Short communication

High-density spherical $Li_4Ti_5O_{12}$/C anode material with good rate capability for lithium ion batteries

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Abstract

$Li_4Ti_5O_{12}$ is a very promising anode material for lithium secondary batteries. To improve the material's rate capability and pile density is considered as the important researching direction. One effective way is to prepare powders composed of spherical particles containing carbon black. A novel technique has been developed to prepare spherical $Li_4Ti_5O_{12}$/C composite. The spherical precursor containing carbon black is prepared via an "outer gel" method, using $TiOCl_2$, C and NH_3 as the raw material. Spherical $Li_4Ti_5O_{12}$/C powders are synthesized by sintering the mixture of spherical precursor and Li_2CO_3 in N_2. The investigation of TG/DSC, SEM, XRD, Brunauer–Emmett–Teller (BET) testing, laser particle size analysis, tap-density testing and the determination of the electrochemical properties show that the $Li_4Ti_5O_{12}$/C composite prepared by this method are spherical, has high tap-density and excellent rate capability. It is observed that the tap-density of spherical $Li_4Ti_5O_{12}$/C powders (the mass content of C is 4.8%) is as high as $1.71\,g\,cm^{-3}$, which is remarkably higher than the non-spherical $Li_4Ti_5O_{12}$. Between 1.0 and 3.0 V versus Li, the initial discharge specific capacity of the sample is as high as $144.2\,mAh\,g^{-1}$, which is still $128.8\,mAh\,g^{-1}$ after 50 cycles at a current density of $1.6\,mA\,cm^{-2}$.
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Keywords: Lithium secondary batteries; $Li_4Ti_5O_{12}$; High tap-density; Spherical; Conductivity

1. Introduction

The spinel lithium titanate $Li_4Ti_5O_{12}$ is a so-called zero-strain insertion material as the negative-electrode material of lithium secondary batteries [1]. Recently, this material has attracted attention because of the low cost, satisfactory safety and easy preparation. Therefore, it is regarded as one of the most promising anode materials.

However, there are two main obstacles preventing $Li_4Ti_5O_{12}$ to be put into commercially used. One is the low conductivity, which leads to initial capacity loss and poor rate capability. The other is the low pile density, which leads to low volumetric specific capacity and batteries' energy density. Both problems are related to this material's structure and electrode preparation process.

To improve the conductivity, several effective ways have been proposed, including synthesis of nano-particle $Li_4Ti_5O_{12}$ [2], substitution of a small quantity of Li^+ or Ti^{4+} by supervalent metal ions [3–6] (V^{5+}, Mn^{4+}, Fe^{3+}, Ni^{2+}, Cr^{3+} and Mg^{2+}), synthesis of electronic conductor composites [7] (carbon), etc. Unfortunately, little attention has been fixed on improving the pile density of $Li_4Ti_5O_{12}$ so far. The $Li_4Ti_5O_{12}$ powders are usually prepared via conventional solid-state reaction and sol–gel method. The obtained $Li_4Ti_5O_{12}$ powders always show irregular particle morphology with broad particle size distribution. According to our test, the tap-density of the powders is not more than $1.0\,g\,cm^{-3}$. For improving the tap-density of product, it is expected that preparing spherical powders may be an effective way [8]. The authors have developed an "inner gel" technique to prepare spherical $Li_4Ti_5O_{12}$ anode material with high tap-density of $1.64\,g\,cm^{-3}$ [9]. But the rate capability of the product is not satisfied. To obtain $Li_4Ti_5O_{12}$ anode material with both high conductivity and high tap-density, the authors developed a novel method to prepare spherical $Li_4Ti_5O_{12}$/C composite.

In this work, the authors develop the "outer gel" process to prepare spherical $Li_4Ti_5O_{12}$/C anode material. The structure, the morphology and the electrochemical performance of

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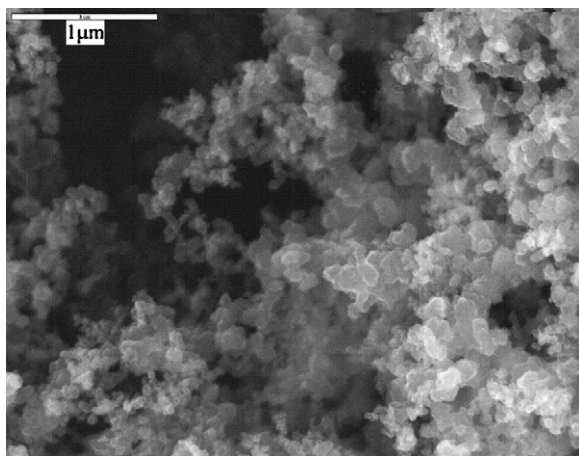*E-mail address:* gaoj@mail.tsinghua.edu.cn (J. Gao).

