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Preparation of Micro/Nano-$LiFePO_4$/C Cathode Material for Li-ion Batteries

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Abstract: *$LiFePO_4$/C composite with micro/nano structure was synthesized via controlled crystallization-dry mixing-carbon thermal reduction method. As prepared micro/nano $LiFePO_4$/C composite show both excellent high-rate performance and high tap density as the cathode for lithium ion batteries. The tap density is 1.39 $g\cdot cm^{-3}$ while the discharge specific capacities of 148.9, 145.3, 143.3 and 132.6 $mAh\cdot g^{-1}$ are achieved at rates of 1 C, 2 C, 5 C and 10 C, respectively. This as-prepared micro/nano $LiFePO_4$/C composite material is suitable for large-scale application, such as electric vehicles and plug-in hybrid electric vehicles.*

Keywords: $LiFePO_4$; micro/nano; cathode

1. INTRODUCTION

Olivine-structured $LiFePO_4$ proposed by Padhi et al. [1] is recognized as promising positive electrode material for lithium-ion batteries due to its low cost, long cycle life, environmental friendliness and thermal stability. Despite these advantages, pristine $LiFePO_4$ has inherently poor electrical conductivity and sluggish lithium ion motion ability. Intensive efforts have been made to overcome the low electronic conductivity of $LiFePO_4$ [2-7]. Modifications of $LiFePO_4$ by decreasing particle size, doping with foreign atoms and coating with electronically conductive agents have been reported as effective ways to enhance its kinetics. Especially, decreasing particle size of $LiFePO_4$ to nanometer scale can improve the high-rate performance by shortening the diffusion length for electrons and lithium ions and increasing the effective reaction areas [8-10].

However, increasing the high-rate performance solely by decreasing the particle size will increase the surface area of the material, result in decreasing both the volumetric and the gravimetric energy density of the $LiFePO_4$/C composite significantly. Furthermore, nano-sized particles will fall off the current collector easily and the tap density of $LiFePO_4$/C composite with nanoscale particles is smaller than that of micro-sized particles. $LiFePO_4$/C composite with micro/nano structure can combine the advantages of enhanced kinetics of nano-sized structure and good stability of micro-sized structure [11-13].

There have been some reports of micro-nano $LiFePO_4$/C composite material in recent years. Wang etal. [14] synthesized micro-nano $LiFePO_4$/C composite material with both high-rate performance and high tap density, shown discharge capacities of more than 120,110 and 90 $mAh\cdot g^{-1}$ at rates of 5 C, 10 C and 20 C, respectively, and high tap density of 1.4 $g\cdot cm^{-3}$. Su etal.[15] prepared self-assembled $LiFePO_4$/C nano/microspheres by using PA as phosphorus source, shown a high tap density of 1.2 $g\cdot cm^{-3}$ and a high reversible specific capacity of 155 $mAh\cdot g^{-1}$ at 0.1 C.

In this paper, $LiFePO_4$/C composite with micro/nano structure was synthesized via controlled crystallization-dry mixing-carbon thermal reduction method. As prepared micro/nano $LiFePO_4$/C composite show both excellent high-rate performance and high tap density as the cathode for lithium ion batteries.

2. EXPERIMENTAL

In this paper, micro/nano $LiFePO_4$/C composite material was prepared via dry mixing and carbon thermal reduction method using nano-sized $FePO_4$ as precursor.

Nano-sized $FePO_4$ precursor was synthesized by modified controlled crystallization method[16] followed by preheated at 520° C for 10 h in air, using Fe $(NO_3)_3$, H_3PO_4 and NH_3 as the raw material, according to the reaction:

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

To synthesize micro/nano $LiFePO_4$/C powders, as-obtained

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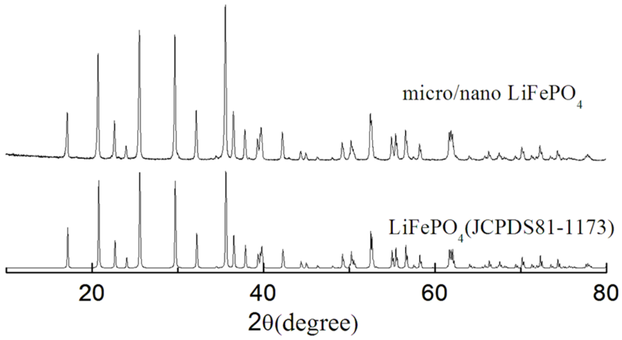

