Journal of Power Sources 304 (2016) 354–359

Contents lists available at ScienceDirect

Journal of Power Sources

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

Direct formation of $LiFePO_4$/graphene composite via microwave-assisted polyol process

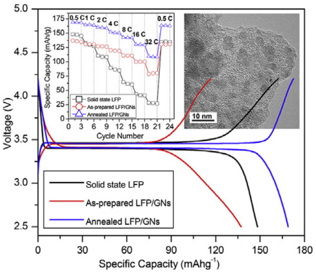
Jinsub Lim [a,1], Jihyeon Gim [b,1], Jinju Song [b], Dang Thanh Nguyen [b], Sungjin Kim [b], Jeonggeun Jo [b], Vinod Mathew [b], Jaekook Kim [b,*]

[a] *Korea Institute of Industrial Technology (KITECH), 6, Cheomdan-gwagiro 208-gil, Buk-gu, Gwangju 500-480, South Korea*
[b] *Department of Materials Science and Engineering, Chonnam National University, 300 Yongbongdong, Bukgu, Gwangju 500-757, South Korea*

HIGHLIGHTS

- One-step synthesis of $LiFePO_4$ particles and graphene nanosheets simultaneously.
- Microwave-assisted polyol reaction directly produces LFP/GNs composite cathode.
- The LFP/GNs cathode exhibited enhanced electrochemical properties versus lithium.
- The study offers opportunities to produce graphene based composite electrodes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 August 2015
Received in revised form 3 November 2015
Accepted 18 November 2015
Available online 6 December 2015

Keywords:
Lithium ion battery
Nanocomposite cathodes
Graphene nanosheets
Microwave-assisted polyol synthesis
Electrochemistry

ABSTRACT

The present study reports on the direct synthesis of $LiFePO_4$ nanoparticles and graphene nanosheets to form a composite cathode (LFP/GNs) in a one-step microwave-assisted polyol reaction. The polyol reaction induced by microwave irradiation for a few minutes produces nanocrystalline LFP and graphene nanosheets simultaneously from lithium, iron and phosphorus and carbon (5 wt% of graphite oxide) sources, respectively, used as starting precursors. Powder X-ray diffraction (XRD), electron microscopy, and atomic force microscopy (AFM) studies on microwave-reacted sample obtained using just graphite oxide confirms the formation of graphene nanosheets separately. Whereas, electron microscopy studies on the LFP/GNs composite reveals that olivine nanoparticles of average sizes ranging between 5 and 20 nm are well-dispersed on the graphene nanosheets. Electrochemical measurements reveal that the $LiFePO_4$/GNs nanocomposite cathodes registered enhanced discharge capacities (79 and 108 mAh g^{-1} for the as-prepared and annealed composite cathodes, respectively) at 32 C rates with good capacity retention capabilities. The AC impedance measurements confirm that the enhanced cathode properties of the LFP/GNs nanocomposite are ascribed to the improved electronic conductivity of the graphene nanosheets and the nano-sized particles. The slightly better electrochemical properties of the annealed LFP/GNs are attributed to its higher crystallinity.

1. Introduction

The growing market of electric transportation systems including hybrid, plug-in hybrid, and pure electric vehicles has undoubtedly accelerated the research on Li-ion batteries (LIBs) as an efficient energy storage device for renewable green energy. To satisfy the

---

[*] Corresponding author.
E-mail address: jaekook@chonnam.ac.kr (J. Kim).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2015.11.069
0378-7753/

demands of high energy/power density LIBs in this emerging commercial market, significant research efforts to upgrade its components viz., the cathode, anode, electrolyte, and separator is required to be undertaken. In particular, the development of high capacity cathodes with great thermal stability remains essential for long-distance electric vehicles in the near future. In this regard, olivine-type $LiFePO_4$ has been intensively investigated as a cathode material because it is not only inexpensive, nontoxic and environmentally benign, but also has a relatively high theoretical capacity of 170 mAh g^{-1} and a suitably flat voltage-region of 3.4 V within the electrolyte window. Despite these advantages, $LiFePO_4$ suffers from intrinsic limitations, such as a low electronic conductivity and Li ion diffusion rates across the $LiFePO_4/FePO_4$ interface. To surmount these drawbacks, various attempts including the deposition of a carbon coating on the surface of the olivine particles [1], mixing with conducting materials such as carbon [2], graphene [3] and polymers [4], partial cation substitution in the Li or transition metal sites [5], reducing particle size [6,7], and customizing particle morphologies [8–12] have been attempted. Among these strategies, the nanocomposite cathode comprised of olivine and graphene nanosheets shows improved electronic conductivity and hence results in better high rate performance. Obviously, graphene is intensively attractive for a variety of applications including fuel cells [13], rechargeable batteries [14] and solar cells [15] because of its excellent electrical, mechanical, optical, and thermal properties [16–20]. In specific, 2-Dimensional graphene nanosheets (GNs) tends to contribute to higher electrical conductivities due to the unique geometrical dimension that offers a favored path for the rapid flow of electrons and therefore aid in the energy storing capabilities of electrode hosts in LIBs. Recent literature reports improved electrochemical properties during Li-insertion/de-insertion in $LiFePO_4$-graphene nanocomposite cathodes containing single layer carbon sheets formed via co-precipitation [3], solvothermal [21–23], microwave [24,25] and spray drying [26]. However, all the reported methods have either adopted two-step approaches or have maintained high pressure/temperature during reaction in order to obtain homogeneous LFP/GNs. Our previous work showed that monodispersed $LiFePO_4$ nano-rods directly synthesized by microwave-assisted polyol process under a few minutes without any post heat treatments exhibited high reversible discharge capacities (~161 mAh g^{-1}) with excellent capacity retention until 100 cycles [27]. In this reaction, microwave energy plays the roles of a heating source whereas the polyol solvent serves as a suitable microwave irradiation susceptor because of its high permanent dipole and thereby results in the rapid heating of the solution and the subsequent formation of nanocrystalline $LiFePO_4$. Therefore, the simultaneous utilization of the high microwave energy and the reducing environment of polyol to directly synthesize $LiFePO_4$/Graphene nanocomposites remain significant.

