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Trans. Nonferrous Met. Soc. China 21(2011) 529-534

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

# Effects of calcination temperature on properties of Li<sub>2</sub>SiO<sub>3</sub> for precursor of Li<sub>2</sub>FeSiO<sub>4</sub>

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Received 13 July 2010; accepted 4 October 2010

**Abstract:** Li<sub>2</sub>SiO<sub>3</sub> was synthesized by combination of sol-gel method and calcination at high temperature using Li<sub>2</sub>CO<sub>3</sub>, HNO<sub>3</sub>, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH as starting materials. The effects of calcination temperature and refluxing system on the composition and properties of lithium silicate were investigated. The samples were characterized by TGA/DTA, XRD, SEM and particle size analysis. Li<sub>2</sub>FeSiO<sub>4</sub> was prepared by the solid-state reaction between Li<sub>2</sub>SiO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. The XRD patterns show that the use of refluxing system in the sol-gel preparation can decrease the Li<sub>2</sub>SiO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. The XRD patterns show that the use of temperature plays an important role in the properties of the Li<sub>2</sub>SiO<sub>3</sub> samples. The sample calcined at 700 °C has high purity of 97% Li<sub>2</sub>SiO<sub>3</sub> and good morphology as precursor of Li<sub>2</sub>FeSiO<sub>4</sub>. It consists of primary particles with size of 1–3  $\mu$ m, and the primary particle clusters form agglomerates with loose and porous appearance.

Key words: lithium ion batteries; Li<sub>2</sub>FeSiO<sub>4</sub>; Li<sub>2</sub>SiO<sub>3</sub>; sol-gel method

### **1** Introduction

Among the novel cathode materials for lithium ion batteries, iron-based active materials seem to be one of the most ideal candidates. The well-known examples are LiFePO<sub>4</sub> and Li<sub>2</sub>FeSiO<sub>4</sub> distinguished from other materials by their excellent stability [1]. However, the lower electronegativity of Si vs P will result in a lowering of the Fe<sup>II</sup><=>Fe<sup>III</sup> couple[2]. So Li<sub>2</sub>FeSiO<sub>4</sub> should have a lower electronic band gap, and therefore a higher electronic conductivity compared with LiFePO<sub>4</sub>, and it will become a prospective novel cathode material in lithium ion batteries.

Similar to other cathode materials, one of the important methods for synthesis of  $Li_2FeSiO_4$  is the solid-state reaction between  $Li_2SiO_3$  and iron compounds at high temperature. For example, NYTÉN et al [2] and ZAGHIB et al [3] have reported the synthesis of  $Li_2FeSiO_4$  powder by this method using  $Li_2SiO_3$  and  $FeC_2O_4$ ·2H<sub>2</sub>O as the starting materials.

In previous studies [4–5], the lithium silicates were mainly synthesized by the solid-state reaction,

precipitation and sol-gel methods. By the solid-state reaction between amorphous silica and a lithium compound, lithium silicates were synthesized at high temperature in air [4, 6–7]. But the obtained products were a mixture of Li<sub>2</sub>SiO<sub>3</sub>, Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Li<sub>4</sub>SiO<sub>4</sub> and quartz compounds. In the precipitation method [4, 8], the reaction between amorphous silica (SiO<sub>2</sub>) suspended in water and aqueous solution of LiOH has been proposed. And lithium silicate sample with 87% Li<sub>2</sub>SiO<sub>3</sub> was prepared by the precipitation method in Ref.[4]. Compared with the conventional solid-state reaction, the sol-gel method shows advantages in the lower calcination temperature during the synthesis and the higher ionic conductivity for the final Li<sub>2</sub>SiO<sub>3</sub> product [9]. This method involves the controlled hydrolysis of an alkoxide and gelation. Gels are prepared by hydrolysis of tetraethylorthosilicate with an alcohol containing a lithium compound such as LiOH, LiNO3 or CH3OLi. The properties of the final materials depend remarkably on the factors such as pH, refluxing temperature, initial concentration, reactant stability and impurities. In Ref.[4], the highest content of Li<sub>2</sub>SiO<sub>3</sub> (94%) was obtained for molar ratio 2 of Li to Si by sol-gel method.

