Preparation of Micro–Nano-Structured FePO4·2H2O for LiFePO4 Cathode Materials by the Turbulent Flow Cycle Method

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ABSTRACT: The micro–nano-structured FePO4·2H2O was prepared from mixed solution of FeSO4 oxidized in diluted H3PO4 with H2O2 and NaOH solution in the turbulent flow cycle state at 95 °C. The resulting products were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Constant current charge/discharge tests were adopted to investigate the electrochemical performance and the rate capability (from 0.1C to 5C) of the carbon-coated LiFePO4 composite materials prepared from the micro–nano-structured FePO4. The carbon-coated LiFePO4 composite materials deliver a high specific discharge capacity of 153.7 mAh·g−1, exhibit excellent cycle performance with 98.6% of the capacity retained after 30 cycles. This study demonstrates that the turbulent flow cycle method may be an economical and effective method for industrial production of fine and uniform micro–nano-structured FePO4·2H2O particles for LiFePO4 cathode materials for Li-ion batteries.

INTRODUCTION

Currently, lithium-ion batteries have been widely used in large scale electrochemical energy storage; digital electronic products such as mobile phones, cameras, tablets, and laptop computers; and electrical equipment such as electric tools, electric bicycles, and electric vehicles. China is a major producer of lithium-ion batteries, and battery companies attach great importance to the power application technology of lithium-ion battery energy storage.1–4 Today there are 7.19 billion active mobile phones,5 close to 1 billion laptop computers, and another billion tablets worldwide.6 It is estimated that the number of electric vehicles will reach 245 million in 2030, more than 30 times today’s 7.2 million level.7

As the core of lithium-ion batteries, cathode materials have always been the focus of research. Therefore, the ideal cathode materials need to have the following characteristics, such as high electric potential, high specific capacity, high density (including compaction density and tap density), good safety, good rate performance, and long life. Whereas, a series of approaches have been adopted, including doping,14–16 compounding,17–19 changing the morphology and size of raw materials,20–22 etc. Furthermore, different preparation processes and reaction conditions may have a great influence on the structure and morphology of the prepared samples and further affect the quality and consistency.23–25 The synthesis of traditional iron phosphate was mainly carried out in a liquid phase reaction system with an anchor stirrer.

In fact, the particles are in fluid movement under the stirring state of anchor or paddle. The form of fluid movement not only depends on the stirring method, but also affects the collision process between molecules and the aggregation state of the formed products, and its role in the synthesis process cannot be ignored. As a common phenomenon in environmental fluid mechanics, turbulence is a disordered state in the process of fluid particles changing from one stable state to another.

At present, the production of LiFePO4 was realized from Li2CO3, FePO4·2H2O, and organic compounds. However, the low electronic conductivity and slow ion diffusion coefficient of pure LiFePO4 resulted in low discharge capacity and poor rate performance. To solve these problems, various approaches have been adopted, including doping,14–16 compounding,17–19 changing the morphology and size of raw materials,20–22 etc. Furthermore, different preparation processes and reaction conditions may have a great influence on the structure and morphology of the prepared samples and further affect the quality and consistency.23–25 The synthesis of traditional iron phosphate was mainly carried out in a liquid phase reaction system with an anchor stirrer.

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another stable state, of which the flow elements such as the speed and pressure change randomly with time and space. The process significantly affects the flow structure and blending, and the movement form is shown in Figure 1.

![Figure 1. Turbulent flow cycle process in flow movement.](image)

Based on the turbulent flow phenomenon, a new stirring form is designed in the liquid phase reaction system to allow the reactants to collide and react between molecules in the turbulent flow mode, and synthesize a series of inorganic particles with micro–nano structures. The turbulent flow cycle method changed the flow direction of the materials during the stirring process, so that the materials were in a turbulent state. In this work, the objective of the work is the preparation of micro–nano-structured FePO₄·2H₂O by the turbulent flow cycle method. The composition and structure of micro–nano-structured FePO₄·2H₂O are investigated. The electrochemical performances of the final carbon-coated LiFePO₄ composite materials were measured. The electrochemical performances and the rate capability test (from 0.1C to 5C) between our materials were measured. The electrochemical performances of the final carbon-coated LiFePO₄ composite materials were measured. The electrochemical performances and the rate capability test (from 0.1C to 5C) between our LiFePO₄ and LiFePO₄ prepared without the turbulent flow cycle method were compared to prove that the turbulent flow cycle method is preferable to synthesize LiFePO₄ cathodes.

