Synthesis and electrochemical properties of $LiFePO_4$/C cathode material

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Since Goodenough *et al.* [1] found lithium iron phosphate ($LiFePO_4$) could be used as cathode material for the lithium ion batteries, many research groups are devoted to improving the performance of this material [2–6]. They thought $LiFePO_4$ was one of the most promising cathode materials for the lithium ion batteries because it is abundant, environmentally benign, stable and safe.

The main problem of the $LiFePO_4$ is its low electronic conductivity and low lithium ion diffusivity. In order to overcome these defaults, one way is to coat the $LiFePO_4$ with electronically conductive materials like carbon [7], the other way is to produce small fine particles of $LiFePO_4$ through solution methods like coprecipitation, sol–gel and hydrothermal synthesis [6, 8]. $LiFePO_4$ coated with carbon was usually synthesized by solid-state reaction, which required a long firing time at 400–800 °C. The carbon sources in the previous work are sugar, carbon gel, sucrose, carbon black and aqueous gelatin. Obviously, these carbon sources did not react with other reactants. They were only decomposed into native carbon onto the particles in the sintering process.

We have synthesized $LiMn_2O_4$, $ZnCo_2O_4$ electrode materials successfully by rheological phase reaction in our laboratory [9, 10]. In this work, small fine $LiFePO_4$ particles coated with carbon were obtained by the rheological phase reaction using comparatively lower temperature and fewer sintering time, and the native carbon on the particles came from citric acid, which is a new carbon source and acted as one of the reactants. We also describe the electrochemical properties of the powders.

In order to obtain $LiFePO_4$/C, $CH_3COOLi\cdot 2H_2O$, $NH_4H_2PO_4$, $FeC_2O_4\cdot 2H_2O$ and citric acid were ground and fully mixed in stoichimetric rations. After the powders were ground homogeneously, a proper amount of water was added to obtain the rheological body. All of the above operations were finished in a glove box, which is full of argon. Then a precursor was formed through the rheological body at 100 °C for 8 hr. The precursor was sintered at 550 °C in a tube furnace with flowing argon gas for 12 hr, a black powder $LiFePO_4$/C was obtained.

The $LiFePO_4$/C was analyzed by X-ray diffractometer (XRD), element analysis (EA) and scanning electron microscope (SEM). The test cells were fabricated using lithium foil as the anode, $LiFePO_4$/C powders mixed with 10% acetylene back and 5% polytetrafluorothetylene (PTFE) as the cathode and 1 M $LiPF_6$ (EC/DEC = 1:1) as the electrolyte. A porous polypropylene film (Celgard 2400) was used as the separator. The cell was cycled at a constant current density of 10 mA/g and 100 mA/g at different temperatures, with a charge-discharge voltage limit of 2.0–4.4 V.

Fig. 1 shows the XRD patterns of the $LiFePO_4$/C powders. The peaks are in line with the olive-type $LiFePO_4$ except the Li_3PO_4 impurity, which is pointed by the asterisk (*). The content of the carbon in the $LiFePO_4$ powders is 7.8% through the element analysis. The carbon comes from the citric acid. But we cannot find the characteristic peaks of the carbon, which indicates the presence of the carbon does not influence the structure of the $LiFePO_4$. The grain size is estimated to be about 80 nm through the SEM image in Fig. 2. From the above XRD and TEM analysis, we can see that small grain size of $LiFePO_4$ coated with carbon can be obtained by rheological phase reaction.

The charge–discharge curves of the cells with $LiFePO_4$/C as a cathode at room temperature are shown in Fig. 3. The first discharge capacity of the $LiFePO_4$/C is 121 mAh/g at 10 mA/g at room temperature. After 10 cycles, the discharge capacity is 135 Ah/g. When the current density increased from 10 mA/g to 100 mA/g, the first discharge capacity decreased from 121 mAh/g to 110 mAh/g, which is consistent with the previous reports [1].

Many papers have already reported that the discharge capacity of $LiFePO_4$/C increased at an elevated temperature because of the higher Li diffusion rate in $LiFePO_4$ particles [3, 11]. This idea is approved by our experiments. The first discharge capacity is 117 mAh/g at 100 mA/g at 55 °C, which is higher than that of $LiFePO_4$/C tested at room temperature at 100 mA/g.

