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(54) **SULFIDE-BASED SOLID ELECTROLYTE AND METHOD FOR THE PREPARATION THEREOF**  
SULFIDBASIERTER FESTELEKTROLYT UND VERFAHREN ZUR HERSTELLUNG DESSELBEN  
ÉLECTROLYTE SOLIDE À BASE DE SULFURE ET SON PROCÉDÉ DE PRÉPARATION

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(73) Proprietor: **Hyundai Motor Company**  
**Seoul 06797 (KR)**

(72) Inventors:  
• **SUNG, Ju Young**  
**18280 Hwaseong-si, Gyeonggi-do (KR)**

• **LEE, Ho Taek**  
**18280 Hwaseong-si, Gyeonggi-do (KR)**  
• **LIM, Jae Min**  
**18280 Hwaseong-si, Gyeonggi-do (KR)**  
• **JANG, Yong Jun**  
**18280 Hwaseong-si, Gyeonggi-do (KR)**

(74) Representative: **Viering, Jentschura & Partner mbB**  
**Patent- und Rechtsanwälte**  
**Am Brauhaus 8**  
**01099 Dresden (DE)**

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**Description****TECHNICAL FIELD**

5 [0001] The present disclosure relates to a sulfide-based solid electrolyte and a preparation method thereof.

**BACKGROUND**

10 [0002] Today, secondary batteries have been widely used from large devices such as a vehicle and a power storage system to small devices such as a mobile phone, a camcorder, and a laptop.

[0003] As the secondary battery is widely used and applied, the demand for improved safety and high performance of the battery has been increased.

[0004] A lithium secondary battery which is one of the secondary batteries has an advantage that energy density is higher and a capacity per unit area is larger than a nickel-manganese battery or a nickel-cadmium battery.

15 [0005] However, most of the electrolytes used in the lithium secondary batteries in the related art are liquid electrolytes such as organic solvents. Accordingly, safety problems such as leakage of electrolytes and the risk of fire resulting therefrom have been constantly raised.

[0006] As a result, recently, to increase safety, an interest in all-solid-state batteries using solid electrolytes rather than liquid electrolytes as the electrolytes has been increased.

20 [0007] The solid electrolyte has higher safety than the liquid electrolyte due to a non-combustible or flame-retardant property.

[0008] The solid electrolytes are divided into an oxide-based electrolyte and a sulfide-based electrolyte. The sulfide-based solid electrolyte has high lithium-ionic conductivity compared to the oxide-based solid electrolyte and is stable in a wide voltage range and thus the sulfide-based solid electrolyte is frequently used.

25 [0009] In Mizuno et al., high lithium ion conducting glass-ceramics in the system  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ , Solid State Ionics, 177(2006), 2721-2725 (hereinafter, referred to as 'non-patent document'), there is provided an amorphous solid electrolyte such as  $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$  and  $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$  among the sulfide-based solid electrolytes. According to the non-patent document, the amorphous solid electrolyte has ion conductivity at  $1 \times 10^{-3}$  S/cm at the time of heat-treating (crystallizing) at a relatively low temperature of 200°C to 300°C, whereas the amorphous solid electrolyte has ion conductivity at  $1 \times 10^{-6}$  S/cm at the temperature or higher.

30 [0010] In Korean Patent Application Publication No. 10-2015-0132265 (hereinafter, referred to as 'patent document'), there is provided a crystalline solid electrolyte such as  $\text{Li}_6\text{PS}_5\text{Cl}$  among sulfide-based solid electrolytes. According to the patent document, the crystalline solid electrolyte has ion conductivity at  $1 \times 10^{-3}$  S/cm at the time of heat-treating (crystallizing) at a temperature of about 500°C, whereas the crystalline solid electrolyte has ion conductivity at  $1 \times 10^{-4}$  S/cm at the temperature or less.

35 [0011] As described in non-patent documents and the patent document, there is a limitation that the sulfide-based solid electrolyte in the related art has high ion conductivity only in a predetermined temperature range of either a low temperature (about 250°C) or a high temperature (about 500°C). From e.g. JP 2001 006674 A a solid electrolyte is known, comprising: diphosphorus pentasulfide, nickel sulfide and lithium halide. From e.g. US 2014/193693 A1 a lithium-ion conductive sulfide is known. From e.g. DE 112014 002991 T5 a solid electrolyte sulfide material is known. From e.g. EP 2 779 298 A1 a solid electrolyte is known.

40 [0012] The above information disclosed in this Background section is only for enhancement of understanding of the background of the invention and therefore it may contain information that does not form the prior art that is already known in this country to a person of ordinary skill in the art.

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**SUMMARY**

[0013] The present invention provides a sulfide-based solid electrolyte according to claim 1 and a method of preparing a sulfide-based solid electrolyte according to claim 7. Further embodiments of the electrolyte and the method are described in the respective dependent claims. Embodiments of the present disclosure relates to a sulfide-based solid electrolyte having high ion conductivity in a wide crystallization temperature range, as a sulfide-based solid electrolyte containing a nickel (Ni) element and a halogen element.

[0014] Embodiments of the present invention can overcome the limitation of a sulfide-based solid electrolyte in the related art and provide a sulfide-based solid electrolyte having high ion conductivity in a wide crystallization temperature range and a preparing method thereof.

55 [0015] The present invention may include a number configurations in order to achieve advantages, for example, solving above-described problems associated with the prior art.

[0016] In one aspect, the present invention provides a sulfide-based solid electrolyte including 5 parts by mole to 20

parts by mole of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and 5 parts by mole to 40 parts by mole of lithium halide with respect to 100 parts by mole of a mixture of lithium sulfide ( $\text{Li}_2\text{S}$ ) and diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ), wherein the sulfide-based solid electrolyte has a cubic crystal structure.

[0017] In a preferred embodiment, the mixture may include 60 mole% to 90 mole% of lithium sulfide and 10 mole% to 40 mole% of diphosphorus pentasulfide.

[0018] In another preferred embodiment, the lithium halide may be expressed by  $\text{LiX}$  (X is Cl, Br or I).

[0019] In still another preferred embodiment, the crystallization temperature may be 200°C to 400°C and the sulfide-based solid electrolyte may have a cubic crystal structure.

[0020] In yet another preferred embodiment, the crystallization temperature may be 400°C to 600°C and the sulfide-based solid electrolyte may have a cubic crystal structure.

[0021] In still yet another preferred embodiment, the cubic crystal structure may have diffraction peaks in an area of diffraction angles  $2\theta$  of  $15.5\pm 0.5^\circ$ ,  $18\pm 0.5^\circ$ ,  $25.5\pm 0.5^\circ$ ,  $30\pm 0.5^\circ$ ,  $31.5\pm 0.5^\circ$ ,  $40\pm 0.5^\circ$ ,  $45.5\pm 0.5^\circ$ ,  $48\pm 0.5^\circ$ ,  $53\pm 0.5^\circ$ ,  $55\pm 0.5^\circ$ ,  $56.5\pm 0.5^\circ$  and  $59.5\pm 0.5^\circ$  in an X-ray diffraction spectrum.

[0022] In another aspect, the present invention provides a method of preparing a sulfide-based solid electrolyte including: (1) preparing a starting material by adding 5 parts by mole to 20 parts by mole of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and 5 parts by mole to 40 parts by mole of lithium halide with respect to 100 parts by mole of a mixture of lithium sulfide ( $\text{Li}_2\text{S}$ ) and diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ); (2) milling and amorphizing the starting material; and (3) heat-treating and crystallizing the amorphized starting material to obtain a crystallized sulfide-based solid electrolyte having a cubic crystal structure.

