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微波合成法制备锂离子电池正极材料 $\text{Li}_2\text{FeSiO}_4$

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摘要: 研究了一种制备锂离子电池正极材料 $\text{Li}_2\text{FeSiO}_4$ 的新方法. 采用机械球磨结合微波热处理合成了 $\text{Li}_2\text{FeSiO}_4$ 正极材料. 通过 XRD、SEM 和恒流充放电测试, 对样品结构、形貌和电化学性能进行了表征和分析. 与传统固相法合成的材料在晶体结构、微观形貌以及充放电性能方面进行了比较. 结果表明, 微波合成法可以快速制备具有正交结构的 $\text{Li}_2\text{FeSiO}_4$ 材料; 在 650 °C 下处理 12 min, 获得了纯度高、晶粒细小均匀的产物, 该产物具有较高的放电比容量和良好的循环性能. 在 60 °C 下以 C/20 倍率(电流密度, $1C=160 \text{ mA} \cdot \text{g}^{-1}$)进行充放电, 首次放电容量为 $119.5 \text{ mAh} \cdot \text{g}^{-1}$, 10 次循环后放电容量为 $116.2 \text{ mAh} \cdot \text{g}^{-1}$. 与传统高温固相法相比, 微波合成法制备的材料具有较高的纯度、均匀的形貌和较好的电化学性能.

关键词: 锂离子电池; 正极材料; $\text{Li}_2\text{FeSiO}_4$; 微波合成

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Preparation of $\text{Li}_2\text{FeSiO}_4$ Cathode Material for Lithium-Ion Batteries by Microwave Synthesis

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Abstract: We report a novel synthetic route for the preparation of the $\text{Li}_2\text{FeSiO}_4$ cathode material by microwave processing. The $\text{Li}_2\text{FeSiO}_4$ material was synthesized using mechanical ball-milling and subsequent microwave processing. The prepared samples were characterized by X-ray diffraction, scanning electron microscopy, and electrochemical methods. Properties of the prepared materials and electrochemical characteristics of the samples were investigated and compared to samples prepared by the conventional solid-state reaction. The obtained results indicated that highly pure $\text{Li}_2\text{FeSiO}_4$ material with uniform and fine particle size was quickly and successfully synthesized by microwave (MW) heating at 650 °C for 12 min. This compound showed high specific capacity and good cycle ability. The initial discharge capacity of the sample obtained by MW heating delivered $119.5 \text{ mAh} \cdot \text{g}^{-1}$ at 60 °C at a current density of C/20 rate ($1C=160 \text{ mA} \cdot \text{g}^{-1}$). After 10 cycles the discharge capacity maintained $116.2 \text{ mAh} \cdot \text{g}^{-1}$. The $\text{Li}_2\text{FeSiO}_4$ material displayed higher phase purity, better microstructure, and better electrochemical properties than the sample prepared by the conventional solid-state method.

Key Words: Li-ion battery; Cathode material; $\text{Li}_2\text{FeSiO}_4$; Microwave synthesis

Since introduction of polyanionic-based cathode materials by Goodenough's group^[1], there is great interest in polyanion compounds as lithium storage cathodes because of their low raw materials cost, nontoxicity, environmental friendliness, and high safety^[2,3]. Particularly, LiFePO_4 becomes a promising cathode

material for large-scale Li-ion power battery applications^[4-6]. Indeed, safety and environmental respects nowadays have become two major concerns, which assure thermal stability, great chemical and electrochemical stability. Recently, the silicate-based materials of polyanionic compound are developed as a new class

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of safe cathode materials^[7-12]. The orthosilicate family of Li_2MSiO_4 ($M=\text{Fe, Mn, Co}$) has similar crystalline structure, chemical and thermal stability with LiFePO_4 ^[8-10]. Furthermore, with more abundant resources, lower raw materials cost, and being more environmentally friendly than LiFePO_4 , the Li-Fe-Si-O system holds great attraction as potentially cheap cathode material^[8,13-15]. Its theoretical capacity is $166 \text{ mAh} \cdot \text{g}^{-1}$ based on one Li ion intercalation/extraction reaction. The first testing of $\text{Li}_2\text{FeSiO}_4$ by Nytén *et al.*^[8] has shown reversible capacity around $130 \text{ mAh} \cdot \text{g}^{-1}$ cycled at $60 \text{ }^\circ\text{C}$ at a $C/16$ rate. Then the cycling stability is also quite good ($<3\%$ of degradation over 120 cycles)^[16,17]. However, similarly as in the case of LiFePO_4 material the rate performance is still poor due to the problems of low electronic conductivity and low lithium diffusivity, as well as the difficulty in synthesizing a single-phase material. Synthesis of ultra-fine and well-crystallized $\text{Li}_2\text{FeSiO}_4$ powders has been used by various synthetic methods such as solid-state reaction^[8,14], sol-gel route, and hydrothermal reaction^[13,15,18,19]. In all of these studies, $\text{Li}_2\text{FeSiO}_4$ was synthesized for very long processing time with high energy consuming. Thus there is a need for development of novel synthesis methods to reduce required processing time ensuring control of particle size and modification of particle surface to improve the electrochemical performance.

