

Wang Qinghua, Wang Bengen, Xu Yan, Liu Hongyu

## Preparation of lithium fast ionic conductor by sol-gel-hydrothermal method

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**Abstract** The solid fast ionic conductor was synthesized by the sol-gel-hydrothermal method. The influences of the dispersion reagent, the alkalinity and the calcination temperature on the surface morphology of nanopowders, and the electric conductivity were discussed. When PEG 12000 was used as the dispersion reagent, the alkalinity was 1.0% and the calcination temperature was 550°C; the electric conductivity at ambience temperature of the inorganic nanopowder of lithium fast ionic conductor synthesized was  $2.59 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ .

**Keywords** lithium fast ionic conductor, inorganic nanopowder, sol-gel-hydrothermal method

### 1 Introduction

Fast ionic conductors, which are also called solid electrolytes [1], are a type of solid materials that have ionic electric ability. Solid lithium ionic cell is one of the research hot-spots of lithium ionic cells because of its safety and good plasticity. Solid electrolytes of high ionic conductivity are of utmost priority in the research of lithium ionic cells. Nanometer materials exhibit the small-size effect and the interface effect due to their quanta sizes, and these make nanometer materials special because of some of their physical and chemical properties. Nanometer materials and nanometer multiplex materials used as embedded lithium material may improve material-reversible embedded lithium capacity and the life cycle of the material because of their special nanometer microstructure and their surface morphology [2]. Nanometer active materials have large specific surface area, shallow depth of embed-emerge lithium ion and short

journey, and these electrodes consequently have little charge-discharge polarization extent, high reversible capacity and long circular life span with large current. The high interspace ratio of nanometer materials offers enough space for lithium ionic embed-emerge, and this improves embedded lithium capacity and energy density.

Inorganic nanopowder coagulates easily and reunites during synthesis because of its large specific surface area and upper specific surface area, and then forms the second particle. The diameter of the second particle increases and hence the nanopowder loses its function [3]. Investigation on the prevention of the dispersion reagent and the surface decoration reagent from reuniting on the course of synthesis is relatively active at present [4–8].

This research integrated the strongpoint of liquid-phase method, and the sol-gel-hydrothermal method was used to synthesize the inorganic nanopowder of lithium fast ionic conductor. The influences of the PEG dispersion reagent, the alkalinity and the calcination temperature on the diameter of inorganic nanopowder and the surface description of nanopowder were discussed.

### 2 Experimental

#### 2.1 Reagents

$\text{Al}(\text{ClO}_4)_3$  solution,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , PEG, 25% hartshorn, ethanol without water, distilled water.

#### 2.2 Apparatuses

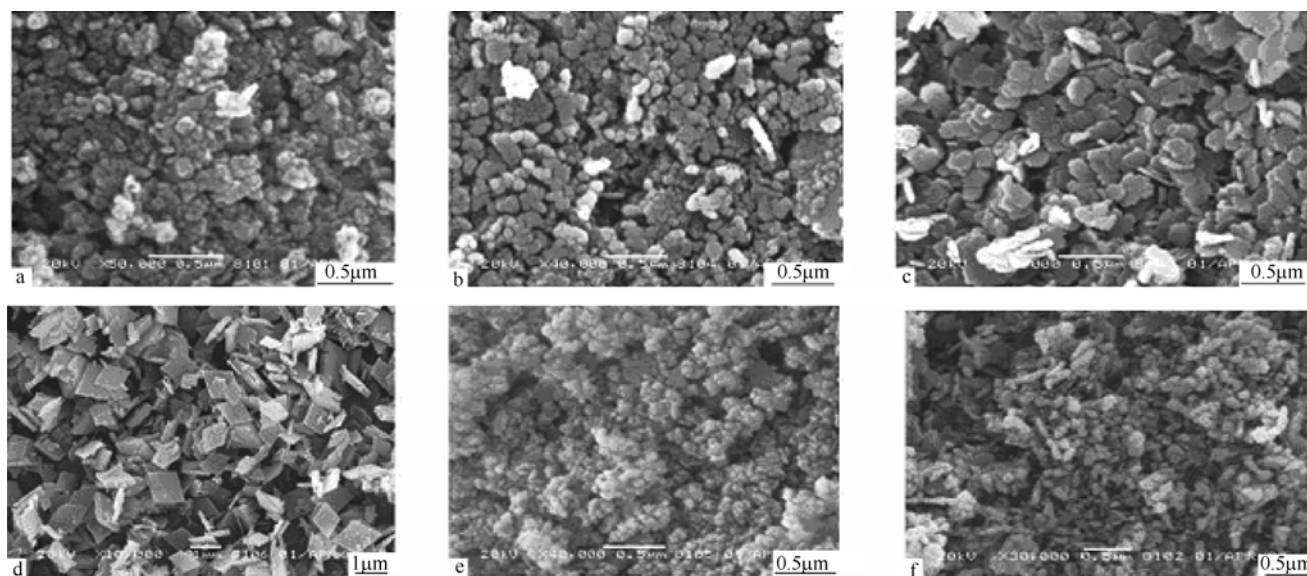
Scanning electron microscopy (SEM), X-ray diffraction (XRD), high pressure autoclave, electrical conductivity apparatus.

