(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
07 June 2018 (07.06.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/100470 A1

(51) International Patent Classification:
H01M 10/0568 (2010.01) *H01M 2/16* (2006.01)
H01G 11/52 (2013.01) *H01M 4/66* (2006.01)
H01G 11/62 (2013.01) *H01M 10/0525* (2010.01)
H01M 2/02 (2006.01) *H01M 10/0569* (2010.01)
H01M 2/10 (2006.01)

(21) International Application Number:
PCT/IB2017/057316

(22) International Filing Date:
22 November 2017 (22.11.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2016-234674 02 December 2016 (02.12.2016) JP

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

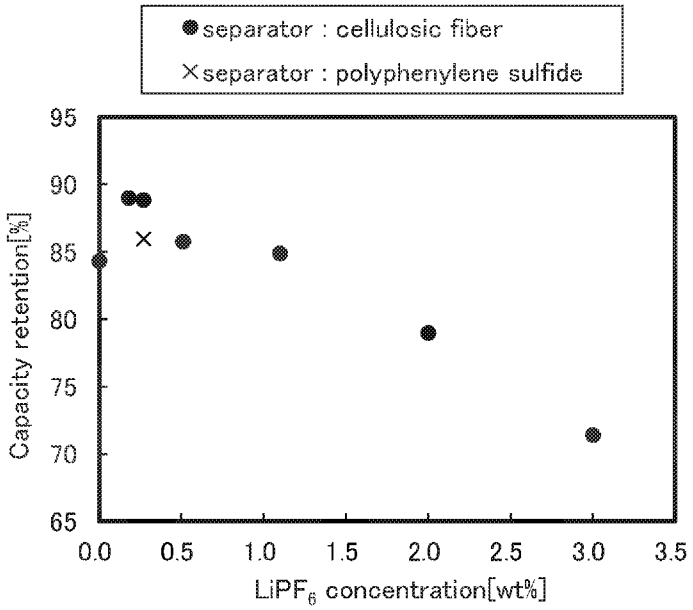
(72) Inventors: **NARITA, Kazuhei**; c/o Semiconductor Energy Laboratory Co., Ltd., 398, Hase, Atsugi-shi, Kanagawa 2430036 (JP). **TAJIMA, Ryota**; c/o Semiconductor Energy Laboratory Co., Ltd., 398, Hase, Atsugi-shi, Kanagawa 2430036 (JP).

(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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,

WO 2018/100470 A1

(54) Title: POWER STORAGE DEVICE AND ELECTRONIC DEVICE

FIG. 43A



(57) Abstract: Provided is a power storage device whose charging and discharging characteristics are unlikely to be degraded by heat treatment or a power storage device that is highly safe against heat treatment. The power storage device includes a positive electrode, a negative electrode, a separator, an electrolyte, and an exterior body. The separator is positioned between the positive electrode and the negative electrode and includes polyphenylene sulfide or cellulosic fiber. The electrolyte includes propylene carbonate, ethylene carbonate, and vinylene carbonate, lithium hexafluorophosphate, and lithium bis(pentafluoroethanesulfonyl)amide. A concentration of lithium hexafluorophosphate with respect to the electrolyte is more than or equal to 0.01 wt percent and less than or equal to 1.9 wt percent in a weight ratio.

[Continued on next page]

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, ST, 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))*

DESCRIPTION

POWER STORAGE DEVICE AND ELECTRONIC DEVICE

TECHNICAL FIELD

[0001]

One embodiment of the present invention relates to a power storage device and an electronic device.

[0002]

Note that one embodiment of the present invention is not limited to the above technical field. One embodiment of the invention disclosed in this specification and the like relates to an object, a method, and a manufacturing method. One embodiment of the present invention relates to a process, a machine, manufacture, or a composition of matter. Specifically, examples of the technical field of one embodiment of the invention disclosed in this specification include a semiconductor device, a display device, a light-emitting device, a power storage device, a memory device, an imaging device, a driving method thereof, and a manufacturing method thereof.

[0003]

In this specification, the power storage device is a collective term describing units and devices having a power storage function. For example, a power storage device (also referred to as a secondary battery) such as a lithium-ion secondary battery, a lithium-ion capacitor, and an electric double layer capacitor are included in the category of the power storage device.

BACKGROUND ART

[0004]

In recent years, a variety of power storage devices such as lithium-ion secondary batteries, lithium-ion capacitors, and air batteries have been actively developed. In particular, demand for lithium-ion secondary batteries with high output and high energy density has rapidly grown with the development of the semiconductor industry, for portable information terminals such as mobile phones, smartphones, and laptop computers, portable music players, and digital cameras; medical equipment; next-generation clean energy vehicles such as hybrid electric vehicles (HEV), electric vehicles (EV), and plug-in hybrid electric vehicles (PHEV); and the like. The lithium-ion secondary batteries are essential as rechargeable energy supply sources for today's information society.

[0005]

As described above, lithium-ion secondary batteries have been used for a variety of purposes in various fields. Properties necessary for such lithium-ion secondary batteries are high energy density, excellent cycle performance, safety in a variety of operation environments, and the like.

[0006]

A lithium-ion secondary battery includes at least a positive electrode, a negative electrode, and an electrolyte (Patent Document 1).

[Reference]

[Patent Document]

[0007]

[Patent Document] Japanese Published Patent Application No. 2012-009418

DISCLOSURE OF INVENTION

[0008]

Power storage batteries that are to be mounted in electronic devices such as a wearable device and a portable information terminal need to resist heat treatment performed when the electronic devices are processed. Particularly in the case where a housing of the electronic device and a lithium-ion power storage battery are integrally formed, the lithium-ion power storage battery needs to have heat resistance to a temperature higher than or equal to the manufacturing temperature of the housing.

[0009]

High heat resistance of an electrolyte is necessary for high heat resistance of the power storage device. In order to increase the heat resistance of the electrolyte, it is considered effective to suppress the decomposition of the electrolyte by heat or to suppress the decomposition of the electrolyte due to a reaction of the electrolyte with other members by heat. Examples of the reaction between the electrolyte and other members include a reaction with a positive electrode, a negative electrode, a separator, or an exterior body.

[0010]

In view of the above, an object of one embodiment of the present invention is to provide a power storage device whose charging and discharging characteristics are unlikely to be degraded by heat treatment. Another object of one embodiment of the present invention is to provide a power storage device that is highly safe against heat treatment. Another object of one embodiment of the present invention is to provide a power storage device having high flexibility. Another object of one embodiment of the present invention is to provide a novel power storage device, a novel electronic device, or the like.

[0011]

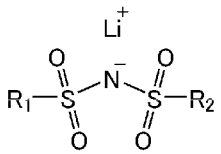
Note that the descriptions of these objects do not disturb the existence of other objects. In one embodiment of the present invention, there is no need to achieve all the objects. Other objects will be apparent from and can be derived from the description of the specification, the drawings, the claims, and the like.

[0012]

One embodiment of the present invention is a power storage device comprising a positive electrode, a negative electrode, a first separator, an electrolyte, and an exterior body. The positive electrode includes a positive electrode active material layer and a positive electrode current collector. The negative electrode includes a negative electrode material layer and a negative electrode current collector. The first separator is positioned between the positive electrode and the negative electrode. The first separator includes polyphenylene sulfide or cellulosic fiber. The electrolyte includes propylene carbonate, ethylene carbonate, and vinylene carbonate, lithium hexafluorophosphate, and lithium salt expressed by General Formula (G1).

[0013]

[Chemical Formula 1]



(G1)

[0014]

In General Formula (G1), R^1 and R^2 independently represent fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 10 carbon atoms.

[0015]

The power storage device preferably includes a second separator. The second separator is preferably positioned between one or both of the positive electrode and negative electrode and the exterior body and includes polyphenylene sulfide or cellulosic fiber.

[0016]

In the power storage device, the concentration of lithium hexafluorophosphate with respect to the electrolyte is preferably more than or equal to 0.01 wt% and less than or equal to 1.9 wt% in a weight ratio.

[0017]

In the power storage device, the lithium salt represented by General Formula (G1) is preferably lithium bis(pentafluoroethanesulfonyl)amide.

[0018]

In the power storage device, the positive electrode current collector preferably includes

aluminum or stainless steel.

[0019]

One embodiment of the present invention is an electronic device comprising the above-mentioned power storage device, a band, a display panel, and a housing. The power storage device includes a positive electrode lead and a negative electrode lead. The positive electrode lead is electrically connected to the positive electrode. The negative electrode lead is electrically connected to the negative electrode. The power storage device is embedded in the band. Part of the positive electrode lead and part of the negative electrode lead protrude from the band. The power storage device has flexibility. The power storage device is electrically connected to the display panel. The display panel is included in the housing. The band is connected to the housing. The band includes a rubber material.

[0020]

In the electronic device, the rubber material is preferably fluorine rubber or silicone rubber.

[0021]

One embodiment of the present invention can provide a power storage device whose charging and discharging characteristics are unlikely to be degraded by heat treatment. One embodiment of the present invention can provide a power storage device that is highly safe against heat treatment. One embodiment of the present invention can provide a power storage device having high flexibility. One embodiment of the present invention can provide a novel power storage device, a novel electronic device, or the like.

[0022]

Note that the description of these effects does not preclude the existence of other effects. One embodiment of the present invention does not necessarily achieve all the effects listed above. Other effects will be apparent from and can be derived from the description of the specification, the drawings, the claims, and the like.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

FIGS. 1A to 1C illustrate examples of a power storage device and electrodes.

FIGS. 2A and 2B each illustrate an example of a power storage device.

FIGS. 3A and 3B illustrate examples of a power storage device.

FIGS. 4A and 4B illustrate examples of a power storage device.

FIGS. 5A and 5B illustrate examples of a power storage device.

FIGS. 6A to 6F illustrate examples of embossing.

FIGS. 7A and 7B illustrate examples of a power storage device.

FIG. 8 illustrates an example of a power storage device.

FIG. 9 illustrates an example of a power storage device.

FIGS. 10A to 10C illustrate an example of a method for manufacturing a power storage device.

FIGS. 11A to 11C illustrate an example of a method for manufacturing a power storage device.

FIGS. 12A to 12C illustrate an example of a method for manufacturing a power storage device.

FIG. 13 illustrates an example of a method for manufacturing a power storage device.

FIGS. 14A to 14C illustrate examples of an electronic device, a band, and a power storage device.

FIGS. 15A to 15C illustrate examples of a band and a power storage device.

FIGS. 16A and 16B illustrate an example of a power storage device.

FIG. 17A to 17C illustrate an example of a method for detecting leakage.

FIGS. 18A and 18B illustrate an example of a power storage device.

FIGS. 19A and 19B illustrate an example of a power storage device.

FIG. 20 illustrates an example of a power storage device.

FIGS. 21A to 21D illustrate a method for manufacturing a power storage device.

FIGS. 22A, 22B, 22C1, and 22C2 illustrate an example of a power storage device.

FIG. 23 illustrates an example of a power storage device.

FIGS. 24A to 24D illustrate a method for manufacturing a power storage device.

FIG. 25 illustrates an example of a power storage device.

FIGS. 26A to 26F each illustrate an example of an electronic device.

FIGS. 27A to 27D each illustrate an example of an electronic device.

FIGS. 28A to 28C each illustrate an example of an electronic device.

FIG. 29 illustrates an example of an electronic device.

FIGS. 30A and 30B each illustrate an example of an electronic device.

FIGS. 31A to 31D each show charge and discharge curves in Example 1.

FIGS. 32A to 32D each show charge and discharge curves in Example 1.

FIGS. 33A to 33D each show charge and discharge curves in Example 1.

FIGS. 34A to 34D each show charge and discharge curves in Example 1.

FIGS. 35A to 35D each show cycle characteristics in Example 1.

FIGS. 36A to 36D each show cycle characteristics in Example 1.

FIGS. 37A to 37D each show cycle characteristics in Example 1.

FIGS. 38A to 38D each show cycle characteristics in Example 1.

FIGS. 39A to 39D each show cycle characteristics in Example 1.

FIGS. 40A to 40D each show cycle characteristics in Example 1.

FIGS. 41A to 41D each show cycle characteristics in Example 1.

FIGS. 42A to 42D each show cycle characteristics in Example 1.

