



The important role of adipic acid on the synthesis of nanocrystalline lithium iron phosphate with high rate performance

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ARTICLE INFO

Article history:

Received 17 November 2009
Received in revised form 15 January 2010
Accepted 21 January 2010
Available online 1 February 2010

Keywords:

Adipic acid
LiFePO₄
Nanocrystalline material
Carbon coating
Rate capability

ABSTRACT

A simple, low-cost, adipic acid-assisted, solid-state method was used to prepare carbon-coated, nanocrystalline LiFePO₄ material. Scanning electron microscopy (SEM) images revealed that the majority of the particles lay between 200 and 400 nm for pure LiFePO₄, while the carbon-coated LiFePO₄ particles were sized from 70 to 250 nm. Cycling studies indicated a high and stable discharge capacity of 150 mAh g⁻¹ for the Li/carbon-coated nanocrystalline LiFePO₄ at room temperature. High rate capability studies from 0.5C to 20C demonstrated an excellent capacity retention efficiency of over 99.9%.

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1. Introduction

Since the pioneering work of Padhi et al. [1], LiFePO₄ has proffered several unique advantages over conventional cathode materials such as LiCoO₂, LiNiO₂, and LiMn₂O₄ with respect to cost effectiveness, environmental soundness, and thermal stability in the charged state. In addition, a high theoretical capacity (170 mAh g⁻¹) and very flat potential window located at ~3.4 V that were achieved through inductive effects are also appealing [2]. However, LiFePO₄ suffers the disadvantages of low electronic conductivity and sluggish Li⁺ ion diffusion kinetics across LiFePO₄/FePO₄ interfaces given its intrinsic character, resulting in a reversible capacity loss at high current rates [3]. The poor rate performance of LiFePO₄ thereby complicates its use in high-power-density batteries.

As such, focus upon improving the rate performance of LiFePO₄ materials is the basic premise of current research. Two procedures have been implemented to circumvent the aforementioned setbacks: reduction of grain size of the active particles, which would lead to a suppression of the diffusion lengths for both electrons and ions, and use of surface-modified LiFePO₄ with a conductive matrix such as carbon [2–5]. Carbon coating is an effective route to improve the electrochemical performance of LiFePO₄ and avoid the formation of Fe³⁺. Recently, Zhang et al. [6] reported the synthesis of composite LiFePO₄ that achieved a discharge capacity

of ~142 mAh g⁻¹ by ball milling and subsequent heat treatments. Furthermore, this synthetic procedure required additional carbon materials, including amorphous and graphitized carbons as well as a complex agent. This method also leads to the formation of inactive Fe₂P and FeP₂ phases from the reduction of Fe and P, consequently reducing the electrochemical performance of the cell during prolonged cycles [6,7].

Recently, we firstly reported the synthesis and electrochemical characterization of LiFePO₄ material prepared by an adipic acid-assisted, simple sol–gel method [8]. This Li/LiFePO₄ cell showed a high initial discharge capacity of more than 150 mAh g⁻¹ at 1C as well as good cycleability at a high current density of over 30C without any additional treatment, such as carbon coating, or the use of additives or ball milling, to improve the cycle performance. During this study, we found that adipic acid plays a very effective role in forming a nanocrystalline LiFePO₄ as a carbon source and as a chelate agent.

In this study, we used adipic acid in the grinding process with various starting materials to produce nanocrystalline LiFePO₄ particles by solid-state method. Adipic acid is very cheap and affords effective control of the particle size, thereby obviating the need for further treatment for carbon coating. We report the synthesis and electrochemical characterization of LiFePO₄ material prepared by an adipic acid-assisted, simple solid-state method without any additional treatment to improve the battery performance.

