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(54) Title: METHOD OF SYNTHESIS OF $\text{LiTi}_2(\text{PS}_4)_3$

(57) Abstract: The present invention relates to a method of synthesis of lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ comprising the steps of: (a) providing a mixture of lithium sulfide Li_2S , phosphorus sulfide P_2S_5 and titanium sulfide TiS_2 ; (b) subjecting the mixture prepared in step (a) to a preliminary reaction step through mechanical milling or melt-quenching to produce an intermediate amorphous sulfide mixture; (c) subjecting the mixture prepared in step (b) to a heat treatment step at a maximum plateau temperature of at least 350°C and less than 500°C.



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Method of synthesis of $\text{LiTi}_2(\text{PS}_4)_3$

Field of the invention

The present invention relates to a method of synthesis of lithium
5 titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$.

Background art

The all-solid-state battery system offers the possibility of high energy
density of the battery pack. In order to realize such systems, a solid electrolyte
10 which exhibits high ionic conductivity is demanded. $\text{LiTi}_2(\text{PS}_4)_3$ is a candidate for
such a solid electrolyte, and has been described in Kim et al., *Chem. Mater.*
2008, 20, 470–474; Kim et al., *Electrochemistry Communications* 10 (2008)
497–501; and Shin et al., *Journal of The Electrochemical Society*, 161 (1) A154-
A159 (2014).

15 According to the method of synthesis described in Kim et al., *Chem.*
Mater. 2008, 20, 470–474, a stoichiometric mixture of Li_2S , TiS_2 and P_2S_5 is
mixed and heated under vacuum according to the following temperature
profile:

20 20 h 150 h air quench
 → → →
 750°C 400°C
 (10 h)

However, the synthesis conditions proposed in the literature were not
optimized with respect to the generation of secondary phases and ionic
conductivity.

25

Summary of the invention

With a view to solving the above-referenced problems in the synthesis of
lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$, the present inventor has studied

different aspects of the preparation of this material, and this work has led to the achievement of the present invention.

In one aspect, the present invention thus relates to a method of synthesis of lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ comprising the steps of:

5 (a) providing a mixture of lithium sulfide Li_2S , phosphorus sulfide P_2S_5 and titanium sulfide TiS_2 ;

(b) subjecting the mixture prepared in step (a) to a preliminary reaction step through mechanical milling or melt-quenching to produce an intermediate amorphous sulfide mixture;

10 (c) subjecting the mixture prepared in step (b) to a heat treatment step at a maximum plateau temperature of at least 350°C and less than 500°C .

Here "maximum plateau temperature" refers to the maximum temperature maintained in a heating vessel as commonly used in solid state chemistry, the temperature vs. time profile typically including a gradual ascent phase with a controlled rate of increase of temperature starting from room temperature, a chosen reaction temperature maintained effectively constant over a period of time (the "maximum plateau temperature"), and then a descent phase wherein the temperature is brought back down to room temperature.

20

Brief description of the drawings

Figure 1a shows a schematic view of a high temperature heat treatment process according to a prior art method, with a temperature incline prior to heat treatment, a maximum plateau temperature maintained at 700°C during heat treatment and then a programmed temperature decrease. Figure 1b shows an illustrative and non-limiting embodiment of a process according to the present invention with a first amorphasizing step, followed by low-temperature heat treatment, with a preferred maximum plateau temperature T maintained during heat treatment at $375^\circ\text{C} \leq T \leq 450^\circ\text{C}$.

Figure 2 shows X-ray diffraction patterns (XRD) of lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ samples obtained according to the process of the present invention (embodiments illustrated in a non-limiting manner by Examples 1 to 3) or according to the conventional synthesis process (Comparative Example 1) or according to other processes not according to the present invention (Comparative Examples 2 to 4).

Figure 3 shows thermogravimetric analysis (TGA) study of high temperature heat treatment of amorphasized $\text{LiTi}_2(\text{PS}_4)_3$ (Comparative Example 4).

Figure 4 shows ionic conductivity values observed for lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ samples obtained according to illustrative and non-limiting embodiments of the present invention (Examples 1 to 3), or according to embodiments not according to the present invention (Comparative Examples 3 and 4).

Detailed description of the invention

Without wishing to be bound by any particular theory, it is believed that the low ionic conductivity of $\text{LiTi}_2(\text{PS}_4)_3$ obtained according to literature methods may be due to the impurity of TiS_2 included in the synthesized material.

Because of the incongruent melting behavior of $\text{LiTi}_2(\text{PS}_4)_3$, it is important to avoid melting of the material during heat treatment. By "incongruent melting", reference is made here to chemical transformation of the material upon melting, with new chemical bonds being formed. Without control of undesired melting and impurity formation, it is very difficult to obtain a single phase of $\text{LiTi}_2(\text{PS}_4)_3$.

To solve the above-mentioned problems, the present invention provides a new synthesis procedure of $\text{LiTi}_2(\text{PS}_4)_3$.