Foundation item: Project (2007CB613607) support by the National Basic Research Program of China; Project (2010QZZD0101) supported by the Basic Research Foundation for the Chinese Central Universities

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In addition, lithium metasilicate was also synthesized by a modified combustion method using LiOH, SiO<sub>2</sub>, H<sub>2</sub>O and urea as starting materials [5]. The distinct difference between this method and other ones is that the precursors are only heat-treated at temperatures between 450 and 750 °C for 5 min.

Among those methods, the sol-gel method is the most promising one for the synthesis of  $Li_2SiO_3$ . Although many researches have been done on the preparation of lithium metasilicate by the sol-gel method, the effects of the calcination temperature on the properties of  $Li_2SiO_3$  have not been well classified. Furthermore, as a precursor of  $Li_2FeSiO_4$ , the  $Li_2SiO_3$  should have a loose and porous morphology, which will facilitate the solid-state reaction between  $Li_2SiO_3$  and iron compounds. In this work, the effects of calcination temperature on the properties of  $Li_2SiO_3$  sample were investigated and  $Li_2SiO_3$  was synthesized with high purity and good morphology, and  $Li_2FeSiO_4$  cathode was prepared using the  $Li_2SiO_3$  precursor.

#### 2 Experimental

 $Li_2SiO_3$  samples were synthesized by the combination of the sol-gel method and the calcination at high temperature. Stoichiometric amounts of  $Li_2CO_3$  and  $Si(OC_2H_5)_4$  were used as the starting materials. Lithium carbonate was dissolved in a nitric acid solution, and then the aqueous solution, alcohol as solubilizing agent, and ethyl orthosilicate  $[Si(OC_2H_5)_4]$  were mixed. De-ionized water was added slowly to adjust the solution to pH 2. The mixture was transferred into a refluxing system and heat-treated at 80 °C for 8 h, and then the mixture was aged at 70 °C for 8 h to transform into gel. The gel was dried in a vacuum oven at 120 °C for 24 h and then ground, and the obtained powders were calcined at different temperatures for 8 h.

In order to investigate the effect of refluxing on the characteristics of  $Li_2SiO_3$ , a contrast experiment was conducted, where no refluxing was used during the sol-gel preparation and the mixture was directly heated and agitated at 80 °C to vaporize the solvent. The sol-gel transition time of the sample was only 6 h. The other steps were similar to the above ones.

 $Li_2FeSiO_4$  was prepared by solid-state reaction between  $Li_2SiO_3$  and  $FeC_2O_4$ ·2H<sub>2</sub>O. These starting materials were dispersed in acetone, mixed thoroughly and then ground together with 10% (mass fraction) carbon gel. After evaporating the acetone, the mixture was heated to 750 °C for 24 h in Ar atmosphere [3].

The thermo gravimetric analysis and differential thermal analysis (TGA/DTA) were conducted on a Perkin Elmer TGA 7 thermal analyzer. The data were recorded between 20 and 900 °C at a heating rate of 5

°C/min in N<sub>2</sub> atmosphere. The samples were characterized by X-ray diffraction (XRD) on a Rigaku D/max2550VB diffractmeter equipped with Cu K<sub> $\alpha$ </sub> radiation. The relative volume fractions of the various compounds in the samples were estimated from the total area under the most intense diffraction peak for each phase identified by the corresponding JCPDS files [4]. The morphologies of the samples were observed by a scanning electron microscope (SEM).

#### **3 Results and discussion**

The thermo gravimetric analysis and differential thermal analysis were conducted on the dried gel to find suitable calcination temperature for the synthesis of Li<sub>2</sub>SiO<sub>3</sub>, and the results are shown in Fig.1. The first mass loss occurs below 120 °C, and a corresponding endothermic peak is observed on the DTA curve, which is caused by the dehydration of the sample and the evaporation of remained ethanol. The DTA curve presents a sharp endothermic peak around 250 °C, but little mass loss can be observed on the TGA curve. It is due to the melting of the lithium nitrate. A large mass loss, corresponding to two united endothermic peaks, is detected between 520 and 630 °C. It may result from the polycondensation of silicon hydroxide, the decomposition of lithium nitrate, and the complicated reactions between the lithium compounds and silicon compounds [9-10]. The mass of the sample keeps nearly constant when the temperature is above 630 °C. According to the results of the TGA-DTA, the dried gel was calcined at temperatures between 650 and 900 °C for 8 h in this work.



