



(43) International Publication Date  
7 March 2013 (07.03.2013)

(10) International Publication Number  
**WO 2013/031995 A1**

- (51) **International Patent Classification:**  
*C01B 25/45* (2006.01) *H01M 4/58* (2010.01)
- (21) **International Application Number:**  
PCT/JP2012/072280
- (22) **International Filing Date:**  
27 August 2012 (27.08.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
2011-189027 31 August 2011 (31.08.2011) JP
- (71) **Applicant (for all designated States except US): SEMI-CONDUCTOR ENERGY LABORATORY CO., LTD.**  
[JP/JP]; 398, Hase, Atsugi-shi, Kanagawa, 2430036 (JP).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only): MIWA, Takuya**  
[JP/JP]; c/o SEMICONDUCTOR ENERGY LABORATORY CO., LTD., 398, Hase, Atsugi-shi, Kanagawa, 2430036 (JP). **NOMOTO, Kuniharu. MOMO, Junpei.**
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))

(54) **Title:** MANUFACTURING METHOD OF COMPOSITE OXIDE AND MANUFACTURING METHOD OF POWER STORAGE DEVICE

(57) **Abstract:** An object is to reduce variation in shape of crystals that are to be formed. Solutions containing respective raw materials are made in an environment where an oxygen concentration is lower than that in air, the solutions containing the respective raw materials are mixed in an environment where an oxygen concentration is lower than that in air to form a mixture solution, and with use of the mixture solution, a composite oxide is formed by a hydrothermal method.



**WO 2013/031995 A1**

## DESCRIPTION

**MANUFACTURING METHOD OF COMPOSITE OXIDE AND  
MANUFACTURING METHOD OF POWER STORAGE DEVICE**

5

## TECHNICAL FIELD

[0001]

The present invention relates to a composite oxide and further relates to a power storage device.

10

## BACKGROUND ART

[0002]

In recent years, power storage devices such as lithium ion secondary batteries have been developed.

15

[0003]

Examples of such power storage devices include a power storage device having an electrode formed using lithium iron phosphate ( $\text{LiFePO}_4$ ), which is a composite oxide, as an active material. The power storage device having an electrode formed using  $\text{LiFePO}_4$  has high thermal stability and favorable cycle characteristics.

20

[0004]

As an example of a method for forming a composite oxide such as  $\text{LiFePO}_4$ , a hydrothermal method can be used (e.g., Patent Document 1). A hydrothermal method is a method, which is performed in the presence of hot water, for synthesizing a compound or growing crystal of a compound.

25

[0005]

By using a hydrothermal method, even a material which is less likely to be dissolved in water at ordinary temperatures and pressures can be dissolved, and thus a substance which is hardly obtained by a production method performed at ordinary temperatures and pressures can be synthesized or crystal growth of such a substance can be conducted. Further, by using a hydrothermal method, microparticles of single crystals of an objective substance can be easily synthesized.

30

[0006]

Using a hydrothermal method, for example, enables a desired compound to be formed in the following manner: a solution containing a raw material is introduced into a container resistant to pressure and be subjected to heat and pressure treatment; and the treated solution is filtered.

5 [Reference]

[0007]

[Patent Document 1] Japanese Published Patent Application No. 2004-095385

#### DISCLOSURE OF INVENTION

10 [0008]

However,  $\text{LiFePO}_4$  formed by the conventional hydrothermal method has a problem of large variation in crystal shape of  $\text{LiFePO}_4$ .

[0009]

When variation in crystal shape is large, for example, the bulk density of crystals in an active material of an electrode is low, and the charge-discharge characteristics of a power storage device are reduced. In order to suppress a reduction in the charge-discharge characteristics of the power storage device, crystal shapes are preferably regulated, so that the crystal shapes in the active material of the electrode are uniform.

20 [0010]

An object of one embodiment of the present invention is to reduce variation in shape of crystals formed by using a hydrothermal method.

[0011]

In one embodiment of the present invention, a mixture solution containing a raw material is made in an environment where an oxygen concentration is lower than that in air, and with use of the mixture solution, a composite oxide is formed by using a hydrothermal method, whereby difference in crystal shape in the formed composite oxide is suppressed.

[0012]

30 One embodiment of the present invention is a production method of a composite oxide including the steps of: forming a solution containing lithium (Li) with use of a compound containing Li in an atmosphere where an oxygen concentration is

lower than that in air; forming a solution containing phosphorus (P) with use of a compound containing P in an atmosphere where an oxygen concentration is lower than that in air; forming a solution containing one or more transition metals selected from iron (Fe), cobalt (Co), nickel (Ni), and manganese (Mn) with use of one or more compounds containing any one transition metal of Fe, Co, Ni, and Mn in an atmosphere where an oxygen concentration is lower than that in air; mixing the solution containing Li and the solution containing P in an atmosphere where an oxygen concentration is lower than that in air and forming a solution containing Li and P; mixing the solution containing Li and P and the solution containing the transition metal in an atmosphere where an oxygen concentration is lower than that in air and forming a mixture solution; and forming a composite oxide by a hydrothermal method in an atmosphere where an oxygen concentration is lower than that in air. The thus obtained composite oxide is represented by a general formula,  $\text{LiMPO}_4$  (M denotes one or more of Fe, Co, Ni, and Mn).

[0013]

According to one embodiment of the present invention, shapes of formed crystals can be regulated. Thus, difference in crystal shape can be reduced.

#### BRIEF DESCRIPTION OF DRAWINGS

[0014]

FIGS. 1A and 1B are flow charts showing an example of a production method of a composite oxide.

FIG. 2 is a schematic view illustrating an example of a crystal structure of a composite oxide.

FIG. 3 illustrates an example of a power storage device.

FIGS. 4A and 4B each illustrate a structure example of an electrode in a power storage device.

FIG. 5 illustrates an example of a power storage device.

FIG. 6 illustrates examples of electric devices.

FIG. 7A is a schematic view illustrating an example of an electric device and FIG. 7B is a block diagram thereof.

FIG. 8 shows an observation result of  $\text{LiFePO}_4$ , which is obtained with a

scanning electron microscope.

FIG. 9 shows an observation result of  $\text{LiFePO}_4$ , which is a comparison example and obtained with a scanning electron microscope.

## 5 BEST MODE FOR CARRYING OUT THE INVENTION

[0015]

Examples of embodiments of the present invention will be described with reference to the drawings below. Note that it will be readily appreciated by those skilled in the art that details of the embodiments can be modified in various ways  
10 without departing from the spirit and scope of the invention. Thus, the present invention should not be limited to the description of the following embodiments.

[0016]

Note that the contents in different embodiments can be combined with one another as appropriate. In addition, the contents of the embodiments can be replaced  
15 with each other as appropriate.

[0017]

Further, the ordinal numbers such as "first" and "second" are used to avoid confusion between components and do not limit the number of each component.

[0018]

### 20 (Embodiment 1)

In this embodiment, an example of a composite oxide having crystals will be described.

[0019]

An example of a production method of a composite oxide of this embodiment  
25 is described with reference to flow charts in FIGS. 1A and 1B.

[0020]

In the example of a production method of a composite oxide in this embodiment, as shown in FIG. 1A, a mixture solution used for synthesizing a composite oxide is formed in an atmosphere where an oxygen concentration is lower than that in  
30 air (the atmosphere is also referred to as "low-oxygen concentration atmosphere") as a step S11. Then, a composite oxide is formed with use of the obtained mixture solution by a hydrothermal method as a step S12.

[0021]

Details of the production method of a composite oxide is described with a flow chart shown in FIG. 1B.

[0022]

5 In the example of a production method of a composite oxide of this embodiment, as shown in FIG. 1B, a compound containing lithium (Li), which is also referred to as "lithium compound", is weighed as a step S11\_1. Further, a compound containing phosphorus (P), which is also referred to as "phosphorus compound", is weighed as a step S11\_2. Further, a compound containing a transition metal, which is  
10 also referred to as "transition metal compound", is weighed as a step S11\_3.

[0023]

Examples of lithium compounds that can be used include lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ), anhydrous lithium hydroxide ( $\text{LiOH}$ ), lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium oxide ( $\text{Li}_2\text{O}$ ), lithium nitrate ( $\text{LiNO}_3$ ), and lithium acetate  
15 ( $\text{CH}_3\text{COOLi}$ ).

[0024]

Examples of phosphorus compounds that can be used include phosphoric acid such as orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and ammonium hydrogenphosphates such as ammonium dihydrogenphosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ).

20 [0025]

As a transition metal compound, for example, one or more compounds containing any one of iron (Fe), cobalt (Co), nickel (Ni), and manganese (Mn) can be used. Examples thereof include iron chloride tetrahydrate ( $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ), iron sulfate heptahydrate ( $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ), iron acetate ( $\text{Fe}(\text{CH}_3\text{COO})_2$ ), manganese chloride  
25 tetrahydrate ( $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ ), manganese sulfate-hydrate ( $\text{MnSO}_4\cdot \text{H}_2\text{O}$ ), manganese acetate tetrahydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ), cobalt chloride hexahydrate ( $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ), cobalt sulfate ( $\text{CoSO}_4$ ), cobalt acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ), nickel chloride hexahydrate ( $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ ), nickel sulfate hexahydrate ( $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ ), and nickel acetate tetrahydrate ( $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ).

