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Synthesis of Size-controllable $LiFePO_4$/C Cathode Material by Controlled Crystallization

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Abstract: *The preparation of $LiFePO_4$/C materials with particle size ranging from 10μm to 100-200nm was attempted by controlled crystallization-carbothermal reaction, which has been experienced as an effective process for mass production of electrode materials. The structure, morphology and electrochemical performance of different materials were carefully characterized. With the decrease of particle size for $LiFePO_4$ powders, the $LiFePO_4$/C composite exhibit better capacity performance at high current density. This paves an effective way to synthesize size-controllable $LiFePO_4$/C materials by mass production.*

Keywords: $LiFePO_4$; size-controllable; mass production

1. INTRODUCTION

Olivine-structured $LiFePO_4$ is recognized as a potential positive electrode material for use in lithium-ion batteries [1]. It has advantages of low cost, excellent thermal stability, satisfactory safety and low toxicity, etc. However, poor electronic conductivity and slow lithium-ion diffusion prevent $LiFePO_4$ to be put into commercially application. Several techniques have been applied to overcome its limitations, including synthesis of $LiFePO_4$/C composite [2, 3], substitution of a small quantity of Li^+ by supervalent metal ions [4, 5] and preparation of $LiFePO_4$ powders with fine particles [6, 7], etc. Especially, minimizing particle size is an effective mean to enhance ion diffusion of $LiFePO_4$ material.

In our laboratory, the high-density spherical carbon-coated $LiFePO_4$ cathode material has been prepared via a controlled crystallization-carbothermal reduction method [8-10]. The spherical carbon-coated $LiFePO_4$ has excellent fluidity and dispersivity and much higher tap density, which is advantageous for preparation of high performance electrodes. However, the prepared spherical precursor of $LiFePO_4$ powders have the particle size distribution of about 7~12μm. The pyrolytic carbon is coated on the surface of spherical $LiFePO_4$ particles. Their electronic conductivity is still low in the interior of particles. Moreover, large particle size of $LiFePO_4$ results in long distances of Li^+ diffusion. These entire disadvantages lead to the unsatisfactory rate capability of $LiFePO_4$ materials.

The fine particles of $LiFePO_4$ cathode material could shorten the diffusion distances of Li^+ in the particles, meanwhile the increased specific surface area of the fine material provide more area for electrochemical reaction to improve the performance of the $LiFePO_4$ electrode.

In previous studies, fine-particle $LiFePO_4$ material was synthesized mostly by sol-gel and co-precipitation methods. The prepared $LiFePO_4$ powders by the above approaches have achieved the good electrochemical properties to some extent. Delacourt [7] et al. synthesized $LiFePO_4$ with particle size around 100-200nm via liquid-state co-precipitation method, which possessed high discharge capacity of 147mAh/g at 5C rate. Huang [11] et al prepared nano-$LiFePO_4$/C composite material using CH_3COOLi, Fe $(CH_3COO)_2$, $NH_4H_2PO_4$ and carbon gel as raw material. The discharge capacity of this material at 5C rate can reach 120mAh/g. Although nano-$LiFePO_4$/C cathode material with better electrochemical performance can be obtained via sol-gel method, these methods spend longer time.

The controlled crystallization process has been experienced as an effective way for mass production of electrode materials [10].

In this study, the synthesis of $LiFePO_4$/C cathode materials with particle size ranging from 10μm to 100-200nm was attempted by

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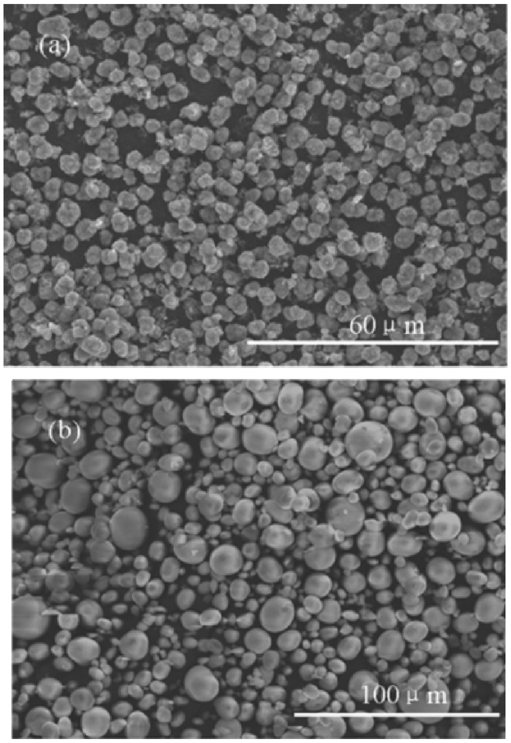