In the backdrop of these considerations, the present work reports on the direct one-step formation of a $LiFePO_4$/graphene nanocomposite via a polyol reaction induced by microwave absorption. The highlight of this study is that simultaneous synthesis of LFP and graphene is achieved by the polyol reaction induced by the microwave absorption for a few minutes. The physical, chemical and electrochemical properties of the prepared sample were investigated by powder X-ray Diffraction, high resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), elemental analysis, impedance measurement, and galvanostatic tests.

2. Experimental section

2.1. Synthesis

Synthesis of Graphite oxide: Initially, graphite oxide was prepared by the oxidation of graphite using a modified Hummers method [28]. In brief, natural graphite powder (1 g, Daejung Chemical) was treated with 40 ml of HNO_3 aqueous solution (64–66%, Duksan Reagents) and 60 ml of H_2SO_4 aqueous solution (95%, Daejung Chemical) in an ice water bath maintained at 0 °C. After magnetic stirring for 20 min, 5 g of $KMnO_4$ (extra pure, Junsei Chemicals) was gradually added and reacted for 2 h. Then, 200 ml of deionized water and 5 ml of H_2O_2 aqueous solution (30%, Daejung Chemical) were added to the system, followed by washing with 15 ml of HCl aqueous solution (35%, Daejung Chemical). The resulting solid was dried in an oven at 60 °C for 24 h and thereafter stirred with deionized water for 2–3 h (pH 6–7). Graphite oxide powder was finally obtained after ultrasonication, washing with deionized water and drying.

Synthesis of $LiFePO_4$/Graphene Nanocomposite: The $LiFePO_4$/graphene nanocomposite was synthesized by microwave-assisted polyol method. Fe-acetate [$Fe\text{-}(CH_3COO)_2$], phosphoric acid (H_3PO_4) and Li-acetate ($Li–CH_3COO$) weighed out to corresponding molar stoichiometric composition of 1:1:1, respectively, were dissolved in a polyol medium of TTEG (tetraethylene glycol). In specific, a slightly extra amount (~3 wt%) of the lithium precursor was taken to compensate for anticipated lithium evaporation at elevated temperatures. 5 wt% of graphite oxide (GO) was added to the precursor solution and the resulting solution was treated by ultrasonication for 10 min to ensure a homogeneous dispersion. After stirring for 3 h, the resulting mixture was then heated at moderate temperatures (~300 °C) for close to 20 min in a conventional microwave oven (1000 W, 2450 MHz). Precaution need to be taken during the reaction as rapid solution evaporation occurs followed by the release of exothermic energy and subsequent formation of precipitated powders in solution. The precipitate obtained was washed and filtered by using ceramic membrane funnels with acetone and methanol several times in order to ensure the removal of residual organic matters. The filtered powder was dried at 120 °C for 12 h in a vacuum oven for moisture evaporation. The as-prepared sample was then dried and annealed at 600 °C for 12 h under H_2/Ar (5:95, v/v) atmosphere to obtain a highly crystalline sample.

2.2. Structural and physical characterization

Powder X-ray Diffraction: Powder X-ray diffraction (XRD) patterns of the prepared samples were measured using Shimazu X-ray diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 30 mA within the scanning angle, 2θ, range of 10–80° in steps of 0.02°.

High Resolution TEM: The particle morphologies and sizes were determined by high resolution transmission electron microscopy (HR-TEM). The TEM pictures were recorded using an FEI Tecnai F20 at the Korea Basic Science Institute (KBSI, Gwangju center) at 200 kV.

AFM: The sample for AFM imaging was prepared by depositing colloidal suspensions of graphene and NMP (*N*-Methyl-2-pyrrolidone) solution on a pre-cleaned and silanized 1×1 cm silicon wafer. The silanization process of silicon wafer has been reported earlier [29]. The prepared silicon wafer substrate was immersed into graphene dispersed suspension (50 μg ml^{-1}) for 10 s followed by air-dried treatment. AFM images were taken by non-contact mode using silicon/aluminum coated cantilevers (PPP-NCHR 10, Park systems). All images were collected under ambient conditions with the scan size of 5×5 μm and a scanning raster rate of 247.26 kHz.

CHN Analysis: The amount of graphene in the samples was analyzed using an elemental analyzer (EA-1110, Thermo Quest, Italy).

RAMAN Spectroscopy: Raman spectroscopy measurements were conducted using a JASCO Laser Raman Spectrometer NRS-5100 series (KBSI, Gwangju center), with an excitation laser wavelength of 532 nm, at a power density of 5.6 mW cm^{-2}.