Fig.1 TGA-DTA curves for dry gel at heating rate of 5 °C/min in  $N_2$  atmosphere

Comparisons were made to investigate the effects of refluxing on the properties of Li<sub>2</sub>SiO<sub>3</sub>. Fig.2 shows the XRD patterns of Li<sub>2</sub>SiO<sub>3</sub> samples made with different sol-gel preparation methods. A refluxing system was



**Fig.2** XRD patterns of  $Li_2SiO_3$  samples calcined at 700 °C using refluxing system (a) and without refluxing system (b)

applied in the preparation of sample (a), while not in that of sample (b). The XRD patterns of the two samples can be indexed to the JCPDS file 29–0829 of the *Cmc*21 space group structure [11]. Four intense diffraction peaks have been found at 18.9°, 27.0°, 33.0° and 38.5° corresponding to Miller indexes [2 0 0], [1 1 1], [0 2 0] and [3 1 1], where the [1 1 1] plane produces the most intense peak at 27.0. This indicates that Li<sub>2</sub>SiO<sub>3</sub> is obtained in both cases. However, the samples are not pure Li<sub>2</sub>SiO<sub>3</sub>. A little Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurity was detected in both samples. To determine the volume fraction,  $\varphi$ , of the compounds detected by XRD, it was assumed that the most intense diffraction peak of each compound was proportional to the volume fraction in the sample, and it was calculated by Eq. (1):

$$\varphi = C_i / \Sigma C_j \tag{1}$$

where  $C_i$  represents the integral intensity corresponding to each compound identified, and  $\Sigma C_i$  is the addition of the integral intensity corresponding to all the compounds identified in the sample [4,11-12]. Thus the contents of  $Li_2Si_2O_5$  impurity in samples (a) and (b) can be calculated to be 3% and 7%, respectively. Furthermore, a trace amount of Li<sub>4</sub>SiO<sub>4</sub> impurity occurred in sample (b). The phase diagram of the Li<sub>2</sub>O-SiO<sub>2</sub> system indicates that Li<sub>4</sub>SiO<sub>4</sub> and Li<sub>2</sub>SiO<sub>3</sub> can coexist and retransform to each other, and so can Li<sub>2</sub>SiO<sub>3</sub> and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> [13-14]. The relative content of them depends on the calcination temperature, time, and molar ratio of Li to Si, etc. The higher impurities for the sample without refluxing may be attributed to the locally uneven distribution of lithium in the precursors, which results in the occurrence of Li<sub>4</sub>SiO<sub>4</sub> and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurities where the lithium is insufficient. The refluxing system prolongs the sol-gel transition time and the compounds are well distributed in the precursor, which facilitates the formation of Li<sub>2</sub>SiO<sub>3</sub> and the reduction of impurities during the calcination.

Fig.3 shows the particle size analysis curves for the

samples made with different sol-gel transition methods. Sample (b) without refluxing exhibits a low and broad profile with two united peaks, while sample (a) using the refluxing system shows a much more intense and narrower particle size distribution, which facilitates achieving uniform reactivity of the  $Li_2SiO_3$  precursor and large density of the final  $Li_2FeSiO_4$  product. The difference in the particle size distribution may be owing to the fact that the refluxing enables the sufficient sol-gel transition and good distribution of compounds, and then suppresses the excess aggregation of the  $Li_2SiO_3$ particles.



**Fig.3** Particle size analysis curves of  $Li_2SiO_3$  samples calcined at 700 °C using refluxing system (a) and without refluxing system (b)

According to the results of XRD and particle size analysis, the use of refluxing system in the sol-gel transition facilitates the preparation of  $Li_2SiO_3$  with high purity and small uniform particles, so the refluxing system was adopted in the following study.

