A comprehensive study on Li$_4$Si$_{1-x}$Ti$_x$O$_4$ ceramics for advanced tritium breeders

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Abstract

Hetero-elements doped lithium orthosilicate has been considered as advanced tritium breeders due to its superior performances. In this work, Li$_4$Si$_{1-x}$Ti$_x$O$_4$ ceramics were prepared by proprietary hydrothermal process and multistage sintering. The reaction mechanism of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ was put forward. XRD and SEM analyses indicate that insertion of Ti leads to lattice expansion, enhances the sinterability and changes the fracture mode. The compressive tests show that the crush load increases almost four times by increasing $x$ from 0 to 0.2. However, the thermal conductivity and ionic conductivity are the best when $x$=0.05 and $x$=0.1, respectively. Thermal cycling stability of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ pebbles was further appraised through investigating the changes of microstructure and crush load. After undergoing thermal cycling, the Li$_4$Si$_{1-x}$Ti$_x$O$_4$ still show higher crush load compared with Li$_4$SiO$_4$, despite Ti segregation in some samples. The $x$=0.05 sample exhibits excellent thermal cycling stability. To be sure, Ti doping improves the overall performance of Li$_4$SiO$_4$.

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1. Introduction

Tritium breeding materials (TBMs) are taken as one of the key functional materials for fusion reactor blanket. Neutrons generated from the reaction between deuterium (D) and tritium (T) can react with Li element to produce tritium, thus achieving tritium self-sustaining of a D–T fusion reactor [1-3]. With preferable chemical stability, efficient tritium extraction, high temperature resistance and no magnetohydrodynamic effect, lithium-based ceramics have long been recognized as promising TBMs [2, 4-6]. However, the overall performance of conventional lithium ceramics (i.e. Li$_4$SiO$_4$, Li$_2$TiO$_3$, Li$_2$O, LiAlO$_2$, Li$_2$ZrO$_3$ etc.) is still difficult to achieve satisfactory results. In order to improve their corresponding performance, diverse advanced TBMs, such as Li$_{2+x}$TiO$_{3+y}$ [7-9], mixed-phase ceramics represented by Li$_2$TiO$_3$/Li$_4$SiO$_4$ [10-13], oxides modified ceramics [14-16] and hetero-element doped ceramics (notably Li$_{4+x}$Si$_{1-x}$Al$_x$O$_4$) were prepared in recent years [17-20]. And previous studies have shown that Al doped lithium orthosilicate exhibits the enhanced crushing strength [17, 19, 20], thermal and ionic conductivity [17, 20-22], and tritium release performance [18].

Since TBMs should endure long periods of harsh operating conditions (high temperature, thermal gradient, irradiation by neutron and energetic particles), thermal and irradiation stability are two important parameters and deserve more attention. However, the influence of doping elements on the thermal cycling stability of TBMs has not been investigated so far. Meanwhile, fine-grained ceramics are identified as the most promising, regarding tritium release behavior and mechanical strength [23]. But with the grain refinement, surface energy of ceramic particles increases, and thus
the structural and functional instability of materials may get more acute in high temperature environment. Therefore, it is significant to fabricate fine-grained lithium ceramic solid solution and investigate its thermal cycling stability.

The aim of this work is to prepare \( \text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4 \) by proprietary hydrothermal process and multistage sintering (Ti has lower neutron activation than Al), and to investigate the influences of Ti doping on the microstructure, mechanical and physical properties of \( \text{Li}_4\text{SiO}_4 \). Furthermore, the thermal cycling stability of \( \text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4 \) pebbles is further studied. These results can cast light for future development of advanced tritium breeding materials.

2. Experimental details

Lithium hydroxide monohydrate, fumed \( \text{SiO}_2 \) (Hydrophilic-300) and \( \text{TiO}_2 \) (30 nm, anatase, hydrophilic) were purchased from Aladdin Ltd. (Shanghai, China). All chemicals were used without further purification.