2. Experimental

Using a conventional solid-state method, nanocrystalline LiFePO₄ materials were synthesized from the following high-purity starting materials: Li₂CO₃;

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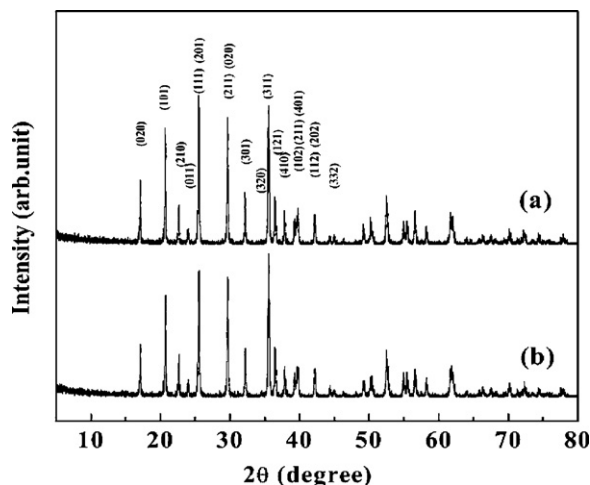


Fig. 1. Powder XRD patterns of (a) pristine and (b) carbon-coated LiFePO_4 .

$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{HPO}_4$; $\text{C}_6\text{H}_{10}\text{O}_4$ (Sigma–Aldrich, USA). Stoichiometric amounts of starting materials without and with adipic acid (molar ratio of adipic acid to total metal ions was 0.1) were used for the LiFePO_4 and carbon-coated LiFePO_4 synthesis, respectively. Initially, the starting materials were finely ground using a mortar and precalcined at 400°C for 3 h. The resulting compound was again finely ground using a mortar and fired at 670°C for 5 h under an Ar atmosphere to obtain nanocrystalline LiFePO_4 .

Structural studies were performed using powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) under $\text{Cu K}\alpha$ radiation. The carbon content of the synthesized LiFePO_4 particles was determined using an elemental analyzer (CHN Flash EA series, CE Instruments, Italy). Surface morphological features of the olivine phase materials were observed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Particle size distribution was analyzed through a dynamic light scattering (DLS) system (DLS-7000(AL), Otsuka Electronics, Japan). The internal structure of the samples was observed by transmission electronic microscopy (TEM, TECNAI, Philips, Netherlands). The composite cathode was fabricated with 20.0 mg of accurately weighed active material, 3.0 mg of Ketzen black, and 3.0 mg of conductive binder (2.0 mg of teflonized acetylene black and 1.0 mg of graphite), which was pressed on a 200 mm^2 stainless steel mesh, serving as the current collector, under a pressure of 300 kg cm^{-2} and dried at 130°C for 5 h in an oven. The cell (CR2032) was composed of a cathode and a metallic lithium anode separated by a porous polypropylene film (Celgard 3401). A mixture of 1.0 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v, Techno Semichem Co., Ltd, Korea) was used as the electrolyte solution. The current density of the charge and discharge cycles was 0.1 mA cm^{-2} with a cut-off voltage of 2.8–4.0 V. The cycling test was also conducted at the same test condition with various current densities (0.1C–20C) at room temperature.

3. Results and discussion

Fig. 1 shows the powder XRD pattern of LiFePO_4 and carbon-coated LiFePO_4 (hereafter designated C- LiFePO_4) olivine phases prepared by the solid-state method. Both materials exhibited a well-crystallized orthorhombic structure with a $pnma$ space group. The observed patterns were in excellent agreement with the JCPDS card No. 40-1499 and were indexed accordingly. Further, the