FIGS. 43A and 43B show the relationship between the concentration of lithium hexafluorophosphate and cycle chracteristics.

FIGS. 44A to 44D each show charge and discharge curves in Example 2.

FIGS. 45A and 45B each show charge and discharge curves in Example 2.

FIGS. 46A to 46C each show cycle characteristics in Example 2.

FIGS. 47A to 47C each show cycle characteristics in Example 2.

FIGS. 48A to 48C each show cycle characteristics in Example 2

FIGS. 49A to 49C each show cycle characteristics in Example 2.

FIGS. 50A and 50B show the relationship between the concentration of lithium hexafluorophosphate and cycle chracteristics.

FIG. 51 shows an XPS measurement position in Example 3.

FIGS. 52A to 52C each show XPS spectra in Example 3.

FIGS. 53A to 53C each show XPS spectra in Example 3.

FIGS. 54A to 54C each show XPS spectra in Example 3.

FIGS. 55A and 55B each show XPS spectra in Example 3.

FIGS. 56A and 56B show TG-DTA measurement results in Example 3.

FIG. 57 shows TG-DTA measurement results in Example 4.

BEST MODE FOR CARRYING OUT THE INVENTION

[0024]

Embodiments will be described in detail with reference to the drawings. It will be readily appreciated by those skilled in the art that modes and details of the present invention can be modified in various ways without departing from the spirit and scope of the present invention. Thus, the present invention should not be construed as being limited to the description in the following embodiments.

[0025]

Note that in structures of the present invention described below, the same portions or portions having similar functions are denoted by the same reference numerals in different drawings, and a description thereof is not repeated. Further, the same hatching pattern is

applied to portions having similar functions, and the portions are not especially denoted by reference numerals in some cases.

[0026]

Note that the position, size, range, or the like of each structure illustrated in drawings and the like is not accurately represented in some cases for easy understanding. Therefore, the disclosed invention is not necessarily limited to the position, size, range, or the like as disclosed in the drawings and the like.

[0027]

In this specification and the like, flexibility refers to a property of an object being flexible and bendable. In other words, it is a property of an object that can be changed in form in response to an external force applied to the object, and elasticity or restorability to the former shape is not taken into consideration. A power storage device having flexibility, i.e., a flexible power storage device, can be changed in shape in response to an external force. A flexible power storage device can be used with its shape fixed in a state of being changed in shape, can be used while repeatedly changed in shape, or can be used in a state of not being changed in shape. In this specification and the like, the inside of an exterior body refers to a region surrounded by the exterior body of a power storage battery, in which a structure such as a positive electrode, a negative electrode, an active material layer, and a separator, and an electrolyte are stored.

[0028]

Note that the terms "film" and "layer" can be interchanged with each other depending on the case or circumstances. For example, the term “conductive layer” can be changed into the term “conductive film” in some cases. Also, the term “insulating film” can be changed into the term “insulating layer” in some cases.

[0029]

(Embodiment 1)

In this embodiment, power storage devices of embodiments of the present invention will be described with reference to FIGS. 1A to 1C to FIG. 13.

[0030]

The power storage device of one embodiment of the present invention includes a positive electrode, a negative electrode, a separator, an electrolyte, and an exterior body.

[0031]

High heat resistance of an electrolyte is necessary for high heat resistance of the power storage device. In order to increase the heat resistance of the electrolyte, it is considered effective to suppress the decomposition of the electrolyte by heat or to suppress the

decomposition of the electrolyte due to a reaction of the electrolyte with other members by heat. Examples of the reaction between the electrolyte and other members include a reaction with a positive electrode, a negative electrode, a separator, or an exterior body.

[0032]

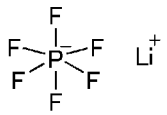
Note that in this specification, an electrolyte means a substance having electric conductivity. The electrolyte is not limited to liquid and may be a gelled one or solid. An electrolyte in a liquid state is referred to as an electrolytic solution in some cases. An electrolytic solution can be made by dissolving a solute in a solvent. An electrolyte in a solid state is referred to as a solid electrolyte in some cases.

[0033]

For example, lithium hexafluorophosphate ($LiPF_6$) represented by General Formula (100) is widely used as a lithium salt serving as a solute of an electrolyte. However, lithium hexafluorophosphate is poor in chemical and thermal stability. For example, a trace of moisture causes hydrolysis reaction to generate HF, which might be a cause of deterioration of a power storage device. It is also said that lithium hexafluorophosphate is decomposed into LiF and PF_5 at high temperature, and PF_5 decomposes the solvent. The solute probably has a low stability at high temperature. Lithium hexafluorophosphate has a thermal decomposition temperature of approximately 154°C. Note that the thermal decomposition temperature is a temperature at which the weight in a powder state decreases by 5 % due to thermal decomposition. The change in weight by thermal decomposition can be shown by thermogravimetry-differential thermal analysis (TG-DTA) and the like.

[0034]

[Chemical Formula 2]



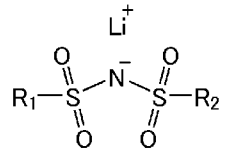
(100)

[0035]

General Formula (G1) represents the lithium salt used in one embodiment of the present invention.

[0036]

[Chemical Formula 3]



(G1)

[0037]

In General Formula (G1), R^1 and R^2 independently represent fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 10 carbon atoms.

[0038]

In this specification and the like, the fluoroalkyl group refers to a group in which some or all hydrogen atoms of an alkyl group are substituted with fluorine atoms. It is preferable that 60 % or more of hydrogen atoms of the alkyl group be substituted for fluorine atoms. The fluoroalkyl group may have atoms other than carbon, hydrogen, and fluorine, such as oxygen, sulfur, and nitrogen.

[0039]

The lithium salt represented by General Formula (G1) has high chemical and thermal stability. The lithium salt also has high decomposition temperature and thermal resistance; thus, the thermal resistivity of a storage battery including the lithium salt as a solute can be increased. Moreover, the lithium salt represented by General Formula (G1) contains fluorine having high electronegativity; thus, a fluoroalkylsulfonyl group shows a strong electron-withdrawing property and the dissociation level of a lithium ion is very high. For these reasons, the lithium salt is suitable as an electrolyte solute in a power storage device, such as a lithium ion secondary battery. The more fluorine atom the fluoroalkyl group has, the more preferable it is.

[0040]

In General Formula (G1), it is more preferable that R^1 be fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 7 carbon atoms. In General Formula (G1), it is more preferable that R^2 be fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 7 carbon atoms. When such a lithium salt is used as an electrolyte solute, the thermal resistivity of the power storage device can be increased.

[0041]

In General Formula (G1), it is more preferable that R^1 be fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 5 carbon atoms. In General Formula (G1), it is more preferable that R^2 be fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 5 carbon atoms. In that case, the dissociation level of the lithium salt represented by General Formula (G1) is increased. As a result, the electrolyte can have high ion conductivity. Moreover, the molecular weight of the lithium salt represented by

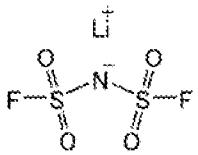
General Formula (G1) is not increased, and the weight of the lithium salt dissolved in a solvent is small. Thus, an increase in viscosity of the electrolyte and the degradation of battery characteristics can be suppressed. The cost can also be reduced.

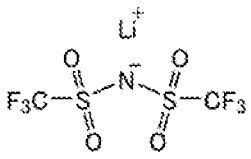
[0042]

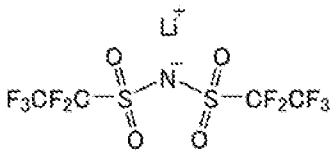
Specific structural formulae of the lithium salt represented by General Formula (G1) are shown below. The following is preferably used as a solute: lithium bis(fluorosulfonyl)amide ($LiN(FSO_2)_2N$, abbreviation: LiFSA) represented by Structural Formula (101), lithium bis(trifluoromethanesulfonyl)amide ($Li(CF_3SO_2)_2N$, abbreviation: LiTFSA) represented by Structural Formula (102), lithium bis(pentafluoroethanesulfonyl)amide ($Li(C_2F_5SO_2)_2N$, abbreviation: LiBETA) represented by Structural Formula (103), lithium (perfluorobuthanesulfonyl)(trifluoromethanesulfonyl))amide ($LiN(C_4F_9SO_2)(CF_3SO_2)$) represented by Structural Formula (104), and the like. These materials have high thermal decomposition temperatures. Thus, storage devices including these materials as solutes can have higher thermal resistance. For example, the melting point and thermal decomposition temperature of lithium bis(fluorosulfonyl)amide is 140 °C and about 300 °C, respectively. The melting point and thermal decomposition temperature of lithium bis(trifluoromethanesulfonyl)amide is 233 °C and about 380 °C, respectively. The melting point and thermal decomposition temperature of lithium bis(pentafluoroethanesulfonyl)amide is 328 °C and about 350 °C, respectively.

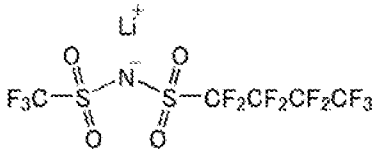
[0043]

[Chemical Formula 4]


(101)


(102)


(103)


(104)

[0044]

However, the lithium salt represented by General Formula (G1) might react with a current collector, leading to corrosion of the current collector. The corrosion of the current collector might become a cause of a reduction in battery capacity.

[0045]

The above described lithium hexafluorophosphate represented by Structural Formula (100) might react with a current collector to form a passivation film on the current collector surface and suppress the corrosion of the current collector.

[0046]

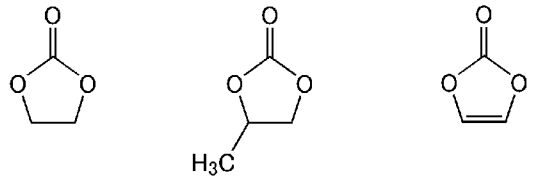
For this reason, in one embodiment of the present invention, the electrolyte solute preferably contains the lithium salt represented by General Formula (G1) and lithium hexafluorophosphate ($LiPF_6$) represented by Structural Formula (100). Lithium hexafluorophosphate ($LiPF_6$) can form a passivation film on the current collector surface and suppress the corrosion of the current collector. Lithium hexafluorophosphate ($LiPF_6$) is desirably used at an amount sufficient for forming a passivation film on the current collector surface. Moreover, the lithium salt represented by General Formula (G1) mainly supplies lithium ions which serve as carrier ions, and also has high thermal resistance. In addition, the use of the lithium salt represented by General Formula (G1) and lithium hexafluorophosphate ($LiPF_6$) represented by Structural Formula (100) can make a power storage device have high thermal resistance. The power storage device is unlikely to have a decrease in capacity and energy density after charging and discharging are repeated even when a storage battery is subjected to heat treatment.

[0047]

To increase the thermal resistance of the power storage device, a solvent contained in the electrolyte preferably has a high boiling point and low vapor pressure. The solvent preferably has high dielectric constant and high ability of dissolving a solute. As such a solvent, carbonate can be used. The carbonate means a compound containing at least one carbonic ester in its molecular structure and includes both cyclic carbonate and chain carbonate in its category. The chain includes both straight-chain and branched-chain. As cyclic carbonate, ethylene carbonate (EC) represented by Structural Formula (301), propylene carbonate (PC) represented by Structural Formula (302), and vinylene carbonate (VC) represented by Structural Formula (303) can be used. The boiling points of ethylene carbonate (EC), propylene carbonate (PC), and vinylene carbonate (VC) are 243 °C, 242 °C, and 162 °C, respectively. Moreover, these carbonates have high thermal resistance and low vapor pressure and thus are preferably used as a solvent.

[0048]

[Chemical Formula 5]



(301) (302) (303)

[0049]

When graphite (layered graphite) is used as the negative electrode, propylene carbonate (PC) does not form a passivating film on the graphite surface but is intercalated between graphite layers together with lithium ions, separating part of the graphite layers from a graphite particle in some cases. In view of this, it is preferable to mix an electrolyte with a solvent having a function of forming a passivation film on the graphite surface. Examples of the solvent having a function of forming a passivation film on the graphite surface includes ethylene carbonate (EC), vinylene carbonate (VC), and the like. In one embodiment of the present invention, propylene carbonate (PC), ethylene carbonate (EC), and vinylene carbonate (VC) are used for the electrolyte solvent. This can suppress the separation of part of the graphite layers from a graphite particle.

