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Ceramics International 34 (2008) 1349–1351
CERAMICS INTERNATIONAL
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Short communication

Electrochemical properties of carbon-mixed $LiFePO_4$ cathode material synthesized by the ceramic granulation method

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Received 25 October 2006; received in revised form 19 January 2007; accepted 12 March 2007
Available online 29 April 2007

Abstract

$LiFePO_4$/carbon composite cathode material was prepared using polyvinyl alcohol (PVA) as carbon source by pelleting and subsequent pyrolysis in N_2. The samples were characterized by XRD, SEM and TGA. Their electrochemical performance was investigated in terms of charge–discharge cycling behavior. It consists of a single $LiFePO_4$ phase and amorphous carbon. The special micro-morphology via the process is favorable for electrochemical properties. The discharge capacity of the $LiFePO_4$/C composite was 145 mAh/g, closer to the theoretical specific capacity of 170 mAh/g at 0.1 C low current density. At 3 C modest current density, the specific capacity was about 80 mAh/g, which can satisfy for transportation applications if having a more planar discharge flat.

Keywords: Lithium-ion batteries; Cathode material; Carbon mixed $LiFePO_4$; Spray-pelleting

1. Introduction

Recently, the phosphate $LiFePO_4$ has been studied as the cathode-active material in Li batteries, because it is expected to have low-cost, low toxicity and high theoretical specific capacity of 170 mAh/g [1]. However, due to their very poor conductivity, initial reports indicated that Li^+ can only be partially extracted/inserted at room temperature at modest rates. Many studies have been performed to overcome this problem, and it has been found that particle-size reduction, doping to improve the intrinsic conductivity and electronic conductivity enhancement by means of conducting agents are effective [2–4]. These factors are largely affected by the method of preparation, that is, $LiFePO_4$ has a large range of electrochemical properties that depend on the synthesizing conditions. Therefore, to produce commercially available $LiFePO_4$, a proper preparation method is a worthwhile research target.

In this study, a spray granulation and followed calcination method has been employed as a new solid–liquid-phase synthesis route for making carbon-containing $LiFePO_4$, which used polyvinyl alcohol (PVA), a usual polymer binder in ceramic powder granulation process as the carbon source.

2. Experimental

$LiFePO_4$ was first prepared by a solid-state reaction involving a mixture of $FeC_2O_4{\cdot}2H_2O$, $NH_4H_2PO_4$, and Li_2CO_3 in a stoichiometric molar ratio (1:1:1). The precursors were planetary milled in alcohol for at least 6 h, and then heated under purified N_2 gas for 8 h at 400 °C to decompose the oxalate and phosphate. The resulting gray powder was subsequently mixed with 5 wt% PVA aqueous solution to form slurry, which was peristaltically pumped into a spray drying tower operating at 200 °C. The dry granulation powders were collected and then sintered at 700 °C for 8 h under flowing N_2 gas.

In order to determine the exact amount of carbon coated on the olivine particles, thermogravimetric analysis (TGA2050, TA USA) was carried out under a dry flow of air over both coated (C-$LiFePO_4$) and uncoated ($LiFePO_4$) olivine material

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doi:10.1016/j.ceramint.2007.03.021

in independent measurements. The structure of this composite was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements.

For electrochemical evaluation, the cathode was consisted of active material (75%), acetylene black (17%) and PVdF binder (8%) on Al foil current collector. These electrodes were dried under vacuum at 120 °C for at least 6 h before the 2032 coin cells assembly inside an Argon-filled glove box. The cell was soaked in 1 M $LiPF_6$ (DMC:EC = 1:1) electrolyte together with lithium metal as the counter electrode. The charge–discharge experiment data were collected galvanostatically on a LAND Cell test system (Wuhan, China) between 2.5 and 4.2 V versus Li by applying from 0.1 to 5 C current densities at room temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of $LiFePO_4$ olivine before and after the carbon mixing experiment. The X-ray diffraction peaks for $LiFePO_4$ can be indexed in the orthorhombic system (space group *Pnma*) with cell parameters: $a = 6.008$, $b = 10.334$ and $c = 4.693$ Å. After the carbon mixing process, the olivine structure of C-$LiFePO_4$ was maintained with no evidence of impurities that may be caused by the reduction of iron during the mixing process. The cell parameters for C-$LiFePO_4$ was decreased with $a = 5.994$, $b = 10.315$ and $c = 4.688$ Å.

Fig. 2 shows an SEM photograph of C-$LiFePO_4$ material that was prepared using our ceramic powder granulation technique. The granulation with hollow, "donut" structures appears in Fig. 2(a) due to instant evaporation of water. The single powder is constituted of agglomerates of an average primary particle size of approximately 200 nm in Fig. 2(b). The hollow microstructure favors the penetrating and soakage between the cathode material and electrolyte. To confirm how the carbon is distributed within the $LiFePO_4$ powder, a part of the $LiFePO_4$ powder was observed under TEM as shown in Fig. 3. It is clear from the image that the surface of the $LiFePO_4$ powder is modified by amorphous carbon. This means that the nano-sized carbon (marked primary particles by arrows) are agglomerated and coated on $LiFePO_4$.