Figure 1. SEM images of micron $FePO_4 \cdot xH_2O$: a, D50=4.37 μm and b, D50=12.32 μm

controlled crystallization-carbothermal reaction process, which can be applied for mass production. The effects of particle size, morphology and electrochemical performance of different materials were investigated.

2. EXPERIMENTAL

In this work, Fe $(NO_3)_3$, H_3PO_4, $NH_3 \times H_2O$, Li_2CO_3 and sucrose ($C_{12}H_{22}O_{11}$) were used as raw materials. Firstly, amorphous $FePO_4 \cdot xH_2O$ powders were synthesized by controlled crystallization according to the following reaction:

$$Fe(NO_3)_3 + H_3PO_4 + 3NH_3 + xH_2O = FePO_4 \cdot xH_2O + 3NH_4NO_3 \quad (1)$$

In this work, the particle size of $LiFePO_4$ powders can be controlled effectively by controlling the particle size of precursor $FePO_4 \cdot xH_2O$ powders. The controlled crystallization parameters were as follows. The concentration of the Fe $(NO_3)_3$ and H_3PO_4 solution were both 0.2 mol/L. The concentration of the NH_3 solution was 0.6 mol/L. The agitating intensity was 80-100W/L. The average rest time was 30-45min. The temperature was 30°C. The pH value was 2.1.

The amorphous $FePO_4 \cdot xH_2O$ powders with different particle sizes were pre-heated at 520°C for 10h in air to obtain anhydrous $FePO_4$ powders.

To synthesize $LiFePO_4$/C powders, as-obtained $FePO_4$ precursor, Li_2CO_3, $C_{12}H_{22}O_{11}$ and deionized water (H_2O) were mixed uniformly in a mole ratio of Li_2CO_3: $FePO_4$: $C_{12}H_{22}O_{11}$: H_2O = 0.485:1:0.2:2, forming slurry. The slurry was dried and then sintered at 700°C for 16h in N_2. The spherical carbon-coated $LiFePO_4$/C powders with different size distribution were finally obtained through above carbothermal reduction process.

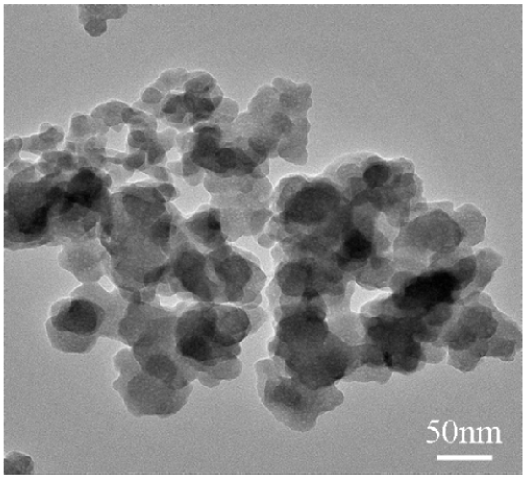

Figure 2. TEM images of nano $FePO_4 \cdot xH_2O$

The morphology of the precursor $FePO_4$ and the $LiFePO_4$/C composite materials with different size distribution were observed by scanning electron microscopy (SEM, Hitachi S-5500) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin).

The crystalline phase of as-synthesized $LiFePO_4$/C composite material was characterized by powder X-ray diffraction (XRD, D/max-rB) measurement using Cu K_α radiation.

