(010) facets dominated LiFePO₄ nano-flakes confined in 3D porous graphene network as a high-performance Li-ion battery cathode

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ABSTRACT

Olivine-structured LiFePO₄ (LFP) has been widely considered as one of the most promising and safest high-power positive electrode materials for lithium-ion batteries (LIBs) as a power source in the electric transportation. However, the electrochemical behavior of LFP for lithium-storage is seriously restrained by its intrinsic feature of low electrical conductivity and poor lithium-ion diffusion ability. In this research, LFP nano-flakes with oriented (010) facets were prepared through the solvothermal method, and 3D porous composite of LFP nano-flakes confined on graphene (LFP@G) was synthesized by freeze-drying concentrated graphene-oxide-gel containing LFP nano-flakes followed by a heat-treatment process. As the cathode materials for LIBs, LFP@G composite can release a reversible specific capacity of 129 mAh g⁻¹ at a high current rate of 20 C. Meanwhile, a long cycling stability for LFP@G composite with a capacity of 139.8 mAh g⁻¹ over 600 cycles up to 10 C can be achieved. The superior electrochemical Li-storage properties of LFP@G composite can be ascribed to the fast lithium-ion transfer channels of LFP originated from the exposed (010) planes, shortened lithium-ion diffusion distance, and the excellent two-phase electric contact between LFP and graphene in the 3D porous graphene conductive network for fast electron and lithium-ion transport.

1. Introduction

Electrochemical energy storage devices of high energy and power density have become the main energy source to power hybrid electric vehicles (HEVs) and electric vehicles (EVs). As one of the most important energy storage devices, lithium-ion batteries (LIBs) have been greatly developed to meet the huge demand in portable electric equipment [1–3]. However, the current LIBs still need to be advanced for further improving the power and energy densities to fulfill the increasing request of EVs and HEVs, competing with other electrochemical energy system, like the electrochemical capacitors [1,3,4]. It is believed that major advances to optimize the transport kinetics of ions and electrons in the electrode materials are essentially required to further enhance the electrochemical performance of LIBs.

Olivine-structured LiFePO₄ (LFP) has been considered as one of the most promising positive electrode materials for LIBs due to its low-cost, high safety, desirable theoretical specific capacity (170 mAh g⁻¹), environmental-compatibility, low toxicity, and good thermal stability [5–7]. In spite of these advantages, the main obstacle for applicable electrochemical properties of LFP is its slow Li-ion diffusivity velocity and low electronic conductivity [6–8]. Various methods have been proposed to remedy the inherent drawbacks of the LFP, such as surface modification of LFP by good electrically conductive layers [9–11], optimization of morphology, structure, and particle size [3,8], foreign hetero-atom doping [12–15], and hierarchical nano-/micro-structure assembly [16–18]. The above-mentioned strategies can address the issues of the intrinsic properties of LFP. However, their electrochemical performance is also determined by the properties of the entire electrode. As a result, the structure and composition of LFP cathode should be tuned to improve its electrochemical performance.

Graphene (G) with superior physic-chemical, electrical, and mechanical properties has become an ideal matrix for active electrode materials to accelerate the transport of electrons and Li ions, which can enhance electrochemical lithium-storage properties of the anchored guest materials [19–21]. Hitherto, some graphene modified LFP materials have been reported. However, most of the as-prepared LFP/G composite only can have a low efficient electric contact between the two components caused by the irregular structure of LFP and the

uneven dispersion of graphene. Thus, a limited improvement of electrochemical properties of LFP can be achieved. Recently, experimental [22–30] and computational [31,32] studies acknowledged that lithium-ion preferentially migrated through the spatial channels oriented along the (010) facet in the olivine-structured of LFP because of the low activation barrier along this facet and short distance of lithium-ion diffusion. Therefore, for the high-rate lithium-storage performance, the component of LFP as thin as possible in thickness along the b-axis and as much crystal orientation growing along the ac-facet as possible in LFP/G composite needs to be increased.

On the basis of the above argument, three aspects of research are proposed to facilitate the improvement of electrochemical performance of LFP/G composite: (1) obtaining LFP particles with small size; (2) increasing the component of the LFP with crystal orientation growing along the ac-facet and a thin b-axis direction, and (3) designing a more reliable conductive channel between LFP particles to increase ionic and electronic conductivity. Wang *et al.* [12] prepared the three dimensional (3D) porous LFP/G composite by using the electrostatic attraction and hydrothermal method and the as-obtained material showed a superior electrochemical performance. However, the whole process is too cumbersome. Yang *et al.* [33] used a sol-gel approach to prepare 3D LFP composite. However, the poor combination of G and LFP and lack of oriented (010) facets of LFP crystal cause a poor electrochemical performance.

Herein, a high-performance LIB cathode material of LFP nano-flakes confined in 3D porous graphene network (LFP@G) is needed through a facile synthesis route. On one hand, the LFP nano-flakes can be uniformly confined in the 3D conductive scaffold of graphene. The intimate electrical contact between LFP and graphene can be formed. Thus, the overall conductivity of cathode is greatly improved by 3D conductive network of graphene, in which the migrating speed of charged particles (Li^+ or e^-) is accelerated. On the other hand, LFP nano-flakes exposed in the electrolyte has a shortened electronic and ionic transport distance, leading to the enhanced rate capability. Moreover, 3D porous LFP@G electrode can be directly used for LIBs without additional conductive agents and binders, thereby overcoming the adverse side reactions between the inactive components and lithium. Consequently, 3D porous LFP@G cathode material can exhibit a high-rate capability with the direct exposure of G into electrolyte, ensuring the desirable electrode/electrolyte interactions.