The microwave heating technique is widely applied to prepare advanced materials in the field of inorganic synthesis due to its advantages of convenience, energy efficiency, and environmental compatibility. A great deal of interest has been shown in the microwave synthesis of cathode materials^[20-23]. Unlike the conventional heating, microwave heating can achieve very uniform and rapid heating through the direct absorption of microwave energy into the materials. Therefore, microwave processing with flexibility for thermal treatment can be expected to produce fine particles with high purity and homogeneous microstructure.

We introduced microwave heating into the preparation of the $\text{Li}_2\text{FeSiO}_4$ cathode material in this study, and this method is very quick and simple for synthesizing $\text{Li}_2\text{FeSiO}_4$. The obtained $\text{Li}_2\text{FeSiO}_4$ materials exhibited higher phase purity, homogeneous microstructure, and better electrochemical properties, compared with those of sample by conventional solid-state process.

1 Experimental

1.1 Preparation and characterization of $\text{Li}_2\text{FeSiO}_4$ cathode material

$\text{Li}_2\text{FeSiO}_4$ cathode material was prepared by ball-milling and subsequent microwave heating. Li_2CO_3 (99.5%), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.0%), and nano SiO_2 (99.5%) were used as starting materials with 15% (*w*, mass fraction) glucose (98.0%) as carbon source, then were weighed in stoichiometric ratios, dispersed into acetone, and thoroughly mixed by wet ball milling for 6 h in polypropylene bottles using alumina balls (the charge to balls ratio was 1:3) at $300 \text{ r} \cdot \text{min}^{-1}$. After evaporating the acetone, the mixture was ground by ball-milling for 0.5 h. The starting materials were first heated at $400 \text{ }^\circ\text{C}$ for 6 h in flowing pure Ar

(99.99%) to pre-decompose the oxalate. After cooling down, the pre-decomposed precursor mixtures were divided into two parts, pressed into pellets, and then placed in alumina crucible, respectively.

One part of mixture was heat-treated by conventional method (CM) in a flow of Ar at 650 and $700 \text{ }^\circ\text{C}$ for 20 h to synthesize cathode material and the obtained samples were referred as CM1 and CM2, respectively. The other part was treated by microwave heating at $650 \text{ }^\circ\text{C}$ for 8 and 12 min in Ar atmosphere and the obtained samples were denoted as MW1 and MW2, respectively. The microwave irradiation to the crucible was conducted with a controllable temperature HAMiLab-V3 multimode microwave heating oven (SYNOTHERM Corporation, China).

Thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) was carried out on SDTQ 600 simultaneous thermal analysis (TA Instruments Corporation, USA) to determine the treating temperature. The mixture was heated from room temperature to $900 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in Ar flow.

The structures of the samples were determined by X-ray diffraction (XRD, D/max-rA type $\text{Cu K}_{\alpha 1}$, 40 kV, 300 mA, 10° – 70° , Japan). The microstructures of all products were observed by scanning electron microscopy (SEM, JEOL JSM-6360LV, USA). The amounts of carbon in the samples were obtained using vario EL III elemental analyzer (Elementar Company, Germany).

1.2 Cell fabrication and electrochemical testing

The electrochemical properties of the $\text{Li}_2\text{FeSiO}_4$ samples were assessed using CR2025 coin cells. The cathode was prepared by mixing 75% (*w*) of the active material with 15% (*w*) carbon black and 10% (*w*) poly-vinylidene fluoride (PVdF). The mixture was made into slurry by milling using *N*-methyl-2-pyrrolidone (NMP) as the solvent. The electrodes were formed by coating the slurry onto Al foils. After drying overnight at 393 K in a vacuum, the electrode disks with 12 mm in diameter were punched and weighed. The cells were assembled with the as-prepared cathode, with lithium metal as the anode and with Celgard 2400 film as a separator. The electrolytes were $0.8 \text{ mol} \cdot \text{L}^{-1}$ lithium bis(oxalato)borate (LiBOB) dissolved in ethylene carbonate (EC)/propylene carbonate (PC)/ethyl methyl carbonate (EMC) (1:1:3, volume ratio). Cell assembly was carried out in an ultra-pure Ar-filled glove box. The electrochemical measurements were performed using a battery test system (LAND CT2001A) between 2.0 and 4.0 V at $60 \text{ }^\circ\text{C}$.