**RESULTS AND DISCUSSION**

**Reaction State.** The turbulent flow cycle method provides high shear and mechanical effects. When the rotor of the stirrer runs at high speed, negative pressure is generated at the bottom of the rotor to form a negative pressure zone. The materials in the negative pressure zone are sucked by the rotor into the narrow shearing “working zone” between the stator and the rotor, which is the gap between the stator and the rotor. The materials are sheared by a strong force formed between the gap, forcing them to spray out through the stator holes and turn back to the mixture in the reaction vessel when they hit the wall of the reaction vessel. The sheared materials are again sucked between the rotor and stator by the negative pressure at the bottom of the rotor and subjected to strong force, thus forming a continuous circulation. In this state, the movement direction of each substance in the mixture had the characteristics of randomness. Therefore, the mixing or dispersion between the materials was more rapid and uniform, and the reactants could quickly contact in a short time, thus forming a uniform microcrystalline particle product. This method is conducive to promoting micro-mixing and preparing nano or micro–nano materials.

**Composition and Structure of the Prepared FePO₄·2H₂O.** White crystal powders were obtained by the turbulent flow cycle method. The results of X-ray fluorescence (XRF) spectroscopy indicate that the mass ratio of Fe:P is 1.80 in the prepared samples, and it agrees with the theoretical value in FePO₄·2H₂O. This result demonstrates that all of the ferrous iron atoms were oxidized into ferric iron atoms and reacted with an equimolar amount of PO₄³⁻ to form FePO₄ products. The TG/DSC measurement was carried out to study the crystal water content in the FePO₄ products. Figure 2 shows the TG/DSC curves of the FePO₄·2H₂O powders in N₂.

![Figure 2. TG-DSC curves of the FePO₄·2H₂O powders in N₂.](image)

**Structure and Electrochemical Properties of LiFePO₄/C Composite Materials.** The XRD patterns of the carbon-coated LiFePO₄ composite materials and the precursor are...
LiFePO₄ particles. The coated carbon exists in an amorphous form on the surface of the LiFePO₄/C are presented in Figure 5. As can be seen, the XRD patterns of the final product LiFePO₄/C are similar to those of the precursor and can match well with the JCPDS (40-1499) standard olivine LiFePO₄ patterns. The calculated cell parameters of LiFePO₄/C are a = 10.3163 Å, b = 6.0070 Å, c = 4.6909 Å, and V = 290.70 Å³, which are close to those of the standard olivine LiFePO₄, indicating that the crystal structure of LiFePO₄ wasn’t changed carbon coated. There are no C and precursor diffraction peaks in LiFePO₄/C, which demonstrates that coated carbon exists in an amorphous form on the surface of LiFePO₄ particles.

The color of the final LiFePO₄/C powders is black, which indicates that the LiFePO₄ crystal particles are well carbon coated. Figure 6 presents the SEM images and TEM images of the carbon-coated LiFePO₄ final product. As shown in Figure 6a, all of the particles are uniformly distributed and have almost the same shape in comparison with the precursor. In addition, no significant agglomeration can be observed, that’s probably because the homogeneously coated carbon layer prevented the adjacent fine particles from aggregation. The average particle size of the composites is about 1 μm, and there is no obvious increase in the grain size after calcination at 680 °C for 3 h during the in situ coating process, which is confirmed by the image shown in Figure 6b. It is considered that the coated carbon hindered grain growth at high temperatures. Therefore, the particle size similar to that of the precursor was maintained.

The details of the morphological features of final product particles can be observed in the TEM images shown in Figure 6c, d. As shown in Figure 6c, the particle size is about 1.5 μm and this is in agreement with the results of SEM. It can be easily observed that a thin carbon layer is uniformly coated on the surface of the LiFePO₄ particle, indicating that the phenolic resin is a suitable carbon resource for in situ carbon coating in the preparation of cathode materials. Figure 6d shows the partially enlarged view of the LiFePO₄/C particle. As can be seen, a uniform carbon layer with nearly the same thickness of about 15 nm is clearly displayed (arrow). The in situ carbon coating approach has proved to be an effective way to significantly improve the electrical conductivity of the cathode materials and to obtain excellent electrochemical performances of the Li-ion batteries.

