



Low-temperature sintering of Li_4SiO_4 spheres with high crushing load using mesoporous silica as Si sources

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Abstract

Li_4SiO_4 has been widely studied as tritium breeder and high temperature CO_2 capture material. Tritium breeding rate and CO_2 adsorption capacity are closely related to lithium content and microstructure. Since high sintering temperatures result in grain coarsening and lithium sublimation, it is a great challenge to prepare Li_4SiO_4 ceramics with a satisfactory mechanical strength at low sintering temperature. In this work, mesoporous silica was used as Si source to prepare Li_4SiO_4 spheres. The mesoporous structure might provide more reaction sites for lithium ions, thereby facilitating the reaction between LiOH and mesoporous silica. The sintering temperature of Li_4SiO_4 spheres was greatly reduced by using mesoporous silica as Si source. The Li_4SiO_4 spheres with a homogenous fine-grained microstructure (the average grain size of $2.2\ \mu\text{m}$) and high crushing load (41.65 N) could be obtained at $675\ ^\circ\text{C}$.

Keywords: Li_4SiO_4 pellets, low-temperature sintering, mesoporous silica, crushing load

I. Introduction

Lithium orthosilicate (Li_4SiO_4) has drawn worldwide research interest because of its wide applications in tritium breeding materials and high temperature carbon dioxide capture materials [1–4]. Given its practical application in tritium-producing blanket and coal combustion power plants, the preparation of spherical Li_4SiO_4 samples with both excellent physicochemical properties and mechanical performance is a common topic that researchers have to face.

Extrusion-spheronization technique, graphite moulding method, wet method, etc. have been employed to generate Li_4SiO_4 spheres [5–10]. Hu *et al.* [6] prepared the Li_4SiO_4 samples with enriched porosity by an extrusion-spheronization technique using microcrystalline cellulose as pore former and the prepared samples exhibited excellent cyclic CO_2 sorption performance. Ni *et al.* [3] produced Li_4SiO_4 spheres via graphite moulding method, which showed good sphericity and cyclic stability. They suggested that adding agar or using organic lithium source could improve the mesoporous structure and specific surface area, thereby ef-

fectively increasing the sorption capacities of pellets. Graphite bed method was proposed by researchers from University of Science and Technology Beijing to prepare Li_4SiO_4 pebbles. The tritium release behaviour was investigated and the results demonstrated that greater porosity encouraged tritium release at lower temperatures [2]. To summarize, whether used as tritium breeding materials or high temperature CO_2 capture materials, the pore structure design of Li_4SiO_4 samples is critical. High sintering temperature is advantageous to yield high mechanical strength, but it is not advantageous to obtain high porosity and fine-grained structures. Moreover, high temperature processing leads to lithium sublimation and lack of microstructure control. Therefore, it is still a challenge to prepare Li_4SiO_4 samples with fine-grained structure and high mechanical strength at a low temperature.

Mesoporous silica, with its large specific surface area and abundant pore volume, may provide more reactive sites for Li^+ to facilitate the reaction with Li sources, and act as a template to control the particle size and reduce the agglomeration of Li_4SiO_4 . The usage of mesoporous silica as Si source is an effective way to improve the sintering activity of Li_4SiO_4 , and thus achieve a balance between porosity and mechanical strength. However, the research on mesoporous silica as silicon source

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is currently limited. Accordingly, mesoporous silica was synthesized and employed to prepare Li_4SiO_4 and the influences of sintering temperature on the microstructure and crushing load of Li_4SiO_4 spheres were investigated.

II. Experimental

2.1. Preparation of Li_4SiO_4 spheres

2.5 g of CTAB (cetyltrimethylammonium bromide) was added in a mixed solution consisting of 50 ml of deionized water and 200 ml of ethanol and sonicated for 5 min to dissolve completely. Then, 1 ml of TEOS (tetraethyl orthosilicate) was added to the solution. After sonication for another 5 min, 5 ml of ammonium hydroxide solution (28%) was added into the mixture to catalyse the hydrolysis of TEOS. The reaction was carried out at room temperature under continuous stirring for 12 h. The products were harvested by centrifugation, washed thoroughly with ethanol and dried in oven at 60 °C. The dried products were further heat treated at 500 °C for 2 h in air to obtain mesoporous silica.

Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$) and the prepared mesoporous silica were weighted in a molar ratio of 4 : 1.05 and dispersed in 60 ml of equal volumes of deionized water and ethanol, keeping the Li^+ concentration at 1 mol/l. Subsequently, the above-obtained suspension was transferred to a 100 ml Teflon-lined stainless-steel autoclave and heated in a drying oven at 200 °C for 12 h. Finally, precursor powder could be yielded by drying the hydrothermal products at 70 °C.

Wet method was employed to generate ceramic spheres [11]. The precursor powder (4 g) was mixed with 4 ml of ethylene glycol solution (20 vol.%) to form a slurry. Subsequently, the slurry was extruded through a syringe onto a copper wire, which was secured to an-

other syringe. The slurry droplets on the copper wire formed green spheres under vibration and then dropped into liquid nitrogen by gravity (Fig. 1). The slurry was extruded at a rate of about 20 drops/min. After freezing in liquid nitrogen for half an hour, the green spheres were salvaged and placed on filter papers to dry. Then, these green spheres were dried in a drying oven at 70 °C for 12 h. Finally, the dried Li_4SiO_4 spheres with 1.35–2 mm in diameter were sintered at several temperatures (between 600–750 °C) for 4 h.

2.2. Characterization

The phase composition and crystal structure were investigated by X-ray diffractometry (Shimadzu XRD-7000). The samples were ground into powders for XRD tests. The morphology was observed by scanning electron microscope (Hitachi S-4800 & TESCAN VEGA3 XMU) and grain sizes were measured by Nano Measure 1.2 software from SEM images. The density was determined by an electronic density balance using ethanol as immersion medium (HANGPING FA2104J). The crushing load was tested by a universal material strength-testing machine with a 5 kN load cell and cross-head speed of 0.25 mm/min (WANCE ETM105D).

III. Results and discussion

XRD pattern of the prepared mesoporous silica is shown in inset of Fig. 2a. A broad band at 15°–30° can be detected, indicating the formation of amorphous SiO_2 . The results are in accordance with a number of previous studies [12–14]. As shown in Fig. 2a, the mesoporous silica consists of sub-microspheres with various diameters. According to Fig. 2b, magnified yellow rectangular area of Fig. 2a, it can be seen that there is abundance of pores in the sub-microspheres (Fig. 2b).