2 Results and discussion

Fig.1 presents the TGA-DSC curves of the starting materials for preparation of $\text{Li}_2\text{FeSiO}_4$. It is found that two endothermic peaks at 188 and $400 \text{ }^\circ\text{C}$ in the DSC curve are observed, and obvious mass loss is also seen in TGA curve, corresponding to losing lattice water and the decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, respectively. As the temperature rises, a wide endothermic peak appears at $604 \text{ }^\circ\text{C}$ in DSC curve, and continual mass loss is observed in TGA curve, indicating the decomposition of Li_2CO_3

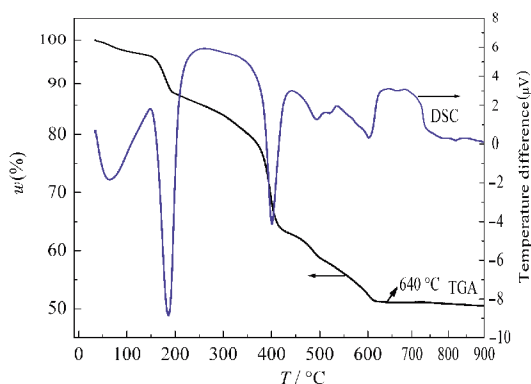


Fig.1 TGA-DSC curves of the mixture sample

and formation of silicate. The mass of raw materials does not decrease over 640 °C. It can be concluded that the reaction cannot be achieved at the annealing temperature below 640 °C.

Typical XRD profiles of the as-prepared $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite by microwave process for 8 and 12 min are shown in Fig.2. The XRD pattern shows that incomplete phase transformation of MW1 sample is obtained at 650 °C for 8 min and the crystallinity of $\text{Li}_2\text{FeSiO}_4$ increases with prolonging irradiation time. Highly pure $\text{Li}_2\text{FeSiO}_4$ phase with good crystallization is achieved for 12 min. The diffraction peaks of the obtained sample MW2 are in good accord with previous reports^[8,17,19]. It has been confirmed by XRD analysis that the crystal structure of the obtained sample can be fitted using orthorhombic $Pmn2_1$ space group. No diffraction response of the carbon content is observed due to its amorphous state, and the result of element analysis indicates that the amount of carbon in the sample MW2 is about 5.41% (*w*). Fig.3 shows the XRD patterns of the as-prepared samples by solid-state reaction at 650 and 700 °C for 20 h. Although experienced at higher temperature 700 °C for much longer calcination time, the sample CM2 contains an appreciable amount of impurity phases of Li_2SiO_3 (marked by +) and $\text{LiFeSi}_2\text{O}_6$ (marked by *), compared with the sample MW2. And the sample CM2 contains about 5.06% (*w*) carbon by element analysis. From the difference in the above results by two methods, it suggests that $\text{Li}_2\text{FeSiO}_4$ with higher phase purity can be quickly and successfully synthe-

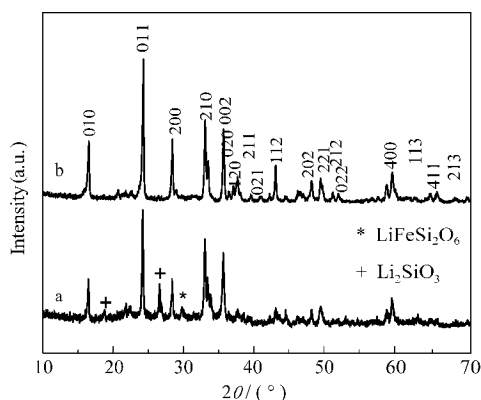


Fig.2 XRD patterns of as-prepared samples by microwave processing at 650 °C for 8 min (a, MW1) and 12 min (b, MW2)

