$

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{Li}^2 \sigma^2}. \quad (2)$$

Here, R is the gas constant, T is the absolute temperature, n is the number of electrons transferred per molecule during redox reaction, F refers to the Faraday constant, A is the surface area of the working electrode, C_{Li} stands for the concentration of lithium ions, ω is the angular frequency, and σ is the Warburg factor. The Warburg factor is connected with the real part of the impedance (Z_{re}), and it can be gotten from the slope of the lines in Fig. 9b. The calculated lithium-ion diffusion coefficients are given in Fig. 9c. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ obviously shows the largest lithium-ion diffusion coefficients among all samples, and the highest electrochemical activity during cycling. It is therefore reasonable to infer that the excellent rate capability of $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ originates from the dramatically enhanced ionic conductivity and reduced redox polarization.

CONCLUSIONS

In this work, $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) anode materials were synthesized by a simple solid state method. All XRD peak signal of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$) compounds correspond to the orthorhombic structure $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ phase with *Cmca* space group. A different morphology appears between $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ and $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$ prepared by the same method, suggesting the successful fabrication of Li-site doping by Na in the structure of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$. EDS results supply a strong evidence of the uniform element distribution of Na, Ba, Ti and O elements in $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$, suggesting the successful doping by Na in the structure. After 50 cycles, the delithiation capacities of $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0, 0.05, 0.1, 0.15$ and 0.2) between 0 and 3 V at a current density of 50 mA g^{-1} are 140.8, 140.4, 117.1, 163.9 and $123.6 \text{ mA h g}^{-1}$, respectively. The corresponding capacity retentions are 86.4%, 72.8%, 70.8%, 100%, and 84.4%, respectively. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ exhibits the highest delithiation capacity among all samples. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ also shows the greatest rate performance among all samples, and the delithiation capacity of $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ delivered at 300 mA g^{-1} is corresponding to 87.6% of that obtained at 50 mA g^{-1} . In addition, the novel $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$ as anode also shows an acceptable electrochemical performance. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ with cycling performance, simple synthesis route and wide discharge voltage range can be used as possible anode candidate for rechargeable batteries.