2.1 Preparation of precursor powders

The precursor powders were hydrothermally synthesized using lithium hydroxide monohydrate, fumed \( \text{SiO}_2 \) and \( \text{TiO}_2 \) nanopowders with a ratio of 4:1-x:x (x=0, 0.05, 0.1, 0.2). Briefly, lithium hydroxide monohydrate (0.14 mol) was thoroughly dissolved in 70 ml of deionized water under magnetic stirring. Meanwhile, fumed \( \text{SiO}_2 \) (0.035(1-x) mol) was uniformly dispersed in 70 ml of ethanol. Subsequently, the above two solutions were mixed under magnetic stirring at room temperature. After that, \( \text{TiO}_2 \) nanopowders (0.035x mol) were added, and continued stirring for 30 min. Then, the mixed solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 200 ml and performed at 180 °C for 12 h. Finally, hydrothermal products were dried at 80 °C for overnight, and ground in an agate mortar to obtain precursor powders.
2.2 Fabrication of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ pebbles

The as-prepared precursor powders and deionized water were mixed in a mass ratio of 5:4 to form the slurry, then the green spheres could be produced by dropping the slurry through a nozzle (0.7 mm in diameter) into a container of liquid nitrogen. By freezing for more than 15 min, the green spheres were salvaged and placed on filter papers, dried in air for 30 min and then in drying oven of 70 °C for overnight. Li$_4$Si$_{1-x}$Ti$_x$O$_4$ pebbles could be finally obtained by sintering the dried green spheres in a box-type resistance furnace. To be specific, the samples were heated to 420 °C, dwelling for 1h, then heated to 720 °C, dwelling for 1h, finally sintered at 800 °C for 4 h. The heating rate was 5 °C/min.

2.3 Characterization

Thermal behavior of the precursor powders was studied by thermogravimetry and differential scanning calorimetry (NETZSCH 409 PC) in air at a constant heating rate of 10 °C/min. The phase composition and crystal structure were investigated by X-ray diffractometry (XRD-7000), and the cell parameters were refined via Jade 6.5 software. The morphology was observed by scanning electron microscope (Model S-4800, Hitachi, Japan), and grain size was measured by Nano Measure 1.2 software from SEM images. The density was measured by an electronic density balance using ethyl alcohol as the immersion medium. The crush load was tested by a universal material strength-testing machine with a 5 kN load cell and cross-head speed of 0.1 mm/min (HT-2402). To minimize the influence caused by the pebble size, the pebbles with a diameter of 1.2~1.3 mm were used for the test. The average crush load was estimated based on the results of more than ten pebbles. For thermal and ionic conductivity tests, the precursor powders were pressed into pellets and sintered at the same sintering process. The thermal conductivity was measured by LFA 457 Micro
Flash Analyzer of NETZSCH. The ionic conductivity was determined by AC impedance spectra measured using an Agilent E4980A impedance analyzer in the frequency range from 100 to $10^6$ Hz, and analyzed by fitting the equivalent circuit model using the ZView software. For thermal cycling tests, the ceramic pebbles were heated to 800 °C in a box-type resistance furnace, dwelling for 4 h, then cooled down to room temperature (set the heating and cooling rate to 5 °C/min). After each three cycles, a batch of ceramic pebbles were fetched out for microstructure characterization and compressive strength testing.

3. Results and discussion

3.1 Phase composition of precursor powders

Fig. 1 shows the XRD patterns of the precursor powders synthesized via hydrothermal process. The undoped samples consist of Li$_2$SiO$_3$ and Li$_2$CO$_3$, suggesting LiOH and SiO$_2$ tend to generate stable Li$_2$SiO$_3$ instead of Li$_4$SiO$_4$ in the hydrothermal reaction system, and the rest of Li$^+$ changes to Li$_2$CO$_3$ when drying the hydrothermal products. The diffraction peaks of the Ti doped samples are basically the same as that of the undoped one, except the emergence of Li$_2$TiO$_3$ peaks. Moreover, with the increase of Ti content, the proportion of Li$_2$CO$_3$ decreases. It reveals there are two competitive reactions.