Figure 7a shows the initial charge/discharge curves of the as-prepared LiFePO₄/C sample at a 0.1C rate between 2 and 4.2 V vs Li⁺/Li. The cathode material exhibits a relatively high voltage plateau at around 3.5 V in the charge curve and a stable discharge plateau at around 3.4 V, which is attributed to the polarization effect during the first charge/discharge process. The first charge capacity is about 160 mAh·g⁻¹ which is close to the theoretical capacity, and the initial discharge capacity reaches up to 153.7 mAh·g⁻¹. The initial Coulombic efficiency is 96.1%. This indicates that the lithium ion could undergo intercalation and deintercalation reversibly in the lattice of the prepared cathode materials.

Figure 7b presents the charge/discharge curves of the 2nd and 31st cycles. As can be seen, the polarization of the cathode material between the charge/discharge plateau becomes lower and remains unchanged after the first cycle. The stable charge and discharge plateaus can be observed at around 3.5 and 3.4 V, which is in agreement with the reported figures.²⁷–³⁰ The charge capacity is 153.8 mAh·g⁻¹ in the 2nd cycle and 152.3 mAh·g⁻¹ in the 31st cycle, the corresponding discharge capacities are 153.6 and 151.5 mAh·g⁻¹, respectively. The result shows that 98.6% of the capacity is retained after 30 cycles.

The LiFePO₄/C sample also exhibits outstanding cycle performance with a stable capacity of about 153 mAh·g⁻¹ and no noticeable capacity fading occurs in the 30 cycles, as shown in Figure 7c. The Coulombic efficiency is maintained at a high level near 100%. The discharge capacity and cycle performance at a low rate of the LiFePO₄/C sample prepared by the turbulent flow cycle method is improved in comparison with the LiFePO₄/C sample prepared without the turbulent flow method.
cycle method, as shown in Figure 7c. The above results indicate high purity LiFePO4/C cathode material was obtained through the carbon thermal reduction method and the micro–nano-structured FePO4·2H2O was synthesized by the turbulent flow cycle method.

Figure 8 shows the rate capability of LFP prepared by the turbulent flow cycle method and LFP prepared without the turbulent flow cycle method from 0.1C to 5C. Throughout the test, the rate capability of the materials under a high current charge and discharge can be clearly observed. It can be seen from the test results that the rate capability of LFP prepared by the turbulent flow cycle method was significantly better than that of LFP prepared without the turbulent flow cycle method. As a cathode material, the materials still possess adequate electronic conductivity, fair structural stability, and excellent cycle performance even at high rates.

**CONCLUSIONS**

The micro–nano-structured FePO4·2H2O has been synthesized by the turbulent flow cycle method. The secondary particles were agglomerated from large amounts of primary particles. The D50 and D90 of the prepared FePO4 particles were 2.4 and 4.2 μm, respectively. The LiFePO4/C composite materials prepared from FePO4 by the carbon thermal reduction method exhibit a reversible capacity of 153 mAh·g⁻¹ at 0.1C and excellent cycle performance. The turbulent flow cycle method provides the possibility for industrial production with a micro–nano structure.

**EXPERIMENTAL SECTION**

**Reagents.** Ferrous sulfate (FeSO4·7H2O), phosphoric acid (H3PO4), hydrogen peroxide (H2O2), sodium hydroxide (NaOH), and lithium carbonate (Li2CO3) were of analytical grade (AR) and were purchased from Sinopharm Chemical Reagent Co., Ltd. Phenolic resin (PF-8010) was chemically pure (CP) and was purchased from Sinopharm Chemical Reagent Co., Ltd. Acetylene black, poly(vinylidene difluoride) (PVDF), N-methyl-2-pyrrolidone (NMP), lithium hexafluorophosphate (LiPF6), ethylene carbonate (EC), and dimethyl carbonate (DMC) were of battery-grade purity and were purchased from Aladdin Chemistry Co., Ltd. Lithium foil (provided by San Tong Metal Co., Ltd.) was used as the anode and a Celgard 2300 microporous polypropylene membrane was used as the separator for assembling CR2032 coin-type cells. Deionized water and anhydrous ethanol were used as solvents in the experimental process.