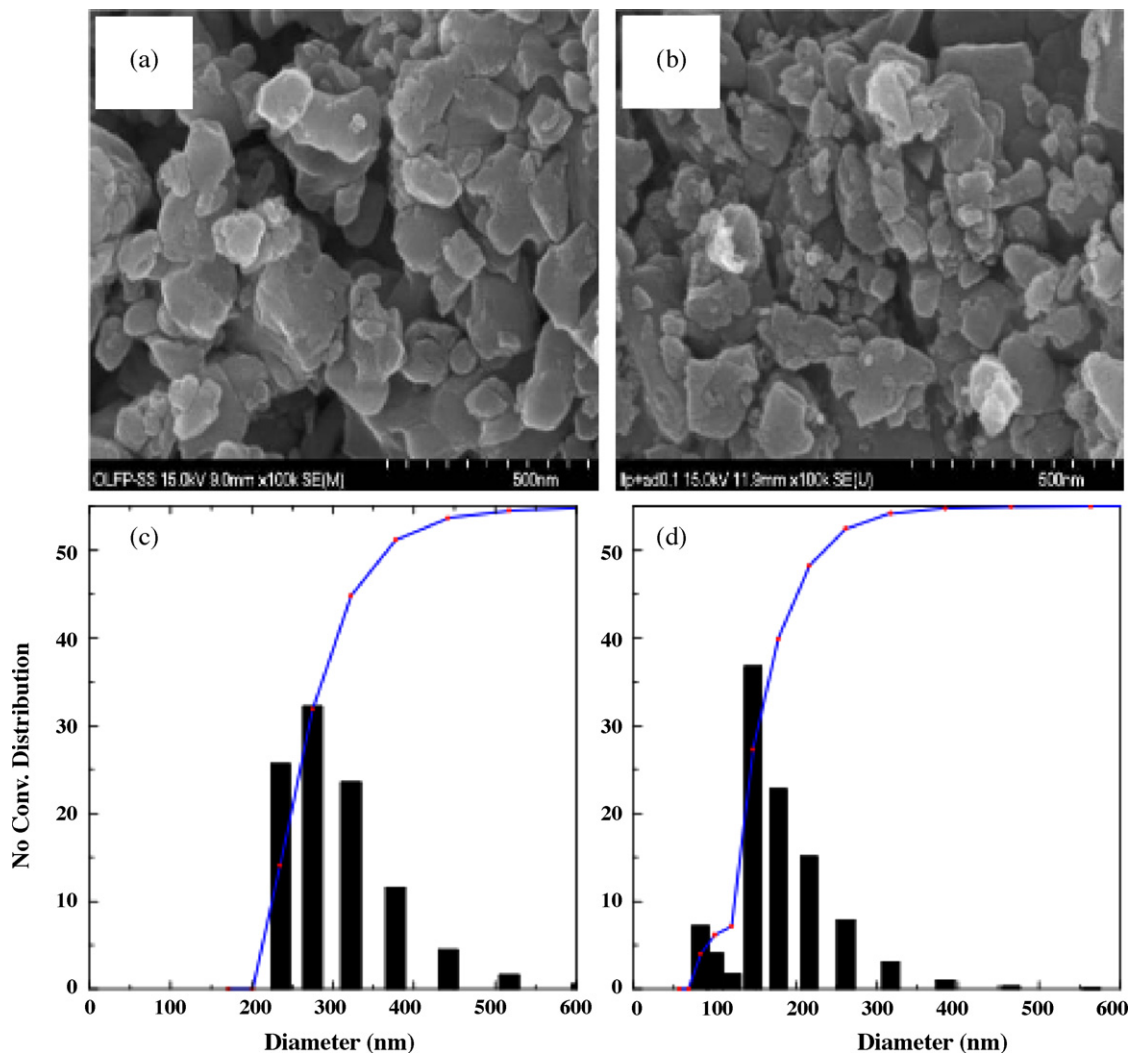


Fig. 2. Particle morphology and size distribution plots of (a and c) pristine and (b and d) carbon-coated LiFePO_4 .