Fig.4 shows the XRD patterns for the Li<sub>2</sub>SiO<sub>3</sub> samples synthesized at different temperatures for 8 h. The XRD patterns of samples fit well with the JCPDS file 29-0829, indicating that Li<sub>2</sub>SiO<sub>3</sub> was synthesized in the temperature range of 650-900 °C. However, the contents of Li2SiO3 and impurities change dramatically with increasing the calcination temperature. The peaks of Li<sub>4</sub>SiO<sub>4</sub> are most intense in the sample calcined at 650 °C, and the least intense in the sample calcined at 700 °C. On the other hand, the peaks of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> are most intense in sample calcined at 900 °C, and the least intense in the sample calcined at 700 °C. The samples synthesized at 650, 700, 800 and 900 °C have Li<sub>2</sub>SiO<sub>3</sub> contents of 92%, 97%, 88%, 88%, and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> contents of 4%, 3%, 11% and 12%, respectively. Furthermore, 4% Li<sub>4</sub>SiO<sub>4</sub> was also found in the sample calcined at 650 °C and trace amounts of Li<sub>4</sub>SiO<sub>4</sub> impurity was found in the samples calcined at 800 and 900 °C. The results indicate that the



Fig.4 XRD patterns of  $Li_2SiO_3$  samples calcined at 650 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d)

Li<sub>4</sub>SiO<sub>4</sub> impurity mainly occurs in the sample synthesized at 650 °C, and the content of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurity rises with increasing calcination temperature. The occurrence of Li<sub>4</sub>SiO<sub>4</sub> phase and a large amount of  $Li_2Si_2O_5$  impurity can be attributed to the insufficient reaction between the lithium compound and silicon compound at low calcination temperature. As a result, a Li<sub>4</sub>SiO<sub>4</sub> phase occurs in the site where the lithium exceeds locally, and a Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> phase occurs where the lithium is insufficient. The undesired effects of difference in lithium distribution in the precursors can be overcome by enhancing the calcination temperature, which can improve the diffusion of lithium in the precursor and product. So the purity of the sample synthesized at 700 °C was improved dramatically compared with that synthesized at 650 °C. The content of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurity increases with increasing the calcination temperature from 700 to 900 °C, and it can be attributed to the lithium sublimation at high temperature, which results in the insufficiency of lithium compound for the synthesis of Li<sub>2</sub>SiO<sub>3</sub>. Therefore, the Li<sub>2</sub>SiO<sub>3</sub> sample with the highest purity of 97% was achieved at 700 °C in this work.

Fig.5 shows the SEM images of  $Li_2SiO_3$  samples synthesized at different temperatures. The  $Li_2SiO_3$ powders calcined at 700 °C consist of primary particles of 1–3 µm. The primary particle clusters form agglomerates with loose and porous appearance. The  $Li_2SiO_3$  powders calcined at 800 °C are similar to those at 700 °C, except that the agglomerates and the primary particles become large. However, the  $Li_2SiO_3$  powders calcined at 900 °C show a much more compact surface morphology compared with those obtained at 700 °C or 800 °C. It can be attributed to the calcination of the particles at high temperature.

According to the above results, the  $Li_2SiO_3$  sample synthesized by calcination at 700 °C and using refluxing



Fig.5 SEM images of  $Li_2SiO_3$  calcined at 700 °C (a), 800 °C (b) and 900 °C (c)

during the sol-gel preparation has excellent properties for the precursor of Li<sub>2</sub>FeSiO<sub>4</sub>. The Li<sub>2</sub>SiO<sub>3</sub> sample obtained at the optimized conditions shows a high purity of 97% Li<sub>2</sub>SiO<sub>3</sub> and a primary particle size of 1–3  $\mu$ m. It has higher purity and smaller particle size than those reported by PFEIFFER et al[4], where an optimized sample with 94% Li<sub>2</sub>SiO<sub>3</sub> and 6% Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurities was achieved using a similar sol-gel process with refluxing. In addition, a calcination temperature of 900 °C was used[4], which is much higher than that used in this work. The low calcination temperature can prevent serious aggregation of the primary particles and excessive-growth of the crystals and primary particles, which facilitates to improve the reactivity of Li<sub>2</sub>SiO<sub>3</sub> precursor in the synthesis of Li<sub>2</sub>FeSiO<sub>4</sub> cathode material.