[0050]

In one embodiment of the present invention, it is preferable that the electrolyte solvent contain ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC) and that the electrolyte solute contain the lithium salt represented by General Formula (G1) and lithium hexafluorophosphate ($LiPF_6$).

[0051]

In a power storage device of one embodiment of the present invention, an electrolyte formed in the following manner is preferably used: vinylene carbonate (VC) is mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) are mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate are dissolved in the solution.

[0052]

Specifically, the amount of vinylene carbonate (VC) dissolved in the electrolyte is more than or equal to 0.1 wt% and less than or equal to 5.0 wt%, preferably 1.0 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte is more than or equal to 0.1 mol/L and less than or equal to 5.0mol/L, preferably 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate with respect to the electrolyte is preferably more than or equal to 0.01 wt% and less than or equal to 1.9 wt%, further preferably, 0.05 wt% and less than or equal to 1.2 wt%, still further preferably 0.1 wt%

and less than or equal to 0.8 wt% in the weight ratio.

[0053]

The composition of electrolyte can be examined by X-ray photoelectron spectroscopy (XPS), gas chromatography mass spectrometry (GC-MS), liquid chromatography mass spectrometry (LC-MS), ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES), atomic absorption spectrometry (AAS), glow discharge mass spectrometry (GD-MS), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and the like.

[0054]

Polyethylene, polypropylene, and the like, which are generally used as a separator, are sensitive to heat. Minute pores of a separator might be blocked at high temperature, resulting in malfunction of the power storage device.

[0055]

In view of the above, a separator containing polyphenylene sulfide (PPS) or cellulosic fiber is preferably used for the power storage device of one embodiment of the present invention.

[0056]

The separator containing polyphenylene sulfide and the separator containing solvent-spun regenerated cellulosic fiber have high heat resistance and high chemical resistance.

[0057]

Moreover, the separator containing polyphenylene sulfide and the separator containing solvent-spun regenerated cellulosic fiber have low reactivity to the electrolytic solution at high temperature. Thus, degradation of the output characteristics and the charge and discharge cycle performance can be inhibited.

[0058]

<Structural example of power storage device>

Next, a specific structure of the power storage device of one embodiment of the present invention will be described below.

[0059]

FIG. 1A illustrates a power storage device 500, which is a power storage device of one embodiment of the present invention. Although FIG. 1A illustrates a mode of a thin power storage device as an example of the power storage device 500, one embodiment of the present invention is not limited to this example.

[0060]

As illustrated in FIG. 1A, the power storage device 500 includes a positive electrode 503, a negative electrode 506, a first separator 507, a second separator 520, and an exterior body

509. The power storage device 500 may include a positive electrode lead 510 and a negative electrode lead 511. A bonding portion 518 corresponds to a thermocompression bonding portion in the outer region of the exterior body 509.

[0061]

FIG. 1B illustrates the appearance of the positive electrode 503. The positive electrode 503 includes the positive electrode current collector 501 and the positive electrode active material layer 502.

[0062]

As illustrated in FIG. 1B, the positive electrode 503 preferably includes the tab region 281. The positive electrode lead 510 is preferably welded to part of the tab region 281. The tab region 281 preferably includes a region where the positive electrode current collector 501 is exposed. When the positive electrode lead 510 is welded to the region where the positive electrode current collector 501 is exposed, contact resistance can be further reduced. Although FIG. 1B illustrates the example where the positive electrode current collector 501 is exposed in the entire tab region 281, the tab region 281 may partly include the positive electrode active material layer 502.

[0063]

FIG. 1C illustrates the appearance of the negative electrode 506. The negative electrode 506 includes the negative electrode current collector 504 and the negative electrode active material layer 505.

[0064]

As illustrated in FIG. 1C, the negative electrode 506 preferably includes the tab region 282. The negative electrode lead 511 is preferably welded to part of the tab region 282. The tab region 282 preferably includes a region where the negative electrode current collector 504 is exposed. When the negative electrode lead 511 is welded to the region where the negative electrode current collector 504 is exposed, contact resistance can be further reduced. Although FIG. 1C illustrates the example where the negative electrode current collector 504 is exposed in the entire tab region 282, the tab region 282 may partly include the negative electrode active material layer 505.

[0065]

As shown in FIG. 1A, the first separator 507 includes a region overlapping with the positive electrode 503 and the negative electrode 506. The second separator 520 includes a region overlapping with the tab regions 281 and 282. Note that the second separator 520 is not necessarily provided.

[0066]

FIGS. 2A and 2B each illustrate an example of a cross-sectional view along dashed-dotted line A1-A2 in FIG. 1A. FIGS. 2A and 2B each illustrate a cross-sectional structure of the power storage device 500 that is formed using a pair of the positive electrode 503 and the negative electrode 506.

[0067]

As illustrated in FIGS. 2A and 2B, the power storage device 500 includes the positive electrode 503, the negative electrode 506, the first separator 507, the second separator 520, an electrolyte 508, and the exterior body 509. The first separator 507 is located between the positive electrode 503 and the negative electrode 506. The second separator 520 is located between the positive electrode 503 and the exterior body 509 and between the negative electrode 506 and the exterior body 509. The exterior body 509 is filled with the electrolyte 508.

[0068]

The positive electrode 503 includes a positive electrode active material layer 502 and a positive electrode current collector 501. The negative electrode 506 includes a negative electrode active material layer 505 and a negative electrode current collector 504. The active material layer is formed on one surface or opposite surfaces of the current collector. The first separator 507 is positioned between the positive electrode current collector 501 and the negative electrode current collector 504.

[0069]

The power storage device includes one or more positive electrodes and one or more negative electrodes. For example, the power storage device can have a layered structure including a plurality of positive electrodes and a plurality of negative electrodes.

[0070]

The positive electrode 503 and the negative electrode 506 preferably include tab regions so that a plurality of stacked positive electrodes can be electrically connected to each other and a plurality of stacked negative electrodes can be electrically connected to each other. Furthermore, a lead is preferably electrically connected to the tab region.

[0071]

FIGS. 3A and 3B are examples of cross-sectional views taken along dashed-dotted lines B3-B4 and B5-B6 in FIG. 1A, respectively. The cross-sectional view taken along dashed-dotted line B3-B4 corresponds to a region including the positive electrode lead 510 and the positive electrode 503. The cross-sectional view taken along dashed-dotted line B5-B6 corresponds to a region including the negative electrode lead 511 and the negative electrode 506. FIGS. 3A and 3B illustrate cross-sectional structures of the power storage device 500 formed using a pair of the positive electrode 503 and the negative electrode 506.

[0072]

As shown in FIG. 3A, the second separator 520 is provided between the positive electrode 503 and the exterior body 509. The second separator 520 preferably includes a region overlapping with the tab region 281 included in the positive electrode and with the positive electrode lead 510. As shown in FIG. 3B, the second separator 520 is provided between the negative electrode 506 and the exterior body 509. The second separator 520 preferably includes a region overlapping with the tab region 282 included in the negative electrode and with the negative electrode lead 511.

[0073]

When a conductive material is used for the outer surface of the exterior body 509, and an insulating resin is used for the inner side (the positive electrode and negative electrode side) of the exterior body 509, the resin is melted by heat treatment and the conductive material on the outer side is exposed in some cases. When the conductive material of the exterior body is in contact with the positive electrode lead 510, the negative electrode lead 511, the positive electrode current collector 501, or the negative electrode current collector 504, leakage might occur. When the second separator 520 is provided between the positive electrode 503 and the exterior body 509 and between the negative electrode 506 and the exterior body 509, the leakage can be suppressed. Note that the second separator 520 is not necessarily provided.

[0074]

FIG. 4A illustrates another example of a cross-sectional view along dashed-dotted line A1-A2 in FIG. 1A. FIG. 4B is a cross-sectional view along dashed-dotted line B1-B2 in FIG. 1A.

[0075]

FIGS. 4A and 4B each illustrate a cross-sectional structure of the power storage device 500 that is formed using a plurality of pairs of the positive and negative electrodes 503 and 506. There is no limitation on the number of electrode layers of the power storage device 500. In the case of using a large number of electrode layers, the power storage device can have high capacity. In contrast, in the case of using a small number of electrode layers, the power storage device can have a small thickness and high flexibility.

[0076]

The examples in FIGS. 4A and 4B each include two positive electrodes 503 in each of which the positive electrode active material layer 502 is provided on one surface of the positive electrode current collector 501; two positive electrodes 503 in each of which the positive electrode active material layers 502 are provided on opposite surfaces of the positive electrode current collector 501; and three negative electrodes 506 in each of which the negative electrode

active material layers 505 are provided on opposite surfaces of the negative electrode current collector 504. In other words, the power storage device 500 includes six positive electrode active material layers 502 and six negative electrode active material layers 505. Note that although the first separator 507 has a bag-like shape in the examples illustrated in FIGS. 4A and 4B, the present invention is not limited to this example and the first separator 507 may have a stripe shape or a bellows shape.

[0077]

Alternatively, one positive electrode in which both surfaces of the positive electrode current collector 501 are provided with the positive electrode active material layers 502 in FIGS. 4A and 4B is preferably replaced with two positive electrodes in each of which one surface of the positive electrode current collector 501 is provided with the positive electrode active material layer 502. Similarly, one negative electrode in which both surfaces of the negative electrode current collector 504 are provided with the negative electrode active material layers 505 is preferably replaced with two negative electrodes in each of which one surface of the negative electrode current collector 504 is provided with the negative electrode active material layer 505. In the power storage device 500 in FIGS. 5A and 5B, surfaces of the positive electrode current collectors 501 on the side not provided with the positive electrode active material layer 502 face and are in contact with each other, and surfaces of the negative electrode current collectors 504 on the side not provided with the negative electrode active material layer 505 face and are in contact with each other. Such a structure allows the interface between the two positive electrode current collectors 501 and the two negative electrode current collectors 504 to serve as sliding planes when the power storage device 500 is curved, relieving stress caused in the power storage device 500.

[0078]

Although FIG. 1A illustrates the example where the ends of the positive electrode 503 and the negative electrode 506 are substantially aligned with each other, part of the positive electrode 503 may extend beyond the end of the negative electrode 506.

[0079]

In the power storage device 500, the area of a region where the negative electrode 506 does not overlap with the positive electrode 503 is preferably as small as possible.

[0080]

In the example illustrated in FIG. 2A, the end of the negative electrode 506 is located inward from the end of the positive electrode 503. With this structure, the entire negative electrode 506 can overlap with the positive electrode 503 or the area of the region where the negative electrode 506 does not overlap with the positive electrode 503 can be small.

[0081]

The areas of the positive electrode 503 and the negative electrode 506 in the power storage device 500 are preferably substantially equal. For example, the areas of the positive electrode 503 and the negative electrode 506 that face each other with the first separator 507 therebetween are preferably substantially equal. For example, the areas of the positive electrode active material layer 502 and the negative electrode active material layer 505 that face each other with the first separator 507 therebetween are preferably substantially equal.

[0082]

In the example illustrated in FIG. 2B, the end of the positive electrode 503 is located inward from the end of the negative electrode 506. With this structure, the entire positive electrode 503 can overlap with the negative electrode 506 or the area of the region where the positive electrode 503 does not overlap with the negative electrode 506 can be small. In the case where the end of the negative electrode 506 is located inward from the end of the positive electrode 503, a current sometimes concentrates at the end portion of the negative electrode 506. For example, concentration of a current in part of the negative electrode 506 results in deposition of lithium on the negative electrode 506 in some cases. By reducing the area of the region where the positive electrode 503 does not overlap with the negative electrode 506, concentration of a current in part of the negative electrode 506 can be inhibited. As a result, for example, deposition of lithium on the negative electrode 506 can be inhibited, which is preferable.

[0083]

As shown in FIGS. 4A and 4B, the end portion of the positive electrode 503 can be positioned on an inner side than the negative electrode 506 even when a plurality of positive electrodes 503 and the negative electrodes 506 is used. The end portion of the positive electrode 503 may be substantially aligned with the end portion of the negative electrode 506. The end portion of the negative electrode 506 may be positioned on an inner side than the positive electrode 503.

