Characteristics of Li$_{0.98}$Cu$_{0.01}$FePO$_4$ prepared from improved co-precipitation

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Abstract

Pure lithium iron phosphates and stoichiometric Cu-doped lithium iron phosphates were synthesized via improved co-precipitation, followed by sintering at high temperature for crystallization. The improved co-precipitation process allowed the homogeneous mixing of the ingredient reactants at atomic level. All samples were pure single phase indexed with orthorhombic $Pnma$ space group. The particle size of the Li$_{0.98}$Cu$_{0.01}$FePO$_4$ was drastically fine with 100–200 nm, compared with the undoped LiFePO$_4$. The electrochemical performance of Li$_{0.98}$Cu$_{0.01}$FePO$_4$, including reversible capacity, cycle number and charge–discharge characteristics, exhibited better than those of LiFePO$_4$.

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1. Introduction

Among cathode candidates, LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$ spinel have been widely used as cathode materials in lithium-ion batteries currently. More recently, LiFePO$_4$ has become one of the most promising compounds due to the relative lack of toxicity and inexpensive and abundant raw materials [1–5]. LiFePO$_4$ has a high lithium intercalation voltage of 3.4 V versus lithium metal and a high theoretical capacity of 170 mAh g$^{-1}$. However, there are two drawbacks for the use of LiFePO$_4$ as a commercial cathode material. One is its poor electronic conductivity [1]. Another problem is that it is difficult to synthesize LiFePO$_4$ because of ion oxidation state [6].

It is an effective method to improve electrochemical property of LiFePO$_4$ by supervalent ion doping and carbon coating [7–16].Comparatively, volumetric capacity of cell is difficult to increase because the addition of carbon will decrease the practical density of cathode material. And the doping of 1% supervalent ion will hardly change the practical density of cathode material. Therefore, this mean will promote the practical utilization of LiFePO$_4$. Chung et al. [7,8] proposed that LiFePO$_4$ doped with high valence metal ions could improve its electronic conductivity as high as eight orders of magnitude. Shi et al. [9,10] not only proved the feasibility of Cr$^{3+}$ ion doping LiFePO$_4$ in theory, but also synthesized the sample. Wen et al. [17] also investigated the structure and properties of LiFe$_{0.9}$V$_{0.1}$PO$_4$ and indicated that the cathode properties of LiFe$_{0.9}$V$_{0.1}$PO$_4$, including reversible capacity, cycle number and charge–discharge characteristics, were better than those of pure LiFePO$_4$. Moreover, it was not easy to dope ion uniformly by solid phase confused with 1.0% (molar ratio) ion, which may limit the function of doping. In present investigation, we are trying to put forward an improved co-precipitation route to prepare ion-doped LiFePO$_4$. In this method, olivine LiFePO$_4$ will be gained by the precursor which was prepared by co-precipitation sintered in the N$_2$, in which inexpensive and stable Fe$^{3+}$ compound was used as raw material and inert gas was not used during the processes of co-precipitation. It is convenient to operate according to this preparation method with the purpose of industrial manufacture.

2. Experimental

The pure LiFePO$_4$ and doped Li$_{1-x}$Cu$_x$FePO$_4$ were synthesized by improved co-precipitation, followed by sintering at high temperature. The ingre-
The chemical compositions of Cu-doped lithium iron phosphates were analyzed by atomic absorption spectrometry. Determination of Fe²⁺ from the samples by spectrophotometry showed up to 99.95% of total iron, and the Fe²⁺ was hardly oxidized.

Fig. 1 shows that among all samples prepared, the discharge specific capacity of Li₀.⁹₈Cu₀.₀₁FePO₄ is better than others. That is, the small amounts of Cu²⁺ doped are benefit to the increase of specific capacities.

