

Effect of graphene nanosheets content on the morphology and electrochemical performance of LiFePO₄ particles in lithium ion batteries



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ABSTRACT

Few layers graphene nanosheets (GS) are obtained by the reduction of graphite oxide (GO) via Lithium aluminium tetrahydride (LiAlH₄) and Phosphorus tribromide (PBr₃) as the deoxidizer. The LiFePO₄/GS composite is prepared using a solution phase method followed by a calcination process with only 2 h at 600 °C. The effect of the GS content in LiFePO₄/GS on the morphology and electrochemical performance of LiFePO₄ particles is extensively investigated. Results show that the optimized amount of GS in LiFePO₄/GS is 5%. The primary particle size of LiFePO₄/5%GS is 100~150 nm which are wrapped and connected homogeneously and loosely by GS with ~4 layers. The GS can restrict the growth of LiFePO₄ particle and construct an effective conductive network LiFePO₄/GS composite, which all can enhance the conductivity of LiFePO₄ particle. The LiFePO₄/5%GS composite delivers a capacity of 155.4 mAhg⁻¹ at 0.2 C, which is much higher than pure LiFePO₄ (125.3 mAhg⁻¹). Even at high rate of 5 C, a specific capacity of 124.3 mAhg⁻¹ is achievable, with no obvious capacity fading after 100 cycles.

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1. Introduction

Lithium iron phosphate (LiFePO₄) has been recognized as a promising positive electrode material, due to its high theoretical capacity (170 mAhg⁻¹), environment benignity and excellent cycling stability [1,2]. Nonetheless, LiFePO₄ has some intrinsic shortcomings, including low electronic conductivity (~10⁻⁹ Scm⁻¹) and slow lithium ion diffusion across the LiFePO₄/FePO₄, which all can lead to a poor high rate performance [3,4]. In recent years, many efforts such as carbon coating [1,5], metal doping [6,7] and size controlling [8] have been made to improve the conductivity of LiFePO₄ to enhance its rate capacity and cycling performance. It is commonly recognized that this goal could be achieved by adding different carbon sources to obtain LiFePO₄ particle with both small size and high electronic conductivity that contribute to an excellent electrochemical performance.

Graphene nanosheets are one-atomic thickness planar of sp²-hybridized carbon atoms packed into two-dimensional (2D)

honeycomb lattices, which have attracted much attention for various applications in thermal, mechanical, and electronic fields [9,10]. Graphene based materials also have a wide-range of industrial applications such as supercapacitors [11], composite materials [12,13] and lithium ion batteries [14]. Graphene has a thinner wrinkled paper-like structure and higher electrical conductivity than graphite carbon. It has been demonstrated that the cathode material such as LiFePO₄ modified by a few layers graphene has a better electrochemical performance [15]. However, it is difficult to optimize the structure of LiFePO₄ particle modified by a few graphene layers, resulting in only a restricted enhancement in electrochemical activity of LiFePO₄ [12]. Therefore, the improvement of rate performance on LiFePO₄/GS composite should be further researched.

In this paper, the graphene was prepared by a special chemical reduction method for exfoliated graphite oxide and was used to in-situ modify the LiFePO₄ to form LiFePO₄/GS composite, which exhibits a high rate capability and an excellent cyclic stability. At the same time, the effects of carbon coating and graphene content on the morphology and electrochemical performance of LiFePO₄ were compared in the following sections.

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2. Experimental

2.1. Material preparation

GO was prepared by a modified Hummers method, which was reduced by our previous reported method that using LiAlH_4 and PBr_3 as the chemical reduction reagents to form GS [16,17]. First, GO was first dispersed in anhydrous tetrahydrofuran to form a suspension solution with the concentration of 1.0 mg ml^{-1} , and then the suspension was transferred to Ultrasonic cell crusher (300W, JY92-IIN, SCIENTZ) for 30 min. Subsequently, a certain amount of LiAlH_4 was slowly added into the GO suspension under stirring. After 4 h, the mixture was filtered and washed by anhydrous tetrahydrofuran. The obtained powder was then immersed in 1 wt% HCl solution for 15 min under stirring, which was filtered and washed by ethanol and last dried in an oven at 40°C . Second, the as-prepared powder was dispersed into dichloromethane (containing trace of water) solution to form a suspension solution with the concentration of 1.0 mg ml^{-1} , and the deoxidizer PBr_3 was slowly dropped into above suspension under stirring for 2 h. The obtained mixture solution was filtered and washed again with 50 ml ethanol, and the GS was obtained after dried in an oven at 40°C .

GS modified LiFePO_4 composite was prepared as follows: ethylene glycol was added to 0.5 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_3PO_4 solution with equimolar concentration. $\text{LiOH} \cdot \text{H}_2\text{O}$ was gradually added to the above mixed solution and yielding a final solution with Li:Fe:P molar ration of 3:1:1. The solution was stirred for 30 min under nitrogen atmosphere and then was heated to 130°C with the continuous stirring for 5 h to obtain a green product. After being cooled slowly to ambient temperature, the obtained green precipitate was washed several times with distilled water and finally dried in an oven under 80°C . The obtained precipitate and GS were mixed and dissolved in N-methyl-2-pyrrolidinone (NMP) under ultrasound for 2 h. After that, the sample was grinded by ball-milling for 12 h and dried at 120°C under a vacuum atmosphere to form the precursors. Finally, the precursors were sintered at 600°C for 2 h under nitrogen atmosphere to obtain GS modified LiFePO_4 composite. The 2.5%, 5% and 7.5% GS was used in the synthesis of $\text{LiFePO}_4/\text{GS}$ composite. In order to compare the effects between GS and glucose on the morphology and electrochemical performance of LiFePO_4 , 10 wt% glucose as carbon source was also used to synthesize the LiFePO_4/C sample. The glucose and LiFePO_4 precursor were dissolved in ethanol and grinded by ball-milling for 12 h and dried at 80°C to form LiFePO_4/C precursor. The LiFePO_4/C precursor was sintered at 600°C for 2 h under nitrogen atmosphere to obtain LiFePO_4/C composite.