Received 24 May 2017; accepted 16 June 2017;
published online 21 July 2017

- Massé RC, Uchaker E, Cao G. Beyond Li-ion: electrode materials for sodium- and magnesium-ion batteries. *Sci China Mater*, 2015, 58: 715–766
- Zhou X, Chen S, Yang J, *et al.* Metal-organic frameworks derived okra-like SnO_2 encapsulated in nitrogen-doped graphene for lithium ion battery. *ACS Appl Mater Interfaces*, 2017, 9: 14309–14318
- Yang J, Xu Z, Sun H, *et al.* A three-dimensional interlayer composed of graphene and porous carbon for long-life, high capacity lithium-iron fluoride battery. *Electrochim Acta*, 2016, 220: 75–82
- Yang J, Yan B, Ye J, *et al.* Carbon-coated LiCrTiO_4 electrode material promoting phase transition to reduce asymmetric polarization for lithium-ion batteries. *Phys Chem Chem Phys*, 2014, 16: 2882–2891
- Yang L, Zhang X, Li Y, *et al.* Graphene-encapsulated $\text{Li}_2\text{MnTi}_3\text{O}_8$ nanoparticles as a high rate anode material for lithium-ion batteries. *Electrochim Acta*, 2015, 155: 272–278
- Chen C, Ai C, Liu X, *et al.* High performance $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$ anode material fabricated by a facile method without an additional carbon source. *J Alloys Compd*, 2017, 698: 692–698
- Han JT, Huang YH, Goodenough JB. New anode framework for rechargeable lithium batteries. *Chem Mater*, 2011, 23: 2027–2029
- Wang C, Wang S, Tang L, *et al.* A robust strategy for crafting monodisperse $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanospheres as superior rate anode for lithium ion batteries. *Nano Energ*, 2016, 21: 133–144
- Tang L, He YB, Wang C, *et al.* High-density microporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microbars with superior rate performance for lithium-ion batteries. *Adv Sci*, 2017, 4: 16003117 pages
- Wang C, Wang S, He YB, *et al.* Combining fast Li-ion battery cycling with large volumetric energy density: grain boundary induced high electronic and ionic conductivity in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres of densely packed nanocrystallites. *Chem Mater*, 2015, 27: 5647–5656
- Shu J, Wu K, Wang P, *et al.* Lithiation and delithiation behavior of sodium lithium titanate anode. *Electrochim Acta*, 2015, 173: 595–606
- Koseva I, Chaminade JP, Gravereau P, *et al.* A new family of isostructural titanates, $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ ($M = \text{Sr, Ba, Pb}$). *J Alloys Compd*, 2005, 389: 47–54
- Fan SS, Zhong H, Yu HT, *et al.* Hollow and hierarchical $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ microspheres with high electrochemical performance as anode material for lithium-ion battery. *Sci China Mater*, 2017, 60: 427–437
- Li H, Shen L, Ding B, *et al.* Ultralong $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ nanowires composed of single-crystalline nanoparticles: promising candidates for high-power lithium ions batteries. *Nano Energ*, 2015, 13: 18–27
- Liu J, Wu B, Wang X, *et al.* Study of the Li^+ intercalation/de-intercalation behavior of $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ by *in-situ* techniques. *J Power Sources*, 2016, 301: 362–368
- Lin X, Li P, Wang P, *et al.* $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$: a probable host material for high performance lithium storage. *Electrochim Acta*, 2015, 180: 831–844
- Li P, Qian S, Yu H, *et al.* $\text{PbLi}_2\text{Ti}_6\text{O}_{14}$: a novel high-rate long-life anode material for rechargeable lithium-ion batteries. *J Power Sources*, 2016, 330: 45–54
- Liu J, Li Y, Wang X, *et al.* Synthesis process investigation and electrochemical performance characterization of $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ by *ex situ* XRD. *J Alloys Compd*, 2013, 581: 236–240
- Cheng F, Shen J, Peng B, *et al.* Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts. *Nat Chem*, 2011, 3: 79–84
- Dambournet D, Belharouak I, Amine K. $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ ($M = \text{Sr, Ba, Na}$) lithium insertion titanate materials: a comparative study. *Inorg Chem*, 2010, 49: 2822–2826
- Yu H, Yan L, Qian S, *et al.* Fabrication of $\text{Ba}_{0.95}\text{M}_{0.05}\text{Li}_2\text{Ti}_6\text{O}_{14}$ ($M=\text{Ag, Pb, Al}$) as high performance anode candidates for lithium secondary batteries. *Electrochim Acta*, 2017, 228: 453–461
- Yu H, Luo M, Lan H, *et al.* Comparative study of $\text{Pb}_{1-x}\text{Ba}_x\text{Li}_2\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 1$) as lithium storage materials for secondary batteries. *J Power Sources*, 2017, 357: 179–187
- Yu H, Luo M, Qian S, *et al.* $\text{Ba}_{0.9}\text{La}_{0.1}\text{Li}_2\text{Ti}_6\text{O}_{14}$: advanced lithium storage material for lithium-ion batteries. *Electrochim Acta*, 2017, 232: 132–141
- Yi TF, Yang SY, Li XY, *et al.* Sub-micrometric $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 0.2$) spinel as anode material exhibiting high rate capability. *J Power Sources*, 2014, 246: 505–511
- Yin X, Huang K, Liu S, *et al.* Preparation and characterization of Na-doped LiFePO_4/C composites as cathode materials for lithium-ion batteries. *J Power Sources*, 2010, 195: 4308–4312
- Kuang Q, Zhao Y, Liang Z. Synthesis and electrochemical properties of Na-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials for Li-ion batteries. *J Power Sources*, 2011, 196: 10169–10175

