Synthesis and characterization of Cu-doped LiFePO₄ with/without carbon coating for cathode of lithium-ion batteries

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The Cu-doped LiFePO₄ with/without carbon coating was synthesized by sol-gel method. The material was characterized by X-ray diffraction, Raman spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectroscopy and its electrochemical properties were investigated by charge–discharge tests. For the carbon coated sample presents a high uniformity and a particle size around 50–100 nm. Electrochemical tests show that the specified capacity was 102 mAh/g measured 0.25 C (1.5 mA) regime discharge rate, voltage range (2.5–3.7 V). Optimization of this composite would be required, but the Cu doping and carbon coating to LiFePO₄ showed a promising material for use as cathode material in lithium ion battery.

Key-words: Lithium-ion batteries, Sol-gel synthesis, Cathode material, Lithium iron phosphates, Ion doping

1. Introduction

Lithium iron phosphate (LiFePO₄) has attracted a great deal of attention for its applications as cathode materials for next-generation Li-ion batteries because of a relatively large theoretical capacity (170 mAh/g), cost-effectiveness, and high cycling stability. However, its low electronic conductivity (10⁻¹⁰ S cm⁻¹) and low lithium ion diffusivity led to a poor rate capability that has limited its wide application. In order to increase the charge capacity and to improve the conductivity of this material, many works on its synthesis have been performed, using different approaches as solid-state reaction, co-precipitation, hydrothermal synthesis, solution, emulsion drying. To improve Li⁺ ion diffusion some authors have coated with an electron-conductive layer as conductive carbon, dispersed a metal nanosized Cu and Ag. Also doping the structure with ions such as Mg²⁺, Ti⁴⁺ and others have been reported. Croce et al. report the preparation and electrochemical performance of kinetically improved Cu-doped LiFePO₄ composite cathode materials. The added Cu metal powders do not affect the structure of LiFePO₄ but clearly improve its kinetics in terms of capacity delivery and cycling life due to a reduction of the particle size and an increase of the bulk intra- and inter-particle electronic conductivity of LiFePO₄.

The objective of this study is to prepare copper (Cu)-doped LiFePO₄ with/without carbon coating by sol-gel method and evaluate its properties to look the potential of this material as cathode of lithium ion battery.

2. Experimental

2.1 Synthesis

Cu-doped LiFePO₄ was synthesized via sol-gel method. CH₃COOLi·2H₂O, FeCl₂·4H₂O, H₃PO₄, and CuCl₂ were used as reactants. For the sample with carbon coating, a mixture of PEG and D-fructose was used as carbon source. Initially, solutions of 1M H₃PO₄ and 1M FeCl₂·4H₂O dissolved in ethanol were prepared and stirred for approximately 3 h. After addition of 1M CH₃COOLi·2H₂O and 1M CuCl₂ dissolved in ethanol, the mixture was stirred for 2 h at rt. For the sample with carbon coating, PEG/fructose (1:1 weight ratio) mixture 10% w/w was mixed in the previous step and then the mixture was stirred for 2 h. For both samples the resulting mixture was calcined at 700°C in an argon atmosphere for 5 h.

2.2 Analysis techniques

The Cu-doped LiFePO₄ was characterized by X-ray diffraction (XRD), Raman spectroscopy, Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM). The SEM observation was performed on a JSM-6700F, the Energy Dispersive Spectroscopy (EDS) on a JSM-6700F JET 2300 and the X-ray diffraction was carried out under the following conditions: Cu Kα radiation, 40 kV and 40 mA. The charge and discharge measurements were conducted using two-electrode coin-type cell (CR2016) of Li/EC:PC:LiPF₆ (1:1:1 in volume ratio)/LiFePO₄.

The cathode was prepared by mixing 85% of the Cu-doped LiFePO₄/C, 10% of an acetylene black as conducting agent and 5% of an poly (vinylidene fluoride) as binder, pressing in an aluminum mesh and drying in an oven at 80°C for 12 h.

The cells were assembled in an Ar-filled glove box using 1.0 M/L of LiPF₆ in ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio of 1:1 as electrolyte and metallic lithium foil as counter electrode. The charge and discharge tests were performed between 3.5 and 4.3 V at 0.5 C (3 mA) and 0.25 C (1.5 mA).