30 [0026]

Then, as a step S12\_1, the lithium compound is dissolved in a solvent in an

atmosphere where an oxygen concentration is lower than that in air, so that a solution containing Li (also referred to as "lithium containing solution") is formed. Further, as a step S12\_2, the phosphorus compound is dissolved in a solvent in an atmosphere where an oxygen concentration is lower than that in air, so that a solution containing P (also referred to as "phosphorus containing solution") is formed. Further, as a step S12\_3, the transition metal compound is dissolved in a solvent in an atmosphere where an oxygen concentration is lower than that in air, so that a solution containing a transition metal (also referred to as "transition metal-containing solution") is formed.

[0027]

As the solvent in which the lithium compound, the phosphorus compound, or the transition metal compound is dissolved, water can be used for example. In addition, the oxygen concentration in the solvent is preferably 4.5 ppm or lower. For example, nitrogen bubbling is performed in the solvent, whereby the oxygen concentration in the solvent can be reduced. Reduction in the oxygen concentration in the solvent enables suppression of oxidation of a substance which is to be produced.

[0028]

Further, as the atmosphere where an oxygen concentration is lower than that in air, for example, a nitrogen atmosphere or a mixed atmosphere of nitrogen and hydrogen can be employed.

[0029]

Next, as a step S13, the solution containing Li and the solution containing P are mixed in an atmosphere where an oxygen concentration is lower than that in air, so that a solution containing Li and P (also referred to as "lithium-phosphorus-containing solution") is formed. The solution containing Li and P is slightly alkaline.

[0030]

Then, as a step S14, the solution containing Li and P and the solution containing the transition metal are mixed in an atmosphere where an oxygen concentration is lower than that in air, so that a mixture solution is formed.

[0031]

In this step, it is preferable, for example, to drip the solution containing Li and P little by little while stirring the solution containing the transition metal. Thus, a

hydrogen ion in the solution containing the transition metal and a hydroxide ion in the solution containing Li and P are reacted (neutralization reaction) prior to a reaction of a transition metal ion and a hydroxide ion. As a result, production of unnecessary transition metal hydroxide can be reduced.

5 [0032]

Then, as a step S15, a composite oxide is formed using the mixture solution by a hydrothermal method.

[0033]

10 For example, the mixture solution is introduced into a container resistant to pressure, subjected to pressure and heat treatment, and cooled. Then, the cooled solution is filtered. In this manner, the composite oxide can be formed.

[0034]

As a container resistant to pressure, an autoclave or the like can be used, for example.

15 [0035]

A preferable temperature at which the pressure and heat treatment is performed is, for example, higher than or equal to 100 °C and lower than or equal to the critical temperature of water. A preferable pressure at which the pressure and heat treatment is performed is, for example, higher than or equal to 0.1 MPa and lower than or equal to the critical pressure of water. A preferable time during which the pressure and heat treatment is performed is, for example, 0.5 hours or longer. In addition, the atmosphere in the container resistant to pressure is set to have lower oxygen concentration than that in air, whereby the treatment can be performed by a hydrothermal method in an atmosphere where an oxygen concentration is lower than that in air. For example, the preferable atmosphere in the container resistant to pressure is a nitrogen atmosphere or a mixed atmosphere of nitrogen and hydrogen. Thus, unnecessary oxygen in the container resistant to pressure can be removed. Further, even when the solution is oxidized during the step, the solution can be reduced. Therefore, adverse effect of oxidation can be suppressed.

30 [0036]

Alternatively, the pressure and heat treatment may be performed after addition of a reducing agent. For example, a reducing agent is added to the mixture solution,

and then the pressure and heat treatment can be performed. Further, without limitation thereto, for example, a reducing agent may be added to the solution containing the transition metal, and then the mixture solution may be formed.

[0037]

5           Examples of a reducing agent include ascorbic acid, sulfur dioxide, sulfurous acid, sodium sulfite, sodium hydrogen sulfite, ammonium sulfite, and phosphorous acid. With use of a reducing agent, the solution can be reduced even when the solution is oxidized during the step; thus, adverse effect of oxidation can be reduced.

[0038]

10           The composite oxide obtained by a hydrothermal method has a plurality of crystals. The crystal shape of the composite oxide is, for example, a rectangular solid 161 as illustrated in FIG. 2. Variation in shapes of the plurality of crystals, which are rectangular solids, is small. This is because impurities in the composite oxide formed under the condition where oxidation is suppressed are reduced. Note that it is  
15           preferable that a crystal structure of the composite oxide be an olivine structure.

[0039]

The foregoing has described an example of a production method of a composite oxide according to this embodiment.

[0040]

20           As described with reference to FIGS. 1A and 1B and FIG. 2, according to the example of a production method of a composite oxide of this embodiment, a solution containing lithium (Li) and phosphorus (P) is formed by mixing a solution containing Li and a solution containing P in an atmosphere where an oxygen concentration is lower than that in air, and then a mixture solution is formed by mixing the solution containing  
25           Li and P and a solution containing a transition metal in an atmosphere where an oxygen concentration is lower than that in air, so that generation of by-product due to oxidation can be suppressed. Thus, variation in crystal shape of composite oxide formed by using a hydrothermal method can be small.

[0041]

30           (Embodiment 2)

In this embodiment, an example of a power storage device having an electrode in which the composite oxide described in Embodiment 1 is used for an active material

will be described.

[0042]

A structure example of a power storage device in this embodiment is described with reference to FIG. 3.

5 [0043]

The power storage device illustrated in FIG. 3 includes a positive electrode 201, a negative electrode 202, an electrolyte 203, and a separator 204.

[0044]

10 The positive electrode 201 includes a positive electrode current collector 211 and a positive electrode active material layer 212.

[0045]

For the positive electrode current collector 211, aluminum, copper, nickel, titanium, or the like can be used. Further, an alloy including a plurality of materials capable of being used for the positive electrode current collector 211 may be used.

15 [0046]

For the positive electrode active material layer 212, for example, the composite oxide described in Embodiment 1 can be used. In this case, the composite oxide can be formed, for example, by the production method described in Embodiment 1. The composite oxide functions as an active material.

20 [0047]

For example, a conduction auxiliary agent, a binder, and a solvent are added to the composite oxide described in Embodiment 1, whereby a paste is formed. The paste is applied on the positive electrode current collector 211 and baked, so that the positive electrode active material layer 212 can be formed.

25 [0048]

The negative electrode 202 includes a negative electrode current collector 221 and a negative electrode active material layer 222.

[0049]

30 For the negative electrode current collector 221, iron, copper, nickel, or the like can be used. Alternatively, for the negative electrode current collector 221, an alloy of a plurality of materials capable of being used for the negative electrode current collector 221 may be used.

[0050]

For the negative electrode active material layer 222, silicon, graphite, or the like can be used. In this case, silicon or graphite functions as an active material.

[0051]

5 Further, the negative electrode active material layer 222 may have a structure including a plurality of whiskers, for example.

[0052]

Further, for the negative electrode active material layer 222, graphene can be used for example.

10 [0053]

Graphene refers to a one-atom-thick sheet of carbon molecules having  $sp^2$  bonds and holes through which ions pass, or refers to a stack in which a plurality of one-atom-thick sheets (the number of sheets is 2 to 100) are stacked (the stack is also referred to as multilayer graphene). Further, net-like graphene is referred to as  
15 graphene net. Note that in graphene, an element other than carbon may be contained to account for 30 at.% or less, or an element other than carbon and hydrogen may be contained to account for 15 at.% or less. Thus, graphene analogue is also regarded as graphene.

[0054]

20 Characteristics of graphene are high conductivity, sufficient flexibility, high mechanical strength and high heat resistance. In addition, graphene has capacity of storing ions.

[0055]

In the case where silicon or graphite is used for an active material, for example,  
25 silicon or graphite may be covered with graphene. Further, in the case of multilayer graphene, for example, microparticles of silicon, graphite, or the like may be included between a plurality of graphene layers.

[0056]

By using graphene, conductivity of an electrode can be increased.  
30 Accordingly, graphene can have a function of a binder. Further, by using graphene, an electrode can be formed without a conventional conductive auxiliary agent or a binder.

[0057]

Furthermore, by using graphene, deformation and damage of the electrode can be suppressed.

[0058]

5           Note that graphene may be used not only for the negative electrode active material layer 222 but also for the positive electrode active material layer 212. For example, a plurality of crystals of the composite oxide described in Embodiment 1 may be covered with graphene. Further, in the case of multilayer graphene, for example, microparticles of the composite oxide may be provided between a plurality of graphene  
10 layers.

[0059]

FIG. 4A illustrates a structure example of the negative electrode 202 including the negative electrode active material layer 222. In this example, the negative electrode active material layer 222 has a plurality of whiskers.

15 [0060]

The electrode illustrated in FIG. 4A includes the negative electrode current collector 221 and the negative electrode active material layer 222. The negative electrode active material layer 222 includes a layer 251 having whiskers.

[0061]

20           As the layer 251 having whiskers, for example, silicon can be used.

[0062]

In the layer 251 having whiskers, it is preferable that a core portion of each whiskers have crystallinity (the core portion is also referred to as crystalline portion) and the peripheral portion of the core portion be amorphous. For example, in the  
25 amorphous portion, change in volume, which occurs due to store and release of ions, is small. The crystalline portion has high conductivity and high ion conductivity; thus, in the crystalline portion, the rate of storing ions and the rate of releasing ions can be increased.