$$2\text{LiOH} + \text{SiO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{H}_2\text{O}$$

$$2\text{LiOH} + \text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3 + \text{H}_2\text{O}$$

3.2 TD/DSC analyses

The TG/DSC curves of precursor powders with varying Ti doping amount are illustrated in Fig. 2. Slight weight loss at around 425 °C in the TG curves can be ascribed to the reaction of residual SiO$_2$/TiO$_2$ with Li$_2$CO$_3$ [24]. Major weight loss occurs in the range of 650–750 °C, accompanied by a sharp exothermic peak at 709 °C,
which is attributed to the formation of Li$_4$Si$_{1-x}$Ti$_x$O$_4$. The weight loss decreases with increasing Ti content due to the reduced lithium carbonate in the samples, in accordance with XRD results. Compared with the undoped sample, the exothermic peak of Ti doped samples shifts to lower temperature, indicating Ti doping can reduce the reaction temperature and raise the reaction efficiency. This is due to the lattice distortion caused by the substitution of Ti$^{4+}$ for Si$^{4+}$, which may reduce the activation energy [25]. No obvious weight changes are found above 800 °C, suggesting the synthesis process is finished. Moreover, considering the release of CO$_2$ caused by above mentioned two reactions, multistage sintering is adopted to reduce the pores and impurities (i.e. 425 °C for 1h, 710 °C for 1h and 800 °C for 4h).

3.3 Phase composition

Fig. 3 shows the XRD patterns of the Li$_4$Si$_{1-x}$Ti$_x$O$_4$ ($x$=0, 0.05, 0.1, 0.2) samples fabricated via multistage sintering. It can be seen that the undoped sample is composed of Li$_4$SiO$_4$, with a small amount of Li$_2$CO$_3$. And for the doped samples, the diffraction peaks belonging to Li$_4$SiO$_4$ can be obviously observed, and the weak diffraction peaks of Li$_2$TiO$_3$ are found. The diffraction peaks of Li$_4$SiO$_4$ shift to small angle with increasing Ti content, and the increase in the lattice volumes shown in Table 1 indicates the insertion of Ti in the Li$_4$SiO$_4$ structure. However, the deviation of Li$_2$TiO$_3$ peaks does not occur, which reveals the entrance of Si into Li$_2$TiO$_3$ lattice is rather difficult. More secondary Li$_2$TiO$_3$ can be observed in $x$=0.2 sample. This is due to the low content of Li$_2$CO$_3$ in the precursor, so Li$_2$TiO$_3$ is retained. Previous researches show that Li$_2$TiO$_3$ can hardly be incorporated into the Li$_4$SiO$_4$ giving Li$_4$Si$_{1-x}$Ti$_x$O$_4$ solid solution [26, 27]. Hence, the possible formation process of Li$_4$Si$_{1-x}$Ti$_x$O$_3$ in this work can be concluded as: Li$_2$TiO$_3$ reacts with Li$_2$CO$_3$ to form Li$_4$TiO$_4$, subsequently incorporates into Li$_4$SiO$_4$ to generate solid solution [28].
\[
\text{Li}_4\text{TiO}_3 + \text{Li}_2\text{CO} \rightarrow \text{Li}_4\text{TiO}_4 + \text{CO}_2
\]
\[
x\text{Li}_4\text{TiO}_4 + \text{Si}_4\text{SiO}_4 \rightarrow \text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4
\]