Fig. 1. SEM image of the carbon black powders.

the spherical $Li_4Ti_5O_{12}$/C composite have been investigated in detail.

2. Experimental

The spherical precursor containing carbon black was prepared by an "outer gel" method as the follows. Titanium tetrachloride ($TiCl_4$) was dissolved in deionized water and $TiOCl_2$ solution was prepared. Then a certain quantity of carbon was dispersed uniformly in this solution. The mixed solution was pumped continuously into coal oil by stirring, having a volume water/oil ratio of 1:10. A certain quantity of Span 80 was dissolved in coal oil as the surface active reagent. After this, the mixed slurry was heated to 50 °C and NH_3 was blown into the mixed slurry. The spherical gel precursor deposited along with the increase of pH. The mixture in the reactor was filtered, washed and dried. Thus, the spherical precursor powders containing carbon black were obtained. Then the dried spherical gel precursor and Li_2CO_3, in a certain molar ratio of Li:Ti, were mixed uniformly. The spherical $Li_4Ti_5O_{12}$/C powders are synthesized by sintering the mixture at 800 °C for 16 h in N_2. In this work, the input quantity of carbon (C/(C + $Li_4Ti_5O_{12}$) quantity ratio) is 5% and it is tested that the fact quantity of carbon is 4.8%.

TG/DSC of the mixture of precursor and Li_2CO_3 was used to direct the heat treatment. Powder X-ray diffraction (XRD, D/max-rB) using Cu Kα radiation was used to identify the crystalline phase and crystal lattice parameters of the powders. The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F). The powders' particle size and particle size distribution were identified by laser particle size analyzer (OMEC LS-POP(III)). The specific surface area of the powders was identified by BET analyzer (Builder SSA-4200). The tap-density of the powders was tested as the following method. A certain quality of powders was added into a dry measuring cylinder, and then taped the measuring cylinder until the volume of the powders did not change anymore. The ratio of the quality and the volume was the tap-density of the powders.

Experimental test cells for measurements used the cathode with the composition of 80 wt.% $Li_4Ti_5O_{12}$/C, 10 wt.% carbon black and 10 wt.% PTFE. The separator was a Celguard 2400 microporous polylene membrane. The electrolyte was 1 M $LiPF_6$ EC + DEC(1:1 by volume). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The discharge–charge cycling was galvanostatically performed at different current density of 0.08–3.2 mA cm^{-2} with cut-off voltages of 1.0–3.0 V (versus Li/Li$^+$) at 20 °C.

3. Results and discussion

Fig. 1 shows the morphology of the carbon black. The powders are composed of dispersed nano-crystalline grains. So it can be distributed uniformly in each of spherical $Li_4Ti_5O_{12}$ particles.

Fig. 2 shows the morphology of the precursor powders. The powders are all composed of well-dispersed spherical particles, as shown in Fig. 2(a). The surface of every spherical particle is smooth, and there are also some carbon fragments adhering to the spherical particle, as shown in Fig. 2(b). It is tested that the tap-density of the precursor is 1.38 g cm^{-3}.

