



(51) International Patent Classification:

C01G 45/00 (2006.01) H01M 4/505 (2010.01)
H01M 4/36 (2006.01)

(21) International Application Number:

PCT/JP20 14/062542

(22) International Filing Date:

1 May 2014 (01.05.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2013-100358 10 May 2013 (10.05.2013) JP
2013-100383 10 May 2013 (10.05.2013) JP

(71) Applicant: SEMICONDUCTOR ENERGY LABORATORY CO., LTD. [JP/JP]; 398, Hase, Atsugi-shi, Kanagawa, 2430036 (JP).

(72) Inventors: KAWAKAMI, Takahiro; c/o SEMICONDUCTOR ENERGY LABORATORY CO., LTD., 398, Hase, Atsugi-shi, Kanagawa, 2430036 (JP). YOSHITOMI, Shuhei. OCHIALI, Teruaki. SEO, Satoshi. MOMMA, Yohei. SAITO, Yumiko.

(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, IR, IS, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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.

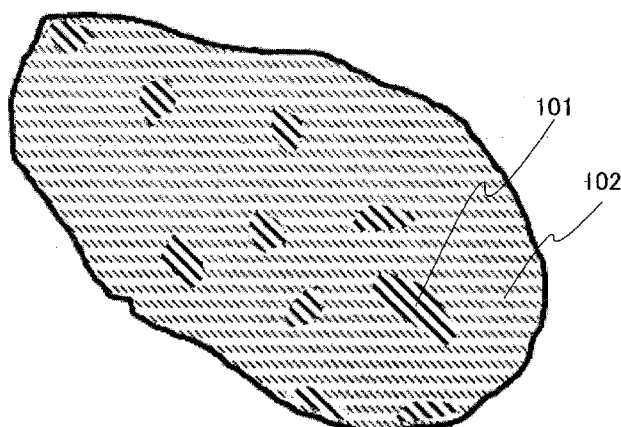
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: LITHIUM MANGANESE OXIDE COMPOSITE, SECONDARY BATTERY, AND MANUFACTURING METHOD THEREOF

FIG. 1



(57) Abstract: To increase the amount of lithium ions that can be received and released in and from a positive electrode active material to achieve high capacity and high energy density of a secondary battery. A composite material of crystallites of LiMn_2O_4 (crystallites with a spinel crystal structure) and crystallites of Li_2MnO_3 (crystallites with a layered rock-salt crystal structure) is used as a positive electrode active material. The lithium manganese oxide composite has high structural stability and high capacity.

DESCRIPTION

**LITHIUM MANGANESE OXIDE COMPOSITE, SECONDARY BATTERY,
AND MANUFACTURING METHOD THEREOF**

5

TECHNICAL FIELD

[0001]

The present invention relates to the structure and a manufacturing method of a secondary battery. In particular, the present invention relates to a positive electrode active material of a lithium-ion secondary battery.

10

BACKGROUND ART

[0002]

Examples of the secondary battery include a nickel-metal hydride battery, a lead-acid battery, and a lithium-ion secondary battery.

15

[0003]

Such secondary batteries are used as power sources in portable information terminals typified by mobile phones. In particular, lithium-ion secondary batteries have been actively developed because capacity thereof can be increased and size thereof can be reduced.

20

[0004]

In a lithium-ion secondary battery, as a positive electrode active material, a phosphate compound having an olivine structure and containing lithium (Li) and iron (Fe), manganese (Mn), cobalt (Co), or nickel (Ni), such as lithium iron phosphate (LiFeP0₄), lithium manganese phosphate (LiMnPO₄), lithium cobalt phosphate (LiCoPO₄), and lithium nickel phosphate (LiNiPO₄), which are disclosed in Patent Document 1, has been known.

25

[Reference]

[0005]

30

[Patent Document 1] Japanese Published Patent Application No. H11-25983

DISCLOSURE OF INVENTION

[0006]

LiCoO₂ is used as a positive electrode active material of a lithium-ion secondary battery. However, cobalt, a raw material of LiCoO₂, is expensive. In view of this problem, an object is to provide a positive electrode active material that can be
5 formed at low cost with the use of manganese, which is an inexpensive material.

[0007]

Another object is to increase the amount of lithium ions that can be received and released in and from a positive electrode active material to achieve high capacity and high energy density of a secondary battery.

10 [0008]

Further, high ion conductivity and high electric conductivity are required as properties of a positive electrode active material of a lithium-ion secondary battery. Thus, another object is to provide a positive electrode active material having high ion conductivity and high electric conductivity.

15 [0009]

The inventors have found that a novel material can be formed by combining lithium manganese oxides, LiMn₂O₄ with a spinel crystal structure and Li₂MnO₃ with a layered rock-salt (a-NaFeO₂ type) crystal structure.

[0010]

20 The novel material is a lithium manganese oxide composite having a spinel crystal structure in part of the surface of each particle with a layered rock-salt crystal structure. In the case of using this novel material as a positive electrode active material of a lithium-ion secondary battery, lithium inside the particle is released or diffused through the region with a spinel crystal structure of the surface of the particle,
25 resulting in high capacity. Furthermore, the novel material includes a plurality of portions each with a spinel crystal structure such that the each particle is dotted with them. Note that in each particle of the novel structure, a region with a layered rock-salt crystal structure is larger than the regions each with a spinel crystal structure.

[0011]

30 Each particle contains a plurality of crystallites and the size of each crystallite is smaller than that of the particle, specifically, less than or equal to 1 μm. Note that

whether the particle contains a plurality of crystallites can be determined with a high resolution transmission electron microscope (TEM). Furthermore, a crystal structure can be determined with the use of a fast Fourier transformation pattern (FFT pattern) using a high resolution TEM image (multiple wave interference image). By comparison with data (e.g., an incident angle or a diffraction intensity) on Li_2MnO_3 with a layered rock-salt crystal structure or data (e.g., an incident angle or a diffraction intensity) on LiMn_2O_4 with a spinel structure, which is contained in a JCPDS card (database on index minerals for powder X-ray diffraction patterns), a crystal structure can be determined. Thus, when some portions in the same particle of the novel material are determined, at least a spot corresponding to a spinel crystal structure and a spot corresponding to a layered rock-salt crystal structure are observed. Note that a crystallite means the largest aggregation that can be regarded as a single crystal and refers to a fine single crystal. The size of one crystallite can be calculated (by Scherrer formula) from peak broadening of a diffraction pattern obtained using a powder X-ray diffraction method.

[0012]

The novel material can also be referred to as a composite material of crystallites of LiMn_2O_4 (crystallites with a spinel crystal structure) and crystallites of Li_2MnO_3 (crystallites with a layered rock-salt crystal structure). FIG. 1 is a model diagram illustrating one particle of this novel material.

[0013]

In FIG. 1, one particle includes at least two kinds of crystallites of a crystallite 101 with a spinel crystal structure and a crystallite 102 with a layered rock-salt crystal structure. As in FIG. 1, the novel material is a lithium manganese oxide composite where each particle has a spinel crystal structure and a layered rock-salt crystal structure in contact with the spinel crystal structure. When a lithium battery using this material as a positive electrode active material is charged or discharged, lithium of Li_2MnO_3 in each particle is released or received through the crystallites 101 with a spinel crystal structure which are scattered on the surface of the particle.

[0014]

FIG. 11A illustrates comparative example 1, and FIG. 11B illustrates comparative example 2. The novel material is greatly different from comparative

examples 1 and 2 in structure and property. FIG. 11A illustrates a mixture of a plurality of particles, that is, a mixture of particles each having a spinel crystal structure and a size of several micrometers (Spi-LiMn₂O₄ particles 104) and Li₂MnO₃ particles 103 each having a layered rock-salt crystal structure and a size of several micrometers.

FIG. 11B illustrates a material 105 obtained by sintering the mixture in FIG. 11A at high temperature (e.g., 1000 °C). In obtaining the Li₂MnO₃ particles 103 from comparative example 1 or 2, Li₂CO₃ (lithium carbonate) and MnCO₃ (manganese carbonate) are weighed so that the ratio of Li₂CO₃ to MnCO₃ is 1:1, and they are pulverized in a ball mill or the like and fired. In obtaining the Spi-LiMn₂O₄ particles 104, Li₂CO₃ and MnCO₃ are weighed so that the ratio of Li₂CO₃ to MnCO₃ is 0.5:2, and they are pulverized in a ball mill or the like and fired.

[0015]

There are at least two methods for forming the novel material. As for one of the methods, in the case where the ratio for weighing (also referred to as the ratio of materials) is made to be different from that of the comparative example so that the crystallites 101 with a spinel crystal structure are included at approximately 2 %, Li₂CO₃ and MnCO₃ are weighed so that the ratio of Li₂CO₃ to MnCO₃ is 0.98:1.01, and they are pulverized in a ball mill or the like and fired at higher than or equal to 800 °C and lower than or equal to 1100 °C. Note that "the crystallites 101 with a spinel crystal structure are included at approximately 2 %" means that the crystallites 102 with a layered rock-salt crystal structure are included at approximately 98 %". In the case where each particle includes the crystallites 101 with a spinel crystal structure at approximately 5 % (the crystallites with a layered rock-salt crystal structure at approximately 95 %), Li₂CO₃ and MnCO₃ are weighed so that the ratio of Li₂CO₃ to MnCO₃ is 0.955:1.03, and they are pulverized in a ball mill or the like and fired. In the case where the crystallites 101 with a spinel crystal structure are included at approximately 50 %, Li₂CO₃ and MnCO₃ are weighed so that the ratio of Li₂CO₃ to MnCO₃ is 0.64:1.28, and they are pulverized in a ball mill or the like and fired. The novel material is formed by intentionally changing the ratio of materials so that the crystallites 101 with a spinel crystal structure are included at greater than or equal to approximately 2 % and less than or equal to 50 %.

[0016]

In another method for forming the novel material, Li_2CO_3 (lithium carbonate) and MnCO_3 (manganese carbonate) are weighed so that the ratio of Li_2CO_3 to MnCO_3 is 1:1, and they are pulverized in a ball mill or the like and fired at higher than 380 °C and lower than 950 °C, preferably at approximately 500 °C. When the firing is performed at lower than 380 °C, only $\text{Spinel-LiMn}_2\text{O}_4$ particles are formed, whereas when firing is performed at higher than or equal to 950 °C, only Li_2MnO_3 particles with a layered rock-salt crystal structure are formed. Thus, firing at 500 °C enables formation of a lithium manganese oxide composite where crystallites with a spinel structure and crystallites with a layered rock-salt crystal structure exist in each particle.

[0017]

When a lithium manganese oxide where crystallites with a spinel structure and crystallites with a layered rock-salt crystal structure exist in each particle is formed, a battery including the oxide is fabricated, and the oxide is chemically analyzed to examine the element composition, the composition might be different from that calculated from the ratio of materials by less than 10 %. The present invention can be implemented without departing from the technical idea and should not be construed as being out of the scope of the present invention only because the composition of a formed substance does not exactly correspond to the ratio of materials.

[0018]

The inventors have found that a novel lithium manganese oxide composite can be formed by mixing Li_2CO_3 particles and MnCO_3 particles so that the ratio (molar mixing ratio) of Li_2CO_3 to MnCO_3 is in the range from 0.88:1.09 (= Li_2CO_3 : MnCO_3) to 0.98:1.01 (= Li_2CO_3 : MnCO_3), preferably from 0.91:1.06 (= Li_2CO_3 : MnCO_3) to 0.95:1.03 (= Li_2CO_3 : MnCO_3) and performing heat treatment at higher than or equal to 500 °C and lower than or equal to 1000 °C.

[0019]

The raw materials of the novel material are not limited to only two kinds of material; NiO among other materials, in addition to Li_2CO_3 and MnCO_3 , may be weighed and added, and they may be pulverized in a ball mill or the like and fired. The novel material can be obtained under either the air or a nitrogen atmosphere in the

firing process.

[0020]

The use of the novel material, the lithium manganese oxide composite, as a positive electrode active material of a lithium secondary battery increases the capacity and energy density of the secondary battery.

[0021]

The positive electrode active material can be used for a secondary battery that is used in a portable information terminal, a home-use constant power source device, an electric motor cycle, an electric vehicle, hybrid electric vehicle, or the like.