In the present invention, an intermediate step is proposed, before the high-temperature reaction to produce final $\text{LiTi}_2(\text{PS}_4)_3$ product, the intermediate step consisting of subjecting the mixture prepared in step (a), based on

ordinary solid samples of each of the three reaction components (as may be obtained from commercial suppliers) to a preliminary reaction step through mechanical milling or melt-quenching to produce an intermediate amorphous sulfide mixture. This intermediate step may also be referred to hereinafter as an "amorphasizing step", and provides amorphous materials derived from Li_2S - TiS_2 - P_2S_5 . This amorphous material is able to be heat-treated at over 400°C without melting. Without the intermediate step, the specimens are melted due to the low melting point of P_2S_5 ($\sim 270^\circ\text{C}$). Elemental phosphorus and sulfur also have lower melting points and will thus melt before the temperatures needed to produce $\text{LiTi}_2(\text{PS}_4)_3$ product in the solid phase reaction. It is considered that the most important effect of the intermediate step is allowing Li_2S , TiS_2 and P_2S_5 to completely mix and react with each other – the intermediate step may, as well as ensuring intimate physical mixing, begin the chemical transformations which will lead to the final product. The intermediate step may thus act to react the low melting material of P_2S_5 with Li_2S (or at least start this reaction).

In terms of starting material mole ratios, the method is appropriately carried out with as close as possible to a stoichiometric ratio thereof in view of the final product $\text{LiTi}_2(\text{PS}_4)_3$ product to be produced. Thus, the lithium sulfide Li_2S , phosphorus sulfide P_2S_5 and titanium sulfide TiS_2 starting materials are generally used in a $\text{Li}_2\text{S} : \text{P}_2\text{S}_5 : \text{TiS}_2$ mole ratio of 1:3:4.

The amorphous material obtained through the "amorphasizing step" can advantageously be heat-treated at the temperature of $350^\circ\text{C} \leq T < 500^\circ\text{C}$. More generally, in heat treatment step (c), the maximum plateau temperature is appropriately not more than 475°C , and preferably at least 375°C , more preferably at least 400°C and at most 450°C . Further, in heat treatment step (c), the maximum plateau temperature during heat treatment is appropriately maintained for at least 1 hour and at most 300 hours. In terms of the speed of temperature increase going from room temperature up to the maximum plateau temperature, before the heat treatment step, a generally appropriate range is

from $0.1^{\circ}\text{C min}^{-1}$ to $20^{\circ}\text{C min}^{-1}$. A preferred speed is in the range of $1^{\circ}\text{C min}^{-1}$ to $5^{\circ}\text{C min}^{-1}$. Analogous rates of temperature decrease after the heat treatment step, may also be used to bring the sample back down to room temperature.

When $\text{LiTi}_2(\text{PS}_4)_3$ is produced by using the method of the present invention, it can be obtained substantially as a single phase without any impurity of TiS_2 . Values of about three times higher ionic conductivity can be observed as compared to that of $\text{LiTi}_2(\text{PS}_4)_3$ produced by a conventional process.

In the method according to the present invention, each of the method steps (a), (b) and (c) is advantageously carried out under an inert gas, for example, nitrogen or argon, preferably argon.

As mentioned above, in one way of carrying out the present invention, the intermediate step (b), also referred to herein as an "amorphasizing step", the intermediate step giving rise to an intermediate amorphous sulfide mixture, may be carried out by a "melt-quenching" procedure. In an appropriate melt-quenching step, the starting materials are heated to a temperature higher than the melting point of the final product $\text{LiTi}_2(\text{PS}_4)_3$, i.e. to over 700°C . A quick heating procedure may be used to avoid evaporation when attaining the high temperature of over 700°C . However, in most cases, it is preferable for a sample to be in the equilibrium state before quenching. Therefore, it is appropriate to wait for a relatively longer period and heat up more slowly, for example with a heating rate of $0.05^{\circ}\text{C min}^{-1}$ to $20^{\circ}\text{C min}^{-1}$, with a holding time of appropriately 3 hours to 300 hours. To quench the molten mixture, raised to a temperature above 700°C , a rapid cooling rate is used, appropriately between 300 to 1000 K s^{-1} , to bring the mixture to room temperature or below. A generally appropriate method for sulfide amorphous materials is ice quenching. In such a method, a heated quartz tube containing the material to be quenched is placed in ice water.

In preferred embodiments for carrying out the present invention, the intermediate step (b), also referred to herein as an "amorphasizing step", the

intermediate step giving rise to an intermediate amorphous sulfide mixture, is carried out by a mechanical milling procedure, such as planetary ball milling, vibration milling or jet milling. Where the preferred method of planetary ball milling is used, a generally appropriate ball size range is chosen within the
5 range $1 \text{ mm} \leq \phi \leq 10 \text{ mm}$, the temperature range is chosen within the range $0^\circ\text{C} \leq T \leq 60^\circ\text{C}$, the rotation speed is chosen within the range $200 \text{ rpm} \leq R \leq 500 \text{ rpm}$, and the duration is chosen within the range $5 \text{ h} \leq t \leq 200 \text{ h}$.

