Journal of Power Sources 347 (2017) 29–36

Contents lists available at ScienceDirect

Journal of Power Sources

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

A simple route to improve rate performance of $LiFePO_4$/reduced graphene oxide composite cathode by adding Mg^{2+} via mechanical mixing

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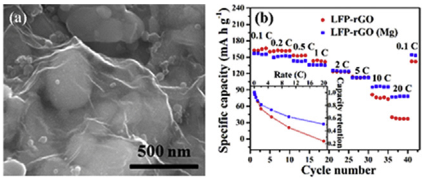
HIGHLIGHTS

- Adding Mg^{2+} alone into LFP results in little improvement of rate performance.
- Introducing rGO to LFP results in moderately increased capacity at high rate.
- Adding Mg^{2+} into LFP/rGO cathode brings significantly improved rate performance.
- Enhanced reduction of Fe^{2+} to Fe^0 occurs in simultaneous presence of Mg^{2+} and rGO.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 September 2016
Received in revised form
8 February 2017
Accepted 12 February 2017

Keywords:
Mg^{2+}
Reduced graphene oxide
$LiFePO_4$
Li-ion battery
Rate performance

ABSTRACT

Introducing Mg^{2+} to $LiFePO_4$ and reduced graphene oxide composite via mechanical mixing and annealing leads to largely improved rate performance of the cathode (e.g. ~78 mA h g^{-1} at 20 C for $LiFePO_4$ and reduced graphene oxide composite with Mg^{2+} introduction vs. ~37 mA h g^{-1} at 20 C for $LiFePO_4$ and reduced graphene oxide composite). X-ray photoelectron spectroscopy unravels that the enhanced reduction of Fe^{2+} to Fe^0 occurs in the simultaneous presence of Mg^{2+} and reduced graphene oxide, which is beneficial for the rate capability of cathode. The simple fabrication process provides a simple and effective means to improve the rate performance of the $LiFePO_4$ and reduced graphene oxide composite cathode.

1. Introduction

$LiFePO_4$ (LFP) is one of the most promising cathode materials for lithium ion batteries (LIBs), due to its abundant material supply with its high theoretical capacity (170 mA h g^{-1}), low cost, good environmental compatibility, and excellent safety [1–3]. Nevertheless, it suffers from low rate capability mainly due to its low electronic conductivity [2–5].

Many attempts have been made to tackle this problem, including conductive surface coating on LFP particles [4], cation

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http://dx.doi.org/10.1016/j.jpowsour.2017.02.043
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doping of LFP [6–8], reduction of LFP size [9], and addition of conductive additive into the electrode [10], etc. Introducing conductive materials to the LFP cathode has been commonly employed in preparing the LFP based cathode. Among various choices of conductive materials, graphene based materials are the most promising. Reduced graphene oxide (rGO) is cheap and easy to process with LFP to form composite electrode by mechanical mixing [10], hydrothermal reaction [11] or electrophoresis [12]. The LFP/rGO electrodes indeed exhibit superior rate capability to those of the conventional LFP electrodes (e.g., ~82 mA h g^{-1} at 10 C for LFP/rGO composite vs. ~60 mA h g^{-1} at 10 C for conventional LFP electrodes [12]). On the other hand, doping of Mg^{2+} into the LFP lattice has also been found to be beneficial for the rate capability of the LFP cathode [7]. It has been theoretically suggested that Mg^{2+} taking the substitutional site of Fe^{2+} in LFP can effectively improve the electronic conduction and ionic conductivity of the LFP [13]. Experimentally, improved electronic and ionic transport properties of LFP crystals has been found in Mg^{2+} doped mesoporous carbon-coated LFP nanocrystals, in which the Mg^{2+} doping is suggested by X-ray diffraction (XRD) and Rietveld refinement data [7].

In the present work, we show that introducing Mg^{2+} and rGO to LFP together via simple mechanical mixing and annealing leads to largely improved rate performance of the cathode, while adding Mg^{2+} or rGO alone results in little, or moderate performance (specific capacity) improvement of the same cathode, respectively. We discover that the additional improvement on rate performance of the LFP cathode (with Mg^{2+} and rGO) results from the enhanced reduction of Fe^{2+} to Fe^0 in the simultaneous presence of Mg^{2+} and rGO, rather than having Mg^{2+} doped into the LFP lattice. Our work provides a simple method that effectively improves the rate performance of the LFP/rGO cathode without disturbing the growth process of the active materials.

2. Experimental

2.1. Preparation of the LFP (Mg), LFP-rGO, LFP-rGO (Mg) composite

The commercial LFP powders (Advanced Lithium Electrochemistry Co., Ltd., Taiwan) were employed for the preparation of cathode electrode. LFP was dispersed in isopropyl alcohol (IPA) by sonication for 3 h, followed by adding $Mg(NO_3)_2 \cdot 6H_2O$ (LFP/Mg mass ratio 130/1). After drying, the powders were collected and annealed at 700 °C for 1 h under H_2 (volume 10%)/Ar atmosphere. The annealed LFP powders without adding $Mg(NO_3)_2 \cdot 6H_2O$ were also prepared following the same procedure for comparison.