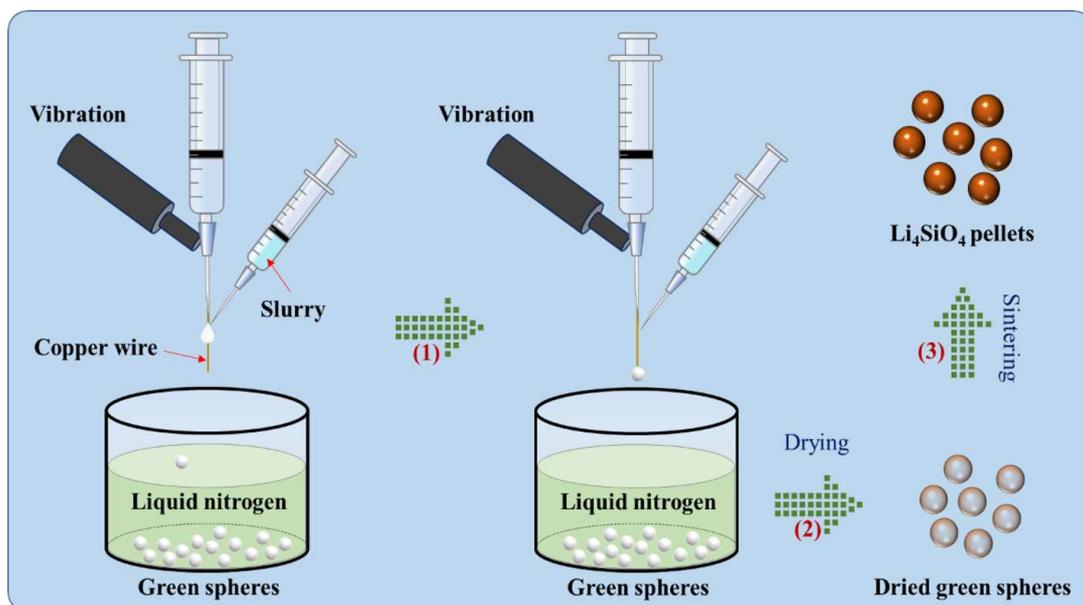


Figure 1. Scheme of Li_4SiO_4 sphere processing

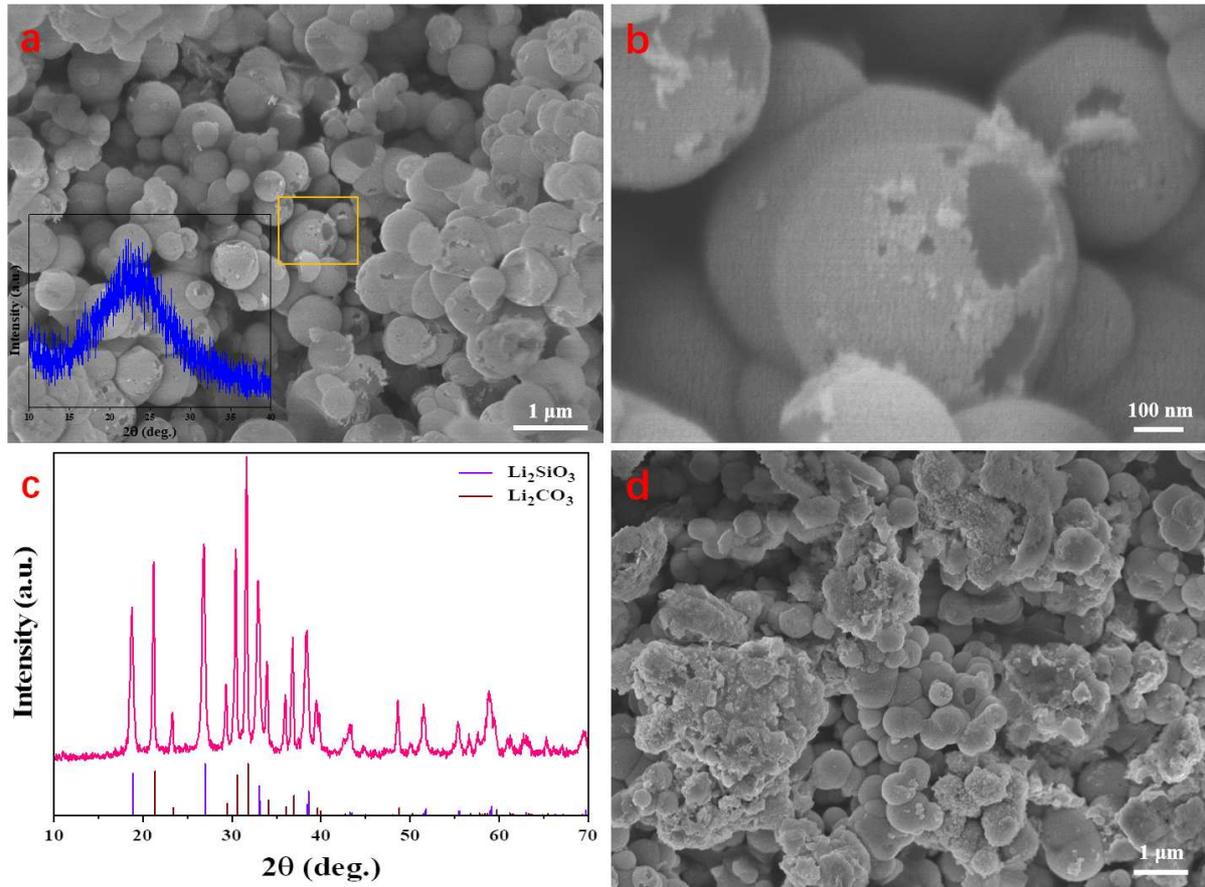
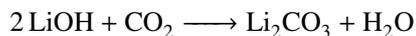
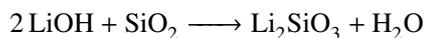


Figure 2. SEM images of mesoporous silica with corresponding XRD pattern shown in inset (a) and magnified yellow rectangular area of Fig. 2a (b). XRD pattern (c) and SEM image (d) of precursor powder

The existence of pores can increase the contact area between Li^+ and silica and thus facilitate the reaction between LiOH and silica.

