



Phase composition and electrochemical performance of sodium lithium titanates as anode materials for lithium rechargeable batteries



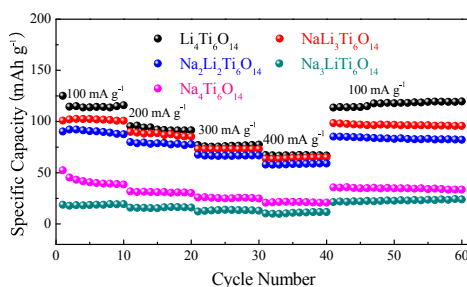
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HIGHLIGHTS

- $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) samples are prepared by a solid state reaction.
- Different Na/Li ratios result in the formation of different titanates.
- Phase composition of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ is identified and compared.
- Electrochemical behaviors of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ are different from each other.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) are prepared by solid-state method and their structures, morphologies and electrochemical properties are compared by changing the Na/Li atomic ratio. It can be found that two single-phase samples of $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ and $\text{Na}_4\text{Ti}_6\text{O}_{14}$ and three multi-phase samples of $\text{Li}_4\text{Ti}_6\text{O}_{14}$ ($\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$), $\text{NaLi}_3\text{Ti}_6\text{O}_{14}$ ($\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}/\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$) and $\text{Na}_3\text{LiTi}_6\text{O}_{14}$ ($\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}/\text{Na}_2\text{Ti}_3\text{O}_7$) can be formed by using a stoichiometric ratio of starting materials based on the formula of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$. Besides, different Na/Li atomic ratios in $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ also induce the morphology evolution shifting from round-shape to polyhedron-shape, and then to square-shape with the increase of Na content. Electrochemical tests show that $\text{Li}_4\text{Ti}_6\text{O}_{14}$ delivers the highest charge capacities of 116 mAh g^{-1} at 100 mA g^{-1} , 91.5 mAh g^{-1} at 200 mA g^{-1} , 77.5 mAh g^{-1} at 300 mA g^{-1} and 66.9 mAh g^{-1} at 400 mA g^{-1} among five samples. For comparison, $\text{Na}_4\text{Ti}_6\text{O}_{14}$ only reveals the reversible capacities of 38.6 mAh g^{-1} at 100 mA g^{-1} , 30.2 mAh g^{-1} at 200 mA g^{-1} , 24.8 mAh g^{-1} at 300 mA g^{-1} and 20.9 mAh g^{-1} at 400 mA g^{-1} . It suggests that $\text{Li}_4\text{Ti}_6\text{O}_{14}$ is the most potential lithium storage material among all the $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ samples.

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1. Introduction

Lithium-ion batteries (LIBs), due to their high energy density and long cycle life, are widely used as the power supplies of electric vehicles and hybrid electric vehicles [1–5]. To replace the unsafe

carbonaceous anode materials, various titanates (such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{SrTi}_6\text{O}_{14}$, $\text{Li}_2\text{Ti}_3\text{O}_7$, $\text{Li}_2\text{ZnTi}_3\text{O}_8$, $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$, etc.) have been developed as potential anode materials in high-power LIBs for their high operating potential plateau ($>1.0 \text{ V}$ versus Li/Li^+) and low-strain characteristic in the past decade [6–11]. However, most of titanates suffer from low electronic conductivity (10^{-13} – $10^{-12} \text{ S cm}^{-1}$) and Li^+ diffusion coefficient (10^{-13} – $10^{-10} \text{ cm}^2 \text{ s}^{-1}$) [12–14], which hinder their commercial application.