[0022]

The lithium manganese oxide composite disclosed in this specification has high structural stability and high capacity. Furthermore, the lithium manganese oxide composite disclosed in this specification can be formed through a simple forming process where a plurality of materials are weighed, pulverized in a ball mill or the like, and mixed, and then the mixture is fired; thus, an effect of reducing cost can be obtained and excellent mass productivity is achieved.

[0023]

Firing at a high temperature of 800 °C or higher in a synthesis process of the lithium manganese oxide composite disclosed in this specification allows the oxide to have high crystallinity and excellent cycle characteristics.

BRIEF DESCRIPTION OF DRAWINGS

[0024]

In the accompanying drawings:

FIG. 1 is a model diagram illustrating one embodiment of the present invention;

FIG. 2 is a cross-sectional TEM image of one embodiment of the present invention;

FIG. 3 is an enlarged partial image of FIG. 2;

FIG. 4 is a graph showing the relation between discharge capacity and voltage of one embodiment of the present invention and comparative examples;

FIG. 5 is a graph showing the relation between discharge capacity and voltage

of one embodiment of the present invention;

FIGS. 6A to 6C illustrate a coin-type secondary battery;

FIG. 7 illustrates a laminated secondary battery;

FIGS. 8A and 8B illustrate a cylindrical secondary battery;

FIG. 9 shows a cross-sectional TEM image and an FFT analysis result of an example;

FIG. 10 shows a cross-sectional TEM image and an FFT analysis result of an example;

FIGS. 11A and 11B are model diagrams each illustrating a comparative example;

FIG. 12 is a graph showing the relation between discharge capacity and voltage of one embodiment of the present invention; and

FIG. 13 is X-ray diffraction data of one embodiment of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0025]

Embodiments and an example of the present invention will be described below in detail with reference to the drawings. However, the present invention is not limited to the following descriptions, and it is easily understood by those skilled in the art that modes and details disclosed herein can be modified in various ways. Furthermore, the present invention is not construed as being limited to descriptions of the embodiments and the example.

[0026]

(Embodiment 1)

A method for forming a novel material will be described below in detail.

[0027]

First, starting materials lithium carbonate (Li_2CO_3), manganese carbonate (MnCO_3), and nickel oxide (NiO) are weighed.

[0028]

In this embodiment, the ratio of raw materials is adjusted according to the idea of changing the ratio. The ratio is changed to form a lithium manganese oxide composite having a spinel crystal structure in part of the surface of each particle with a

layered rock-salt crystal structure.

[0029]

In the case where Li_2CO_3 , MnCO_3 , and NiO are used at a ratio of 1:0.7:0.3 (= $\text{Li}_2\text{CO}_3:\text{MnCO}_3:\text{NiO}$), $\text{Li}_2\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ is obtained. Thus, it is important to change this ratio.

[0030]

In this embodiment, Li_2CO_3 , MnCO_3 , and NiO are weighed such that the ratio thereof is 0.84:0.8062:0.318 (= $\text{Li}_2\text{CO}_3:\text{MnCO}_3:\text{NiO}$). Note that the ratio is represented as a molar ratio. Acetone is added to the powder of these materials, and then, they are mixed in a ball mill to prepare mixed powder.

[0031]

After that, heating is performed to volatilize acetone, so that a mixed material is obtained.

[0032]

Then, the mixed material is put into a melting pot, and is fired at a temperature in the range from 800 °C to 1100 °C in the air for 5 to 20 hours inclusive to synthesize a novel material.

[0033]

Subsequently, grinding is performed to separate the sintered particles. For the grinding, acetone is added and then mixing is performed in a ball mill.

[0034]

After the grinding, heating is performed to volatilize acetone, and then, vacuum drying is performed, so that a powdery novel material is obtained.

[0035]

FIG. 2 shows a cross-sectional TEM image of the thus obtained novel material.

[0036]

FIG. 3 is an enlarged image of one of a plurality of particles in FIG. 2. As shown in FIG. 3, a region surrounded by a black dotted line corresponds to a crystallite 101 having a spinel crystal structure, and a region surrounded by a white dotted line corresponds to a crystallite 102 having a layered rock-salt crystal structure.

[0037]

When an FFT pattern is obtained by the FFT analysis from a part of the region surrounded by the black dotted line in FIG. 3, the values determined by the positional relation (e.g., a distance and an angle) of the obtained spots correspond to the data of JCPDS card No. 35-0782 (e.g., an incident angle and a diffraction intensity) on
5 LiMn_2O_4 with a spinel crystal structure which belongs to the space group $FcBm$ (number 227). Thus, the region can be identified as a spinel crystal structure.

[0038]

When an FFT pattern is obtained by the FFT analysis from a part of the region surrounded by the white dotted line in FIG. 3, the lattice constant can be determined by
10 the positional relation (a distance and an angle) of the obtained spots. Thus, the crystal structure of the region can be identified as a layered rock-salt crystal structure by Li_2MnO_3 JCPDS card No. 81-1953 (a space group $C2/c$, number 15).

[0039]

The use of this novel material as a positive electrode active material enables
15 fabrication of a positive electrode.

[0040]

FIG. 4 shows measured discharge capacity of this novel material. The vertical axis represents voltage (V), and the horizontal axis represents discharge capacity (mAh/g).

20 [0041]

In addition, comparative examples 1 and 2 will be described.

[0042]

Comparative example 1, which corresponds to FIG. 11A, is sample 1 formed in such a manner that particles each having a size of several micrometers and a spinel
25 crystal structure ($\text{Spi-LiMn}_2\text{O}_4$ particles 104) and the Li_2MnO_3 particles 103 each having a size of several micrometers and a layered rock-salt crystal structure are separately synthesized and the $\text{Spi-LiMn}_2\text{O}_4$ particles 104 and the Li_2MnO_3 particles 103 are mixed.

[0043]

30 Comparative example 2, which corresponds to FIG. 11B, is sample 2 obtained by firing sample 1 at 1000 °C.

[0044]

As shown in FIG. 4, the discharge capacity of the novel material is higher than those of comparative examples 1 and 2. Thus, the novel material, that is, a lithium manganese oxide composite having a spinel crystal structure in part of the surface of each particle with a layered rock-salt crystal structure has a high capacity although synthesized at a high temperature.

[0045]

In this embodiment, Li_2CO_3 , MnCO_3 , and NiO are used as starting materials; however, materials are not particularly limited thereto and any other material may be used as long as a lithium manganese oxide composite having a spinel crystal structure in part of the surface of each particle with a layered rock-salt crystal structure can be formed.

[0046]

(Embodiment 2)

In this embodiment, a novel material is obtained by a forming method different from that in Embodiment 1.

[0047]

First, starting materials lithium carbonate (Li_2CO_3) and manganese carbonate (MnCO_3) are weighed.

[0048]

In this embodiment, firing temperature is adjusted to synthesize a novel material.

[0049]

In this embodiment, Li_2CO_3 and MnCO_3 are weighed such that the ratio thereof is 1:1 ($= \text{Li}_2\text{CO}_3:\text{MnCO}_3$). Acetone is added to the powder of these materials, and then, they are mixed in a ball mill to prepare mixed powder. After that, heating is performed to volatilize acetone, so that a mixed material is obtained.

[0050]

Then, the mixed material is put into a melting pot, and is fired at a temperature higher than 380 °C and lower than 950 °C, preferably at approximately 500 °C, in the air for 5 to 20 hours inclusive.

[0051]

Subsequently, grinding is performed to separate the sintered particles. For the grinding, acetone is added and then mixing is performed in a ball mill.

[0052]

After the grinding, heating is performed to volatilize acetone, and then, vacuum drying is performed, so that a powdery novel material is obtained.

[0053]

When an FFT pattern is obtained by the FFT analysis using a cross-sectional TEM image of the thus obtained novel material from a region of the particle of the novel material, the region can be identified as the one with a spinel crystal structure by LiMn_2O_4 JCPDS card No. 35-0782 (a space group $Fd\bar{3}m$, number 227). When an FFT pattern is obtained by the FFT analysis from another region of the same particle, the region can be identified as the one with a layered rock-salt crystal structure by Li_2MnO_3 JCPDS card No. 81-1953 (a space group $C2/c$, number 15). Thus, the regions in the same particle can be identified as the ones with two kinds of crystal structures as in

Embodiment 1.

[0054]

These results show that the novel material substantially the same as that in Embodiment 1 can be formed. Note that since the firing temperature in Embodiment 1 is high, the crystallinity of the novel material in Embodiment 1 is higher than that of the novel material obtained in this embodiment.

[0055]

The use of the novel material of this embodiment as a positive electrode active material enables fabrication of a positive electrode.

[0056]

FIG. 5 shows measured discharge capacity of the novel material of this embodiment. FIG. 5 also shows the discharge capacity of the novel material of Embodiment 1.

[0057]

A comparative material is formed at a firing temperature lower than or equal to 380 °C, and an FFT pattern is obtained by the FFT analysis using a cross-sectional TEM image of the material. As a result, only the region identified as the one with a spinel crystal structure by LiMn_2O_4 JCPDS card No. 35-0782 (a space group $Fd\bar{3}m$, number

227) can be observed. The discharge capacity of this comparative material is measured to be as low as 110 mAh/g.

[0058]

When a comparative material is formed at a firing temperature higher than or equal to 950 °C, and an FFT pattern is obtained by the FFT analysis using a cross-sectional TEM image of the material, only the region identified as a spinel crystal structure by Li_2MnO_3 JCPDS card No. 81-1953 (a space group C2/c, number 15) can be observed. The discharge capacity of this comparative material is measured to be a low value of 18 mAh/g.

[0059]

The above results suggest that whether a particle has two kinds of crystal structures depends on the firing temperature.

[0060]

(Embodiment 3)

A method for forming a novel material will be described below in detail.

[0061]

First, starting materials Li_2CO_3 and MnCO_3 are weighed.

[0062]

In this embodiment, the ratio of materials is adjusted according to the idea of changing the ratio of materials. The ratio of materials is changed to form a lithium manganese oxide composite having a spinel crystal structure in part of the surface of each particle with a layered rock-salt crystal structure.

[0063]

Table 1 shows the target percentage of part with a spinel crystal structure in each of materials formed in this embodiment (samples A to D and comparative examples 1 to 5), the target percentage of part with a layered rock-salt crystal structure in each of the materials, and the ratios of materials. Note that forming methods of samples A to D and comparative examples 1 to 5 are substantially the same except for the ratio of materials.

[0064]

[Table 1]

	Percentage (%)		Feed ratio of materials
	Li_2MnO_3	$\text{spinel-LiMn}_2\text{O}_4$	
comperative example 1	100	0	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=1:1$
sample A	98	2	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.98:1.01$
sample B	95	5	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.955:1.03$
sample C	90	10	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.91:1.06$
sample D	85	15	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.88:1.09$
comperative example 2	80	20	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.84:1.12$
comperative example 3	60	40	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.71:1.23$
comperative example 4	50	50	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.64:1.28$
comperative example 5	0	100	$\text{Li}_2\text{CO}_3:\text{MnCO}_3=0.5:2$

[0065]

According to Table 1, the materials are weighed.

[0066]

- 5 Acetone is added to the powder of these materials, and then, they are mixed in a ball mill to prepare mixed powder. In this embodiment, the weighed materials, a zirconia ball with a diameter of 3 mm, and acetone are put into a pot made of zirconia, and wet ball milling using a planetary ball mill is performed at 400 rpm for 2 hours.

[0067]

- 10 After that, heating is performed to volatilize acetone, so that a mixed material is obtained. In this embodiment, acetone in slurry subjected to the ball milling is volatilized at 50 °C in the air to obtain the mixed material.

[0068]

- 15 Then, the mixed material is put into a melting pot, and is fired at a temperature in the range from 500 °C to 1000 °C in the air for 5 to 20 hours inclusive to synthesize a novel material. In this embodiment, a melting pot made of aluminum is filled with the mixed material that has been dried, and heating is performed at 900 °C for 10 hours.

[0069]

- 20 Subsequently, grinding is performed to separate the sintered particles. In this embodiment, the fired material, a zirconia ball with a diameter of 3 mm, and acetone are put into a pot made of zirconia, and wet ball milling using a planetary ball mill is

performed at 200 rpm for 2 hours.

