



## Improved lithium storage performance of lithium sodium titanate anode by titanium site substitution with aluminum



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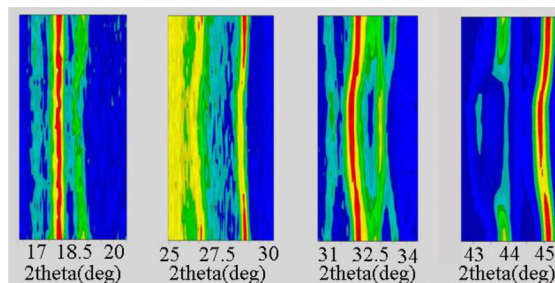
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### HIGHLIGHTS

- Ti-site substitution in  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  anode is reported at the first time.
- $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  (M = Al, Zr, V) are prepared by a solid-state reaction.
- $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$  exhibits enhanced electrochemical property.
- $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$  delivers a charge capacity of  $180.7 \text{ mAh g}^{-1}$  at  $1000 \text{ mA g}^{-1}$ .

### GRAPHICAL ABSTRACT



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### ABSTRACT

$\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  and its Ti-site substitution  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  (M = Al, Zr, V) are prepared by a solid-state reaction method and used as anode materials for lithium-ion batteries. It is found that metal doping can effectively enhance the electronic conductivity and ionic diffusion coefficient of  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$ . Especially for  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$ , it reveals the highest electronic conductivity ( $1.02 \times 10^{-9} \text{ S cm}^{-1}$ ) and lithium ion diffusion coefficient ( $8.38 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ) among all the samples. As a result,  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$  reveals the best electrochemical performance. It can deliver a charge specific capacity of  $270.3 \text{ mAh g}^{-1}$  at  $50 \text{ mA g}^{-1}$ . Even cycled at  $1000 \text{ mA g}^{-1}$ , it still can present a charge capacity of  $180.7 \text{ mAh g}^{-1}$ . All these enhanced lithium storage capabilities of  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$  should be attributed to the increased electronic/ionic conductivities and the decreased charge transfer resistance induced by Al doping. Besides, in-situ X-ray diffraction observation also confirms that the structural change of  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{Al}_{0.1}\text{O}_{14}$  is highly reversible process for lithium storage.

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## 1. Introduction

In the past two decades, lithium ion batteries have been widely applied as the main power sources for portable electronic products

(e.g. cellular phones, laptops, digital cameras), electric vehicles and large-scale grid energy storage because of their high energy density, long cycle life and environmental friendliness [1]. However, lithium ion batteries always suffer from poor safety issue, and have the risk of explosion due to the use of unsafe electrode materials [2–4]. Consequently, it is necessary to find high structural/thermal stability electrode materials for solving the safety issue of lithium-ion batteries.

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In recent years, spinel lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) has been extensively studied to replace graphite for its high discharge/charge plateau (about 1.55 V versus  $\text{Li}/\text{Li}^+$ ), high thermodynamic stability and zero strain characteristic [5]. In comparison to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{Li}_2\text{MTi}_6\text{O}_{14}$  ( $M = \text{Sr}$  or  $\text{Ba}$ ) with lower working potential (about 1.4 V) is a novel anode material for lithium ion batteries [6,7]. For instance,  $\text{Li}_2\text{BaTi}_6\text{O}_{14}$  formed by a solid state reaction can deliver a reversible capacity of 137.7  $\text{mAh g}^{-1}$  with an average working potential of 1.45 V [8].  $\text{Li}_2\text{SrTi}_6\text{O}_{14}$  prepared by using mesoporous brookite  $\text{TiO}_2$  shows good cycling stability and rate capability in  $\text{LiMn}_2\text{O}_4/\text{Li}_2\text{SrTi}_6\text{O}_{14}$  full cell [9]. Thus, it is concluded that this class of materials ( $\text{Li}_2\text{MTi}_6\text{O}_{14}$ ,  $M = \text{Ba}$  or  $\text{Sr}$ ) could be of practical use in high-power lithium-ion batteries for transportation applications [6–11].

As reported, the structure of  $\text{Li}_2\text{MTi}_6\text{O}_{14}$  ( $M = \text{Sr}$  or  $\text{Ba}$ ) can be described as a network of intercalated edge and corner-sharing octahedral [12–14].  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$ , an isostructural titanate with a composition corresponding to the formula  $\text{Li}_2\text{MTi}_6\text{O}_{14}$ , has also been evidenced in the ternary oxide systems  $\text{MO}-\text{Li}_2\text{O}-\text{TiO}_2$  ( $M = \text{Sr}$ ,  $\text{Ba}$ ,  $\text{Pb}$ ,  $2\text{Na}$ ) [14]. Most recently,  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  has been investigated as a probable anode material for lithium-ion batteries [15–19]. Although it reveals a low working potential platform at 1.25 V, the electrochemical properties of  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  is poor due to its unsatisfied intrinsic electronic/ionic conductivities. To enhance the lithium storage capability, carbon coating is developed to form a nano-micro structure for  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  [20,21]. To our knowledge, doping has been considered to be an effective way to improve the intrinsic electronic/ionic conductivities of electrode materials for lithium-ion batteries. The cations and anions including  $\text{Ag}^+$  [22],  $\text{Mg}^{2+}$  [23],  $\text{Ni}^{2+}$  [24],  $\text{Cu}^{2+}$  [25],  $\text{Ca}^{2+}$  [26],  $\text{La}^{3+}$  [27],  $\text{Gd}^{3+}$  [28],  $\text{Nb}^{5+}$  [29],  $\text{F}^-$  [30],  $\text{Br}^-$  [31] and  $\text{N}^{3-}$  [32] have been widely investigated as the doped ions in titanates by researchers all over the world.

