Journal of Power Sources 249 (2014) 311–319

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

In-situ growth of graphene decorations for high-performance $LiFePO_4$ cathode through solid-state reaction

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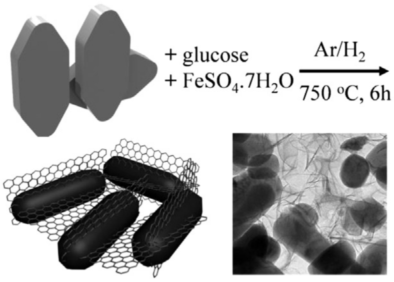
HIGHLIGHTS

- Graphene-decorated $LiFePO_4$ is *in-situ* synthesized through solid-state reaction.
- Graphene is *in-situ* grown through pyrolysis and catalytic graphitization of glucose.
- Graphene forms a compact, uniform and thin coating layer throughout the LFP NPs.
- Graphene cross-links into a conducting network around the LFP NPs.
- Electrochemical performance of LFP@graphene is remarkably improved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 September 2013
Received in revised form
5 October 2013
Accepted 24 October 2013
Available online 5 November 2013

Keywords:
Graphene
In-situ growth
Li-ion batteries
Lithium iron phosphate cathode
Solid-state reaction

ABSTRACT

Graphene-decorated $LiFePO_4$ composite is synthesized for the first time through *in-situ* pyrolysis and catalytic graphitization, in which glucose and a trace amount of $FeSO_4$ are employed as the graphene source and catalyst precursor, respectively. Under Ar/H_2 (95:5) atmosphere at 750 °C, $FeSO_4$ is thermally reduced to Fe nano-particles (Fe NPs) and glucose is pyrolyzed to carbon fragments first, followed by the *in-situ* growth of graphene sheets directly on the $LiFePO_4$ nano-particles (LFP NPs) surface through the realignment of carbon fragments under the catalytic effect of the Fe NPs. The graphene sheets not only form a compact and uniform coating layer throughout the LFP NPs, but also stretch out and cross-link into a conducting network around the LFP particles. The $LiFePO_4$@graphene composite displays a high reversible specific capacity of 167.7 mAh g^{-1} at 0.1C rate, superb rate performance with discharge capacity of 94.3 mAh g^{-1} at 100C rate and much prolonged cycle life. The remarkable electrochemical improvement is attributed to both electric and ionic conductivity increase as a result of *in-situ* grown graphene coatings along the LFP surface and the graphene network intrinsically connecting to the LFP particles.

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1. Introduction

The olivine-structured $LiFePO_4$ (LFP) is widely accepted as a promising cathode candidate used in lithium-ion batteries (LIBs) for powering electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) due to its high theoretical capacity (170 mAh g^{-1}), acceptable operating voltage (3.4 V vs. Li^+/Li), good safety, low cost and toxicity [1–9]. However, one of the major challenges for the commercialization of LFP is the poor high-rate capability, attributed to its intrinsically low electronic conductivity (10^{-9}–10^{-10} s cm^{-1}) and slow ionic diffusivity ($\sim 10^{-14}$ cm^2 s^{-1}) [10–12]. Considerable efforts have been made to overcome the electronic and ionic transport limitations of LFP by reducing the particle size, [13–15] optimizing the morphology [16,17], decorating the surface with

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http://dx.doi.org/10.1016/j.jpowsour.2013.10.106

electrically conducting agents [11,18–22] and doping the host framework with supervalent cations [23–25]. Among these strategies, a combination of nano-sized particles and carbon coating is considered as the most effective route to improve the material utilization and rate performance of LFP cathode [26–28]. Particle size reduction provides both a shorter diffusion path and a large surface area for charge carriers, resulting in a higher ionic diffusion constant. Furthermore, carbon coating not only enhances the surface electrical conductivity and thus alleviating the electrode polarization, but also prevents the iron dissolution and migration [29]. All these factors contribute to great improvements of the reversible capacity, cycling stability and rate capability [26,27].

Although carbon coating of LFP has been extensively studied and successfully commercialized, there still remain several fundamental and technical questions. It is well known that various parameters of carbon coating layer including carbon content, degree of graphitization and morphology, coating thickness, distribution (uniformity and coverage) and carbon surface area can significantly affect the electrochemical performance of LFP cathode [26,27,30–33]. Typically, a thin, uniform and highly-graphitic carbon coating layer throughout the LFP nano-particles (LFP NPs) is regarded as the most promising coating manner for LFP cathode with high electrochemical performance [26,27,34–36]. In addition, intrinsic interconnection between carbon coating layers is also very effective to reduce the contact resistance between active material particles. On the other hand, the graphitic carbon coating layer needs to be very thin (1–3 nm) to allow easy and rapid penetration of Li^+ ions [26,27]. Nevertheless, developing an effective approach to produce ultrathin and uniform graphitic carbon coatings is very challenging given carbon is difficult to graphitize at relatively low temperatures required for synthesis of LFP (600–800 °C) [26,34–36].