[0084]

As illustrated in FIG. 1A, the positive electrode lead 510 is preferably electrically connected to the positive electrode 503. Similarly, the negative electrode lead 511 is preferably electrically connected to the negative electrode 506. The positive electrode lead 510 and the negative electrode lead 511 are exposed to the outside of the exterior body 509 so as to serve as terminals for electrical contact with an external portion.

[0085]

The positive electrode current collector 501 and the negative electrode current collector 504 can double as terminals for electrical contact with an external portion. In that case, the

positive electrode current collector 501 and the negative electrode current collector 504 may be arranged such that part of the positive electrode current collector 501 and part of the negative electrode current collector 504 are exposed to the outside of the exterior body 509 without using electrode leads.

[0086]

Note that part of a surface of the exterior body 509 preferably has projections and depressions. This can relieve stress applied to the exterior body 509 when the power storage device 500 is curved. Thus, the power storage device 500 can have high flexibility. Such projections and depressions can be formed by embossing the exterior body 509 before the power storage device 500 is assembled.

[0087]

Here, embossing, which is a kind of pressing, will be described.

[0088]

FIGS. 6A to 6F are cross-sectional views illustrating examples of embossing. Note that embossing refers to processing for forming unevenness on a film by bringing an embossing roll whose surface has unevenness into contact with the film with pressure. Note that the embossing roll is a roll whose surface is patterned.

[0089]

FIG. 6A illustrates an example where one surface of a film 50 used for the exterior body 509 is embossed.

[0090]

FIG. 6A illustrates the state where a film 50 is sandwiched between an embossing roll 53 in contact with the one surface of the film and a roll 54 in contact with the other surface and the film 50 is transferred in a direction 60. The surface of the film is patterned by pressure or heat.

[0091]

Processing illustrated in FIG. 6A is called one-side embossing, which can be performed by a combination of the embossing roll 53 and the roll 54 (a metal roll or an elastic roll such as a rubber roll).

[0092]

FIG. 6B illustrates the state where a film 51 whose one surface is embossed is sandwiched between the embossing roll 53 and the roll 54 and is transferred in the direction 60. The embossing roll 53 rolls along a non-embossed surface of the film 51; thus, both surfaces of the film 51 are embossed. As described here, one film can be embossed more than once.

[0093]

FIG. 6C is an enlarged view of a cross section of a film 52 whose both surfaces are embossed. Note that H_1 represents the thickness of the film in depressions or projections, and H_2 represents the thickness of the film at a boundary portion between a depression and its adjacent projection or the thickness of the film at a boundary portion between a projection and its adjacent depression. The thickness of the film is not uniform, and H_2 is smaller than H_1.

[0094]

FIG. 6D illustrates another example where both surfaces of a film are embossed.

[0095]

FIG. 6D illustrates the state where the film 50 is sandwiched between the embossing roll 53 in contact with one surface of the film and an embossing roll 55 in contact with the other surface and the film 50 is being transferred in the direction 60.

[0096]

FIG. 6D illustrates a combination of the embossing roll 53 and the embossing roll 55, which are a couple of embossing rolls. The surface of the film 50 is patterned by alternately provided projections and depressions for embossing and debossing part of the surface of the film 50.

[0097]

FIG. 6E illustrates the case of using the embossing roll 53 and an embossing roll 56 whose protrusions have a pitch different from that of protrusions of the embossing roll 55 in FIG. 6D. Note that a protrusion pitch or an embossing pitch is the distance between the tops of adjacent protrusions. For example, a distance P in FIG. 6E is a protrusion pitch or an embossing pitch. FIG. 6E illustrates the state where the film 50 is sandwiched between the embossing roll 53 and the embossing roll 56 and is transferred in the direction 60. The film processed using the embossing rolls with different protrusion pitches can have surfaces with different embossing pitches.

[0098]

FIG. 6F illustrates the state where the film 50 is sandwiched between an embossing roll 57 in contact with one surface of the film and an embossing roll 58 in contact with the other surface and the film 50 is transferred in the direction 60.

[0099]

Processing illustrated in FIG. 6F is called tip-to-tip both-side embossing performed by a combination of the embossing roll 57 and the embossing roll 58 that has the same pattern as the embossing roll 57. The phases of the projections and depressions of the two embossing rolls are coordinate, so that substantially the same pattern can be formed on both surfaces of the film 50. Unlike in the case of FIG. 6F, embossing may be performed without coordinating the

phases of the projections and depressions of the same embossing rolls.

[0100]

An embossing plate can be used instead of the embossing roll. Furthermore, embossing is not necessarily employed, and any method that allows formation of a relief on part of the film can be employed.

[0101]

FIG. 7A illustrates an example of the power storage device 500 using an exterior body 529 having projections and depressions formed by the embossing described above. FIG. 7B is a cross-sectional view taken along the dashed-dotted line H1-H2 in FIG. 7A. The structure of FIG. 7B without the exterior body 529 is similar to the structure of FIG. 4B.

[0102]

The projections and depressions of the exterior body 529 are formed so as to include a region overlapping with the positive electrode 503 and the negative electrode 506. In FIG. 7A, the bonding portion 518 does not have projections and depressions, but may have projections and depressions.

[0103]

Furthermore, the projections and depressions of the exterior body 529 are formed at regular intervals in the long axis direction of the power storage device 500 (the Y direction in FIG. 7A). In other words, one depression and one projection are formed so as to extend in the short axis direction of the power storage device 500 (the X direction in FIG. 7A). Such projections and depressions can relieve stress applied when the power storage device 500 is curved in the long axis direction.

[0104]

Note that the projections and depressions of the exterior body 529 may be formed so as to have a geometric pattern in which diagonal lines in two directions cross each other (see FIG. 8). Such projections and depressions can relieve stresses caused by curving the power storage device 500 in at least two directions.

[0105]

Although the positive electrode lead 510 and the negative electrode lead 511 are provided on the same side of the power storage device 500 in FIG. 1A, the positive electrode lead 510 and the negative electrode lead 511 may be provided on different sides of the power storage device 500 as illustrated in FIG. 9. The electrode leads of the power storage device of one embodiment of the present invention can be freely positioned as described above; therefore, the degree of freedom in design is high. Accordingly, a product including the power storage device of one embodiment of the present invention can have a high degree of freedom in design.

Furthermore, a yield of products each including the power storage device of one embodiment of the present invention can be increased.

[0106]

<Example of Manufacturing Method for Power Storage Device>

Next, an example of a manufacturing method for the power storage device 500, which is a power storage device of one embodiment of the present invention, will be described with reference to FIGS. 10A and 10B to FIG. 13.

[0107]

First, the positive electrode 503, the negative electrode 506, and the first separator 507 are stacked. Specifically, the first separator 507 is positioned over the positive electrode 503. Then, the negative electrode 506 is positioned over the first separator 507. In the case of using two or more positive electrode-negative electrode pairs, another separator 507 is positioned over the negative electrode 506, and then, the positive electrode 503 is positioned. In this manner, the positive electrodes 503 and the negative electrodes 506 are alternately stacked and separated by the first separator 507.

[0108]

Alternatively, the first separator 507 may have a bag-like shape. The electrode is preferably surrounded by the first separator 507, in which case the electrode is less likely to be damaged during a fabricating process.

[0109]

First, the positive electrode 503 is positioned over the first separator 507. Then, the first separator 507 is folded along a broken line in FIG. 10A so that the positive electrode 503 is sandwiched by the first separator 507. Although the example where the positive electrode 503 is sandwiched by the first separator 507 is described here, the negative electrode 506 may be sandwiched by the first separator 507.

[0110]

Here, the outer edges of the first separator 507 outside the positive electrode 503 are bonded so that the first separator 507 has a bag-like shape (or an envelope-like shape). The bonding of the outer edges of the first separator 507 can be performed with the use of an adhesive or the like, by ultrasonic welding, or by thermal fusion bonding.

[0111]

Next, the outer edges of the first separator 507 are bonded by heating. Bonding portions 514 are illustrated in FIG. 10A. In such a manner, the positive electrode 503 can be covered with the first separator 507.

[0112]

Note that in the case where the outer edges of the first separator 507 are bonded using an adhesive or the like, the amount of the adhesive is preferably small. The outer edges of the first separator 507 are bonded such that an electrode (the positive electrode 503 in FIG. 10A) sandwiched between facing portions of the first separator 507 does not protrude from the first separator 507; thus, for example, when the bonding portions 514 are formed as illustrated in FIG. 10B, the amount of the adhesive can be reduced. In FIG. 10B, the bonding portions 514 are formed at the following portions of the outer edges of the first separator 507: portions of two sides intersecting with a side where a fold is formed that are close to the fold; and a portion of a side opposite to the side where the fold is formed.

[0113]

Then, the negative electrodes 506 and the positive electrodes 503 each covered with the separator are alternately stacked as illustrated in FIG. 10C. Furthermore, the positive electrode lead 510 and the negative electrode lead 511 each having a sealing layer 115 are prepared. Thermoplastic resin such as polypropylene and the like can be used for the sealing layer 115.

[0114]

After that, the positive electrode lead 510 having the sealing layer 115 is connected to the tab region 281 of the positive electrode 503 as illustrated in FIG. 11A. FIG. 11B is an enlarged view of a connection portion. The tab region 281 of the positive electrode 503 and the positive electrode lead 510 are electrically connected to each other by irradiating the bonding portion 512 with ultrasonic waves while applying pressure thereto (ultrasonic welding). In that case, a curved portion 513 is preferably provided in the tab region 281.

[0115]

This curved portion 513 can relieve stress due to external force applied after fabrication of the power storage device 500. Thus, the power storage device 500 can have high reliability.

[0116]

The negative electrode lead 511 can be electrically connected to the tab region 282 of the negative electrode 506 by a similar method.

[0117]

Subsequently, the positive electrode 503, the negative electrode 506, and the first separator 507 are positioned over the second separator 520.

[0118]

Next, the second separator 520 is folded along a broken line in FIG. 11C so that the positive electrode 503, the negative electrode 506, and the first separator 507 are sandwiched by the second separator 520. Note that the second separator 520 preferably covers the tab regions 281 and 282.

[0119]

Here, it is preferable that the outer edges of the second separator 520 be bonded so that the second separator 520 has a bag-like shape (or an envelope-like shape). The bonding of the outer edges of the second separator 520 can be performed with the use of an adhesive or the like, by ultrasonic welding, or by thermal fusion bonding.

[0120]

Next, the outer edges of the second separator 520 are bonded by heating. FIG. 12A shows a bonding portion 521. In such a manner, the positive electrode 503, the negative electrode 506, and the first separator 507 can be covered with the second separator 520.

[0121]

Note that in the case where the outer edges of the second separator 520 are bonded using an adhesive or the like, the amount of the adhesive is preferably small. The outer edges of the second separator 520 are bonded such that the positive electrode 503 and the negative electrode 506 which are sandwiched between the second separator 520 and the first separator 507 do not protrude from the second separator 520; thus, for example, when the bonding portions 521 are formed as illustrated in FIG. 12B, the amount of the adhesive can be reduced. In FIG. 12B, the bonding portions 521 are formed at the following portions of the outer edges of the second separator 520: portions of two sides that intersect with a side where a fold is formed that are close to the fold; and the vicinity of the tab regions 281 and 282.

[0122]

Note that the second separator 520 is not necessarily provided. If the second separator 520 is not provided, the process related to the second separator 520 can be eliminated.

[0123]

Subsequently, the positive electrode 503, the negative electrode 506, the first separator 507, and the second separator 520 are positioned over an exterior body 509.

[0124]

Then, the exterior body 509 is folded along a portion shown by a dotted line in the vicinity of a center portion of the exterior body 509 in FIG. 12C.

[0125]

In FIG. 13, the thermocompression bonding portion in the outer edges of the exterior body 509 is illustrated as a bonding portion 118. Then, the outer edges of the exterior body 509 except an inlet 119 for introducing the electrolyte 508 are bonded by thermocompression bonding. In thermocompression bonding, sealing layers provided over the leads are also melted, thereby fixing the leads and the exterior body 509 to each other. Moreover, adhesion between the exterior body 509 and the leads can be increased.