3.4 Morphology of ceramic pebbles

Fig. 4 shows the cross-section SEM micrographs of \(\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4\) pebbles \((x=0, 0.05, 0.1, 0.2)\). It can be seen that the \(\text{Li}_4\text{SiO}_4\) sample is made of spherical particles and displays the fracture features of intergranular fracture, which indicate the intergranular bonding is weak. In contrast, the \(\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4\) samples mainly display irregular particles, and stable polygonal structure can be seen (pointed out by red arrows), which indicates that addition of Ti enhances the sinterability. The migration of interface under the interface driving force is responsible for the growth of polygonal grains. Furthermore, the grain size increases with increasing Ti content. The average grain sizes are 0.80 µm, 3.21 µm, 4.09 µm and 5.73 µm, respectively. It has been reported that the grain growth of \(\text{Li}_4\text{SiO}_4\) pebbles is controlled by the lattice diffusion (volume diffusion) at about 850 °C [29]. As discussed above, Ti substitution increases the lattice diffusion, i.e., the activation energy for grain growth decreases and grains grow more easily for the Ti doped samples under the same sintering conditions. Additionally, the proportion of transgranular fracture rises with increasing Ti doping content (pointed out by yellow arrows), suggesting the enhancement of the grain boundary cohesion. The transgranular fracture feature predicts the enhanced mechanical strength.

EDS mapping was performed on the \(\text{Li}_4\text{Si}_{0.9}\text{Ti}_{0.1}\text{O}_4\) sample to depict the distribution of Ti and Si elements. As shown in Fig. 5, Ti and Si elements are detected within the grains, confirming the formation of solid solution. However, the aggregation of Ti element can be found in some regions (marked with red circles). Combined with the XRD results, it can be deduced the small-sized \(\text{Li}_2\text{TiO}_3\) particles
exist as second phase.

3.5 Crush load, density and grain size

The ceramic pebbles need high crush load to prevent the breaking and fragmentation, which lead to plugging of purge circuits and diminished heat transfer [23]. The dependence of crush load, density and grain size on Ti doping amount is illustrated in Fig. 6. The Li₄SiO₄ sample shows low crush load of 11 N, and the crush load is remarkably improved with the increase of Ti doping content. The average crush loads are 27 N (x=0.05), 31 N (x=0.1) and 52 N (x=0.2), respectively. Furthermore, the addition of Ti promotes the grain growth, but has relatively little effect on densification of ceramic pebbles. The ceramic densification is depended on the competition between grain boundary migration and pores removal. The results show that the effect of Ti doping on grain boundary migration prevails. And this is the reason why the density of Ti doped samples is not significantly improved compared to that of Li₄SiO₄ sample.

Grain size and porosity are critical factors affecting the strength of ceramics, which can be expressed by the empirical equation [30]: \( S=kG^{-a}e^{-bP} \). Where \( S \) is the strength, \( G \) is the grain size, \( P \) is the porosity, \( b \) is a constant related to pore shape, and \( k, a \) are positive constants. The Li₄Si₁₋ₓTiₓO₄ samples have a comparable density (78.5~81.0%T.D.) and larger grain size, but higher crushing strength, compared to the Li₄SiO₄ sample. The reasons for this phenomenon are, on one side, with increasing Ti content, the lattice distortion increases and the deformation resistance of the matrix is increased, thereby resulting in a more significant solid solution strengthening effect. On the other side, second phase Li₂TiO₃ contained in the Li₄Si₁₋ₓTiₓO₄ samples may make contribution for the enhanced strength as the crushing strength of Li₂TiO₃ is better than that of Li₄SiO₄. It also should be noted that strength of ceramic pebbles is
also affected by flaws, sphericity and impurities.

3.6 Thermal conductivity

Thermal conductivity can be calculated by multiplying specific heat, thermal diffusivity and density.

\[ k = \rho \cdot \alpha \cdot c_p \]

where \( k \) is thermal conductivity, \( \rho \) is bulk density. \( \alpha \) and \( c_p \) are thermal diffusivity and specific heat, which can be directly measured by laser flash apparatus.

