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Organophosphonic acid as precursor to prepare $LiFePO_4$/carbon nanocomposites for high-power lithium ion batteries

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ABSTRACT

Amino tris(methylene phosphonic acid) (ATMP) is selected as phosphorus and carbon co-source for the synthesis of uniformly nano-sized $LiFePO_4$/C by a quasi-sol–gel method. This strategy using ATMP instead of conventional $NH_4H_2PO_4$ supplies two advantages: firstly, ATMP *in situ* chelates Li^+ onto its framework and subsequently binds with FeC_2O_4 in aqueous solution, forming a molecule-scale homogeneous precursor which can obviously improve the purity of $LiFePO_4$. Secondly, the organic carbon contained in ATMP can form uniformly distributed conductive carbon networks among $LiFePO_4$ particles after calcination, which improves the electrical conductivity. The resultant $LiFePO_4$/C with 1.1 *wt.%* carbon achieves a higher discharge capacity than those of $LiFePO_4$ and $LiFePO_4$/C prepared with inorganic $NH_4H_2PO_4$. Moreover, core-shell structured $LiFePO_4$/C nanocomposites are also fabricated by further introducing sucrose into the synthesis system. The high-quality carbon shell effectively hinders the $LiFePO_4$ particle growth and aggregation under high-temperature treatment, which further enhances the electrical conductivity and lithium-ion diffusion, resulting in the improved electrochemical performance with excellent cycle stability (the optimum discharge capacity of 158.6 mAh g^{-1} at 0.1 C and 138.4 mAh g^{-1} at 2 C). The high purity, nanosize and core-shell structure of $LiFePO_4$/C composites yielded by the novel synthesis strategy account for their outstanding electrochemical performance in high-power lithium-ion batteries.

1. Introduction

Lithium ion batteries, as the promising energy storage devices for emerging electric vehicles, hybrid electric vehicles and intermittent renewable energies, have been widely investigated in recent years due to their high energy density, high capacity and long cycle life [1]. As one of the most popular cathode materials in lithium-ion batteries, the olivine-type $LiFePO_4$ has received considerable attention due to its acceptable flat operating voltage (~3.4 V *vs* Li/Li^+), large theoretical rate capacity (~170 mAh g^{-1}), and good thermal stability, as well as low cost, nontoxicity, and environmental benignity [2,3]. Although $LiFePO_4$ has been applied to practical uses in large-sized Li ion batteries (*e.g.* power battery), the sluggish lithium-ion diffusion (10^{-14}–10^{-16} cm^2 s^{-1}) and low electronic conductivity (10^{-9}–10^{-10} S cm^{-1}) still limit its applicable electrochemical performance, which need to be improved [4–6].

The slow lithium-ion diffusion in the electrodes is closely related to the particle size and material homogeneity, which can be substantially enhanced by decreasing particle size and improving phase purity based on the proper synthesis route and precursor [7–9]. So far, various routes including solid-state reaction [10], sol–gel method [11–13], hydro-/solvothermal approach [4,7], and spray pyrolysis technique [14], et al., have been developed for the synthesis of $LiFePO_4$. Among them, the sol–gel method is particularly attractive for preparing high purity and homogeneity of nanoscaled $LiFePO_4$ with controllable particle size and morphology. Nevertheless, the extra addition of complexants such as oxalic acid [11], citric acid [12], ethylene glycol [13] and tartaric acid [15] to obtain gel precursors not only increases the cost, but also causes the synthesis process complex. For the precursor, H_3PO_4 or ammonium phosphate is normally used as the phosphorus source in the synthesis of $LiFePO_4$. However, the process is not green and suffers from the common problems associated with the use of liquid acids (H_3PO_4) such as corrosion of equipment. Moreover, ammonium phosphate can easily decompose into toxic ammonia which is a cause of air pollution. To meet the demand of economic synthesis, clean environment and high

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performance, there is an urgent necessity for development of new and green precursors as phosphorus source and construction of a simple and effective route to synthesize high-quality $LiFePO_4$.

Recently, the organophosphonic acid, a kind of industrially used water clean compound, which is low-cost and environmental-friendly, has been used to fabricate a variety of multifunctional inorganic-organic hybrid materials [16–18]. In the synthesis process, the terminal RPO_3 groups of organophosphonic acid can *in situ* chelate metal ions such as Ti^{4+}, Ni^{2+}, Zn^{2+}. Meanwhile, the uniformly distributed organic linking units in their framework will hinder the aggregation of precursor at space scale and allow the formation of well-dispersed products. In consideration of appropriate phosphorus atoms in the organic framework, the strong interaction with metal ions and the characteristics of solid acid, the organophosphonic acid can be a potential phosphorus source for $LiFePO_4$.

In addition, to overcome the poor electrical conductivity, modifications of $LiFePO_4$ by coating with electronically conductive agents and doping with supervalent cations have been widely conducted [3,19–22]. Among them, carbon-coating is proved to be the most effective and facile method to improve power performance of $LiFePO_4$ by the multiple positive effects: I) reduction of Fe^{3+} to Fe^{2+}, II) minimization of the particle size, III) enhancement of electrical conductivity. Over the past decades, various carbon sources, including sucrose [23–25], glucose [26,27], poly(ethylene glycol) [28], poly(vinyl alcohol) [29], and citric acid [30], were explored to prepare $LiFePO_4$ through the carbon-coating. Undoubtedly, carbon-coated $LiFePO_4$ achieves good specific capacity and rate performance at relatively low carbon content. However, in most cases, the carbon layers are unevenly coated, incompletely wrapped and not intimately contacted to the $LiFePO_4$ particles, which may suffer the low electrical conductivity in the interface of $LiFePO_4$ and electrolyte, and lead to large charge-transfer resistance. It has been demonstrated that the formation of perfect carbon coating is not only affected by the species of the carbon precursor but depended on the homogeneity of the synthesis system [31–33], and thus a uniform reaction environment is particularly proposed in order to achieve the satisfactory carbon-coating effect in the case of low carbon loading amount.