In a further aspect, the present disclosure relates to an all-solid-state lithium battery comprising the following elements:

- 10 - a positive electrode active material layer;
 - a solid electrolyte layer;
 - a negative electrode active material layer,

wherein the solid electrolyte layer contains a lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ material produced according to the present invention, and is
15 positioned between the positive electrode active material layer and negative electrode active material layer.

In such an all-solid-state lithium battery, using as solid electrolyte, the $\text{LiTi}_2(\text{PS}_4)_3$ sulfide materials produced according to the present invention, concerning the form of the solid electrolyte materials, examples include a
20 particle shape, such as the shape of a true ball and the shape of an elliptical ball, or a thin film form, for example. When solid electrolyte materials have a particle shape, as for the mean particle diameter, it is preferable that their size is within the range of 50 nm to 10 micrometers, more preferably within the range of 100 nm to 5 micrometers.

25 Although it is preferable to have only one or more solid electrolyte materials as mentioned above in a solid electrolyte layer, this layer may also contain a binding agent if needed. As a binding agent used for a solid electrolyte layer, this may be of the same type as mentioned hereunder for the positive active material layer.

As regards the thickness of a solid electrolyte layer, although this may change with the kind of solid electrolyte materials, and the overall composition of an all-solid battery, generally it is preferable that this thickness is within the range of 0.1 micrometer to 1000 micrometers, more preferably within the range of 0.1 micrometer to 300 micrometers.

Concerning the positive active material (cathode active material) to be used in the positive electrode (cathode) active material layer, this is not especially limited if the average operating potential becomes more than 4 V (vs. Li/Li⁺). As an average operating potential of positive active material, this is appropriately more than 4 V (vs. Li/Li⁺), and it is preferable that it is within the limits of 4.0 V to 6.0 V, still more preferably within the limits of 4.5 V to 5.5 V. The average operating potential can be evaluated using cyclic voltammetry, for example. In particular, when cyclic voltammetry is measured at a small electric potential speed like 0.1 mV/sec, it can be considered that the average value of the voltage which gives the peak current on the side of oxidation, and the voltage which gives the peak current on the side of reduction is the average operating potential.

As a positive active material, especially if the average operating potential is made with more than 4 V (vs. Li/Li⁺), there is no specific limitation, but it is preferable that the material is an oxide positive active material, which can have a high energy density.

A compound which has the spinel type structure denoted by general formula LiM_2O_4 (M is at least one kind of transition metal element), as an example of positive active material, can be mentioned as an example. As regards M of the above-mentioned general formula LiM_2O_4 , especially if it is a transition metal element, it will not be limited, but it is preferable that it is at least one kind chosen from the group which consists of Ni, Mn, Cr, Co, V, and Ti, for example, and it is more preferable that it is at least one kind chosen from the group which consists of Ni, Mn, and Cr especially. Specifically,

LiCr_{0.05}Ni_{0.50}Mn_{1.45}O₄, LiCrMnO₄, LiNi_{0.5}Mn_{1.5}O₄, etc. can be mentioned. The compound which has the olivine type structure denoted by general formula LiMPO₄ (M is at least one kind of transition metal element) as other examples of positive active material can be mentioned. M in the above-mentioned general
5 formula will not be limited especially if it is a transition metal element, but it is preferable that it is at least one kind chosen from Mn, Co, Ni, and the group that consists of V, for example, and it is more preferable that it is at least one kind chosen from the group which consists of Mn, Co, and Ni especially. Specifically, LiMnPO₄, LiCoPO₄, LiNiPO₄, etc. can be mentioned. The compound
10 which has the layer structure denoted by general formula LiMO₂ (M is at least 1 type of a transition metal element) as other examples of positive active material can be mentioned. Specifically, LiCoO₂, LiNi_{0.5}Mn_{0.5}O₂ and LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂ etc. can be mentioned. As examples other than the positive active material mentioned above, a Li₂MnO₃-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ solid solution, a Li₂MnO₃-
15 LiNi_{0.5}Mn_{1.5}O₂ solid solution, a Li₂MnO₃-LiFeO₂ solid solution, etc. can be mentioned.

As regards the form of the positive active material, a particle shape, such as the shape of a true ball and the shape of an elliptical ball, thin film form, etc. can be mentioned, as an example. As for the mean particle diameter, when the
20 positive active material has a particle shape, it is preferable that it is within the size range of 0.1 micrometer to 50 micrometers, for example. As for the content of the positive active material in a positive active material layer, it is preferable that it is in the range of 10 % by weight to 99% by weight, for example, more preferably from 20 % by weight to 90% by weight.

25 Concerning the positive active material layer, in addition to the positive active material mentioned above, if needed, the positive active material layer in may contain other materials, for example, solid electrolyte materials etc. As for the content of the solid electrolyte materials in a positive active material layer,

it is preferable that this content is 1 % by weight to 90% by weight, more preferably 10 % by weight to 80% by weight.

