



# Lithium storage performance improvement of $\text{NaTi}_2(\text{PO}_4)_3$ with nitrogen-doped carbon derived from polyaniline

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## ABSTRACT

NASICON-type  $\text{NaTi}_2(\text{PO}_4)_3$  has been acknowledged as a promising anode for energy storage due to high ion conductivity and low cost. Nevertheless, intrinsic low electrical conductivity of  $\text{NaTi}_2(\text{PO}_4)_3$  and low stability in aqueous electrolyte limit its further applications in aqueous lithium rechargeable battery. In this paper, polyaniline as carbon and nitrogen sources was employed to synthesize nitrogen-doped carbon coated  $\text{NaTi}_2(\text{PO}_4)_3$  (NTP-P) composite by sol-gel approach and following calcination treatment. The loose and carbon-coated structure endows NTP-P with good structure stability and improved electrochemical kinetics. Compared with glucose-derived carbon-coated  $\text{NaTi}_2(\text{PO}_4)_3$  composite, NTP-P exhibits superior rate and cycling performance. NTP-P with proper carbon content delivers the discharge capacity of 119.4 and 83.4  $\text{mAh g}^{-1}$  at rate of 0.2 and 15 C, and its capacity retention can maintain 85.8% after 1000 cycles at 5 C. This research reveals that the integration of carbon coating and nitrogen doping by using polyaniline give an excellent method to enhance the electrochemical properties of electrode materials.

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## 1. Introduction

With growing concerns about global energy crisis and environmental pollution, primary energy such as coal, oil, and natural gas cannot meet people's needs [1–5]. Therefore, there is an urgent need to develop renewable energy. However, renewable energy such as solar energy, wind power, etc. is greatly affected by weather and climate, which has brought great challenge to their applications [6–8]. Hence, the development of large-scale energy storage technology is of great significance to use renewable energy efficiently [9–12]. Among various energy storage technology, rechargeable battery system is an efficient way due to flexible installation, fast response, high efficiency, etc. Electricity can be transformed from all forms of energy, such as wind and solar energy, and can be converted into other forms of energy. Battery system can be employed as transfer center of energy.

Lithium ion battery exhibits the most promising prospect in energy storage due to long cycle life and high energy density [13–16]. Besides large-scale energy storage, lithium ion battery has

been extensively used in many portable electronic devices such as notebook computer, camera, etc. Taking high voltage and good cycle performance into account, commercial lithium ion battery mainly uses organic solution as electrolyte. However, organic electrolyte exist toxic, flammable, and other issues. Furthermore, organic electrolyte with large viscosity can prevent the diffusion of Li ions greatly [17,18]. There is an imperative demand for new energy storage system with high reliability, safety, and high-speed charging. Aqueous lithium rechargeable battery can solve those problems that appear in battery system using organic electrolyte [19].

In aqueous lithium rechargeable battery system, aqueous salt solutions such as  $\text{LiNO}_3$ ,  $\text{Li}_2\text{SO}_4$ , etc. are employed as electrolyte. Aqueous salt solution shows many predominances such as low cost, low viscosity, high safety, etc. Besides aqueous electrolyte, cathode and anode are other main materials for aqueous lithium rechargeable battery. Cathode materials including  $\text{LiCoO}_2$  [20],  $\text{LiMn}_2\text{O}_4$  [21], and  $\text{LiFePO}_4$  [22] demonstrate outstanding electrochemical performance due to good intercalation/deintercalation behavior before oxygen evolution reaction. Recently, anode materials is essential for the improvement of the cell performance. Nevertheless, common anodes such as  $\text{VO}_2$ ,  $\text{LiV}_3\text{O}_8$ , and  $\text{Na}_2\text{V}_6\text{O}_{16}$  exhibit inferior cycling performance and low structure stability in aqueous electrolyte, further limiting their applications [23–25].

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$\text{LiTi}_2(\text{PO}_4)_3$  displays very promising prospect as anode in aqueous lithium rechargeable battery because of high power density and good stability [26]. Many research groups tried to further improve the rate capability, cycling performance, and structure stability by high-quality carbon coating, lattice doping, and adding conductive agent, etc. [27–29].

