



A three-dimensional LiFePO₄/carbon nanotubes/graphene composite as a cathode material for lithium-ion batteries with superior high-rate performance



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ABSTRACT

A three-dimensional lithium iron phosphate (LiFePO₄)/carbon nanotubes (CNTs)/graphene composite was successfully synthesized via solid-state reaction. The LiFePO₄/carbon nanotubes/graphene (LFP–CNT–G) composite used as Li-ions battery cathode material exhibits superior high-rate capability and favorable charge–discharge cycle performance under relative high current density compared with that of LiFePO₄/carbon nanotubes (LFP–CNT) composite and LiFePO₄/graphene (LFP–G) composite. Graphene nanosheets and CNTs construct 3D conducting networks are favor for faster electron transfer, higher Li-ions diffusion coefficient and lower resistance during the Li-ions reversible reaction. The synergistic effect of graphene nanosheets and CNTs improves the rate capability and cycling stability of LiFePO₄-based cathodes. The LFP–CNT–G electrode shows reversible capacity of 168.9 mA h g⁻¹ at 0.2 C and 115.8 mA h g⁻¹ at 20 C. The electrochemical impedance spectroscopy demonstrate that the LFP–CNT–G electrode has the smallest charge-transfer resistance, indicating that the fast electron transfer from the electrolyte to the LFP–CNT–G active materials in the Li-ions intercalation/deintercalation reactions owing to the three-dimensional networks of graphene and carbon nanotubes.

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1. Introduction

Lithium-ion battery has attracted much attention as one of the most promising energy storage systems and power sources for electric vehicles (EV), plug-in hybrid electric vehicles (PHEVs), and hybrid electric vehicles (HEVs) due to its outstanding electrochemical performance, high capacity and energy density compared to conventional rechargeable batteries [1–3]. Lithium iron phosphate (LiFePO₄) has many advantages such as low cost, nontoxicity, high theoretical capacity and stable voltage plateau and has been used as the positive electrode of the lithium-ion batteries [4,5]. Since the pioneering work by Padhi et al. [6], LiFePO₄ has been extensively studied compared with other candidates of cathode materials for lithium-ion batteries. However, the poor Li-ions diffusion coefficient and low electronic conductivity of LiFePO₄ limit its commercial application in high-rate batteries [7–10]. Considerable

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methods have been made to overcome the limitations of pristine LiFePO₄ such as carbon coating [11,12], optimizing the LiFePO₄ particle size and shape [13] and cations or oxides doping [14,15]. Among various methods, the combination of LiFePO₄ with high conductive carbon materials (such as conductive carbon black, graphene, and carbon nanotubes) has been proved to be an effective way to improve the electrochemical performance of the lithium-ion batteries [16–18]. For example, Konarova and Taniguchi [19] prepared carbon-coated LiFePO₄ using acetylene black to avoid LiFePO₄ particle growth during heat treatment and the carbon-coated LiFePO₄ showed improved battery performance. Graphene, a two-dimensional carbon material, has distinctive characteristics such as flexible structure, large surface area and superior electrical conductivity and has been widely studied as an additional material for lithium-ion battery [20,21]. Ding et al. [22] prepared LiFePO₄/graphene composites through a co-precipitation method and the composite cathode material delivered an initial discharge capacity of 160 mA h g⁻¹ at 0.2 C and the capacity retained 110 mA h g⁻¹ at a high rate of 10 C. Zhou et al. [23] synthesized graphene modified LiFePO₄ composites by spray-drying and annealing processes and the composite cathode material

delivered a discharge capacity of 70 mA h g⁻¹ at 60 C. Carbon nanotubes (CNTs), another kind of carbon material with high electrical conductivity in the axial direction, have also been intensively applied to cathode in lithium-ion battery [24,25]. Li et al. [26] used CNTs as the conducting additive in LiFePO₄ and LiCoO₂ electrodes. The reversible discharge capacity of LiFePO₄-CNTs composite cathode was 155 mA h g⁻¹ at 0.1 C.