Fig. 3 shows the TG–DSC curves of the mixture of precursor powders and Li_2CO_3 with a heating rate of 10 °C min^{-1} from room temperature to 900 °C in argon. On the DSC curve near
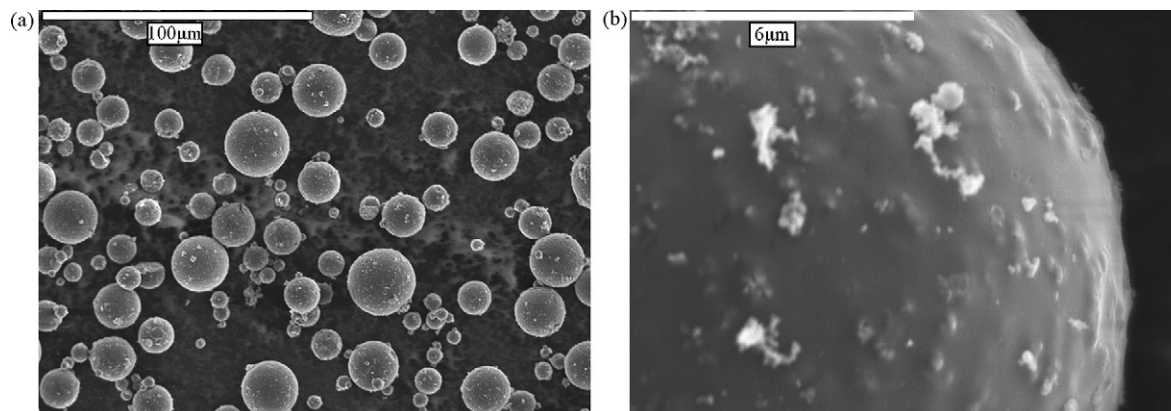

Fig. 2. SEM images of the precursor powders prepared by "outer gel" method.
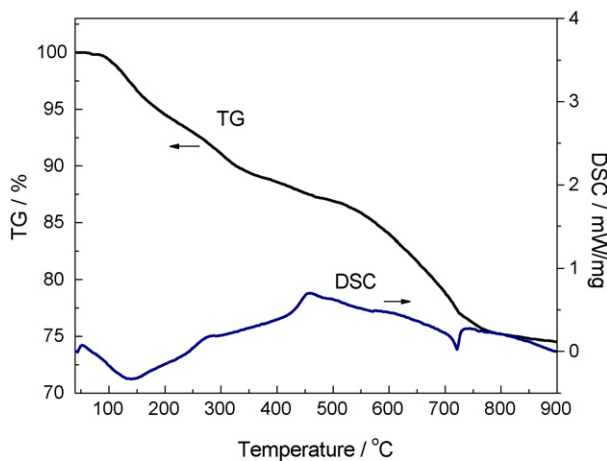
Fig. 3. TG/DSC curves of the mixture of precursor powders and Li_2CO_3.

$140\,^{\circ}C$, there is an obvious endothermic peak, associating with the sharply weight loss on the TG curve, which is related to the quickly dehydration of precursor powders. During $260–550\,^{\circ}C$, there is a broad exothermic peak on the DSC curve, associating with the slowly elimination of residual H_2O in precursor on the TG curve. On the DSC curve near $720\,^{\circ}C$, there is an obvious endothermic peak, which is related to the preparation of $Li_4Ti_5O_{12}$ crystal and the loss of CO_2. When the temperature is high than $750\,^{\circ}C$, the TG curve indicates the weight remains constant. We can conclude that the reaction between the precursor and Li_2CO_3 will finish and the powders' composition will be confirmed when the heat-treating temperature is higher than $750\,^{\circ}C$.

Based on the above analysis, we heat treated the mixture of the spherical precursor and Li_2CO_3 at $800\,^{\circ}C$ for 16 h in N_2 to synthesize the spherical $Li_4Ti_5O_{12}/C$ powders.