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To find a suitable anode, it is necessary to make a comparison of structural characteristic and electrochemical behavior in the same series of titanates. As for $\text{Li}_2\text{MTi}_3\text{O}_8$ ($M = \text{Zn, Co, Cu, Mn, Mg}$) [15–19], it is found that $\text{Li}_2\text{CoTi}_3\text{O}_8$, $\text{Li}_2\text{Co}_{0.5}\text{Zn}_{0.5}\text{Ti}_3\text{O}_8$, and $\text{Li}_2\text{ZnTi}_3\text{O}_8$ have the same cubic structure with a space group of $P4_332$. However, $\text{Li}_2\text{CuTi}_3\text{O}_8$ shows the same cubic structure but a different space group of $Fd-3m$ among the similar complex spinel titanates of $\text{Li}_2\text{CuTi}_3\text{O}_8$, $\text{Li}_2\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Ti}_3\text{O}_8$ ($P4_332$) and $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ($P4_332$) [20]. It indicates that different element substitution and content may result in the structural evolution of titanate. Besides, both reports reveals that $\text{Li}_2\text{M}'_{0.5}\text{M}''_{0.5}\text{Ti}_3\text{O}_8$ with a space group of $P4_332$ has higher reversible capacity and better rate property than that of pristine $\text{Li}_2\text{MTi}_3\text{O}_8$. Similar phenomena can be observed for the $\text{Li}_2\text{MTi}_6\text{O}_{14}$ series ($M = \text{Ba, Sr, Na, Pb}$) [11,21–23]. Different from $\text{Li}_2\text{MTi}_3\text{O}_8$ and $\text{Li}_2\text{MTi}_6\text{O}_{14}$, $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 4$) samples show quite different phases ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{NaLiTi}_3\text{O}_7$, Li_2TiO_3 and $\text{Na}_4\text{Ti}_5\text{O}_{12}$) and electrochemical behaviors with different Na/Li ratios [24]. As a result, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was proved to be the most promising anode among the $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 4$) series. Similar phenomena can be observed for the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ series [25–28]. For comparison, high purity phases were indexed with the same structure and the space group of $R-3c$ for all the $\text{Li}_{1-x}\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ($0 \leq x \leq 1$) samples [29]. It can be also found that the unit cell dimensions anisotropically gradually increased with the increase of Na content, and the reversible capacity reached the maximum value with $x = 0.5$ by using $\text{Li}_{1-x}\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ($0 \leq x \leq 1$) as anode materials for sodium ion batteries. All these previous reports suggest that different compounds can be found as proper candidates for energy storage in different titanate series (end-member titanate in $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ series, and middle-member titanate in $\text{Li}_2\text{MTi}_3\text{O}_8$ and $\text{Li}_{1-x}\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ series).

In former researches, one of titanates, $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$, as a novel promising anode material with low potential plateau (about 1.25 V) was studied in LIBs [30–33], which can offer a higher whole cell potential than $\text{Li}_4\text{Ti}_5\text{O}_{12}$. To find the most potential anode in the same titanate series with $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$, it is better to make a comparison of structural characteristic, operating potential, reversible capacity, diffusion coefficient and rate property between $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ and other similar titanates from the same series (such as $\text{Li}_4\text{Ti}_6\text{O}_{14}$, $\text{NaLi}_3\text{Ti}_6\text{O}_{12}$, $\text{Na}_3\text{LiTi}_6\text{O}_{14}$ and $\text{Na}_4\text{Ti}_6\text{O}_{14}$). Based on the investigation on $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$, a series of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) series are prepared by solid-state method at the first time in this paper with the different of Na/Li atomic ratios. It can be found that different phases form with different Na/Li atomic ratios in the precursor. Their structural characteristics, surface morphologies and electrochemical properties are tested and compared in detail.

2. Experimental

$\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) samples with different Na contents ($x = 0, 1, 2, 3$ and 4) were synthesized by a traditional solid-state method. The stoichiometric amounts of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (Aladdin Chemistry), $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (Aladdin Chemistry), TiO_2 (Aladdin Chemistry) were mixed with oxalic acid dehydrate chelating agent (Aladdin Chemistry) under various Na/Li molar ratios and pre-treated by high energy ball-milling in ethanol at 400 rpm rotational speed for 15 h. The obtained precursor slurry was dried at 80°C and then calcinated at 900°C for 10 h in air atmosphere. Based on the different Na/Li molar ratios, the as-prepared five $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) samples were designated as $\text{Li}_4\text{Ti}_6\text{O}_{14}$, $\text{NaLi}_3\text{Ti}_6\text{O}_{14}$, $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$, $\text{Na}_3\text{LiTi}_6\text{O}_{14}$ and $\text{Na}_4\text{Ti}_6\text{O}_{14}$, respectively.

The crystal structure of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) samples was detected by Bruker AXS D8 Focus X-ray diffraction (XRD) instrument with $\text{Cu K}\alpha$ radiation. Samples were observed by a scan angle range from 5 to 80° with a step size of 0.02° and a count time of 1 s.