[0023] In a preferred embodiment, the mixture may include 60 mole% to 90 mole% of lithium sulfide and 10 mole% to 40 mole% of diphosphorus pentasulfide.

[0024] In another preferred embodiment, the lithium halide may be expressed by  $\text{LiX}$  (X is Cl, Br or I)

[0025] In still another preferred embodiment, step (3) may be a step of heat-treating the amorphized starting material at 200°C to 400°C and crystallizing the heat-treated starting material to have a cubic crystal structure.

[0026] In yet another preferred embodiment, step (3) may be a step of heat-treating the amorphized starting material at 400°C to 600°C and crystallizing the heat-treated starting material to have a cubic crystal structure.

[0027] In still yet another preferred embodiment, the cubic crystal structure may have diffraction peaks in an area of diffraction angles  $2\theta$  of  $15.5\pm 0.5^\circ$ ,  $18\pm 0.5^\circ$ ,  $25.5\pm 0.5^\circ$ ,  $30\pm 0.5^\circ$ ,  $31.5\pm 0.5^\circ$ ,  $40\pm 0.5^\circ$ ,  $45.5\pm 0.5^\circ$ ,  $48\pm 0.5^\circ$ ,  $53\pm 0.5^\circ$ ,  $55\pm 0.5^\circ$ ,  $56.5\pm 0.5^\circ$  and  $59.5\pm 0.5^\circ$  in an X-ray diffraction spectrum.

[0028] The present invention includes the above configurations and thus can have the following effects.

[0029] According to embodiments of the present invention, the sulfide-based solid electrolyte can have high ion conductivity due to a crystal structure of a high ionic conductive phase in a wide temperature range even though a battery is driven in any environment.

[0030] Since the range of the crystallization temperature is wide, the sulfide-based solid electrolyte may be used suitably for changes in a manufacturing process and thus commercialization of the sulfide-based solid electrolyte can be accelerated.

[0031] The effects of the present invention are not limited to the aforementioned effects. It should be understood that the effects of the present invention include all effects inferable from the description below.

[0032] Other aspects and preferred embodiments of the invention are discussed infra.

[0033] It is understood that the term "vehicle" or "vehicular" or other similar term as used herein is inclusive of motor vehicles in general such as passenger automobiles including sports utility vehicles (SUV), buses, trucks, various commercial vehicles, watercraft including a variety of boats and ships, aircraft, and the like, and includes hybrid vehicles, electric vehicles, plug-in hybrid electric vehicles, hydrogen-powered vehicles and other alternative fuel vehicles (e.g. fuels derived from resources other than petroleum). As referred to herein, a hybrid vehicle is a vehicle that has two or more sources of power, for example both gasoline-powered and electric-powered vehicles.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0034] The above and other features of the present invention will now be described in detail with reference to certain exemplary embodiments thereof illustrated in the accompanying drawings which are given hereinbelow by way of illustration only, and thus are not limitative of the present invention, and wherein:

FIG. 1 is a result of measuring impedance values for sulfide-based solid electrolytes in Examples 1 to 4 of the present invention;

FIG. 2 is a result of measuring impedance values for sulfide-based solid electrolytes in Examples 5 to 8 of the present invention;

FIG. 3 is an X-ray diffraction spectroscopy (XRD) result for the sulfide-based solid electrolyte in Example 4 of the present invention;

FIG. 4 is an XRD result for the sulfide-based solid electrolyte in Example 8 of the present invention;

FIG. 5 is a result of measuring discharge capacities of all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 1 to 4 of the present invention; and

FIG. 6 is a result of measuring discharge capacities of all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 5 to 8 of the present invention.

**[0035]** It should be understood that the appended drawings are not necessarily to scale, presenting a somewhat simplified representation of various preferred features illustrative of the basic principles of the invention. The specific design features of the present invention as disclosed herein, including, for example, specific dimensions, orientations, locations, and shapes will be determined in part by the particular intended application and use environment.

**[0036]** In the figures, reference numbers refer to the same or equivalent parts of the present invention throughout the several figures of the drawing.

### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

**[0037]** Hereinafter reference will now be made in detail to various embodiments of the present invention, examples of which are illustrated in the accompanying drawings and described below. While the invention will be described in conjunction with exemplary embodiments, it will be understood that present description is not intended to limit the invention to those exemplary embodiments. On the contrary, the invention is intended to cover not only the exemplary embodiments, but also various alternatives, modifications, equivalents and other embodiments, which may be included within the scope of the invention as defined by the appended claims.

**[0038]** Hereinafter, the present invention will be described in detail through exemplary embodiments. The exemplary embodiments of the present invention may be modified in various forms as long as the gist of the invention is not changed. However, the scope of the present invention is not limited to the following exemplary embodiments.

**[0039]** When it is determined that the description for the known configurations and functions may obscure the gist of the present invention, the description for the known configurations and functions will be omitted. In this specification, the term "comprise" means that other constituent elements may be further included unless noted otherwise.

**[0040]** The present invention is a sulfide-based solid electrolyte including lithium sulfide ( $\text{Li}_2\text{S}$ ), diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ), nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and lithium halide ( $\text{LiX}$ ) and characterized by forming a cubic crystal structure having high ion conductivity in a wide temperature range compared to a sulfide-based solid electrolyte in the related art at the time of heat-treating for crystallization.

**[0041]** A method of preparing a sulfide-based solid electrolyte according to the present invention includes (1) a step of preparing a starting material by adding 5 parts by mole to 20 parts by mole of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and 5 parts by mole to 40 parts by mole of lithium halide with respect to 100 parts by mole of a mixture of lithium sulfide ( $\text{Li}_2\text{S}$ ) and diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ); (2) a step of milling and amorphizing the starting material; and (3) a step of heat-treating and crystallizing the amorphized starting material.

**[0042]** The lithium sulfide, diphosphorus pentasulfide, nickel sulfide and lithium halide are not particularly limited and may be industrially available or synthesized by a conventional method, and may use materials having high purity.

**[0043]** The mixture may include lithium sulfide of 60 mole% to 90 mole%, particularly 70 mole% to 80 mole%, and more particularly 75 mole% to 80 mole%, and diphosphorus pentasulfide of 10 mole% to 40 mole%, particularly 20 mole% to 30 mole%, and more particularly 20 mole% to 25 mole%.

**[0044]** According to the present invention, the sulfide-based solid electrolyte containing a nickel (Ni) element may be prepared by adding nickel sulfide to the mixture of lithium sulfide and diphosphorus pentasulfide in (1) the preparing of a starting material.

**[0045]** The sulfide-based solid electrolyte containing the nickel (Ni) element has high ion conductivity due to a crystal structure formed with nickel (Ni). The sulfide-based solid electrolyte has a specific crystal structure according to binding of respective elements and it is estimated that the lithium ions move by a hopping method through a gap in the crystal structure. Accordingly, as van der Waals radius of the element forming the gap in the crystal structure is decreased, it is advantageous in movement of lithium ions. The van der Waals radii of the elements mainly included in the sulfide-based solid electrolyte in the related art are as follows.

