Electrochimica Acta 231 (2017) 85–93

Contents lists available at ScienceDirect

Electrochimica Acta

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

Dual Layer Coating Strategy Utilizing N-doped Carbon and Reduced Graphene Oxide for High-Performance $LiFePO_4$ Cathode Material

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ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 7 January 2017
Accepted 28 January 2017
Available online 3 February 2017

Keywords:
$LiFePO_4$nanoplates
polydopamine
reduced graphene oxide
nitrogen-doped carbon
rate performance

ABSTRACT

Lithium iron phosphate ($LiFePO_4$, LFP) has two major drawbacks such as low lithium ion diffusivity and poor electric conductivity, which limit the wider application as a cathode material for lithium ion batteries. In this work, we report a dual carbon layer coating strategy for LFP, which uses polydopamine-derived nitrogen-doped carbon (N-doped carbon) and reduced graphene oxide (RGO). These dual carbon layers are prepared by a one-pot polymerization process and thermal treatment. The dual carbon coated LFP has a rate capability with a discharge capacity of 98 mAh/g at 30C, cycling performance with a discharge capacity of 115 mAh/g at 10C, and 96.18% capacity retention after 700 cycles. The high rate performance and the excellent long-term cycling stability can be attributed to the enhanced electric conductivity with N-doped carbon coating, the well-connected electron pathway, and the fast Li^+ ion diffusion induced by the small size of the particles. Consequently, coating of LFP with polydopamine derived N-doped carbon and RGO produces a material suitable for high-performance lithium-ion batteries.

1. Introduction

$LiFePO_4$ has attracted considerable attention as a promising cathode material for lithium ion battery (LIB) since the pioneering report by Padhi et al. [1] $LiFePO_4$, a low cost and nontoxic material, has excellent thermal stability, a high theoretical capacity (170 mAh g^{-1}), an acceptable operation potential (3.4 V *vs.* Li^+/Li) along with its abundant precursors [2–4]. Consequently, many reports on the use of $LiFePO_4$ in large-scale energy storage devices, such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and energy storage systems, have been made [5,6]. Nevertheless, $LiFePO_4$ is not fully utilized in high-performance applications because of its intrinsic drawbacks such as low electronic conductivity ($\sim 10^{-10}$ S cm^{-1}) and Li-ion diffusivity ($\sim 10^{-14}$ cm^2 s^{-1}) [7–9]. To overcome these drawbacks, the use of carbon additives, [10–12] the control of particle size [13–15] and morphology [16–18], and alien ion doping [19,20] have been widely utilized.

For practical use in EV and HEV applications, the rate performance, which depends on fast lithium ion and electron transport in the battery, must be improved [21]. Conductive carbon additives such as amorphous carbon, carbon nanotubes, and reduced graphene oxide (RGO) are commonly added to enhance the electronic conductivity. Another technique to achieve this is particle size reduction [21,22] because small particles have shorter Li-ion and electron diffusion pathways in the solid phase, enhancing the cathode performance of $LiFePO_4$ [23]. However, as the particle size of $LiFePO_4$ powder moves from the micro- to the nanoscale, carbon additives must be added more to connect the active materials, resulting in low loading of active materials. Carbon coating is a good method to enhance the electric conductivity while not lowering the mass loading of active materials. Furthermore, carbon coating can act as a blocking layer between the active material and the electrolyte, preventing unwanted side reactions during the charge/discharge processes [24]; in addition, the carbon coating suppresses particle growth during heat treatment [25].

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http://dx.doi.org/10.1016/j.electacta.2017.01.185
0013-4686/

The properties of carbon coating such as the thickness and crystallinity can affect electrochemical performances. The thin uniform carbon layer can improve the electrochemical performance of LFP significantly because the coating on the $LiFePO_4$ surface can transfer the electrons in all directions during the electrochemical reaction [26]. To achieve a uniform carbon layer, various organic carbon sources, such as citric acid and sucrose, are commonly used [27,28]. Furthermore, most of the carbon layers derived from the organic carbon sources are amorphous carbon, and electrochemical performance is significantly affected by the carbon structure in $LiFePO_4$/C composites [29]. Therefore, the carbon source must be carefully selected to improve electrochemical performance. Dopamine is a well-known, naturally occurring carbon precursor containing catechol and amine functional groups. Polydopamine-derived carbon shows highly graphitic characteristic (nearly 100% sp^2C) [30,31] and produces a highly uniform carbon layer [32]. In addition, dopamine can be easily polymerized to polydopamine on any substrate under weakly basic conditions, and the layer thickness can easily be controlled. These properties make it suitable for electrochemical applications.

However, carbon coating approaches have focused on improving the intrinsic properties of $LiFePO_4$, such as its low electronic conductivity, which, because carbon coated particles are connected in a "point-to-point" mode, is not an efficient way to attain a good rate performance [33,34]. This "point-to-point" mode is not beneficial to fast charge and discharge performance because of the low contact area between $LiFePO_4$ particles. One way to improve rate performance is to increase the interparticle contact area between the carbon coated $LiFePO_4$ particles by using conductive carbon additives. Among the various carbon additives, RGO has attracted attention because of its large specific surface area, excellent electronic conductivity, flexibility, and mechanical strength, favorable properties for increasing interparticle contact area.