#### 2.3 Procedure

Some methods for preparing the inorganic nanopowder of fast ionic conductor are the hydrothermal method, sol-gel method,

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Wang Qinghua(✉), Wang Bengen, Xu Yan, Liu Hongyu  
College of Aerospace and Material Engineering, National University of Defense Technology, Changsha 410073, China  
E-mail: qh1002@sina.com



**Fig. 1** SEM images of the powders prepared by using the PEG dispersion reagent with different molecular weights  
a) PEG 1000; b) PEG 2000; c) PEG 4000; e) PEG 6000; e) PEG 12000; f) PEG 20000;

deposit-calcination method, solid-phase sintering method and vaporize solvent-pyrogeneration method.

This research uses the sol-gel-hydrothermal method to synthesize the inorganic nanopowder of lithium fast ionic conductor. The path of preparation is as follows:  $\text{Al}(\text{ClO}_4)_3$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$  largely dispersed to form sol, hydrothermal reacted to form gel, and then desiccated.

### 3 Results and discussion

#### 3.1 Effect of dispersant

Wang et al. [5] indicated that the reunion level can be alleviated when some organic macromolecular surface active agents with steric effect, such as PCAA, PEG, are added to the deposition process or to the dehydration process of the deposits.

Choosing an appropriate dispersant is an active research project at present. Ma et al. [6], Zhang et al. [7] and Xu et al. [8] reported that the nanopowder can be restrained from reuniting with the help of surface modification or dispersant in the chemical preparation process of the nanometer material.

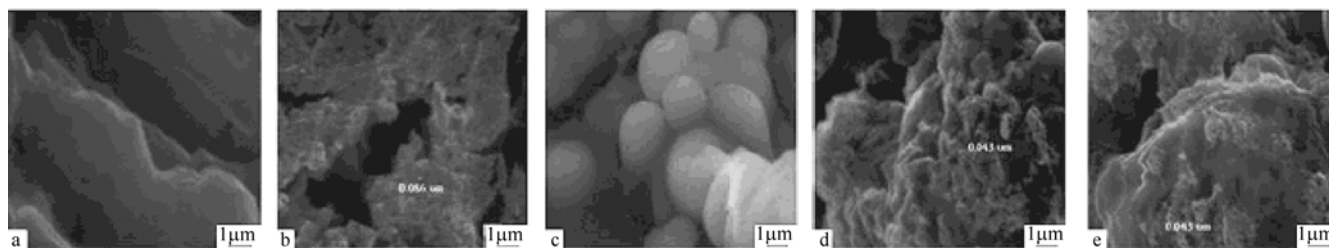
The influences on the reunion of the nanopowder were studied when PEG with different molecular weights was added as the dispersant. Figure 1 shows the SEM photographs of nanopowders prepared by adding the PEG dispersant reagent with different molecular weights (from 1000 to 20 000).