However, the rate-performance enhancement of such carbon-modified electrode materials is still limited since one-dimensional CNTs can hardly form an effective continuous network to enhance the electrical contact [27]. On the other hand, the graphene is difficult to form tightly wrapping on the surface of LiFePO₄ resulting in limited enhancement in electrochemical activity of LiFePO₄ [28–30]. Hence, the combination of LiFePO₄ with carbon nanotubes and graphene is supposed to construct a three dimensional structure that may improve the performance of LiFePO₄ composites. The conducting networks formed by the CNTs and graphene may provide conductive pathways for electron transfer during the insertion/desertion process, shorten the Li⁺ ion diffusion channels and accelerate the penetration of the liquid electrolyte into the LFP-CNT-G composite in all directions. Up to now, there are few reports on the combination of graphene and CNTs with LiFePO₄. In this work, a three dimensional LiFePO₄/carbon nanotubes/graphene (LFP-CNT-G) composite was prepared by wet ball milling followed by a two-step heat treatment process. The LFP-CNT-G cathode material shows remarkably improved charge/discharge capability superior to that of the traditional LiFePO₄/CNTs (LFP-CNT) and LiFePO₄/graphene (LFP-G) cathode materials.

2. Experimental

2.1. Sample preparation

The CNTs (>99 wt.%, Shenzhen Nanotech Pord Co., Ltd) used in this work are about 20–40 nm in diameter and 5–10 μm in length with an approximate surface area of 90–120 m² g⁻¹. Graphite oxide was prepared by a modified Hummers method [31,32]. Graphene was achieved by microwave thermal reduction of the graphite oxide at 200 °C for 8 min.

LFP-CNT-G composite was synthesized by solid-state reaction. The solid-state reaction using wet ball milling was performed with stoichiometric amounts of Li₂CO₃, FeC₂O₄·2H₂O, NH₄H₂PO₄, 3 wt.% CNTs, 1 wt.% graphene in ethanol (>99.9%) at a rotation speed of 300 rpm for 12 h. Mass ratio of the materials to zirconia balls was selected to be 1:10. The precursor mixture after ball milling was dried at 90 °C for 8 h in a vacuum drying oven. The dried powders were subjected to a two-step heat treatment process. It was first heated to 350 °C for 4 h under Ar atmosphere to decompose the carbonate, oxalate, and ammonium mixture of the starting materials followed by heat treatment at 650 °C for 10 h to form LFP-CNT-G composite.

For comparison, LFP-CNT and LFP-G samples were also synthesized under the same condition.

2.2. Characterization

X-ray diffraction (XRD, DMAX-Ultima IV, Rigaku Corporation, Japan) was employed to identify the crystal structure of all the as-prepared samples at a scanning rate of 20 min⁻¹ for 2θ in the range of 10–80°. Raman spectroscopic analysis was performed with a Renishaw Invia system with laser excitation energy of 514 nm. The morphologies of the samples were investigated by scanning electron microscopy (SEM, S3400N, Hitachi, Japan) and transmission electron microscopy (TEM, JEM 2100F, Japan).

All the as-prepared composites were used as cathode and constructed into a 2032 coin-type test cell. The electrochemical performances of the lithium-ion batteries were evaluated from 2.5 to 4.2 V on a LAND battery tester (CT2001A, Wuhan LAND Corporation, China). The working electrodes were produced by dispersing the as-prepared composites (LFP-CNT, LFP-G and LFP-CNT-G), carbon black and polyvinylidene fluoride (PVDF) with a weight ratio of 85:10:5 in an N-methylpyrrolidone (NMP) solvent to form homogeneous slurry. The slurry was uniformly spread onto aluminum foil substrates. The electrodes were dried in a vacuum oven at 80 °C for 10 h and then pressed.