Herein, we report the use of organophosphonic acid ATMP (amino tris(methylene phosphonic acid)) as co-source of phosphorus and carbon to synthesize the nano-sized and high-purity $LiFePO_4$ particles with low carbon content through a quasi-sol–gel route. The introduction of multifunctional ATMP offers a green, low-cost and complexant-free synthesis route. More importantly, the resultant $LiFePO_4$ exhibited superior electrochemical performance to $LiFePO_4$ and $LiFePO_4/C$ derived from inorganic $NH_4H_2PO_4$. Furthermore, with the assistance of sucrose, the prepared $LiFePO_4/C$ nanocomposites with core-shell structure ($LiFePO_4$ as core and carbon as shell) presented the enhanced performance for high-power lithium-ion batteries. The simple alternative route for preparing high-performance $LiFePO_4$ materials from organophosphonic acid is crucial to the practical application of lithium ion batteries.

2. Experimental section

2.1. Material preparation

In a typical synthesis of $LiFePO_4/C$ nanocomposites, stoichiometric amounts of $FeC_2O_4 \cdot 2H_2O$, $LiOH \cdot H_2O$, ATMP and sucrose with a weight ratio of 7.2: 1.7: 4.2: x ($x = 0$, 0.3, 0.6, 0.9 or 1.2, in gram) were added to a corundum mortar. The mixture turned into slurry after 6 ml of deionized water was added. Then, the colloidal compounds were milled continually to form a yellow paste, following the evaporation of water. The obtained yellow paste was dried at room temperature overnight and transferred to a quartz boat. Precalcination was carried out at 350 °C for 3 h in a tubular furnace under nitrogen protection. After cooling to room temperature, the resulting products were further ground and calcinated at 700 °C for 3 h with a heating rate of 2 °C/min under nitrogen protection. The prepared composite was labeled as $LiFePO_4$/AS-*n*, where A and S is the first letter of ATMP and sucrose, respectively; and n ($n = 0, 3, 6, 9, 12$) denotes the amount of sucrose, corresponding to 0, 0.3, 0.6, 0.9 or 1.2 g, respectively. For comparison, we also synthesized the sample $LiFePO_4$/S-*m* ($m = 0$, 3 or 6, standing for the added sucrose with the amount of 0, 0.3 or 0.6 g, respectively) by the same procedure except using $NH_4H_2PO_4$ as phosphorus source.

2.2. Characterization

Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDX) was carried out on a JEOL JSM-7500F microscope at 5 kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010F at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in ethanol and drop-casted onto copper grids covered with carbon film. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA. The diffraction data were collected over the 2θ angle of 10° to 60° at a scan rate of 3°/min. The lattice parameters were refined by using Rietica software. Thermogravimetric analysis (TGA) of the samples were conducted on a TA SDT Q600 analyzer in air or nitrogen atmosphere with a heating rate of 5 K/min. N_2 adsorption–desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). Magnetization studies were performed at room temperature using a LDJ 9600 VSM magnetometer.

2.3. Electrochemical measurement

Electrochemical measurements were performed by using a 2032-type coin cell. The working electrode (*ca.* 3 mg, 0.075 mm) was made by cathode composite $LiFePO_4/C$, carbon black (Super-P) and polyvinylidene fluoride with a weight ratio of 80: 10: 10. The counter electrode was a disk of lithium metal foil (13 mm in diameter, 0.5 mm thick). The electrolyte was a 1 M solution of $LiPF_6$ in 1:1 (v/v) ethylene carbonate/dimethyl carbonate. Celgard 2400 membrane was used as a separator. Galvanostatical charge and discharge measurements were conducted on the electrochemical test instrument (CT2001A, Land Electronic Co., Ltd. Wuhan, China) between 2.5 V and 4.2 V versus Li/Li^+ at room temperature (25 °C). Cyclic voltammetry (CV) was measured by using an IM6 instrument at a scanning rate of 0.1 mV s^{-1} between 2.5 and 4.4 V. Electrochemical impedance spectroscopy measurements were carried out at a discharge state (V_{oc}: *ca.* 2.5 V) with a sinusoidal signal of 5 mV over a frequency range of 100 kHz to 100 mHz.

3. Results and discussion

3.1. Use of ATMP to prepare $LiFePO_4/C$ nanocomposite

By the quasi-sol–gel method, the homogeneous mixing of FeC_2O_4, LiOH and ATMP and the following two-step calcination process render the formation of $LiFePO_4/C$ nanocomposite ($LiFePO_4$/AS-0). Organophosphonic acid ATMP is used as a complexing agent to chelate Li^+, which would further reacted with $Fe(OH)_2$ that arisen from the hydrolysis of $FeC_2O_4 \cdot 2H_2O$ in a basic system at the initial heating stage, giving the precursor of $LiFePO_4/C$. The organic compositions in the precursor would be