**[0046]** - Phosphorus (180 pm), sulfur (180 pm), tin (217 pm), silicon (210 pm), arsenic (185 pm)

**[0047]** Meanwhile, since the van der Waals radius of nickel is 163 pm and very small compared to the above elements, when nickel is included in the crystal structure, the lithium ions may smoothly pass through the gap.

**[0048]** The sulfide-based solid electrolyte containing the nickel (Ni) element has excellent stability. This may be described according to a principle of hard and soft acids and bases (HSAB). Since sulfur (S) is a weak base and phosphorus (P) is a strong acid, sulfur (S) and phosphorus (P) are not stably bound to each other. As a result, when nickel (Ni) which is an intermediate acid with weaker acidity than phosphorus (P) is included in a crystal phase, nickel (Ni) has better reactivity than phosphorus (P) as a weak base and high stability during binding.

**[0049]** The nickel sulfide may be added with 5 parts by mole to 20 parts by mole, preferably 5 parts by mole to 15 parts by mole, and more preferably 5 parts by mole to 10 parts by mole with respect to 100 parts by mole of the mixture of lithium sulfide and diphosphorus pentasulfide. When the content of nickel sulfide is 5 parts by mole or more, ion conductivity and stability of the sulfide-based solid electrolyte may be improved as described above. Further, when the content of nickel sulfide is 20 parts by mole or less, nickel sulfide may be evenly distributed in the mixture and finally, the crystal structure of the sulfide-based solid electrolyte may be evenly formed.

**[0050]** According to the present invention, the sulfide-based solid electrolyte containing a nickel (Ni) element and a halogen element may be prepared by adding nickel sulfide and lithium halide to the mixture of lithium sulfide and diphosphorus pentasulfide in (1) the preparing of a starting material.

**[0051]** The lithium halide may be expressed by LiX (X is Cl, Br or I).

**[0052]** The lithium halide may be added with 5 parts by mole to 40 parts by mole with respect to 100 parts by mole of the mixture of lithium sulfide and diphosphorus pentasulfide. When the content of lithium halide is 5 parts by mole or more, a cubic crystal structure of a high ion conductive phase may be formed. However, when the content of lithium halide is more than 40 parts by mole, an orthorhombic crystal structure in which ion conductivity of the sulfide-based solid electrolyte is reduced at the time of hot heat treatment may be formed.

**[0053]** As such, a precursor (starting material) of the sulfide-based solid electrolyte is formed by adding the specific content of nickel sulfide and lithium halide to the mixture of lithium sulfide and diphosphorus pentasulfide to form a cubic crystal structure having high ion conductivity in a wide temperature range of 200°C to 600°C compared with the sulfide-based solid electrolyte in the related art at the time of heat treatment for crystallization of the starting material.

**[0054]** Step (2) is a step of milling and amorphizing the starting material.

**[0055]** The amorphizing may be performed by a method of wet milling of adding a solvent to the starting material and then milling the solvent or dry milling of milling the starting material without adding the solvent.

**[0056]** When the amorphizing is performed by wet milling, before step (3) to be described below, drying for removing the solvent may be further performed.

**[0057]** Step (3) is a step of heat-treating and crystallizing the amorphized starting material to have a specific crystal structure.

**[0058]** It is described earlier that the sulfide-based solid electrolyte in the related art is formed as a high ion conductive phase only in a specific temperature range of a low temperature of about 250°C or a high temperature of about 500°C.

**[0059]** The sulfide-based solid electrolyte according to the present invention has a wide crystallization temperature to have a cubic crystal structure as a high ion conductive phase in the entire numerical range, at the time of heat treatment at 200°C to 600°C.

**[0060]** Hereinafter, the present invention will be described in more detail through detailed Examples. However, these Examples are to exemplify the present invention and the scope of the present invention is not limited thereto.

## EXAMPLES

**[0061]** The following examples illustrate the invention and are not intended to limit the same.

### Comparative Example 1

**[0062]** After 80Li<sub>2</sub>S-20P<sub>2</sub>S<sub>5</sub> as a sulfide-based solid electrolyte disclosed in Mizuno et al., high lithium ion conducting glass-ceramics in the system Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub>, Solid State Ionics, 177(2006), 2721-2725 was prepared by varying a crystallization temperature, ion conductivity was measured. The preparing method was as follows.

**[0063]** Li<sub>2</sub>S : P<sub>2</sub>S<sub>5</sub> was measured to be in a composition ratio of 80 mol : 20 mol so as to prepare a mixture of 20 g. Xylene as a solvent was added to the mixture and then the mixture was milled by a planetary mill and amorphized. After the amorphizing is completed, the solvent was removed by vacuum drying and the mixture was crystallized by heat-treating under a condition of Table 1 below.

**[0064]** Each sulfide-based solid electrolyte was compressively molded by varying a heat-treatment temperature to form a molding body (a diameter of 13 mm) for measurement. An AC potential of 10mV was applied to the molding body and then ion conductivity was measured by performing a frequency sweeping of 1×10<sup>6</sup> to 100 Hz. The result is illustrated in Table 1.

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[Table 1]

Classification	Heat-treatment (crystallization) condition	Ion conductivity [S/cm]
80Li <sub>2</sub> S-20P <sub>2</sub> S <sub>5</sub>	230°C, 2 hrs	1.3×10 <sup>-3</sup>
	500°C, 4 hrs	2.3×10 <sup>-6</sup>

[0065] Referring to Table 1, in the case of a sulfide-based solid electrolyte in Comparative Example 1, it can be seen that high ion conductivity of 10<sup>-3</sup> S/cm or more is observed at a low crystallization temperature of 230°C, whereas ion conductivity is very low at a high crystallization temperature of 500°C.

### Comparative Example 2

[0066] Li<sub>6</sub>PS<sub>5</sub>Cl as a sulfide-based solid electrolyte disclosed in Korean Patent Application Publication No. 10-2015-0132265 was prepared by varying a crystallization temperature and then ion conductivity was measured. The preparing method was as follows.

[0067] A lithium sulfide powder, a diphosphorus pentasulfide powder, and a lithium chloride (LiCl) powder were measured according to a composition of Li<sub>6</sub>PS<sub>5</sub>Cl to prepare a mixture of 5 g. Xylene as a solvent was added to the mixture, and then the mixture was milled by a planetary mill and amorphized. After the amorphizing is completed, the solvent was removed by vacuum drying and the mixture was crystallized by heat-treating under a condition of Table 2 below.

[0068] Ion conductivity was measured by the same method as Comparative Example 1. The result is illustrated in Table 2 below.

[Table 2]

Classification	Heat-treatment (crystallization) condition	Ion conductivity [S/cm]
Li <sub>6</sub> PS <sub>5</sub> Cl	230°C, 2 hrs	4.31×10 <sup>-4</sup>
	500°C, 4 hrs	1.81×10 <sup>-3</sup>

[0069] Referring to Table 2, in the case of a sulfide-based solid electrolyte in Comparative Example 2, it can be seen that high ion conductivity of 10<sup>-3</sup> S/cm or more is observed at a high crystallization temperature of 500°C, whereas ion conductivity is slightly low at a low crystallization temperature of 230°C.

### Examples 1 to 4

[0070] (Example 1) 6.85 g of lithium sulfide (Li<sub>2</sub>S), 8.28 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 4.48 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 0.39 g of lithium chloride (LiCl) were measured and mixed to be Chemical Formula of Table 3 to prepare 20 g of a starting material.

