



# Self-doping of $Ti^{3+}$ into $Na_2Ti_3O_7$ increases both ion and electron conductivity as a high-performance anode material for sodium-ion batteries



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## ARTICLE INFO

### Article history:

Received 23 May 2018

Received in revised form

10 July 2018

Accepted 16 July 2018

Available online 18 July 2018

### Keywords:

$Na_2Ti_3O_7$

Sodium-ion batteries

Self-doping

Conductivity

Anode materials

## ABSTRACT

As a safe, low-voltage anode material, in recent years,  $Na_2Ti_3O_7$  has become regarded as a highly alternative negative material for high energy room-temperature sodium ion batteries. However, its poor ion and electron conductivity produces very poor electrochemical performance of  $Na_2Ti_3O_7$ , therefore greatly limiting its practical application in future scalable utilization. We report here a self-doping of  $Ti^{3+}$  into the  $Na_2Ti_3O_7$  electrode material, through a very simple post heat-treatment process, that is, annealing the  $Na_2Ti_3O_7$  precursor at an argon atmosphere containing 5%  $H_2$ . By XPS characterization, it is confirmed that  $Ti^{3+}$  is successfully doped into  $Na_2Ti_3O_7$ . Benefiting from this self-doped  $Ti^{3+}$  with larger ionic radius and better electronic conductivity, the obtained  $Na_2Ti_3O_7$  demonstrates improved electron conductivity and ion diffusion properties. Combined with a carbon coating, this self-doped  $Na_2Ti_3O_7$  electrode material exhibits superior electrochemical performance to that of non-doped electrode, e.g., this  $Na_2Ti_3O_7$  sample could delivers a specific capacity of 187.8 and 51.9  $mAh\ g^{-1}$  from 0.1C to 10C at various rate of discharge, respectively. When recycled back to 0.1C, it can still reach 153  $mAh\ g^{-1}$ . Compared with numerous reported nanoscale means, we believe this approach is practical and productive, and may extend to other ti-based electrode materials.

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## 1. Introduction

Sodium-ion batteries (SIBs) have attracted interesting attention in recent years since they offer significantly reduced cost of portable electric devices and of the entire electrical energy storage system [1–4]. At the present stage, developing high performance electrode materials for SIBs is most important, and a key issue in whether SIBs can be applied on a large scale or not. Actually, numerous efforts have been undertaken to obtain the cathode and anode materials with satisfactory electrochemical performance, for instance,  $NaFePO_4$ ,  $Na_{0.44}MnO_2$ ,  $Na_3V_2(PO_4)_3$ , and  $Na_4Fe_3(PO_4)_2(P_2O_7)$  [5–12] have been well studied as superior cathode materials for SIBs. However, compared with the cathode materials,

substantially less work has been done on anode side; therefore, one of most critical challenge for the widespread application of SIBs at present is to develop affordable and available anode materials that can adapt large quantities of  $Na^+$  ions durably and stably. Among various kinds of reported anode electrodes, such as  $MoS_2$ ,  $NiCo_2O_4$ ,  $TiO_2$ ,  $NaTi_2(PO_4)_3$ , organic  $Na_2C_8H_4O_4$  and  $Na_2Ti_3O_7$  employed in SIBs [13–18], the titanium-based electrode materials are attractive promising owing to high safety, assuring high activity, lower prices and environmental friendliness [19,20]. Particularly,  $Na_2Ti_3O_7$  has been regarded as a potential anode material because of its low Na-storage potential and high energy density. The structure of  $Na_2Ti_3O_7$  is made up of a zigzag layered framework of titanium oxygen octahedra which are linked by edges and sodium ions inset in the interlayer space [21,22], furthermore, not only does it provide a competitive capacity ( $177\ mAh\ g^{-1}$ ), but also there is a low discharge voltage platform of 0.1 V versus  $Na^+/Na$  [23–25].