2.2. Structure and morphology characterization

X-ray diffraction (XRD, Rigaku D/max 2500 v/pc, Japan) and Raman spectroscopy (Thermo $\lambda_{\text{EX}} = 532 \text{ nm}$ made in USA) were applied to characterize the structural features of LiFePO_4 , LiFePO_4/C and $\text{LiFePO}_4/\text{GS}$ materials. Morphology and particle sizes were observed by a field-emission scanning electron microscopy (SEM, HITACH S4800, Japan). Crystal structure and GS layers were observed by a transmission electron microscope (TEM, JOEL JSM-2100F, Japan). Raman spectrum was examined using a multi-wavelength micro-Raman spectroscopy (JY HR800) utilizing 532.05 nm incident radiation and a $50\times$ aperture. Thermogravimetric analysis (NETZSCH STA 449 F3 Jupiter) measurement was performed from room temperature to 700°C with the heating rate of $10^\circ\text{C min}^{-1}$ in air atmosphere.

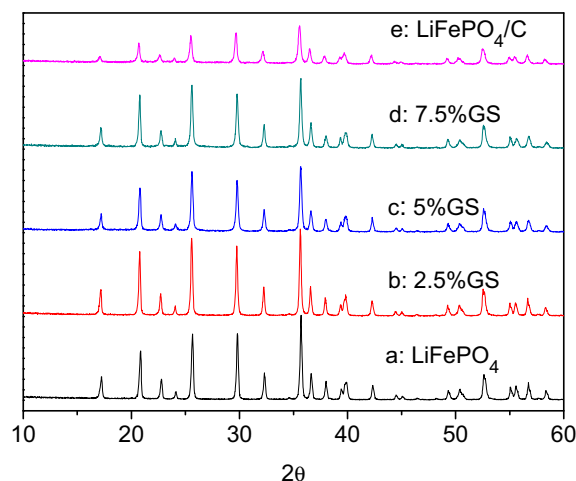


Fig. 1. XRD patterns of pure LiFePO_4 , $\text{LiFePO}_4/\text{GS}$ and LiFePO_4/C .

2.3. Electrochemical measurement

Electrochemical performances of LiFePO_4 , LiFePO_4/C and $\text{LiFePO}_4/\text{GS}$ samples were evaluated using CR 2032-type coin cells. Laminated electrode was prepared as follows: the active material with synthetic graphite (Super P) and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 were mixed and dissolved in N-methyl-2-pyrrolidinone (NMP) to form slurry with the assistance of ultrasound. The slurry was pasted onto an aluminum current collector and dried at 120°C for 12 h under a vacuum atmosphere. A solution of 1 M LiPF_6 was dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/methyl-ethyl carbonate (EMC) (1:1:1, v/v). Celgard 2400 was used as the separator, and Li foil was served as the counter electrode. The active materials load on the current collector was around 2.0 mg. Coin cells were assembled in a pure argon-filled glove box with the content of water and oxygen below 5 ppm. Galvanostatic charge/discharge of electrode was tested on LAND system (CT 2001A, China) in the voltage range of 4.2–2.5 V at room temperature (the current of 1 C is corresponding to 170 mA g^{-1}). The cyclic voltammograms (CVs) of LiFePO_4 , LiFePO_4/C and $\text{LiFePO}_4/5\% \text{GS}$ electrodes were obtained on an electrochemical workstation (Gamry PC 14-750, USA) at a scanning rate of 0.1 mVs^{-1} using the LiFePO_4 , LiFePO_4/C or $\text{LiFePO}_4/\text{GS}$ as the working electrode, and the lithium foil both as the reference and counter electrodes. The corresponding electrochemical impedance spectroscopy (EIS) curves were measured at a frequency range of $10^{-2} \sim 10^5 \text{ Hz}$.

3. Results and discussion

3.1. Crystalline structure analysis

Fig. 1 shows the XRD patterns of the synthesized LiFePO_4 , LiFePO_4/C and $\text{LiFePO}_4/\text{GS}$ samples. All diffraction peaks of the samples in XRD patterns clearly show a single phase formation of an olivine structure without any impurity phase, which are well indexed to an orthorhombic, $Pnmb$ space group (JCPDS Card NO.40-1499), indicating that the obtained samples are high crystallinity of purity LiFePO_4 . Simultaneity, no evidence of graphene and carbon are found in the diffraction patterns, suggesting that their existence does not influence the structure and formation of LiFePO_4 . Compared with the pure LiFePO_4 (Fig. 1a), the intensity of diffraction peaks decreases with the increase of the amount of GS from 2.5% to 5% (Fig. 1b–c), indicating that the amount of GS has an obvious influence on the crystallinity of the products. When the amount of

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