In order to investigate the suitable calcination

temperature and the possible reactions in the synthesis of Li<sub>2</sub>FeSiO<sub>4</sub> by the solid-state reaction between Li<sub>2</sub>SiO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, thermo gravimetric analysis and differential thermal analysis were conducted on the mixture of Li<sub>2</sub>SiO<sub>3</sub> and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in N<sub>2</sub> atmosphere, and the results are shown in Fig.6. An endothermic peak occurs on the DTA curve around 90 °C and a corresponding mass loss is observed on the TGA curve, which is due to the dehydration of physically absorbed water in the sample. The second endothermic peak is revealed around 180 °C on the DTA curve and corresponds to a continuous mass loss on the TGA curve. It can be attributed to dehydration of the chemically combined water in FeC2O4·2H2O. In the temperature range of 300-500 °C, the mass of the sample decreases quickly, corresponding to a sharp and intense exothermic peak around 350 °C and two low and broad exothermic peaks around 270 and 500 °C, respectively. This results from the complicated reactions which may include the decomposition of FeC<sub>2</sub>O<sub>4</sub>, and the reactions between the iron compounds and the lithium compounds. Above 500 °C, the mass of the sample keeps nearly constant. So it could be concluded that the calcination temperature should be above 550 °C for the synthesis of Li<sub>2</sub>FeSiO<sub>4</sub> powder.

Using the optimized  $Li_2SiO_3$  as a precursor,  $Li_2FeSiO_4$  was prepared by the solid-state reaction between  $Li_2SiO_3$  and  $FeC_2O_4 \cdot 2H_2O$  at 750 °C for 24 h. Fig.7 shows the XRD pattern of the  $Li_2FeSiO_4$  powder. The sharp diffraction peaks indicate that the sample has good crystallinity. The XRD pattern agrees well with that reported by DOMINKO et al[15], and the XRD results for the  $Li_2FeSiO_4$  phase can be indexed to the orthorhombic unit cell in space group *Pmn*21. However, some unidentifiable impurity peaks were also observed in the diffraction patterns.



**Fig.6** TGA-DTA curves for mixture of  $Li_2SiO_3$  and  $FeC_2O_4$ ·2H<sub>2</sub>O at heating rate of 5 °C/min in N<sub>2</sub> atmosphere



Fig.7 XRD pattern of Li<sub>2</sub>FeSiO<sub>4</sub> sample

#### 4 Conclusions

1)  $Li_2SiO_3$  was synthesized by the combination of sol-gel method and the calcination at high temperature. The use of refluxing system during the sol-gel preparation decreases the  $Li_2Si_2O_5$  and  $Li_4SiO_4$  impurities in the  $Li_2SiO_3$  samples.

2) The calcination temperature plays an important role in the properties of Li<sub>2</sub>SiO<sub>3</sub>. The purity of the sample synthesized at 700 °C is improved dramatically compared with that synthesized at 650 °C. The content of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> impurity rises with increasing the calcination temperature from 700 to 900 °C, and the Li<sub>2</sub>SiO<sub>3</sub> sample with the highest purity of 97% is achieved at 700 °C. The Li<sub>2</sub>SiO<sub>3</sub> sample calcined at 700 °C shows a good morphology as the precursor of Li<sub>2</sub>FeSiO<sub>4</sub>. It consists of primary particles of 1–3  $\mu$ m, and the primary particle clusters form agglomerates with loose and porous appearance.

3)  $Li_2FeSiO_4$  was prepared by the solid-state reaction between  $Li_2SiO_3$  and  $FeC_2O_4$ ·2H<sub>2</sub>O. The sample has good crystallinity, and the XRD results can be indexed to the  $Li_2FeSiO_4$  phase of orthorhombic unit cell in space group *Pmn*21 and some unidentifiable impurity.

#### References

- DOMINKO R, BELE M, GABERSCEK M, MEDEN A, REMSKAR M, JAMNIK J. Structure and electrochemical performance of Li<sub>2</sub>MnSiO<sub>4</sub> and Li<sub>2</sub>FeSiO<sub>4</sub> as potential Li-battery cathode materials
  [J]. Electrochem Commun, 2006, 8: 217–223.
- [2] NYTÉN A, ABOUIMRANE A, ARMAND M. Electrochemical performance of Li<sub>2</sub>FeSiO<sub>4</sub> as a new Li-battery cathode material [J]. Electrochem Commun, 2005, 7: 156–163.
- [3] ZAGHIB K, SALAH A A, RAVETC N, MAUGER A, GENDRON F, JULIEN C M. Structural, magnetic and electrochemical properties of lithium iron orthosilicate [J]. J Power Sources, 2006, 160: 1381–1387.