Herein, we report a crystalline $LiFePO_4$ nanoplate (LFP NP) that is coated with a dual carbon layer composed of polydopamine-derived nitrogen-doped carbon (NC) and RGO. This coated LFP NP material has an excellent rate performance and long cycling stability, and we believe that polydopamine plays three important roles in this material. First, polydopamine connects the active materials and conductive additives; secondly, it is a thickness-controlled conductive N-doped carbon layer due to amine groups in the dopamine monomer; thirdly, it prevents LFP NP particles from agglomerating during thermal treatment. The RGO layer forms a well-interconnected structure that may enlarge the particle-to-particle contact area, resulting in efficient electron transport pathway between the active materials. Furthermore, the thickness-controlled N-doped carbon layers are not sufficiently thick to impede Li-ion transport, and N-doped carbon layers enhance the electronic conductivity of $LiFePO_4$. Moreover, these dual carbon layers can be prepared easily in a one-pot polymerization and thermal treatment process. To confirm the effect of carbon structural difference of mono- and dual carbon coating on battery performance, we compared the electrochemical performances of $LiFePO_4$ nanoplate@N-doped carbon@RGO (LFP NP@NC@RGO), $LiFePO_4$ nanoplate@N-doped carbon (LFP NP@NC), and $LiFePO_4$ nanoplate@RGO (LFP NP@RGO) composites.

2. Experimental section

Dopamine hydrochloride, Tris-buffer, and lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, 99%) were purchased from Sigma-Aldrich. Phosphoric acid (H_3PO_4, 85%) was purchased from ACROS. Iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%) was purchased from Alfa Aesar. Ethylene glycol was purchased from SAMCHUN. All chemicals were used without further purification.

2.1. Preparation of graphene oxide (GO)

GO was synthesized by a modified Hummers method [35]. Graphite (3 g, Aldrich, <20 microns), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g) were mixed in H_2SO_4 (80 mL). This mixture was stirred at 95 °C for 5 h and then cooled to room temperature, and then deionized water (DI water) was slowly added. The mixture was filtered and dried. Subsequently, pre-oxidized graphite was poured into the H_2SO_4 aqueous solution with stirring and cooling. Then, $KMnO_4$ (15 g) was slowly added to above mixture. Subsequently, H_2O_2 (10 mL, 30 wt%) was added. Finally, the mixture was washed with aqueous HCl (10:1 v/v) and then filtered with DI water. The mixture was then dried, yielding the GO powder.

2.2. Preparation of bare LFP nanoplates (bare LFP NP)

$LiFePO_4$ nanoparticles were prepared by solvothermal synthesis using $LiOH{\cdot}H_2O$ (99%, Sigma-Aldrich), H_3PO_4 85% (Acros), and $FeSO_4{\cdot}7H_2O$ (99% Alfa Aesar) as precursors in the stoichiometric ratio of 2.7:1:1.5, respectively. First, an appropriate quantity of $LiOH{\cdot}H_2O$ was dissolved in ethylene glycol (45 mL, SAMCHUN). Then, H_3PO_4 was added dropwise into the above solution with vigorous stirring. $FeSO_4.7H_2O$ was dissolved in ethylene glycol (30 mL). Subsequently, the $LiOH{\cdot}H_2O$ solution was added into the iron sulfate solution with stirring. The obtained olive green suspension was transferred into a Teflon-lined stainless steel autoclave and then heated at 180 °C for 10 h. After heating, the autoclave was cooled to room temperature. The obtained gray precipitates were washed with EtOH and DI water several times. Finally, the LFP residues were dried in an oven overnight.

2.3. Preparation of LFP nanoplate@N-doped carbon@RGO (LFP NP@NC@RGO) and LFP nanoplate@N-doped carbon (LFP NP@NC)

The as-prepared bare LFP NP powder was dispersed in Tris-buffer solution (10 mM) by sonication. Then, dopamine hydrochloride (3 mg/mL, 200 mL H_2O) was added to the above suspension and stirred for 15 min. Then, graphene oxide suspension (3 wt% in H_2O) was added to the dopamine solution over 10 min. After reacting for 5 min, the suspension of LFP, dopamine, and graphene oxide suspension was washed three times with DI water and dried at 70 °C in an oven for 10 h. The collected $LiFePO_4$ nanoplate@polydopamine@GO composite was calcined at 700 °C for 5 h in Ar-filled Swagelok container to form LFP NP@NC@RGO. For comparison, LFP NP@NC samples were also prepared under the same condition without RGO.

2.4. Preparation of LFP nanoplate@RGO (LFP NP@RGO)

The as-prepared bare LFP NP powder was dispersed in DI water. The graphene oxide suspension (3 wt% in H_2O) was added. The mixture was stirred for 30 min. And then, the suspension of LFP and graphene oxide suspension was filtered and dried at 70 °C in an oven for 10 h. The collected $LiFePO_4$ nanoplate@GO composite was calcined in Ar-filled Swagelok container at 700 °C for 5 h.

2.5. Cell fabrication and electrochemical analysis

The electrode was prepared by mixing the as-prepared active materials, Super P (Timcal, carbon black), and poly(vinylidene fluoride) (PVDF) with *N*-methyl-2-pyrrolidone (NMP, Aldrich) in a weight ratio of 70:15:15. The mixed slurry was spread onto an aluminum foil current collector and dried at 120 °C under vacuum for 10 h. Then, coin type 2016 cell was assembled in an Ar-filled glove box with a lithium foil as the counter electrode and Celgard 2450 membrane was used as the separator. The loading mass of