Figure 1. XRD patterns of micro/nano LiFePO$_4$/C composite material

nano FePO$_4$ precursor, Li_2CO_3, $C_{12}H_{22}O_{11}$ and deionized water (H_2O) were mixed uniformly in a molar ratio of Li_2CO_3:FePO$_4$:$C_{12}H_{22}O_{11}$:H_2O =0.485:1:0.1:2 and ball-milled for 2 h in a planetary miller to form a kind of uniform slurry. A small amount of water-soluble binder was added into the slurry in order to bind nano FePO$_4$ particles to each other.

The slurry was dried at 80^o C and agitated vigorously at the same time for almost 2 h, finally, we obtained a kind of well-dispersed mixed powders which were consisted of hierarchical structures, with nanosized primary structures and micro-sized secondary structures. The mixed powders were sintered at 700^o C for 16 h in N_2. the micro/nano LiFePO$_4$/C composite was finally obtained through carbothermal reduction process.

The crystalline phase of the synthesized LiFePO$_4$/C composite was characterized by powder X-ray diffraction (XRD, D/max-rB) measurement using Cu Kα radiation. The morphologies of the nano FePO$_4$ precursor and micro/nano LiFePO$_4$/C composite material were observed by scanning electron microscopy (SEM, ZEISS Supra55). To measure the tap density, about 4 g of powder was placed in a small glass vial and tapped on the lab bench for 10 min by hand. The measured volume of the tapped powder and its mass was used to calculate the ‘‘tap’’ density. [17]

We also tested the carbon content of LiFePO$_4$/C powders by dissolving the LiFePO$_4$/C in diluted HNO_3, filtering, drying and weighing the mass of the residual carbon.

The cathode was prepared with the composition of 80 wt% active material, 10 wt% carbon black and 10 wt% PVDF. The separator was Celguard 2400 micro porous polypropylene membrane. The electrolyte was 1M LiPF$_6$ dissolved in EC+DEC (1:1 by volume). A lithium metal anode was used in this study. The cells were galvanostatically charged and discharged over a voltage rang of 2.5-4.3 V (vs. Li/Li+) at 0.1 C rate and 1.5-4.3 V (vs. Li/Li$^+$) at other different C rates (1 C=150 mAh·g^{-1}).

3. RESULTS AND DISCUSSION

The XRD patterns of micro/nano LiFePO$_4$/C composite material are shown in Fig.1. All diffraction peaks of the composite material can be indexed to pure LiFePO$_4$ with an orthorhombic olivine-type structure (JCPDS card no. 81-1173). The strong diffraction peaks in the pattern suggest a perfect crystallinity of the synthesized materials with no impurities.