[0126]

After that, in a reduced-pressure atmosphere or an inert gas atmosphere, a desired amount of electrolyte 508 is introduced to the inside of the exterior body 509 from the inlet 119. Lastly, the inlet 119 is sealed by thermocompression bonding. Through the above steps, the power storage device 500, which is a thin power storage device, can be fabricated.

[0127]

Aging may be performed after fabrication of the power storage device 500. The aging can be performed under the following conditions, for example. Charge is performed at a rate of 0.001 C or more and 0.2 C or less. The temperature may be higher than or equal to room temperature and lower than or equal to 50 °C. In the case where an electrolyte is decomposed and a gas is generated and accumulates between the electrodes, the electrolyte cannot be in contact with a surface of the electrode in some regions. That is to say, an effectual reaction area of the electrode is reduced and effectual resistance is increased.

[0128]

When the resistance is extremely increased, the negative electrode potential is decreased. Consequently, lithium is intercalated into graphite and lithium is deposited on the surface of graphite. The lithium deposition might reduce capacity. For example, if a coating film or the like is grown on the surface after lithium deposition, lithium deposited on the surface cannot be dissolved again. This lithium cannot contribute to capacity. In addition, when deposited lithium is physically collapsed and conduction with the electrode is lost, the lithium also cannot contribute to capacity. Therefore, the gas is preferably released to prevent the potential of the negative electrode from reaching the potential of lithium because of an increase in a charging voltage.

[0129]

In the case of performing degasification, for example, part of the exterior body of the thin power storage device is cut to open the power storage device. When the exterior body is expanded because of a gas, the form of the exterior body is preferably adjusted. Furthermore, the electrolyte may be added as needed before resealing. In the case where degasification cannot be performed, a space for releasing a gas may be provided in the cell so that a gas that accumulates between the electrodes can be released from between the electrodes. A space formed by the use of the embossed laminate exterior body described above can be utilized as a space for releasing a gas.

[0130]

After the release of the gas, the charging state may be maintained at a temperature higher than room temperature, preferably higher than or equal to 30 °C and lower than or equal

to 60 °C, more preferably higher than or equal to 35 °C and lower than or equal to 50 °C for, for example, 1 hour or more and 100 hours or less. In the initial charging, an electrolyte decomposed on the surface forms a coating film. The formed coating film may thus be densified when the charging state is held at a temperature higher than room temperature after the release of the gas, for example.

[0131]

Here, a charging rate and a discharging rate will be described. The charging rate (also referred to as C rate) refers to the relative ratio of constant current charging current to battery capacity (current value in charging [A] ÷ battery capacity [Ah]) and is expressed in a unit C. For example, the case where a battery having a capacity of 10 Ah is charged at a constant current of 2 A is rephrased as follows: charging is performed at 0.2 C. A charging rate of 1 C refers to the amount of current with which a battery is charged completely for one hour. The higher the charging rate is, the faster charging is completed. Furthermore, a discharging rate (also referred to as C rate) refers to the relative ratio of constant current discharging current to battery capacity (current value in discharging [A] ÷ battery capacity [Ah]) and is expressed in a unit C. For example, the case where a battery having a capacity of 10 Ah is discharged at a constant current of 2 A is rephrased as follows: discharging is performed at 0.2 C. A discharging rate of 1 C refers to the amount of current with which a battery is discharged completely for one hour. The higher the discharging rate is, the faster discharging is completed.

[0132]

<Components of power storage device>

Other components of the power storage device of one embodiment of the present invention are described in detail below. When a flexible material is selected from materials of the members described in this embodiment and used, a flexible power storage device can be fabricated.

[0133]

<<Electrolyte >>

The electrolyte contains a solute and a solvent.

[0134]

As a solvent of the electrolyte, a material with carrier ion mobility is used. In particular, the solvent preferably has high heat resistance and low reactivity to a graphite negative electrode. In the power storage device of one embodiment of the present invention, propylene carbonate, ethylene carbonate, and vinylene carbonate are mixed and used for the solvent.

[0135]

As the solvent, an aprotic organic solvent is preferably used. For example, propylene carbonate, ethylene carbonate, vinyl ethylene carbonate, one of EC, PC, butylene carbonate, γ-butyrolactone, γ-valerolactone, dimethyl sulfoxide, methyl diglyme, benzonitrile, and sulfolane can be used, or two or more of these solvents can be used in an appropriate combination in an appropriate ratio.

[0136]

When a gelled high-molecular material is used as the solvent of the electrolyte, safety against liquid leakage and the like is improved. Further, the power storage device can be thinner and more lightweight. Typical examples of gelled high-molecular materials include a silicone gel, an acrylic gel, an acrylonitrile gel, a polyethylene oxide-based gel, a polypropylene oxide-based gel, a gel of a fluorine-based polymer, and the like.

[0137]

Alternatively, the use of one or more kinds of ionic liquids (room temperature molten salts) which have features of non-flammability and non-volatility as a solvent of the electrolyte can prevent the power storage device from exploding or catching fire even when the power storage device internally shorts out or the internal temperature increases owing to overcharging and others. Thus, the power storage device has improved safety.

[0138]

As the solute, a material that has carrier ion mobility and contains carrier ions can be used. In the case where carrier ions are lithium ions, the solute is a lithium salt. As a lithium salt, LiBETA, lithium bis(trifluoromethanesulfonyl)amide ($Li(CF_3SO_2)_2N$, abbreviation: LiTFSA), lithium bis(fluorosulfonyl)amide ($Li(FSO_2)_2N$, abbreviation: LiFSA), $LiBF_4$, lithium bis(oxalate)borate ($LiB(C_2O_4)_2$, abbreviation: LiBOB), or the like, which has high heat resistance, is preferably used.

[0139]

In the power storage device, when a metal included in the positive electrode current collector is dissolved by a battery reaction between the electrolyte and the current collector, the capacity of the power storage device is decreased and the power storage device deteriorates. That is, the capacity is significantly decreased as charging and discharging are repeated through the cycle performance test of the power storage device, and the lifetime of the power storage device becomes short. Furthermore, when metal dissolution from the current collector at a connection portion between the lead and the current collector proceeds, disconnection might occur. In one embodiment of the present invention, a material which is unlikely to react with the current collector and thus is unlikely to cause the dissolution of the metal in the current collector is used for the solute material contained in the electrolyte.

[0140]

Examples of a metal in materials for the positive electrode current collector include aluminum and stainless steel. In one embodiment of the present invention, for a solute material used for the electrolyte, the solute that is unlikely to dissolve such a metal included in the positive electrode current collector is used. Specifically, lithium salt represented by General Formula (G1) and $LiPF_6$ can be given as a lithium salt that can be used as the solute in one embodiment of the present invention.

[0141]

In the power storage device of one embodiment of the present invention, the dissolution of the metal included in the positive electrode current collector into the electrolyte is inhibited, so that the deterioration of the positive electrode current collector is inhibited. In addition, the deposition of the metal on a surface of the negative electrode is inhibited, so that the capacity reduction is small, and the power storage device can have a favorable cycle lifetime.

[0142]

Other than the above solute, one of lithium salts such as $LiPF_6$, $LiClO_4$, $LiAsF_6$, $LiAlCl_4$, LiSCN, LiBr, LiI, Li_2SO_4, $Li_2B_{10}Cl_{10}$, $Li_2B_{12}Cl_{12}$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiC(CF_3SO_2)_3$, $LiC(C_2F_5SO_2)_3$, $LiN(FSO_2)_2$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, and $LiN(C_4F_9SO_2)(CF_3SO_2)$ can be used, or two or more of these lithium salts can be used in an appropriate combination in an appropriate ratio.

[0143]

Although the case where carrier ions are lithium ions in the above electrolyte is described, carrier ions other than lithium ions can be used. When the carrier ions other than lithium ions are alkali metal ions or alkaline-earth metal ions, instead of lithium in the lithium salts, an alkali metal (e.g., sodium or potassium) or an alkaline-earth metal (e.g., calcium, strontium, barium, beryllium, or magnesium) may be used as the solute.

[0144]

Furthermore, an additive agent such as vinylene carbonate (VC), propane sultone (PS), *tert*-butylbenzene (TBB), fluoroethylene carbonate (FEC), lithium bis(oxalate)borate (LiBOB), or a dinitrile compound such as succinonitrile or adiponitrile may be added to the electrolyte solution. The concentration of such an additive agent in the whole solvent is, for example, higher than or equal to 0.1 wt% and lower than or equal to 5 wt%.

[0145]

With the use of the above solvent and the above electrolyte, an electrolyte of the power storage device of one embodiment of the present invention can be formed.

[0146]

<<Current Collector>>

There is no particular limitation on the current collector as long as it has high conductivity without causing a significant chemical change in a power storage device. For example, the positive electrode current collector and the negative electrode current collector can each be formed using a metal such as stainless steel, gold, platinum, zinc, iron, nickel, copper, aluminum, titanium, tantalum, or manganese, an alloy thereof, sintered carbon, or the like. Alternatively, copper or stainless steel that is coated with carbon, nickel, titanium, or the like may be used. Alternatively, the current collectors can each be formed using an aluminum alloy to which an element that improves heat resistance, such as silicon, titanium, neodymium, scandium, or molybdenum, is added. Still alternatively, a metal element that forms silicide by reacting with silicon can be used to form the current collectors. Examples of the metal element that forms silicide by reacting with silicon include zirconium, titanium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, cobalt, and nickel.

[0147]

An irreversible reaction with an electrolyte is sometimes caused on surfaces of the positive electrode current collector and the negative electrode current collector. Thus, the positive electrode current collector and the negative electrode current collector preferably have low reactivity to an electrolyte.

[0148]

The positive electrode current collector and the negative electrode current collector can each have any of various shapes including 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, a porous shape, and a shape of non-woven fabric as appropriate. The positive electrode current collector and the negative electrode current collector may each be formed to have micro irregularities on the surface thereof in order to enhance adhesion to the active material layer. The positive electrode current collector and the negative electrode current collector each preferably have a thickness of 5 μm to 30 μm inclusive.

[0149]

An undercoat layer may be provided over part of a surface of the current collector. The undercoat layer is a coating layer provided to reduce contact resistance between the current collector and the active material layer or to improve adhesion between the current collector and the active material layer. Note that the undercoat layer is not necessarily formed over the entire surface of the current collector and may be partly formed to have an island-like shape. In addition, the undercoat layer may serve as an active material to have capacity. For the undercoat layer, a carbon material can be used, for example. Examples of the carbon material

include graphite, carbon black such as acetylene black, and a carbon nanotube. Examples of the undercoat layer include a metal layer, a layer containing carbon and high molecular compounds, and a layer containing metal and high molecular compounds.

[0150]

<<Active Material Layer>>

The active material layer includes the active material. An active material refers only to a material that is involved in insertion and extraction of ions that are carriers. In this specification and the like, a layer including an active material is referred to as an active material layer. The active material layer may include a conductive additive and a binder in addition to the active material.

[0151]

The positive electrode active material layer includes one or more kinds of positive electrode active materials. The negative electrode active material layer includes one or more kinds of negative electrode active materials.

[0152]

The positive electrode active material and the negative electrode active material have a central role in battery reactions of a power storage device, and receive and release carrier ions. To increase the lifetime of the power storage device, the active materials preferably have a little capacity involved in irreversible battery reactions, and have high charge and discharge efficiency.

[0153]

Examples of positive electrode active materials are a composite oxide with a layered rock-salt crystal structure and a composite oxide with a spinel crystal structure. Alternatively, an example of a positive electrode active material is a polyanionic positive electrode material. Examples of polyanionic positive electrode materials are a material with an olivine crystal structure and a material with a NASICON structure. Alternatively, an example of a positive electrode active material is a positive electrode material containing sulfur.

[0154]

As the positive electrode active material, various composite oxides can be used. For the active material particles, a compound such as $LiFeO_2$, $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, Li_2MnO_3, V_2O_5, Cr_2O_5, or MnO_2 can be used.

[0155]

An example of a material with a layered rock-salt crystal structure includes a composite oxide represented by $LiMO_2$. The element M is preferably one or more elements selected from Co and Ni. $LiCoO_2$ is preferable because it has high capacity, stability in the air, and thermal stability to a certain extent, for example. As the element M, one or more elements selected

from Al and Mn may be included in addition to one or more elements selected from Co and Ni.