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- [4] PFEIFFER H, BOSCH P, BULBULIAN S. Synthesis of lithium silicates [J]. J Nucl Metar, 1998, 257: 309–317.
- [5] CRUZ D, BULBULIAN S. Synthesis of lithium silicate tritium breeder powders by a modified combustion method [J]. J Nucl Metar, 2003, 312: 263–270.
- [6] KNITTERA R, ALM B, ROTH G. Crystallisation and microstructure of lithium orthosilicate pebbles [J]. J Nucl Mater, 2007, 367–370: 1378–1385.
- [7] SAAD K B, HAMZAOUI H, LABIDI A, BESSAÏS B. Growth of lithium silicate crystals inside porous silicon film and their exploitation for ozone detection [J]. Appl Surf Sci, 2008, 254: 3955–3960.
- [8] MORALES A A, PFEIFFER H, DELFIN A, BULBULIAN S. Phase transformations on lithium silicates under irradiation [J]. Mater Lett, 2001, 50: 37–41.
- [9] CHEN R F, SONG X Q, MA J F, JIA M Y. Synthesis of Li<sub>2</sub>SiO<sub>3</sub> by sol-gel method and study of its ionic conductivity [J]. Materials Review, 1999, 13: 69–74.
- [10] SONG X Q, CHEN R F. Influence of rare-earth oxide dopants on

conductivities of  $Li_2SiO_3$  ion conductor [J]. Journal of Functional Material and Devices, 1999, 6: 157–164.

- [11] CRUZ D, BULBULIAN S, LIMA E, PFEIFFER H. Kinetic analysis of the thermal stability of lithium silicates (Li<sub>4</sub>SiO<sub>4</sub> and Li<sub>2</sub>SiO<sub>3</sub>) [J]. J Solid State Chem, 2006, 179: 909–915.
- [12] FU Y P, CHANG C C, LIN C H, CHIN T S. Solid-state synthesis of ceramics in the BaO-SrO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system [J]. Ceram Int, 2004, 30: 41–47.
- [13] CLAUS S, KLEYKAMP H, SMYKATZ-KLOSS W. Phase equilibria in the Li<sub>4</sub>SiO<sub>4</sub>-Li<sub>2</sub>SiO<sub>3</sub> region of the pseudobinary Li<sub>2</sub>O-SiO<sub>2</sub> system [J]. J Nucl Metar, 1996, 230: 9–15.
- [14] JACQUIN J R, TOMOZAWA M. Crystallization of lithium metasilicate from lithium disilicate glass [J]. J Non-Cryst Solids, 1995, 190: 224–230.
- [15] DOMINKO R, CONTE D E, HANZEL D, GABERSCEK M, JAMNIK J. Impact of synthesis conditions on the structure and performance of Li<sub>2</sub>FeSiO<sub>4</sub> [J]. J Power Sources, 2008, 178: 842–847.

## 焙烧温度对 Li<sub>2</sub>FeSiO<sub>4</sub> 前驱体 Li<sub>2</sub>SiO<sub>3</sub> 性能的影响

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摘 要:以Li<sub>2</sub>CO<sub>3</sub>, HNO<sub>3</sub>,Si(OC<sub>2</sub>H<sub>3</sub>)<sub>4</sub>为原材料,采用溶胶–凝胶和高温焙烧法合成Li<sub>2</sub>SiO<sub>3</sub>;研究焙烧温度和回流系统对硅酸锂组分和性能的影响;利用TGA/DTA,XRD,SEM和粒径分析等手段对样品进行表征;采用Li<sub>2</sub>SiO<sub>3</sub>和Fe<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O固相反应制备Li<sub>2</sub>FeSiO<sub>4</sub>。XRD结果表明,在溶胶–凝胶制备过程中使用回流系统能减少Li<sub>2</sub>SiO<sub>3</sub>样品中Li<sub>2</sub>SiO<sub>5</sub>和Li<sub>4</sub>SiO<sub>4</sub>杂质。焙烧结温度对Li<sub>2</sub>SiO<sub>3</sub>的性能有重要的作用,当温度为700℃时,Li<sub>2</sub>SiO<sub>3</sub>前驱体材料样品纯度为97%,并具有良好的形貌;它是由粒径为1~3 μm的一次粒子组成,一次粒子束形成疏松、多孔的团聚体。

关键词: 锂离子电池; Li<sub>2</sub>FeSiO<sub>4</sub>; Li<sub>2</sub>SiO<sub>3</sub>; 溶胶-凝胶法

(Edited by YANG Hua)