[0070]

After the grinding, heating is performed to volatilize acetone, and then, vacuum drying is performed, so that powdery novel materials are obtained. In this embodiment, heating is performed on the mixture subjected to wet ball milling at 50 °C in the air to volatilize acetone, and then, vacuum drying is performed at 170 °C.

[0071]

The use of these novel materials (samples A to D) as positive electrode active materials enables fabrication of positive electrodes.

10 [0072]

FIG. 12 shows measured discharge capacity of these novel materials (samples A to D) and comparative example 1.

[0073]

As shown in FIG. 12, sample A, in which part with a spinel crystal structure occupies approximately 2 % of the whole, has higher discharge capacity than comparative example 1, which is the material containing only LiMn_2O_4 with a spinel crystal structure. Sample D, in which part with a spinel crystal structure occupies approximately 15 % of the whole, has higher discharge capacity than sample A. Sample C, in which part with a spinel crystal structure occupies approximately 10 % of the whole, has higher discharge capacity than sample D. Among all the samples, sample B, in which part with a spinel crystal structure occupies approximately 5 % of the whole, has the highest discharge capacity.

[0074]

FIG. 13 shows X-ray diffraction (XRD) patterns of samples A to D and comparative examples 1 to 5 that are obtained by measurement. Although FIG. 13 shows all the data in one graph for comparison, the way to show the data is not particularly limited.

[0075]

The XRD patterns of samples A to D each have diffraction peaks (at around 2θ of approximately 36° and approximately 44°) peculiar to a particle with a spinel crystal structure ($\text{Sp-LiMn}_2\text{O}_4$) and diffraction peaks (at around 2θ of approximately 21° and

approximately 22°) peculiar to a particle with a layered rock-salt crystal structure (Li_2MnO_3). Similarly, the XRD patterns of comparative examples 2 to 4 each have diffraction peaks peculiar to a particle with a spinel crystal structure ($\text{Spi-LiMn}_2\text{O}_4$) and diffraction peaks peculiar to a particle with a layered rock-salt crystal structure (Li_2MnO_3).

[0076]

The XRD pattern of comparative example 1 has diffraction peaks peculiar to a particle with a layered rock-salt crystal structure (Li_2MnO_3). The XRD pattern of comparative example 5 has diffraction peaks peculiar to a particle with a spinel crystal structure ($\text{Spt-LiMn}_2\text{O}_4$).

[0077]

(Embodiment 4)

In this embodiment, the structure of a storage battery including the positive electrode active material formed by the forming method described in Embodiment 1, 2, or 3 will be described with reference to FIGS. 6A to 6C, FIG. 7, and FIGS. 8A and 8B.

[0078]

(Coin-type Storage Battery)

FIG. 6A is an external view of a coin-type (single-layer flat type) storage battery, and FIG. 6B is a cross-sectional view thereof.

[0079]

In a coin-type storage battery 300, a positive electrode can 301 doubling as a positive electrode terminal and a negative electrode can 302 doubling as a negative electrode terminal are insulated from each other and sealed by a gasket 303 made of polypropylene or the like. A positive electrode 304 includes a positive electrode current collector 305 and a positive electrode active material layer 306 provided in contact with the positive electrode current collector 305. The positive electrode active material layer 306 may further include a binder for increasing adhesion of positive electrode active materials, a conductive additive for increasing the conductivity of the positive electrode active material layer, and the like in addition to the active materials. As the conductive additive, a material that has a large specific surface area is preferably used; for example, acetylene black (AB) can be used. Alternatively, a carbon material such as a carbon nanotube, graphene, or fullerene can be used.

[0080]

A negative electrode 307 includes a negative electrode current collector 308 and a negative electrode active material layer 309 provided in contact with the negative electrode current collector 308. The negative electrode active material layer 309 may further include a binder for increasing adhesion of negative electrode active materials, a conductive additive for increasing the conductivity of the negative electrode active material layer, and the like in addition to the negative electrode active materials. A separator 310 and an electrolyte (not illustrated) are provided between the positive electrode active material layer 306 and the negative electrode active material layer 309.

[0081]

A material with which lithium can be dissolved and precipitated or a material into and from which lithium ions can be inserted and extracted can be used for the negative electrode active materials used for the negative electrode active material layer 309; for example, a lithium metal, a carbon-based material, and an alloy-based material can be used. The lithium metal is preferable because of its low redox potential (3.045 V lower than that of a standard hydrogen electrode) and high specific capacity per unit weight and per unit volume (3860 mAh/g and 2062 mAh/cm³).

[0082]

Examples of the carbon-based material include graphite, graphitizing carbon (soft carbon), non-graphitizing carbon (hard carbon), a carbon nanotube, graphene, carbon black, and the like.

[0083]

Examples of the graphite include artificial graphite such as meso-carbon microbeads (MCMB), coke-based artificial graphite, or pitch-based artificial graphite and natural graphite such as spherical natural graphite.

[0084]

Graphite has a low potential substantially equal to that of a lithium metal (0.1 V to 0.3 V vs. Li/Li⁺) when lithium ions are intercalated into the graphite (while a lithium-graphite intercalation compound is formed). For this reason, a lithium-ion secondary battery can have a high operating voltage. In addition, graphite is preferable because of its advantages such as relatively high capacity per unit volume, small volume expansion, low cost, and safety greater than that of a lithium metal.

[0085]

For the negative electrode active materials, an alloy-based material which enables charge-discharge reactions by an alloying reaction and a dealloying reaction with lithium can be used. In the case where carrier ions are lithium ions, a material containing at least one of Al, Si, Ge, Sn, Pb, Sb, Bi, Ag, Au, Zn, Cd, In, Ga, and the like can be used for example. Such elements have higher capacity than carbon. In particular, silicon has a significantly high theoretical capacity of 4200 mAh/g. For this reason, silicon is preferably used for the negative electrode active materials. Examples of the alloy-based material using such elements include SiO, Mg₂Si, Mg₂Ge, SnO, SnO₂, Mg₂Sn, SnS₂, V₂Sn₃, FeSn₂, CoSn₂, Ni₃Sn₂, Cu₆Sn₅, Ag₃Sn, Ag₃Sb, Ni₂MnSb, CeSb₃, LaSn₃, La₃Co₂Sn₇, CoSb₃, InSb, SbSn, and the like. Note that SiO refers to the powder of a silicon oxide including a silicon-rich portion and can also be referred to as SiO_y (2 > y > 0). Examples of SiO include a material containing one or more of Si₂O₃, Si₃O₄, and Si₂O and a mixture of Si powder and silicon dioxide (SiO₂). Furthermore, SiO may contain another element (e.g., carbon, nitrogen, iron, aluminum, copper, titanium, calcium, and manganese). In other words, SiO refers to a colored material containing two or more of single crystal silicon, amorphous silicon, polycrystal silicon, Si₂O₃, Si₃O₄, Si₂O, and SiO₂. Thus, SiO can be distinguished from SiO* (x is 2 or more), which is clear and colorless or white. Note that in the case where a secondary battery is fabricated using SiO as a material thereof and the SiO is oxidized because of repeated charge and discharge cycles, SiO is changed into SiO₂ in some cases.

[0086]

Alternatively, for the negative electrode active materials, an oxide such as titanium dioxide (TiO₂), lithium titanium oxide (Li₄Ti₅O₁₂), lithium-graphite intercalation compound (Li_xC₆), niobium pentoxide (Nb₂O₅), tungsten oxide (WO₂), and molybdenum oxide (MoO₂) can be used.

[0087]

Still alternatively, for the negative electrode active materials, Li_{3-*}M_xN (M = Co, Ni, or Cu) with a Li₃N structure, which is a nitride containing lithium and a transition metal, can be used. For example, Li_{2.6}Co_{0.4}N₃ is preferable because of high charge and discharge capacity (900 mAh/g and 1890 mAh/cm³).

[0088]

A nitride containing lithium and a transition metal is preferably used, in which case lithium ions are contained in the negative electrode active materials and thus the negative electrode active materials can be used in combination with a material for a positive electrode active material which does not contain lithium ions, such as V_2O_5 or Cr_3O_8 . In the case of using a material containing lithium ions as a positive electrode active material, the nitride containing lithium and a transition metal can be used for the negative electrode active material by extracting the lithium ions contained in the positive electrode active material in advance.

[0089]

Alternatively, a material which causes a conversion reaction can be used for the negative electrode active materials; for example, a transition metal oxide which does not cause an alloy reaction with lithium, such as cobalt oxide (CoO), nickel oxide (NiO), and iron oxide (FeO), may be used. Other examples of the material which causes a conversion reaction include oxides such as Fe_2O_3 , CuO, Cu_2O , RuO_2 , and Cr_2O_3 , sulfides such as $CoS_{0.89}$, NiS, and CuS, nitrides such as Zn_3N_2 , Cu_3N , and Ge_3N_4 , phosphides such as NiP_2 , FeP_2 , and CoP_3 , and fluorides such as FeF_3 and BiF_3 .

[0090]

The current collectors 305 and 308 can each be formed using a highly conductive material which is not alloyed with a carrier ion of lithium among other elements, such as a metal typified by stainless steel, gold, platinum, zinc, iron, nickel, copper, aluminum, titanium, and tantalum or an alloy thereof. Alternatively, an aluminum alloy to which an element which improves heat resistance, such as silicon, titanium, neodymium, scandium, and molybdenum, is added can be used. Still alternatively, a metal element which forms silicide by reacting with silicon can be used.

Examples of the metal element which forms silicide by reacting with silicon include zirconium, titanium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, cobalt, nickel, and the like. The current collectors can each have a foil-like shape, a plate-like shape (sheet-like shape), a net-like shape, a cylindrical shape, a coil shape, a punching-metal shape, an expanded-metal shape, or the like as appropriate.

The current collectors each preferably have a thickness of 10 μm to 30 μm inclusive.

[0091]

Any of the positive electrode active materials described in Embodiments 1 to 3

can be used for the positive electrode active material layer 306.

[0092]

As the separator 310, an insulator such as cellulose (paper), polyethylene with pores, and polypropylene with pores can be used.

5 [0093]

As an electrolyte in the electrolytic solution, a material which contains carrier ions is used. Typical examples of the electrolyte are lithium salts such as LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, and $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$. One of these electrolytes may be used alone, or two or more of them may be used in an appropriate combination and in an appropriate ratio.

10 [0094]

Note that when carrier ions are alkali metal ions other than lithium ions, alkaline-earth metal ions, beryllium ions, or magnesium ions, instead of lithium in the above lithium salts, an alkali metal (e.g., sodium and potassium), an alkaline-earth metal (e.g., calcium, strontium, barium, beryllium, and magnesium) may be used for the electrolyte.

[0095]

As a solvent of the electrolytic solution, a material in which carrier ions can transfer is used. As the solvent of the electrolytic solution, an aprotic organic solvent is preferably used. Typical examples of aprotic organic solvents include ethylene carbonate (EC), propylene carbonate, dimethyl carbonate, diethyl carbonate (DEC), γ -butyrolactone, acetonitrile, dimethoxyethane, tetrahydrofuran, and the like, and one or more of these materials can be used. When a gelled high-molecular material is used as the solvent of the electrolytic solution, safety against liquid leakage and the like is improved. Furthermore, the storage battery can be thinner and more lightweight. Typical examples of gelled high-molecular materials include a silicone gel, an acrylic gel, an acrylonitrile gel, polyethylene oxide, polypropylene oxide, a fluorine-based polymer, and the like. Alternatively, the use of one or more of ionic liquids (room temperature molten salts) which have features of non-flammability and non-volatility as a solvent of the electrolytic solution can prevent the storage battery from exploding or catching fire even when the storage battery internally shorts out or the internal temperature increases owing to overcharging and others.

20

25

30

[0096]

Instead of the electrolytic solution, a solid electrolyte including an inorganic material such as a sulfide-based inorganic material or an oxide-based inorganic material, or a solid electrolyte including a macromolecular material such as a polyethylene oxide (PEO)-based macromolecular material may alternatively be used. When the solid electrolyte is used, a separator and a spacer are not necessary. Furthermore, the battery can be entirely solidified; therefore, there is no possibility of liquid leakage and thus the safety of the battery is dramatically increased.