Fig. 7 shows the dependence of the thermal diffusivity, specific heat and thermal conductivity on the temperature and Ti doping amount. The relative densities of the pellets are 84.10% \((x=0)\), 80.16% \((x=0.05)\), 81.53% \((x=0.1)\), 81.57% \((x=0.2)\), respectively. It can be seen that the thermal diffusivity and specific heat of the Ti doped samples are roughly higher than that of the \( \text{Li}_4\text{SiO}_4 \) sample. The thermal conductivity does not increase monotonically with the increase of Ti content, and the \( x=0.05 \) sample has the best thermal conductivity. Compared with the reported \( \text{Li}_{4+\alpha}\text{Si}_{1-x}\text{Al}_x\text{O}_4 \) [17], the prepared \( \text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4 \) in this work exhibits lower thermal conductivity. There may be two reasons: (1) Heat conduction of \( \text{Li}_4\text{SiO}_4 \) can be carried out through photons and carriers. The formation of interstitial lithium, as the result of aluminum addition, contributes to the thermal conductivity. (2) Generally, thermal conductivity decreases with increasing porosity and is very sensitive to impurities. Hence, the presence of pores and \( \text{Li}_2\text{TiO}_3 \) may be detrimental to the thermal conductivity. Even so, the thermal conductivity of \( \text{Li}_4\text{SiO}_4 \) is obviously improved through the substitution of Ti, it is foreseen that solid solution ceramics should be a good candidate for advanced tritium breeders.

3.7 Ion conductivity

Tritium diffusion process can be envisaged as lithium-ion migration which acts
as the charge carrier in the ceramics [22, 31], the tritium release behavior can be evaluated by measuring the conductivity of breeder materials. Fig. 8 are the impedance spectra of the samples recorded at room temperature in the frequency range of 100~10⁶ Hz. The equivalent circuit is composed of a resistance R1 in series with a component consisting of another resistance R2 in parallel to a CPE element. The depressed semicircle is present in the plot, the right intercept of the semicircle with the real axis corresponds to the bulk resistance (grain interior resistance plus grain boundary resistance). The ion conductivity can be calculated in accordance with the relation:

\[ \sigma = \frac{L}{R \cdot S} \]

where \( \sigma \) is ion conductivity, \( L \) is the sample thickness, \( R \) is the bulk resistance and \( S \) is the area of the electrode. The calculated ion conductivity is illustrated in Table 2. It can be seen that substitution of Ti for Si causes an increase in ionic conductivity, signifying the improvement in tritium release performance. The insertion of Ti⁴⁺ enlarges the lattice size of the Li₄SiO₄-type structure, i.e. the size of migration channels of Li⁺ increases [32]. Moreover, since Ti–O bond is stronger than Si–O bond, the Li–O bond interaction in Li₄SiO₄ structure is decreased when the Si atom is replaced by Ti atom, thus the ionic conductivity is improved [33]. However, the ionic conductivity decreases with increasing \( x \) from 0.1 to 0.2, this is probably due to the increased proportion of second-phase Li₂TiO₃. According to the research by Tanigawa et al. [34], lithium orthosilicate has better conductivity than lithium titanate, and the electrical conductivity of Li₄SiO₄ is about two orders larger than that of Li₂TiO₃ at 975 K.

3.8 Thermal cycling

It is important to study the microstructure and crushing strength changes during
the thermal cycling tests. As shown in Fig. 9, the grain size of Li$_4$SiO$_4$ sample increases following thermal cycles, small-sized pores merge with each other, and coarse grains with a transgranular fracture morphology can be observed. EDS analyses indicate both fine grains and coarse grains in Fig. 9b2 are Li$_4$SiO$_4$ (Fig. S1 and S2), confirming the secondary growth of grains. The crush load increases slightly after 9 cycles (Fig. 13a), which is ascribed to the change of fracture mode and the decrease of pores. However, due to the presence of intracrystalline pores and cracks, the crush load decreases after 12 cycles.

For the Li$_4$Si$_{0.95}$Ti$_{0.05}$O$_4$ sample, no obvious changes in the microstructure and the crush load after 6 thermal cycles (Fig. 10 and Fig. 13b). Many tiny particles precipitate on the grain boundaries and the surface of grains. EDS analysis (see Fig. S3) shows that Si/Ti ratio is lower than the designed value (viz. 8.3 vs 19), suggesting the segregation of Ti toward the grain surface during long-time thermal cycling. This can lead to the slight decrease of strength after 9 cycles.