The cathode was prepared with the composition of 80 wt% active materials, 10 wt% carbon black, and 10 wt % PTFE. The separator was Celguard 2400 microporous polypropylene membrane. The electrolyte was 1M $LiPF_6$ EC+DEC (1:1 by vol.). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The cells were galvanostatically charged and discharged over a voltage rang of 2.5-4.2V (vs. Li/Li^+) at different C rates.

3. RESULTS AND DISCUSSION

The scanning electron micrographs of spherical precursor $FePO_4 \cdot xH_2O$ powders with size distribution of 4μm and 12μm are shown in Fig.1. The particles are spherical and spherical alike, non-agglomerative and well-dispersed. This is the distinguishing feature of powders synthesized by controlled crystallization method.

The transmission electron micrograph of nano-$FePO_4 \cdot xH_2O$ powders synthesized by controlled crystallization is shown in Fig.2. The morphology of nano-$FePO_4 \cdot xH_2O$ powders is not very clear due to the accumulation and overlap among the particles. The nano powders are easy to disperse in the medium of water. The particle size of nano-$FePO_4 \times xH_2O$ powders is around 30nm.

The scanning electron micrographs of nano-$FePO_4$ and nano-$LiFePO_4$/C powders are shown in Fig.3. Contrast to Fig.2, the particle size of nano-$FePO_4$ powders increases from 30nm to 100~200nm after pre-heating, which is caused by growth of $FePO_4$ grains at high temperature crystallization process. However, compared with the particle size of $FePO_4$ powders, the particle size of nano-$LiFePO_4$/C powders do not increase significantly. It is probably because that sucrose as carbon source dissolved into the water

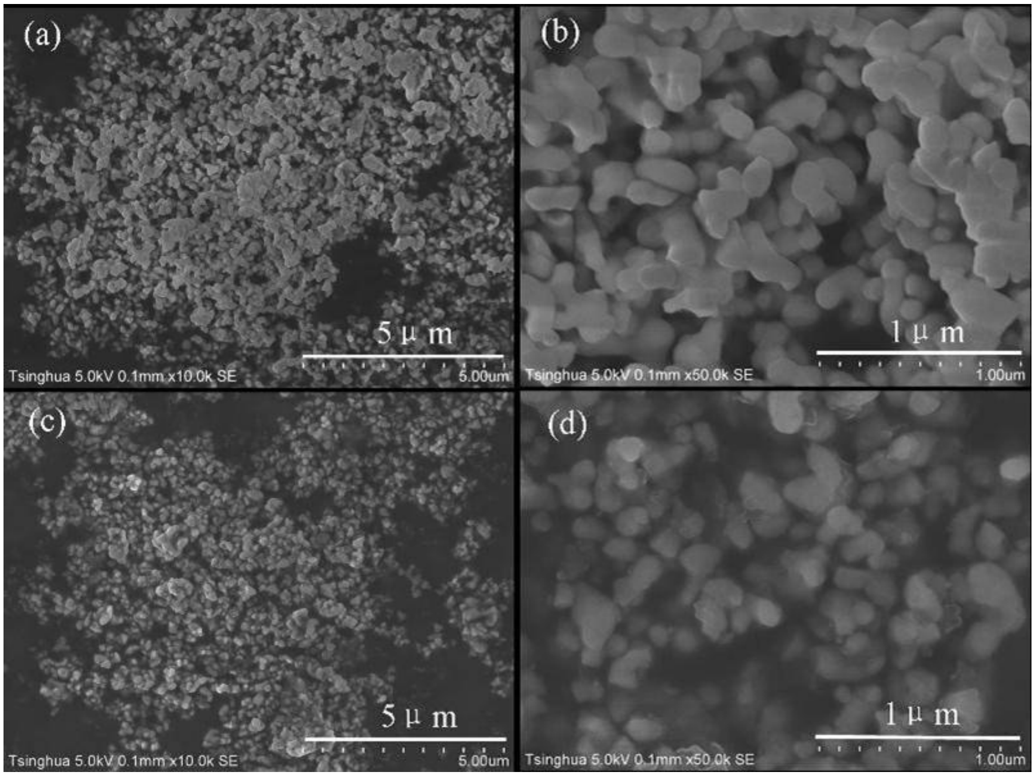

Figure 3. SEM images of nano-$FePO_4$ (a and b) and nano-$LiFePO_4/C$ (c and d)