[0097]

For the positive electrode can 301 and the negative electrode can 302, a metal having a corrosion-resistant property to an electrolytic solution in charging and discharging a secondary battery, such as nickel, aluminum, and titanium, an alloy of any of the metals, an alloy containing any of the metals and another metal (e.g., stainless steel), a stack of any of the metals, a stack including any of the metals and any of the alloys (e.g., a stack of stainless steel and aluminum), or a stack including any of the metals and another metal (e.g., a stack of nickel, iron, and nickel) can be used. The positive electrode can 301 and the negative electrode can 302 are electrically connected to the positive electrode 304 and the negative electrode 307, respectively.

[0098]

The negative electrode 307, the positive electrode 304, and the separator 310 are immersed in the electrolytic solution. Then, as illustrated in FIG. 6B, the positive electrode 304, the separator 310, the negative electrode 307, and the negative electrode can 302 are stacked in this order with the positive electrode can 301 positioned at the bottom, and the positive electrode can 301 and the negative electrode can 302 are subjected to pressure bonding with the gasket 303 interposed therebetween. In such a manner, the coin-type storage battery 300 can be manufactured.

[0099]

Here, a current flow in charging a battery will be described with reference to FIG. 6C. When a battery using lithium is regarded as a closed circuit, lithium ions transfer and a current flows in the same direction. Note that in the battery using lithium, an anode and a cathode change places in charge and discharge, and an oxidation reaction and a reduction reaction occur on the corresponding sides; hence, an electrode

with a high redox potential is called a positive electrode and an electrode with a low redox potential is called a negative electrode. For this reason, in this specification, the positive electrode is referred to as a "positive electrode" and the negative electrode is referred to as a "negative electrode" in all the cases where charge is performed, discharge is performed, a reverse pulse current is supplied, and a charging current is supplied. The use of the terms "anode" and "cathode" related to an oxidation reaction and a reduction reaction might cause confusion because the anode and the cathode change places at the time of charging and discharging. Thus, the terms "anode" and "cathode" are not used in this specification. If the terms "anode" or "cathode" is used, it should be mentioned that the anode or the cathode is which of the one at the time of charging or the one at the time of discharging and corresponds to which of a positive electrode or a negative electrode.

[0100]

Two terminals in FIG. 6C are connected to a charger, and a storage battery 400 is charged. As the charge of the storage battery 400 proceeds, a potential difference between electrodes increases. The positive direction in FIG. 6C is the direction in which a current flows from one terminal outside the storage battery 400 to a positive electrode 402, flows from the positive electrode 402 to a negative electrode 404 in the storage battery 400, and flows from the negative electrode 404 to the other terminal outside the storage battery 400. In other words, a current flows in the direction of a flow of a charging current.

[0101]

Next, an example of a laminated storage battery will be described with reference to FIG. 7.

[0102]

A laminated storage battery 500 illustrated in FIG. 7 includes a positive electrode 503 including a positive electrode current collector 501 and a positive electrode active material layer 502, a negative electrode 506 including a negative electrode current collector 504 and a negative electrode active material layer 505, a separator 507, an electrolytic solution 508, and an exterior body 509. The separator 507 is provided between the positive electrode 503 and the negative electrode 506 in the exterior body 509. The exterior body 509 is filled with the electrolytic solution 508.

[0103]

In the laminated storage battery 500 illustrated in FIG. 7, the positive electrode current collector 501 and the negative electrode current collector 504 also serve as terminals for an electrical contact with an external portion. For this reason, each of the positive electrode current collector 501 and the negative electrode current collector 504 is arranged so that part of the positive electrode current collector 501 and part of the negative electrode current collector 504 are exposed on the outside the exterior body 509.

[0104]

As the exterior body 509 in the laminated storage battery 500, for example, a laminate film having a three-layer structure in which a highly flexible metal thin film of aluminum, stainless steel, copper, nickel, or the like is provided over a film formed of a material such as polyethylene, polypropylene, polycarbonate, ionomer, or polyamide, and an insulating synthetic resin film of a polyamide-based resin, a polyester-based resin, or the like is provided as the outer surface of the exterior body over the metal thin film can be used. With such a three-layer structure, permeation of the electrolytic solution and a gas can be blocked and an insulating property can be obtained.

[0105]

<Cylindrical Storage battery>

Next, an example of a cylindrical storage battery will be described with reference to FIGS. 8A and 8B. As illustrated in FIG. 8A, a cylindrical storage battery 600 includes a positive electrode cap (battery cap) 601 on the top surface and a battery can (outer can) 602 on the side surface and bottom surface. The positive electrode cap 601 and the battery can 602 are insulated from each other by a gasket (insulating gasket) 610.

[0106]

FIG. 8B is a diagram schematically illustrating a cross section of the cylindrical storage battery. Inside the battery can 602 having a hollow cylindrical shape, a battery element in which a strip-like positive electrode 604 and a strip-like negative electrode 606 are wound with a stripe-like separator 605 interposed therebetween is provided. Although not illustrated, the battery element is wound around a center pin. For the battery can 602, a metal having corrosion resistance to an electrolytic solution, such as

nickel, aluminum, or titanium, an alloy of such a metal, or an alloy of such a metal and another metal (e.g., stainless steel) can be used. Alternatively, the battery can 602 is preferably covered with nickel, aluminum, or the like in order to prevent corrosion caused by a nonaqueous electrolytic solution. Inside the battery can 602, the battery element in which the positive electrode, the negative electrode, and the separator are wound is provided between a pair of insulating plates 608 and 609 which face each other. Inside the battery can 602, the battery element in which the positive electrode, the negative electrode, and the separator are wound is interposed between a pair of insulating plates 608 and 609 which face each other. Furthermore, a nonaqueous electrolytic solution (not illustrated) is injected inside the battery can 602 provided with the battery element. As the nonaqueous electrolytic solution, a nonaqueous electrolytic solution which is similar to those of the above coin-type storage battery and the laminated power storage device can be used.

[0107]

Although the positive electrode 604 and the negative electrode 606 can be formed in a manner similar to that of the positive electrode and the negative electrode of the coin-type storage battery described above, the difference lies in that, since the positive electrode and the negative electrode of the cylindrical storage battery are wound, active materials are formed on both sides of the current collectors. A positive electrode terminal (positive electrode current collecting lead) 603 is connected to the positive electrode 604, and a negative electrode terminal (negative electrode current collecting lead) 607 is connected to the negative electrode 606. Both the positive electrode terminal 603 and the negative electrode terminal 607 can be formed using a metal material such as aluminum. The positive electrode terminal 603 and the negative electrode terminal 607 are resistance-welded to a safety valve mechanism 612 and the bottom of the battery can 602, respectively. The safety valve mechanism 612 is electrically connected to the positive electrode cap 601 through a positive temperature coefficient (PTC) element 611. The safety valve mechanism 612 cuts off electrical connection between the positive electrode cap 601 and the positive electrode 604 when the internal pressure of the battery exceeds a predetermined threshold value. The PTC element 611, which serves as a thermally sensitive resistor whose resistance increases as temperature rises, limits the amount of current by increasing the resistance, in order to

prevent abnormal heat generation. Note that barium titanate (BaTiO_3)-based semiconductor ceramic can be used for the PTC element.

[0108]

Note that in this embodiment, the coin-type storage battery, the laminated storage battery, and the cylindrical storage battery are given as examples of the storage battery; however, any of storage batteries with a variety of shapes, such as a sealed storage battery and a square-type storage battery, can be used. Furthermore, a structure in which a plurality of positive electrodes, a plurality of negative electrodes, and a plurality of separators are stacked or wound may be employed.

[0109]

For each of the positive electrodes of the storage batteries 300, 500, and 600, which are described in this embodiment, a positive electrode active material formed by the method for forming a positive electrode active material of one embodiment of the present invention is used. Thus, the discharge capacity of the storage batteries 300, 500, and 600 can be increased.

[0110]

This embodiment can be implemented in combination with any of the other embodiments as appropriate.

[Example 1]

[0111]

In this example, novel materials were synthesized according to Table 2, FFT patterns were obtained by the FFT analysis measurement in the range shown in a cross-sectional TEM image of one of the samples and part of the cross-sectional TEM image, and the crystal structures were determined. FIGS. 9 and 10 show the results.

[0112]

[Table 2]

	Percentage (%)		Synthesis condition Ratio of materials
	Li_2MnO_3	spi- LiMn_2O_4	
1	100	0	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 1 : 1$
2	98	2	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.98 : 1.01$

3	95	5	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.955 : 1.03$
4	90	10	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.91 : 1.06$
5	85	15	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.88 : 1.09$
6	80	20	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.84 : 1.12$
7	60	40	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.71 : 1.23$
8	50	50	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.64 : 1.28$
ref.	0	100	$\text{Li}_2\text{CO}_3 : \text{MnCO}_3 = 0.5 : 2$

[0113]

Under condition 1 in Table 2, a novel material was formed according to Embodiment 2. Note that under the condition of a reference in Table 2, a novel material cannot be obtained.

[0114]

A procedure for synthesis of the novel materials will be described below in detail.

[0115]

10 Weighed materials, a zirconia ball with a diameter of 3 mm, and acetone were put into a pot made of zirconia, and wet ball milling using a planetary ball mill was performed at 400 rpm for 2 hours.

[0116]

15 Then, the slurry subjected to acetone in slurry subjected to the ball milling was volatilized at 50 °C in the air, so that a mixed material is obtained.

[0117]

Then, the mixed material was dried and a crucible made of aluminum was filled with the dried mixed material, and firing was performed at 800 °C to 1100 °C in the air for 10 hours to obtain an objective.

20 [0118]

Subsequently, grinding was performed to separate the sintered-particles.- The fired material, a zirconia ball with a diameter of 3 mm, and acetone were put into a pot

made of zirconia, and wet ball milling using a planetary ball mill was performed at 200 rpm for 2 hours.

[0119]

After the grinding, heating is performed on the mixture subjected to wet ball milling at 50 °C in the air to volatilize acetone, and then, vacuum drying was performed at 170 °C, so that a positive electrode active material that is a novel material was obtained.

[0120]

A cross section of each sample was observed with a high-resolution transmission electron microscope (TEM) ("H9000-NAR" manufactured by Hitachi, Ltd.) at an acceleration voltage of 200 kV. FIG. 9 shows the cross-sectional TEM image of the novel material. An FFT analysis portion is shown by a black frame in FIG. 9. An FFT analysis result is shown in a lower right portion in FIG. 9. In addition, data on LiMn_2O_4 with a spinel crystal structure that is described in a JCPDS card is shown in an upper right portion in FIG. 9. The region surrounded by the black frame in FIG. 9 can be identified as a region with a spinel crystal structure.

[0121]

FIG. 10 shows a cross-sectional TEM image of the novel material. An FFT analysis portion is shown by a white frame in FIG. 10. The obtained FFT analysis result is shown in a left portion in FIG. 10. In addition, data on Li_2MnO_3 with a layered rock-salt crystal structure that is described in a JCPDS card is shown in a lower right portion in FIG. 10. The region surrounded by the white frame in FIG. 10 can be identified as the one with a layered rock-salt crystal structure.

EXPLANATION OF REFERENCE

[0122]

101: crystallite with spinel crystal structure, 102: crystallite with layered rock-salt crystal structure, 103: Li_2MnO_3 particle, 104: Spi- LiMn_2O_4 particle, 105: material obtained by sintering, 300: storage battery, 301: positive electrode can, 302: negative electrode can, 303: gasket, 304: positive electrode, 305: positive electrode current collector, 306: positive electrode active material layer, 307: negative electrode, 308:

negative electrode current collector, 309: negative electrode active material layer, 310: separator, 400: storage battery, 402: positive electrode, 404: negative electrode, 500: storage battery, 501: positive electrode current collector, 502: positive electrode active material layer, 503: positive electrode, 504: negative electrode current collector, 505: negative electrode active material layer, 506: negative electrode, 507: separator, 508: electrolytic solution, 509: exterior body, 600: storage battery, 601: positive electrode cap, 602: battery can, 603: positive electrode terminal, 604: positive electrode, 605: separator, 606: negative electrode, 607: negative electrode terminal, 608: insulating plate, 609: insulating plate, 611: PTC element, 612: safety valve mechanism

10

This application is based on Japanese Patent Application serial no. 2013-100358 filed with Japan Patent Office on May 10, 2013 and Japanese Patent Application serial no. 2013-100383 filed with Japan Patent Office on May 10, 2013, the entire contents of which are hereby incorporated by reference.