[0063]

30           The layer 251 having whiskers can be formed by, for example, a low pressure CVD (LPCVD) method.

[0064]

For example, in the case where the layer 251 having whiskers is formed using silicon, a deposition gas containing silicon can be used as a source gas for forming the layer 251 having whiskers by an LPCVD method. For the deposition gas containing silicon, silicon hydride, silicon fluoride, or silicon chloride can be used for example.

5 [0065]

The pressure is preferably set to 10 Pa to 1000 Pa inclusive, further preferably 20 Pa to 200 Pa inclusive. By adjusting pressure, the crystalline portion and the amorphous portion can be each formed.

[0066]

10 Alternatively, the negative electrode active material layer 222 can have such a structure that a layer having graphene is provided to cover the layer 251 having whiskers. FIG. 4B illustrates a structure example of the negative electrode 202 including the negative electrode active material layer 222 in which a layer having graphene is provided to cover the layer having whiskers.

15 [0067]

The electrode illustrated in FIG. 4B includes a layer 252 having graphene in addition to the structure illustrated in FIG. 4A.

[0068]

20 The layer 252 having graphene is provided in contact with the layer 251 having whiskers.

[0069]

For example, the layer 252 having graphene can be formed in the following manner: a graphene oxide layer is formed over the layer 251 having whiskers and then heated, so that the graphene oxide layer is reduced.

25 [0070]

As an example illustrated in FIG. 4B, the negative electrode active material layer has a structure in which a layer having graphene is provided in contact with the layer having whiskers, whereby even when the volume of the layer having whiskers is changed due to store and release of ions, for example, the layer having graphene contributes to reduce stress caused by change in volume. As a result, the whisker structure in the layer having whiskers can be prevented from being damaged. Therefore, cycle characteristics of the power storage device can be improved.

30

[0071]

As the separator 204 illustrated in FIG. 3, for example, paper, nonwoven fabric, glass fiber, or synthetic fiber may be used. As the synthetic fiber, materials such as nylon (polyamide), vinylon (also called vinalon) (polyvinyl alcohol fiber), polyester, acrylic, polyolefin, and polyurethane may be used. More examples of materials of the separator 204 are polymer materials (high-molecular compounds) such as fluorine-based polymer, polyether (e.g., polyethylene oxide and polypropylene oxide), polyolefin (e.g., polyethylene and polypropylene), polyacrylonitrile, polyvinylidene chloride, polymethyl methacrylate, polymethylacrylate, polyvinyl alcohol, polymethacrylonitrile, polyvinyl acetate, polyvinylpyrrolidone, polyethyleneimine, polybutadiene, polystyrene, polyisoprene, and polyurethane, derivatives thereof, a cellulose based material such as paper and film, and nonwoven fabric. These materials can be used either alone or in combination. However, it is necessary to choose a material which will not dissolve in the electrolyte 203, as the separator 204.

[0072]

The electrolyte 203 can be formed using a material including ions serving as carriers, a material through which ions serving as carriers transfer, or the like. Examples of such a material include lithium chloride (LiCl), lithium fluoride (LiF), lithium perchlorate (LiClO<sub>4</sub>), and lithium tetrafluoroborate (LiBF<sub>4</sub>). These materials can be used either alone or in combination in the electrolyte 203. Alternatively, for the electrolyte 203, a lithium salt material containing fluorine can be used, e.g., lithium hexafluorophosphate (LiPF<sub>6</sub>), lithium hexafluoroarsenate (LiAsF<sub>6</sub>), lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>), lithium bis(trifluoromethanesulfonyl)imide (LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>), lithium bis(pentafluoroethanesulfonyl)imide (LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>), or the like.

[0073]

Alternatively, the electrolyte 203 can be formed by dissolving the above material into a solvent. Examples of the solvent include a cyclic carbonate such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC); an acyclic carbonate such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC), isobutyl methyl carbonate, and dipropyl carbonate (DPC); an aliphatic carboxylic acid

ester such as methyl formate, methyl acetate, methyl propionate, and ethyl propionate; a  $\gamma$ -lactone such as  $\gamma$ -butyrolactone; an acyclic ether such as 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), and ethoxymethoxy ethane (EME); a cyclic ether such as tetrahydrofuran and 2-methyltetrahydrofuran; an alkyl phosphate ester such as dimethylsulfoxide, 1,3-dioxolane, trimethyl phosphate, triethyl phosphate, and trioctyl phosphate; and fluorides thereof. These materials can be used either alone or in combination as the solvent of the electrolyte 203.

[0074]

As an example of a power storage device according to this embodiment, a structure example of a coin-type secondary battery is described with reference to FIG. 5.

[0075]

The power storage device illustrated in FIG. 5 includes a positive electrode 301, a negative electrode 302, a separator 304, a housing 305, a housing 306, a ring-shaped insulator 307, a spacer 308, and a washer 309.

[0076]

The positive electrode 301 corresponds to the positive electrode 201 in FIG. 3, for example. A positive electrode current collector 311 corresponds to the positive electrode current collector 211, and a positive electrode active material layer 312 corresponds to the positive electrode active material layer 212.

[0077]

The negative electrode 302 corresponds to the negative electrode 202 in FIG. 3, for example. A negative electrode current collector 321 corresponds to the negative electrode current collector 221, and a negative electrode active material layer 322 corresponds to the negative electrode active material layer 222.

[0078]

The separator 304 corresponds to the separator 204 in FIG. 3, for example.

[0079]

The housing 305, the housing 306, the spacer 308, and the washer 309 each of which is made of metal (e.g., stainless steel) are preferably used. The housing 305 and the housing 306 have a function of electrically connecting the positive electrode 301 and the negative electrode 302 to the outside.

[0080]

As in the case of the power storage device illustrated in FIG. 5, the positive electrode 301, the negative electrode 302, and the separator 304 are soaked in the electrolyte; the negative electrode 302, the separator 304, the ring-shaped insulator 307, the positive electrode 301, the spacer 308, the washer 309, and the housing 305 are stacked in this order with the housing 306 positioned at the bottom; and the housing 305 and the housing 306 are subjected to pressure bonding. In such a manner, the coin-type secondary battery is manufactured.

[0081]

The foregoing has described an example of a power storage device according to this embodiment.

[0082]

Note that not being limited to use for the above coin-type secondary battery, the composite oxide according to Embodiment 1 can be used for a rectangular or cylindrical secondary battery, for example.

[0083]

As described with reference to FIG. 3, FIGS. 4A and 4B, and FIG. 5, in the example of a power storage device according to this embodiment, the positive electrode of the power storage device is formed using the composite oxide according to the above embodiment, whereby the bulk density of an active material can be increased. As a result, the energy density of the power storage device can be increased.

[0084]

(Embodiment 3)

In this embodiment, examples of electric devices each provided with a power storage device will be described.

[0085]

Examples of electric devices using the power storage device are as follows: display devices, lighting devices, desktop personal computers or notebook personal computers, image reproduction devices (for example, which reproduce a still image or a moving image stored in a storage medium such as a digital versatile disc (DVD)), mobile phones, portable game machines, portable information terminals, e-book readers, video cameras, digital still cameras, high-frequency heating apparatus such as microwaves, electric rice cookers, electric washing machines, air-conditioning systems

such as air conditioners, electric refrigerators, electric freezers, electric refrigerator-freezers, freezers for preserving DNA, dialysis devices, and the like. In addition, moving objects driven by an electric motor using electric power from a power storage device are also included in the category of electric devices. As examples of the moving objects, electric vehicles, hybrid vehicles which include both an internal-combustion engine and an electric motor, motorized bicycles including motor-assisted bicycles, and the like can be given.

[0086]

Examples of electric devices of this embodiment are described with reference to FIG. 6 and FIGS. 7A and 7B.

[0087]

A display device 5000 shown in FIG. 6 includes a housing 5001, a display portion 5002, a speaker portion 5003, a power storage device 5004, and the like. The display device 5000 corresponds to a display device for TV broadcast reception.

[0088]

Note that the display device disclosed in this specification includes, in its category, all of information display devices for personal computers, advertisement displays, and the like besides TV broadcast reception.

[0089]

As the display portion 5002, a display device such as a liquid crystal display device, a light-emitting device in which a light-emitting element such as an organic EL element is provided in each pixel, an electrophoresis display device, a digital micromirror device (DMD), a plasma display panel (PDP), or a field emission display (FED) can be used, for example.

[0090]

The power storage device 5004 is provided in the housing 5001. As the power storage device 5004, the power storage device described in Embodiment 2 can be used for example.

[0091]

The display device 5000 can receive electric power from a commercial power supply. Alternatively, the display device 5000 can use electric power stored in the power storage device 5004. Thus, even when electric power cannot be supplied from

the commercial power supply because of power outage or the like, the display device 5000 can be operated with use of the power storage device 5004 as a power supply.

[0092]

A lighting device 5100 shown in FIG. 6 is an installation lighting device. The lighting device 5100 includes a housing 5101, a light source 5102, and a power storage device 5103.

[0093]

As the light source 5102, an artificial light source which emits light artificially by using electric power can be used. Examples of artificial light source include discharge lamps such as an incandescent lamp and a fluorescent lamp, and light-emitting elements such as a light-emitting diode and an organic EL element.

[0094]

The power storage device 5103 is provided in a ceiling 5104 on which the housing 5101 and the light source 5102 are installed. Note that the power storage device 5103 may be provided in the housing 5101, not being limited to the above case.