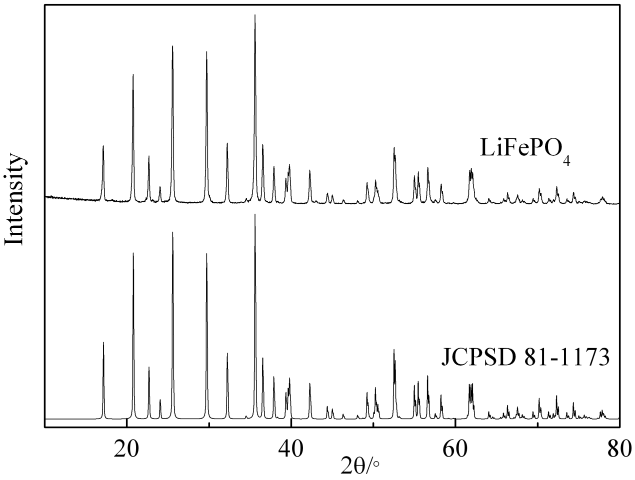

Figure 4. XRD pattern of nano-$LiFePO_4/C$

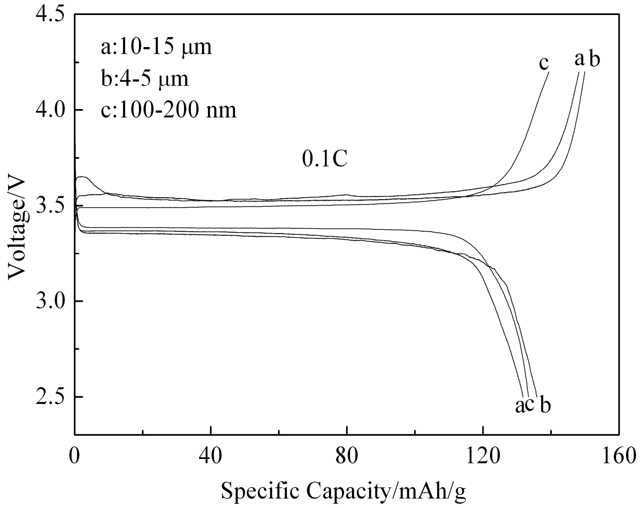

Figure 5. Initial charge-discharge curves of $LiFePO_4$ with different size distribution at 0.1C rate, 2.5-4.2 V

medium completely during the mixing process, and then dispersed uniformly on the surface of nano-$FePO_4$ powders when the slurry was drying, the coating layer of pyrolytic carbon restrains the growth of the grains as well as improves the conductivity of nano-$LiFePO_4$ particles during the sintering.

The XRD pattern of nano-$LiFePO_4/C$ powders is shown in Fig.4. The strong and sharp peaks in the pattern of the powders indicate the product is well crystallized. The spectrum of nano-$LiFePO_4/C$ powders is almost the same as the spectra of pure ordered orthorhombic olivine structured $LiFePO_4$ (JCPDS 81-1173). There is no evidence of diffraction peaks for carbon, indicating the residual pyrolytic carbon in the product is amorphous.

The charge-discharge curves of $LiFePO_4$ with different size distribution at 0.1C rate to a cut-off voltage between 2.5V to 4.2V are shown in Fig.5. The $LiFePO_4$ powders with particle size of 10-15μm, 4-5μm and 100-200nm have the first charge capacity of