15

CLAIMS

1. A particle comprising:
a first crystallite with a layered rock-salt crystal structure; and
a second crystallite with a spinel crystal structure in part of a surface of the
5 particle,
wherein a percentage of part with a layered rock-salt crystal structure in the
particle is 50 % or more and 98 % or less, and
wherein the particle is lithium manganese oxide.
- 10 2. The particle according to claim 1, wherein the first crystallite has the same
crystal structure as that of a crystallite of Li_2MnO_3 .
3. The particle according to claim 1, wherein the first crystallite belongs to a
space group C2/c.
- 15 4. The particle according to claim 1, wherein the percentage of part with the
layered rock-salt crystal structure in the particle is 85 % or more and 98 % or less.
5. The particle according to claim 1, wherein the first crystallite is Li_2MnO_3 .
- 20 6. The particle according to claim 1, wherein the second crystallite is LiMn_2O_4 .
7. An electrode comprising the particle according to claim 1.
- 25 8. A storage battery comprising the electrode according to claim 7.
9. An electronic device comprising the storage battery according to claim 8.
10. A particle comprising:
a crystal of Li_2MnO_3 ; and
a crystal of LiMn_2O_4 ,
wherein a percentage of Li_2MnO_3 in the particle is 50 % or more and 98 % or
- 30

less.

11. The particle according to claim 10, wherein a percentage of LiMn_2O_4 in the particle is 2 % or more and 50 % or less.

5

12. The particle according to claim 10, wherein the percentage of Li_2MnO_3 in the particle is 85 % or more and 98 % or less.

13. An electrode comprising the particle according to claim 10.

10

14. A storage battery comprising the electrode according to claim 13.

15. An electronic device comprising the storage battery according to claim 14.

15

16. A particle comprising:

a crystal of Li_2MnO_3 ; and

a crystal of LiMn_2O_4 ,

wherein a percentage of LiMn_2O_4 in the particle is 2 % or more and 50 % or less.

20

17. The particle according to claim 16, wherein the percentage of LiMn_2O_4 in the particle is 2 % or more and 15 % or less.

18. An electrode comprising the particle according to claim 16.

25

19. A storage battery comprising the electrode according to claim 18.

20. An electronic device comprising the storage battery according to claim 19.

30

21. A method for manufacturing a particle, comprising the steps of:

mixing lithium carbonate and manganese carbonate to obtain a mixture; and

performing heat treatment of the mixture at higher than or equal to 500 °C and

lower than or equal to 1000 °C to obtain an active material particle after mixing lithium carbonate and manganese carbonate,

wherein a molar ratio of lithium carbonate to manganese carbonate is in a range from 0.88:1.09 to 0.98:1.01.

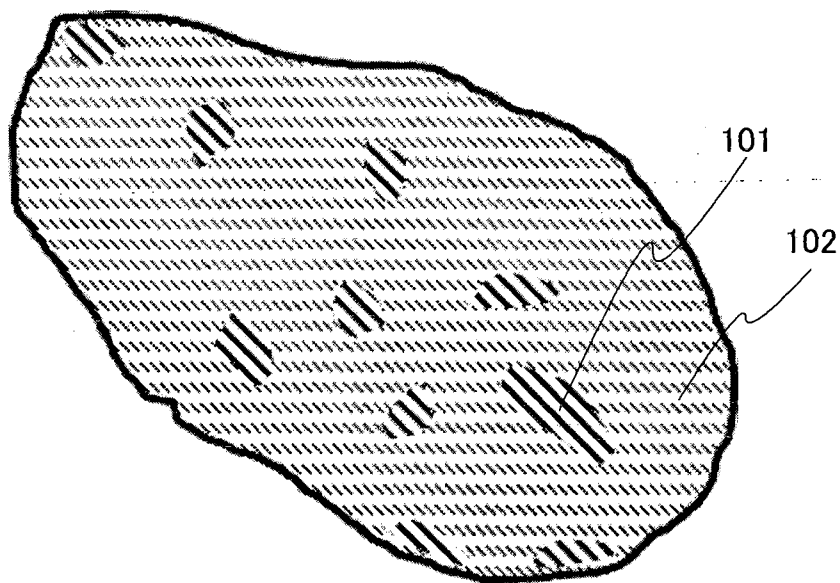
5

22. The method according to claim 21, wherein the molar ratio of lithium carbonate to manganese carbonate is in a range from 0.91:1.06 to 0.95:1.03.