[0095]

The lighting device 5100 can receive power from a commercial power supply. Alternatively, the lighting device 5100 can use power stored in the power storage device 5103. Thus, even when electric power cannot be supplied from the commercial power supply because of power outage or the like, the lighting device 5100 can be operated with use of the power storage device 5103 as a power supply.

[0096]

Note that although the installation lighting device 5100 shown in FIG. 6 is provided in the ceiling 5104, it is not limited thereto. The power storage device can be used in an installation lighting device provided in a wall 5105, a floor 5106, a window 5107, or the like, besides in the ceiling 5104. Alternatively, the power storage device can be used in a tabletop lighting device and the like.

[0097]

An air conditioner in FIG. 6 includes an indoor unit 5200 and an outdoor unit 5204.

[0098]

The indoor unit 5200 includes a housing 5201, a ventilation duct 5202, the

power storage device 5203, and the like. Note that although the power storage device 5203 shown in FIG. 6 is provided in the indoor unit 5200, it is not limited thereto. For example, the power storage device 5203 may be provided in the outdoor unit 5204. Alternatively, the power storage devices 5203 may be provided in both the indoor unit  
5 5200 and the outdoor unit 5204.

[0099]

The air conditioner can receive electric power from the commercial power supply. Alternatively, the air conditioner can use electric power stored in the power storage device 5203. Specifically, in the case where the power storage devices 5203  
10 are provided in both the indoor unit 5200 and the outdoor unit 5204, the air conditioner can be operated with use of the power storage device 5203 as a power supply even when electric power cannot be supplied from the commercial power supply because of power outage or the like.

[0100]

Note that although the separated air conditioner including the indoor unit and the outdoor unit is shown in FIG. 6 as an example, the power storage device may be used in an air conditioner in which the functions of an indoor unit and an outdoor unit are integrated in one housing.  
15

[0101]

An electric refrigerator-freezer 5300 shown in FIG. 6 includes a housing 5301, a door for a refrigerator 5302, a door for a freezer 5303, and the power storage device 5304.  
20

[0102]

The power storage device 5304 is provided in the housing 5301.

25 [0103]

The electric refrigerator-freezer 5300 can receive power from a commercial power supply. Alternatively, the electric refrigerator-freezer 5300 can use power stored in the power storage device 5304. Thus, even when electric power cannot be supplied from the commercial power supply because of power outage or the like, the  
30 electric refrigerator-freezer 5300 can be operated with use of the power storage device 5304 as a power supply.

[0104]

In addition, a high-frequency heating apparatus such as a microwave and an electric device such as an electric rice cooker require high power in a short time. The stop of supplying a commercial power supply in use of electric devices can be prevented by using the power storage device as an auxiliary power supply for supplying electric power which cannot be supplied enough by a commercial power supply.

[0105]

In addition, in a time period when electric devices are not used, specifically when the proportion of the amount of power which is actually used to the total amount of power which can be supplied by a commercial power supply source (such a proportion referred to as usage rate of power) is low, power can be stored in the power storage device, whereby an increase in usage rate of power can be suppressed in a time period when the electric devices are used. In the case of the electric refrigerator-freezer 5300, electric power can be stored in the power storage device 5304 at night time when the temperature is low and the door for a refrigerator 5302 and the door for a freezer 5303 are not opened or closed. The power storage device 5304 is used as an auxiliary power supply in daytime when the temperature is high and the door for a refrigerator 5302 and the door for a freezer 5303 are opened and closed; thus, the usage rate of electric power in daytime can be reduced.

[0106]

Further, the electric device illustrated in FIGS. 7A and 7B is an example of a folding mobile information terminal. FIG. 7A is a schematic external view, and FIG. 7B is a block diagram.

[0107]

The electric device in FIGS. 7A and 7B includes a housing 6000a, a housing 6000b, a panel 6001a, a panel 6001b, a hinge 6002, a button 6003, a connection terminal 6004, and a storage medium insertion portion 6005, as illustrated in FIG. 7A. In addition, the electric device in FIGS. 7A and 7B has a power source portion 6101, a wireless communication portion 6102, an arithmetic portion 6103, an audio portion 6104, and a panel portion 6105, as illustrated in FIG. 7B.

[0108]

The panel 6001a is provided in the housing 6000a.

[0109]

The panel 6001b is provided in the housing 6000b. The housing 6000b is connected to the housing 6000a with the hinge 6002.

[0110]

The panel 6001a and the panel 6001b function as display panels. For example,  
5 the panel 6001a and the panel 6001b may display different images or one image.

[0111]

Further, one of or both the panel 6001a and the panel 6001b may function as a touch panel. In this case, data may be input in such a manner that an image of a keyboard is displayed on one of or both the panel 6001a and the panel 6001b and then  
10 touched with a finger 6010 or the like. Alternatively, the display panel and the touch panel may be stacked, so that one of or both the panel 6001a and the panel 6001b are formed. Further alternatively, one of or both the panel 6001a and the panel 6001b may be formed with use of an input-output panel provided with a display circuit and a light detection circuit.

15 [0112]

In the electric device illustrated in FIGS. 7A and 7B, the housing 6000a is overlapped with the housing 6000b by moving the housing 6000a or the housing 6000b with use of the hinge 6002, so that the electric device can be folded.

[0113]

20 The button 6003 is provided on the housing 6000b. Alternatively, the button 6003 may be provided on the housing 6000a. Further alternatively, a plurality of buttons 6003 may be provided on one of or both the housing 6000a and the housing 6000b. For example, when the button 6003 which is a power button is provided and pushed, the state of the electric device can be controlled, i.e., the electric device can be  
25 set to an on state or an off state, by putting the button 6003.

[0114]

The connection terminal 6004 is provided on the housing 6000a. Alternatively, the connection terminal 6004 may be provided on the housing 6000b. Further alternatively, a plurality of connection terminals 6004 may be provided on one  
30 of or both the housing 6000a and the housing 6000b. For example, when the electric device is connected to a personal computer via the connection terminal 6004, data stored in the electric device may be rewritten using the personal computer.

[0115]

The storage medium insertion portion 6005 is provided on the housing 6000a. Alternatively, the storage medium insertion portion 6005 may be provided on the housing 6000b. Further alternatively, a plurality of storage medium insertion portions 6005 may be provided on one of or both the housing 6000a and the housing 6000b. For example, when a card storage medium is inserted into the storage medium insertion portion, data can be read from the card storage medium and written into to the electric device, or data can be read from the electric device and written to the card storage medium.

[0116]

The power source portion 6101 has a function of supplying power for driving the electric device. For example, from the power source portion 6101, power is supplied to the wireless communication portion 6102, the arithmetic portion 6103, the audio portion 6104, and the panel portion 6105. The power source portion 6101 is provided with a power storage device 6111. The power storage device 6111 is provided in one of or both the housing 6000a and the housing 6000b. As the power storage device 6111, the power storage device described in Embodiment 2 can be employed. Note that a power supply circuit which generates a power supply voltage for driving the electric device may be provided in the power source portion 6101. In this case, in the power supply circuit, the power supply voltage is generated using power supplied from the power storage device 6111. Further, the power source portion 6101 may be connected to a commercial power supply.

[0117]

The wireless communication portion 6102 has a function of transmitting and receiving electric waves. For example, the wireless communication portion 6102 is provided with an antenna, a demodulation circuit, a modulation circuit, and the like. In this case, for example, electric waves are transmitted and received at the antenna, whereby data is exchanged with an external device. Note that a plurality of antennas may be provided in the wireless communication portion 6102.

[0118]

The arithmetic portion 6103 has a function of conducting arithmetic processing in accordance with instruction signals input from the wireless communication portion

6102, the audio portion 6104, and the panel portion 6105, for example. For example, the arithmetic portion 6103 is provided with a CPU, a logic circuit, a memory circuit, and the like.

[0119]

5           The audio portion 6104 has a function of controlling input/output of sound that is audio data. For example, the audio portion 6104 is provided with a speaker and a microphone.

[0120]

10           The power source portion 6101, the wireless communication portion 6102, the arithmetic portion 6103, and the audio portion 6104 are provided, for example, inside one of or both the housing 6000a and the housing 6000b.

[0121]

15           The panel portion 6105 has a function of controlling operation of the panel 6001a (also referred to as panel A) and the panel 6001b (also referred to as panel B). Note that a driver circuit, which controls driving of the panel 6001a and the panel 6001b, is provided in the panel portion 6105, whereby operation of the panel 6001a and the panel 6001b may be controlled.

[0122]

20           Note that a control circuit may be provided in one or a plurality of the power source portion 6101, the wireless communication portion 6102, the arithmetic portion 6103, the audio portion 6104, and the panel portion 6105, thereby controlling operation. Further, a control circuit may be provided in the arithmetic portion 6103, thereby controlling operation of one or a plurality of the power source portion 6101, the wireless communication portion 6102, the audio portion 6104, and the panel portion 6105.

25           [0123]

          Further, a memory circuit may be provided in one or a plurality of the power source portion 6101, the wireless communication portion 6102, the audio portion 6104, and the panel portion 6105, whereby data necessary for operation may be stored in the memory circuit. Thus, operation speed can be improved.

30           [0124]

          The electric device illustrated in FIGS. 7A and 7B can receive electric power from the commercial power supply and use power stored in the power storage device

6111. Thus, even when electric power cannot be supplied from the commercial power supply because of power outage or the like, the electric device can be operated with use of the power storage device 6111 as a power supply.