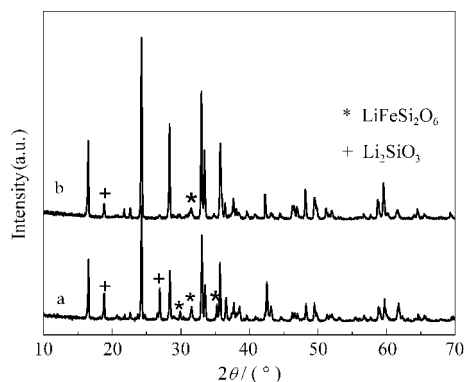


Fig.3 XRD patterns of as-prepared samples by conventional method at 650 °C (a, CM1) and 700 °C (b, CM2) for 20 h

sized through microwave process. And it is derived from the character of microwave effect of microwave irradiation. As a good microwave absorber, the residual carbon greatly improves the absorption ability of microwave energy into the whole reaction sample^[22] and under the microwave irradiation the reaction sample achieves uniform and volume heating on molecular level to fast generate high temperature sufficiently necessary for completing the reaction. In addition, the microwave energy can enhance the ions inter-diffusion movement and decrease the reaction activation energy^[23] to accelerate phase transformation of the reaction sample, consequently leading to higher purity of final product in shorter processing time. Therefore, microwave processing makes it possible to synthesize the target material at temperature lower than that required for conventional heating.

The morphologies of the samples prepared using two methods are displayed in Fig.4(a, b). It is seen that because of longer cal-

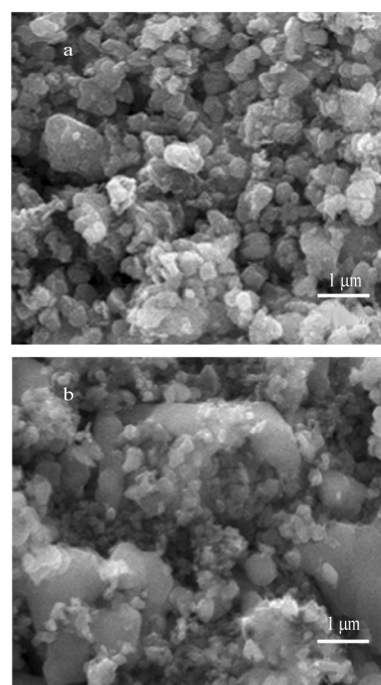


Fig.4 SEM images of the obtained $\text{Li}_2\text{FeSiO}_4$ samples (a) MW2, (b) CM2

ination time at higher temperature, the sample CM2 powders with irregular morphology show smoother particle surface, larger particle size, a wider range of particle size distribution, and an obvious tendency toward agglomeration. On the other hand, the crystallite particles of sample MW2 develop well and form loose agglomerates. The obtained sample MW2 exhibits narrower particle size distribution and smaller particle growth due to the very short treatment time and uniform heating of microwave treatment which suppress active particles abnormal growth and make particles develop homogeneously. Meanwhile, the presence of carbon during microwave heating can control the diffusion process of growing crystallites to hinder particle agglomerations and reduce particle size. Furthermore, reduced particle size and uniform distribution are beneficial for electrical conductivity and the diffusion of lithium ions during charge-discharge cycles.

The obtained samples by two methods possess some difference in the phase purity and microstructure, and thus the electrochemical behaviors of $\text{Li}_2\text{FeSiO}_4$ cathode materials occur differently. Fig.5 shows the initial charge-discharge curves of the as-prepared $\text{Li}_2\text{FeSiO}_4$ materials at 60 °C. It shows that the electrochemical performance of the material synthesized by microwave process is superior to that of sample by conventional solid-state method. The $\text{Li}_2\text{FeSiO}_4$ material by microwave process delivers first discharge capacity of $119.5 \text{ mAh} \cdot \text{g}^{-1}$ when cycled at $C/20$ rate. Whereas the sample by solid-state method has a relatively lower capacity of $104 \text{ mAh} \cdot \text{g}^{-1}$ directly attributed to the presence of the inactive impurity phase and heterogeneous microstructure. The second charge-discharge cycles of the prepared samples are presented in Fig.6. It is obviously higher discharge capacity of MW2 by microwave treatment than that of CM2 by conventional treatment. The variation of discharge capacity with preparation method can be explained in terms of particle size and microstructure homogeneity. It is well known that particle size is critical in determining reversible lithium capacities and cycle rates for low-conductivity polyanion compounds, and the electrochemical performance of material is better in samples with uniform and smaller particles, additionally, where the particles are in intimate contact with carbon^[24,25]. Consequently good electrochemical performance of MW2 indicates that higher phase purity, microstructure, and morphology homogeneity of $\text{Li}_2\text{FeSiO}_4$