[0156]

For example, it is possible to use $LiNi_xMn_yCo_zO_w$ (x, y, and z are each 1/3 or a neighborhood thereof and w is 2 or a neighborhood thereof, for example). For example, it is possible to use $LiNi_xMn_yCo_zO_w$ (x is 0.8 or a neighborhood thereof, y is 0.1 or a neighborhood thereof, z is 0.1 or a neighborhood thereof, and w is 2 or a neighborhood thereof, for example). For example, it is possible to use $LiNi_xMn_yCo_zO_w$ (x is 0.5 or a neighborhood thereof, y is 0.3 or a neighborhood thereof, z is 0.2 or a neighborhood thereof, and w is 2 or a neighborhood thereof, for example). For example, it is possible to use $LiNi_xMn_yCo_zO_w$ (x is 0.6 or a neighborhood thereof, y is 0.2 or a neighborhood thereof, z is 0.2 or a neighborhood thereof, and w is 2 or a neighborhood thereof, for example). For example, it is possible to use $LiNi_xMn_yCo_zO_w$ (x is 0.4 or a neighborhood thereof, y is 0.4 or a neighborhood thereof, z is 0.2 or a neighborhood thereof, and w is 2 or a neighborhood thereof, for example).

[0157]

A neighborhood is a value greater than 0.9 times and smaller than 1.1 times the predetermined value.

[0158]

A material in which part of the transition metal and lithium included in the positive electrode active material is replaced with one or more elements selected from Fe, Co, Ni, Cr, Al, Mg, and the like, or a material in which the positive electrode active material is doped with one or more elements selected from Fe, Co, Ni, Cr, Al, Mg, and the like may be used for the positive electrode active material.

[0159]

As the positive electrode active material, for example, a solid solution obtained by combining two or more composite oxides can be used. For example, a solid solution of $LiNi_xMn_yCo_zO_2$ (x, y, $z > 0$, $x+y+z = 1$) and Li_2MnO_3 can be used as the positive electrode active material.

[0160]

An example of a material with a spinel crystal structure includes a composite oxide represented by LiM_2O_4. It is preferable to contain Mn as the element M. For example, $LiMn_2O_4$ can be used. It is preferable to contain Ni in addition to Mn as the element M because the discharge voltage and the energy density of the secondary battery are improved in some cases. It is preferable to add a small amount of lithium nickel oxide ($LiNiO_2$ or $LiNi_{1-x}M_xO_2$ (M = Co, Al, or the like)) to a lithium-containing material with a spinel crystal structure which contains manganese, such as $LiMn_2O_4$, because the characteristics of the secondary battery can be

improved.

[0161]

The average diameter of primary particles of the positive electrode active material is preferably greater than or equal to 1 nm and less than or equal to 100 μm, further preferably greater than or equal to 50 nm and less than or equal to 50 μm, and still further preferably greater than or equal to 1 μm and less than or equal to 30 μm, for example. Furthermore, the specific surface area is preferably greater than or equal to 1 m^2/g and less than or equal to 20 m^2/g. Furthermore, the average diameter of secondary particles is preferably greater than or equal to 5 μm and less than or equal to 50 μm. Note that the average particle diameters can be measured with a particle diameter distribution analyzer or the like using a laser diffraction and scattering method or by observation with a scanning electron microscope (SEM) or a TEM. The specific surface area can be measured by a gas adsorption method.

[0162]

A conductive material such as a carbon layer may be provided on the surface of the positive electrode active material. With the conductive material such as the carbon layer, the conductivity of the electrode can be increased. For example, the positive electrode active material can be coated with a carbon layer by mixing a carbohydrate such as glucose at the time of baking the positive electrode active material. As the conductive material, graphene, multi-graphene, graphene oxide (GO), or reduced graphene oxide (RGO) can be used. Note that RGO refers to a compound obtained by reducing graphene oxide (GO), for example.

[0163]

Note that a layer containing an oxide and/or a fluoride may be provided on a surface of the positive electrode active material. The oxide and the positive electrode active material may differ or similar in composition.

[0164]

As the polyanionic positive electrode material, for example, a complex oxide containing oxygen, an element X, a metal A, and a metal M. The metal M is one or more elements selected from Fe, Mn, Co, Ni, Ti, V, and Nb, the metal A is one or more elements selected from Li, Na, and Mg, and the element X is one or more elements selected from S, P, Mo, W, As, and Si.

[0165]

As a material with an olivine crystal structure, a complex material ($LiMPO_4$ (general formula) (*M* is one or more of Fe(II), Mn(II), Co(II), and Ni(II))) can be used as the positive electrode active material. Typical examples of the general formula $LiMPO_4$ are lithium compounds such as $LiFePO_4$, $LiNiPO_4$, $LiCoPO_4$, $LiMnPO_4$, $LiFe_aNi_bPO_4$, $LiFe_aCo_bPO_4$,

$LiFe_aMn_bPO_4$, $LiNi_aCo_bPO_4$, $LiNi_aMn_bPO_4$ ($a + b \leq 1$, $0 < a < 1$, and $0 < b < 1$), $LiFe_cNi_dCo_ePO_4$, $LiFe_cNi_dMn_ePO_4$, $LiNi_cCo_dMn_ePO_4$ ($c + d + e \leq 1$, $0 < c < 1$, $0 < d < 1$, and $0 < e < 1$), and $LiFe_fNi_gCo_hMn_iPO_4$ ($f + g + h + i \leq 1$, $0 < f < 1$, $0 < g < 1$, $0 < h < 1$, and $0 < i < 1$).

[0166]

In particular, $LiFePO_4$ is preferable because it meets requirements with balance for the positive electrode active material, such as safety, stability, high capacity density, high potential, and the existence of lithium ions that can be extracted in initial oxidation (charging).

[0167]

The average diameter of primary particles of the positive electrode active material with an olivine crystal structure is preferably greater than or equal to 1 nm and less than or equal to 20 μm, further preferably greater than or equal to 10 nm and less than or equal to 5 μm, and still further preferably greater than or equal to 50 nm and less than or equal to 2 μm, for example. Furthermore, the specific surface area is preferably greater than or equal to 1 m^2/g and less than or equal to 20 m^2/g. Furthermore, the average diameter of secondary particles is preferably greater than or equal to 5 μm and less than or equal to 50 μm.

[0168]

Alternatively, a complex material such as $Li_{(2-j)}MSiO_4$ (general formula) (M is one or more of Fe(II), Mn(II), Co(II), and Ni(II); $0 \leq j \leq 2$) may be used as the positive electrode active material. Typical examples of the general formula $Li_{(2-j)}MSiO_4$ are lithium compounds such as $Li_{(2-j)}FeSiO_4$, $Li_{(2-j)}NiSiO_4$, $Li_{(2-j)}CoSiO_4$, $Li_{(2-j)}MnSiO_4$, $Li_{(2-j)}Fe_kNi_lSiO_4$, $Li_{(2-j)}Fe_kCo_lSiO_4$, $Li_{(2-j)}Fe_kMn_lSiO_4$, $Li_{(2-j)}Ni_kCo_lSiO_4$, $Li_{(2-j)}Ni_kMn_lSiO_4$ ($k + l \leq 1$, $0 < k < 1$, and $0 < l < 1$), $Li_{(2-j)}Fe_mNi_nCo_qSiO_4$, $Li_{(2-j)}Fe_mNi_nMn_qSiO_4$, $Li_{(2-j)}Ni_mCo_nMn_qSiO_4$ ($m + n + q \leq 1$, $0 < m < 1$, $0 < n < 1$, and $0 < q < 1$), and $Li_{(2-j)}Fe_rNi_sCo_tMn_uSiO_4$ ($r + s + t + u \leq 1$, $0 < r < 1$, $0 < s < 1$, $0 < t < 1$, and $0 < u < 1$).

[0169]

Still alternatively, a nasicon compound represented by $A_xM_2(XO_4)_3$ (general formula) (A = Li, Na, or Mg, M = Fe, Mn, Ti, V, or Nb, X = S, P, Mo, W, As, or Si) can be used for the positive electrode active material. Examples of the nasicon compound are $Fe_2(MnO_4)_3$, $Fe_2(SO_4)_3$, and $Li_3Fe_2(PO_4)_3$. Further alternatively, a compound represented by Li_2MPO_4F, $Li_2MP_2O_7$, or Li_5MO_4 (general formula) (M = Fe or Mn) can be used as the positive electrode active material.

[0170]

Further alternatively, a polyanionic positive electrode material containing V can be used. Typical examples are α-$LiVOPO_4$, β-$LiVOPO_4$, α1-$LiVOPO_4$, $LiVPO_4F$, $LiVPO_4O$, $LiVP_2O_7$,

$LiVOSO_4$, Li_2VOSiO_4, and $LiVMoO_6$.

[0171]

Further alternatively, a perovskite fluoride such as $NaFeF_3$ and FeF_3, a metal chalcogenide (a sulfide, a selenide, or a telluride) such as TiS_2 and MoS_2, an oxide with an inverse spinel structure such as $LiMVO_4$, a vanadium oxide (V_2O_5, V_6O_{13}, LiV_3O_8, or the like), a manganese oxide, an organic sulfur compound, or the like can be used as the positive electrode active material.

[0172]

Alternatively, a borate-based positive electrode material represented by $LiMBO_3$ (general formula) (M is Fe(II), Mn(II), or Co(II)) can be used as the positive electrode active material.

[0173]

Another example of the positive electrode active material is a lithium-manganese composite oxide represented by a composition formula $Li_aMn_bM_cO_d$. Here, the element M is preferably a metal element other than lithium and manganese, or silicon or phosphorus, further preferably nickel. Furthermore, in the case where the whole particle of a lithium-manganese composite oxide is measured, it is preferable to satisfy the following at the time of discharging: $0 < a/(b+c) < 2$; $c > 0$; and $0.26 \leq (b+c)/d < 0.5$. To achieve a high capacity, the lithium-manganese composite oxide preferably includes a region where the surface portion and the middle portion are different in the crystal structure, the crystal orientation, or the oxygen content. In order that such a lithium-manganese composite oxide can be obtained, the composition formula is preferably $1.6 \leq a \leq 1.848$; $0.19 \leq c/b \leq 0.935$; and $2.5 \leq d \leq 3$. Furthermore, it is particularly preferable to use a lithium-manganese composite oxide represented by a composition formula $Li_{1.68}Mn_{0.8062}Ni_{0.318}O_3$. In this specification and the like, a lithium-manganese composite oxide represented by a composition formula $Li_{1.68}Mn_{0.8062}Ni_{0.318}O_3$ refers to that formed at a ratio (molar ratio) of the amounts of raw materials of Li_2CO_3:$MnCO_3$:NiO = 0.84:0.8062:0.318. Although this lithium-manganese composite oxide is represented by a composition formula $Li_{1.68}Mn_{0.8062}Ni_{0.318}O_3$, the composition might deviate from this.

[0174]

Note that the ratios of metal, silicon, phosphorus, and other elements to the total composition in the whole particle of a lithium-manganese composite oxide can be measured with, for example, an inductively coupled plasma mass spectrometer (ICP-MS). The ratio of oxygen to the total composition in the whole particle of a lithium-manganese composite oxide can be measured by, for example, energy dispersive X-ray spectroscopy (EDX). Alternatively, the

ratio of oxygen to the total composition in the whole particle of a lithium-manganese composite oxide can be measured by ICP-MS combined with fusion gas analysis and valence evaluation of X-ray absorption fine structure (XAFS) analysis. Note that the lithium-manganese composite oxide is an oxide containing at least lithium and manganese, and may contain at least one selected from chromium, cobalt, aluminum, nickel, iron, magnesium, molybdenum, zinc, indium, gallium, copper, titanium, niobium, silicon, phosphorus, and the like.

[0175]

In the case where carrier ions are alkali metal ions other than lithium ions, or alkaline-earth metal ions, a material containing an alkali metal (e.g., sodium or potassium) or an alkaline-earth metal (e.g., calcium, strontium, barium, beryllium, or magnesium) instead of lithium may be used as the positive electrode active material. For example, the positive electrode active material may be a layered oxide containing sodium.