23. The method according to claim 21, wherein the mixture further comprises
10 nickel oxide.

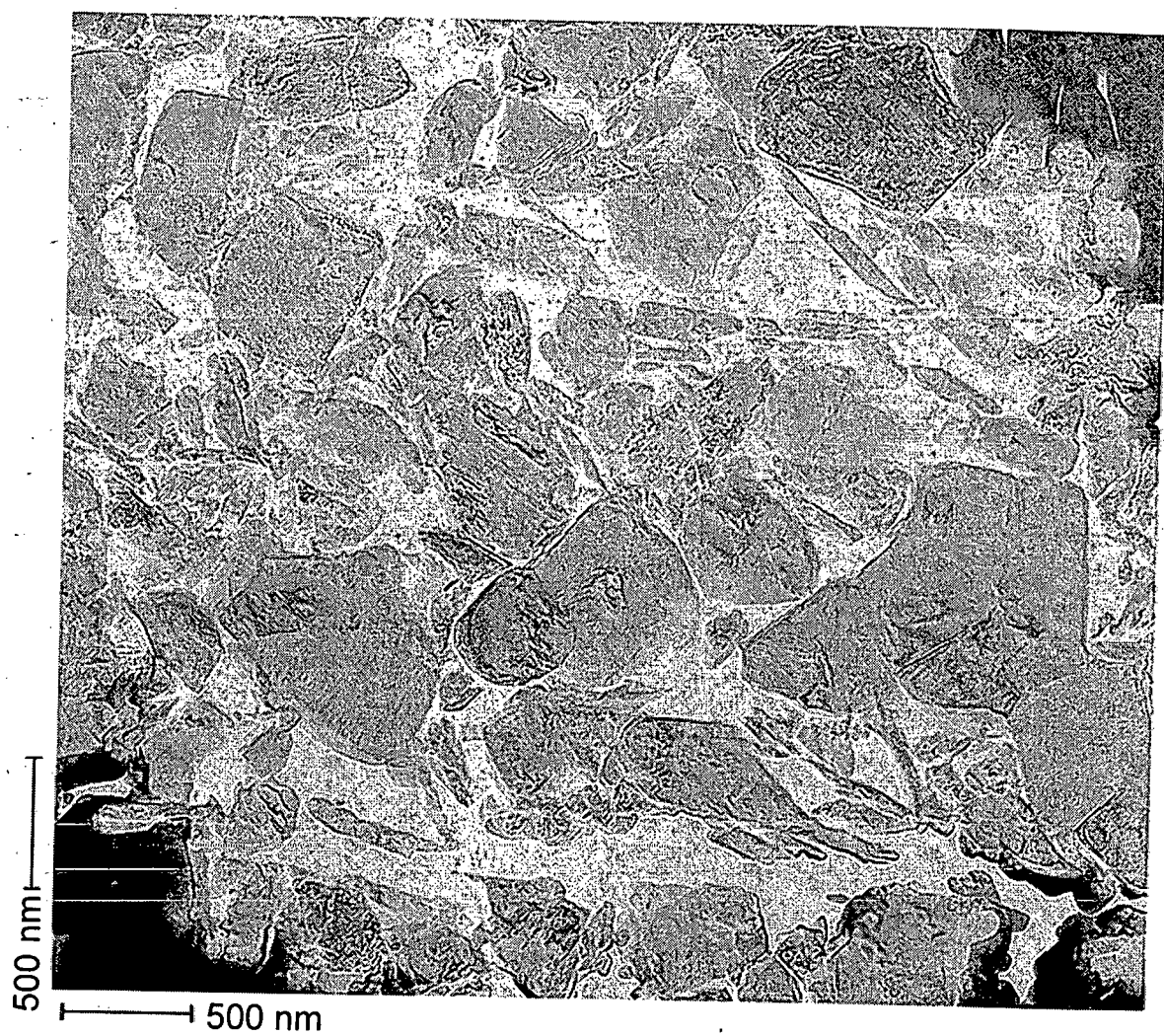
1/13

FIG. 1



2/13

FIG. 2



3/13

FIG. 3

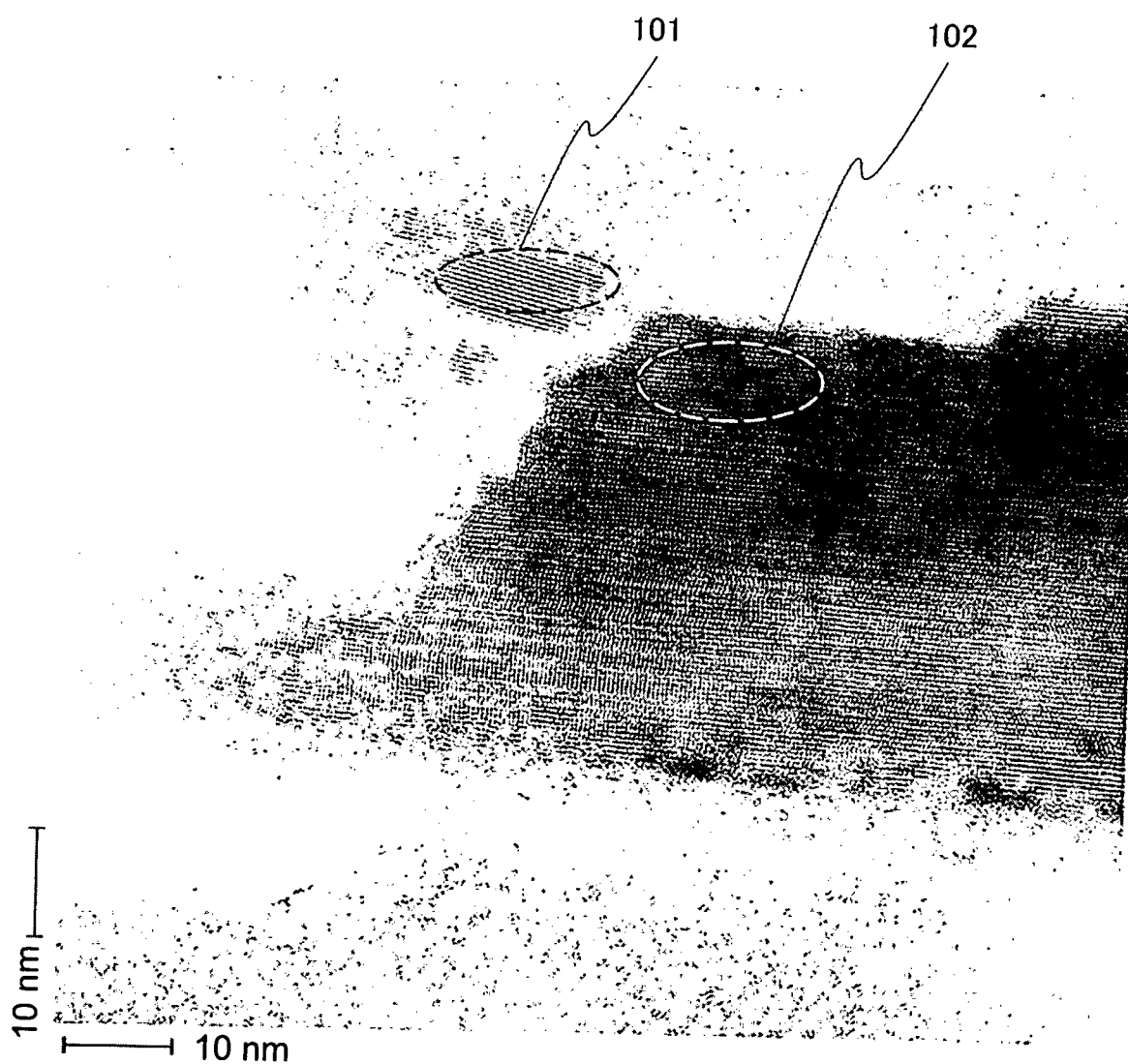


FIG. 4

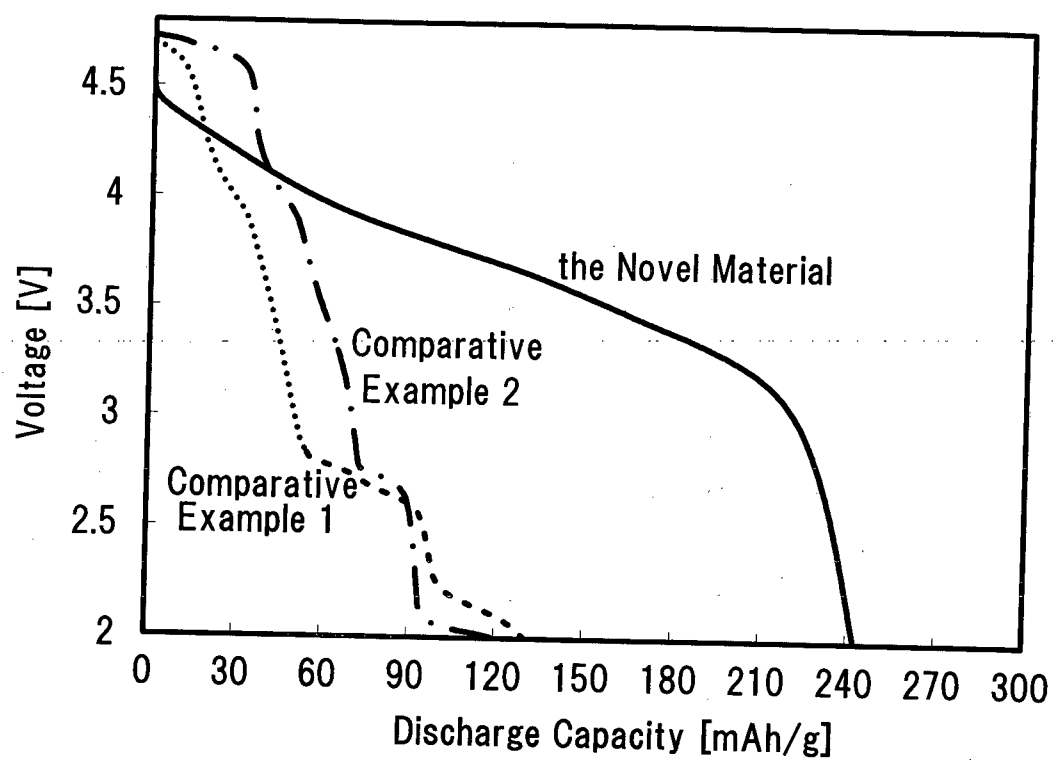
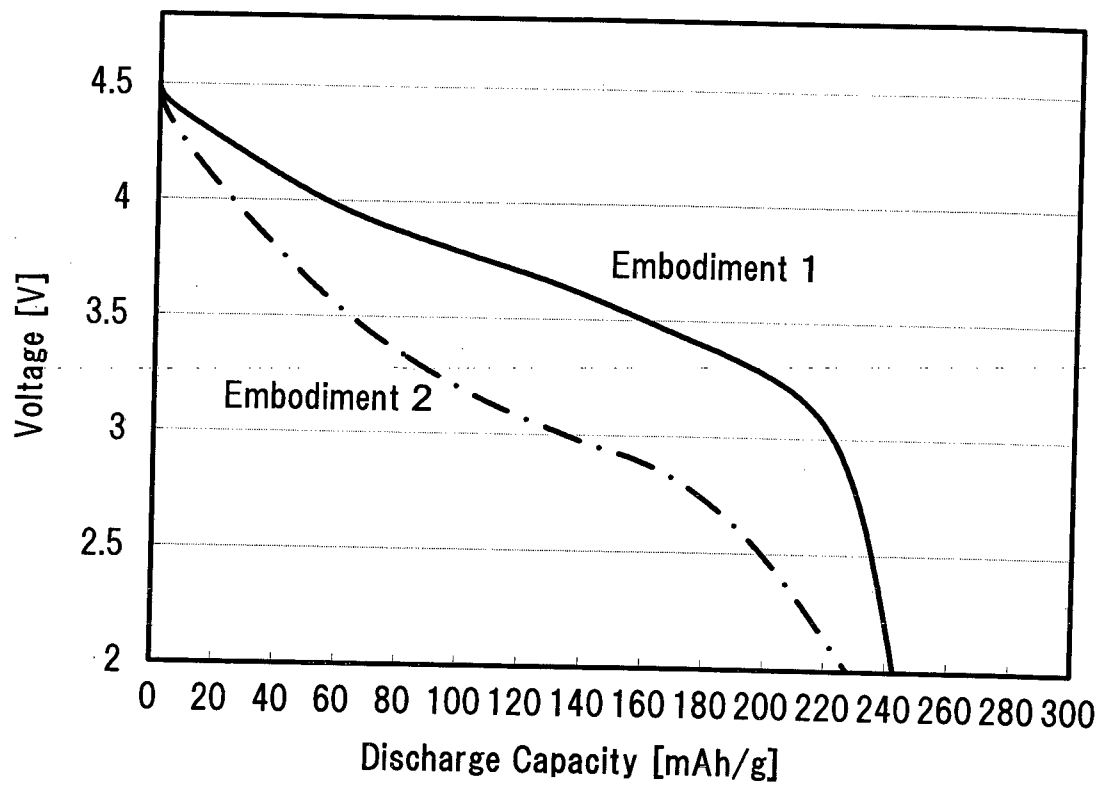


FIG. 5



6/13

FIG. 6A

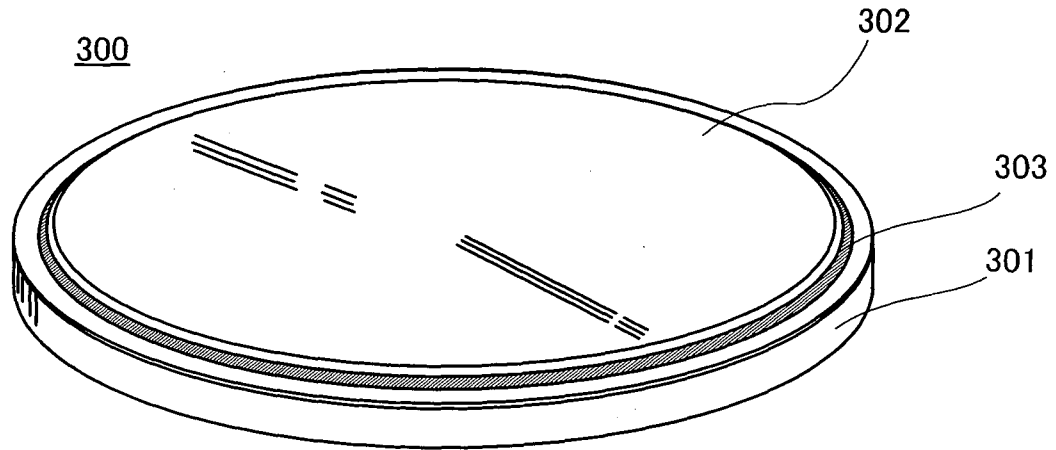


FIG. 6B

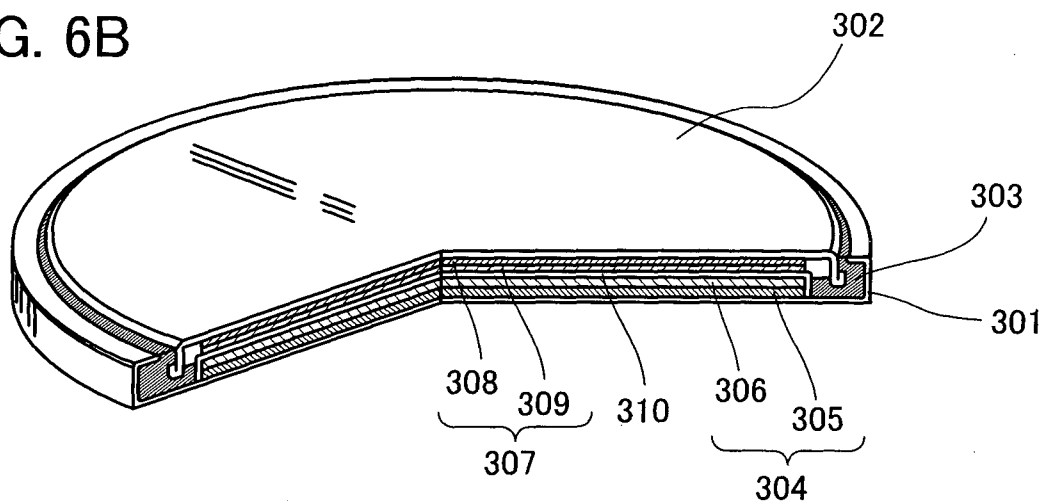
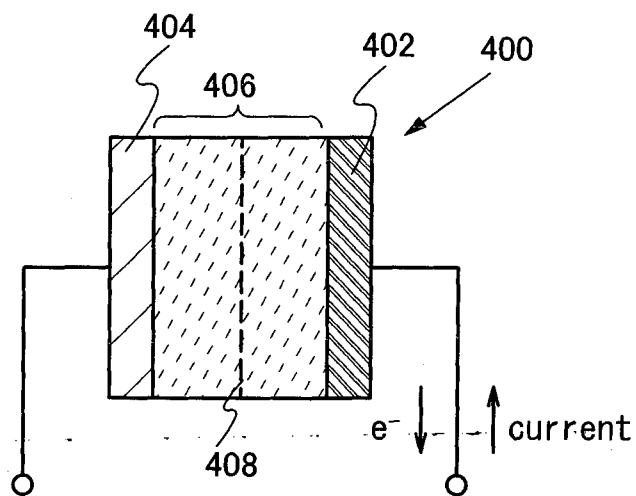