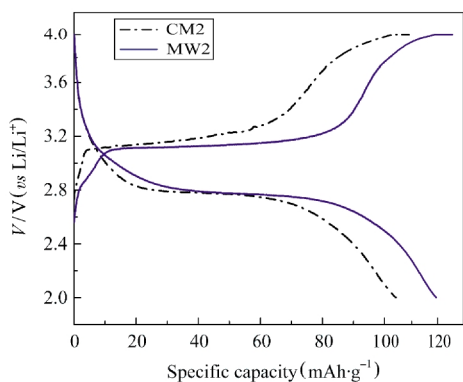


Fig.5 Initial cycle curves of $\text{Li}_2\text{FeSiO}_4$ samples MW2 and CM2

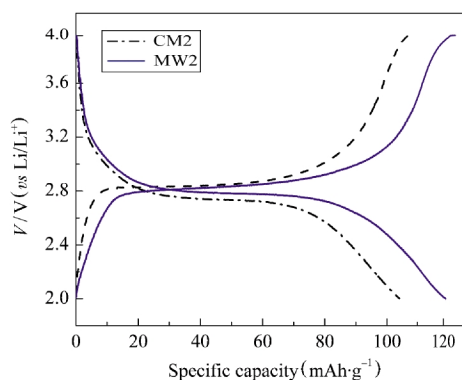


Fig.6 The second cycle curves of $\text{Li}_2\text{FeSiO}_4$ samples MW2 and CM2

cathode material by microwave process are more promising than those of the material prepared by solid-state method.

Compared Fig.5 with Fig.6, it is seen that the specific shift of potential plateau on the first charging to a lower potential on later cycles is observed, similarly as reported and explained by Nytén *et al.*^[8,16] that lithium may be extracted from $\text{Li}_2\text{FeSiO}_4$ through a rather complex non-reversible mechanism as charge voltages are 3.10 and 2.80 V (*vs* Li/Li⁺) for the first and second cycles indicating a phase transition to a more stable structure in which some of the Li ions and Fe ions become interchanged and lead to a structural rearrangement.

On further charge-discharge cycles, the potential plateaus are stable at 2.80 and 2.76 V with good reversibility. Meanwhile the sample MW2 with the larger reversible capacity was electrochemically tested with respect to its cyclic performance at different rates given in Fig.7. The sample shows good cycling stability. After 10 cycles the discharge capacity maintains $116.2 \text{ mAh} \cdot \text{g}^{-1}$ at $C/20$ rate. And the capacity retention at higher rate is quite good: at $C/2$ rate the reversible capacity is still about 80% of that at $C/20$ rate with initial discharge capacity of $96.2 \text{ mAh} \cdot \text{g}^{-1}$, and after 10 cycles the discharge capacity maintains $89.5 \text{ mAh} \cdot \text{g}^{-1}$. The good cycling stability of sample MW2 could be attributed to the high purity and crystallized phase structure, fine and uniform particle size and improved electronic conductivity through carbon connection.

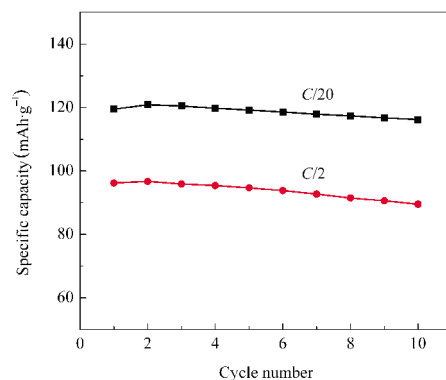


Fig.7 Cycle performance of MW2 sample at $C/2$ and $C/20$ rates

3 Conclusions

The $\text{Li}_2\text{FeSiO}_4$ cathode material was synthesized fast and conveniently by microwave process at 650 °C for 12 min. Compared with the product by conventional solid-state method, the uniform and fine particles of $\text{Li}_2\text{FeSiO}_4$ material with higher purity can be prepared successfully by this novel synthetic method and the obtained sample has larger electrochemical capacity with initial discharge specific capacity of 119.5 mAh · g⁻¹ at 60 °C. In addition, the obtained $\text{Li}_2\text{FeSiO}_4$ material shows good capacity retention on cycling at different rates. Consequently, the results indicate that microwave processing is a promising method for preparing $\text{Li}_2\text{FeSiO}_4$ cathode material.

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