In this work, LFP nano-flakes with oriented (010) facets were prepared through a solvothermal method, and 3D porous composite of LFP nano-flakes anchored on graphene (LFP@G) was synthesized by simply freeze-drying concentrated graphene oxide gel containing LFP nano-flakes followed by heat-treatment. The graphene in the 3D LFP@G porous composite could support the LFP as a conductive skeleton, which can greatly enhance the electronic and ionic conductivity of LFP flakes. As a positive electrode material for LIBs, the LFP@G showed a high reversible specific capacity and good rate capability. The enhanced electrochemical performance of LFP@G composite can be ascribed to the shortened lithium-ion diffusion distance and increased fast lithium-ion diffusion channels with exposed (010) facets of LFP nano-flakes, as well as improved electrical conductivity by 3D porous graphene conductive network.

2. Experimental

2.1. Material preparation

Graphene oxide (GO) was synthesized by chemical oxidization treatment of graphite with a Hummers' method, as reported elsewhere [13]. LFP was obtained through a facile solvothermal procedure. Typically, LiOH, H_3PO_4, and $FeSO_4 \cdot 7H_2O$ were used as the raw material with a molar ratio of 2.7:1.5:1. Ethylene glycol (EG) was invoked as the dispersing agent. Firstly, 1 mL of 85 wt% H_3PO_4 solution was slowly added to 20 mL of 0.028 mg mL^{-1} LiOH·H_2O in ethylene glycol (EG) to form a transparent solution under vigorous stirring. Secondly, 20 mL of 0.0695 mg mL^{-1} $FeSO_4 \cdot 7H_2O$ in EG was slowly introduced to the above solution, resulting in a dark green suspension. After stirring for 1 h, the above-mentioned mixture was removed to a stainless-steel autoclave of 100 mL and kept at 180 °C for 10 h. Thirdly, after naturally cooling to room temperature, the as-formed gray-green sample was obtained by centrifugation and washed by deionized water and anhydrous ethanol, respectively. The LFP sample was then heated to 80 °C and kept for 10 h to remove the solvent in oven. 80 mg of as-prepared LFP sample was added into 100 mL of ethanol to form LFP suspension, and then 0.8 mL of (3-Aminopropyl) trimethoxysilane (APS) were added and stirring for 12 h, the APS-modified LFP was obtained after centrifugation and rinsed by the distilled water. Then, the above modified LFP was sonicated in 100 mL of distilled water to form a suspension. Subsequently, 6.35 mL of 1.26 mg mL^{-1} graphene oxide was introduced to the above suspension and agitated for 2 h. The as-formed LFP/GO suspension was heated and concentrated to form a LFP/GO colloidal gel, which was pasted to a stainless-steel mesh without any binder. Then, the LFP@GO composite was obtained after freeze-drying for 24 h. Finally, the LFP@G electrode with a carbon content of ∼ 6.2% was successfully prepared by directly calcining the LFP@GO composite at 650 °C for 3 h in the mixture of Ar and H_2. For comparison, the LFP/C with a carbon content of ∼ 7.6% was obtained by directly heating the LFP coated by sucrose under the same procedure.

2.2. Characterization

The micro-structure of the as-prepared active materials were characterized by a scanning electron microscope (SEM, FEI Nova Nano230), which is equipped with an energy-dispersive spectroscopy (EDS) and a transmission electron microscope (TEM, Titan G260–300). The crystalline structure of the samples was identified by powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) with a wave length of 0.15406 nm for Cu Kα radiation. Raman spectra of electrode materials were detected in a spectrometer (LabRAM HR800). The specific surface area of electrode materials was measured by the automated analyzer for surface area and pore size (quadrasorb SI), analyzed with the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI) was applied to show the chemical compositions of electrode materials.

2.3. Electrochemical measurement

The electrochemical behaviors of the as-prepared materials were estimated in a half cell consisting of LFP@G composite as a work electrode, a polypropylene microporous membrane as a separator, and metallic Li foil as a counter electrode. In this work, the working electrode of LFP@G composite was directly synthesized through the concentrated gel method. The electrode with LFP/C as active materials was fabricated by dispersing 80 wt% sample, 10 wt% poly (vinylidene fluoride) binder, and 10 wt% acetylene black in the N-methylpyrrolidione solvent to obtain a uniform slurry, which was then pasted on an aluminum foil and heated in vacuum to remove the solvent at 120 °C for 12 h. The electrolyte of 1 M $LiPF_6$ in the mixed solvent of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dmethyl carbonate (DMC) with a volume ratio of 1:1:1 was used. All the batteries were assembled in a sealed Ar-filled glove-box and tested in a potential range of 2.4–4.2 V (versus Li/Li^+) by galvanostatic charge/discharge in a cycler (CT2001A, Wuhan LAND electronics Co. Ltd, China). Electrochemical impedance spectroscopies (EIS) were recorded by an electrochemical testing system (CHI 660D, CH Instruments, China). The frequency ranged from 10^{-2} to 10^5 Hz at an amplitude voltage of 5 mV. The cyclic voltammetry (CV) measurements of half cells with a scan rate of 0.1 mV s^{-1} were carried out at open circuit voltage.