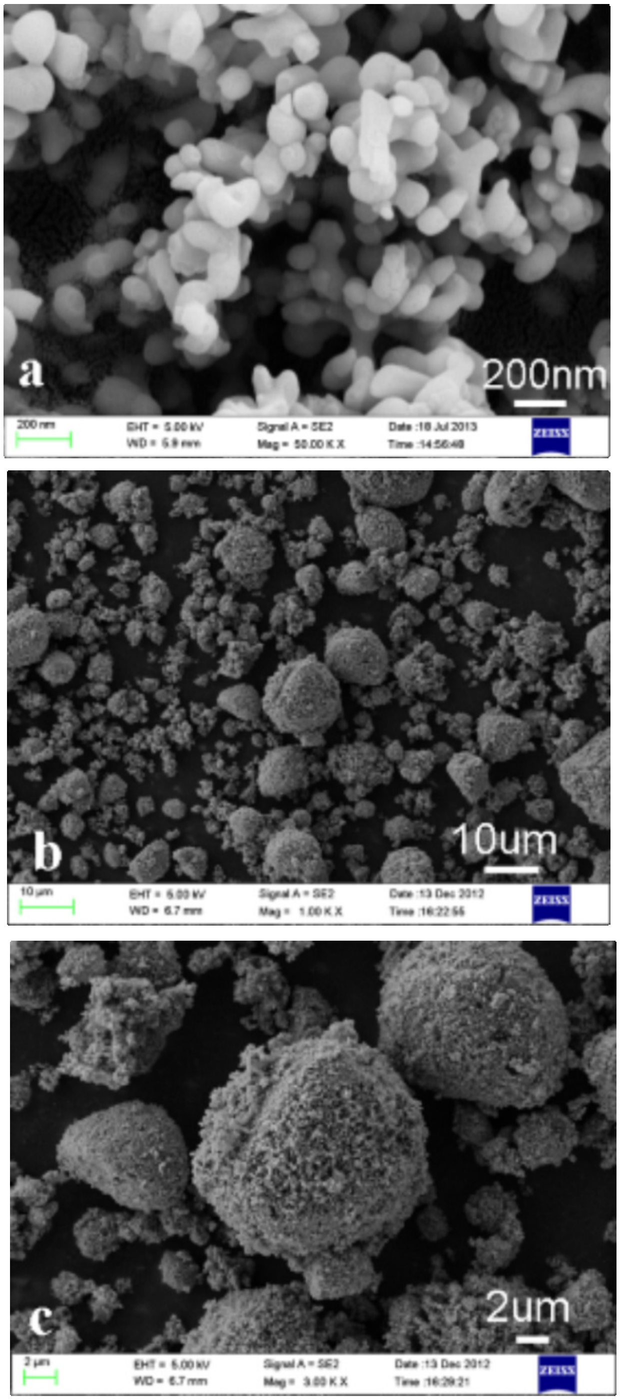

Figure 2. SEM images of nano FePO$_4$ (a) and micro/nano (b and c) LiFePO$_4$/C composite material

The images of nano FePO$_4$ precursor and micro/nano LiFePO$_4$/C composite material are shown in Fig.2. Fig.2a shows the images of nano FePO$_4$ powders, which is well-dispersed and its particle size is around 100 to 200 nm. Fig.2b and Fig.2c display typical SEM images of micro/nano LiFePO$_4$/C product. It is clear that the as-

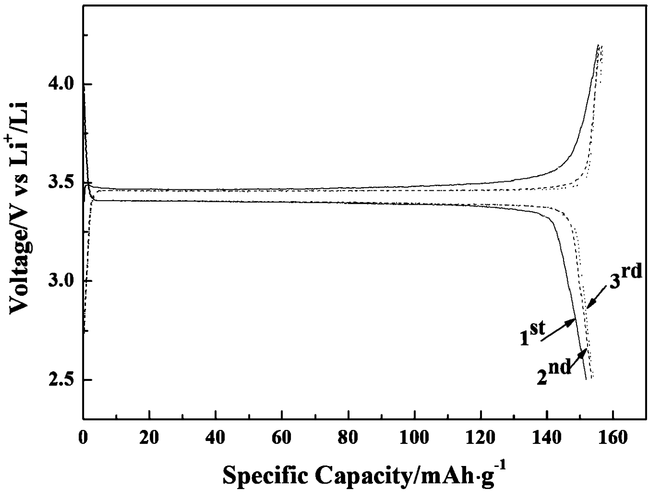

Figure 3. charge/discharge voltage profiles at 0.1 C for the first 3 cycles

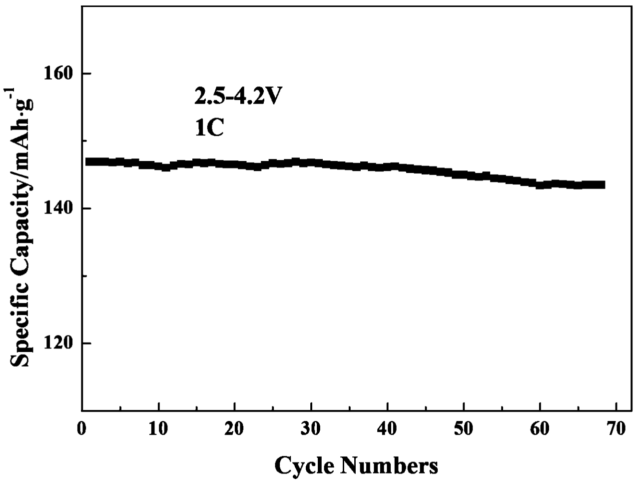

Figure 5. Cycle performance of micro/nano LiFePO$_4$/C at 1 C in the voltage range of 2.5-4.3 V (vs. Li/Li$^+$)