XRD pattern and SEM image of the precursor powder are shown in Figs. 2c and 2d, respectively. The diffraction peaks can be mainly assigned to Li_2SiO_3 (PDF#29-0829) and Li_2CO_3 (PDF#83-1454). The formation of Li_2SiO_3 and Li_2CO_3 can be expressed as follows:



The phase composition is consistent with that of the products synthesized with SiO_2 as Si source [15,16], suggesting Si sources have little effect on the composition of hydrothermal products. SEM image (Fig. 2d) confirms that the precursor powder mainly has spherically shaped particles. The particle size of the precursor powder is comparable to that of mesoporous silica, suggesting that mesoporous silica may act as a template to control the particle size of the resulting precursor powder.

XRD patterns of the Li_4SiO_4 spheres sintered at various temperatures are shown in Fig. 3. The diffraction peaks attributed to Li_4SiO_4 (PDF#74-0307) can be detected in all samples, suggesting that the reaction between Li_2SiO_3 and Li_2CO_3 occurs above 600°C . With

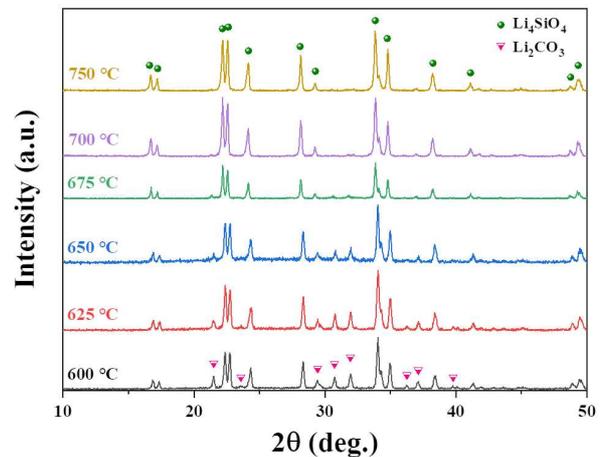


Figure 3. XRD patterns of Li_4SiO_4 spheres sintered at various temperatures

increasing sintering temperature, the XRD peak intensities of Li_4SiO_4 gradually increase, the diffraction peaks of Li_2CO_3 weaken and eventually disappear. The appropriate sintering temperature should exceed 675°C to avoid excessive Li_2CO_3 impurities, because the presence of Li_2CO_3 may affect the tritium release behaviour and CO_2 absorption [17,18].

Figures 4a1-4d1 show SEM images of the Li_4SiO_4 spheres sintered at various temperatures. When the sintering temperature is below 675°C , the Li_4SiO_4 spheres