[0071] To the starting material, 165 g of xylene as a solvent was added and then milled by a planetary ball mill and amorphized. Thereafter, the solvent was removed by vacuum drying under conditions of about 160°C and 2 hrs.

[0072] The amorphized starting material was crystallized by heat-treating under conditions of about 260°C and 2 hrs to obtain the sulfide-based solid electrolyte.

[0073] (Example 2) Except that 6.72 g of lithium sulfide (Li<sub>2</sub>S), 8.12 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 4.39 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 0.77 g of lithium chloride (LiCl) were measured and mixed to be Chemical Formula of Table 3 to prepare 20 g of a starting material, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

[0074] (Example 3) Except that 6.47 g of lithium sulfide (Li<sub>2</sub>S), 7.82 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 4.22 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 1.49 g of lithium chloride (LiCl) were measured and mixed to be Chemical Formula of Table 3 to prepare 20 g of a starting material, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

[0075] (Example 4) Except that 6.02 g of lithium sulfide (Li<sub>2</sub>S), 7.28 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 3.93 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 2.77 g of lithium chloride (LiCl) were measured and mixed to be Chemical Formula of Table 3 to prepare 20 g of a starting material, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

### Examples 5 to 8

[0076] (Example 5) Except for heat-treating and crystallizing the amorphized starting material under conditions of 500°C and 4 hrs, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

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**[0077]** (Example 6) Except for heat-treating and crystallizing the amorphized starting material under conditions of 500°C and 4 hrs, a sulfide-based solid electrolyte was obtained by the same method as Example 2.

**[0078]** (Example 7) Except for heat-treating and crystallizing the amorphized starting material under conditions of 500°C and 4 hrs, a sulfide-based solid electrolyte was obtained by the same method as Example 3.

**[0079]** (Example 8) Except for heat-treating and crystallizing the amorphized starting material under conditions of 500°C and 4 hrs, a sulfide-based solid electrolyte was obtained by the same method as Example 4.

**[0080]** Compositions and crystallization conditions in Examples 1 to 8 are illustrated in Table 3 below.

[Table 3]

Classification	Chemical Formula	Crystallization condition
Example 1	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·5LiCl	260°C / 2 hrs
Example 2	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·10LiCl	
Example 3	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·20LiCl	
Example 4	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·40LiCl	
Example 5	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·5LiCl	500°C / 4 hrs
Example 6	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·10LiCl	
Example 7	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·20LiCl	
Example 8	80Li <sub>2</sub> S·20P <sub>2</sub> S <sub>5</sub> ·10Ni <sub>3</sub> S <sub>2</sub> ·40LiCl	

### Example 9

**[0081]** Except that 5.25 g of lithium sulfide (Li<sub>2</sub>S), 6.35 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 3.43 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 4.96 g of lithium bromide (LiBr) were measured and mixed to be Chemical Formula of 80Li<sub>2</sub>S·20P<sub>2</sub>S<sub>5</sub>·10Ni<sub>3</sub>S<sub>2</sub>·40LiBr to prepare 20 g of a starting material, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

### Example 10

**[0082]** Except that 4.63 g of lithium sulfide (Li<sub>2</sub>S), 5.60 g of diphosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>), 3.03 g of nickel sulfide (Ni<sub>3</sub>S<sub>2</sub>), and 6.74 g of lithium iodide (LiI) were measured and mixed to be Chemical Formula of 80Li<sub>2</sub>S·20P<sub>2</sub>S<sub>5</sub>·10Ni<sub>3</sub>S<sub>2</sub>·40LiI to prepare 20 g of a starting material, a sulfide-based solid electrolyte was obtained by the same method as Example 1.

## TEST EXAMPLES

### Test Example 1

**[0083]** Ion conductivities of the sulfide-based solid electrolytes in Examples 1 to 8 were measured. Each sulfide-based solid electrolyte was compressively molded to form a molding body (a diameter of 13 mm) for measurement. An AC potential of 10 m V was applied to the molding body and then an impedance value was measured by performing a frequency sweeping of 1×10<sup>6</sup> to 100 Hz to obtain ion conductivity.

**[0084]** FIG. 1 is a result of measuring impedance values for the sulfide-based solid electrolytes in Examples 1 to 4 of the present invention.

**[0085]** FIG. 2 is a result of measuring impedance values for the sulfide-based solid electrolytes in Examples 5 to 8 of the present invention.

**[0086]** Table 4 below is a result of measuring ion conductivities for the sulfide-based solid electrolytes in Examples 1 to 8 of the present invention.

[Table 4]

Classification	Ion conductivity [S/cm]
Example 1	7.00×10 <sup>-4</sup>
Example 2	1.03×10 <sup>-3</sup>

(continued)

Classification	Ion conductivity [S/cm]
Example 3	$1.06 \times 10^{-3}$
Example 4	$1.09 \times 10^{-3}$
Example 5	$2.33 \times 10^{-4}$
Example 6	$2.93 \times 10^{-4}$
Example 7	$6.88 \times 10^{-4}$
Example 8	$2.07 \times 10^{-3}$

[0087] Referring to FIGS. 1 and 2, it can be seen that ion conductivity is increased as the content of halogen element in the sulfide-based solid electrolyte is increased. Further, referring to FIG. 2, in the case of crystallization at a high temperature of 500°C, it can be verified that an interface resistance is decreased as the content of halogen element is increased.

[0088] Referring to Table 4, it can be seen that the sulfide-based solid electrolyte according to the present invention has ion conductivity of  $10^{-4}$  S/cm or more in a wide crystallization temperature range. Particularly, it can be verified that Examples 4 and 8 containing 40 parts by mole of lithium halide have very high ion conductivity of  $10^{-3}$  S/cm or more.

### Test Example 2

[0089] With respect to the sulfide-based solid electrolytes in Examples 4 and 8, an X-ray diffraction spectroscopy (XRD) was performed.

[0090] FIG. 3 is an XRD result for the sulfide-based solid electrolyte in Example 4 and FIG. 4 is an XRD result for the sulfide-based solid electrolyte in Example 8.

[0091] Referring to FIG. 3, it can be seen that the sulfide-based solid electrolyte in Example 4 has diffraction peaks in regions having diffraction angles  $2\theta$  of  $15.5 \pm 0.5^\circ$ ,  $18 \pm 0.5^\circ$ ,  $25.5 \pm 0.5^\circ$ ,  $30 \pm 0.5^\circ$ ,  $31.5 \pm 0.5^\circ$ ,  $40 \pm 0.5^\circ$ ,  $45.5 \pm 0.5^\circ$ ,  $48 \pm 0.5^\circ$ ,  $53 \pm 0.5^\circ$ ,  $55 \pm 0.5^\circ$ ,  $56.5 \pm 0.5^\circ$  and  $59.5 \pm 0.5^\circ$  as main peaks, and it can be seen that since the peaks are substantially the same peaks as  $\text{Li}_6\text{PS}_5\text{Cl}$  having high ion conductivity, the sulfide-based solid electrolyte of Example 4 has a high ion conductive cubic crystal structure.

[0092] Referring to FIG. 4, it can be seen that since the sulfide-based solid electrolyte in Example 8 also has substantially the same peaks as  $\text{Li}_6\text{PS}_5\text{Cl}$  as main peaks, the sulfide-based solid electrolyte of Example 8 has a high ion conductive cubic crystal structure.

