



One-pot combustion synthesis of $\text{Li}_3\text{VO}_4\text{-Li}_4\text{Ti}_5\text{O}_{12}$ nanocomposite as anode material of lithium-ion batteries with improved performance



Yujing Sha^{a,1}, Zhaobao Zhang^{a,1}, Yubo Chen^a, Qian Lin^a, Yijun Zhong^a, Xiaomin Xu^a, Zongping Shao^{a,b,c,*}

^aJiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), State Key Laboratory of Materials-Oriented Chemical Engineering, Chemistry and Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing, 210009, PR China

^bDepartment of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia

^cCollege of Energy, Nanjing Tech University, Nanjing, 210009, PR China

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ABSTRACT

Li_3VO_4 -decorated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (denoted as V-LTO) composites were synthesized via a facile one-pot cellulose-assisted combustion route. Homogeneous distribution of the Li_3VO_4 phase to introduce additional lithium ion transport paths in the composites and slight doping of vanadium into the lattice of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase were realized simultaneously through the one-pot synthesis, resulting in enhanced apparent ionic and electronic conductivity of the electrode materials. The product with optimal V content, i.e., V-LTO (1:8), showed much improved rate capacities compared with the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The effect of vanadium incorporation on the over-discharge capability of anode materials at a lower voltage was also studied, and the V-LTO (1:8) electrode demonstrated a capacity of 193.6 mAh g^{-1} at a current density of 2000 mA g^{-1} in the potential window of 0.2–3.0 V, much higher than that of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (141.0 mAh g^{-1}). A fairly good cycling stability was also achieved with a capacity retention ratio of 90.0% after working at 1000 mA g^{-1} between 0.2 and 3.0 V for 200 times for the V-LTO (1:8) electrode, which is much higher compared with the capacity retention ratio of 73% for electrodes prepared with pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under the same condition.

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1. Introduction

Because of their several outstanding features such as high energy density, no memory effect, light weight, near-zero toxicity and eco-friendliness, lithium-ion batteries (LIBs) have experienced a fast development since the very first commercial product was released by Sony Corporation in 1991 [1–3]. Actually, after 25 years' research and development, LIBs have become the main power sources for personal electronics. More recently, their large-scale applications in smart grids and electric vehicles have also been well recognized [4–7]. For such applications, safety and lifetime of LIBs are more strictly concerned, while the commercial graphite anode is questionable from the safety consideration. Graphite exhibits a predominant lithium insertion voltage below 0.1 V [8] very close to the lithium electroplating potential, consequently

reactive lithium dendrite is easily formed on the surface of electrodes when discharged at high rates which can penetrate through the separator, leading to a final short circuit and subsequential serious safety concerns. Development of alternative anode materials which are safe, cheap and stable is crucial in realizing the large-scale applications of LIBs.

During the past decade, tremendous efforts have been directed to exploring alternative electrode materials with better safety performance than graphite anode [9–12]. Among many potential anode materials, spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is particularly promising for next-generation LIBs for large-scale applications. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a relatively high and flat lithium intercalation potential around 1.55 V. Such high insertion voltage effectively suppresses the formation of solid electrolyte interface (SEI) derived from the decomposition of organic electrolyte and the formation of lithium dendrite. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ experiences a near zero-strain lattice expansion (< 1%) during discharge-charge processes, which is helpful to improving cycling stability of the electrode. Unfortunately, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits relatively low electronic conductivity

* Corresponding author.

E-mail address: shaozp@njtech.edu.cn (Z. Shao).

¹ These authors contributed equally to this work.

($10^{-7} \sim 10^{-13} \text{ S cm}^{-1}$) [13,14] and poor lithium-ion diffusion coefficient ($10^{-8} \sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$) [15,16], which greatly limit the rate performance of bulk-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and hinder its practical application in large-size energy storage devices and electric vehicles. A reduction in particle size to the nanometer range is an effective way to improve the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, nanostructuring may also reduce the tap density of a material, which is unfavorable for practical use; in particular in the areas that volume specific energy density matters (such as electric vehicles). Ions doping is an effective method to modify the structural properties and thus enhance the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Doping at tetrahedral 8a Li^+ site and octahedral 16d Ti^{4+} site with cations like, Zn, Ca, W, Mg, Ar, Zr, La Ru and V, as well as oxygen-anion site with Br^- has been widely exploited to improve the electronic conductivity and lithium-ion conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [17–26]. Referring to the recent review by Zhao et al. [27], the doping of alien high-valence metallic ions, such as V^{5+} , into the Ti site of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ will generate some Ti^{3+} in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by charge compensation. For example, Yi et al. reported a series of $\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$ ($0 \leq x \leq 0.3$) oxides prepared by solid-state method which showed enhanced performance as compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [26,28]. However, no rate capability of $\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$ was reported and the apparent capacity attenuation with cycling was still observed.

In addition to nanostructuring and ions doping, the formation of composite is another effective method to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, by compositing it with a second phase which can be an electron conductor (eg. carbon), lithium-ion conductor or a mixed conductor. By generating a composite electrode, both the apparent electron conductivity and lithium-ion conductivity may be improved [29,30]. Orthorhombic Li_3VO_4 was reported as a good lithium-ion conducting material with the ionic conductivity up to $4 \times 10^{-5} \text{ S cm}^{-1}$ even at room temperature after the appropriate doping with cations such as Ge^{4+} and Si^{4+} [31]. By applying ionic conductor Li_3VO_4 , as a surface-coating layer, electrode materials, including LiCoO_2 [32], LiMnPO_4 [33] and $\text{Li}_{1.18}\text{Co}_{0.15}\text{Ni}_{0.15}\text{Mn}_{0.52}\text{O}_2$ [34], exhibit improved specific capacity, rate performance and cycle stability because of improved electrochemical kinetic properties, accelerated charge transfer between electrode/electrolyte surfaces and the reinforced surface of materials.