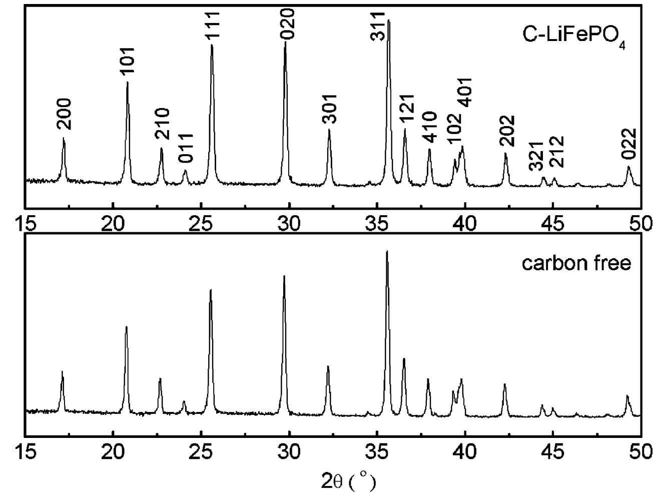

Fig. 1. XRD patterns of $LiFePO_4$ olivine before and after the mixing experiment.

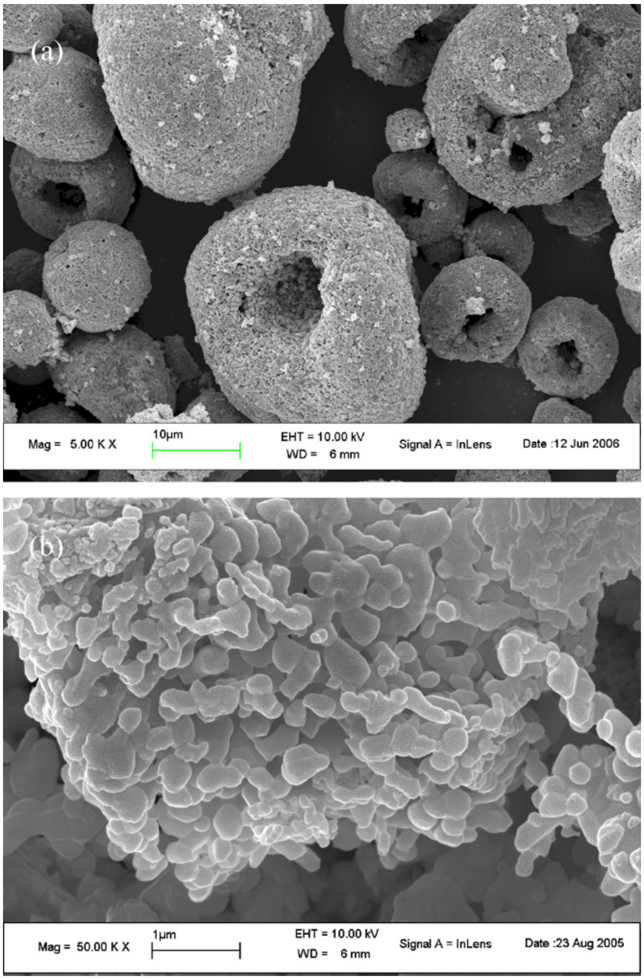

Fig. 2. SEM images of the C-$LiFePO_4$ samples: (a) SEM image (5000×); (b) SEM image (50,000×).

Fig. 4 shows TGA curves performed on both $LiFePO_4$ (gray powder) and carbon-coated C-$LiFePO_4$ (black powder) under air flow, respectively. The experiment was carried out primarily to determine the exact amount of carbon coated on the olivine from PVA pyrolysis process. The TGA curves show a weight

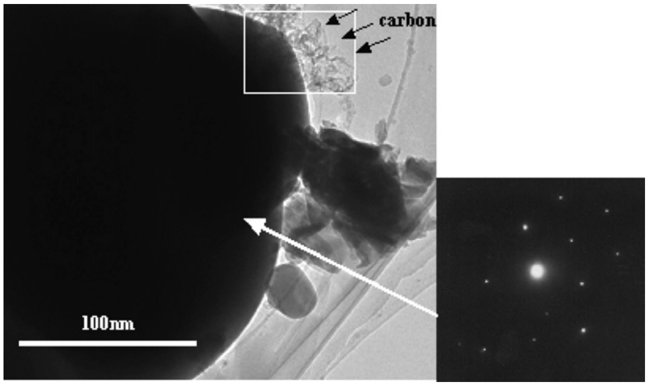

Fig. 3. TEM bright-field images (with corresponding electron diffraction patterns) of the C-$LiFePO_4$ samples.