Fig. 4 shows the morphology of the $Li_4Ti_5O_{12}/C$ powders. In contrast to the precursor, there is obvious difference of particle morphology, particle size, particle size distribution, crystalline phase and tap-density after thermal treatment. It can be found that the spherical particles shrank after sintering and the surface of the spheres is not smooth. The crystalline grains have grown up on the surface of every particle and each of the spherical particles is made up of a large number of fine crystalline grains, as shown in Fig. 4(b). It also can be observed that the crystalline grains of the $Li_4Ti_5O_{12}/C$ are smaller than that of the previous spherical $Li_4Ti_5O_{12}$ [9] and the carbon particles have been uniformly distributed in each of $Li_4Ti_5O_{12}/C$ particles. It indicates that the carbon particles can restrain the growth of the $Li_4Ti_5O_{12}$ crystalline grains and this could benefit to the diffusion of Li^+. The tap-density of the spherical $Li_4Ti_5O_{12}$ powders prepared by this method is as high as $1.80\,g\,cm^{-3}$, which of the spherical $Li_4Ti_5O_{12}/C$ powders prepared in this work still reaches $1.71\,g\,cm^{-3}$. The high-density spherical $Li_4Ti_5O_{12}/C$ anode material can be used in the lithium ion batteries to greatly increase the batteries' energy density. The specific surface area of spherical $Li_4Ti_5O_{12}/C$ powders determined by the Brunauer–Emmett–Teller (BET) method is $8.13\,m^2\,g^{-1}$, which is much higher than the previous spherical $Li_4Ti_5O_{12}$ powders of $0.32\,m^2\,g^{-1}$. Bigger BET could augment the interface of electrode material and electrolyte, which also benefits to the diffusion of Li^+. The particle size distribution of the precursor and $Li_4Ti_5O_{12}/C$ powders is depicted in Fig. 5. As is seen in this fig-
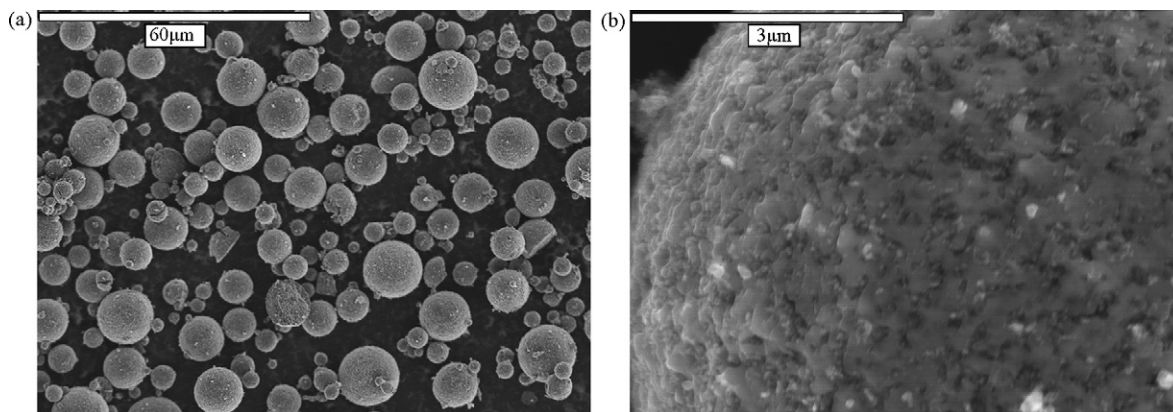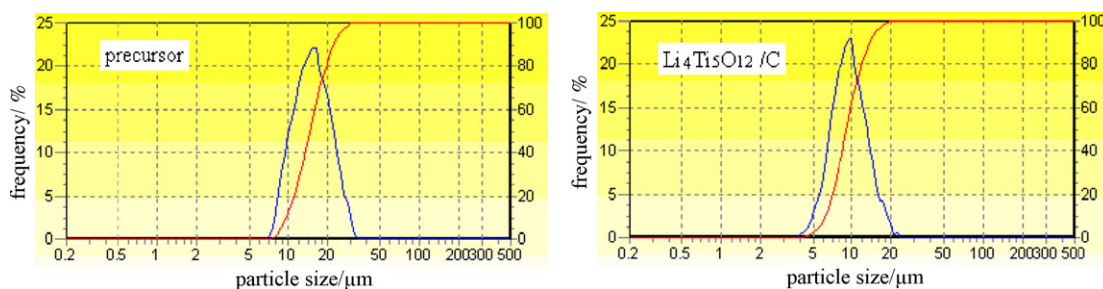

Fig. 4. SEM images of the spherical $Li_4Ti_5O_{12}/C$ powders.

Fig. 5. The particle size distribution of the precursor and $Li_4Ti_5O_{12}/C$ powders.

Table 1
The particle size distribution, BET and tap-density of precursor and $Li_4Ti_5O_{12}$/C powders

Spherical powders	$D_{10}(\mu m)$	$D_{50}(\mu m)$	$D_{90}(\mu m)$	BET ($m^2\,g^{-1}$)	Tap-density ($g\,cm^{-3}$)
Precursor	8.1	14.3	21.7	1.76	1.38
$Li_4Ti_5O_{12}$/C	5.5	9.6	14.1	8.13	1.71

ure, the average particle size of the precursor and $Li_4Ti_5O_{12}$/C powders is 14.3 and 9.6 μm, respectively. The BET and tap-density of the precursor and $Li_4Ti_5O_{12}$/C composite are listed in Table 1.