The graphene oxide (GO) was prepared using the modified Hummers method [14]. The LFP powders and GO were dispersed in IPA by sonication for 3 h, respectively. Then they were mixed, followed by adding different amount of $Mg(NO_3)_2 \cdot 6H_2O$. The mixture was stirred for 1 h after 1hr ultrasonic dispersion. After drying, the composite were collected and annealed at 700 °C for 1 h under H_2 (volume 10%)/Ar atmosphere. The LFP/rGO composite without adding $Mg(NO_3)_2 \cdot 6H_2O$ was also prepared following the same procedure for comparison.

2.2. Structure and morphology characterization

The morphologies and compositions of the samples were characterized by a field emission scanning electron microscope (FESEM, Quanta 200, FEI). Transmission electron microscopy (TEM) was also carried out for more detailed structure analysis using a Tecnai F20 (FEI) microscope operating at 200 kV. The crystallinity and phases of the samples were examined by XRD (SmartLab, Rigaku) with a Cu-Ka radiation source ($d = 0.1541$ nm). Raman analysis was performed using a Micro Raman spectrometer (RM-1000, Renishaw Co., Ltd.) with a 10 mW helium/neon laser at 514 nm. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250) with a monochromatic Al Kα radiation source was used to investigate the elemental composition of composite and its binding state. The binding energy scale of the instrument was calibrated using Ar peak (242.1 eV). Thermal gravimetric analysis (TGA, Perkin-Elmer) was employed to quantify the amount of rGO in the LFP/rGO composite.

2.3. Electrochemical characterization

The electrochemical properties of the LFP/rGO composite were characterized by using CR2032 coin-type cells with Li foil as a counter electrode. The liquid electrolyte was 1.0 M $LiPF_6$ in the mixture of 1:1 (by volume) ethylene carbonate and diethyl carbonate (Novolyte Co.). The final cell was composed of 87 wt% LFP/rGO powder with Mg^{2+} (including 7 wt% rGO, total amount of LFP and Mg kept at ~80 wt%), 3 wt% acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) binder pasted on carbon cloth. As a comparison, conventional cells, consisting of 80 wt% annealed LFP powder or LFP (Mg), 10 wt% acetylene black, and 10 wt% of PVDF binder pasted on carbon cloth were prepared. Galvanostatic charging/discharging cycles were tested between 2.5 and 4.2 V vs. Li^+/Li at different rates on a multichannel battery test system (CT2001A, Wuhan Kingnuo Electronic Co., Ltd.). The electrochemical impedance spectroscopy (EIS) of the batteries was tested in the frequency range from 100 kHz to 2 Hz under an alternating current (AC) stimulus with a 5 mV of amplitude (CHI 660C, Shanghai Chenhua Instrument Co., Ltd.).

3. Results and discussions

3.1. Structure characterizations and electrochemical properties of LFP and LFP (Mg) sample

We first compare the LFP sample with or without Mg^{2+} introduction. rGO is not introduced to such samples. Commercial LFP powder with (LFP/Mg mass ratio of 130/1) or without Mg^{2+} is annealed before it is made into electrode. The two samples are denoted as LFP and LFP (Mg), respectively. The general morphology and crystal structure of the two samples are similar, and here we show the results of a representative one, i.e. LFP (Mg). The characterization of LFP is shown in Fig. S1 (Supporting Information).

The morphology of the LFP (Mg) powder is examined by SEM (Fig. 1(a)). The size of quasi-spherical particles ranges from 50 to 700 nm (with an average size of ~273 nm, Fig. 1(b)). Its crystallinity is examined using XRD and the result is shown in Fig. 1(c). All Bragg peaks can be indexed to the orthorhombic LFP phase. No additional peak or peak shifting is observed. Detailed structural characterization of the LFP (Mg) sample is carried out using TEM. High resolution TEM image taken from the surface region of LFP particle (Fig. 1(d)) discloses an amorphous carbon layer of ~3–4 nm coated on the LFP surface. The spatial distribution of the compositional elements is revealed by EDX elemental mapping (Fig. 1(e)–(k)), showing rather uniform distribution of the compositional elements.

The effect of adding Mg^{2+} on the electronic structure of LFP crystals is investigated by XPS. Fig. 2(a)–(c) compare the typical O 1s, P 2p, and Fe 2p spectra of LFP and LFP (Mg) samples. Fitting of the O 1s XPS spectra (Fig. 2(a)) shows peaks located at around 530.65, 531.50, and 532.60 eV, which are attributed to chemical shifts from Fe-O, P-O, and adsorbed OH^- [15]. The P 2p spectra in Fig. 2(b) shows single peak located at 133.2 eV, which is attributed to P^{5+} state resulting from the PO_4^{3-} group [16]. It can be seen that the Fe 2p spectra is split into $2p_{3/2}$ at ~710.0 eV and $2p_{1/2}$ at