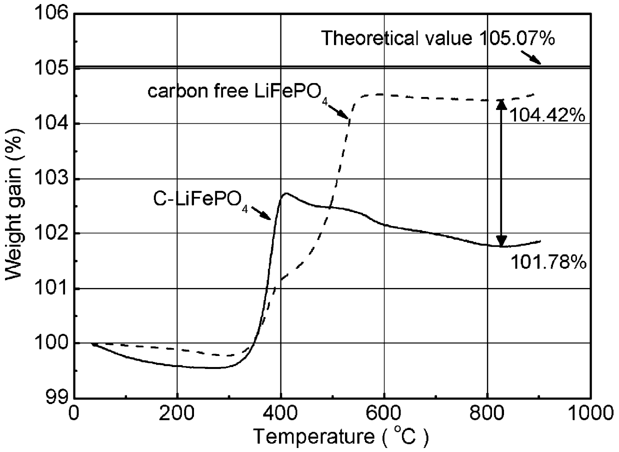

Fig. 4. TGA curves of carbon free $LiFePO_4$ olivine and carbon-mixed C-$LiFePO_4$ (% carbon = 2.64 wt%).

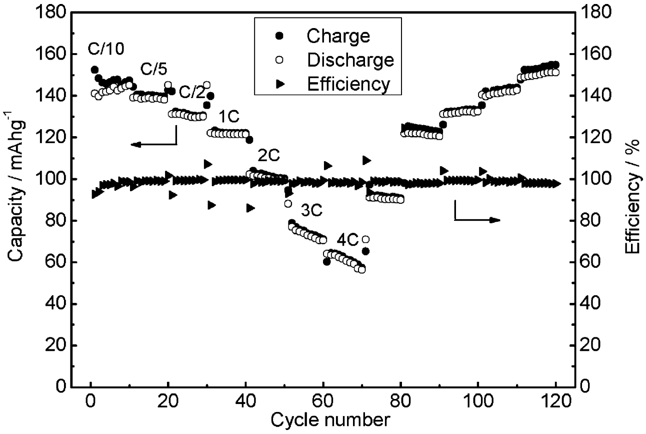

Fig. 5. Charge (solid cycle) and discharge (hollow cycle) capacity cycling performance of C-$LiFePO_4$ electrode at various current densities, and the charge/discharge efficiency (solid trigon).

gain of 4.42% for the carbon free $LiFePO_4$ powder and 1.78% for the C-$LiFePO_4$. Theoretically, when $LiFePO_4$ has been completely oxidized, we expect a 5.07% increase in weight [5]. Finally, the amount of carbon coated on the olivine was calculated to be around 2.64 wt% based on the difference in the TGA weight gain observed in $LiFePO_4$ and C-$LiFePO_4$ according to Eq. (1):

$$\%\,\text{carbon} = (\%\,\text{total weight gain of LiFePO}_4 - \%\,\text{total weight gain of C-LiFePO}_4) \qquad (1)$$

It was expected that this synthesis route would be very effective in enhancing the electrochemical activity of $LiFePO_4$. Fig. 5 shows the cycling performance of electrode made of C-$LiFePO_4$ at various charge/discharge rates, 0.1, 0.2, 0.5, 1, 2, 3 and 4 C (1 C, 170 mAh/g). This result shows the higher discharge rate capability and well cycling stability of this porous-structured electrode, although there is an obvious fluctuation of efficiency at the joint between two different charge/discharge rates, and then the discharge performance come to a stable state. Here the electrode of C-$LiFePO_4$ has shown a relative high cycling capacity as high as 145 mAh/g at a current density of 0.1 C, and can keep a high capacity even at higher discharge rates (130, 122, 101 and 80 mAh/g at current density of 0.5, 1, 2 and 3 C, respectively). Another important features of C-$LiFePO_4$ electrode are relative high coulombic efficiency (ratio of release capacity to insertion capacity) when the charge/discharge cycle comes to a stable state after several cycles even at very high current density, which means that the lithium intercalation and release in C-$LiFePO_4$ are reversible.

The reason for the relative large cycling capacity and cycling stability may arise from the presence of intimate carbon dispersion, thus confirming its role in optimizing the morphology of the $LiFePO_4$ electrode material and, thus, in enhancing the kinetics of its electrochemical process. We think this relatively large capacity for carbon coated $LiFePO_4$ is due to the uniform distribution of carbon webs around the particles by the novel route.

4. Conclusions

In this study, we show that the addition of organic carbon source PVA during the spray-pelleting synthesis route of $LiFePO_4$ can greatly improve its electrochemical performance. The cathode can be discharged at 3 C rate at room temperature with a utilization of about 50%. Discharged at lower current density, the utilization of the material increases, approaching 85% (145 mAh/g), for a 0.1 C discharge rate. When these are carefully controlled by choice of reaction conditions, the $LiFePO_4$/C composite remarkably achieves almost full capacity with good rate capability and excellent stability at room temperature, making this material an almost ideal cathode.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (Nos. 50372003, 50472005) and Tsinghua University Fundamental Research Fund (Project No. JC2003040).

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