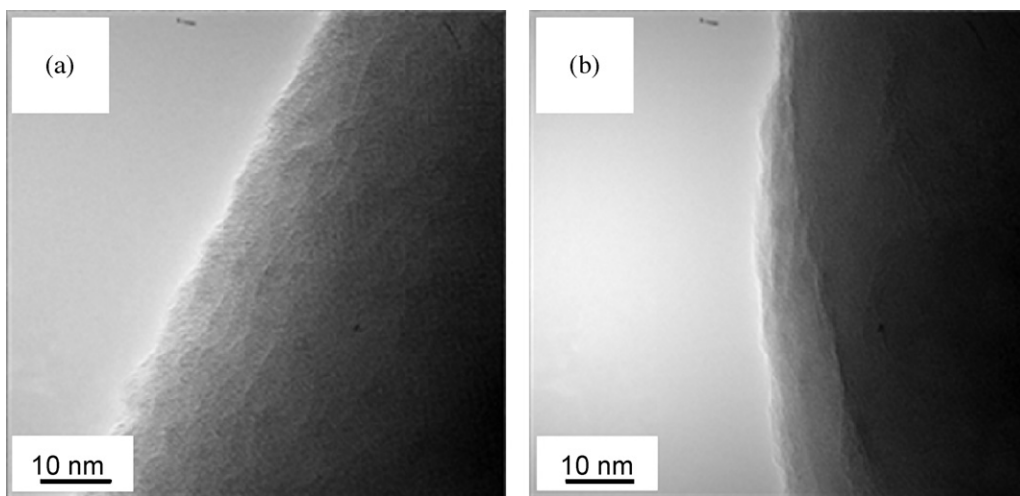


Fig. 3. TEM pictures of (a) pristine and (b) carbon-coated LiFePO₄.

absence of impurity phases within the Li₃PO₄ and metal phosphides (Fe₂P, FeP) revealed the phase purity of the prepared material [9]. To ensure purity of the prepared materials, the following lattice parameters were also calculated: $a = 10.347 \text{ \AA}$, $b = 6.019 \text{ \AA}$, and $c = 4.699 \text{ \AA}$ for pure LiFePO₄, and $a = 10.339 \text{ \AA}$, $b = 6.011 \text{ \AA}$, and $c = 4.663 \text{ \AA}$ for C-LiFePO₄. Saravanan et al. [10] reported a similar variation in lattice parameter values for both thin and thick LiFePO₄ nanoplates. Calculated lattice parameter values compared well with those reported in the literature [11].

SEM images and DLS experiments yielded the particle morphology and size distribution of the prepared olivine phase materials, as shown in Fig. 2. The majority of the particles were between 200 and 400 nm for pure LiFePO₄, and between 70 and 250 nm for the C-LiFePO₄ particles. The drastic reduction in particle size was attributed to the inclusion of adipic acid during the synthesis process, as it is converted into carbon material and coats the active particles during the calcination process. The carbon content of LiFePO₄ and C-LiFePO₄ is 0.26 and 0.92 wt.%, respectively. Coating with such carbon effectively controls the size and hinders the agglomeration of the particles, thereby reducing the grain size of the LiFePO₄ particles [10].

Fig. 3 shows the TEM images of the two materials in order to determine the extent of the carbon coating on the LiFePO₄ surface. It is apparent that a well pronounced coating layer, derived from the carbonization of adipic acid during the calcination process, was coated onto the surface of the LiFePO₄ particles. With a thickness of less than 10 nm, this coating layer of carbon would have improved the electrochemical performance of the cell and was well correlated with a previous report [12].

Fig. 4(a) presents the cycling performance of the olivine phase materials at room temperature. The current density of the charge and discharge cycles was 0.1 mA cm^{-2} with a cut-off voltage of 2.8–4.0 V. Initial discharge capacities of 127 and 145 mAh g⁻¹ were observed for pure LiFePO₄ and C-LiFePO₄, respectively. In the latter, an increasing capacity trend was observed for the first few cycles, after which the Li/C-LiFePO₄ cell delivered a stable discharge behavior (150 mAh g⁻¹) with negligible amounts of variation. In the former, continuous capacity fading resulted. This improved performance was ascribed to the effect of the carbon coating on the LiFePO₄ surface in ensuring a good electronic contact between the active small particles [3]. Previous reports have offered three reasons to explain the poor performance of pure LiFePO₄: (i) dissolution of Fe²⁺ in the conventional electrolyte, due to the presence of HF [13,14]; (ii) an ion exchange reaction between H⁺ and Li⁺, originating from the oxidation of solvents (EC and DMC), as

well as a solid electrolyte interphase [14,15]; (iii) the reaction between LiFePO₄ and HF that leads to the formation and dissolution of H₃PO₄, slowing down the motion of the Li⁺ ions during the cycling process [14]. In C-LiFePO₄, the effective and protective coating of carbon precludes the unwanted and harmful side reaction with HF and, as such, enhances the behavior of the cell. Compared to Zhang et al., this is one of the best results obtained by solid-state synthesis without any additional treatments like ball milling or addition/treatment of carbon or graphite [6,7].