The X-ray diffraction patterns of carbon, the precursor and the $Li_4Ti_5O_{12}$/C composite are shown in Fig. 6. It can be observed that there are few diffraction peaks on the XRD patterns of the precursor powders and these peaks are all assigned to carbon. Thus, the precursors are amorphous except carbon. There are strong and sharp diffraction peaks on the XRD pattern of the $Li_4Ti_5O_{12}$/C composite, and all of them are mostly attributed to $Li_4Ti_5O_{12}$ besides little carbon. The spectra indicate that the amorphous precursor powders have well crystallized into spinel $Li_4Ti_5O_{12}$ powders and carbon still remained in spherical $Li_4Ti_5O_{12}$ particles after heat treatment.

The spherical $Li_4Ti_5O_{12}$/C anode material not only has high tap-density, but also has high specific capacity and good cycling stability. We tested the model cells using the spherical $Li_4Ti_5O_{12}$/C powders prepared in this work as the cathode material. It is tested that carbon has little discharge–charge capacity between 1.0 and 3.0 V, especially in the region of 1.56 V plateau. So the active material in $Li_4Ti_5O_{12}$/C composite is primarily $Li_4Ti_5O_{12}$.

Fig. 7 shows the initial charge–discharge curves of the $Li_4Ti_5O_{12}$/C at the current density of 0.08, 0.32, 1.6 and 3.2 mA cm^{-2}, respectively. At 0.08 mA cm^{-2}, the discharge specific capacity of $Li_4Ti_5O_{12}$/C composite is 158.2 mAh g^{-1} and the $Li_4Ti_5O_{12}$'s discharge specific capacity of 166.2 mAh g^{-1} is very close the theoretical capacity of $Li_4Ti_5O_{12}$ (175 mAh g^{-1}), which indicates that the active material utilization is very close to the theoretical value. At 0.32, 1.6 and 3.2 mA cm^{-2}, the dis-
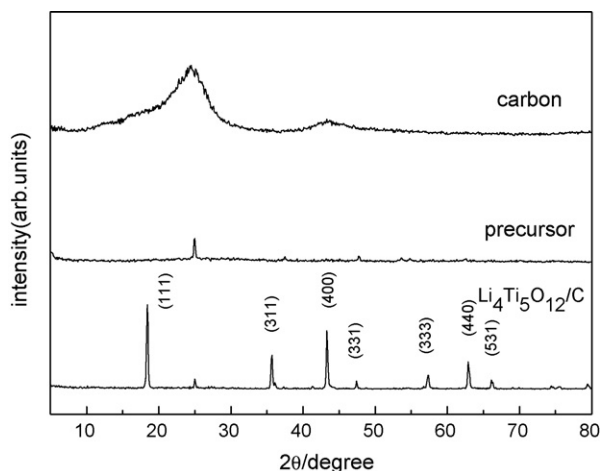
charge specific capacity is 150.6, 144.2 and 132.4 mAh g^{-1}, respectively. Furthermore, the difference between the charge and discharge voltage plateau is small, even at heavy current, which is representative of its good kinetics. The result indicates the rate capability of the prepared $Li_4Ti_5O_{12}$/C composite material has been improved at a certain extent, though uniformly distributing carbon black in each of spherical $Li_4Ti_5O_{12}$ particles, comparing to the previous spherical $Li_4Ti_5O_{12}$ [9].