With prolonging the thermal cycling, the microstructure of Li$_4$Si$_{0.9}$Ti$_{0.1}$O$_4$ sample changes significantly (Fig. 11) and the strength decreases rapidly (Fig. 13c). EDS analysis confirms the tiny particles as titanium-rich (Fig. S4). The atom ratio of Si:Ti is close to 2.5:1 which is much lower than the designed value. It is reasonable to assume that the segregation becomes more serious with the increase of Ti doping content. Furthermore, a great amount of intracrystalline pores can be observed after 12 cycles. As a result, the crush load decreases to less than 20 N, revealing inferior durability of the Li$_4$Si$_{0.9}$Ti$_{0.1}$O$_4$ sample.

For the Li$_4$Si$_{0.8}$Ti$_{0.2}$O$_4$ sample (Fig. 12), laminate structure mainly composed of Ti and O can be seen clearly after 9 cycles (Fig. S5). EDS mapping also indicates Ti with high concentration within the laminate grains (Fig. S6). It suggests the formation
of titanate. Although the microstructure of the Li$_4$Si$_{0.8}$Ti$_{0.2}$O$_4$ sample changes slightly after the thermal cycling, it still exhibits a high crush load (Fig. 13d). Since many factors can affect the strength, such as grain size, porosity, pore size and distribution, sphericity, the content and size of second-phases, humidity, etc., the variation in strength with thermal cycling periods is irregular.

To sum up, the moderate amount of Ti doping can improve the mechanical and physical properties and thermal cycling stability of Li$_4$SiO$_4$. Compared with Al-doped Li$_4$SiO$_4$ [17, 19, 20], Ti doping plays a more significant role in enhancing crushing strength, whilst Al doping contributes more to the improvement of conductivity. Tritium release experiments conducted by Zhao et al. revealed that Li$_{4.2}$Si$_{0.8}$Al$_{0.2}$O$_4$ had lower tritium release temperature and potentially better irradiation resistance compared to Li$_4$SiO$_4$ [18]. The tritium release performance and irradiation resistance of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ solid solution are also worthy of expectation (Ti has lower neutron activation than Al). Since the thermal cycling stability of Li$_{4-x}$Si$_{1-x}$Al$_x$O$_4$ pebbles has not been reported, we cannot make a comparison yet. View from the current studies, solid solution materials should have unique advantages in advanced tritium breeding materials, although more deep studies are still required to further understand the influence of various doping elements.

4. Conclusions

The Li$_4$Si$_{1-x}$Ti$_x$O$_4$ ceramic pebbles were successfully prepared by proprietary hydrothermal process and multistage sintering. The formation of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ solid solution may be result from the incorporation of Li$_4$TiO$_4$ into Li$_4$SiO$_4$. Ti-doping can promote the sinterability and grain growth of Li$_4$SiO$_4$. The crush load of the Li$_4$SiO$_4$ pebbles is improved significantly by doping Ti, and it increases almost four times by increasing $x$ from 0 to 0.2. The thermal and ionic conductivity do not increase...
monotonically with increasing Ti content, the best values are obtained when $x=0.05$ and $x=0.1$, respectively. Thermal cycling tests display that the $\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4$ samples still have higher crush load compared with the $\text{Li}_4\text{SiO}_4$ sample, despite Ti segregation in some samples after undergoing thermal cycling. With the increase of Ti doping content, the segregation becomes more serious. In terms of thermal stability, the optimal Ti doping amount should be $x=0.05$. As titanium has low neutron activation behavior, $\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4$ solid solution may have good application prospect in the field of solid tritium breeders.