[0093] As a result, it can be seen that the sulfide-based solid electrolyte according to the present invention has a high ion conductive cubic crystal structure in a wide crystallization temperature range and it supports the result of Test Example 1.

### Test Example 3

[0094] Charge and discharge capacities of an all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 1 to 8 were measured.

[0095] The all solid-state battery was constituted by a positive electrode, a negative electrode, and a solid electrolyte layer interposed between the positive electrode and the negative electrode. The solid electrolyte layer was formed with a thickness of 500  $\mu\text{m}$  by compressively molding the sulfide-based solid electrolytes in Examples 1 to 8, and as the positive electrode, a powder containing an active material (Nb-coated NCM622), a solid electrolyte (a solid electrolyte used in the solid electrolyte layer), and a conductive material (Super C) was formed on the solid electrolyte layer with an active material loading amount of 5.8  $\text{mg}/\text{cm}^2$  and a thickness of 30  $\mu\text{m}$ , and as the negative electrode, indium foil with a thickness of 100  $\mu\text{m}$  was used.

[0096] With respect to the all solid-state battery, a discharge capacity was measured by performing charging and discharging under a constant current (CC) condition in a range of 2 V to 3.58 V at rate limiting of 0.02 C rate.

[0097] FIG. 5 is a result of measuring charge and discharge capacities of all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 1 to 4 of the present invention and FIG. 6 is a result of measuring charge and discharge capacities of all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 5 to 8 of the present invention. The charge and discharge capacities are numerically illustrated in Table 5.



[Table 5]

Classification	Charge [mAh/g]	Discharge [mAh/g]
Example 1	185	137
Example 2	166	115
Example 3	153	109
Example 4	182	143
Example 5	197	131
Example 6	221	147
Example 7	250	149
Example 8	218	150

[0098] Referring to FIGS. 5 and 6 and Table 5, it can be verified that the all solid-state batteries adopting the sulfide-based solid electrolytes in Examples 1 to 8 have excellent charge and discharge capacities of about 150 mAh/g.

#### Test Example 4

[0099] Ion conductivities for the sulfide-based solid electrolytes in Examples 9 and 10 were measured by the same method as Test Example 1. The result is illustrated in Table 6.

[Table 6]

Classification	Chemical Formula	Ion conductivity [S/cm]
Example 4	$80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5\cdot 10\text{Ni}_3\text{S}_2\cdot 40\text{LiCl}$	$1.09\times 10^{-3}$
Example 9	$80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5\cdot 10\text{Ni}_3\text{S}_2\cdot 40\text{LiBr}$	$5.10\times 10^{-4}$
Example 10	$80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5\cdot 10\text{Ni}_3\text{S}_2\cdot 40\text{LiI}$	$3.00\times 10^{-4}$

[0100] Referring to Table 6, it can be seen that even in the case of using lithium bromide and lithium iodide instead of lithium chloride as the lithium halide, the sulfide-based solid electrolyte having high ion conductivity which has excellent ion conductivity of  $1.0\times 10^{-4}$  S/cm or more can be synthesized.

#### Claims

1. A sulfide-based solid electrolyte comprising:

with respect to 100 parts by mole of a mixture of lithium sulfide ( $\text{Li}_2\text{S}$ ) and diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ ), 5 parts by mole to 20 parts by mole of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ); and 5 parts by mole to 40 parts by mole of lithium halide, wherein the sulfide-based solid electrolyte has a cubic crystal structure.

2. The sulfide-based solid electrolyte of claim 1, wherein the mixture comprises 60 mole% to 90 mole% of the lithium sulfide; and 10 mole% to 40 mole% of diphosphorus pentasulfide.

3. The sulfide-based solid electrolyte of claim 1 or 2, wherein the lithium halide is expressed by  $\text{LiX}$ , where X is Cl, Br or I.

4. The sulfide-based solid electrolyte of any one of claims 1 to 3, wherein

- a crystallization temperature of the sulfide-based solid electrolyte is  $200^\circ\text{C}$  to  $400^\circ\text{C}$ , or  
- a crystallization temperature of the sulfide-based solid electrolyte is  $400^\circ\text{C}$  to  $600^\circ\text{C}$ .

5. The sulfide-based solid electrolyte of claim 4, wherein the cubic crystal structure has diffraction peaks in an area of

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diffraction angles  $2\theta$  of  $15.5\pm 0.5^\circ$ ,  $18\pm 0.5^\circ$ ,  $25.5\pm 0.5^\circ$ ,  $30\pm 0.5^\circ$ ,  $31.5\pm 0.5^\circ$ ,  $40\pm 0.5^\circ$ ,  $45.5\pm 0.5^\circ$ ,  $48\pm 0.5^\circ$ ,  $53\pm 0.5^\circ$ ,  $55\pm 0.5^\circ$ ,  $56.5\pm 0.5^\circ$  and  $59.5\pm 0.5^\circ$  in an X-ray diffraction spectrum.

5 6. The sulfide-based solid electrolyte of any one of claims 1 to 5, wherein the sulfide-based solid electrolyte has high ion conductivity in a wide crystallization temperature range.

7. A method of preparing a sulfide-based solid electrolyte, the method comprising:

10 preparing a starting material by adding 5 parts by mole to 20 parts by mole of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and 5 parts by mole to 40 parts by mole of lithium halide with respect to 100 parts by mole of a mixture of lithium sulfide ( $\text{Li}_2\text{S}$ ) and diphosphorus pentasulfide ( $\text{P}_2\text{S}_5$ );  
milling the starting material to obtain an amorphous material; and  
heat-treating the amorphous material to obtain a crystallized sulfide-based solid electrolyte having a cubic crystal structure.

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8. The method of claim 7, wherein the mixture comprises 60 mole% to 90 mole% of the lithium sulfide; and 10 mole% to 40 mole% of diphosphorus pentasulfide.

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9. The method of claim 7 or 8, wherein the lithium halide is expressed by  $\text{LiX}$ , where X is Cl, Br or I.

10. The method of any one of claims 7 to 9, wherein the heat-treating is performed at  $400^\circ\text{C}$  to  $600^\circ\text{C}$  to obtain the crystallized sulfide-based solid electrolyte.

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11. The method of any one of claims 7 to 9, wherein, the heat-treating is performed at  $200^\circ\text{C}$  to  $400^\circ\text{C}$  to obtain the crystallized sulfide-based solid electrolyte.

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12. The method of claim 10 or 11, wherein the cubic crystal structure has diffraction peaks in an area of diffraction angles  $2\theta$  of  $15.5\pm 0.5^\circ$ ,  $18\pm 0.5^\circ$ ,  $25.5\pm 0.5^\circ$ ,  $30\pm 0.5^\circ$ ,  $31.5\pm 0.5^\circ$ ,  $40\pm 0.5^\circ$ ,  $45.5\pm 0.5^\circ$ ,  $48\pm 0.5^\circ$ ,  $53\pm 0.5^\circ$ ,  $55\pm 0.5^\circ$ ,  $56.5\pm 0.5^\circ$  and  $59.5\pm 0.5^\circ$  in an X-ray diffraction spectrum.

### Patentansprüche

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1. Ein Sulfid-basierter Festelektrolyt, aufweisend:

mit Bezug auf 100 Mol-Teile einer Mischung Lithiumsulfid ( $\text{Li}_2\text{S}$ ) und Diphosphorpentasulfid ( $\text{P}_2\text{S}_5$ ),  
5 Mol-Teile bis 20 Mol-Teile Nickelsulfid ( $\text{Ni}_3\text{S}_2$ ) und  
5 Mol-Teile bis 40 Mol-Teile Lithiumhalogenid,

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wobei der Sulfid-basierte Festelektrolyt eine kubische Kristallstruktur hat.