Furthermore, a positive active material layer may contain an electrically conductive agent from a viewpoint of improving the conductivity of a positive active material layer, other than the solid electrolyte materials mentioned above. As electrically conductive material, acetylene black, Ketjenblack, a carbon fiber, etc. can be mentioned, for example. A positive active material may also contain a binding agent. As such a binding material (binding agent), fluorine-based binding materials, such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE), etc. can be mentioned, for example.

Although the thickness of a positive active material layer may change according to the kind of all-solid-state battery made, it is generally preferable that it is within the range of 0.1 micrometer to 1000 micrometers.

As regards the negative electrode active material layer, this layer at least contains one or more negative electrode active material(s), and may additionally contain at least one or more of solid electrolyte materials and electrically conductive agents if needed. For all-solid-state lithium batteries, the negative electrode active material is not limited provided that occlusion and discharge of the Li ion, which is a conduction ion, are possible. As a negative electrode active material, a carbon active material, a metal active material, etc. can be mentioned, for example. As a carbon active material, black lead, meso carbon micro beads (MCMB), highly ordered / oriented pyrolytic graphite (HOPG), hard carbon, soft carbon, etc. can be mentioned as examples. On the other hand, as a metal active material, charges of an alloy, such as Li alloy and Sn-Co-C, In, Al, Si, Sn, etc. can be mentioned as examples. Oxide stock materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, can be mentioned as examples of other negative electrode active materials.

Concerning solid electrolyte materials used for the negative electrode active material layer, and an electrically conductive agent, these may be the

same as that for the solid electrolyte layer and positive active material layer mentioned above.

The thickness of the negative electrode active material layer will generally be appropriately within the range of 0.1 micrometer to 1000 micrometers.

An all-solid-state battery of the present disclosure has at least the positive active material layer, solid electrolyte layer, and negative electrode active material layer which were mentioned above. It further usually has a positive pole collector which collects a positive active material layer, and a negative pole collector which performs current collection of a negative electrode active material layer. As a material of a positive pole collector, for example, SUS (stainless steel), aluminum, nickel, iron, titanium, carbon, etc. can be mentioned, and SUS is especially preferable. On the other hand as a material of a negative pole collector, SUS, copper, nickel, carbon, etc. can be mentioned, for example, and SUS is especially preferable. Concerning the thickness, form, etc. of a positive pole collector and a negative pole collector, the person skilled in the art may choose suitably according to the use of the all-solid-state battery, etc. The cell case used for a common all-solid-state battery can be used, for example, the cell case made from SUS, etc. can be mentioned. The all-solid-state battery may form a power generation element in the inside of an insulating ring.

The all-solid-state battery of the present disclosure can be considered as a chargeable and dischargeable all-solid-state battery in a room temperature environment. Although it may be a primary battery and may be a rechargeable battery, it is especially preferable that it is a rechargeable battery. Concerning the form of the all-solid-state battery, a coin type, a laminated type, cylindrical, a square shape, etc. can be mentioned, as examples.

As regards the manufacturing method of the all-solid-state battery, this is not particularly limited, and common manufacturing methods of all-solid-state

batteries can be used. For example, when an all-solid-state battery is in the thin film form, a positive active material layer can be formed on a substrate, and the method of forming a solid electrolyte layer and a negative electrode active material layer in order, and laminating them thereafter etc., may be used.

5

Within the practice of the present invention, it may be envisaged to combine any features or embodiments which have hereinabove been separately set out and indicated to be advantageous, preferable, appropriate or otherwise generally applicable in the practice of the invention. The present description
10 should be considered to include all such combinations of features or embodiments described herein unless such combinations are said herein to be mutually exclusive or are clearly understood in context to be mutually exclusive.

15 **Experimental section – Examples**

The following experimental section illustrates experimentally the practice of the present invention, but the scope of the invention is not to be considered to be limited to the specific examples that follow.

20

Example 1

Synthesis of solid electrolytes

Mixture step

The solid electrolyte $\text{LiTi}_2(\text{PS}_4)_3$ was synthesized using starting materials Li_2S (Sigma), TiS_2 (Sigma), and P_2S_5 (Aldrich). They were mixed at the weight
25 ratio listed in Table 1 below:

Table 1: Weight ratio of starting materials for $\text{LiTi}_2(\text{PS}_4)_3$ synthesis

	Weight of starting material (g)	mmol of starting material
Li_2S	0.039584	0.8615
P_2S_5	0.57447	2.5845
TiS_2	0.385946	3.4460

5

Amorphasizing step

The mixed sample was put into a zirconium pot (45 mL) with 18 zirconium balls (ϕ 10mm) under argon. The pot was closed and treated with planetary milling equipment (Fritsch, P7) at 370 rpm for 40 h to obtain the precursor.

