



Well-dispersed rod-like LiFePO_4 nanoparticles on reduced graphene oxide with excellent electrochemical performance for Li-ion batteries

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ABSTRACT

Olivine lithium iron phosphate (LFPO) assimilated with reduced graphene oxide (rGO) was prepared via an easy and cost-effective hydrothermal synthesis, and the resultant composites were employed as active positive electrode for lithium-ion batteries (LIBs). The structural and morphological features were studied by XRD, Raman, SEM, TEM and surface area analysis (BET). The electrochemical properties of the LFPO/rGO composite is evaluated by CV, CP and EIS. The LFPO/rGO composite with a high specific area ($94.7 \text{ m}^2/\text{g}$) was constituted with 74% LFPO and 26% rGO. The LFPO/rGO composite as a LIB cathode displayed a superior initial discharge capacity of 163.3 mAh/g at a current density of 0.2 C and sustained a capacity of 110.6 mAh/g at a high current density of 10 C for 150 consecutive cycles. The existence of highly conductive rGO and a short transportation span for both Li-ions and electrons made LFPO/rGO composite as a promising cathode in LIBs even at high rates.

1. Introduction

Since energy crisis has become a progressively prominent concern, the advance of energy storage devices with high energy density and high power become foremost research over the past few years to meet the growing concerns of the contemporary society. Rechargeable Li-ion batteries (LIBs) are extensively employed as favorable power sources in abundant devices because of their high energy density and extended cyclability [1,2]. Nowadays, the research on electrode materials with desirable properties for instance high energy density, good rate capability and long cyclability is great interest. Since, electrochemical properties of the materials greatly affect by the electrode materials, the development of right and highly effective electrode materials with desirable properties is also a most active field [3,4]. The transition metals oxides (TMOs) play an important role in scientific research, especially for the development of electrode materials in the battery technology for few decades. Remarkable properties such as high theoretical capacities, low cost, environmental friendliness, made TMOs as potential candidate for LIBs [5,6].

The olivine structured transition metal phosphates with general formula LiMPO_4 ($\text{M}=\text{Fe}, \text{Ni}, \text{Mn}, \text{Cu}$ etc.) have been considered as most fortunate positive electrodes of LIBs due to their outstanding properties [7–10]. Among these, LiFePO_4 (LFPO), which belongs to the polyanion-type cathode materials has emerged as promising cathode

material for LIBs because of their matchless properties for example high theoretical capacity (170 mAh/g), long cycling life, high electrochemical potential (3.4 V), outstanding safety performance, thermal stability, cost effective, environmental benignity and abundant iron source in the nature [11,12,18]. The LFPO is a well-organized olivine structured material with $Pnma$ space group, which comprises of corner shared FeO_6 octahedra and edge shared LiO_6 octahedra running parallel to the b-axis and PO_4 polyhedra will be linked together. In addition, PO_4 tetrahedra favor the better phase stability in the course of Li de-intercalation. A stable 3D framework comprising of strong P–O covalent bonds and PO_4 tetrahedral structure provides an outstanding phase stability and safety under misuse conditions for batteries [13]. However, the poor electronic conductivity ($10^{-1} - 10^{-10} \text{ S/cm}$), slow Li-ion diffusion ($10^{-11} - 10^{-14} \text{ cm}^2/\text{s}$) of LFPO limits its widespread applications in LIBs [14]. Tremendous research activities are going on to overcome these constraints. Various synthesis techniques including solid state reaction, solvothermal, hydrothermal, sol-gel, co-precipitation etc., have been used to monitor the particle size and shape [15–18]. The LFPO with various architectures and distinct morphologies including nanorods, nanoparticles, nanosheets, nanoflowers, nanofibers have been constructed for the past few years to facilitate the convenient migration of electrons and lithium ions. The LFPO with lower particle dimensions could tolerate a significant volume change without structural interruption. Nevertheless, electrodes fabricated

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from small-size particles tends to suffer from poor electrical conduction because of the presence of a overprovision of grain boundaries. Carbon coating using various carbon precursors like citric acid, ascorbic acid, adipic acid, pitch carbon, polypropylene, polyvinyl alcohol, polypyrrol, polyacene, polythiophene, starch, glucose, and sucrose etc., have done to improve the electronic conductivity [19–21]. Doping with metal ion like Mn, Co, Ni, V and Ti has been made to improve rate performance. The nanostructured composites can also be controlled by graphene as a conducting support [22–25].

Among these, construction of LFPO on 2D graphene network is one of the most effective approaches due to extraordinary properties of graphene such as outstanding electronic conductivity ($\sim 10^6$ S/cm), high surface area (~ 2630 m²/g), large range potential windows, high charge carrier mobility, structural flexibility, high chemical/thermal stability etc., [26]. Since the pioneering report by Padhi et al. in 1997, LFPO has been studied extensively and reported the discharge capacities almost to theoretical capacity [27,18]. However, the construction of LFPO electrodes by a low cost methodologies with stable electrochemical performance at high current densities are highly desirable. In this work, simple and cost-effective hydrothermal method is opted to fabricate LFPO/rGO composite, which can be used directly as a good cathode material in LIBs. The direct nucleation of LFPO on rGO surface leads to nanostructured hybrid with good interaction between LFPO and conductive frame work. This composite confirmed effective electron supply to the active materials and exhibited superior electrochemical properties.