The 2032 coin-type cells were assembled in a glove box in a high purity argon atmosphere. The cell consisted of the cathode, pure metallic Li anode, micro-porous membrane (Celgard 2400) separator and a non-aqueous electrolyte of 1 mol dm⁻³ LiPF₆ in ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC) (1:1:1 v/v/v).

The electrode performance was investigated in terms of cyclic voltammetry curve (CV) using an electrochemical work station (IM6, Zahner, Germany), charge/discharge curves and cycling capacity using a LAND battery tester within a voltage window of 2.5–4.2 V. CV was carried out at a scanning rate of 0.1 mV s⁻¹. EIS measurements were performed in the frequency range of 100 kHz–10 mHz with an AC amplitude of 5 mV.

3. Results and discussion

3.1. Crystalline structure analysis

The XRD patterns of all the as-prepared composites as well as pure LiFePO₄ and graphene are shown in Fig. 1. It is obviously that the orthorhombic LiFePO₄ phase exists in all composites. The peaks of LFP-CNT-G composite are the sharpest and have the highest intensity, indicating the high purity of this sample. No characteristic peaks from graphene or carbon nanotubes were observed, most probably due to the low content of graphene or carbon nanotubes [33,34]. In addition, the (002) peak of graphene is likely to be eclipsed by the (011) peak of LiFePO₄ [35].

The structure of the LFP-CNT-G composites was further studied by Raman spectra, as shown in Fig. 2. Raman shift evidences the presence of carbon in the LFP-CNT-G composites. The bands at 700–400 cm⁻¹ and 1200–800 cm⁻¹ correspond to the vibrations of Fe–O and PO₄³⁻ in LiFePO₄, respectively, while the strong peaks in the range of 1200–1500 cm⁻¹, 1500–1800 cm⁻¹ and 2350–2750 cm⁻¹ are ascribed to the D-band, G-band and 2D-band, respectively [36,37]. The G-band stands for the presence of graphite carbon, whereas D-band is attributed to disorders or defects in the graphite structure. The broadening of the D and G bands with a strong D band indicates localized in plane sp² domains and disordered graphitic crystal stacking of the graphene nanosheets. The I_D/I_G value (ratio of the intensity of D-band and G-band) generally provides a useful index for comparing the degree of crystallinity of various carbon materials, i.e., the smaller the I_D/I_G ratio, the higher the degree of ordering in the carbon materials [20,32]. The I_D/I_G values of graphene, LFP-CNT, LFP-G and the LFP-CNT-G composite are 1.32, 1.57, 1.65 and 1.71, respectively. The higher I_D/I_G ratio implies that the CNTs and graphene have been successfully incorporated into the LiFePO₄.

3.2. Morphologies

The morphological features of all samples were characterized by SEM and TEM. Fig. 3(a–d) shows the typical SEM images of pristine LiFePO₄ composites and modified LiFePO₄ particles. The pure LiFePO₄ contains well-crystallized and densely aggregated olivine-like nanoparticles with sizes ranging from 200 to 500 nm, as shown in Fig. 3a. For the LFP-CNT composite (Fig. 3b), CNTs are

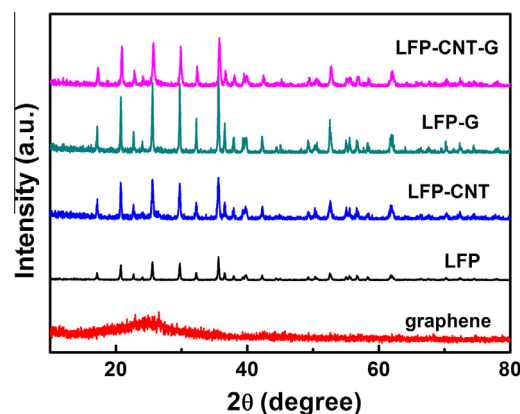


Fig. 1. XRD patterns of the samples.

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