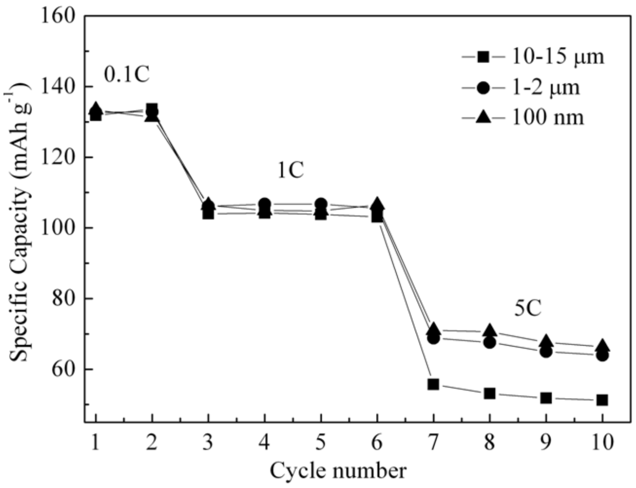

Figure 6. Discharge capacities with increasing cycles for $LiFePO_4$ with different size distributions at different C-rates.

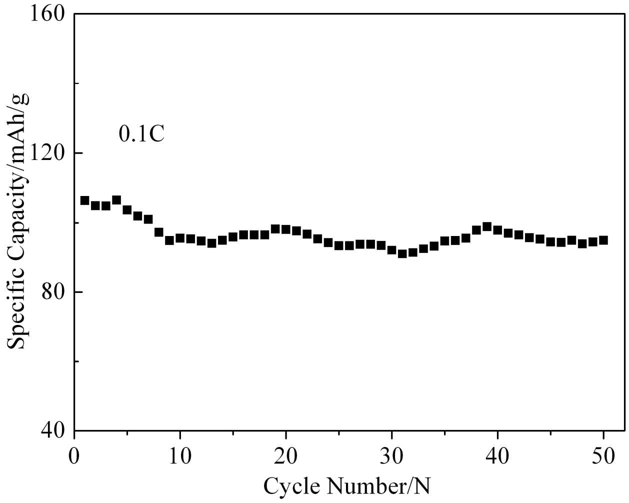

Figure 7. Cycling performance of nano-$LiFePO_4$ at 0.1C rate

148.2, 149.9 and 139.4 mAh/g, respectively. The products have the first discharge capacity of 131.8, 135.8, and 133.4 mAh/g, respectively. The products have the first discharge efficiency are 88.9%, 90.6% and 95.7%. With the particle size decrease from 10-15μm to 100-200nm, the first discharge efficiency of the products increased successively. Although the first charge and discharge capacity of the product with particle size of 100-200nm is less than the other two products, it has both high efficiency and discharge potential plateaus, indicating that synthesis of nano-particles can shorten the diffusion distance of Li^+ and increase its reversibility of insertion and extraction.

The cycling performance of the samples with different size distributions at various charge/discharge rates is shown in Fig.6. The cycle capacities of $LiFePO_4$ with particle size ranging from 10-15μm to 100-200nm at 0.1C are 131.8, 132.7 and 133.4 mAh/g. The cycle capacities remain at 104.2, 106.1 and 106.4 mAh/g at 1C rate, respectively. At 5C rate, the cycle capacities of the samples remain at 55.7, 68.8 and 71 mAh/g. With the decrease of particle size for $LiFePO_4$ powders, the composite exhibit better capacity and cycle performance at high current density, indicating that fine particles can shorten the diffusion distance of Li^+ and improve its electric performance at high current densities.

Fig.7 shows the cycling performance of nano-$LiFePO_4$ at 1C rate. The initial discharge capacity of nano-$LiFePO_4$ at 1C is 106.4 mAh/g. After 50 cycles, the reversible discharge capacity is 95 mAh/g. The capacity retention is 90%, indicating that $LiFePO_4$ with fine particles also remain good cycling performance.

4. CONCLUSIONS

Size-controlled $FePO_4{\cdot}xH_2O$ powders can be prepared by controlled crystallization, which is an effective process for mass production. The $LiFePO_4/C$ materials with particle size ranging from 10μm to 100-200nm can be obtained by carbothermal reaction method successively. With the decrease of particle size for $LiFePO_4$ powders, the $LiFePO_4/C$ composite exhibit better capacity and cycle performance at high current density. This paves a way to synthesize the $LiFePO_4$ powders with different size distribution by controlled crystallization-carbothermal reaction process.

5. ACKNOWLEDGEMENTS

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