2. Der Sulfid-basierte Festelektrolyt gemäß Anspruch 1, wobei die Mischung aufweist

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60 Mol-% bis 90 Mol-% des Lithiumsulfids und  
10 Mol-% bis 40 Mol-% Diphosphorpentasulfid.

3. Der Sulfid-basierte Festelektrolyt gemäß Anspruch 1 oder 2, wobei das Lithiumhalogenid durch  $\text{LiX}$  ausgedrückt ist, in welchem X für Cl, Br oder I steht.

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4. Der Sulfid-basierte Festelektrolyt gemäß irgendeinem der Ansprüche 1 bis 3, wobei

- eine Kristallisationstemperatur des Sulfid-basierten Festelektrolyten  $200^\circ\text{C}$  bis  $400^\circ\text{C}$  ist oder  
- eine Kristallisationstemperatur des Sulfid-basierten Festelektrolyten  $400^\circ\text{C}$  bis  $600^\circ\text{C}$  ist.

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5. Der Sulfid-basierte Festelektrolyt gemäß Anspruch 4, wobei die kubische Kristallstruktur in einem Röntgenbeugungsspektrum Beugungspeaks in einem Bereich von Beugungswinkeln  $2\theta$  von  $15,5\pm 0,5^\circ$ ,  $18\pm 0,5^\circ$ ,  $25,5\pm 0,5^\circ$ ,  $30\pm 0,5^\circ$ ,  $31,5\pm 0,5^\circ$ ,  $40\pm 0,5^\circ$ ,  $45,5\pm 0,5^\circ$ ,  $48\pm 0,5^\circ$ ,  $53\pm 0,5^\circ$ ,  $55\pm 0,5^\circ$ ,  $56,5\pm 0,5^\circ$  und  $59,5\pm 0,5^\circ$  hat.

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6. Der Sulfid-basierte Festelektrolyt gemäß irgendeinem der Ansprüche 1 bis 5, wobei der Sulfid-basierte Festelektrolyt eine hohe Ionenleitfähigkeit in einem weiten Kristallisationstemperaturbereich hat.

7. Ein Verfahren des Herstellens eines Sulfid-basierten Festelektrolyten, das Verfahren aufweisend:

Herstellen eines Ausgangsmaterials durch Hinzugeben von 5 Mol-Teile bis 20 Mol-Teile Nickelsulfid ( $\text{Ni}_3\text{S}_2$ ) und 5 Mol-Teile bis 40 Mol-Teile Lithiumhalogenid mit Bezug auf 100 Mol-Teile einer Mischung Lithiumsulfid ( $\text{Li}_2\text{S}$ ) und Diphosphorpentasulfid ( $\text{P}_2\text{S}_5$ ),

Mahlen des Ausgangsmaterials, um ein amorphes Material zu erhalten und

Wärmebehandeln des amorphen Materials, um einen kristallisierten, Sulfid-basierten Festelektrolyt zu erhalten, welcher eine kubische Kristallstruktur hat.

8. Das Verfahren gemäß Anspruch 7, wobei die Mischung aufweist 60 Mol-% bis 90 Mol-% des Lithiumsulfids und 10 Mol-% bis 40 Mol-% Diphosphorpentasulfid.

9. Das Verfahren gemäß Anspruch 7 oder 8, wobei das Lithiumhalogenid durch  $\text{LiX}$  ausgedrückt ist, in welchem X für Cl, Br oder I steht.

10. Das Verfahren gemäß irgendeinem der Ansprüche 7 bis 9, wobei die Wärmebehandlung bei  $400^\circ\text{C}$  bis  $600^\circ\text{C}$  ausgeführt wird, um einen kristallisierten, Sulfid-basierten Festelektrolyt zu erhalten.

11. Das Verfahren gemäß irgendeinem der Ansprüche 7 bis 9, wobei die Wärmebehandlung bei  $200^\circ\text{C}$  bis  $400^\circ\text{C}$  ausgeführt wird, um einen kristallisierten, Sulfid-basierten Festelektrolyt zu erhalten.

12. Das Verfahren gemäß Anspruch 10 oder 11, wobei die kubische Kristallstruktur in einem Röntgenbeugungsspektrum Beugungspeaks in einem Bereich von Beugungswinkeln  $2\theta$  von  $15,5 \pm 0,5^\circ$ ,  $18 \pm 0,5^\circ$ ,  $25,5 \pm 0,5^\circ$ ,  $30 \pm 0,5^\circ$ ,  $31,5 \pm 0,5^\circ$ ,  $40 \pm 0,5^\circ$ ,  $45,5 \pm 0,5^\circ$ ,  $48 \pm 0,5^\circ$ ,  $53 \pm 0,5^\circ$ ,  $55 \pm 0,5^\circ$ ,  $56,5 \pm 0,5^\circ$  und  $59,5 \pm 0,5^\circ$  hat.

### Revendications

1. Electrolyte solide à base de sulfure comprenant :

pour 100 parties en moles d'un mélange de sulfure de lithium ( $\text{Li}_2\text{S}$ ) et de pentasulfure de diphosphore ( $\text{P}_2\text{S}_5$ ),  
5 parties en moles à 20 parties en moles de sulfure de nickel ( $\text{Ni}_3\text{S}_2$ ) ; et  
5 parties en moles à 40 parties en moles d'halogénure de lithium,

lequel électrolyte solide à base de sulfure a une structure cristalline cubique.

2. Electrolyte solide à base de sulfure selon la revendication 1, dans lequel le mélange comprend  
60 % en moles à 90 % en moles du sulfure de lithium ; et  
10 % en moles à 40 % en moles de pentasulfure de diphosphore.

3. Electrolyte solide à base de sulfure selon la revendication 1 ou 2, dans lequel l'halogénure de lithium est représenté par  $\text{LiX}$ , où X est Cl, Br ou I.

4. Electrolyte solide à base de sulfure selon l'une quelconque des revendications 1 à 3, dans lequel

- le point de cristallisation de l'électrolyte solide à base de sulfure est de  $200^\circ\text{C}$  à  $400^\circ\text{C}$ , ou
- le point de cristallisation de l'électrolyte solide à base de sulfure est de  $400^\circ\text{C}$  à  $600^\circ\text{C}$ .

5. Electrolyte solide à base de sulfure selon la revendication 4, dans lequel la structure cristalline cubique a des pics de diffraction dans une surface d'angles de diffraction  $2\theta$  de  $15,5 \pm 0,5^\circ$ ,  $18 \pm 0,5^\circ$ ,  $25,5 \pm 0,5^\circ$ ,  $30 \pm 0,5^\circ$ ,  $31,5 \pm 0,5^\circ$ ,  $40 \pm 0,5^\circ$ ,  $45,5 \pm 0,5^\circ$ ,  $48 \pm 0,5^\circ$ ,  $53 \pm 0,5^\circ$ ,  $55 \pm 0,5^\circ$ ,  $56,5 \pm 0,5^\circ$  et  $59,5 \pm 0,5^\circ$ , dans un spectre de diffraction des rayons X.