- 27 Hu X, Sun J, Li Z, *et al.* Rechargeable room-temperature Na-CO₂ batteries. *Angew Chem*, 2016, 128: 6592–6596
- 28 Wu MS, Chiang PCJ, Lin JC, *et al.* Correlation between electrochemical characteristics and thermal stability of advanced lithium-ion batteries in abuse tests–short-circuit tests. *Electrochim Acta*, 2004, 49: 1803–1812
- 29 Luo M, Lin X, Lan H, *et al.* Lithiation-delithiation kinetics of BaLi₂Ti₆O₁₄ anode in high-performance secondary Li-ion batteries. *J Electroanalytical Chem*, 2017, 786: 86–93
- 30 Wu X, Li X, Zhu C, *et al.* Electrospun one-dimensional BaLi₂Ti₆O₁₄ nanofibers for high rate performing lithium-ion battery. *Mater Today Energ*, 2016, 1-2: 17–23
- 31 Shu J. Electrochemical behavior and stability of Li₄Ti₅O₁₂ in a broad voltage window. *J Solid State Electrochem*, 2009, 13: 1535–1539
- 32 Shu J. Study of the interface between Li₄Ti₅O₁₂ electrodes and standard electrolyte solutions in 0.0–0.5 V. *Electrochem Solid-State Lett*, 2008, 11: A238
- 33 Yi TF, Yang SY, Xie Y. Recent advances of Li₄Ti₅O₁₂ as a promising next generation anode material for high power lithium-ion batteries. *J Mater Chem A*, 2015, 3: 5750–5777
- 34 Yi TF, Xie Y, Zhu YR, *et al.* Structural and thermodynamic stability of Li₄Ti₅O₁₂ anode material for lithium-ion battery. *J Power Sources*, 2013, 222: 448–454
- 35 Wu K, Shu J, Lin X, *et al.* Phase composition and electrochemical performance of sodium lithium titanates as anode materials for lithium rechargeable batteries. *J Power Sources*, 2015, 275: 419–428
- 36 Yi TF, Mei J, Zhu YR, *et al.* Li₅Cr₇Ti₆O₂₅ as a novel negative electrode material for lithium-ion batteries. *Chem Commun*, 2015, 51: 14050–14053
- 37 Lin X, Wang P, Li P, *et al.* Improved the lithium storage capability of BaLi₂Ti₆O₁₄ by electroless silver coating. *Electrochim Acta*, 2015, 186: 24–33
- 38 Aravindan V, Gnanaraj J, Lee YS, *et al.* Insertion-type electrodes for nonaqueous Li-ion capacitors. *Chem Rev*, 2014, 114: 11619–11635
- 39 Borghols WJH, Wagemaker M, Lafont U, *et al.* Size effects in the Li_{4+x}Ti₅O₁₂ spinel. *J Am Chem Soc*, 2009, 131: 17786–17792
- 40 Lin C, Deng S, Shen H, *et al.* Li₅Cr₃Ti₄O₂₄: a new anode material for lithium-ion batteries. *J Alloys Compd*, 2015, 650: 616–621
- 41 Fang ZK, Zhu YR, Yi TF, *et al.* Li₄Ti₅O₁₂–LiAlO₂ composite as high performance anode material for lithium-ion battery. *ACS Sustain Chem Eng*, 2016, 4: 1994–2003
- 42 Pan D, Wan N, Ren Y, *et al.* Enhanced structural and electrochemical stability of self-similar rice-shaped SnO₂ nanoparticles. *ACS Appl Mater Interfaces*, 2017, 9: 9747–9755
- 43 Yi TF, Han X, Yang SY, *et al.* Enhanced electrochemical performance of Li-rich low-Co Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08–x}Al_xO₂ (0 ≤ x ≤ 0.08) as cathode materials. *Sci China Mater*, 2016, 59: 618–628
- 44 Li P, Wu K, Wang P, *et al.* Preparation, electrochemical characterization and *in-situ* kinetic observation of Na₂Li₂Ti₆O₁₄ as anode material for lithium ion batteries. *Ceramics Int*, 2015, 41: 14508–14516

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (51404002), Anhui Provincial Natural Science Foundation (1508085MB25), the Natural Science Foundation of Guangdong Province (2016A030310127) and Anhui Provincial Science Fund for Excellent Young Scholars (gxyqZD2016066).