[0176]

As the positive electrode active material, for example, an oxide containing sodium, such as $NaFeO_2$, $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$, $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, $Na_2Fe_2(SO_4)_3$, $Na_3V_2(PO_4)_3$, Na_2FePO_4F, $NaVPO_4F$, $NaMPO_4$ (*M* is Fe(II), Mn(II), Co(II), or Ni(II)), Na_2FePO_4F, or $Na_4Co_3(PO_4)_2P_2O_7$ can be used.

[0177]

In addition, as the positive electrode active material, a lithium-containing metal sulfide can be used. Examples of the lithium-containing metal sulfide are Li_2TiS_3 and Li_3NbS_4.

[0178]

As the negative electrode active material, for example, a carbon-based material, an alloy-based material, or the like can be used.

[0179]

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. 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. In addition, examples of the shape of the graphite include a flaky shape and a spherical shape.

[0180]

Graphite has a low potential substantially equal to that of a lithium metal 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. Graphite is preferred because of its advantages described above, such as relatively high capacity

per unit volume, small volume expansion, low cost, and safety greater than that of a lithium metal.

[0181]

Here, a graphite material will be described. Graphite is a layered compound in which a plurality of graphene layers are stacked parallel to each other by van der Waals forces. A surface of the graphite material includes a plane parallel to the graphene layer (also referred to as a basal plane) and a plane where edges of the plurality of graphene layers are arranged (also referred to as an edge plane). In the basal plane, one surface of the outmost layer of the graphene layers composing graphite is exposed. In the edge plane, the edges of the plurality of graphene layers are exposed. In charging and discharging of a secondary battery, the edge plane of the graphite material serves as a main gate for lithium intercalation and deintercalation to and from the graphite material.

[0182]

In the case where graphite is used for the negative electrode active material, the contact between the exposed portion of the edge plane and the electrolyte containing PC might cause a side reaction between graphite and PC in charging and discharging. In spherical natural graphite used for the negative electrode active material included in the power storage device of one embodiment of the present invention, a layer having lower crystallinity than a graphite layer is formed in contact with the edge plane; thus, a side reaction between graphite and PC can be inhibited in some cases.

[0183]

For example, in the case where carrier ions are lithium ions, a material including at least one of Mg, Ca, Ga, Si, Al, Ge, Sn, Pb, As, Sb, Bi, Ag, Au, Zn, Cd, Hg, In, and the like can be used as the alloy-based material. Such elements have a higher capacity than carbon. In particular, silicon has a high theoretical capacity of 4200 mAh/g, and therefore, the capacity of the power storage device can be increased. Examples of an alloy-based material (compound-based material) using such elements include Mg_2Si, Mg_2Ge, Mg_2Sn, SnS_2, V_2Sn_3, $FeSn_2$, $CoSn_2$, Ni_3Sn_2, Cu_6Sn_5, Ag_3Sn, Ag_3Sb, Ni_2MnSb, $CeSb_3$, $LaSn_3$, $La_3Co_2Sn_7$, $CoSb_3$, InSb, and SbSn.

[0184]

Alternatively, for the negative electrode active material, an oxide such as SiO, SnO, SnO_2, titanium dioxide (TiO_2), lithium titanium oxide ($Li_4Ti_5O_{12}$), lithium-graphite intercalation compound (Li_xC_6), niobium pentoxide (Nb_2O_5), tungsten oxide (WO_2), or molybdenum oxide (MoO_2) can be used. Here, SiO is a compound containing silicon and oxygen. When the atomic ratio of silicon to oxygen is represented by α:β, α preferably has an approximate value of

β. Here, when α has an approximate value of β, an absolute value of the difference between α and β is preferably less than or equal to 20 % of a value of β, more preferably less than or equal to 10 % of a value of β.

[0185]

Still alternatively, for the negative electrode active material, $Li_{3-x}M_xN$ (M = Co, Ni, or Cu) with a Li_3N structure, which is a nitride containing lithium and a transition metal, can be used. For example, $Li_{2.6}Co_{0.4}N_3$ is preferable because of high charge and discharge capacity (900 mAh/g and 1890 mAh/cm^3).

[0186]

When a nitride containing lithium and a transition metal is used, lithium ions are contained in the negative electrode active material and thus the negative electrode active material can be used in combination with a material for a positive electrode active material that 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.

[0187]

Alternatively, a material that causes a conversion reaction can be used for the negative electrode active material; for example, a transition metal oxide that 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.

[0188]

The average diameter of primary particles of the negative electrode active material is preferably, for example, greater than or equal to 5 nm and less than or equal to 100 μm.

[0189]

The positive electrode active material layer and the negative electrode active material layer may each include a conductive additive.

[0190]

Examples of the conductive additive include a carbon material, a metal material, and a conductive ceramic material. Alternatively, a fiber material may be used as the conductive additive. The content of the conductive additive in the active material layer is preferably greater than or equal to 1 wt% and less than or equal to 10 wt%, more preferably greater than or

equal to 1 wt% and less than or equal to 5 wt%.

[0191]

A network for electric conduction can be formed in the electrode by the conductive additive. The conductive additive also allows maintaining of a path for electric conduction between the negative electrode active material particles. The addition of the conductive additive to the active material layer increases the electric conductivity of the active material layer.

[0192]

Examples of the conductive additive include natural graphite, artificial graphite such as mesocarbon microbeads, and carbon fiber. Examples of carbon fiber include mesophase pitch-based carbon fiber, isotropic pitch-based carbon fiber, carbon nanofiber, and carbon nanotube. Carbon nanotube can be formed by, for example, a vapor deposition method. Other examples of the conductive additive include carbon materials such as carbon black (e.g., acetylene black (AB)), graphite (black lead) particles, graphene, graphene oxide, and fullerene. Alternatively, metal powder or metal fibers of copper, nickel, aluminum, silver, gold, or the like, a conductive ceramic material, or the like can be used.

[0193]

Flaky graphene has an excellent electrical characteristic of high conductivity and excellent physical properties of high flexibility and high mechanical strength. Thus, the use of graphene as the conductive additive can increase contact points and the contact area of the active materials.

[0194]

Graphene is capable of making low-resistance surface contact and has extremely high conductivity even with a small thickness. Therefore, even a small amount of graphene can efficiently form a conductive path in an active material layer.

[0195]

In the case where an active material with a small average particle diameter (e.g., 1 μm or less) is used, the specific surface area of the active material is large and thus more conductive paths for the active material particles are needed. In such a case, it is particularly preferred that graphene with extremely high conductivity that can efficiently form a conductive path even in a small amount is used.

[0196]

The positive electrode active material layer and the negative electrode active material layer may each include a binder.

[0197]

In this specification, the binder has a function of binding or bonding the active materials and/or a function of binding or bonding the active material layer and the current collector. The binder is sometimes changed in state during fabrication of an electrode or a battery. For example, the binder can be at least one of a liquid, a solid, and a gel. The binder is sometimes changed from a monomer to a polymer during fabrication of an electrode or a battery.

[0198]

As the binder, for example, a water-soluble high molecular compound can be used. As the water-soluble high molecular compound, a polysaccharide or the like can be used. As the polysaccharide, a cellulose derivative such as carboxymethyl cellulose (CMC), methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, diacetyl cellulose, or regenerated cellulose, starch, or the like can be used.

[0199]

As the binder, a rubber material such as styrene-butadiene rubber (SBR), styrene-isoprene-styrene rubber, acrylonitrile-butadiene rubber, butadiene rubber, fluororubber, or ethylene-propylene-diene copolymer can be used. Any of these rubber materials may be used in combination with the aforementioned water-soluble high molecular compound. Since these rubber materials have rubber elasticity and easily expand and contract, it is possible to obtain a highly reliable electrode that is resistant to stress due to expansion and contraction of an active material by charging and discharging, bending of the electrode, or the like. On the other hand, the rubber materials have a hydrophobic group and thus are unlikely to be soluble in water in some cases. In such a case, particles are dispersed in an aqueous solution without being dissolved in water, so that increasing the viscosity of a composition containing a solvent used for the formation of the active material layer (also referred to as an electrode mix composition) up to the viscosity suitable for application might be difficult. A water-soluble high molecular compound having excellent viscosity modifying properties, such as a polysaccharide, can moderately increase the viscosity of the solution and can be uniformly dispersed together with a rubber material. Thus, a favorable electrode with high uniformity (e.g., an electrode with uniform electrode thickness or electrode resistance) can be obtained.

[0200]

Alternatively, as the binder, a material such as PVDF, polystyrene, poly(methyl acrylate), poly(methyl methacrylate) (PMMA), sodium polyacrylate, polyvinyl alcohol (PVA), polyethylene oxide (PEO), polypropylene oxide, polyimide, polyvinyl chloride, polytetrafluoroethylene, polyethylene, polypropylene, polyisobutylene, polyethylene terephthalate, nylon, polyacrylonitrile (PAN), ethylene-propylene-diene polymer, polyvinyl acetate, or nitrocellulose can be used.

[0201]

Two or more of the above materials may be used in combination for the binder.

[0202]

The content of the binder in the active material layer is preferably greater than or equal to 1 wt% and less than or equal to 10 wt%, more preferably greater than or equal to 2 wt% and less than or equal to 8 wt%, and still more preferably greater than or equal to 2 wt% and less than or equal to 5 wt%.

[0203]

<<Separator>>

In view of the above, in the power storage device of one embodiment of the present invention, a separator containing polyphenylene sulfide (PPS) or a separator containing solvent-spun regenerated cellulosic fiber is used. The separator may have a single-layer structure or a stacked-layer structure. A layered structure of a separator containing solvent-spun regenerated cellulosic fiber and another separator may be used, for example.

[0204]

As a material for the separator, one or more materials selected from the following can be used besides polyphenylene sulfide and cellulosic fiber: polypropylene sulfide, a fluorine-based polymer, cellulose, paper, nonwoven fabric, glass fiber, ceramics, synthetic fiber such as nylon (polyamide), vinylon (polyvinyl alcohol fiber), polyester, acrylic, polyolefin, or polyurethane, and the like.

[0205]

<<Exterior Body>>

It is preferred that the surface of the exterior body 509 that is in contact with the electrolyte 508, i.e., the inner surface of the exterior body 509, does not react with the electrolyte 508 significantly. When moisture enters the power storage device 500 from the outside, a reaction between a component of the electrolyte 508 or the like and water might occur. Thus, the exterior body 509 preferably has low moisture permeability.

[0206]

As the exterior body 509, a film having a three-layer structure can be used, for example. In the three-layer structure, a highly flexible metal thin film of aluminum, stainless steel, copper, nickel, or the like is provided over a film formed using polyethylene, polypropylene, polycarbonate, ionomer, polyamide, or the like, 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, the passage of an electrolyte and a gas can be blocked and an insulating property and resistance to

the electrolyte can be provided. The exterior body is folded inside in two, or two exterior bodies are stacked with the inner surfaces facing each other, in which case application of heat melts the materials on the overlapping inner surfaces to cause fusion bonding between the two exterior bodies. In this manner, a sealing structure can be formed.

[0207]

A portion where the sealing structure is formed by fusion bonding or the like of the exterior body is referred to as a sealing portion. In the case where the exterior body is folded inside in two, the sealing portion is formed in the place other than the fold, and a first region of the exterior body and a second region of the exterior body that overlaps with the first region are fusion-bonded, for example. In the case where two exterior bodies are stacked, the sealing portion is formed along the entire outer region by heat fusion bonding or the like.

[0208]

The power storage device 500 can be flexible by using the exterior body 509 with flexibility. When the power storage device 500 has flexibility, it can be used in an electronic device at least part of which is flexible, and the power storage device 500 can be bent as the electronic device changes its form.

[0209]

Note that in one embodiment of the present invention, a graphene compound can be used in a component of the power storage device. As described later, when modification is performed, the structure and characteristics of a graphene compound can be selected from a wider range of alternatives. Thus, a preferable property can be exhibited in accordance with a component in which a graphene compound is to be used. Moreover, a graphene compound has high mechanical strength and therefore can be used in a component of a flexible power storage device. Graphene compounds will be described below.

