Graphene-decorated carbon-coated LiFePO₄ nanospheres as a high-performance cathode material for lithium-ion batteries

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ABSTRACT

Nanohybrids of graphene-decorated carbon-coated LiFePO₄ nanospheres are prepared using a ball milling-assisted rheological phase method combined with a solid-state reaction. The hybrids are characterized by XRD, SEM, TEM, HRTEM, XPS, Raman and TGA, and their electrochemical properties are studied by CV, EIS and galvanostatic charge-discharge. The experimental results exhibit that multilayer graphene films are decorating carbon-coated LiFePO₄ nanospheres without stacking, which results in an abundance of mesopores constituting a unique 3D "sheets-in-pellets" and "pellets-on-sheets" conducting network structure. This structure highlights the improvements of the rate and cyclic performance as a cathode material for lithium-ion batteries, because the highly conductive and plentiful mesopores promote electronic and ionic transport. As a result, the hybrids with approximately 3 wt% graphene exhibit an outstanding rate capability with an initial discharge capacity of 163.8 and 147.1 mA h g^{-1} at 0.1 C and 1 C, and the capacity is retained at 81.2 mA h g^{-1} even at 20 C. Moreover, the composites also reveal an excellent cycling stability with only an 8% capacity decay at 10 C after 500 cycles.

1. Introduction

The increasing energy crisis and environmental pollution, caused by heavy reliance on fossil fuels, have stimulated great interest in the fields of renewable energy and effective energy storage. Since their commercialization by Sony in the early 1990s, lithium ion batteries (LIBs) have been widely recognized as the most important energy storage device [1]. In the past two decades, LIBs have been revolutionary for their applications in electric vehicles (EVs), plug-in hybrid electric vehicles (HEVs) and wholesale energy storage, owing to their advantageous features of high energy density, high efficiency, lightweight and portability [2–6]. However, these new applications demand higher energy and power capabilities with cost-effective, sustainable and environmentally friendly materials [1]. In general, the performance of the electrode material affects the property of LIBs, and its cost directly determines the commercial applications of these materials. Therefore, according to the ever-growing social demand, the rate capability of LIBs must be improved by exploiting electrode materials with better rate capability, cycling stability, lower elemental materials cost and environmental benignity.

Since the seminal work of Goodenough and co-workers [7], the olivine-type lithium iron phosphate (LiFePO₄) has been considered as one of the most promising cathode materials for its high open-circuit voltage (3.45 V vs. Li$^+$/Li), high theoretical discharge capacity (~170 mA h g^{-1}), low cost, natural abundant raw materials, safety, structural stability and environmental-friendliness. The importance for commercial applications is the safety and energy capacity at high power output and at short recharge times [8]. However, for practical application as power batteries, olivine-LiFePO₄ (LFP) exhibit low electronic conductivity (10^{-9} to 10^{-10} S cm^{-1}) [9] and poor lithium ion diffusion coefficient (10^{-14} to 10^{-16} cm^2 s^{-1}) [10]. Such poor electronic conductivity is caused by the lack of mixed valence owing to the low solubility of LiFePO₄ and FePO₄ and the highly localized Fe^{2+} or Fe^{3+} ions, while the poor Li$^+$ conductivity is caused by one-dimensional diffusion of Li$^+$ to

form edge-shared LiO_6 octahedra only along the [010] direction [11]. Thus, seeking strategies to improve the LFP electrochemical performance is still highly desirable.

To date, tremendous efforts have been made to overcome the above problems, which include: i) decreasing the particle size to shorten the ionic and electrical path length [12]; ii) doping with foreign atoms [13]; iii) surface coating or admixing with electronically conductive materials (carbon [14–23], Ag [24], and conducting polymers [25–27]). Among them, carbon-coating is considered as one of the most effective and conventional ways to improve the LFP electrochemical properties.

Graphene, a single atomic monolayer of graphite, has received unprecedented attention over the last decade owing to its ultrahigh theoretical specific surface area (2630 $m^2\ g^{-1}$) [28] and high carrier mobility at room temperature (~10 000 $cm^2\ V^{-1}\ s^{-1}$) [29]. At present, graphene-based materials, including LFP/graphene composite materials, have been used in LIBs electrodes and have shown great potential for LIB applications [30–42]. For example, Zhang et al. [38] reported the preparation of C-LFP/graphene composite through solvothermal route, and Nagaraju et al. [42] fabricated a LFP/rGO composite using a co-precipitation method; these LFP/graphene composites show improved performance in terms of rate capability and stability compared with the bulk LFP. Nevertheless, there still remains great space to develop scalable route with advantages of simplicity, rapid synthesis, safety, low cost, and energy capacity at high power output. On the other hand, for LFP/graphene composite, the problem regarding to graphene agglomeration has not yet been well addressed so far.