2. Experimental

2.1. Material synthesis

Graphite flakes, MnSO₄·H₂O, H₂SO₄, KMnO₄, NaNO₃, H₂O₂ and FeC₂O₄·2H₂O were procured from Tianjin Yongda Chemical Reagent Corporation Limited, China and directly employed without further treatment. Graphene oxide (GO) was prepared by a modified Hummer's process. In a typical synthesis of GO, 1 g of graphite flakes and 0.5 g of NaNO₃ were first placed in a 250 mL flask, followed by the dropwise addition of 25 mL of H₂SO₄ while stirring in an ice-bath. Consequently, 3 g of KMnO₄ was added to the reaction blend. The system was continuously stirred until room temperature was reached. Afterward, the viscous mixture was diluted with 80 mL of pure-water, followed by the addition of 30% H₂O₂ to remove remnants of KMnO₄. The resultant mixture was centrifuged, washed with water and filtered. The resultant material (GO) was dried at 70 °C for 24 h. The LFPO/rGO composite was synthesized by simple and cost effective one step hydrothermal synthesis followed by thermal heat treatment. Typically, FeSO₄·7H₂O, H₃PO₄ and LiOH·H₂O (the molar ratio of Li:Fe:PO₄ was 1:1:3) were orderly dissolved into 80 mL as prepared rGO solution followed by the addition of polyethelene glycol. After vigorously stirring, the resultant mixture was then transferred into 200 mL autoclave and heated at 180 °C for 7 h. The final product was attained after washing (with water and ethanol), drying and then heated at 700 °C for 5 h under Ar flow.

The obtained LFPO/rGO composite was directly used for further characterization without further treatments.

2.2. Material characterization

The surface morphology and particle size were analyzed by SEM (Model: HITACHI-S4700) and TEM (Model: Technai-G2F30). The structural properties of the composites were analyzed by XRD (Model: Rigaku D/Max 2500/PC) patterns recorded in the 2 θ range 10–80° using CuK α radiation. Raman spectra were recorded in the wave-number region from 100 cm⁻¹ to 2000 cm⁻¹ using Renishaw Raman system (Model-RM-1000) equipped with a Nd:YAG green laser as an excitation source. The binding energy states of the composites were examined with XPS with a SPECS GmbH spectrometer (Model: XPS, Thermo K-Alpha). Specific surface area and porosity information of the composites were tested with application of BET and BJH models. Thermo-gravimetric analysis was performed in the temperature range from 30 to 1000 °C at a rate of 5 °C/min in N₂ ambiance to estimate the graphene content in the composite.

2.3. Electrochemical measurements

In order to examine the electrochemical properties of the synthesized composite materials, CR-2032 type cells were organized in an Ar-filled glove-box with controlled environment (< 1 ppm). The positive electrodes were prepared by following the procedure given in previous reports. The circular electrodes with a diameter of 1.5 cm were punched. The final cells were prepared with the prepared circular cathode, Li foil as anode, porous polypropylene (PP) film as separator and 1 M LiPF₆ as electrolyte. The as-prepared batteries were tested after 24 h. The charge-discharge experiments were conducted in the voltage range of 2.5 to 4.2 V on CT-2001A battery testing system. CV and EIS studies were carried out within the frequency from 0.01–10⁵ Hz on a CHI-760C electrochemical workstation.

3. Results and discussion

The fabrication process of the LFPO/rGO composites by a one-step hydrothermal synthesis is schematically represented in Fig. 1. The rod like LFPO NPs were crystallized and anchored onto the rGO sheets during the reaction. GO was reduced to rGO during the calcination at 700 °C for 5 h under Ar flow. The surface morphology and particle size of the composites were studied by SEM and TEM. Fig. 2a–c displays the SEM images of the LFPO/rGO composites. The LFPO NPs were crystallized in rod like shape with the size of 80–100 nm thickness and 200–500 nm length and well dispersed onto rGO nanosheets without distortion of the morphology. The encapsulation of the LFPO NPS onto RGO nanosheets not only effectively facilitate the electron transport between LFPO and RGO, but also significantly enrich the conductivity of the nanocomposite comprising both Li-ions conductivity and electron conductivity [28]. TEM and SAED images of the LFPO NPs and LFPO/rGO composites is shown in Fig. 2d–h. TEM images of the LFPO/rGO

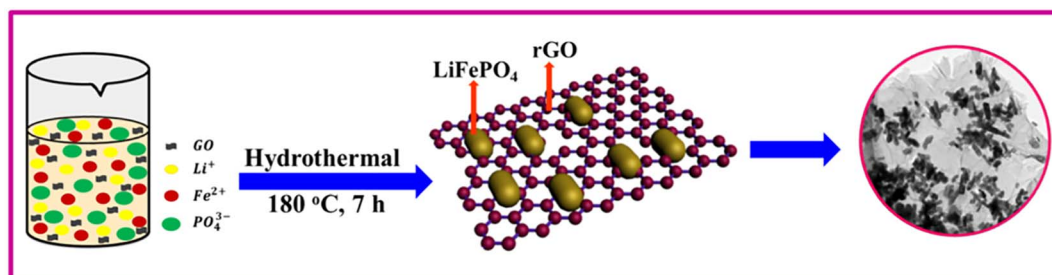


Fig. 1. Schematic diagram for the preparation of LFPO/rGO composite.

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