6. Electrolyte solide à base de sulfure selon l'une quelconque des revendications 1 à 5, lequel électrolyte solide à base de sulfure a une conductivité ionique élevée dans une large plage de températures de cristallisation.

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7. Procédé de préparation d'un électrolyte solide à base de sulfure, le procédé comprenant :

la préparation d'un matériau de départ par addition de 5 parties en moles à 20 parties en moles de sulfure de nickel ( $\text{Ni}_3\text{S}_2$ ) et de 5 parties en moles à 40 parties en moles d'halogénure de lithium, pour 100 parties en moles d'un mélange de sulfure de lithium ( $\text{Li}_2\text{S}$ ) et de pentasulfure de diphosphore ( $\text{P}_2\text{S}_5$ ) ;  
le broyage du matériau de départ pour que soit obtenu un matériau amorphe ; et  
le traitement thermique du matériau amorphe pour que soit obtenu un électrolyte solide à base de sulfure cristallisé ayant une structure cristalline cubique.

8. Procédé selon la revendication 7, dans lequel le mélange comprend 60 % en moles à 90 % en moles du sulfure de lithium ; et 10 % en moles à 40 % en moles de pentasulfure de diphosphore.

9. Procédé selon la revendication 7 ou 8, dans lequel l'halogénure de lithium est représenté par  $\text{LiX}$ , où X est Cl, Br ou I.

10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel le traitement thermique est effectué à une température de 400°C à 600°C pour que soit obtenu l'électrolyte solide à base de sulfure cristallisé.

11. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel le traitement thermique est effectué à une température de 200°C à 400°C pour que soit obtenu l'électrolyte solide à base de sulfure cristallisé.

12. Procédé selon la revendication 10 ou 11, dans lequel la structure cristalline cubique a des pics de diffraction dans une surface d'angles de diffraction  $2\theta$  de  $15,5 \pm 0,5^\circ$ ,  $18 \pm 0,5^\circ$ ,  $25,5 \pm 0,5^\circ$ ,  $30 \pm 0,5^\circ$ ,  $31,5 \pm 0,5^\circ$ ,  $40 \pm 0,5^\circ$ ,  $45,5 \pm 0,5^\circ$ ,  $48 \pm 0,5^\circ$ ,  $53 \pm 0,5^\circ$ ,  $55 \pm 0,5^\circ$ ,  $56,5 \pm 0,5^\circ$  et  $59,5 \pm 0,5^\circ$ , dans un spectre de diffraction des rayons X.