In this work, Li_3VO_4 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites nanocomposites (denoted as V-LTO) with high tap density ($\sim 40\%$ of absolute density) were prepared based on a facile one-pot cellulose-assisted combustion method. Such a one-pot combustion process can realize the formation of homogeneous Li_3VO_4 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocomposite and the doping of V into the oxide lattice of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ simultaneously. The properties and electrochemical performance of the as-prepared Li_3VO_4 -decorated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites and pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were comparatively investigated. Meanwhile, it's well known that discharging at a lower voltage will ensure a higher working voltage in full-cells, greater specific capacity and consequently an elevated energy density of battery. Considering the safety of electrodes working at extreme conditions, the over-discharge behaviors of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at a lower voltage should be emphasized. A broader electrochemical window of 0.2–3.0 V was applied for electrochemical test as well in this study, in addition to the normal working potential range of 1.0–3.0 V. A discharge capacity of 193.6 mAh g^{-1} at a current density of 2000 mA g^{-1} (0.2–3.0 V) and a capacity retention ratio of 90.0% after cycling at 1000 mA g^{-1} for 200 cycles (0.2–3.0 V) were still achieved for the V-LTO (1:8) electrode, much higher than that of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized by a similar process. The improved electrochemical performance of V-LTO (1:8) composite working at both conventional (1.0–3.0 V) and wider (0.2–3.0 V) potential ranges demonstrates its wider application potential in practical cells.

2. Experimental

2.1. Material synthesis

Both pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_3VO_4 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites was synthesized by a one-pot cellulose-assisted combustion method [35,36] with lithium nitrate (LiNO_3 , AR), tetrabutyl titanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$, CP), ammonium vanadate (NH_4VO_3 , AR), and citric acid monohydrate (CA, CP) as raw materials. For the synthesis of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the starting materials were weighed at a molar ratio of Li: Ti: CA = 4.08: 5: 18.06 (8 mol.% Li excess allowing for compensation of possible lithium volatilization during subsequent high-temperature calcination). $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ was firstly dissolved in citric acid solution with vigorous stirring, followed by the addition of LiNO_3 , yielding a transparent solution. Glycine was added as the oxidizer with a molar ratio of 2:1 to that of total metal cation content. Pre-treated cotton fibers were then immersed into the precursor solution. After drying at 80°C , the cotton fibers were pre-calcined at 250°C for 5 h and further calcined at 750°C for 5 h in air. The ramping rate of calcination was fixed at 5°C min^{-1} .

For the preparation of V-LTO composites, precursor solution of Li_3VO_4 was synthesized using the same method of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as mentioned previously. Ammonium vanadate (NH_4VO_3 , AR) was applied as raw material of vanadium source. LiNO_3 (AR), NH_4VO_3 (AR) and citric acid monohydrate were weighed at a mole ratio of Li: V: CA = 3.08: 1: 8.16. Similarly, Li source was 8% excessive considering the possible lithium volatilization during high-temperature calcination. Firstly, the NH_4VO_3 was put into citric acid solution (8.16 g CA in 35 ml deionized water) accompanied with continuous stirring until the NH_4VO_3 was totally dissolved. LiNO_3 was added in sequence, followed by the feeding of glycine (with a mole ratio of 2:1 to that of NH_4VO_3). Finally, a transparent blue solution of Li_3VO_4 precursor was obtained. Two precursor solutions of Li_3VO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were mixed in proper mole ratios (1:8, 1:4, 1:2, 1:1 and 2:1) with continuous stirring for 30 minutes. Then the solution was absorbed into pre-treated cotton fibers. After drying at 80°C , the cotton fibers were pre-calcined at 250°C for 5 h and further calcined at 750°C for 5 h in air.

2.2. Electrochemical performance test

Electrochemical characterizations were performed using CR 2016 half coin cells. A lithium metal foil was used as the reference and counter electrode. Active material mixed with polyvinylidene fluoride (PVDF) and carbon black (Super P) at a mass ratio of 70: 10: 20, was dispersed in N-methyl-2-pyrrolidone (NMP). Homogenous slurry was obtained and coated on copper foil by a blading method. After drying at 100°C for 12 h in a vacuum oven, electrode plates with a diameter of 14 mm were tailored. Cells were assembled in Argon-filled glove-box with 1 M LiPF_6 in EC/DMC (1:1 in volume) as the electrolyte and microporous polyethylene film (Celgard 2400) as the separator. Galvanostatic discharge-charge performance was conducted on Neware battery testers. Cyclic voltammograms (CVs) were recorded by a Princeton Applied Research potentiostat/galvanostatic model 273A at a scan rate of 0.1 mV s^{-1} . The specific capacity of V-LTO was calculated based on the composite weight of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_3VO_4 .

2.3. Material characterization

The crystal structure of the as-synthesized samples were characterized by X-ray diffraction (XRD), performed on a D8 advance diffractometer equipped with $\text{Cu K}\alpha$ radiation. The GSAS and EXPGUI software package was used for the Rietveld refinement of the diffraction patterns. The morphologies of as-synthesized samples were observed by field-emission scanning electron

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