[0125]

5 When the structure shown in FIGS. 7A and 7B is employed, the electric device can have one or a plurality of functions of a telephone set, an e-book reader, a personal computer, and a game machine, for example.

[0126]

The foregoing has described an example of an electric device according to this  
10 embodiment.

[0127]

As described with reference to FIG. 6 and FIGS. 7A and 7B, in an example of an electric device according to this embodiment, a power storage device is provided, whereby the electric device can be driven with electric power supplied from the power  
15 storage device. Thus, even when, for example, external electric power is not supplied, the electric device can be driven.

[Example 1]

[0128]

In this example,  $\text{LiFePO}_4$  (lithium iron phosphate) formed by a production  
20 method described in Embodiment 1 will be described.

[0129]

First, a production method of  $\text{LiFePO}_4$  is described.

[0130]

In the production method of  $\text{LiFePO}_4$  according to this example, raw materials  
25 were weighed so that a molar ratio,  $\text{LiOH}\cdot\text{H}_2\text{O}:\text{FeCl}_2\cdot 4\text{H}_2\text{O}:\text{NH}_4\text{H}_2\text{PO}_4 = 2:1:1$ , was obtained. At this time, Fe was weighed to have a concentration of 0.2 M with respect to 100 ml of water.

[0131]

Next, in a nitrogen atmosphere, the weighed  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ , and  
30  $\text{NH}_4\text{H}_2\text{PO}_4$  were each dissolved in 30 ml of water which had been subjected to nitrogen bubbling, so that a solution containing Li, a solution containing P, and a solution

containing Fe were made.

[0132]

Next, the solution containing Li was dripped into the solution containing P in a nitrogen atmosphere, so that a solution containing Li and P was made. At this time,

5  $\text{Li}_3\text{PO}_4$  was deposited in the mixed solution.

[0133]

Next, the solution containing Fe was dripped into the solution containing Li and P in a nitrogen atmosphere, so that a mixture solution containing Li, P, and Fe was made. At this time, a  $\text{LiFePO}_4$  precursor was deposited in the mixture solution.

10 [0134]

Next, 10 ml of water which had been subjected to nitrogen bubbling was added to the mixture solution. As a result, the amount of the mixture solution was 100 ml. The oxygen concentration of the thus obtained mixture solution was 4.5 ppm.

[0135]

15 Next, after the mixture solution was transferred into an autoclave, the solution was reacted for 15 hours at a temperature of 150 °C while being stirred in a nitrogen atmosphere. Note that the pressure at this step was 0.4 MPa.

[0136]

20 Then, the solution reacted in the autoclave was filtered in an air atmosphere, and the left compound was washed ten times with pure water. After washing, the compound was dried in a vacuum at a temperature of 50 °C.

[0137]

Through the above steps,  $\text{LiFePO}_4$  was formed.

[0138]

25 In addition, the formed  $\text{LiFePO}_4$  was observed with a scanning electron micrograph (SEM). The observation result is shown in FIG. 8.

[0139]

30 Furthermore, a comparison example  $\text{LiFePO}_4$  was formed. In a process for forming the comparison example  $\text{LiFePO}_4$ , all the treatment was performed in an air atmosphere whereas some of the treatment in the process for forming the above-described  $\text{LiFePO}_4$  was performed in a nitrogen atmosphere. Other than the

atmosphere, the production conditions were the same as those of the above  $\text{LiFePO}_4$ . The formed comparison example  $\text{LiFePO}_4$  was observed with a SEM. The observation result is shown in FIG. 9.

[0140]

As shown in FIG. 8, the  $\text{LiFePO}_4$  has a plurality of crystals which are rectangular solids. In addition, variation in crystal shape of the  $\text{LiFePO}_4$  in FIG. 8 is small as compared with that of the  $\text{LiFePO}_4$  in FIG. 9. The above results indicate that variation in crystal shape in the case where  $\text{LiFePO}_4$  is formed in a nitrogen atmosphere can be reduced as compared with the case where  $\text{LiFePO}_4$  is formed in an air atmosphere.

#### EXPLANATION OF REFERENCE

[0141]

161: rectangular solid, 201: positive electrode, 202: negative electrode, 203: electrolyte, 204: separator, 211: positive electrode current collector, 212: positive electrode active material layer, 221: negative electrode current collector, 222: negative electrode active material layer, 301: positive electrode, 302: negative electrode, 304: separator, 305: housing, 306: housing, 307: ring-shaped insulator, 308: spacer, 309: washer, 5000: display device, 5001: housing, 5002: display portion, 5003: speaker portion, 5004: power storage device, 5100: lighting device, 5101: housing, 5102: light source, 5103: power storage device, 5104: ceiling, 5105: wall, 5106: floor, 5107: window, 5200: indoor unit, 5201: housing, 5202: ventilation duct, 5203: power storage device, 5204: outdoor unit, 5300: electric refrigerator-freezer, 5301: housing, 5302: door for refrigerator, 5303: door for freezer, 5304: power storage device, 6000a: housing, 6000b: housing, 6001a: panel, 6001b: panel, 6002: hinge, 6003: button, 6004: connection terminal, 6005: storage medium insertion portion, 6010: finger, 6101: power source portion, 6102: wireless communication portion, 6103: arithmetic portion, 6104: audio portion, 6105: panel portion, 6111: power storage device

This application is based on Japanese Patent Application serial no. 2011-189027 filed with Japan Patent Office on August 31, 2011, the entire contents of which are hereby incorporated by reference.

## CLAIMS

1. A production method of a compound, comprising the steps of:

forming a solution containing lithium (Li) in an atmosphere where an oxygen

5 concentration is lower than an oxygen concentration in air;

forming a solution containing phosphorus (P) in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air;

forming a solution containing one or more transition metals selected from iron (Fe), cobalt (Co), nickel (Ni), and manganese (Mn) in an atmosphere where an oxygen  
10 concentration is lower than an oxygen concentration in air;

mixing the solution containing Li and the solution containing P in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air, whereby forming a solution containing Li and P;

mixing the solution containing Li and P and the solution containing the  
15 transition metal in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air, thereby forming a mixture solution; and

forming a compound by a hydrothermal method in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air,

wherein the compound is represented by a general formula  $\text{LiMPO}_4$ , and

20 wherein M denotes one or more of Fe, Co, Ni, and Mn.

2. The production method according to claim 1, wherein an oxygen concentration of the mixture solution is lower than or equal to 4.5 ppm.

25 3. The production method according to claim 1, wherein the atmosphere where an oxygen concentration is lower than an oxygen concentration in air is a nitrogen atmosphere.

4. The production method according to claim 1, wherein the atmosphere where  
30 an oxygen concentration is lower than an oxygen concentration in air is a mixed atmosphere of nitrogen and hydrogen.

5. The production method according to claim 1, wherein the compound has a crystal shape of a rectangular solid.

6. A method for manufacturing a power storage device, wherein a positive  
5 electrode of the power storage device is formed using the compound formed by the production method according to claim 1.

7. A production method of a compound, comprising the steps of:

forming a solution containing lithium (Li) in an atmosphere where an oxygen  
10 concentration is lower than an oxygen concentration in air;

forming a solution containing phosphorus (P) in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air;

forming a solution containing one or more transition metals selected from iron (Fe), cobalt (Co), nickel (Ni), and manganese (Mn) in an atmosphere where an oxygen  
15 concentration is lower than an oxygen concentration in air;

mixing the solution containing Li and the solution containing P in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air, thereby forming a solution containing Li and P;

mixing the solution containing Li and P and the solution containing the  
20 transition metal in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air, thereby forming a mixture solution;

adding a reducing agent to the mixture solution; and

forming a compound by a hydrothermal method in an atmosphere where an oxygen concentration is lower than an oxygen concentration in air,

25 wherein the compound is represented by a general formula  $\text{LiMPO}_4$ , and wherein M denotes one or more of Fe, Co, Ni, and Mn.

8. The production method claim 7, further comprising the steps of:

introducing the reducing agent into a container resistant to pressure before  
30 adding the reducing agent to the mixture solution;

introducing the mixture solution into the container resistant to pressure; and

forming the compound by the hydrothermal method in the container resistant to

pressure.

9. The production method according to claim 7, wherein an oxygen concentration of the mixture solution is lower than or equal to 4.5 ppm.

5

10. The production method according to claim 7, wherein the atmosphere where an oxygen concentration is lower than an oxygen concentration in air is a nitrogen atmosphere.

10

11. The production method according to claim 7, wherein the atmosphere where an oxygen concentration is lower than an oxygen concentration in air is a mixed atmosphere of nitrogen and hydrogen.

15

12. The production method according to claim 7, wherein the compound has a crystal shape of a rectangular solid.

13. A method for manufacturing a power storage device, wherein a positive electrode of the power storage device is formed using the compound formed by the production method according to claim 7.

