



One-pot synthesis of carbon-coated nanosized $\text{LiTi}_2(\text{PO}_4)_3$ as anode materials for aqueous lithium ion batteries



Zhantao Liu ^{a, b}, Xusong Qin ^{a, b, *}, Hui Xu ^b, Guohua Chen ^{a, b, c, *}

^a Fok Ying Tung Graduate School, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

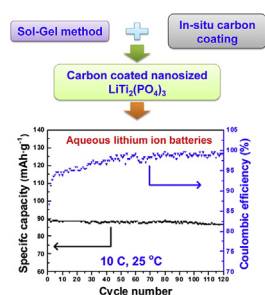
^b Center for Green Products and Processing Technologies, Guangzhou HKUST Fok Ying Tung Research Institute, Guangzhou 511458, China

^c Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- Sol–gel preparation route & carbon coating used for $\text{LiTi}_2(\text{PO}_4)_3$ (LTP/C).
- Turbostratic carbon coating layer achieved for LTP/C.
- Good electrochemical performance achieved in aqueous electrolyte.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a one-pot sintering process incorporating sol–gel preparation route and in-situ carbon coating was proposed for the synthesis of carbon-coated nanosized $\text{LiTi}_2(\text{PO}_4)_3$. Experimental results show that the prepared $\text{LiTi}_2(\text{PO}_4)_3$ particles are of high crystallinity and well-coated by turbostratic carbon. Attributed to nanosized particles and enhanced conductivity provided by turbostratic carbon coating, the carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ showed high rate performance and good cycling life in aqueous electrolyte. Particularly, the carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ exhibited initial specific capacities of 103 and 89 mAh g^{-1} , and retained 80.6% and 97% of the initial capacities after 120 cycles at 1C and 10C in aqueous electrolyte, respectively. The high rate performance and good cycling life of carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ in aqueous electrolyte reveal its potential as negative electrode in aqueous lithium-ion batteries for electric vehicles and industrial-scale energy storage systems.

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1. Introduction

In order to lower the consumption of fossil fuels and meet the ever-increasing demands on the green energies, especially the solar

and wind powers, considerable efforts have been devoted to the development of energy storage systems [1,2]. Among those energy storage systems, rechargeable battery systems, especially the lithium ion batteries, have received significant attention because of their unique properties such as high voltage, high energy density and long service life. Nowadays, lithium ion batteries have been widely applied as power sources for mobile electronic devices like digital camera, cell-phone, laptop, etc. In addition, they show potential applications for electric vehicles and large-scale energy

* Corresponding authors. Fok Ying Tung Graduate School, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China.

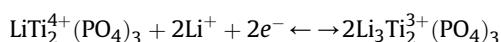
E-mail addresses: qinxusong@ust.hk (X. Qin), kechengh@ust.hk (G. Chen).

storage systems in smart grids. However, the highly flammable characteristic of the organic electrolyte and high cost of commercial lithium ion batteries obstacle their further applications, especially when safety and cost issues are of particular interest.

On the contrary, rechargeable batteries based on aqueous electrolyte are inherently nonflammable. Although the electrochemically stable window of aqueous electrolyte is not as wide as that of organic one, the ionic conductivity of aqueous electrolyte is much higher. In addition, the cost of aqueous electrolyte is cheaper comparing with organic electrolyte. Moreover, the facility and the environment required for battery assembling are easier to be achieved and the associated capital/operational cost would be much lower due to the excellent tolerance of the atmosphere humidity of the aqueous lithium ion batteries (ALIBs).

Because of the above advantages of lithium ion battery based on aqueous electrolyte over that based on organic electrolyte, many efforts have been made in the synthesis of the anode and cathode materials and the battery system design. In 1994, the lithium ion batteries using LiMn_2O_4 as cathode and VO_2 as anode in aqueous electrolyte were first proposed by Dahn's group [3]. After that, cathode materials like LiMn_2O_4 , LiFePO_4 and LiCoO_2 were used as the cathode materials in other groups [4–7]. The electrochemical potentials of these cathode materials are within or near the boundaries of the water's electrochemically stable window and they all exhibited good cycling performance [8]. However, searching for suitable anode materials for aqueous lithium ion battery to match the cathode materials is not easy and remains a big challenge.

Recently, lithium titanium phosphate, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), which has a NASICON-type (sodium superionic conductor) framework structure was used as solid state electrolyte [9]. The insertion and extraction of lithium ions into/from LTP lattice occurs at around -0.5 V with respect to standard hydrogen electrode (SHE), which is approximating the decomposition voltage of aqueous electrolyte [10]. This makes it an ideal candidate as an anode material for aqueous lithium ion battery. In principle, there are two tetravalence titanium atoms in one formula of LTP. At the end of insertion process of Li^+ , the two Ti^{4+} are all reduced to Ti^{3+} , leading to a specific capacity of 138 mAh g^{-1} as shown below.