The particle morphologies and structures of five samples were observed by Hitachi S3400 scanning electron microscopy (SEM), JEOL JEM-2010 high resolution transmission electron microscopy (HRTEM) and corresponding selected area electron diffraction (SAED).

For electrochemical evaluations, the working electrodes were composed of $\text{Li}_4\text{Ti}_6\text{O}_{14}$, $\text{NaLi}_3\text{Ti}_6\text{O}_{14}$, $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$, $\text{Na}_3\text{LiTi}_6\text{O}_{14}$ or $\text{Na}_4\text{Ti}_6\text{O}_{14}$ as active material, carbon black as conductive additive and polyvinylidene fluoride as binder with a weight ratio of 8:1:1. These materials were uniformly mixed in agate mortar with *N*-methylpyrrolidinone as a solvent. Then, the homogeneous slurry was spread on a Cu foil by a doctor-blade technique and dried at 120°C in a vacuum oven for 24 h. After that, the dried thin film was punched into discs with a diameter of 15 mm and used as working electrode for electrochemical investigations. The homemade Swagelok cells were assembled in an Ar-filled glove box, which prevented the sample exposure to oxygen, nitrogen and water. In the half cells, lithium disc was used as counter electrode and Whatman glass fiber was treated as separator. The Li-containing electrolyte was a 1 mol L^{-1} solution of LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate with a volume proportion of 1:1.

The charge–discharge properties of Swagelok cells were measured with a current density of 50 mA g^{-1} between 1.0 and 3.0 V by multi-channel Land battery test system (Wuhan Jinnuo, China) at room temperature. Cyclic voltammograms (CVs) were carried out between 1.0 and 3.0 V with a scan rate of 0.1 mV s^{-1} by CHI 1000B electrochemical workstation (Shanghai Chenhua, China) at room temperature. Electrochemical impedance spectroscopy (EIS) analysis was carried out by CHI 660D electrochemical workstation with the frequency range of 10^5 – 10^{-2} Hz.

3. Results and discussion

XRD patterns of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) samples are shown in Fig. 1. It can be found that an obvious structural transformation can be observed with different Na/Li molar ratios in $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ ($0 \leq x \leq 4$) series. Fig. 1a shows the XRD pattern of as-prepared $\text{Li}_4\text{Ti}_6\text{O}_{14}$ powder, which can be indexed to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase (JCPDS card No. 49–0207) as the dominant phase and rutile TiO_2 phase as the impurity phase with its diffraction peaks at 27.5 , 36.1 , 41.3 , 54.4 and 69.1° (JCPDS card No. 87–0920) as marked by green square (in web version). This phenomenon, in which rutile TiO_2 phase coexists with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase by solid state synthesis way, can be also observed in the former studies on the preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with improper Li/Ti molar ratio in the precursor [34–37]. In these tasks, the absence of lithium source always results in the formation of co-existed $\text{TiO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ phases. With one mole of Li atoms is substituted by Na atoms in $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ sample ($x = 1$, $\text{NaLi}_3\text{Ti}_6\text{O}_{14}$), $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ phase with orthorhombic structure (JCPDS card No. 52–0690) becomes the dominant phase in the as-prepared $\text{NaLi}_3\text{Ti}_6\text{O}_{14}$ powder. At the same time, the feature peaks of rutile TiO_2 phase (27.5°) marked by green square (in web version) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase (35.6 , 43.3 , 57.3 and 63.0°) marked by brown triangle (in web version) as the impurity phases are also indexed in Fig. 1b. For comparison, pure $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ phase with orthorhombic structure can be observed in Fig. 1c, when the molar ratio of Li to Na is 1:1 in the precursor of $\text{Na}_x\text{Li}_{4-x}\text{Ti}_6\text{O}_{14}$ sample ($x = 2$) that is well consistent with the former study results on the preparation of $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ by a similar solid state synthesis way or an oxalic acid assisted sol–gel route [31–33]. The orthorhombic structure of $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ phase is composed of a framework of intercalated edge and corner-sharing distorted TiO_6 octahedrons, and isolated and distorted LiO_4 tetrahedrons. Besides, its lattice parameters are $a = 16.4784$, $b = 5.7358$ and $c = 11.227 \text{ \AA}$ with the space group of $Fmmm$. With one more Li atoms replacement by Na

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