FIG. 1A

1/9

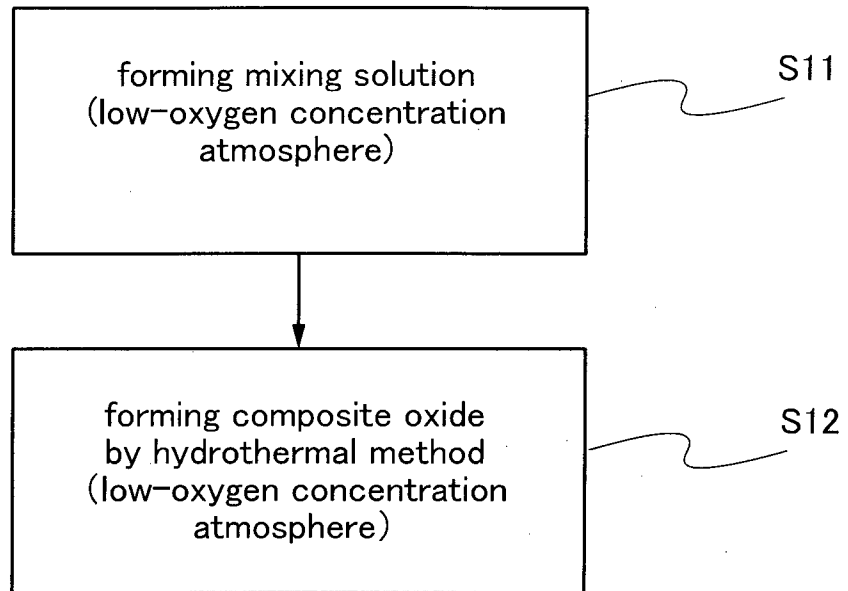
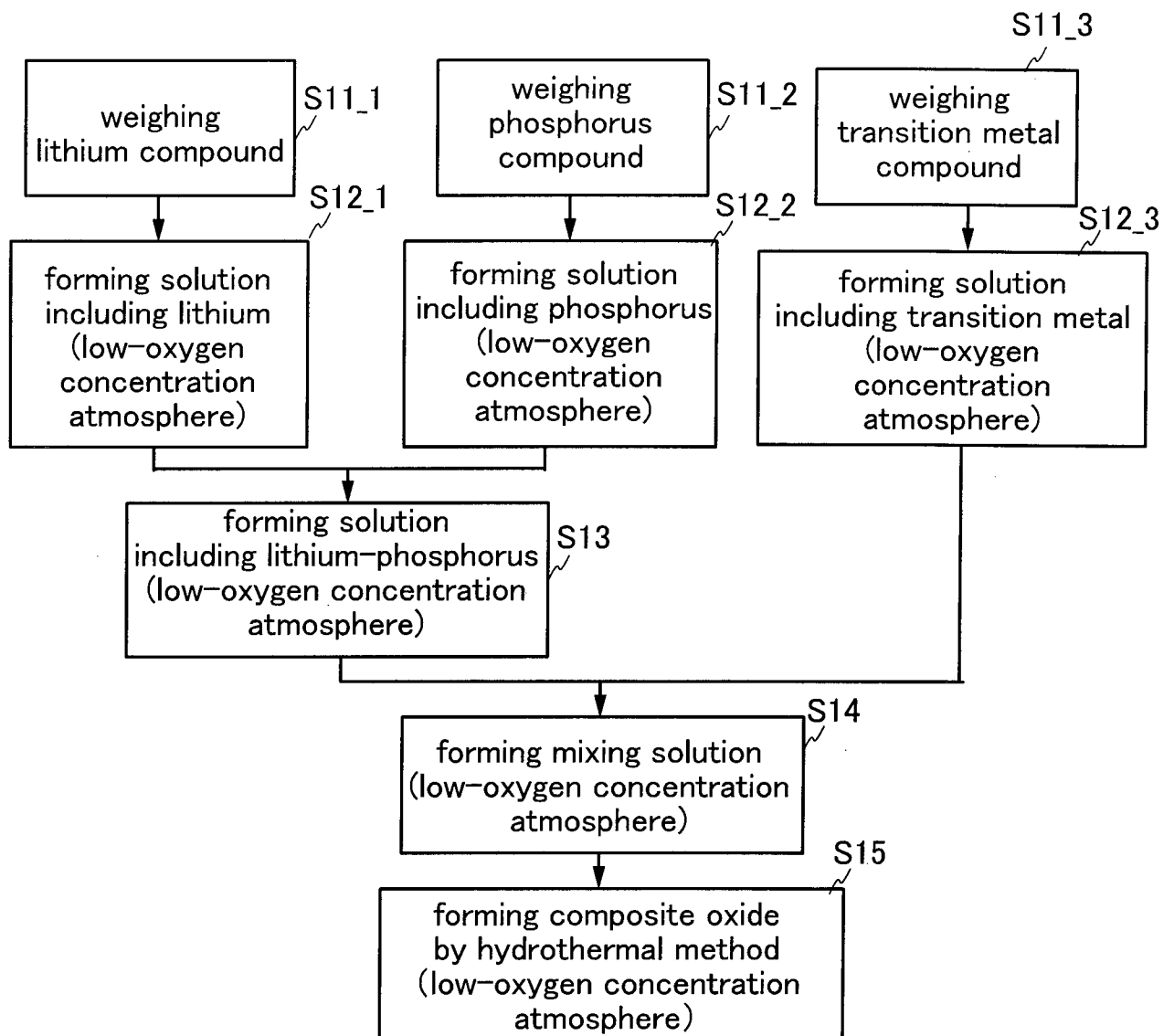


FIG. 1B



2/9

FIG. 2

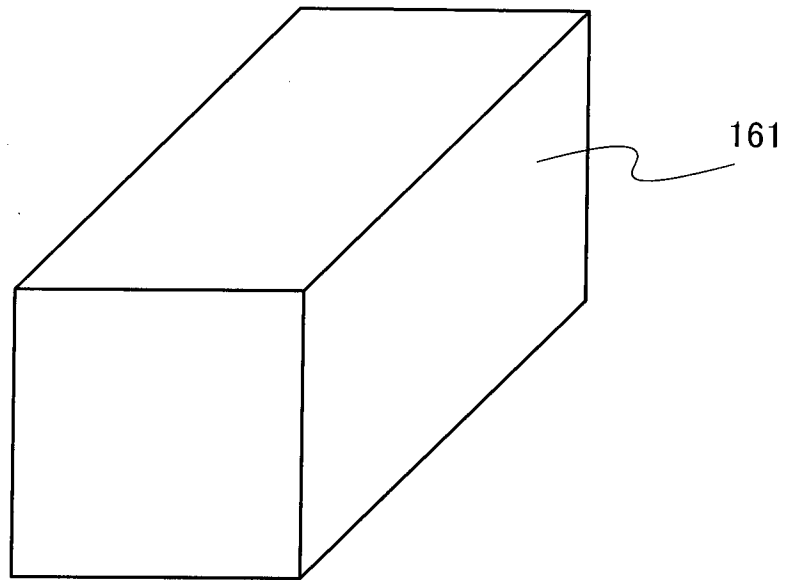
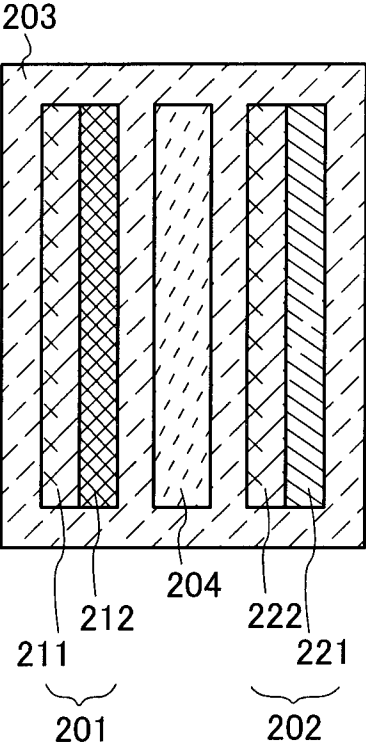