However, it should be noted that NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$ is of poor electronic conductivity. The poor electronic conductivity of LTP has significant impacts on the rate performance and the cycling life of the battery when it is used as anode materials in either organic or aqueous electrolytes. Furthermore, side reactions would happen when it is directly contacted with water, resulting in quick capacity fading [10–12]. In order to improve the electronic conductivity and the isolation from water, chemical vapour deposition (CVD) was incorporated by Luo and co-workers to form a thin carbon layer on the LTP particle surface [12,13]. Carbon coating of the LTP particles was also realized by Wessells and co-workers by calcining the mixture of carbon source and LTP particles [10,14]. With enhanced conductivity provided by the carbon coating, the rate performance and the cycling life of LTP could be significantly improved.

Traditionally, $\text{LiTi}_2(\text{PO}_4)_3$ was synthesized through solid state reaction route. The typical calcination temperature was about 1200°C [15]. In addition to high energy consumption, loss of lithium could be expected under such high calcination temperature, which may cause appearance of impurity phases [16,17]. In-situ carbon coating method has been applied to the preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using pitch as carbon source. Improved high-rate performance of the carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was achieved with the

enhanced conductivity provided by the carbon coating layer [18]. Therefore, considering the fact that sol–gel method could provide molecular level of mixing in solution phase and requires lower reaction temperature in the later calcination procedure comparing to solid state reaction route, a simple one-pot sintering process incorporating sol–gel method and in-situ carbon coating was proposed to prepare carbon-coated nanosized $\text{LiTi}_2(\text{PO}_4)_3$ in this study. Interesting results were obtained as discussed subsequently.

2. Experimental

2.1. Synthesis

The nanosized LTP was prepared by a one-pot sintering process which is similar to the sol–gel method developed by Hara and co-workers [19]. Homogeneous Li-Ti- PO_4 mixture was prepared using analytical grade CH_3COOLi (99%, Aladdin, USA), $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (99+%, Aladdin, USA), $\text{NH}_4\text{H}_2\text{PO}_4$ (Analytical grade, Guangzhou Chemical Reagent Factory, China), $n\text{-C}_4\text{H}_9\text{OH}$ (99%, Aladdin, USA) and distilled water. Typically, 6.8 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved in 45 ml $n\text{-C}_4\text{H}_9\text{OH}$ while 0.66 g of CH_3COOLi and 3.45 g of $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in 150 ml distilled water. The latter solution was then added into the former one dropwise and kept at 60°C for 2 h with magnetic stirring. After that, the temperature was elevated to 100°C overnight to dry the gel. The dried gel was then pulverized and mixed with pitch (Grade I-C, SINOPEC, China) homogeneously in a weight ratio of 5:3. The pitch content in the obtained mixture was therefore of 37.5 wt%, and the obtained mixture was then calcined at different temperatures. During the calcination, Ar gas was used as protective atmosphere.

Samples without adding carbon source were also prepared in a similar process. Specially, two samples were calcined at 850 and 900°C using Ar gas as protective atmosphere while one sample was calcined at 850°C in air. Pure pitch residue sample was obtained by calcining pitch at 850°C for 12 h in Ar atmosphere.

2.2. Characterization

The crystalline structure and morphology of the prepared LTP with/without carbon coating were characterized by X-Ray Diffraction (XRD, Bruker D8 Advance, Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$), Raman spectroscopy (Renishaw RM3000), Scanning Electron Microscope (SEM, JEOL 6300F) and Transmission Electron Microscope (TEM, Philips TECNAI F30). Specific surface areas and total pore volumes of the prepared LTPs with/without carbon coating were estimated from nitrogen adsorption/desorption isotherms at 77 K using a Micromeritics ASAP 2020. The carbon content was determined by thermogravimetric analyser (TGA, TA Q5000).

The charge–discharge test in organic electrolyte was carried out using 2025 coin cell assembled in a glove box (Glove Box MB 20G, MBraun) filled with Ar gas. Metallic lithium was used as negative electrode and the electrolyte was 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume) mixture. Celgard® 2500 was used as separator. The working electrode was fabricated by compressing a mixture of the active materials (carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$), conductive material (super P, SP), and binder (carboxymethyl cellulose, CMC) in a weight ratio of 80:15:5 onto aluminium foil at 10 MPa after the vacuum drying at 80°C . The typical mass loading of active materials is about 0.3 mg cm^{-2} . The coin cells were cycled in galvanostatic mode between 1.0 and 3.0 V at different charge–discharge rates on a multichannel battery test system (Neware CT-3008W) at room temperature. The cell capacity was calculated based on the weight of the active material.

For galvanostatic charge–discharge test in aqueous electrolyte,

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