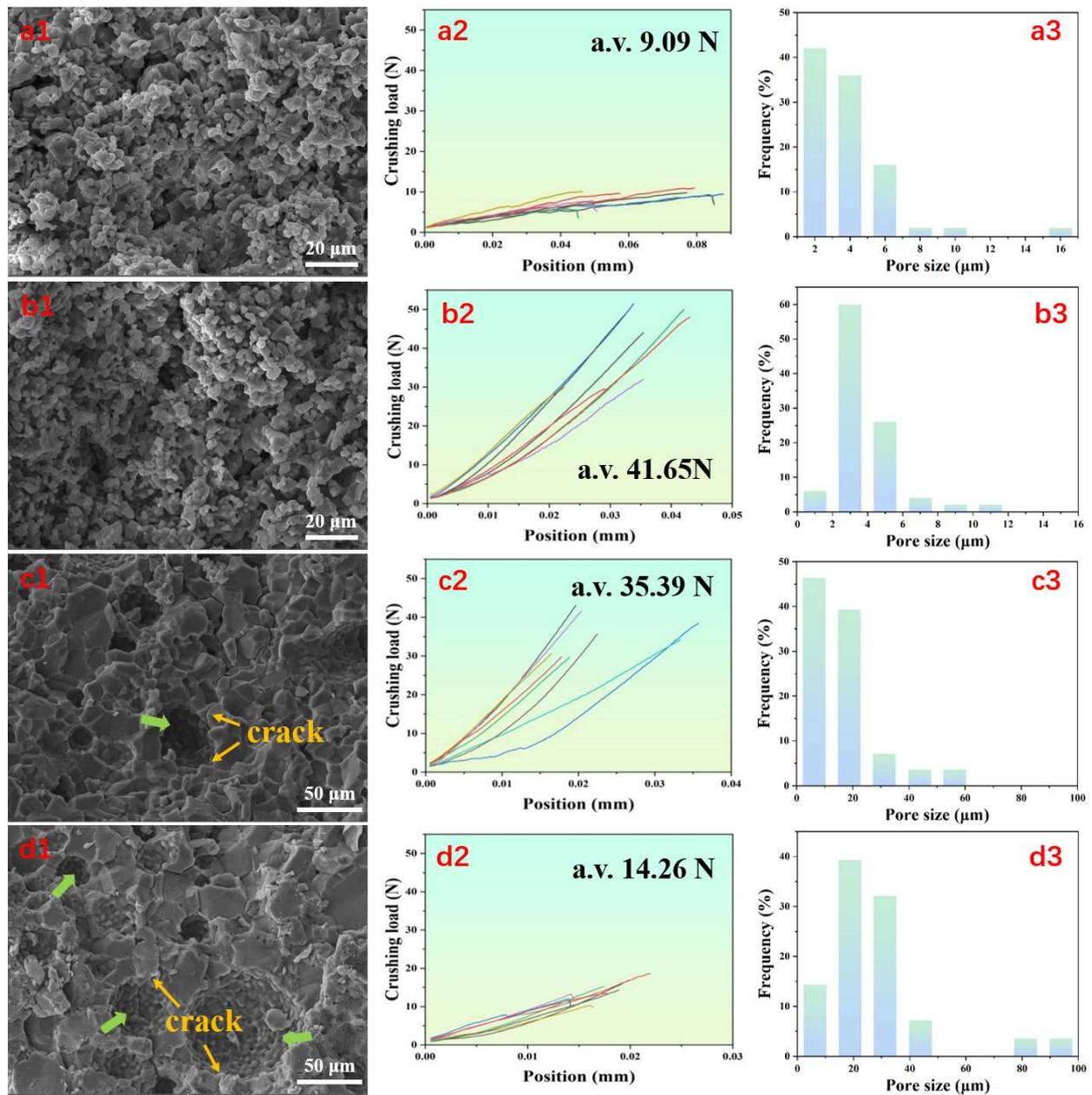


Figure 4. SEM images (1), crushing loads (2) and pore size distribution (3) of the Li_4SiO_4 pellets sintered at: a) 650 °C, b) 675 °C, c) 700 °C and d) 750 °C

have a uniform microstructure and plenty of pores. The average grain size of the sample Li_4SiO_4 sintered at 675 °C is 2.2 μm. It should be noted that small pores evenly distributed in Li_4SiO_4 structure (Fig. 4b3) are favourable for the tritium release and CO_2 absorption, although they may have a negative effect on crushing load of Li_4SiO_4 spheres. With the rise in the sintering temperature up to 700 °C, obvious grain growth occurs (Fig. 4c1). It can be seen from Figs. 4c1 and 4d1 that large pores (marked with green arrows) having tens of microns in diameter appear in the Li_4SiO_4 samples sintered at 700 °C and 750 °C (Figs. 4c3 and 4d3). Higher sintering temperature results in rapid grain growth and fails to eliminate pores in time, leading to the formation of large pores.

Li_4SiO_4 spheres should have enough mechanical strength to cope with the service conditions whether used as tritium breeders or high-temperature CO_2 capture materials. The uniaxial compressive test of the Li_4SiO_4 spheres was done and the results are shown in Figs. 4a2-4d2. The average crushing loads of the Li_4SiO_4 spheres sintered at 650, 675, 700 and 750 °C were calculated to be 9.09, 41.65, 35.39 and 14.26 N, respectively. The crushing load depends on grain size and porosity and the relationship is in accordance with the equation: $S = k \cdot G^{-a} \cdot e^{-bP}$ [19]. In this equation, G is the grain size, P is the porosity, and k , a and b are positive constants. Relative densities of the Li_4SiO_4 spheres sintered at 650, 675, 700 and 750 °C are 79.84, 81.75, 84.00 and 86.43 %TD, respectively. Hence, the