FIG. 3



4/9

FIG. 4A

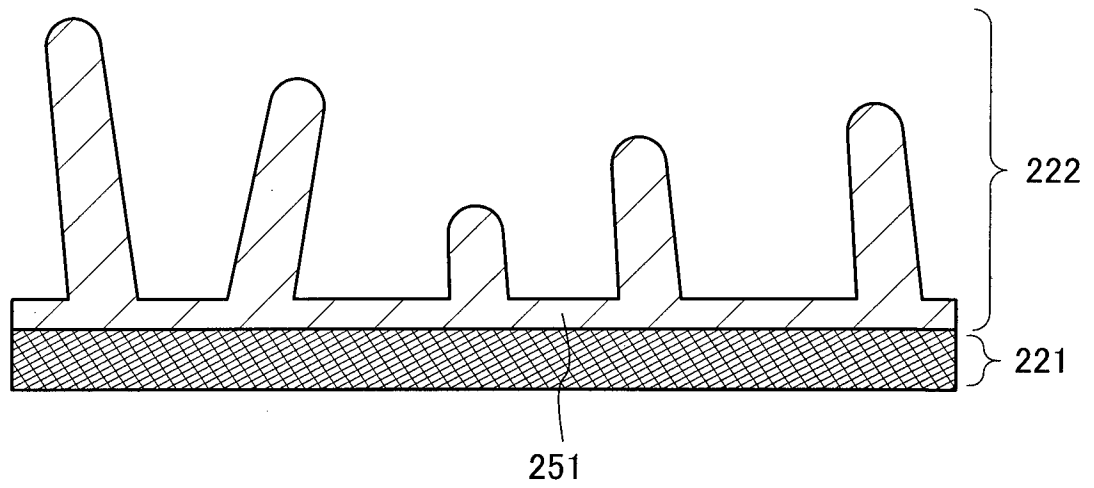
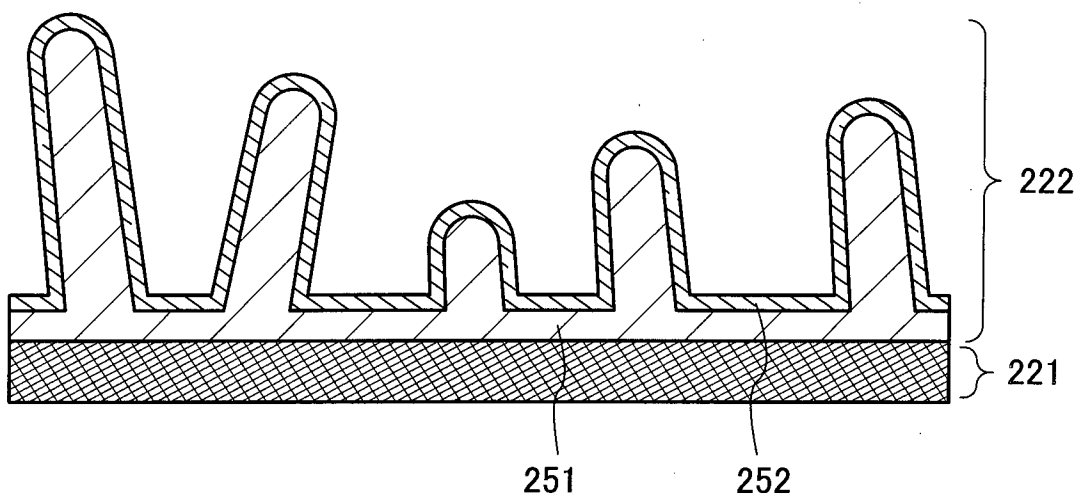
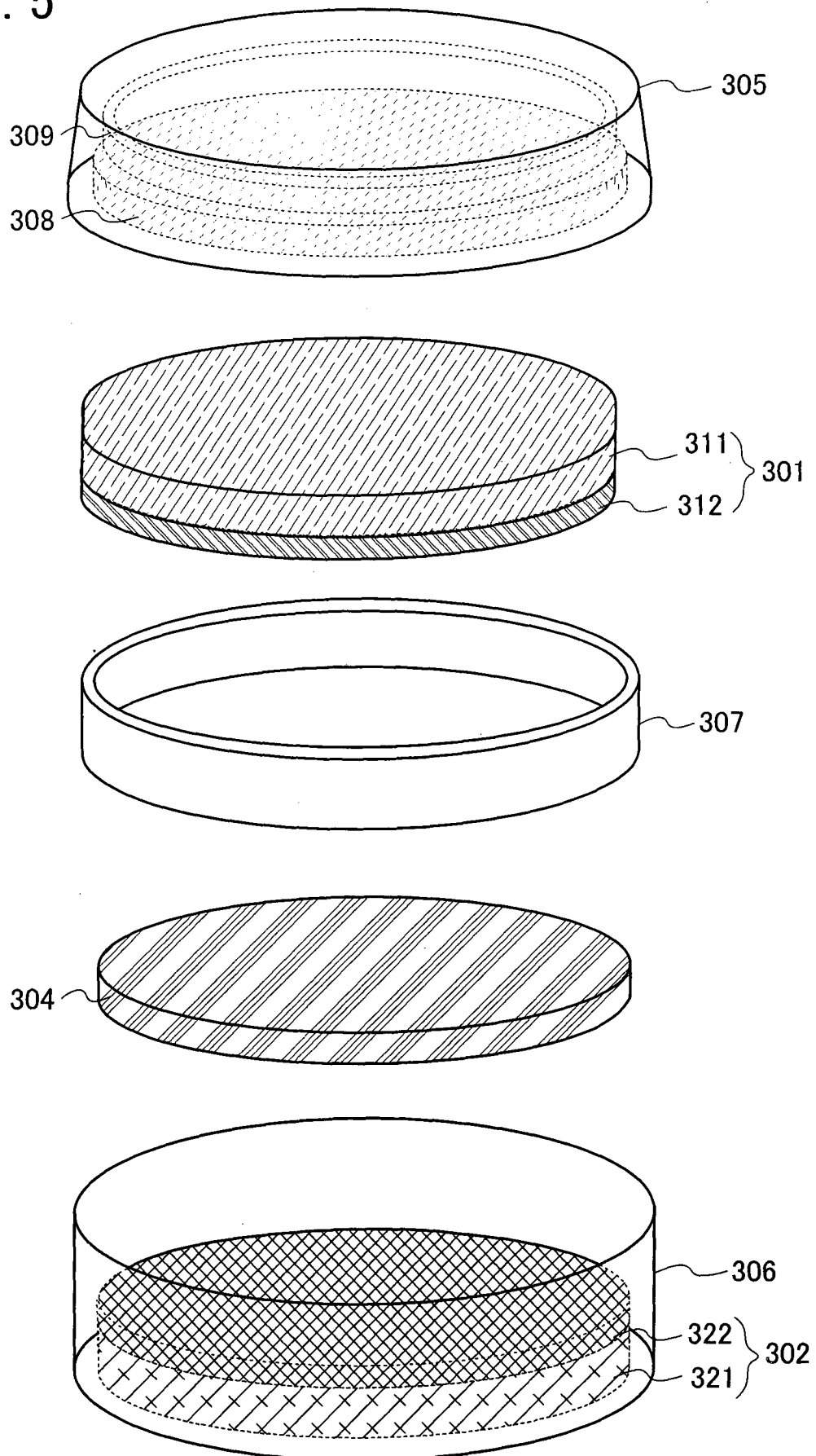