Fig. 8 shows the cycling performance of the spherical $Li_4Ti_5O_{12}$/C composite at different current density. The related data of electrochemical performance is illustrated in Table 2. According to the test, this composite material makes no difference of excellent cycling stability at different current, although the reversible specific capacity is different.
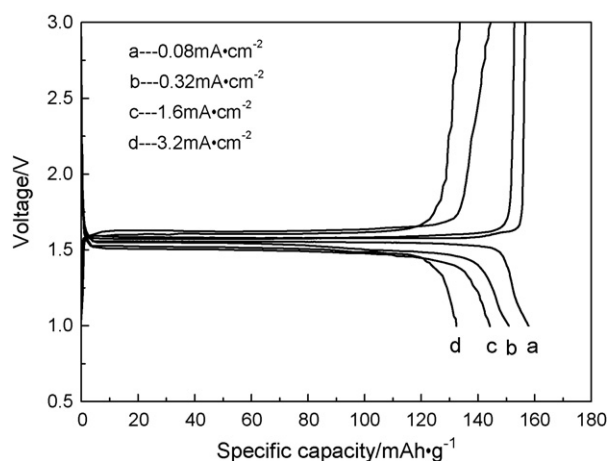

Fig. 7. Initial charge–discharge curves of the $Li_4Ti_5O_{12}$/C composite at different current density.

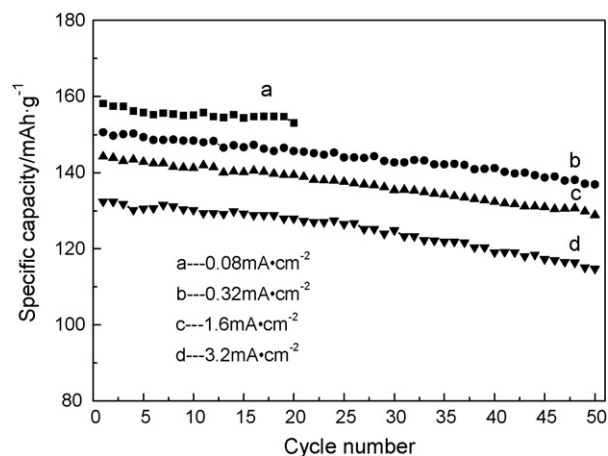Fig. 6. X-ray diffraction patterns of carbon, the precursor and the $Li_4Ti_5O_{12}$/C powders.

Fig. 8. Cycle performance of the spherical $Li_4Ti_5O_{12}$/C composite at different current density.

Table 2
The electrochemical performance of the spherical $Li_4Ti_5O_{12}$/C composite

Charge–discharge current density (mA cm^{-2})	0.08	0.32	1.6	3.2
Initial discharge specific capacity of (mAh g^{-1})	158.2	150.6	144.2	132.4
Discharge specific capacity at 100th cycle (mAh g^{-1})	153.1	136.9	128.8	114.8
Capacity retention after 50 cycles (%)	96.8[a]	90.9	89.3	86.7

[a] Twentieth cycle at 0.08 mA cm^{-2}.

The spherical $Li_4Ti_5O_{12}$/C powders prepared in this work have both high specific capacity and high tap-density. The contradiction between high specific capacity and high tap-density of the materials has been solved satisfactorily. We improve the $Li_4Ti_5O_{12}$ powders' tap-density by controlling the powders' particle morphology, particle size and particle size distribution and improve the $Li_4Ti_5O_{12}$ powders' conductivity by doping carbon in the spherical $Li_4Ti_5O_{12}$ particles. Now, some measures are being taken to further improve the $Li_4Ti_5O_{12}$ material's cycling stability in our lab, such as doping other metal elements to substitute the element of Ti or Li in the $Li_4Ti_5O_{12}$. We will report the results elsewhere.

4. Conclusion

The spherical $Li_4Ti_5O_{12}$/C composite with high specific capacity and excellent cycling performance have been synthesized via a novel technique in this work. At current density of 0.08, 0.32, 1.6 and 3.2 mA cm^{-2}, the composite material has initial discharge specific capacity of 158.2, 150.6, 144.2 and 132.4 mAh g^{-1}, respectively. The material also results the attainment of excellent cycling performance. The tap-density of the spherical $Li_4Ti_5O_{12}$/C composite powders is as high as 1.71 g cm^{-3}, which is remarkably higher than the non-spherical $Li_4Ti_5O_{12}$ powders reported. The high-density of electrode material can result the lithium ion batteries' high power density.

High tap-density and excellent electrochemical performance of the spherical $Li_4Ti_5O_{12}$/C anode material is partly attributed to the advanced preparation. So this preparation technique should be a suitable method to synthesize spherical $Li_4Ti_5O_{12}$/C anode material.

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