Electrochimica Acta 53 (2008) 7946–7951

Contents lists available at ScienceDirect

Electrochimica Acta

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

Rate performance and structural change of Cr-doped $LiFePO_4$/C during cycling

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ARTICLE INFO

Article history:
Received 25 March 2008
Received in revised form 1 June 2008
Accepted 4 June 2008
Available online 12 June 2008

Keywords:
$LiFePO_4$
Carbon coating
Doping
In situ X-ray diffraction
Lithium batteries

ABSTRACT

Structural change of Cr-doped $LiFePO_4$/C during cycling is investigated using conventional and synchrotron-based in situ X-ray diffraction techniques. The carbon-coated and Cr-doped $LiFePO_4$ particles are synthesized by a mechanochemical process followed by a one-step heat treatment. The $LiFe_{0.97}Cr_{0.03}PO_4$/C has shown excellent rate performance, delivering the discharge capacity up to 120 mAh/g at 10 C rate. The results suggest that the improvement of the rate performance is attributed to the chromium doping, which facilitates the phase transformation between triphylite and heterosite during cycling, and conductivity improvement by carbon coating. Structural analysis using the synchrotron source also indicates that the doped Cr replaces Fe and/or Li sites in $LiFePO_4$.

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1. Introduction

Olivine-type $LiFePO_4$ has gained a great deal of interest as a cathode material for lithium-based secondary batteries. This is because $LiFePO_4$ has advantages over ordinary $LiCoO_2$ such as low material cost, nontoxicity, and better thermal stability and is known as one of the candidate cathode materials for a power source in the electric and hybrid electric vehicles (EV and HEV) [1–3]. However, $LiFePO_4$ suffers from poor rate capability at high rates due to low electrical conductivity and poor electrochemical performances at low temperatures. Recent research activities for $LiFePO_4$, therefore, have been devoted to the improvement of the electrical conductivity by mixing carbonaceous conductors [4–7], doping of metallic elements such as Cr, Mg, Ni, or Co [8–10], or optimization of the particle size [11].

In the literature, various mechanisms have been proposed to explain the role of doping elements in the electrochemical properties of $LiFePO_4$. Chung et al. suggested that doping with super-valent ions into Li sites increased the conductivity of $LiFePO_4$ by p-type and n-type conduction [8]. The simulation based on the first-principle calculation reported that the enhancement of electronic conductivity could be achieved by replacing Li ions with higher valence cations [9]. Meanwhile, others proposed that the improved conductivity did not rely on the lattice doping but attributed to the conductive layer existed on the particle surface, that consisted of metal elements, C, O, and P [12,13].

The main focus of this work is to find the role of Cr doping and carbon coating on the improvement of rate performance by investigating the correlation between rate performance and structural changes during cycling using synchrotron-based in situ X-ray diffraction (XRD) technique.

2. Experimental

A mixture of Li_2CO_3 (Aldrich, ≥99%), $FeC_2O_4{\cdot}2H_2O$ (Aldrich, ≥99%), and $(NH_4)_2H{\cdot}PO_4$ (Aldrich, ≥99%) were used as a starting material. The mixture was placed in a zirconia bowl and mechanochemical activation was performed for 3 h using a planetary mill (FRITSCH Pulverisette 5). The rotating speed was 250 rpm and the ball-to-powder weight ratio was 20:1. For the synthesis of $LiFePO_4$, the powder was heat treated at 600 °C using a tube furnace for 10 h in an Ar + 5% H_2 atmosphere. For the carbon coating and Cr doping, 3 wt% carbon black powder and a stoichiometric amount of $(CH_3CO_2)_7Cr_3(OH)_2$ were added to the starting material before mechanochemical activation. Then the mixture was heat treated at 750 °C and followed by furnace cooling. High-resolution XRD patterns were collected on a beam line 8C2 at Pohang Accelerator Laboratory (PAL) to investigate the structure of the sample. The surface morphology and the particle size of the powder were analyzed by scanning electron microscopy (Hitachi

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doi:10.1016/j.electacta.2008.06.005

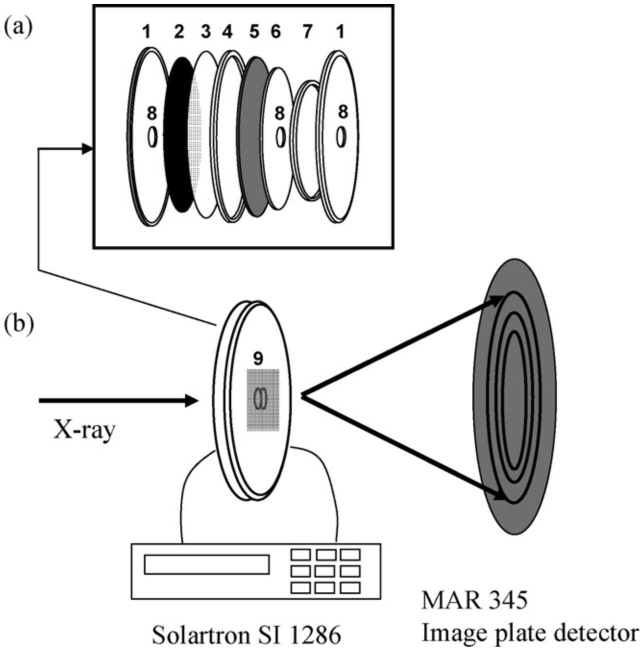

Fig. 1. Schematic diagram of (a) the in situ cell and (b) experiment set-up; (1) case of the cell, (2) cathode, (3) separator, (4) Teflon seal-ring, (5) anode (Li), (6) disc, (7) spring, (8) hole (X-ray path), (9) Kapton windows.