Variations of the discharge capacity with increasing cycles for the $LiFePO_4$/C measured at 100 mA/g at different temperatures are shown in Fig. 4. The

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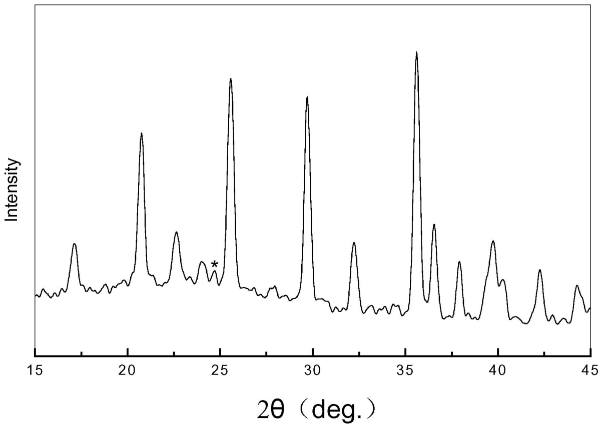

Figure 1 XRD patterns of $LiFePO_4/C$.

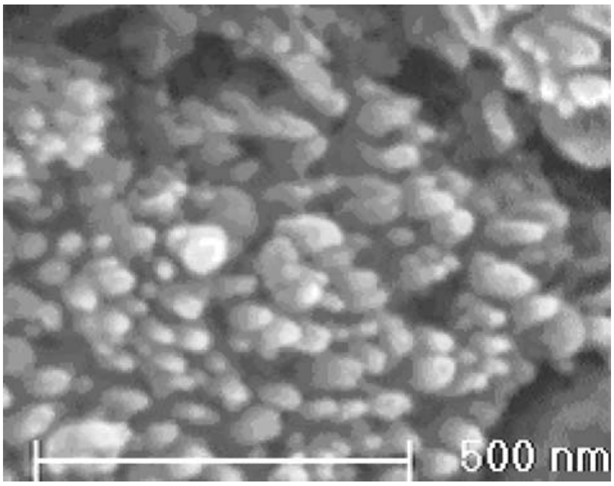

Figure 2 TEM patterns of $LiFePO_4/C$.

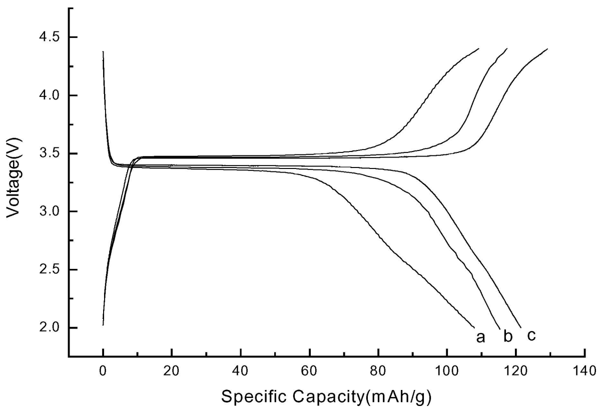

Figure 3 The charge-discharge curves of $LiFePO_4/C$ at (a) 100 mA/g, room temperature; (b) 100 mA/g, 55 °C; (c) 10 mA/g, room temperature.

$LiFePO_4/C$ measured at room temperature shows excellent cycle ability. The discharge capacity is over 100 mAh/g after 100 cycles, which is better than that of $LiFePO_4$ prepared by solid-state reaction method [12]. However, when the testing temperature increased to 55 °C, the discharge capacity fade gradually after 20 cycles. This might be related to the oxidation and decomposition of the electrolyte at elevated temperature.

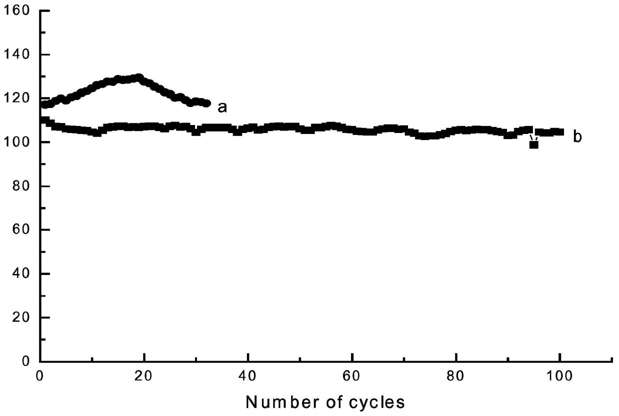

Figure 4 The variation in the discharge capacity with increasing cycling for the $LiFePO_4/C$ at (a) 100 mA/g, 55 °C and (b) 100 mA/g, room temperature.

The $LiFePO_4/C$ was synthesized by rheological phase reaction using lower temperature and fewer sintering time, and the carbon came from the reactant. The sample shows a good electrochemical capacity and cycle ability at a large current density (100 mA/g). The result indicated that rheological phase reaction is a feasible and economical method to obtain $LiFePO_4/C$.

Acknowledgments

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