



Hydrothermal synthesis and electrochemical performance of nanoparticle $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials for lithium ion batteries



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ARTICLE INFO

Article history:

Received 12 January 2015

Received in revised form 20 March 2015

Accepted 23 March 2015

Available online 25 March 2015

Keywords:

Lithium ion batteries

Cathode

Lithium iron silicate

Nanoparticles

Hydrothermal

ABSTRACT

$\text{Li}_2\text{FeSiO}_4$ nanoparticles are successfully synthesized via hydrothermal approach, with the hydrothermal process monitored in detail. Structural characterizations by XRD, FTIR, SEM and HRTEM measurements reveal that the $\text{Li}_2\text{FeSiO}_4$ nanoparticles have a high crystalline degree and monodisperse nanoparticle shape with a size around of 50–200 nm. To further improve the electronic conductivity, the $\text{Li}_2\text{FeSiO}_4$ nanoparticles are coated by a carbon layer using in situ polymerization of dopamine. Moreover, the effect of carbon content for electrochemical performance of $\text{Li}_2\text{FeSiO}_4/\text{C}$ is systematically investigated, and as a result, the composite with a ratio of $\text{Li}_2\text{FeSiO}_4$ and dopamine of 3:1 demonstrate the best electrochemical performance with a discharge specific capacity of 148 mA h g^{-1} at a rate of 0.1 C at room temperature. Furthermore, the electrochemical performance of $\text{Li}_2\text{FeSiO}_4/\text{C}$ at high temperature of 55°C is also investigated, and it also exhibits a good performance with a discharge specific capacity of 240 mA h g^{-1} at a current rate of 0.2 C.

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1. Introduction

Expansion of lithium-ion batteries (LIBs) technology into electric vehicles (EVs), hybrid electric vehicles (HEVs), aerospace, and power-grid applications demands the development of lightweight, high-longevity batteries [1–3]. Increasing the specific capacity of LIBs cathode is considered as an attractive route to lower the battery weight, volume, and cost. Up to now, olivine-structured LiFePO_4 [4,5], which shows advantage of good electrochemical performance and environmental benignity, has been utilized in large scale energy storage system. However, the available energy discharge capacity of LiFePO_4 approaches theoretical limits that far less than the capacity of anode material

at present. Thus, novel electrode materials with high capacity are explored constantly in researchers' endeavors.

Lithium transition metal orthosilicates [6,7] (Li_2MSiO_4 , M = Co, Mn and Fe et al.) could store and release two lithium ion along with transfer reaction of $\text{M}^{2+}/\text{M}^{3+}$ and $\text{M}^{3+}/\text{M}^{4+}$ redox couples, suggesting orthosilicate Li_2MSiO_4 posses a high theoretic specific capacity. Among orthosilicate materials, lithium iron silicate, which was firstly explored by Nyttén et al. [8], has been successfully synthesized and characterized as cathode material for lithium ion battery. $\text{Li}_2\text{FeSiO}_4$ was deemed to one of the most promising candidates for LiFePO_4 because of its high specific capacity, excellent chemical stability, inexpensive and abundant materials, and environmental benignancy.

However, $\text{Li}_2\text{FeSiO}_4$ has some defects like poor electrical conductivity and slow diffusion rate of lithium ion as same as LiFePO_4 , of which limit its electrochemical performance significantly. Therefore, numerous strategies should be attempted to improve the rate performance, such as decreasing the particle size [9], doping with supervalent or isovalent cation [10] and coating with conductive material [11]. Moreover, special morphologies for $\text{Li}_2\text{FeSiO}_4$ also be beneficial to improve its electrochemical performance, including hierarchical shuttle-

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like $\text{Li}_2\text{FeSiO}_4$ [12], rod like $\text{Li}_2\text{FeSiO}_4$ [13], hollow spherical structure $\text{Li}_2\text{FeSiO}_4$ [14] and nanoparticle- $\text{Li}_2\text{FeSiO}_4$ [15]. So far, to synthesize different morphologies of $\text{Li}_2\text{FeSiO}_4$, various synthetic methods, such as sol-gel method [16], solid-state method [17,18], hydrothermal method [19] and supercritical hydrothermal method [20] has been extensively employed. Among them, hydrothermal reaction receives particular interest due to simple operation, mild temperature, controllable particle size and special morphology, etc. On the other hand, it is generally believed that small particles, typically nanoparticles, have major advantages in LIBs, since size reduction dramatically reduces the path for mass and charge transport and mitigates the volumetric changes during electrode operation. In addition, nanoparticles allow quite efficient mixing of the active electrode materials with other component such as the binder, conductive additives and so on.

Therefore, in this work, we reported a hydrothermal synthesis process for the $\text{Li}_2\text{FeSiO}_4$ nanoparticle combined with conductive carbon framework using in situ polymerization of dopamine [21,22]. Its formation mechanism, structural characteristics and electrochemical performance were investigated in detail. The results demonstrated that $\text{Li}_2\text{FeSiO}_4/\text{C}$ nanoparticle showed excellent electrochemical performance both at room temperature and high temperature ($55 \pm 2^\circ\text{C}$).