In the present work,  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  and its Ti-site substitution products are prepared by a high temperature solid state reaction method. The structure and morphology of as-prepared  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  ( $M = \text{Al}$ ,  $\text{Zr}$  and  $\text{V}$ ) are investigated and compared with each other. Electrochemical results show that the dopings of  $\text{Al}^{3+}$  and  $\text{Zr}^{4+}$  can effectively enhance the electronic/ionic conductivities and reduce the charge transfer resistance of  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$ , which contribute greatly to the improvement of reversible specific capacity, cycling calendar life and rate performance of  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$ .

## 2. Experimental

In this investigation, pure  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  was synthesized via a high temperature solid-state reaction route. The starting materials 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),  $\text{TiO}_2$  (Aladdin Chemistry) and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ , Aladdin Chemistry) with molar ratio of 1:1:3:1 were pretreated by planetary high energy ball milling in ethanol for 12 h, then dried in a vacuum oven at 80 °C for 6 h. The as-obtained powder was ground and placed in an alumina boat. After that, it was initially calcined at 400 °C for 4 h, and then calcined at 800 °C for 10 h in an air atmosphere to obtain the final product. In the preparation of precursor for  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$ , 1.67% molar ratio of  $\text{TiO}_2$  was replaced by  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Aladdin Chemistry),  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (Aladdin Chemistry) or  $\text{NH}_4\text{VO}_3$  (Aladdin Chemistry) before ball milling. The calcinations process of  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  ( $M = \text{Al}$ ,  $\text{Zr}$ ,  $\text{V}$ ) is the same as the pure sample.

Phase analysis of the as-prepared samples was performed on a Bruker AXS D8 Focus X-ray diffraction (XRD) instrument with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). Samples were observed with a scan angle between 10 and 80°. In-situ XRD patterns were conducted on the same instrument based on the homemade technique [33]. Particle morphologies of samples were examined by Hitachi S3400 scanning electron microscopy (SEM). The electronic conductivities of the samples were analyzed by using the four-electrode method on a Bio-Logic VSP EC-Lab electrochemical workstation. For electronic conductivity investigation, all the powder samples were pelleted to slices with 15 mm in diameter and 3 mm in thickness.

To evaluate electrochemical performance, the  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  electrodes were composed of 80 wt.% as-prepared powder as active material, 10 wt.% acetylene black as the conductive agent, and 10 wt.% poly(vinylidene difluoride) as the binder. The powder was mixed in 1-methyl-2-pyrrolidinone solvent and then pressed onto a Cu foil substrate. The film coated Cu foil was dried at 120 °C in a vacuum oven for 12 h, and then cut into slices with a diameter of 15 mm. Galvanostatic charge–discharge measurements were carried out using CR2032 coin-type cells. In a typical cell, lithium metal was used as the counter electrode, the separator was Whatman glass fiber, and 1 mol  $\text{L}^{-1}$  solution of  $\text{LiPF}_6$  dissolved in ethylene carbonate/dimethyl carbonate (1:1 in volume) was used as electrolyte. Charge–discharge properties of sample cells were measured with different current densities of 50–1000  $\text{mA g}^{-1}$  on multi-channel Land CT2001A battery test system (Wuhan Jinnuo, China). Cyclic voltammetry (CV) study was examined by using a three-electrode system on a CHI 1000B electrochemical analyzer (Shanghai Chenhua, China) over a potential range of 0.0–3.0 V at a scan rate of 0.1  $\text{mV s}^{-1}$ . Electrochemical impedance spectra (EIS) were collected by using a three-electrode system on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) with an amplitude of 5 mV in a frequency range between 0.01 and 100,000 Hz. In a typical three-electrode system, lithium metal slices were used as the counter and reference electrodes.

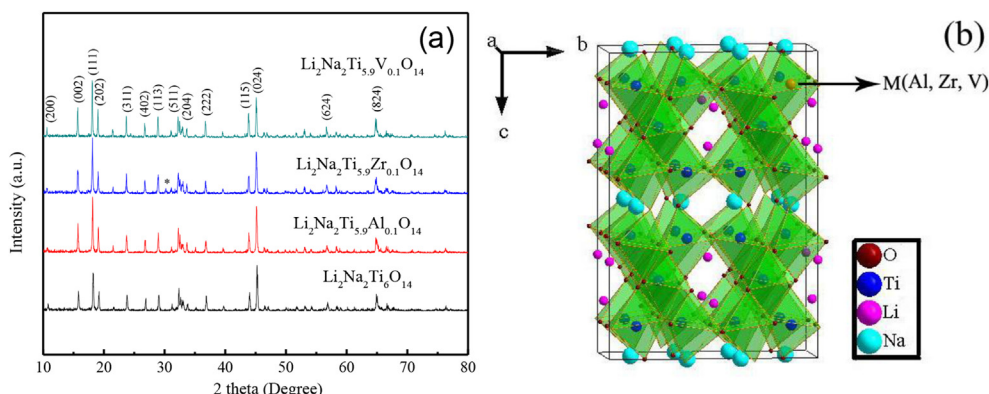


Fig. 1. XRD patterns (a) and crystal structure (b) of  $\text{Li}_2\text{Na}_2\text{Ti}_6\text{O}_{14}$  and  $\text{Li}_2\text{Na}_2\text{Ti}_{5.9}\text{M}_{0.1}\text{O}_{14}$  ( $M = \text{Al}$ ,  $\text{Zr}$ ,  $\text{V}$ ).

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