FIG. 6C



in case of Charge

FIG. 7

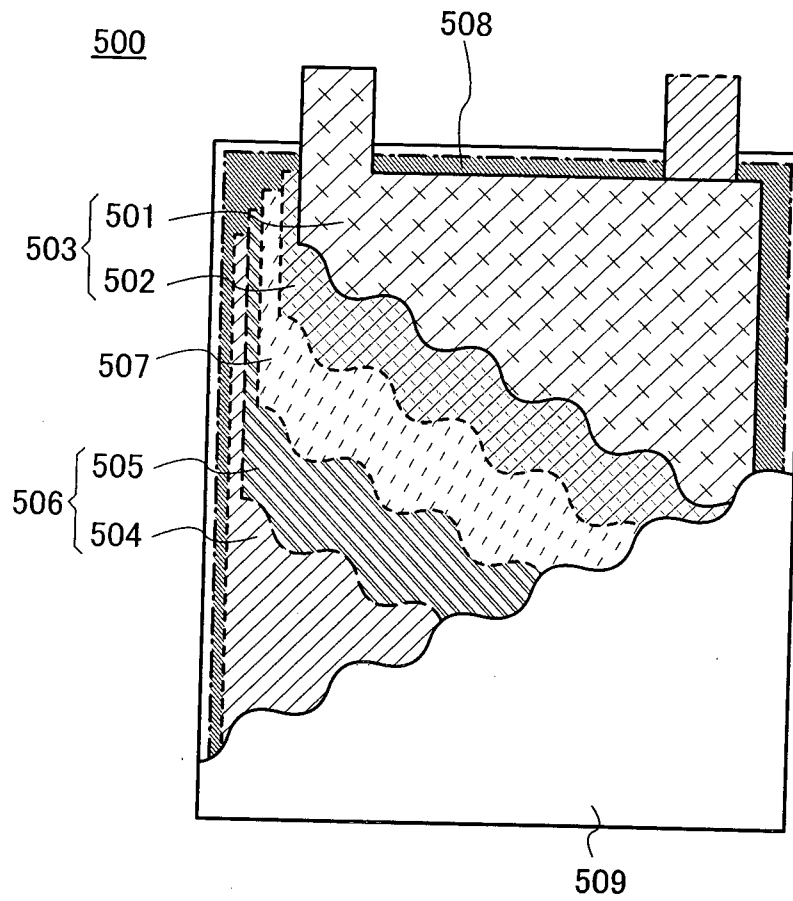


FIG. 8A

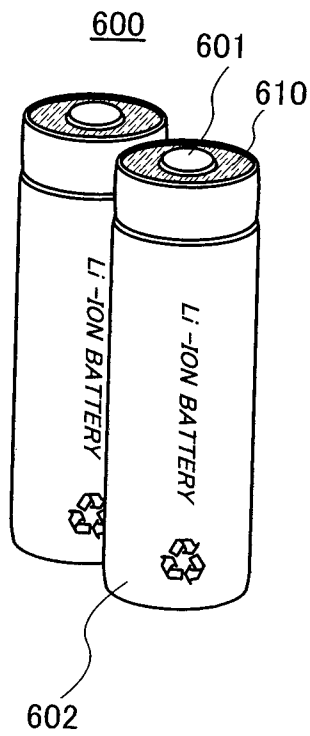


FIG. 8B

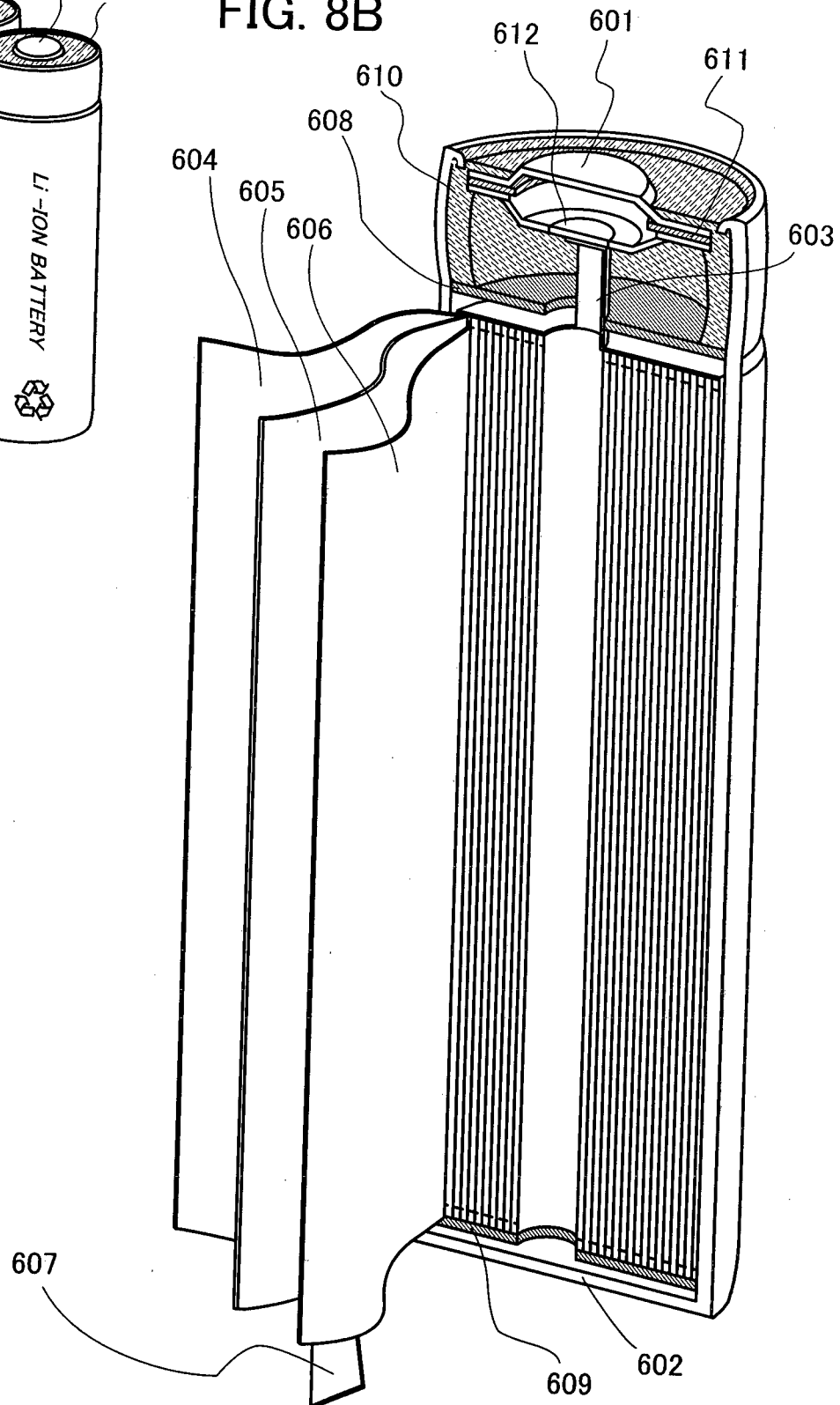


FIG. 9

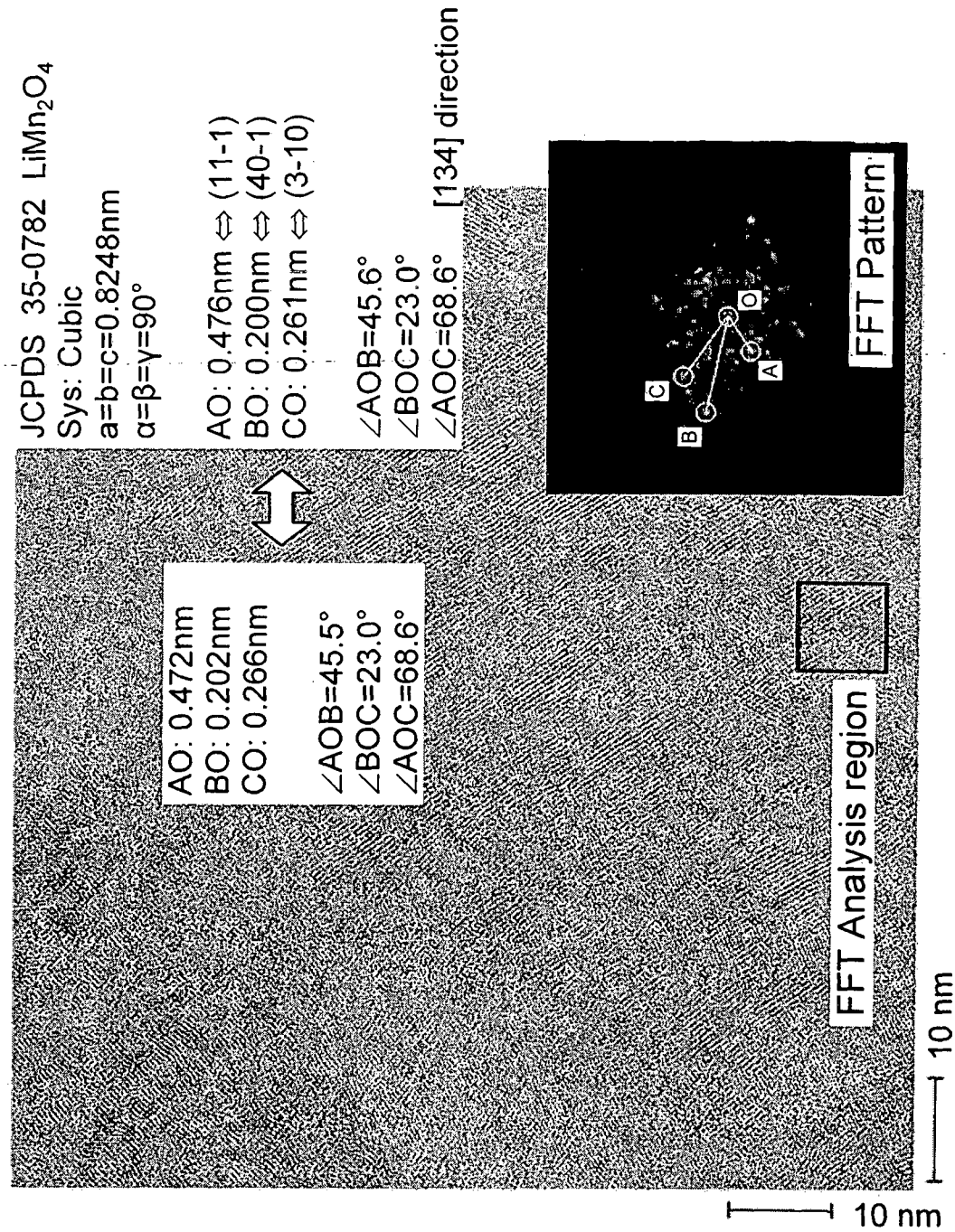
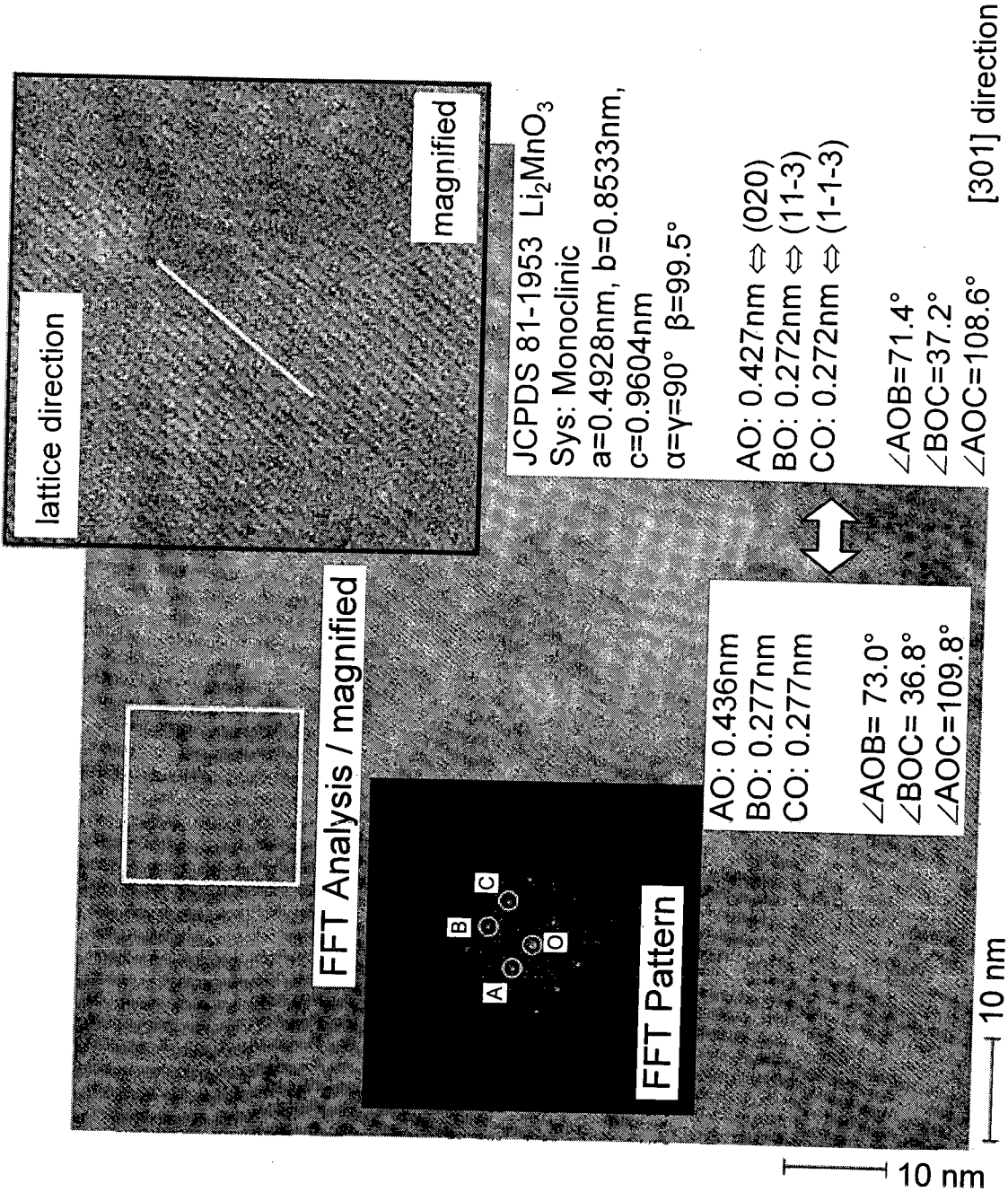