Herein, we report the synthesis of graphene-decorated carbon-coated $LiFePO_4$ nanospheres (denoted as LFP@C/G). We first synthesized the precursor, using a high-energy ball milling assisted rheological phase method [43], which could effectively solve the problem of graphene agglomeration and reduce the particle size of raw materials to decrease the calcination temperature and holding time owing to the uniform distribution of the solid particles and liquid substances in the rheological body [39]. After calcination at 700 °C, the carbon obtained from glucose pyrolysis was exploited as the reducing agent to inhibit the transformation of Fe^{2+} to Fe^{3+}, and the residual carbon could combine with graphene to form a 3D conductive network. The as-synthesized LFP@C/G cathode showed low polarization, high electrical conductivity, excellent rate capability and stable cycle performance, compared with a carbon-coated LFP sample (designated as LFP@C) prepared by the same method without the presence of G.

2. Experimental

2.1. Materials preparation

The graphene was obtained from the Suzhou Tanfeng graphene Technology Co. Ltd, which was prepared by a physical stripping method. We chose unfolded physical exfoliated graphene as a 3D conducting network for LFP nanoparticles growth. Compared with rGO and stacked graphene, which have a wrinkled structure and the problem of agglomeration, unfolded exfoliated graphene can be better dispersed in LFP nanoparticles and allow each LFP nanoparticle to be attached to the conducting layer, which could greatly enhance the electric conductivity. Moreover, multi-layer exfoliated graphene is much less expensive than single-layer graphene and few-layer graphene.

The LFP@C/G composite was synthesized by a solid-state reaction as described below and shown in Fig. 1. The precursor was prepared through a high-energy ball milling assisted rheological phase method. An appropriate amount of Li_2CO_3 (AR, Aladdin), $FeC_2O_4\cdot2H_2O$ (AR, Aladdin), $NH_4H_2PO_4$ (AR, Aladdin), glucose (the weight ratio of glucose to LFP was 10:90) and graphene (the weight ratio of graphene to LFP was 3:97), ultrasonically dispersed in acetone for 2 h, was placed in acetone with a Fe: P: Li molar ratio of 1:1:1 under high-energy ball milling for 6 h. The yellow rheological body was dried under an argon flow at 40 °C for 10 h to evaporate the excess acetone. The yellow platelets were dried at 80 °C under vacuum for 10 h. The obtained powder was ground and annealed at 350 °C for 2 h, followed by sintering at 700 °C under a reducing atmosphere (5 vol% of hydrogen in argon) for 10 h with a heating rate of 1 °C min^{-1}. For comparison, pure LFP and LFP@C were synthesized in the same way except that glucose and graphene were not added, respectively. This method has several advantages: (1) the precursor can be rapidly prepared using our method without impurity using a ball milling assisted rheological phase method in 6 h, which is applied to industrial production; (2) can well solve the problem of impurity materials upon synthesis of LFP nanoparticles due to the instability of Fe^{2+}; (3) effectively solving the problem of graphene agglomeration; (4) providing a prerequisite for the synthesis of highly crystalline LFP@C/G composites.

2.2. Measurements

2.2.1. Materials characterization

The phase purity and crystalline structure of the samples were determined by X-ray diffraction (XRD) with a Miniflex600 powder X-ray diffractometer at 40 kV and 40 mA, using Cu Kα radiation in a 2θ range from 10° to 80° at a scan rate of 0.05° s^{-1} (λ = 1.54178 Å). A thermogravimetric analyzer (TGA; TGA 4000, Perkin Elmer) was used to study the degradation behavior of different samples under non-isothermal conditions. The samples were heated between 30 °C and 850 °C at a heating rate of 5 °C min^{-1} in air, and the flow rate of the synthetic air was 10 mL min^{-1}. The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, FEI SU-8010) equipped with a field-emission gun at an accelerated voltage of 15 kV. Transmission electron microscopy (TEM, JEM-2010 HRTEM) was operated at an acceleration voltage of 200 kV. The XPS spectra of the samples were recorded by an X-ray photoelectron spectrometer (Shimadza-Kratos Analytical, Axis Ultra DLD). Raman measurements were recorded in a Renishaw inVia Raman Microscope using 532 nm laser. Nitrogen adsorption/desorption isotherms were obtained using a surface area and porosity analyzer (Tri Star II 3020) at 77 K. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method.

2.2.2. Electrochemical measurements

The working electrodes were fabricated by using LFP@C or LFP@C/G as the active material, conductive carbon black (Super-P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:15:5. They were mixed in a mortar for 1 h and then dispersed in N-methyl-2-pyrrolidone (NMP) solvent to form a homogeneous slurry. The slurry was coated on aluminum foil and dried in a vacuum oven at 120 °C for 10 h. The electrochemical measurements were carried out using CR2032 coin type cells, which were assembled into half-battery in an argon-filled glove box under concentrations of moisture and oxygen below 1 ppm. Lithium pellets were used as the counter/reference electrodes and Celgard 2400 was used as separator. The electrolyte solution was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) with a volume ratio of EC: DMC = 1:1. The loading of the active mass was approximately 1.5–2.0 mg in LFP@C and LFP@C/G electrodes without deducting the mass of carbon and graphene. Fig. S1† shows illustration of the preparation process of working electrodes of LFP@C and LFP@C/G. Cyclic voltammetry (CV)