It can be seen that when PEG with different molecular weights were added, the appearance of particles and the diameter of particles prepared were different. When the molecular weights of PEG are 1,000, 2,000, 12,000 and 20,000,

respectively, the particles prepared are the pellets. As the molecular weight of PEG increases, the particles become regular and the diameter of particles becomes smaller. When the molecular weight of PEG is 4,000, the particles are regular sheet hexagon and the diameter of the particles varies from 200 to 300 nm. When the molecular weight of PEG is 6,000, the particles become prismatic sheet and the diameter of particles is above 1  $\mu\text{m}$ . The reason may be that PEG used as the surface modifying reagent is selective on microcrystalline surface adsorption, and it cannot be wrapped completely. The growth of particles shows tropism, and then changes to regular polygons. When the molecular weight of PEG is 12,000, the nanopowder is restrained from reuniting well. At this time, the particles become orbicular and the diameter of particles varies from 20 to 50  $\mu\text{m}$ , and the particles become symmetrical in size and show a relaxed configuration.

#### 3.2 Effect of alkalinity

The alkalinity obviously influences the diameter of the particles prepared. The higher the alkalinity, the smaller the granularity of the crystal phase in the molecular sieve. However, at the same time, the alkalinity quickens the deposition velocity and increases the granularity. In this research system,  $\text{LiOH}$  is used as an alkali. The alkali content influences the size of particles on the course of deposition and the content of  $\text{Li}^+$  in the molecular sieve. Finally, the alkali content also influences the electric conductivity. When the alkali contents are 0.8%, 0.9%, 1.0%, 1.2% and 1.5%, the five samples a~e prepared were analyzed with SEM and the electric conductivity was measured with DDS-11A electric conductivity apparatus, respectively.



**Fig. 2** SEM images of the powders prepared from different alkali contents  
a) 0.8%; b) 0.9%; c) 1.0%; d) 1.2%; e) 1.5%

**Table 1** The electric conductivity of the sample prepared from different LiOH compositions

LiOH composition (mass%)	0.8	0.9	1.0	1.2	1.5
Electric conductivity ( $\times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ )	0.131	1.64	2.59	0.567	0.348

It can be seen from Fig. 2 that the samples a, d and e are amorphous. The diameter of particles for the crystal samples b and c are about 20  $\mu\text{m}$ , and the configuration of particles is relaxed. Therefore, the best alkali content is about 1.0%. It can be also seen from Table 1 that the LiOH composition obviously influences the electric conductivity of samples prepared. When the LiOH composition is 1.0%, the electric conductivity at ambience temperature of samples prepared is the highest ( $2.59 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ ).

### 3.3 Effect of calcination temperature

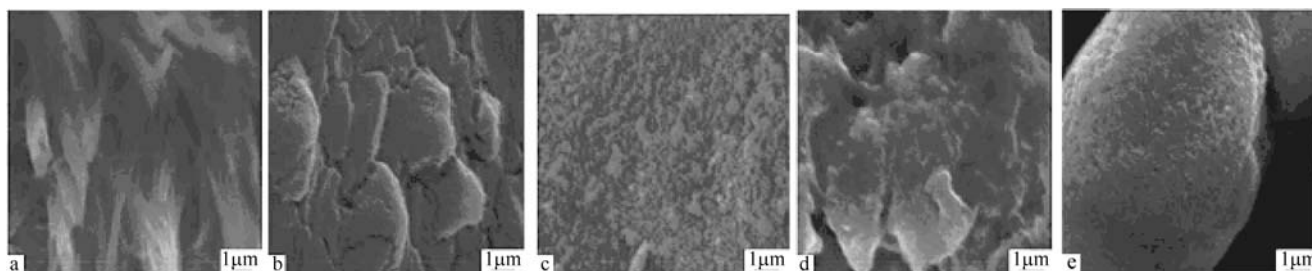
The reaction temperature of sol-gel-hydrothermal method is only 120°C. However, the calcination temperature after desiccation obviously influences the composition of products, the diameter of particles and the diversification of crystal phase, and finally influences the electric conductivity of the samples prepared. The main factors influencing the calcination process are the speed of heating and the calcination temperature. When the speed of heating is rapid, the sample rapidly reaches a high temperature state and the group in the sample such as  $-\text{OH}$  is not eliminated entirely. It leads to the formation of the macroaggregate and increase in the diameters of the particles. When the calcination temperature is lower, the reaction is incomplete and the group in the sample such as  $-\text{OH}$  cannot be eliminated, and the particles are easily coagulated. When the calcination temperature is higher, the reaction activity increases, and the growth rate

of crystal particles also increases, which makes it easy to form an agglomerate.