FIG. 10



11/13

FIG. 11A

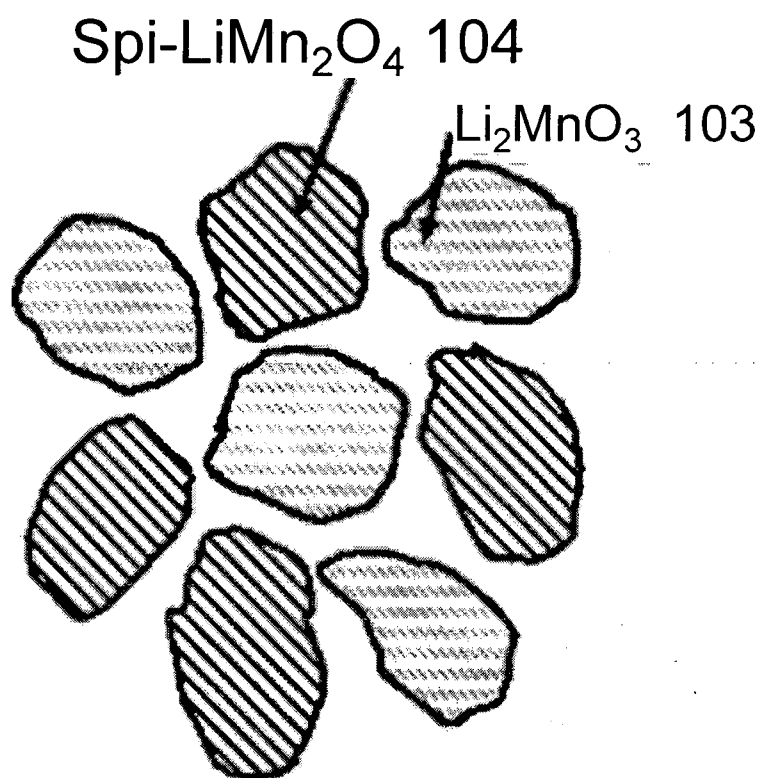
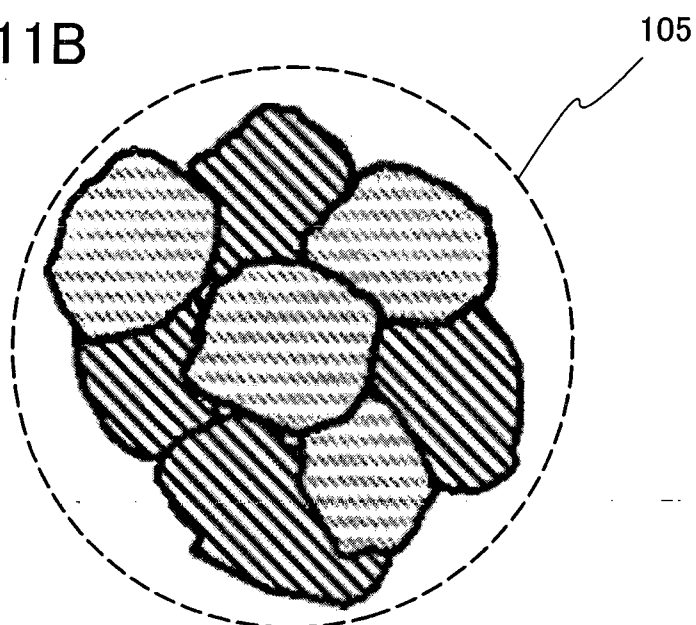


FIG. 11B



12/13

FIG. 12

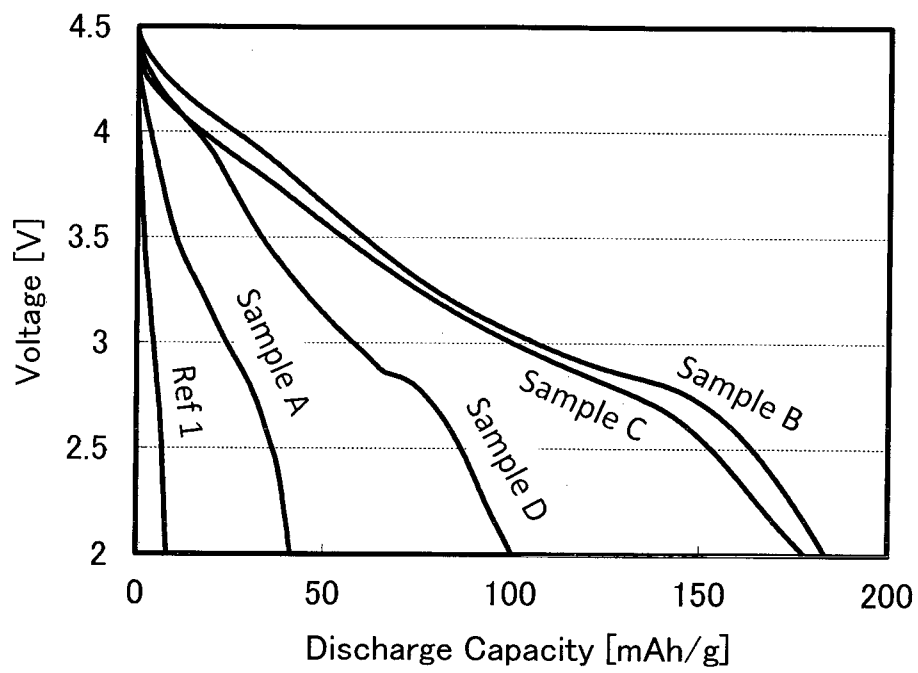
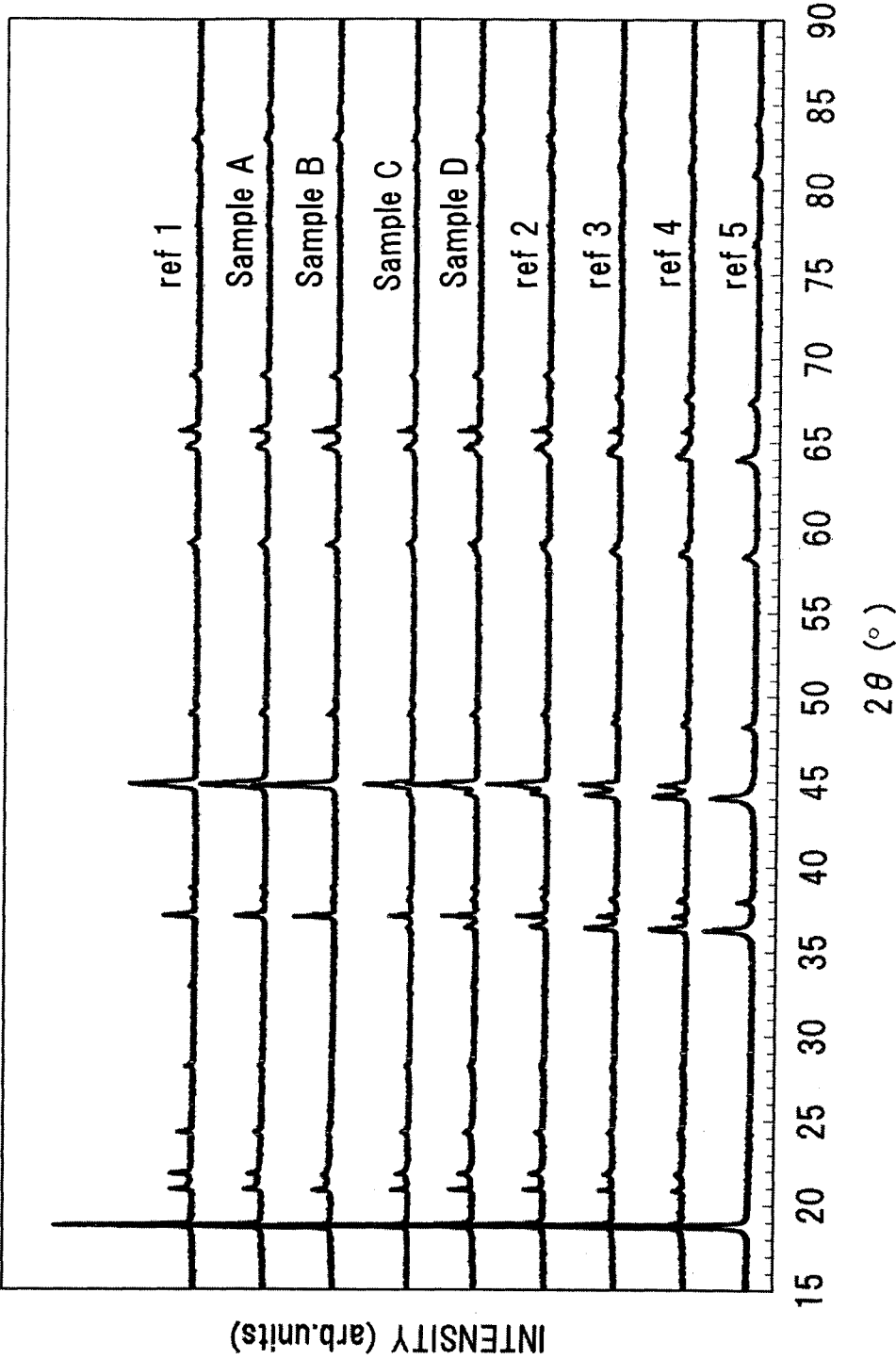


FIG. 13



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP20 14/ 0 6254 2

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. C01G4 5/ 00 (2006.01)i, H01M4/ 36 (2006.01)i, H01M4/ 505 (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. C01G4 5/ 00, H01M4/ 36, H01M4/ 505		
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 1971-2014 Registered utility model specifications of Japan 1996-2014 Published registered utility model applications of Japan 1994-2014		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
Science Direct		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 6-342658 A (TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED) 1994.12.13, claims, paragraph [0013], examples & US 5240794 A & GB 2251119 A & GB 9126884 D0 & DE 4142370 A & FR 2670952 A & CA 2057946 A & ZA 9109814 A	1-3, 5-11, 13-- 16, 18-20 A, 12, 17 21-23
X Y A	JP 2008-511960 A (UCHICAGO ARGONNE, LLC) 2008.04.17, claims, paragraph [0029], example 1, 3-5 & US 2006/0051671 A1 & US 2006/0051673 A1 & US 2009/0123842 A1 & US 2010/0143784 A1 & EP 1807888 A & WO 2006/028476 A2 & CA 2578870 A & KR 10-2007-0083550 A & CN 101080830 A	1-20 4, 12, 17 21-23
☒ 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 "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
30.07.2014		12.08.2014
Name and mailing address of the ISA/JP Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		Authorized officer Shuichi NOBUHIRA Telephone No. +81-3-3581-1 101 Ext. 3416

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/062542

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 2012-84257 A (TOYOTA INDUSTRIES CORP.) 2012.04.26, claims, example 3 (Family: none)	1-3, 5-11, 13-16, 18-20 4, 12, 17 21-23
X Y A	V. BERBENNI et al., Thermogravimetry and X-ray diffraction study of the thermal decomposition processes in Li ₂ CO ₃ -MnCO ₃ mixtures, Journal of Analytical and Applied Pyrolysis, 2002, Vol.62, pp. 45-62	1-3, 5-11, 13-16, 18-20 4, 12, 17 21-23

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/062542

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims NOS.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The technical feature of the invention in claim 1 is publicly known, as disclosed in documents 1-4.

Consequently, claims 1-23 are classified into the main invention of claims 1-9 and invention of other claims; therefore, claims 1-23 involve two or more inventions.

Document 1: JP 6-342658 A (TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED)

Document 2: JP 2008-511960 A (UCHICAGO ARGONNE, LLC)

Document 3: JP 2012-84257 A (TOYOTA INDUSTRIES CORP.)

Document 4: V. BERBENNI et al., Thermogravimetry and X-ray diffraction study of the thermal decomposition processes in Li_2CO_3 - MnCO_3 mixtures, Journal of Analytical and Applied Pyrolysis

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.