



Boosting the performance of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ anode for aqueous lithium ion battery by Sn doping on Ti sites



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ABSTRACT

In this paper, $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.2, 0.3, 0.4$) composites were synthesized by sol-gel approach, and were investigated as anodes for aqueous lithium ion battery. Sn doping with proper content has no obvious influence on phase and morphology of the composite, while excessive dosage of Sn can affect its crystal structure. Sn doping can enhance the electrochemical properties of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ (LC). Among $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ composites, $\text{LiTi}_{1.7}\text{Sn}_{0.3}(\text{PO}_4)_3/\text{C}$ (LC-Sn-0.3) demonstrates the best electrochemical properties. Most importantly, the rate performance of LC can be improved dramatically by Sn doping on Ti sites. LC-Sn-0.3 delivers a discharge capacity of 118.9, 115.3, and 104.2 mAh g^{-1} at 0.2, 6, and 20 C (1 C = 150 mA g^{-1}), respectively, with significant increase of 15.2, 27.4, and 41.9 mAh g^{-1} compare with LC. In addition, LC-Sn-0.3 exhibits superior cycling performance. The capacity retention for LC-Sn-0.3 can keep 76.8% after 1000 cycles at relatively high rate of 10 C, while only 51.7% of initial discharge capacity is retained for LC. Our study reveals that Sn doping on Ti sites is an efficient and facile method to improve the performance of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite for aqueous lithium ion battery.

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1. Introduction

In the 21st century, energy and environmental issues are two major challenges for mankind [1,2]. Coal, oil, and natural gas can't meet people's needs. Although many secondary energies such as solar, wind, and tide are utilized, the geographical conditions, climate, and other factors have great impact on them. In order to achieve the full use of secondary energies, the development of energy storage systems is pushed onto the agenda [3–5]. Battery is one of the most well-suited storage systems due to that electric energy can be transformed into and out in a variety of energy forms [6]. Rechargeable batteries are getting increasingly crucial in daily life, particularly in electronic devices such as laptops and cameras

[7–9]. Conventional lithium ion battery has the advantages of good stability, high voltage, and high energy density, etc. [10–14]. While the used organic electrolyte has the disadvantages of safety risk, high cost, and poor conductivity, which restricts the wide use of lithium ion battery [15,16].

Aqueous lithium ion battery (ALIB) can overcome these issues of conventional organic lithium ion battery by using aqueous salt solution due to low viscosity, high conductivity, and low price [17–19]. Cathode and anode are two important materials for ALIB. Many cathodes such as LiCoO_2 [20,21], LiFePO_4 [22], and LiMn_2O_4 [23] have demonstrated excellent electrochemical performance and stability for ALIB owing to the good electrochemical kinetics of cathodes and the proper potential of 3–4 V for intercalation/deintercalation of Li ions before oxygen evolution reaction [15]. Nevertheless, common anodes such as vanadium oxides and vanadates (VO_2 [24], LiV_3O_8 [25,26], NaV_3O_8 [27]) exhibit relatively poor electrochemical performance. These vanadium-based anodes are still facing the problems of low actual capacity, poor cycling and rate performance. As a result, improving the properties of anodes is crucial for the development of ALIB.

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Poly-anionic compound is a three-dimensional pore structure with many tetrahedral and octahedral structural units connected by covalent bonds in the form of a total of apexes or co-edges, so the structure is relatively stable. $\text{LiTi}_2(\text{PO}_4)_3$, as a typical representative of poly-anionic materials, shows a promising application in ALIB due to large power density and long cycling life [28,29]. And the main research work about $\text{LiTi}_2(\text{PO}_4)_3$ -based materials focuses on carbon coating and size miniaturization [30]. As reported by Xia et al. [7], carbon coating for $\text{LiTi}_2(\text{PO}_4)_3$ could effectively slow down the erosion of electrolyte for electrode and improve the electrical conductivity. Wessells et al. [31] prepared $\text{LiTi}_2(\text{PO}_4)_3$ by Pechini approach, and the prepared materials exhibited excellent cycling performance with capacity retention of 90% after 100 cycles at 0.2 C. Wang et al. [30] synthesized carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ composite by in situ coating method using phenolic resin. The composite demonstrated excellent cycling performance with capacity retention of 84% after 1300 cycles at 150 mA g^{-1} .

So far, very little work about lattice doping has been reported for enhancing the performance of $\text{LiTi}_2(\text{PO}_4)_3$ -based materials in ALIB. Wang et al. [28] studied the influence of Na doping on electrochemical performance of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite. They found that partial substitution of Li by Na didn't change the lattice structure, but can increase lattice volume. Among the Na doped $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composites, $\text{Li}_{0.97}\text{Na}_{0.03}\text{Ti}_2(\text{PO}_4)_3/\text{C}$ exhibited the best electrochemical properties. Liu et al. [32] adopted the electrospinning approach to synthesize Sn doped $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ fibers. The intercalation/deintercalation ability of Li ions of Sn doped composite were improved significantly, and the as-prepared composite demonstrated excellent electrochemical properties in organic and aqueous lithium ion batteries. However, the electrospinning preparation approach needs long time and large energy consumption. Herein, Sn doped $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ on Ti sites was synthesized by sol-gel method using phenolic resin as carbon source. The effect of the dosage of doped Sn on the electrochemical properties and intercalation/deintercalation behavior of Li ions were investigated.