Unfortunately, taking into account the practical application of  $Na_2Ti_3O_7$  as anode material, it obviously still needs to ameliorate its

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low electronic conductivity and structural instability in the intercalated phase, and this is exactly what the reason is for its unsatisfactory and poor rate and cyclic capability. In order to overcome these drawbacks, far-reaching efforts have been carried out to design  $\text{Na}_2\text{Ti}_3\text{O}_7$  nanostructures in previous reported, including nanocrystallization, ion doping, carbon coating and nanocomposites with conductive materials [26–30]. Ni and co-workers have successfully synthesized a novel  $\text{Na}_2\text{Ti}_3\text{O}_7$  nanotube arrays as anode materials through surface engineering [31]. This self-supported NTO nanotube arrays exhibit excellent reversible capacity of  $221 \text{ mAh g}^{-1}$  at 0.2 C and also demonstrate a capacity of 227, 151, 111, and  $84 \text{ mAh g}^{-1}$  at 0.5C, 2C, 5C, and 10 C, respectively. This rate capability is one of the best results for different rate of NTO materials in the reported. It also retains a capacity of  $78 \text{ mAh g}^{-1}$  after 10 000 cycles at 10 C. Indeed, to date, a large variety of nanostructured  $\text{Na}_2\text{Ti}_3\text{O}_7$  has been fabricated and reported, and their electrochemical performance did get better. Nevertheless, it should be pointed out that in most cases, it is somewhat difficult to realize mass production for these nano-sized  $\text{Na}_2\text{Ti}_3\text{O}_7$  materials. Therefore, it is quite a big challenge but desirable to develop a real practical preparation method for  $\text{Na}_2\text{Ti}_3\text{O}_7$  electrode materials with satisfactory and competitive electrochemical properties.

It is well known that the titanium element in most Ti-based materials exists in the form of  $\text{Ti}^{4+}$ , which is a semiconductive element and also has poor conductivity [32]. On the contrary, it is demonstrated that partial of  $\text{Ti}^{4+}$  was reduced to  $\text{Ti}^{3+}$  in host Ti-based materials in some reported studies, it is unexpectedly found that the electronic conductivity of the materials is significantly improved; for example, a proper nano-sized  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  through synergistic modification of  $\text{Ti}^{3+}$  and carbon was reported by Wang et al. and it could availably restrict the particle size growth of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  through the carbonization of PANI and reduced the surface  $\text{Ti}^{4+}$  into  $\text{Ti}^{3+}$  through heat treating under an Ar atmosphere containing 5%  $\text{H}_2$  in this work [33]. This  $\text{Ti}^{3+}$  modified  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  displayed remarkable electrochemical performance for lithium storage and a high specific capacity of  $75 \text{ mAh g}^{-1}$  was obtained at  $3 \text{ A g}^{-1}$  (about 20C). It is clear that the surface modification by  $\text{Ti}^{3+}$  in Ti-based electrode materials is quite effective; however, this strategy has not been tried and reported for SIBs electrode materials, because compared with LIBs, SIBs have to face and overcome more serious issues.

For SIBs, the  $\text{Na}^+$  ionic radius ( $1.02 \text{ \AA}$ ) is larger than  $\text{Li}^+$  ionic radius ( $0.76 \text{ \AA}$ ), so  $\text{Na}^+$  inserted into and extracted from the electrode materials might cause the larger volume change, resulting in cyclic instability and structural instability [34]. Furthermore, it is much more difficult for  $\text{Na}^+$  to diffuse in these electrode materials due to its larger ionic radius, in other words, except for the electronic conductivity, the ion conductivity (or ion diffusion in bulk phase) is another key role for an electrode material, especially for SIBs. Just because of this, many of the materials which are applied in LIBs cannot be suitable for SIBs although they have the same working principles and chemical properties. Particularly, the foreign ions-doping has been demonstrated to the benefit of increasing the intrinsic ion conductivity. In addition, the foreign ions-doping could effectually enhance the stability of materials because they can act as braces in the lattice structure to prevent the lattice from collapsing and suppress cacoethic phase transformations [35].

In this work, we present a self-doping of  $\text{Ti}^{3+}$  into the  $\text{Na}_2\text{Ti}_3\text{O}_7$  electrode material through a very simple post heat-treatment process in an Ar atmosphere containing 5%  $\text{H}_2$ . It is found that the self-doping  $\text{Ti}^{3+}$  can increase layer spacing of  $\text{Na}_2\text{Ti}_3\text{O}_7$ , which is beneficial to  $\text{Na}^+$  inserted/extracted and thus further improves electrochemical performance. At the same time, due to the presence of one more electron in  $\text{Ti}^{3+}$  than in  $\text{Ti}^{4+}$ , the electronic

conductivity of  $\text{Na}_2\text{Ti}_3\text{O}_7$  is also enhanced. Combined with a carbon coating layer, these  $\text{Ti}^{3+}$  self-doping  $\text{Na}_2\text{Ti}_3\text{O}_7$  electrode materials demonstrate better electrochemical performance than that of non-doping ones.