$\text{NaTi}_2(\text{PO}_4)_3$  with NASICON-type structure similar to  $\text{LiTi}_2(\text{PO}_4)_3$  has been paid attention by researchers due to open three-dimension framework, high ion conductivity, and plentiful resource [30,31]. Compared with  $\text{LiTi}_2(\text{PO}_4)_3$ ,  $\text{NaTi}_2(\text{PO}_4)_3$  can provide more migration channels for Li ions because of its bigger cell volume, which can promote diffusion process of Li ions. While the intrinsic low electrical conductivity and direct attacking from  $\text{H}_2\text{O}$  restrict further improvement of electrochemical performance. Wang et al. [31] synthesized  $\text{NaTi}_2(\text{PO}_4)_3$  nanoparticles embedded in carbon matrix by two-step method. They found that the composite exhibited good stability with capacity retention of 95% at  $1500 \text{ mA g}^{-1}$  after 3600 cycles.

In this work, we first employ polyaniline as carbon and nitrogen sources to synthesize nitrogen-doped carbon coated  $\text{NaTi}_2(\text{PO}_4)_3$  nanocomposite with loose structure. The as-synthesized nanoparticles present many advantages as follows. Firstly, the loose structure can provide more channels for diffusion of Li ions. Secondly, high-quality nitrogen-doped carbon layer can prevent the corrosion caused by  $\text{H}_2\text{O}$  in charge-discharge process, and improve the electrical conductivity of materials. Finally, nitrogen doping for carbon layer can lead to more defects, further accelerate the diffusion of Li ions. As anode for aqueous lithium rechargeable battery, this composite demonstrates outstanding rate and cycling performance. It delivers the discharge capacity of  $119.4$  and  $83.4 \text{ mAh g}^{-1}$  at  $0.2$  and  $15 \text{ C}$ , respectively. The capacity retention can reach  $85.8\%$  after 1000 cycles at  $5 \text{ C}$ .

## 2. Experimental

### 2.1. Synthesis of materials

Chemical reagents were provided by Aladdin Industrial Corp., China. Polyaniline was prepared by chemical oxidation approach as follows.  $11.4 \text{ g}$  of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was dissolved in  $25 \text{ mL}$  of distilled water for standby application.  $4.6 \text{ mL}$  of aniline and  $50 \text{ mL}$  of  $2 \text{ mol L}^{-1}$  hydrochloric acid were added into conical flask with stirring in sequence. Then  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution was added dropwise into aniline solution with separatory funnel. The system was kept for  $1 \text{ h}$  at  $10^\circ\text{C}$ . Then the polyaniline product was obtained and applied for preparation of anode after water washing, sucking filtration, and vacuum drying.

$\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  composites were synthesized by sol-gel approach.  $0.3404 \text{ g}$  of  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ ,  $0.8566 \text{ g}$  of  $\text{H}_3\text{PO}_4$ , and polyaniline with fixed dosage were dissolved into  $15$ ,  $10$ , and  $20 \text{ mL}$  of ethanol by ultrasonication for standby application, respectively.  $1.7204 \text{ g}$  of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  was dissolved in  $20 \text{ mL}$  of ethanol with stirring. Then,  $\text{CH}_3\text{COONa}$  solution, polyaniline solution, and  $2 \text{ mL}$  of concentrated  $\text{HCl}$  were added into  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  solution in sequence. After that,  $\text{H}_3\text{PO}_4$  solution was added into above mixed solution through a separatory funnel. The mixture was sealed with plastic wrap and stirred for  $2 \text{ h}$  at  $65^\circ\text{C}$ . After reaction, the water bath was heated to  $70^\circ\text{C}$  to evaporate ethanol with the opening condition of the system to get precursor. After grinding of precursor, the prepared precursor was calcined in tube furnace at  $800^\circ\text{C}$  for  $5 \text{ h}$  under  $\text{Ar}$  protection with a ramp rate of  $5^\circ\text{C min}^{-1}$ .  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  composites using polyaniline with dosage of  $0.07$ ,  $0.12$ , and  $0.19 \text{ g}$  were denoted as NTP-P-1, NTP-P-2, and NTP-P-3, respectively. For comparison,  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  composite was prepared with the same procedure except for using glucose with  $0.19 \text{ g}$ ,

and the corresponding product was denoted as NTP-G.