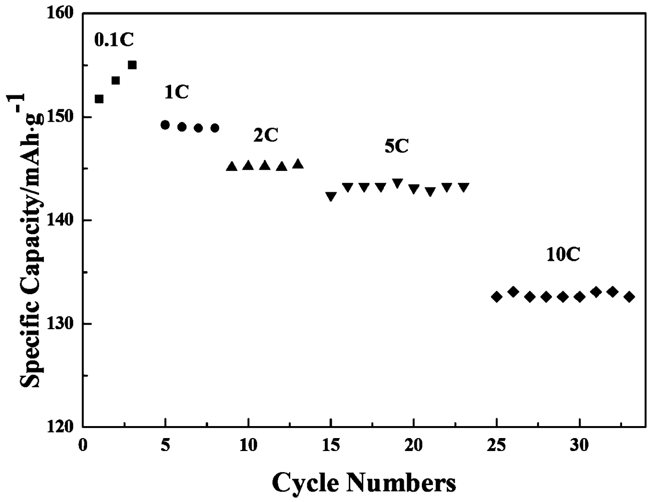

Figure 4. Rate performance of micro/nano LiFePO$_4$/C

prepared LiFePO$_4$/C composite material have micro/nano hierarchical structure with nano particles as the primary structure and micro quasi-spheres particles as the secondary structure.

In order to test the electrochemical performance of micro/nano LiFePO$_4$/C as cathode materials for LIBs, charge/discharge voltage profiles cycled at 0.1 C are shown in Fig.3. The discharge specific capacity and efficiency of this material increase from 97.6% to 99% and 151.7 to 154 mAh·g^{-1} after 3 cycles, accompanied with gradually decreased polarization. These phenomena can be attributed to the progressive penetration of the liquid electrolyte into the particles' interior.

The LiFePO$_4$/C material with micro/nano structure showed excellent high-rate capability, which is displayed in Fig.4. The discharge specific capacities of this micro/nano structured LiFePO$_4$/C composite material can stabilize at 149.2, 145.3, 143.3 and 132.6 mAh·g^{-1} at high rates of 1 C, 2 C, 5 C and 10 C. The results indicated that micro/nano LiFePO$_4$/C composite material has good electrical conductivity. The actual carbon content of the micro/nano LiFePO$_4$/C powders is about 4.7 wt%, determined by the method described above. In addition, the tap density of micro/nano LiFePO4/C composite material can reach to 1.39 g·cm^{-3}.

The cycling performance of micro/nano structured LiFePO$_4$/C material at 1 C is shown in Fig.5. The reversible discharge capacity was 146.9 mAh·g^{-1} at first and remains approximately 143.5 mA h·g^{-1} after 70 cycles.

All the results demonstrate that the micro/nano LiFePO$_4$/C composite material is promising cathode material for LIBs. These superior performances can be attributed to the following factors: (1) Primary nano-sized particles provide short transport distance for lithium-ion and high specific surface area for particles contact efficiently with electrolyte. (2) Carbon coating on the surface of nano particles further improve the electrical conductivity of LiFePO$_4$. (3) Secondary micro-sized particles guarantee a high tap density and can be generally used in manufacturing real batteries for application.

4. CONCLUSIONS

In summary, micro/nano structured LiFePO$_4$/C composite was synthesized via controlled crystallization-dry mixing-carbon thermal reduction method. This special structured LiFePO$_4$/C composite show both excellent high-rate performance and high tap density as the cathode for lithium ion batteries, which is suitable for large-scale application, such as electric vehicles and plug-in hybrid electric vehicles.

5. ACKNOWLEDGEMENTS

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