Some experiments on the different calcination temperatures such as 250°C, 350°C, 550°C, 750°C and 900°C with the speed of heating at 10°C/min were carried out. The powder samples after calcination were examined by using SEM and X-ray diffraction. The results of SEM and X-ray diffraction are shown in Figure 3 and 4, respectively.

It can be seen from Fig. 3 that the appearance of the samples prepared changes largely along with the different calcination temperatures. When the calcination temperature is 250°C, the appearance of the sample is a long bar and the diameter of the sample is about 200 nm. When the calcination temperatures are 350°C and 750°C, the samples are amorphous. When the calcination temperature is 950°C, the diameter of the sample is 50 nm and some particles constitute the larger granule whose diameter is about 1  $\mu\text{m}$ . Only when the calcination temperature is 550°C, the diameter of the sample is 50 nm, which is powdery and the dispersion of particles is also preferable.

It can be seen from Fig. 4 that the uncrystallizable components of the samples decrease when the calcination temperature increases. When the calcination temperature changes from 350°C to 550°C, there is an obvious diversification, and the characteristic peaks of  $\text{LiClO}_4$  disappear. Instead, when the calcination temperature reaches 550°C, some new peaks of  $\text{LiAlSi}_2\text{O}_6$  appear. It shows that  $\text{LiClO}_4$  is decomposed when the calcinations temperature increases



**Fig. 3** SEM images of the powders calcinated at different temperatures  
a) 250°C; b) 350°C; c) 550°C; d) 750°C; e) 950°C

from 350°C to 550°C, and the hydrolysate of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  reacts with the hydrolysate of  $\text{LiClO}_4$  to produce a new crystal phase. When the calcination temperature is increased from 550°C to 950°C, the structure of the crystal phase of  $\text{LiAlSi}_2\text{O}_6$  no longer changes but only the size of the crystal granule increases.

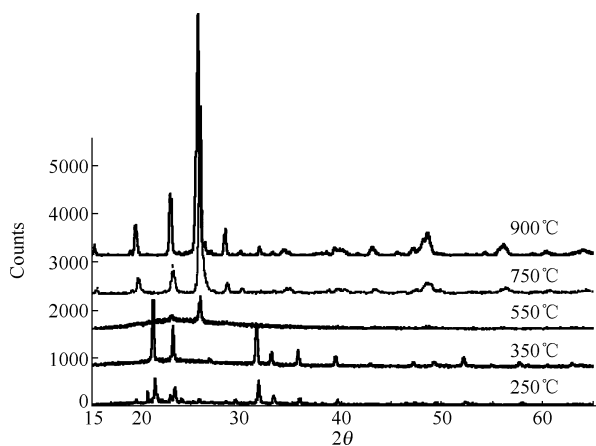


Fig. 4 X-ray diffraction patterns of the powders calcinated at different temperatures

#### 4 Conclusions

The research results on the preparation of inorganic nanopowder of lithium fast ionic conductor by sol-gel-hydrothermal method indicated that when the molecular weight of PEG used as the dispersant was 12,000, the nanopowder can be restrained from reuniting because the nanopowder was orbicular and the diameter of particles was from 20 to 50 nm. The particles have symmetrical size and relaxed configuration. When the alkali content was 1.0%, the diameter of particles was about 20 nm and the particles were dispersed well. When the calcination temperature was increased from 550°C to 950°C, the structure of the crystal phase of  $\text{LiAlSi}_2\text{O}_6$  no longer changed but only

the size of the crystal granule increased. The electric conductivity at ambience temperature of the inorganic nanopowder of lithium fast ionic conductor synthesized was  $2.59 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ .

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