The X-ray diffraction profiles of Li₀.⁹₈Cu₀.₀₁FePO₄ are shown in Fig. 1. The sample is pure single phase indexed with orthorhombic Pnmb space group. During the synthesis process, the ingredient ions Li⁺, Cu²⁺, Fe²⁺, and [PO₄]³⁻ are homogeneously mixed in atomic level. The precursor powders contain uniformly distributed reactants. After sintering, the pure lithium phospho-olivine structure is formed for Cu-doped lithium iron phosphates. No second phase is found as there are small amounts of doped ion and doped ion exist in the form of solid-solution.

The lattice parameters of samples calculated from the XRD patterns (Fig. 2) are shown in Table 1. From Table 1, we can see that the unit-cell parameter and unit-cell volume of LiFePO₄ doped by 1% Cu²⁺ has changed obviously, that is, the length of a-axis, b-axis and c-axis and unit-cell volume are both decreased. It shows that, compared with the pure LiFePO₄, the unit-cell parameter and unit-cell volumes of Li₀.⁹₈Cu₀.₀₁FePO₄ are both shrunk. The reason is that the ion radius of Cu²⁺ is 0.073 nm and smaller than Li⁺ and it caused the decrease of length of c-axis. Another reason is that the binding force between Cu²⁺ and O²⁻ is larger than that between Li⁺ and O²⁻ and the unit-cell volume of Li₀.⁹₈Cu₀.₀₁FePO₄ shrunk. These reasons cause the change of charge–discharge characteristics.

The SEM image in Fig. 3(a) illustrates that the grains of the precursor are small and uniform, whose grain size is about 10 μm. The precursor is the coexisting of two different crystallized shapes of particles. One shape is sector with the size of 3 μm and another is plush spherical with the size of 10 μm. The particles size which grained from solid-state grinding were about 80 μm, whereas the particles size which grained from improved co-precipitation were about 10 μm and uniform.

SEM images of LiFePO₄ and Li₀.⁹₈Cu₀.₀₁FePO₄ samples are shown in Fig. 4. It is found that, after sintering at 600 °C for 10 h, well-crystallized powders are obtained with an average crystal

![Fig. 1. Effect of quantity of Cu²⁺ doped on discharge specific capacity of samples.](image)

![Fig. 2. XRD patterns of Li₀.⁹₈Cu₀.₀₁FePO₄ sample.](image)

![Table 1](table)

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>V (nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO₄</td>
<td>1.033</td>
<td>0.6006</td>
<td>0.4687</td>
<td>0.2908</td>
</tr>
<tr>
<td>Li₀.⁹₈Cu₀.₀₁FePO₄</td>
<td>1.0316</td>
<td>0.6002</td>
<td>0.4682</td>
<td>0.2899</td>
</tr>
<tr>
<td>Padhi et al. [1]</td>
<td>1.0334 (4)</td>
<td>0.6008 (3)</td>
<td>0.4693 (1)</td>
<td></td>
</tr>
<tr>
<td>Barker et al. [11]</td>
<td>1.0288</td>
<td>0.5976</td>
<td>0.4672</td>
<td></td>
</tr>
<tr>
<td>Wen et al. [17]</td>
<td>1.03155 (8)</td>
<td>0.60032</td>
<td>0.47011 (3)</td>
<td>0.29112 (2)</td>
</tr>
</tbody>
</table>
size of 300 nm of LiFePO₄ crystals (Fig. 4a) and another average crystal size of 100–200 nm of Li₀.₉₈Cu₀.₀₁FePO₄ crystals (Fig. 4b). The average size of Li₀.₉₈Cu₀.₀₁FePO₄ is fined evidently compared with that of LiFePO₄. The small particle size of Li₀.₉₈Cu₀.₀₁FePO₄ would be beneficial to reduce the diffusion length of the lithium ion inside, resulting in fast reaction and diffusion kinetics, which can increase charge–discharge capacity and cycling behavior.