10

Heat treatment step

The precursor was sealed into a glass tube at a pressure of 30 Pa and then heated at $T=375\text{ }^\circ\text{C}$ for 8 h. A temperature incline of $2.2\text{ }^\circ\text{C min}^{-1}$ was used to bring the sample up to this heat treatment temperature.

15

At the heat treatment temperature of $375\text{ }^\circ\text{C}$, the sample was not melted.

The procedure is shown in Figure 1 as well as the literature process.

20

Measurement of Li ion conductance

Li ion conductance at a temperature of $25\text{ }^\circ\text{C}$ was measured using the sulfide solid electrolyte material obtained. First, 100 mg of the sulfide solid electrolyte material was added to a cylinder made of alumina and pressed at 4 ton/cm^2 to form a solid electrolyte layer. The pellet was sandwiched by SUS current collector for measuring impedance spectroscopy.

25

An impedance gain-phase analyzer manufactured by Biologic (VMP3) was used for the measurement as FRA (Frequency Response Analyzer). The

measurement was started from a high-frequency range with the conditions of an alternating voltage of 5 mV and a frequency range of 1 Hz to 1 MHz.

The ionic conductivity of the material prepared in Example 1 was 2.1×10^{-5} S/cm.

5

X-Ray Diffraction Measurement

X-ray diffraction measurement (using a $\text{CuK}\alpha$ line) was performed by using the sulfide solid electrolyte materials obtained in Examples and in Comparative Examples. The results are shown in Figure 2.

10 For samples prepared according to the Examples, essentially only the peaks of $\text{LiTi}_2(\text{PS}_4)_3$ were detected.

Example 2

15 Only the heat treatment temperature was different from Example 1 - here the heat treatment temperature was 400 °C and the sample was not melted. The ionic conductivity of the material produced by Example 2 was 2.5×10^{-5} S/cm. Essentially only the peaks of $\text{LiTi}_2(\text{PS}_4)_3$ were detected by XRD.

Example 3

20 Only the heat treatment temperature was different from Example 1 - here the heat treatment temperature was 450 °C and the sample was not melted. The ionic conductivity of the material produced by Example 3 was 2.0×10^{-5} S/cm. Essentially only the peaks of $\text{LiTi}_2(\text{PS}_4)_3$ were detected by XRD.

Comparative Example 1 (= synthesized via literature process)

25 Unlike Example 1, no amorphasizing step was performed. The heat treatment temperature was 750 °C and the sample was melted. The ionic conductivity of this sample was 0.9×10^{-5} S/cm. Peaks of TiS_2 were detected by XRD in addition to those attributed to $\text{LiTi}_2(\text{PS}_4)_3$.

Comparative Example 2

As a difference from Example 1, no amorphasizing step was performed. The heat treatment temperature was 750 °C and the sample was melted. The ionic conductivity of this sample was 0.6×10^{-5} S/cm. Peaks of unknown phase were detected by XRD.

Comparative Example 3

As a difference from Example 1, the amorphasizing step was performed but a heat treatment temperature of 300 °C was used, and the sample was not melted. The ionic conductivity of this sample was 0.2×10^{-5} S/cm. A halo pattern was detected by XRD, indicating an amorphous product.

Comparative Example 4.

As a difference from Example 1, the amorphasizing step was performed but a heat treatment temperature of 500 °C was used, and the sample was not melted. The ionic conductivity of this sample was 1.2×10^{-5} S/cm. Peaks of TiS_2 were detected in addition to $\text{LiTi}_2(\text{PS}_4)_3$ by XRD.

From the TGA measurement, weight loss was observed at around 400 °C (Figure 3). This indicates evaporation of the material. Such an evaporation may lead to the decomposition of $\text{LiTi}_2(\text{PS}_4)_3$ and the generation of TiS_2 at 500 °C. Here, it is considered that this is not unreacted titanium disulfide but instead (re)generated TiS_2 , issuing from $\text{LiTi}_2(\text{PS}_4)_3$ already produced. It is observed that once the TiS_2 is (re)generated during heat treatment, it is very difficult to remove it by heat treatment (a very long time is needed)

Importance of the amorphasizing step

From the results Comparative Example 1 and Comparative Example 2 without an amorphasizing step, it is very difficult to avoid the melting of the material due to the low melting point of P_2S_5 ($\sim 270^\circ\text{C}$). $\text{LiTi}_2(\text{PS}_4)_3$ was obtained at a high temperature heat treatment condition of $T=750^\circ\text{C}$. However, the material obtained included TiS_2 as impurity. Possibly as a result of this, its ionic conductivity was low. Even though the low temperature of $T=400^\circ\text{C}$ (same as Example 1) was applied, the material was melted, resulting in an unknown phase and low ionic conductivity. The amorphasizing step allows one to apply a temperature of over 400°C without melting. Therefore it is possible to synthesize a single phase of $\text{LiTi}_2(\text{PS}_4)_3$ exhibiting high ionic conductivity.