3. Results and discussion

The Cu-doped LiFePO₄ powders were analyzed by XRD to verify phase purity. As shown in Fig. 1, all of the peaks for both
samples in the X-ray diffraction patterns can be assigned to those of orthorhombic LiFePO$_4$ (space group: Pnma) as reported in the literature.\textsuperscript{16} For the sample Cu-doped LiFePO$_4$ with carbon coating no evidence of diffraction peaks for crystalline carbon (graphite) appeared in the diffraction pattern, which indicating that the carbon generated from the carbon source (PEG/fructose) mixture was amorphous and that its presence did not influence the structure of Cu-doped LiFePO$_4$. Additionally, in some previous work, the introduction of carbon or a carbon precursor into a lithium iron phosphate has led to produce iron or iron phosphides during the thermal treatment by carbothermal reduction,\textsuperscript{15} but no copper neither as iron relative peak was detected in the XRD pattern in the present work.

The presence of 1 atomic \% copper was confirmed from EDS measurements. 

\textbf{Figure 2} shows the scanning electron micrograph images corresponding to the Cu-doped LiFePO$_4$ with/without carbon coating. In the case of Cu-doped LiFePO$_4$ without carbon coating rounded particles with high crystallinity and a size distribution of 1–5 \textmu m were observed. However, the Cu-doped LiFePO$_4$ with carbon coating has a particle size between 50–100 nm with more uniform and narrow size distribution (50 to 100 nm). Hence, the carbon as an additive inhibits the particle growth yielding a homogeneous particle size distribution with an average particle size of under 100 nm. The carbon had played an important role in controlling the particle size. The nanosize particles would influence (shorten) the diffusion length of Li ion in the discharge and charge to improve ion conductivity of the material.

The Cu-doped LiFePO$_4$/C powder presents a dark color suggesting total carbonization of carbon source. The carbon content determined by TD-DTA was below the 10% targeted. The residual carbon amount in the final product of Cu-doped LiFePO$_4$/C was around 5%. The Raman spectra at various points of the Cu-doped LiFePO$_4$/C powder are presented in \textbf{Fig. 3}. The spectra are dominated by the intense carbon D- and G-bands at 1360 and 1600 cm$^{-1}$. The weak PO$_4^{3-}$ $\nu_1$ symmetric stretch band at 945 cm$^{-1}$ was observed still visible together with a band at 340 cm$^{-1}$. As shown in \textbf{Fig. 3}, the carbon coating is well homoge-
LiFePO₄ with carbon coating the 1st and 2nd discharge capacity were 23 and 0.5 C and 2nd cycle at 0.25 C rate. Without carbon coating, the 1st and 2nd discharge capacity were 92.3 and 0.25 C. This difference is associated with the presence of carbon, confirming its role in optimizing the morphology of the Cu-doped LiFePO₄ and thus enhancing the kinetics of its electrochemical process.

The Cu-doped LiFePO₄ with carbon coating proved to be far better compared to the Cu-doped LiFePO₄ without coating as it enhanced electronic conductivity. Decrease in particle size for the Cu-doped LiFePO₄ with carbon coating would be beneficial in reducing the diffusion length of the lithium ion inside, resulting in fast reaction and diffusion kinetics.

4. Conclusions

The olivine type Cu-doped LiFePO₄ with/without carbon coating composite was prepared by sol-gel method using CH₃COOLi·2H₂O, FeCl₂·4H₂O, H₃PO₄, and CuCl₂ as raw materials. The particle size obtained by this method presented a high uniformity size around 50–100 nm for carbon coating sample. Electrochemical tests show that the specified capacity was 102 mAh/g measured 0.25 C (1.5 mA) regime discharge rate, voltage range (2.5–3.7 V). Optimization of this composite would be required, but the Cu doping and carbon coating to LiFePO₄ showed a promising material for use as cathode material in lithium ion battery.

Table 1. Capacity values of the Cu-doped LiFePO₄

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Charge capacity</th>
<th>Discharge capacity</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mAh</td>
<td>mAh/g</td>
<td>mAh</td>
</tr>
<tr>
<td>Carbon coating 1</td>
<td>4.083</td>
<td>95.0</td>
<td>3.970</td>
</tr>
<tr>
<td>Carbon coating 2</td>
<td>4.395</td>
<td>102.2</td>
<td>4.408</td>
</tr>
<tr>
<td>Without carbon coating 1</td>
<td>0.77</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Without carbon coating 2</td>
<td>1.25</td>
<td>37</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Fig. 4. Charge–discharge curves of the sol–gel synthesized Cu-doped LiFePO₄ A) without carbon coating B) with carbon coating 1st cycle at 0.5 C and 2nd cycle at 0.25 C rate.

References