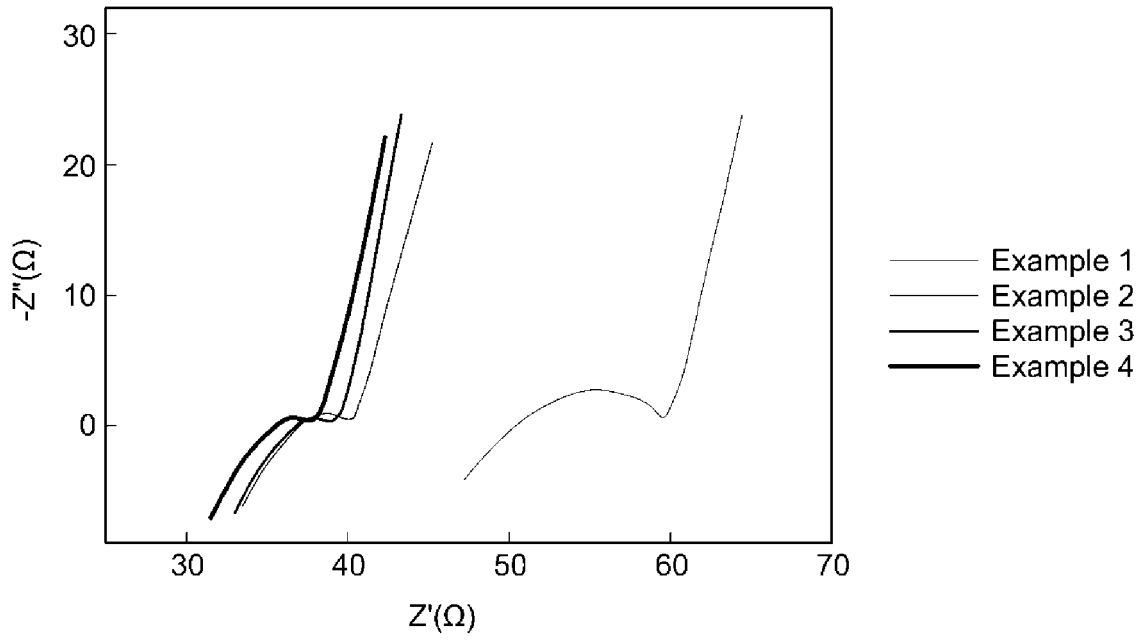


FIG. 1

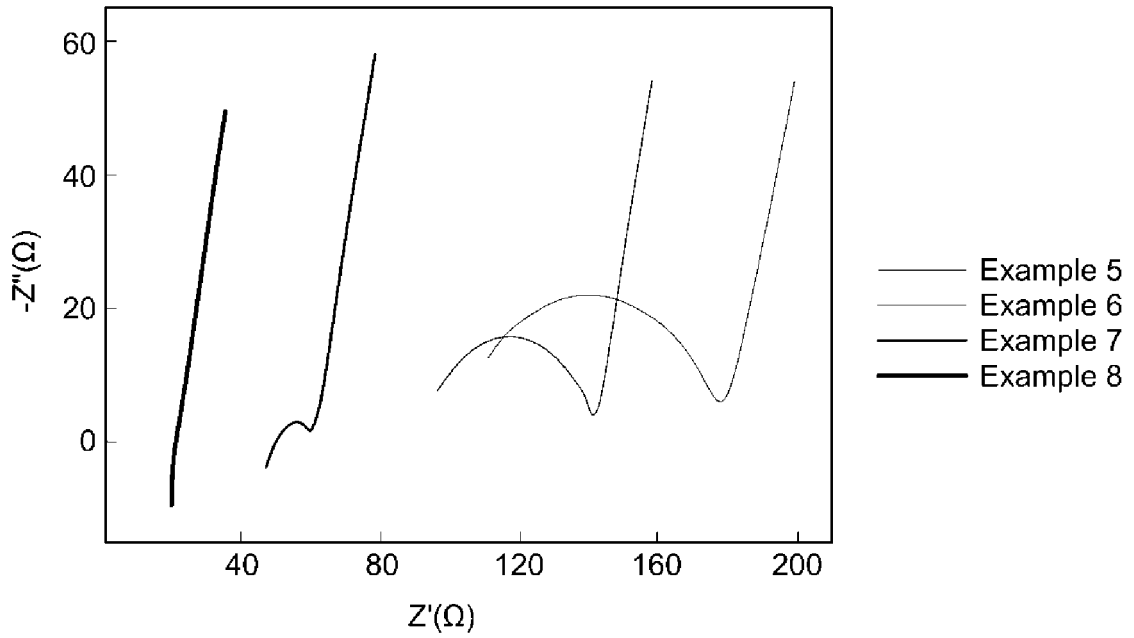


FIG. 2

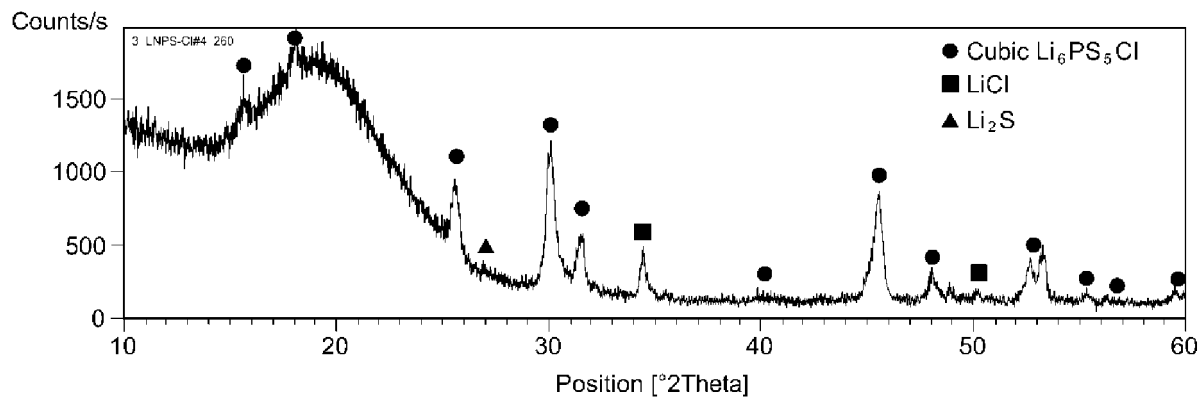


FIG. 3

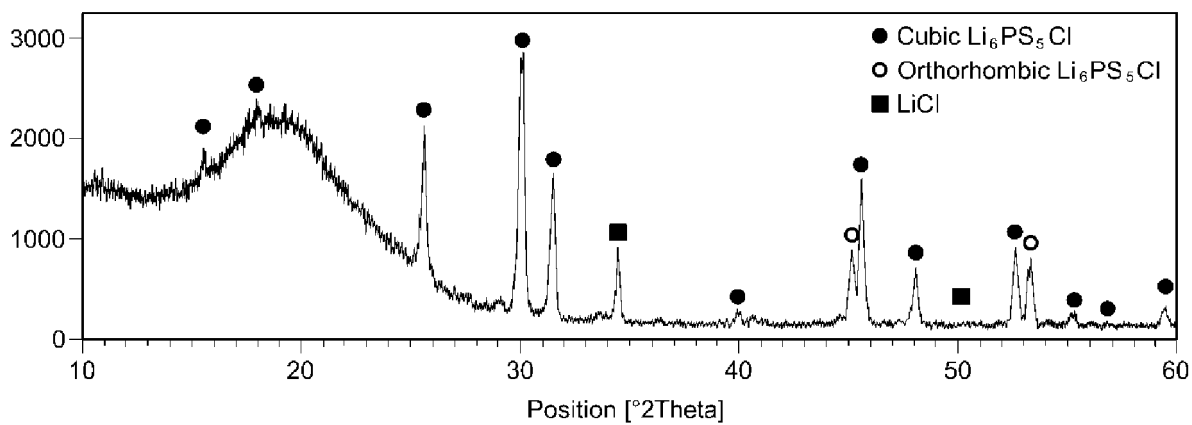
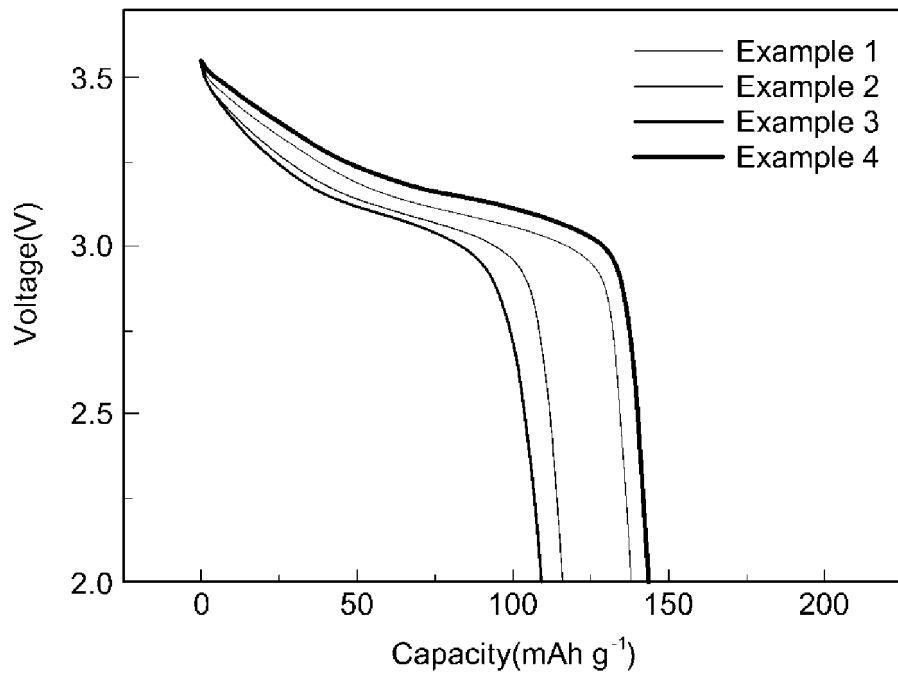
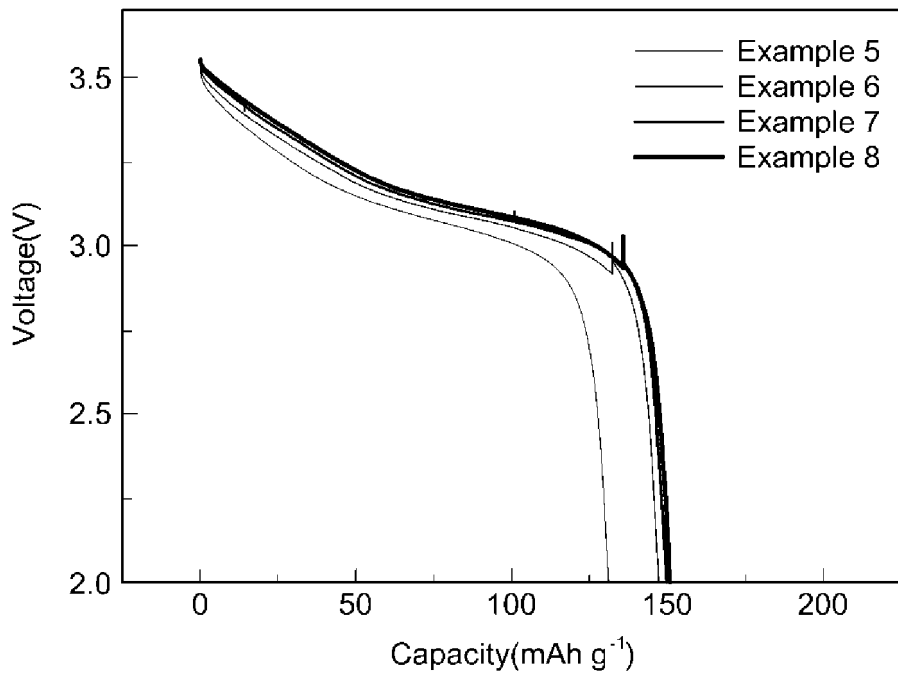


FIG. 4



**FIG. 5**



**FIG. 6**

**REFERENCES CITED IN THE DESCRIPTION**

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