2. Experimental

2.1. Chemicals and preparation

$\text{Li}_2\text{FeSiO}_4$ was prepared via a hydrothermal method. Firstly, 0.01 mol of tetraethyl orthosilicate (TEOS) was hydrolyzed reasonably in 20 mL de-ionized water with the help of a little hydrochloric acid. Then, 20 mL basic solution of 0.04 mol of $\text{LiOH} \cdot 2\text{H}_2\text{O}$ was rapidly added to TEOS mixture under intense vigorous stirring. After a white turbid liquid formed, a solution with 0.01 mol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added. The molar ratio of $\text{Li}:\text{Fe}:\text{Si}$ was kept at 4:1:1. The mixture was then transferred to a 100 mL of Teflon-lined stainless steel autoclave after stirring about 15 min. The autoclave was maintained at 180°C for different time. After cooling down to room temperature, the grayish precipitation was harvested by centrifugation and washed with de-ionized water and ethanol for several times. The samples hydrothermal at 12 h, 18 h and 24 h were prepared and marked as LFS-12 h, LFS-18 h and LFS-24 h, respectively.

Due to the low electronic conductivity of $\text{Li}_2\text{FeSiO}_4$, the modification approach of carbon coating is indispensable. In this study, a continuous and uniform carbon coating $\text{Li}_2\text{FeSiO}_4$ was achieved by means of the in situ polymerization of dopamine due to its outstanding viscosity. The obtained nanoparticle LFS-24 h sample was ultrasonic dispersed in 50 mL de-ionized water. Then, 60 mg of trihydroxy methyl-aminomethane (TRIS) and 100 mg of dopamine were added into the solution. The ratio of $\text{Li}_2\text{FeSiO}_4$ sample and dopamine was 4:1, 3:1, 2:1 in quality. After vigorous stirring for 24 h at room temperature, the resultant black powers were collected after centrifugation, washed by distill water several times and dried at 80°C . Finally, the product was pre-heated at 350°C for 4 h and sintered at 650°C for 10 h under flow nitrogen atmosphere. The final $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites with various molar ratios of $\text{Li}_2\text{FeSiO}_4$ to dopamine with 4:1, 3:1 and 2:1 were marked as LFSC-4, LFSC-3, LFSC-2, respectively.

2.2. Characterization

The crystalline structure of the as-prepared sample was characterized by power X-ray diffraction (XRD, Shimadzu XRD-6000, Japan) in the 2θ range from 10° to 70° with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154\text{ nm}$). The Fourier transformed infrared

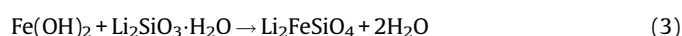
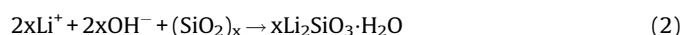
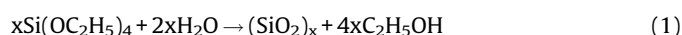
spectroscopy (FTIR) was performed on Vector-22 (Bruker, Germany). The morphology of the samples were characterized by field-emission scanning electron microscopy (FESEM, Zeiss Supra 55) and high-resolution transmission electron microscopy (HRTEM, Hitachi, JEM-2100). The surface area and pore volume was analyzed by Brunauer–Emmett–Teller nitrogen adsorption-desorption measurement (Quantachrome Autosorb-1C-VP, USA). The sample was degassed at 120°C for 24 h before it measured.

2.3. Electrochemical tests

The electrochemical performance of prepared $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites as cathode material was tested by assembled 2032-type coin half cell. The solvent of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (EC/DMC/DEC = 1:1:1 by volume,) was used as electrolyte. A polypropylene microporous film (Cell-gard 2300) was used as the separator. The composite electrode was prepared by mixing active materials, acetylene black and polyvinylidene fluoride (PVDF) binder with a weight ratio of 7:2:1. Before carried out coin cell in an argon-filled glove box, the electrode films were dried at 100°C for at least 12 h in vacuum. The electrochemical tests were performed on a multichannel battery testing system (LAND CT2001A, Wuhan, China) with voltage window of 1.5–4.8 V (versus Li^+/Li) under various current densities at room temperature and high temperature about 55°C .

3. Results and Discussion

In order to confirm the effects of hydrothermal time on the crystalline structure, XRD and FTIR observations of $\text{Li}_2\text{FeSiO}_4$ at different hydrothermal time were tested and displayed in Fig. 1. In the XRD patterns (Fig. 1a), it is noted that the hydrothermal time has a significant impacts on the cation disorder and structural defects in the crystallization process of $\text{Li}_2\text{FeSiO}_4$. Moreover, three main space groups of $\text{Li}_2\text{FeSiO}_4$ are proposed from recent research: $\text{Pmn}2_1$, $\text{P}2_1$ and Pmnb [23–25]. There is a structural evolutionary trend from $\text{P}2_1$ to Pmnb with an increase of calcinations temperatures. In Fig. 1(a), it can be easily found that the patterns of LFS-12 h and LFS-18 h are indexed to Fe_3O_4 . When extending hydrothermal time to 24 h, the obtained LFS-24 h can be well assigned to space group of $\text{P}2_1$ without any reflection peak from impurity phases, especially Fe_3O_4 , suggesting that the as-prepared LFS-24 h sample is a pure-phase material. Satisfactorily, $\text{Li}_2\text{FeSiO}_4$ obtained by hydrothermal reaction only need 24 hours, which is much quicker than other reports [12,19] as same as hydrothermal method, for example, Mu et al. [12] synthesized shuttle like $\text{Li}_2\text{FeSiO}_4$ hydrothermal for at least 6 days and the mechanism of hydrothermal reaction has been proposed as follows:



Based on above equations, it is reasonable that pre-treatment of TEOS with HCl that can slow down the rate of hydrolysis reaction, and therefore, TEOS was controlled to hydrolyze completely and retard from dramatic polymerization. Consequently, the nano-scale $\text{Li}_2\text{FeSiO}_4$ particles were formed during hydrothermal process. In Fig. 1a, it is clearly seen that LFS-24 h and further coated with carbon and calcined at 650°C for 10 h, all the

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