In order to establish the high rate performance of the Li/LiFePO₄ and C-LiFePO₄ cells, they were subjected to different current densities from 0.5C to 20C, Fig. 4(b). The C-LiFePO₄ cell exhibited excellent capacity retention as it delivered discharge capacities of 139 and 81 mAh g⁻¹ for 0.5C and an extremely high 20C rate. Furthermore, the cell retained its capacity with 99.9% efficiency even as the current rate was again changed over to 0.5C and repeated as a cycle. However, the original LiFePO₄ material exhibited a very

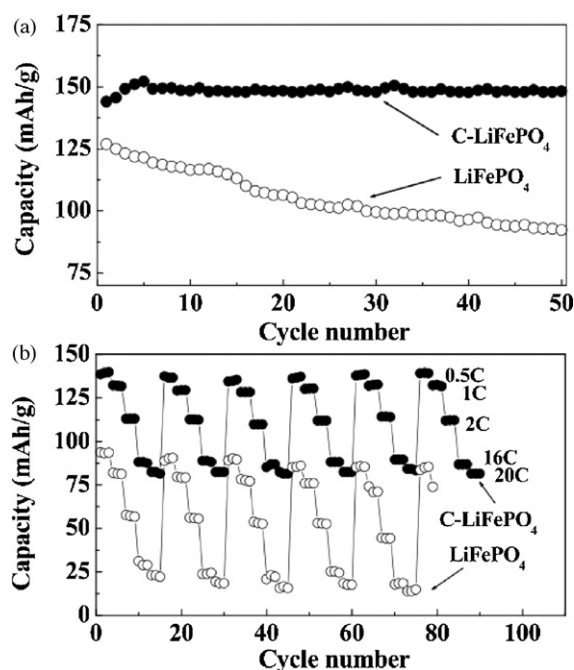


Fig. 4. Cycling performance of (a) Li/LiFePO₄ and carbon-coated LiFePO₄ and (b) rate capability studies of a Li/LiFePO₄ and carbon-coated LiFePO₄ cells.

small discharge capacity depending on the increase of current density when compared to carbon-coated LiFePO₄. Although, Fey et al. [16] also reported the synthesis of LiFePO₄ using adipic acid with improved battery performance. However, there is no optimization on the adipic acid based solid-state route is described, which results poor performance of the cell. Herein, we optimized the adipic acid content (0.1 mol against the total metal ions) to achieve the excellent rate performance of the cell. In conclusion, the role of the carbon coating in reducing the grain size and enlarging contact area by adipic acid is beneficial for improving the rate capability *via* the improved Li⁺ diffusion kinetics. This excellent capacity retention under high current rates may be ascribed to the phase purity, reduced nanoparticle presence, and effective carbon coating by adipic acid.

4. Conclusions

Pristine and carbon-coated nanocrystalline LiFePO₄ materials were synthesized by a simple solid-state method under an Ar atmosphere. The particle sizes were analyzed by DLS and the formation of the carbon layer was verified by TEM. The thickness of the coating layer of carbon was less than 10 nm. The carbon-coated LiFePO₄ material exhibited a superior and stable electrochemical performance of 150 mAh g⁻¹ at room temperature. The rate capability study revealed an excellent capacity retention exceeding 99.5% that was achieved *via* an adipic acid-assisted, solid-state route.

Acknowledgements

This work was supported by the grant from the Technology Innovation Program of the Ministry of Knowledge Economy of Korea (Project No. K1002176).

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