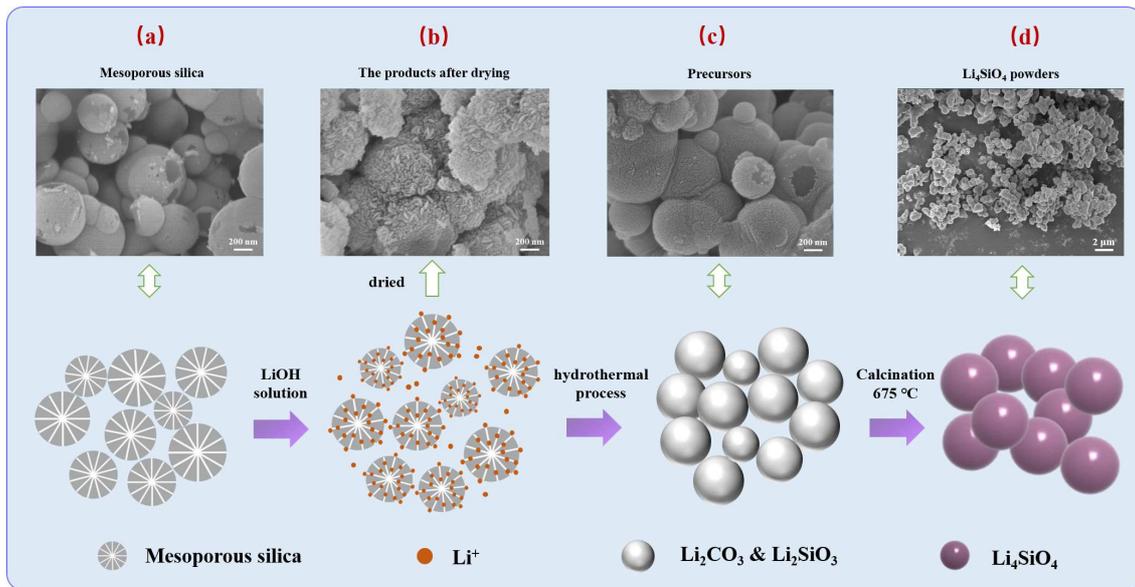


Figure 5. SEM images and scheme of the process and products in each step

poor crushing load of the Li_4SiO_4 spheres sintered at 650°C is ascribed to the high porosity and Li_2CO_3 impurities. The remarkable reduction of crushing load of the sample sintered at 750°C could be attributed to the abnormal grain growth and the presence of large pores.

Our results showed that the sintering temperature of Li_4SiO_4 pellets was greatly reduced by using mesoporous silica as Si source. Moreover, the presence of large pores in the fractured Li_4SiO_4 sample was also confirmed, suggesting that the stress cracking takes place around pores. Thus, to improve the crushing load of Li_4SiO_4 pellets, further studies are needed to avoid the formation of large pores.

To clarify the role of mesoporous silica in controlling the Li_4SiO_4 structure, the products in each step were obtained and characterized. The mesoporous silica and LiOH solution were mixed and dried and the microstructure of the dried powder is shown in Fig. 5b. The microspheres wrapped by nanoparticles could be observed. It could be inferred from the SEM image that Li^+ adsorbs on the surface and in the pore channels of the mesoporous silica and then recrystallize. The pore channels of the mesoporous silica are beneficial to increase the contact area with Li^+ and thus accelerate the reaction between LiOH and mesoporous silica. Figures 5c and 5d showed microstructures of the dried and sintered Li_4SiO_4 spheres, both of them appeared as microspheres with diameters ranging from hundreds of nanometers to several microns. The Li_4SiO_4 spheres prepared from mesoporous silica have small grain size and narrow size distribution (Fig. 5d). Therefore, mesoporous silica plays the role of a template in the preparation of Li_4SiO_4 samples.

IV. Conclusions

The precursor powder consisting of Li_2CO_3 and Li_2SiO_3 was synthesized using mesoporous silica and

lithium hydroxide monohydrate as raw materials. The precursor powder was used for generation of Li_4SiO_4 ceramic spheres by wet method and sintering at low temperature. The mesoporous silica structure might provide more reaction sites for lithium ions, thereby facilitating the reaction between silica and LiOH. Furthermore, the mesoporous silica played the role of a template in the preparation of Li_4SiO_4 spheres. The Li_4SiO_4 spheres sintered at 675°C had a small grain size ($2.2\ \mu\text{m}$) and high crushing load ($41.65\ \text{N}$). With increasing the sintering temperature, large pores were formed due to the rapid grain growth, resulting in the degradation of crushing loads. Consequently, the sintering temperature of the Li_4SiO_4 samples was greatly reduced by using mesoporous silica as Si source. The results can provide a reference for overcoming grain growth and lithium loss caused by high sintering temperature.

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