Author contributions Tao W, Xu ML performed the materials synthesis, characterization and electrochemical measurements. Zhang Q was involved in data analysis and discussion. Yi TF and Zhu YR conceived the strategy, supervised the design of experiments, and wrote the manuscript, and all authors participated in the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The charge/discharge specific capacities of BaLi_{2–x}Na_xTi₆O₁₄ (x=0.0, 0.5, 1.0, 1.5, 2.0) samples at different cycle numbers are available in the online version of the paper.

Wei Tao received his BE degree from Anhui University of Technology in 2015. He is now a second year Master student in Prof. Ting-Feng Yi's group at Anhui University of Technology. His research focuses on the application of functional materials in lithium-ion batteries.

Qianyu Zhang received his PhD degree from Fudan University, China. He was a visiting scholar at the University of California, San Diego from 2013 to 2014. He worked as an assistant researcher at Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences from 2015 to 2017. Currently, he is an associate professor at Dongguan University of Technology, China. His research involves exploring high-performance electrode materials for Li-ion battery.

Ting-Feng Yi received his BE degree in chemical engineering and technology from Liaocheng University in 2001. He then obtained his MSc degree in applied chemistry in 2004 and PhD degree in chemical engineering and technology from Harbin Institute of Technology in 2007. He joined Anhui University of Technology as an assistant professor of chemistry in 2007. He is currently a professor of Anhui University of Technology, China. His research interests include the synthesis of electrochemical functional materials and their application in lithium-ion battery, supercapacitor and lead-acid battery. For detail please see his research ID: <http://www.researcherid.com/rid/F-4594-2012>.

锂离子电池 $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$)负极材料的结构与电化学性能

陶伟¹, 徐茂莲¹, 朱彦荣^{1*}, 张千玉^{2*}, 伊廷锋^{1*}

摘要 本文采用简单的高温固相法制备了 $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$)系列化合物作为储锂材料. XRD Rietveld精确表明Bragg点与 $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ 相对应, 由于 Na^+ 的半径比 Li^+ 的半径大55%, 因此 Na^+ 掺杂的 $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ 化合物具有比纯 $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ 更大的晶胞体积. SEM测试结果表明, $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=0, 0.5, 1$)粉末呈相似的不规则的颗粒状, 粒径大约在500到1000 nm之间. 但是, $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($x=1.5, 2$)展示了棒状的形貌. 循环伏安结果表明, 钝化膜主要在第一次嵌锂过程时形成, $\text{BaLi}_{2-x}\text{Na}_x\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 2$)表面的SEI膜主要在第一次循环且电位在0.7 V以下时形成. 相对于其他样品, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ 具有较高的可逆容量, 较好的倍率性能和优异的循环性能. 电流密度为50、100、150、200、250和300 mA g^{-1} 时, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ 的脱锂容量分别为162.1、158.1、156.7、152.2、147.3和142 mA h g^{-1} . 有趣的是, $\text{BaNa}_2\text{Ti}_6\text{O}_{14}$ 作为阳极也展示了可接受的电化学性能. $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ 所提高的电化学性能可以归因于其最小的极化和最高的锂离子扩散系数. 因具有优异的循环性能、简单的合成路线和宽的放电区间, $\text{BaLi}_{0.5}\text{Na}_{1.5}\text{Ti}_6\text{O}_{14}$ 可作为锂离子电池负极候选材料.