### 2.2. Characterizations

$\text{NaTi}_2(\text{PO}_4)_3$  phase of composites was identified by DX-2700 diffractometer with  $\text{Cu K}\alpha$  radiation. Morphology and microstructure of anodes and cycled electrodes were examined by JEOL 4800 scanning electron microscope and Tecnai G12 transmission electron microscope. Carbon content of composite was determined by thermal analyzer (NETZSCH STA 449 F3) in air with heating rate of  $10^\circ\text{C min}^{-1}$ . The surface composition of composite was examined by X-ray photoelectron spectroscopy (K-Alpha 1063), and the fitting for spectrum was performed by XPSPEAK41 software. Raman spectra were recorded on LabRAM Aramis spectrometer (HORIBA Jobin Yvon). Before SEM measurements of cycled electrodes, the electrodes were washed with distilled water after disassembly, followed by drying at  $80^\circ\text{C}$  for  $8 \text{ h}$ .

### 2.3. Electrochemical measurements

Electrochemical measurements were conducted by using CR2016 coin-type cell on Shanghai Chenhua CHI660D electrochemical workstation. The cell was constituted by  $\text{LiMn}_2\text{O}_4$  (cathode),  $\text{NaTi}_2(\text{PO}_4)_3$  composite (anode), and saturated  $\text{Li}_2\text{SO}_4$  aqueous solution (electrolyte).  $\text{NaTi}_2(\text{PO}_4)_3$  composite and  $\text{LiMn}_2\text{O}_4$  were controlled with a suitable mass ratio (about 2:1). The electrode chip was obtained as follows: polytetrafluoroethylene (binder), acetylene black (conductive agent), and active materials were mixed together in a mass ratio of 1:1:8 with ethanol as solvent. The slurry was pressed on steel mesh (current collector) with a diameter of  $14 \text{ mm}$  by rolling process, followed by drying treatment. Cyclic voltammetry of the cell were conducted in the range of  $0$ – $1.85 \text{ V}$  at a scan rate of  $0.4 \text{ mV s}^{-1}$ . Electrochemical impedance spectroscopy of the cell were performed over the frequency range of  $10^5$ – $10^{-2} \text{ Hz}$ , and the cell was activated by charge-discharge test for 2 cycles at  $0.2 \text{ C}$  before measurements. The rate and cycling performance of the cell was investigated by constant-current charge-discharge measurements on a Neware Battery Test System (CT-3008W) at a voltage window of  $0.1$ – $1.85 \text{ V}$ . Three-electrode system was employed to study intercalation/deintercalation behaviors by cyclic voltammetry at  $0.4 \text{ mV s}^{-1}$ . Three-electrode system consisted of electrode chip (working electrode), saturated calomel electrode (reference electrode), and Pt sheet (counter electrode).

## 3. Results and discussion

XRD patterns for all as-prepared materials are displayed in Fig. 1. It is observed that the peaks for all composites can be well indexed to  $\text{NaTi}_2(\text{PO}_4)_3$  with R-3c space group (JCPDS no. 72-2457). Furthermore, diffraction peaks for carbon does not appear for all samples, which is probably due to amorphous structure of carbon and low content. No other impurity peaks are found, indicating that pure  $\text{NaTi}_2(\text{PO}_4)_3$  is obtained by sol-gel method. XRD results reveal that all composites prepared by sol-gel method exhibit pure phase of  $\text{NaTi}_2(\text{PO}_4)_3$ , and the polyaniline cannot affect the crystal structure.

SEM images of NTP-G and NTP-P-2 at different magnifications are presented in Fig. 2a–d. As seen, particle size of NTP-G is larger than that of NTP-P-2. Moreover, the agglomeration of NTP-G is more serious than that of NTP-P-2, which leads to loose structure of NTP-P-2. This phenomenon probably comes from carbon source difference between glucose and polyaniline, and the existence of nitrogen element prevents agglomeration in the calcination process [32]. Smaller particle size and loose structure can facilitate the migration of Li ions, further improving electrochemical properties

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