## 2. Experimental section

### 2.1. Materials preparation

Synthesis of  $\text{Na}_2\text{Ti}_3\text{O}_7$  was carried out as follows via a convenient sol-gel process. Sodium acetate anhydrous ( $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ ) and citric acid, which were used as a sodium source and a carbon source, respectively, were dissolved in the solvent of 100 ml anhydrous ethanol with continuous stirring until it was completely dissolved. Tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ) along with a little acetic acid was then dissolved in the solution to form a homogeneous solution ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$  and  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$  molar ratio of Na:Ti to 2:3). After that, the gel was heated under continuous stirring to evaporate a maximum of residual alcohol at  $100^\circ\text{C}$  for 2 h, and the precursors were dried at  $60^\circ\text{C}$  for about 8 h to obtain a white powder. Finally, the white powder was calcined in a tube furnace at  $800^\circ\text{C}$  for 6 h in a  $\text{N}_2$ ,  $\text{H}_2/\text{Ar}$ , Ar atmosphere to obtain the final  $\text{N}_2$ - $\text{Na}_2\text{Ti}_3\text{O}_7$  (N-NTO),  $\text{H}_2/\text{Ar}$ - $\text{Na}_2\text{Ti}_3\text{O}_7$  (H-NTO), Ar- $\text{Na}_2\text{Ti}_3\text{O}_7$  (A-NTO) material, respectively. The target sample (H-NTO) was calcined under an argon atmosphere containing 5%  $\text{H}_2$ . The contrast sample was calcined under an argon (A-NTO) and nitrogen (N-NTO) atmosphere. The electrochemical performances of N-NTO was almost the same as A-NTO. However, argon is much more expensive than nitrogen. So all contrast samples were N-NTO in this work.

### 2.2. Materials characterization

The X-ray diffraction patterns were carried out at a sweep speed of  $3 \text{ min}^{-1}$  in  $10^\circ$ – $70^\circ$  by using a Bruker D8 advanced with Cu-K $\alpha$  radiation (40 kV, 40 mA). The  $\text{Na}_2\text{Ti}_3\text{O}_7$  phase was identified by comparison with the JCPDS cards. The morphology and particle size of the as-synthesized products was characterized on field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 55). The HRTEM images were investigated through using a high-resolution transmission electron microscope (Hitachi H-800) equipped with energy-dispersive X-ray spectroscopy (EDS). The percentage of carbon of H-NTO and N-NTO was determined by TGA from 25 to  $700^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$  in air. The structural properties of the H-NTO sample were performed on a labRAM ARAMIS laser Raman spectroscopy. The XPS was carried out on a PHI Quantera SXM scanning X-ray microprobe with a 100 mm beam size at room temperature, which use an Al-K $\alpha$  ( $\lambda = 0.83 \text{ nm}$ ,  $h\nu = 1486.7 \text{ eV}$ ) X-ray source (2 kV, 20 mA). The specific surface area was calculated through using the Brunauer-Emmett-Teller (BET) formula. Powder electronic conductivity measurement was performed at a pressure of 6 MPa on a Powder Resistivity Meter (ST2722, Jingge Electronic Co., Ltd, Suzhou, China).

### 2.3. Electrochemical measurement

The electrochemical performances of the H-NTO and N-NTO electrode materials were carried out by assembling them as an anode in coin cells (type CR2016). The NTO electrodes were prepared by mixture of 70 wt% active material, 20 wt% Super P and 10 wt% of polyvinylidene difluoride (3 wt%). Afterwards, the paste was uniformly spread on copper foil and the electrode slices which the average mass load of the active materials was 1.5–2 mg were dried in a vacuum at  $120^\circ\text{C}$  for 10 h. 1 M  $\text{NaClO}_4$  in PC (propylene carbonate)/EC (ethylene carbonate) with a volume ratio of 1:1 was used as the electrolyte. The glass microfiber fiber (Whatman GF/C)

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