2. Experimental

2.1. Synthesis of materials

All reagents provided by Aladdin Industrial Corporation were in analytical grade, and were directly used without further treatments. $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.2, 0.3, 0.4$) composites were synthesized by sol-gel approach. In a typical process, firstly, 0.8920 g of H_3PO_4 and 15 mL of anhydrous ethanol were mixed with the assistance of ultrasonication for the standby application. 1.7914 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ as Ti source was dissolved in 20 mL of anhydrous ethanol. Then, 0.2658 g of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ as Li source was added into the above solution until it completely dissolved, followed by adding of 0.1700 g of phenolic resin as C source. The dissolution process was conducted at ambient temperature with the magnetic stirring at the rate of 350 r min^{-1} . Afterwards, the prepared H_3PO_4 solution was added into the mixture dropwise, then the system was transferred into water bath and kept at 55 °C for 3 h hermetically. Then, opened the system and increased the temperature to 70 °C to evaporate the solution to obtain the precursor. After grinding, the precursor was calcined at 750 °C for 5 h in Ar atmosphere. The resultant $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ was denoted as LC. $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0.2, 0.3, 0.4$) composites were synthesized on the base of LC by partial replacing $\text{Ti}(\text{OC}_4\text{H}_9)_4$ with $\text{Sn}(\text{C}_4\text{H}_9)_4$ as Sn source with the same molar dosage. The as-prepared $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0.2, 0.3, 0.4$) composites were named as LC-Sn-0.2, LC-Sn-0.3, and LC-Sn-0.4, respectively.

2.2. Characterizations

X-ray diffraction patterns of composites and cycled anodes were identified with D/MAX2500PC X-ray diffractometer (Rigaku, Japan). Morphology of composites and cycled anodes was examined using S-4800 field-emission scanning electron microscope (Hitachi, Japan). Before characterizations, the cycled anodes obtained by disassembling of the cell were washed by distilled water, then dried at 80 °C for 8 h. Thermal gravimetric analysis measurements were conducted on STA 449 F3 thermal analyzer (NETZSCH, Germany) in the range of 25–700 °C in air atmosphere.

2.3. Electrochemical measurements

The anodes and cathodes for electrochemical measurements were prepared as follows: Active materials were mixed with PTFE as adhesive agent and acetylene black as conductive agent in the mass ratio of 8:1:1 using distilled water as solvent. The slurry was pressed on steel mesh as current collector by rolling process using tableting machine, and then dried at 80 °C for 10 h. The intercalation/deintercalation behaviors of Li ions were investigated by cyclic voltammetry measurements utilizing three-electrode system at 0.2 mV s^{-1} . $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$, LiMn_2O_4 , and steel mesh were used as working electrode in corresponding proper potential range, matched with platinum sheet as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. Electrochemical measurements were conducted on CHI660E electrochemical workstation (Shanghai Chenhua) by using CR2016 coin-type cells, which were constructed of LiMn_2O_4 as cathode, $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ composites as anodes, glass fiber membrane as separator, and saturated Li_2SO_4 solution as electrolyte. The mass ratio of cathode to anode was kept at 2:1. Cyclic voltammetry (CV) measurements were performed in the potential range of 0–1.85 V at 0.2 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range of 10^5 – 10^{-2} Hz with the amplitude of 5 mV. Before EIS measurement, the cell was activated by 5 cycles at 0.2 C followed by charging at a constant voltage of 1.6 V for 2 h. Charge-discharge measurements were conducted on battery testing system (CT2001C, Wuhan Land Co.) in the voltage range of 0–1.85 V at fixed rates.

3. Results and discussion

SEM images of LC and LC-Sn-0.3 composites at different magnifications are displayed in Fig. 1a–d. As observed, LC and LC-Sn-0.3 exhibit similar morphology. Many primary particles in nano scale constitute secondary particles in micro scale thanks to the agglomeration effect in the synthesis process of composites. It is well known that the small primary nanoparticles obtained by sol-gel approach can shorten the transporting channel of Li ions, further enhancing the electrochemical properties of composites. SEM characterizations reveal that the as-prepared composites exist in the form of nano and micro scale, and the doping of Sn can't change the morphology of the composites.

XRD patterns of $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0.0, 0.2, 0.3, 0.4$) composites are presented in Fig. 1e. As revealed in Fig. 1e, the main diffraction peaks of all composites are attributed to NASICON-type rhombohedral $\text{LiTi}_2(\text{PO}_4)_3$ structure with R3c space group. LC-Sn-0.2 and LC-Sn-0.3 demonstrate the same diffraction peaks compared with LC, suggesting the pure $\text{LiTi}_2(\text{PO}_4)_3$ phase of these three composites. This indicates that Sn doping with little amount has no influence on the crystal structure of $\text{LiTi}_2(\text{PO}_4)_3$. However, three impurity peaks (Li_8SnO_6 : 17.4°, Li_3PO_4 : 22.2°, 23.0°) appear for LC-Sn-0.4. This is probably ascribed to that NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$ has limited doping capacity on Ti sites, and excessive

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