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Fig. 1 XRD patterns of the precursor powders synthesized by hydrothermal method

Fig. 2 TG/DSC of the precursor powders
Fig. 3 XRD patterns of $\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4$

Table 1 Rietveld refinement parameters for $\text{Li}_4\text{Si}_{1-x}\text{Ti}_x\text{O}_4$

| samples | cell parameters (Å) | $\beta$ (°) | cell volume (Å$^3$) | theoretical density (g/cm$^3$) |
|---------|---------------------|-------------|----------------------|-------------------------------|
|         | a       | b       | c   |                        |                             |                               |
| $x = 0$ | 5.14282 | 6.09982 | 5.29247 | 90.2805 | 166.02 | 2.397 |
| $x = 0.05$ | 5.15371 | 6.11125 | 5.30074 | 90.2042 | 166.95 | 2.384 |
| $x = 0.1$ | 5.16278 | 6.12278 | 5.31046 | 90.276 | 167.86 | 2.371 |
| $x = 0.2$ | 5.16304 | 6.1465 | 5.32568 | 89.9426 | 169.01 | 2.355 |
Fig. 4 SEM fracture micrographs of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ pebbles fabricated via multistage sintering: (a) $x=0$; (b) $x=0.05$; (c) $x=0.1$; (d) $x=0.2$

Fig. 5 SEM micrographs of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ with Ti content $x=0.1$ and corresponding EDS mapping of Si, Ti and O elements
Fig. 6 The dependence of crush load, density and grain size on Ti doping content

Fig. 7 Thermal diffusivity, specific heat and thermal conductivity of Li$_4$Si$_{1-x}$Ti$_x$O$_4$ samples ($x=0, 0.05, 0.1, 0.2$)
Fig. 8 AC impedance spectra for Li$_{4}$Si$_{1-x}$Ti$_x$O$_4$ samples

Table 2 Conductivity of Li$_{4}$Si$_{1-x}$Ti$_x$O$_4$ samples

| samples | R (Ω)     | L (m)       | A (m$^2$)   | conductivity (S/m) |
|---------|-----------|-------------|-------------|--------------------|
| $x = 0$ | $4.512 \times 10^6$ | $1.91 \times 10^{-3}$ | $1.5592 \times 10^{-3}$ | $2.715 \times 10^{-6}$ |
| $x = 0.05$ | $4.365 \times 10^6$ | $2.71 \times 10^{-3}$ | $1.5562 \times 10^{-3}$ | $3.990 \times 10^{-6}$ |
| $x = 0.1$ | $1.003 \times 10^6$ | $2.64 \times 10^{-3}$ | $1.5562 \times 10^{-3}$ | $1.6914 \times 10^{-5}$ |
| $x = 0.2$ | $3.506 \times 10^6$ | $2.70 \times 10^{-3}$ | $1.5851 \times 10^{-3}$ | $4.858 \times 10^{-6}$ |
Fig. 9 SEM micrographs of Li$_4$SiO$_4$ pebbles after (a) 3 cycles, (b) 6 cycles, (c) 9 cycles, (d) 12 cycles. (1) cross section, (2) surface
Fig. 10 SEM micrographs of Li$_4$Si$_{0.95}$Ti$_{0.05}$O$_4$ pebbles after (a) 3 cycles, (b) 6 cycles, (c) 9 cycles, (d) 12 cycles. (1) cross section, (2) surface
Fig. 11 SEM micrographs of Li$_4$Si$_{0.9}$Ti$_{0.1}$O$_4$ pebbles after (a) 3 cycles, (b) 6 cycles, (c) 9 cycles, (d) 12 cycles. (1) cross section, (2) surface
Fig. 12 SEM micrographs of Li₄Si₀.5Ti₀.2O₄ pebbles after (a) 3 cycles, (b) 6 cycles, (c) 9 cycles, (d) 12 cycles. (1) cross section, (2) surface
Fig. 13 Relationship between the crush load and thermal cycles: (a) Li$_4$SiO$_4$ pebbles, (b) Li$_4$Si$_{0.95}$Ti$_{0.05}$O$_4$ pebbles, (c) Li$_4$Si$_{0.9}$Ti$_{0.1}$O$_4$ pebbles, (d) Li$_4$Si$_{0.8}$Ti$_{0.2}$O$_4$ pebbles