Temperature optimization

From the results of Example 1&2 and Comparative Examples 3&4, the heat treatment temperature T range of $375^\circ\text{C} \leq T < 500^\circ\text{C}$ is preferable to obtain the single phase of $\text{LiTi}_2(\text{PS}_4)_3$ and high ionic conductivity (Figure 4). A temperature of 300°C or lower gives rise to amorphous product and a temperature of 500°C or higher appears to be correlated with the continued presence of TiS_2 and evaporation.

Claims

1. Method of synthesis of lithium titanium thiophosphate $\text{LiTi}_2(\text{PS}_4)_3$ comprising the steps of:

5 (a) providing a mixture of lithium sulfide Li_2S , phosphorus sulfide P_2S_5 and titanium sulfide TiS_2 ;

(b) subjecting the mixture prepared in step (a) to a preliminary reaction step through mechanical milling or melt-quenching to produce an intermediate amorphous sulfide mixture;

10 (c) subjecting the mixture prepared in step (b) to a heat treatment step at a maximum plateau temperature of at least 350°C and less than 500°C .

2. Method of synthesis according to claim 1, wherein the mechanical milling procedure used in step (b) to produce an intermediate amorphous sulfide
15 mixture is planetary ball milling, vibration milling or jet milling.

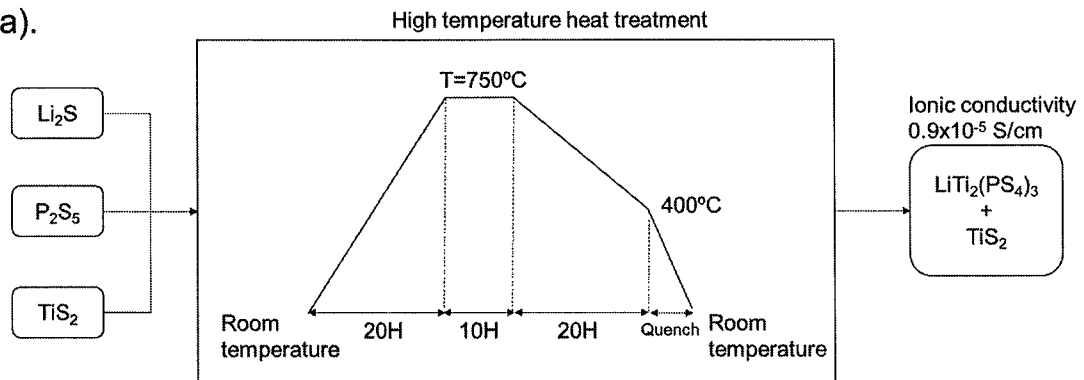
3. Method of synthesis according to claim 2, wherein planetary ball milling is used, and the ball size range is chosen within the range $1\text{ mm} \leq \phi \leq 10\text{ mm}$), the temperature range is chosen within the range $0^\circ\text{C} \leq T \leq 60^\circ\text{C}$, the
20 rotation speed is chosen within the range $200\text{ rpm} \leq R \leq 500\text{ rpm}$, and the duration is chosen within the range $5\text{ h} \leq t \leq 200\text{ h}$.

4. Method according to any of claims 1 to 3, wherein in heat treatment step (c), the maximum plateau temperature is not more than 475°C , and preferably
25 at least 375°C and at most 450°C .

5. Method according to any of claims 1 to 4, wherein in heat treatment step (c), the maximum plateau temperature during heat treatment is maintained for at least 1 hour and at most 300 hours.

6. Method according to any of claims 1 to 5, wherein the lithium sulfide Li_2S , phosphorus sulfide P_2S_5 and titanium sulfide TiS_2 starting materials are used in an $\text{Li}_2\text{S} : \text{P}_2\text{S}_5 : \text{TiS}_2$ mole ratio of 1:3:4.

(a).



(b).