Recent studies have introduced graphene as a two-dimensional (2D) graphitic carbon nano-material in the LFP cathode in order to produce a three-dimensional (3D) conducting matrix [37–47]. However, the specific capacity and rate performance of LFP/graphene composite were not significantly improved compared to the amorphous carbon coated LFP [42,47]. The main reason is that LFP particles just loosely contact with the graphene frames. When the LFP particles were tightly anchored onto and entirely encapsulated into highly graphitized graphene sheets, the electrical conductivity of LFP can be greatly enhanced at the expense of hindering the quick transport of the Li^+ ions to the active materials. Several groups have proposed a coating strategy solution by combing a complete carbon coating layer and a cross-linked graphene conducting network outside the LFP particles. The graphene network plays a key role in providing good inter-particle electrical connection and creating available voids for electrolyte storage and Li^+ ions transport [37–39]. In terms of the graphene-based composite materials, chemically exfoliated graphene oxide (GO) or reduced graphene oxide (RGO) sheets are so far the preferred choice [26,37–47]. This choice leads to two major technical problems: first, GO and RGO need to be specially produced prior to the synthesis of the final product; second, achieving uniform dispersion (or growth) of LFP or carbon coated LFP within the crumpled micrometer-size graphene sheets is difficult or almost impossible with graphene sheets and LFP produced separately.

To overcome the shortcomings in the composite architecture and preparation technology of the carbon-coated LFP, we designed a bottom–up strategy to synthesize a graphene-decorated $LiFePO_4$ composite (LFP@graphene) through an *in-situ* pyrolysis and catalytic graphitization process. Glucose and a trace amount of $FeSO_4$ were employed as the graphene source and catalyst precursors, respectively. Under the catalysis of thermally reduced iron nanoparticles (Fe NPs), nanometer-size graphene sheets were *in-situ* grown on the LFP surface through the realignment of carbon fragments aroused from the pyrolysis of glucose. The graphene sheets not only form a compact and uniform coating layer along the LFP surface, but also stretch out and cross-link into a conducting network around the LFP particles. Therefore, the electrochemical performance of the mono-dispersed quasi-hexahedral LFP NPs obtained from a hydrothermal process is remarkably improved with the assistance of the graphene decorating. To the best of our knowledge, this is the first report about synthesizing graphene decorations for cathode materials using *in-situ* technique at low synthesis temperature. This low-cost and effective graphene surface decorating technique can be applied as a general strategy for more electroactive composite materials used in energy storage devices.

2. Experimental

2.1. Synthesis of LFP NPs and LFP@graphene composite

LFP NPs were synthesized through an optimized hydrothermal method. The starting materials of $FeSO_4 \cdot 7H_2O$ (AR grade), H_3PO_4 (85 wt%) and $LiOH \cdot H_2O$ (AR grade) were used as received. First, 0.25 mol $LiOH \cdot H_2O$ and 0.083 mol H_3PO_4 were dissolved into 150 mL de-ionized water under magnetic stirring. Then, 0.83 mol $FeSO_4$ aqueous solution was added to the $LiOH/H_3PO_4$ solution. The molar ratio of Li:Fe:P was kept at 3:1:1. After stirring for 30 min under an argon gas, the resulting mixture was transferred into a 500-mL-capacity Teflon-lined stainless steel autoclave. The sealed autoclave was then placed into a 200 °C oven for 10 h. Subsequently, the autoclave was cooled down to room temperature and the resulting gray white precipitate (LFP powder) was filtered with de-ionized water and ethanol several times. Finally, the obtained powder was dried at 120 °C in vacuum for 2 h.

To prepare the LFP@graphene composite, D-(+)-glucose ($C_6H_{12}O_6 \cdot H_2O$, AR grade) and $FeSO_4 \cdot 7H_2O$ were chosen as the carbon source and the catalyst precursor, respectively. LFP NPs (1.58 g) were firstly mixed with $FeSO_4 \cdot 7H_2O$ and D-(+)-glucose, and the mole ratio between LFP and $FeSO_4$ varied from 50:1 to 500:1 while the mass ratio between LFP and carbon contained in glucose was kept at 95:5. After careful grinding, 100 mL Milli-Q (Millipore) water was put into the mixture. Under vigorous stirring, the mixture was heated at 100 °C till the water was completely evaporated. The dried mixture was put into a quartz boat and then transferred into the center of a tube furnace with the protection of Ar/H_2 (95:5) atmosphere. The furnace was heated up to 750 °C at the rate of 5 °C min^{-1} and held at this temperature for 6 h. After cooling down to room temperature, the as-prepared composites were used as the cathode material without further purification. As a reference, conventional LFP@amorphous carbon (LFP@AC) was synthesized under the same processing conditions in the absence of $FeSO_4 \cdot 7H_2O$ catalyst precursor.

2.2. Structural characterization

The percentage (wt%) of carbon (including amorphous carbon and graphene) in the as-prepared composites was estimated using a high-precision thermogravimetric analysis system (TG/DTA 7300, SII Nano Technology Inc., Shanghai) in a dry flowing air environment. Morphologies of the materials were observed with scanning electron microscopy (SEM) using a Hitachi S-4700 operated at 15 kV accelerating voltage. Transmission electron microscopy (TEM) micrographs and High-resolution transmission electron microscopy (HRTEM) micrographs were captured on the JEM-2100 instrument at an acceleration voltage of 200 kV. The elemental and structural analysis was identified by X-ray diffraction (XRD, PANalytical X'Pert PRO, Ni-filtered Cu Kα radiation, Netherlands).

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