Fig. 5 illustrates EDS of Li₀.₉₈Cu₀.₀₁FePO₄. It could verify the homogeneous existence of Cu²⁺ dopant in LiFePO₄ crystal. It is a conceivable fact with the reason that the doping process of co-precipitation could undergoes in aqueous solution, which can easily blend all soluble components uniformly even for low content ion dopant.

The charge/discharge curves are shown in Fig. 6. The cell is cycled between 2.5 and 4.0 V using a low current density of 0.1 C (17 mAh g⁻¹) at room temperature. Li₀.₉₈Cu₀.₀₁FePO₄ demonstrates a flatter charging and discharging plateau than that of pure LiFePO₄. The potential for charging is about 3.49 V and discharging potential is around 3.37 V, which is in consistent with the result from the CV test. The small voltage difference between the charge/discharge plateaus is representative of its good kinetics. The discharge capacities stay at 153 mAh g⁻¹.

Fig. 7 shows the cyclic voltammogram of a Li₀.₉₈Cu₀.₀₁FePO₄ electrode at a scanning rate of 0.05 mV s⁻¹. The anodic and cathodic peaks appeared in the CV curves correspond to the two-phase charge–discharge reaction of the Fe²⁺/Fe³⁺ redox couple. During anodic sweep, the lithium ions were extracted from LiₓFePO₄ structure. An oxidation peak formed at 3.51 V during scanning potential from 4.0 to 2.8 V when lithium ions inserted into LiₓFePO₄ structure. The corresponding reduction peaks formed at 3.32 V. The 0.29 V difference between the anodic and cathodic peaks is representative of its good kinetics. Hence, the sharp oxidation and reduction peaks in CV curves indicate that strong lithium intercalation and de-intercalation reactions occurred for Li₀.₉₈Cu₀.₀₁FePO₄ electrode.

To investigate the rate capability, cycle performance of Li₀.₉₈Cu₀.₀₁FePO₄ at various rates is shown in Fig. 8. Although the discharge specific capacity has decreased with increasing charge/discharge rate, the capacity retention remained very good for all the different rates. At 0.1 C, the discharge capacity decreased from 154.5 to 140.9 mAh g⁻¹. The capacity decreased
to 139.0 mAh g$^{-1}$ (1 C) and 130.2 mAh g$^{-1}$ (2 C) at the current densities increase. At higher discharge rate of 2 C, the cell could deliver a capacity of 120.1 mAh g$^{-1}$ after 30 cycle. As a whole, the capacities of Li$_{0.98}$Cu$_{0.01}$FePO$_4$ seem to be stable upon cycling.

Above results which demonstrated good rate performance and cycling density of Li$_{0.98}$Cu$_{0.01}$FePO$_4$ could be attributed to the fact that the small particle size distribution and improved conductivity through doping Cu$^{2+}$. Especially, after substitution, balance of electrical valence induced Li$^+$ defect in LiFePO$_4$ and residue of Fe$^{2+}$/Fe$^{3+}$ coexistence state, so cation defects are of benefit to the diffusion of Li$^+$ in solid phase and increase electrical conductivity of crystal, further the charge–discharge characteristics of material.

4. Conclusion

The lithium iron phosphate and its doped derivatives have been successfully synthesized by improved co-precipitation. Cu$^{2+}$ uniform distribution in LiFePO$_4$ crystal and lead no impurity growth. The Cu-doped lithium iron phosphates demonstrated a better electrochemical property in terms of capacity delivery, cycle performance and electrochemical reversibility, which is attributed to the enhancement of the electronic inductivity by ion dopant, compared with undoped LiFePO$_4$. And small size of Li$_{0.98}$Cu$_{0.01}$FePO$_4$ synthesized by improved co-precipitation may allow intercalation and de-intercalation of lithium ions to occur with ease during the charge–discharge processes and exhibit high discharge capacity and good reversibility. Ion-doped samples show that such ion doping by the improved co-precipitation is an effective method to improve the electrochemical performance of LiFePO$_4$.

References