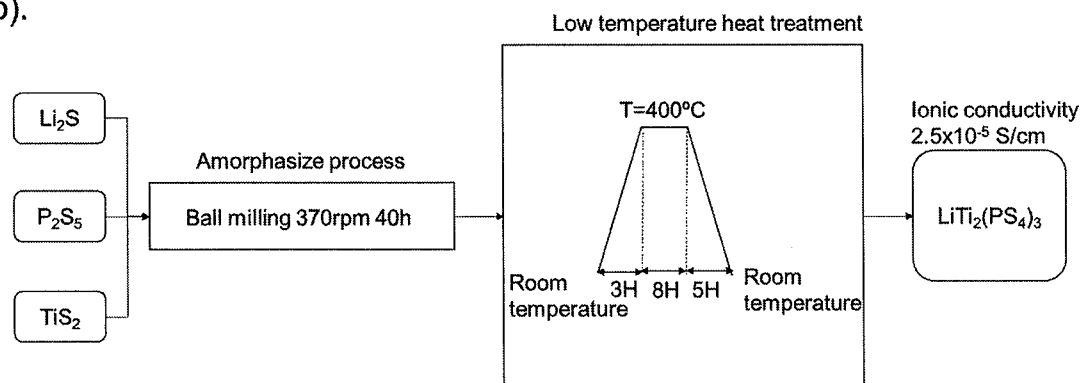


Figure 1

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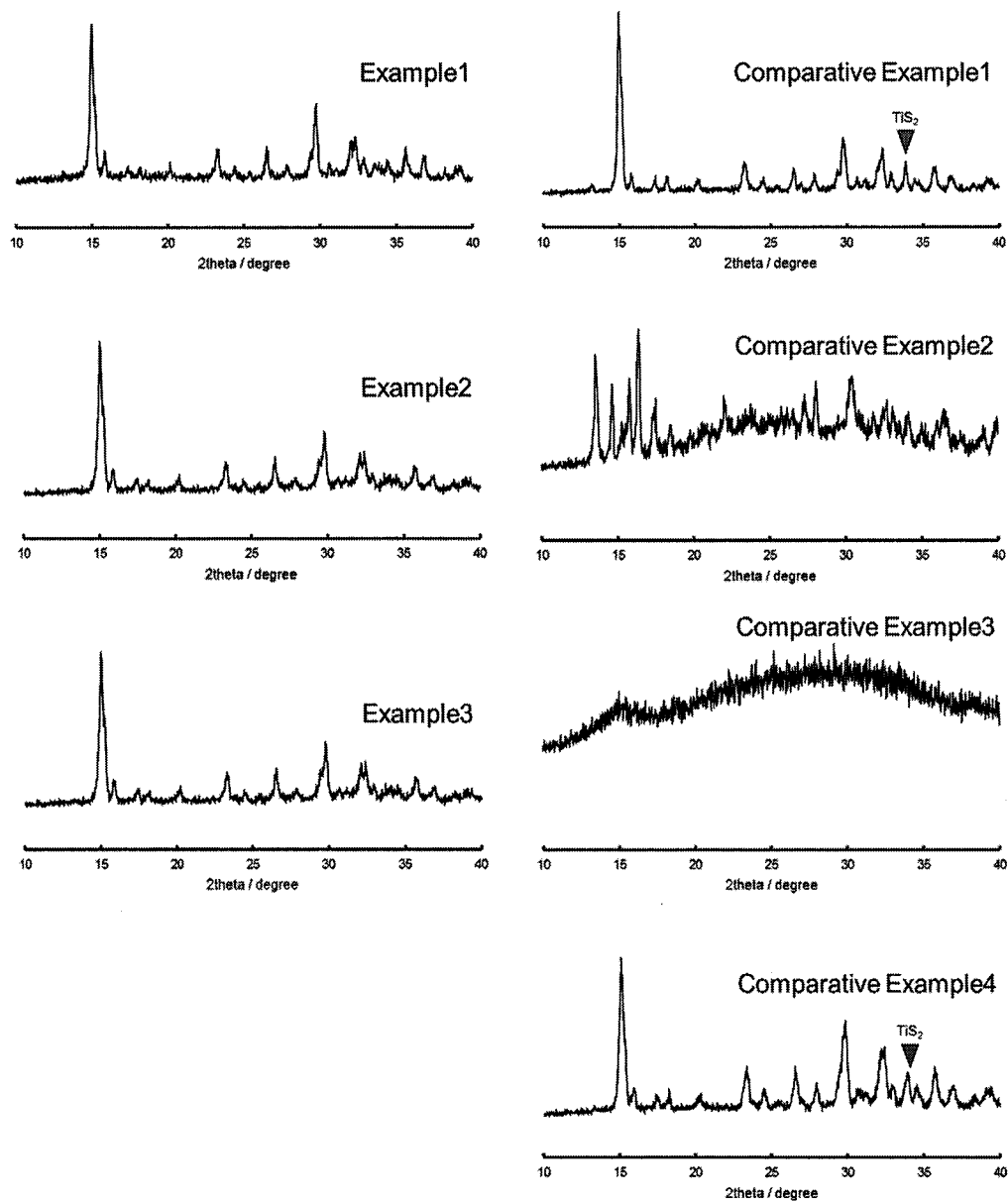