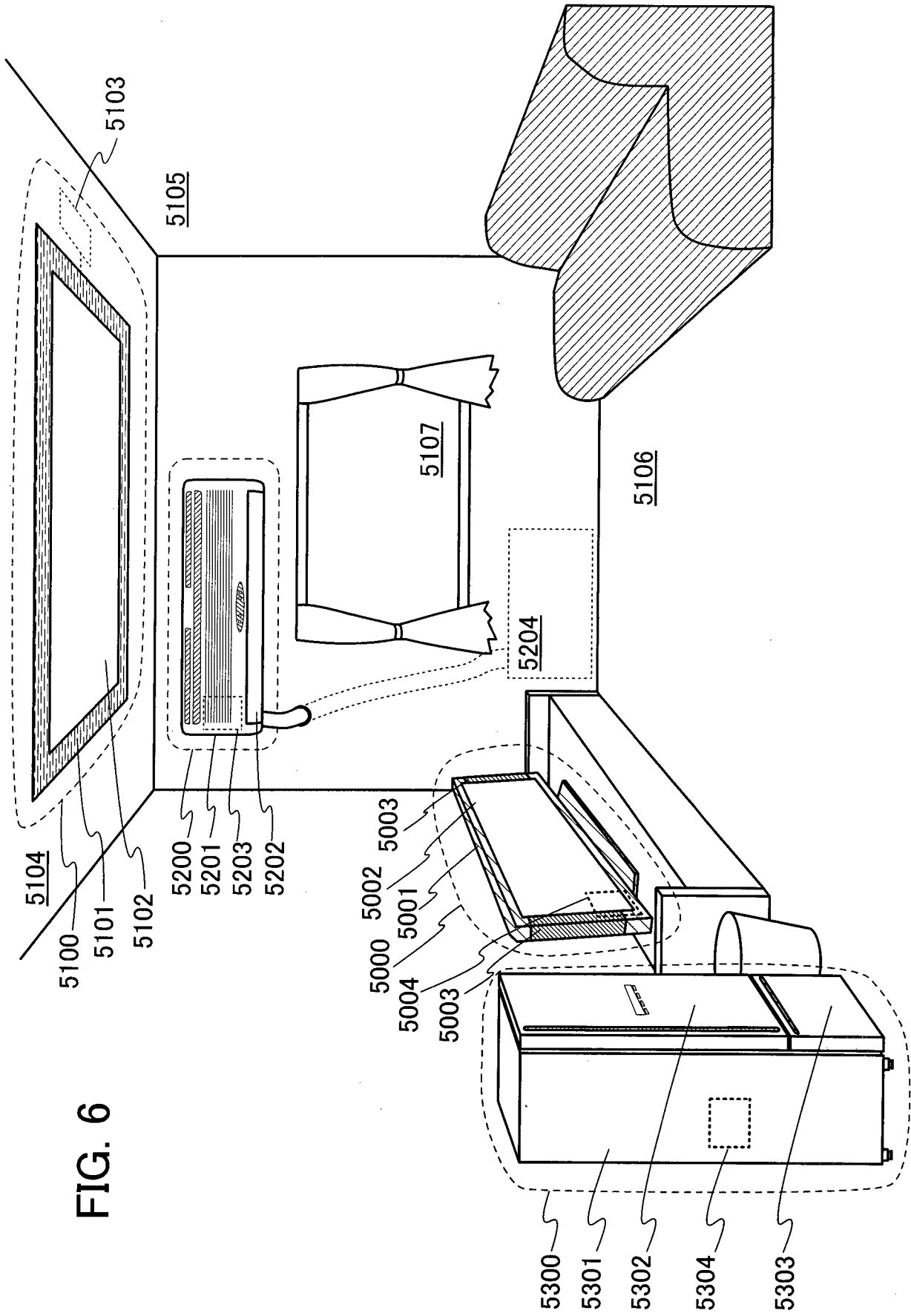
FIG. 4B



5/9

FIG. 5





7/9

FIG. 7A

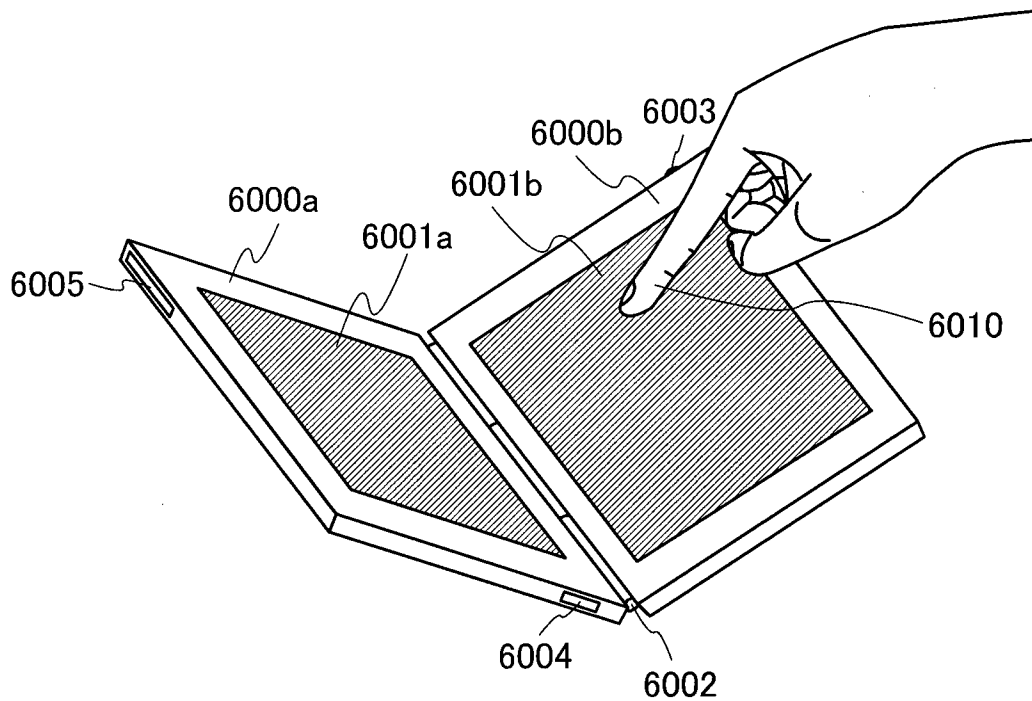


FIG. 7B

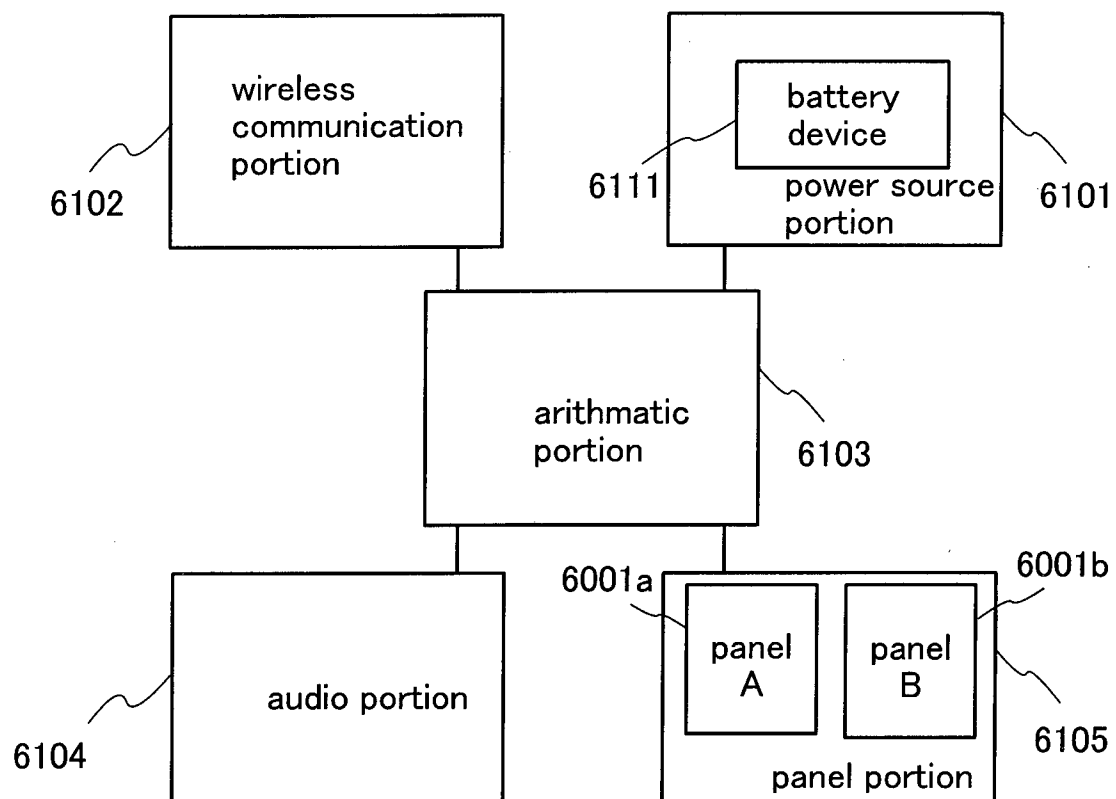


FIG. 8

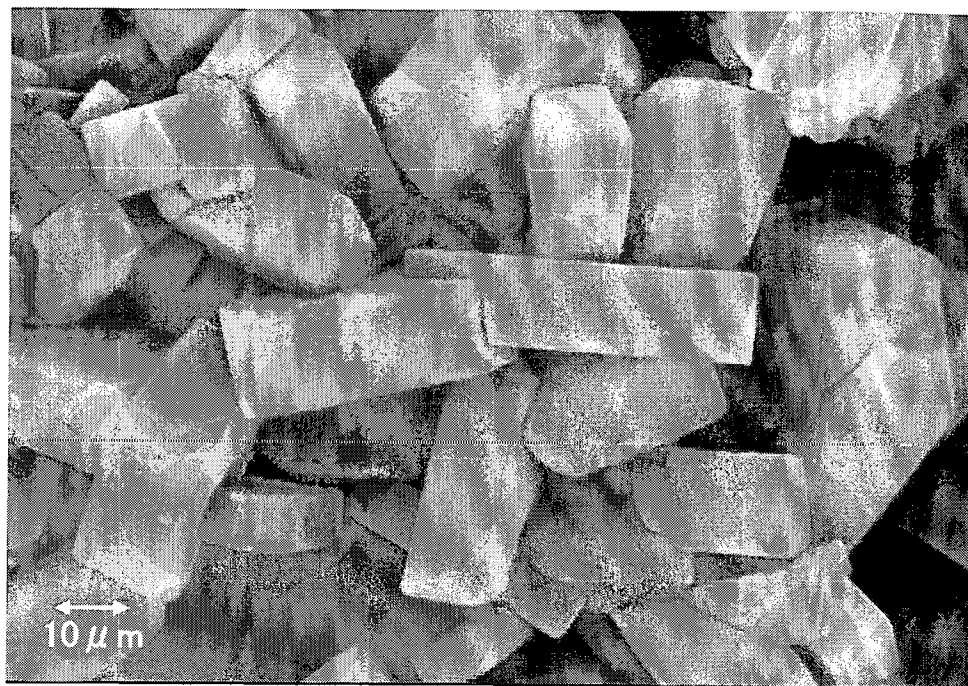


FIG. 9



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/072280

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C01B25/45 (2006.01) i, H01M4/58 (2010.01) i

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)

Int.Cl. C01B25/45, H01M4/58

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

Published examined utility model applications of Japan 1922-1996  
 Published unexamined utility model applications of Japan 1971-2012  
 Registered utility model specifications of Japan 1996-2012  
 Published registered utility model applications of Japan 1994-2012

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                              | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X<br>Y    | JP 2007-511458 A (SÜD-CHEMIE AG) 2007.05.10, claims 1, 4, 22, 23, page 5 lines 7-8, page 9 lines 17-19 & US 2007/0054187 A1 & EP 1682446 A1 & WO 2005/051840 A1 | 1-3, 5, 6<br>4, 7-13  |
| Y         | JP 2011-121802 A (TDK KABUSHIKIGAISHA) 2011.06.23, claim 1, [0023] (Family: none)                                                                               | 4, 11                 |
| Y         | JP 2009-266813 A (TODAKOGYO KABUSHIKIGAISHA) 2009.11.12, claim 3 (Family: none)                                                                                 | 7-13                  |
| E, X      | WO 2012/147766 A1 (SHOWA DENKO K.K.) 2012.11.01, [0001], [0070] (Family: none)                                                                                  | 1-3, 5, 6             |

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“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

“&amp;” document member of the same patent family

Date of the actual completion of the international search

22.11.2012

Date of mailing of the international search report

04.12.2012

Name and mailing address of the ISA/JP

**Japan Patent Office**

3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer

**Yoshiyuki Nishiyama**

Telephone No. +81-3-3581-1101 Ext. 3416

4G

3129