S-4200). The cathodes used in this study were prepared by slurring the active material with 5% poly-vinylidene fluoride (PVDF) and 10% (w/w) acetylene black in an *n*-methyl pyrrolidone (NMP) solvent, and then the mixture was coated onto an Al foil. After drying at 80 °C for 12 h, the electrode disks (1.96 cm^2) were punched and weighed. The cathodes were 60 μm thick and contained approximately 5–7 mg/cm^2 of active materials. The charge and discharge characteristics of the cathodes were examined using a standard coin cell (2032 type). The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution and a lithium foil was used as a counter electrode. The galvanostatic charge–discharge experiments were performed using a Maccor 4000 battery cycler.

Modified 2032 coin cells were used as in situ XRD cells. The cells had a 3 mm diameter hole in the center with Kapton windows, which served as a beam path. In situ XRD patterns were collected on a beam line 5 A at PAL using a MAR345 image plate detector. The MAR345 image plate detector collected one XRD scan in a period as short as a few minutes with a good S/N (signal to noise) ratio. It significantly reduced the data collection time for each scan and provided us a great advantage in studying the phase transition during high rate cycling. The schematic of the in situ XRD cell and the experiment set-up were shown in the Fig. 1. The two theta angles of all the XRD spectra presented in this paper have been converted to the corresponding angles for $\lambda = 1.54$ Å, which is the wavelength of conventional X-ray tube source with Cu Kα radiation to compare with previous results in the literature.

3. Results and discussion

The size distribution of the $LiFePO_4$ particles after heat treatments was examined using an SEM since the particle size affects the electrochemical performance of the cathode. Fig. 2 shows the SEM images of $LiFePO_4$, $LiFePO_4$/C, and $LiFe_{0.97}Cr_{0.03}PO_4$/C particles used in this study. The bare $LiFePO_4$ was heat treated at a lower temperature than other samples because the particle size of bare $LiFePO_4$ increased dramatically as the heat-treatment temperature was increased, which degraded electrochemical performances of the cathode [14,15]. The preliminary experiments indicated that the heat-treatment temperatures showing good electrochemical performances for bare $LiFePO_4$ and $LiFePO_4$/C were 600 and 750 °C, respectively. The mean coherent domain sizes were obtained from XRD peak analysis and they were approximately 73, 95, and 100 nm for $LiFePO_4$, $LiFePO_4$/C, and $LiFe_{0.97}Cr_{0.03}PO_4$/C.

Only slightly bigger $LiFePO_4$/C particles were observed compared to the bare $LiFePO_4$, although the heat-treatment temperature for $LiFePO_4$/C was considerably higher. This suggested that the carbon coating layer suppressed the particle growth during

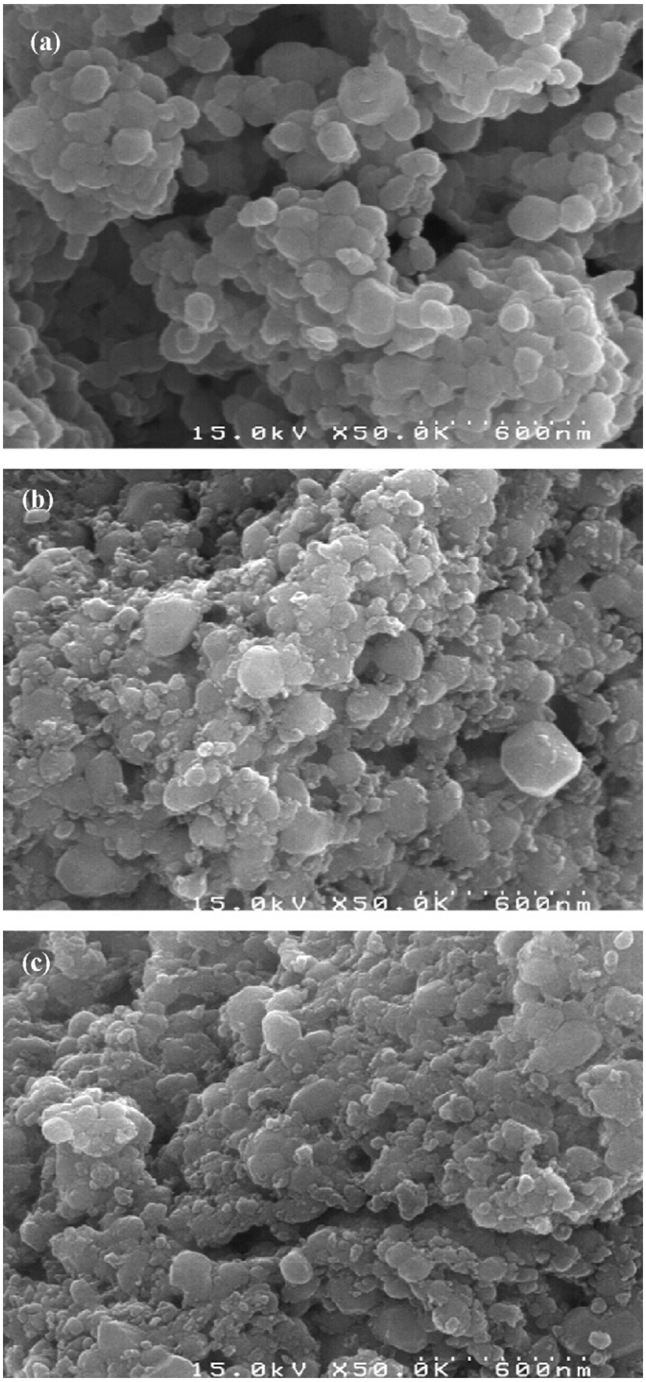

Fig. 2. SEM micrographs of (a) bare, (b) carbon-coated, and (c) carbon coated and Cr-doped $LiFePO_4$.

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