Figure 2

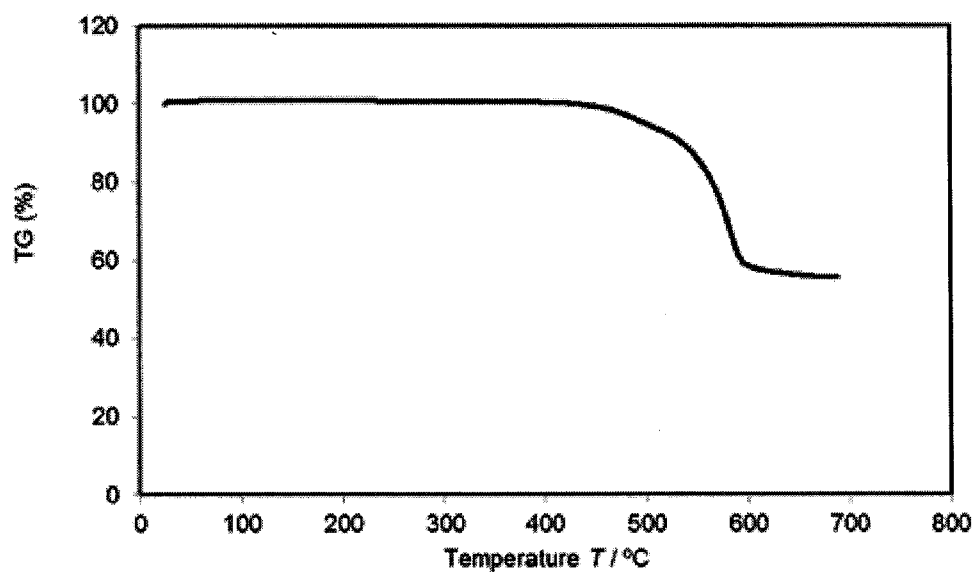


Figure 3

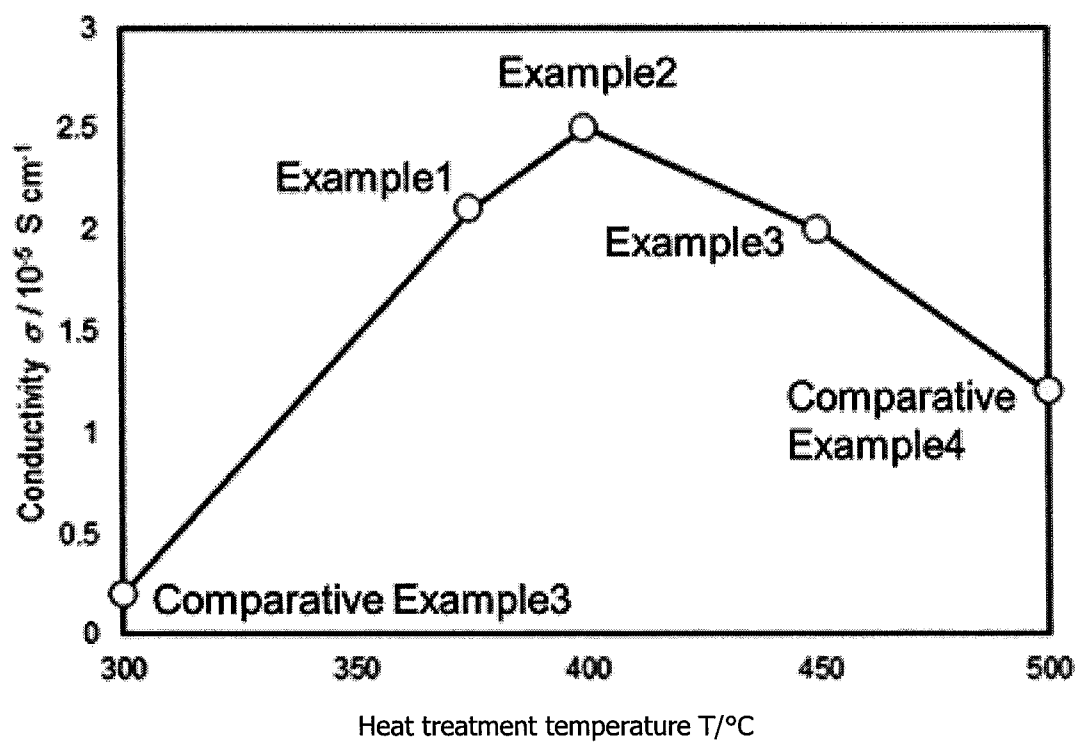


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/070867

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B25/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YOUNGSIK KIM ET AL: "3D framework structure of a new lithium thiophosphate, LiTi₂(PS₄)₃, as lithium insertion hosts", CHEMISTRY OF MATERIALS AMERICAN CHEMICAL SOCIETY USA, vol. 20, no. 2, 22 January 2008 (2008-01-22), pages 470-474, XP002763349, ISSN: 0897-4756 cited in the application abstract page 471, Figure 1 and paragraph "Synthesis" ----- -/-	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 October 2016

Date of mailing of the international search report

18/11/2016

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Authorized officer

Rigondaud, Bernard

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/070867

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 555 307 A1 (TOKYO INST TECH [JP]; TOYOTA MOTOR CO LTD [JP]) 6 February 2013 (2013-02-06) claims 12-17 paragraphs [0001], [0022] - [0030] figure 5 -----	1-6
A	DE 10 2011 121681 A1 (FRAUNHOFER GES FORSCHUNG [DE]) 13 June 2013 (2013-06-13) claims 1, 6 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/070867

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		CN 102823049 A	12-12-2012
		EP 2555307 A1	06-02-2013
		EP 2988361 A1	24-02-2016
		JP 5527673 B2	18-06-2014
		KR 20120136372 A	18-12-2012
		US 2013040208 A1	14-02-2013
		WO 2011118801 A1	29-09-2011

DE 102011121681 A1	13-06-2013	NONE	