**Characterization.** The phase identification of the samples was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation, λ = 0.154 nm) at a scan rate of 4°·min⁻¹. The main elemental content of the samples was tested by X-ray fluorescence (XRF) spectroscopy (S4 PIONEER). The morphology and particle size of the prepared samples were observed using a FEI Quanta 200 scanning electron microscopy (SEM) system. Transmission electron microscopy (TEM) images were obtained using a JEM-2100 (HR) TEM with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) of the samples was carried out using a NETZSCH STA449C thermal analyzer at a heating rate of 10 K·min⁻¹ with FePO4·2H2O under an N2 atmosphere. The particle size distribution of the FePO4·2H2O was measured using a Malvern MasterSizers 2000 analyzer.

**Preparation of Micro–Nano-Structured FePO4·2H2O.** Scheme 1 shows the flowchart for the preparation of high purity FePO4·2H2O with a micro–nano structure by the turbulent flow cycle method. The reaction installation for the turbulent flow cycle method is shown in Figure 9. It consists of a motor, a stirrer that would make the reaction solution form a turbulent flow cycle state, a reaction vessel, a constant temperature water bath device, and a speed governor. The motor power was 300 W, the frequency was 50 Hz, and the speed was 200–11 000 rpm. The stirrer with a diameter of 6.5 cm, a height of 3.5 cm, and evenly distributed small holes (diameter of 0.5 cm) was placed in the reaction solution, which was a combination of a stator and a rotor.

Stoichiometric amounts of FeSO4·7H2O and H3PO4 were dissolved in 74 mL of deionized water in the reaction vessel, and then a certain amount of H2O2 was added into the mixed solution to turn all Fe²⁺ into Fe³⁺ through oxidation tested...
using phenanthroline in ethanol. The abovementioned oxidized solution in the reaction vessel was placed in a constant temperature water bath device, heated to 90 °C, churned up at 800 rpm to create a turbulent flow cycle, and then reacted for 0.5 h. Then, 10% NaOH solution was added into the reaction vessel from the top via a pipette to adjust the pH of the oxidized solution at 2.15 to 2.18. After the pH stabilized, FePO₄·2H₂O crystals continued to react for 4 h in a turbulent flow cycle state, and the yellow precipitate completely turned into a white precipitate. The micro−nano-structured FePO₄·2H₂O crystals were obtained. In addition, this method has many advantages, such as small reactor volume, high yield, high efficiency, and complete reaction. FePO₄·2H₂O crystals were washed with deionized water and dried at 120 °C for 12 h. The yield reached 99.5%. FePO₄ powder without crystal water was obtained by heat treatment in a muffle furnace at 600 °C for 4 h, which was collected for later use.

Preparation of Carbon-Coated LiFePO₄ Composite Materials. The carbon-coated LiFePO₄ composite materials were prepared by a carbon thermal reduction method. PF-8010 was chosen as the carbon resource for the in situ carbon coating. PF-8010 (2.5 wt %) was adequately dissolved in 20 wt % anhydrous ethanol and mixed well with 50 wt % deionized water, 50 wt % anhydrous FePO₄ powder, and 12.53 wt % Li₂CO₃ to form the mixed solution. After being vigorously stirred and mixed well, the mixture was dried at 100 °C in a
vacuum oven. Then, LiFePO4/C composite materials were obtained by carbon thermal reduction at 680 °C.

**Electrochemical Measurements.** The electrochemical measurements were performed by testing CR2032 coin-type cells. The cathodes of the cells were fabricated by blending 89 wt % prepared LiFePO4/C powder, 9 wt % acetylene black, and 2 wt % poly(vinylidene difluoride) (PVDF) binder in N-methyl-2-pyrrolidone (NMP) to form a slurry. The active substance mass was the total mass of C and LiFePO4. The slurry was then pasted on Al foil and dried at 70 °C for 24 h in a vacuum oven. The loading density of the electrode is ca. 7.2 mg cm⁻². Lithium metal was used as the anode and a Celgard 2300 microporous polypropylene membrane was used as the separator. The electrolyte was 1 M LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (volume ratio of 1:1). The cells were assembled in an Ar-filled glove box and the battery performance was measured using a Land CT2001A (Wuhan, China) battery tester. The tests were performed at a 0.1C to 5C current rate in a voltage range of 2.0−4.2 V vs Li/Li⁺ at room temperature.

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### Notes

The authors declare no competing financial interest.

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