[0210]

Graphene has carbon atoms arranged in one atomic layer. A π bond exists between the carbon atoms. Graphene including two or more and one hundred or less layers is referred to as multilayer graphene in some cases. The length in the longitudinal direction or the length of the major axis in a plane in each of graphene and multilayer graphene is greater than or equal to 50 nm and less than or equal to 100 μm or greater than or equal to 800 nm and less than or equal to 50 μm.

[0211]

In this specification and the like, a compound including graphene or multilayer graphene as a basic skeleton is referred to as a graphene compound. Graphene compounds include graphene and multilayer graphene.

[0212]

Graphene compounds will be detailed below.

[0213]

A graphene compound is, for example, a compound where graphene or multilayer graphene is modified with an atom other than carbon or an atomic group with an atom other than carbon. A graphene compound may be a compound where graphene or multilayer graphene is modified with an atomic group composed mainly of carbon, such as an alkyl group or alkylene. An atomic group that modifies graphene or multilayer graphene is referred to as a substituent, a functional group, a characteristic group, or the like in some cases. Modification in this specification and the like refers to introduction of an atom other than carbon, an atomic group with an atom other than carbon, or an atomic group composed mainly of carbon to graphene, multilayer graphene, a graphene compound, or graphene oxide (described later) by a substitution reaction, an addition reaction, or other reactions.

[0214]

Note that the surface and the rear surface of graphene may be modified with different atoms or atomic groups. In multilayer graphene, multiple layers may be modified with different atoms or atomic groups.

[0215]

An example of the above-described graphene modified with an atom or an atomic group is graphene or multilayer graphene that is modified with oxygen or a functional group containing oxygen. Examples of a functional group containing oxygen include an epoxy group, a carbonyl group such as a carboxyl group, and a hydroxyl group. A graphene compound modified with oxygen or a functional group containing oxygen is referred to as graphene oxide in some cases. In this specification, graphene oxides include multilayer graphene oxides.

[0216]

As an example of modification of graphene oxide, silylation of graphene oxide will be described. First, in a nitrogen atmosphere, graphene oxide is put in a container, *n*-butylamine ($C_4H_9NH_2$) is added to the container, and stirring is performed for one hour with the temperature kept at 60 °C. Then, toluene is added to the container, alkyltrichlorosilane is added thereto as a silylating agent, and stirring is performed in a nitrogen atmosphere for five hours with the temperature kept at 60 °C. Then, toluene is further added to the container, and the resulting solution is suction-filtrated to give solid powder. The powder is dispersed in ethanol, and the resulting solution is suction-filtered to give solid powder. The powder is dispersed in acetone, and the resulting solution is suction-filtered to give solid powder. A liquid of the solid powder is vaporized to give silylated graphene oxide.

[0217]

The modification is not limited to silylation, and silylation is not limited to the above-described method. Furthermore, the modification is not limited to introduction of an atom or an atomic group of one kind, and the modification of two or more types may be performed to introduce atoms or atomic groups of two or more kinds. By introducing a given atomic group to a graphene compound, the physical property of the graphene compound can be changed. Therefore, by performing desirable modification in accordance with the use of a graphene compound, a desired property of the graphene compound can be exhibited intentionally.

[0218]

A formation method example of graphene oxide will be described below. Graphene oxide can be obtained by oxidizing the aforementioned graphene or multilayer graphene. Alternatively, graphene oxide can be obtained by being separated from graphite oxide. Graphite oxide can be obtained by oxidizing graphite. The graphene oxide may further be modified with the above-mentioned atom or atomic group.

[0219]

A compound that can be obtained by reducing graphene oxide is referred to as reduced graphene oxide (RGO) in some cases. In RGO, in some cases, all oxygen atoms contained in the graphene oxide are not extracted and part of them remains in a state of oxygen or an atomic group containing oxygen that is bonded to carbon. In some cases, RGO includes a functional group, e.g., an epoxy group, a carbonyl group such as a carboxyl group, or a hydroxyl group.

[0220]

A graphene compound may have a sheet-like shape where a plurality of graphene compounds partly overlap with each other. Such a graphene compound is referred to as a graphene compound sheet in some cases. The graphene compound sheet has, for example, an area with a thickness larger than or equal to 0.33 nm and smaller than or equal to 10 mm, preferably larger than or equal to 0.34 nm and smaller than or equal to 10 μm. The graphene compound sheet may be modified with an atom other than carbon, an atomic group containing an atom other than carbon, an atomic group composed mainly of carbon such as an alkyl group, or the like. A plurality of layers in the graphene compound sheet may be modified with different atoms or atomic groups.

[0221]

A graphene compound may have a five-membered ring composed of carbon atoms or a poly-membered ring that is a seven- or more-membered ring composed of carbon atoms, in addition to a six-membered ring composed of carbon atoms. In the neighborhood of a

poly-membered ring which is a seven- or more-membered ring, a region through which a lithium ion can pass may be generated.

[0222]

Furthermore, a plurality of graphene compounds may be gathered to form a sheet-like shape, for example.

[0223]

A graphene compound has a planar shape, thereby enabling surface contact.

[0224]

In some cases, a graphene compound has high conductivity even when it is thin. The contact area between graphene compounds or between a graphene compound and an active material can be increased by surface contact. Thus, even with a small amount of a graphene compound per volume, a conductive path can be formed efficiently.

[0225]

In contrast, a graphene compound may also be used as an insulator. For example, a graphene compound sheet can be used as a sheet-like insulator. Graphene oxide, for example, has a more excellent insulation property than a graphene compound that is not oxidized, in some cases. A graphene compound modified with an atomic group may have an improved insulation property, depending on the type of the modifying atomic group.

[0226]

A graphene compound in this specification and the like may include a precursor of graphene. The precursor of graphene refers to a substance used to form graphene. The precursor of graphene may contain the above-described graphene oxide, graphite oxide, or the like.

[0227]

Graphene containing an alkali metal or an element other than carbon, such as oxygen, is referred to as a graphene analog in some cases. In this specification and the like, graphene compounds include graphene analogs.

[0228]

A graphene compound in this specification and the like may include an atom, an atomic group, and ions of them between the layers. The physical properties, such as electric conductivity and ionic conductivity, of a graphene compound sometimes change when an atom, an atomic group, and ions of them exist between layers of the compound. In addition, a distance between the layers is increased in some cases.

[0229]

A graphene compound has excellent electrical characteristics of high conductivity and

excellent physical properties of high flexibility and high mechanical strength in some cases. A modified graphene compound can have extremely low conductivity and serve as an insulator depending on the type of the modification. A graphene compound has a planar shape. A Graphene compound enables low-resistance surface contact.

[0230]

This embodiment can be combined with any of the other embodiments as appropriate.

[0231]

(Embodiment 2)

In this embodiment, electronic devices of embodiments of the present invention will be described with reference to FIG. 14A to 14C to FIGS. 17A to 17C.

[0232]

<Structural Example 1 of Smartwatch>

FIG. 14A is a perspective view of a watch-type portable information terminal (also called a smartwatch) 700. The portable information terminal 700 includes a housing 701, a display panel 702, a clasp 703, bands 705A and 705B, and operation buttons 711 and 712.

[0233]

The display panel 702 mounted in the housing 701 doubling as a bezel includes a rectangular display region. The display region has a curved surface. The display panel 702 preferably has flexibility. Note that the display region may be non-rectangular.

[0234]

The bands 705A and 705B are connected to the housing 701. The clasp 703 is connected to the band 705A. The band 705A and the housing 701 are connected to each other with a pin such that they can pivot around the pin at a connection portion, for example. In a similar manner, the band 705B and the housing 701 are connected to each other and the band 705A and the clasp 703 are connected to each other.

[0235]

FIGS. 14B and 14C are perspective views of the band 705A and a power storage device 750, respectively. The band 705A includes the power storage device 750. As the power storage device 750, the power storage device 500 described in Embodiment 1 can be used, for example. The power storage device 750 is embedded in the band 705A, and part of the positive electrode lead 751 and part of the negative electrode lead 752 protrude from the band 705A (see FIG. 14B). The positive electrode lead 751 and the negative electrode lead 752 are electrically connected to the display panel 702. The surface of the power storage device 750 is covered with an exterior body 753 (see FIG. 14C). Note that the pin may function as an electrode. Specifically, the positive electrode lead 751 and the display panel 702 may be electrically

connected to each other through the pin that connects the band 705A and the housing 701, and the negative electrode lead 752 and the display panel 702 may be electrically connected to each other through the pin. In that case, the structure of the connection portion between the band 705A and the housing 701 can be simplified.

[0236]

The power storage device 750 has flexibility. Specifically, a surface of the exterior body 753 preferably has projections and depressions formed by the embossing described in Embodiment 1. Furthermore, the power storage device 750 preferably has sliding planes of the power storage device 500 illustrated in FIGS. 5A and 5B.

[0237]

The band 705A can be formed so as to incorporate the power storage device 750. For example, the power storage device 750 is set in a mold that the outside shape of the band 705A fits and a material of the band 705A is poured in the mold and cured, so that the band 705A illustrated in FIG. 14B can be formed.

[0238]

In the case where a rubber material is used as the material of the band 705A, rubber is cured through heat treatment. For example, in the case where fluorine rubber is used as a rubber material, it is cured through heat treatment at 170 °C for 10 minutes. In the case where silicone rubber is used as a rubber material, it is cured through heat treatment at 150 °C for 10 minutes. The power storage device of one embodiment of the present invention has high heat resistance, which can inhibit breakage and degradation of the charge and discharge characteristics due to heat treatment performed when the power storage device and the rubber material are integrally formed.

[0239]

Examples of the material of the band 705A include fluorine rubber, silicone rubber, fluorosilicone rubber, and urethane rubber.

[0240]

Note that energization of the power storage device 750, including aging, is preferably performed after the power storage device 750 is formed to be incorporated in the band 705A. In other words, heat treatment is preferably performed on the power storage device 500 described in Embodiment 1 before energization of the power storage device 500. The heat treatment is preferably performed at 110 °C to 190 °C inclusive for a period of time suitable for vulcanization of the rubber material, for example, at 170 °C for 10 minutes. This can inhibit degradation of the charge and discharge characteristics of the power storage device 500 due to heat treatment.

[0241]

The portable information terminal 700 in FIG. 14A can have a variety of functions such as a function of displaying a variety of data (e.g., a still image, a moving image, and a text image) on the display region, a touch panel function, a function of displaying a calendar, date, time, and the like, a function of controlling processing with a variety of software (programs), a wireless communication function, a function of being connected to a variety of computer networks with a wireless communication function, a function of transmitting and receiving a variety of data with a wireless communication function, and a function of reading out a program or data stored in a recording medium and displaying it on the display region.

[0242]

The housing 701 can include a speaker, a sensor (a sensor having a function of measuring force, displacement, position, speed, acceleration, angular velocity, rotational frequency, distance, light, liquid, magnetism, temperature, chemical substance, sound, time, hardness, electric field, current, voltage, electric power, radiation, flow rate, humidity, gradient, oscillation, odor, or infrared rays), a microphone, and the like. Note that the portable information terminal 700 can be manufactured using the light-emitting element for the display panel 702.

[0243]

Although FIGS. 14A to 14C illustrate the example where the power storage device 750 is incorporated in the band 705A, the power storage device 750 may be incorporated in the band 705B. The band 705B can be formed using a material similar to that of the band 705A.

[0244]

The rubber material used for the band 705A preferably has high chemical resistance. Specifically, the rubber material preferably has low reactivity to an electrolyte contained in the power storage device 750.

[0245]

When the band 705A is cracked or chipped despite of its high chemical resistance, a user of the portable information terminal 700 might touch the electrolyte that leaks from the power storage device 750. In the case where the portable information terminal 700 has a function of detecting leakage of the electrolyte, the user can stop operation of the portable information terminal 700 and remove it as soon as the electrolyte leakage is detected. Consequently, the portable information terminal 700 can be highly safe.

[0246]

<Structural Example 2 of Smartwatch>

FIG. 15A is a perspective view of a band 735A having a structure different form that of

the band 705A illustrated in FIG. 14B. A housing 731 connected to the band 735A includes a leakage detection circuit (not illustrated) having a function of detecting leakage of the electrolyte of the power storage device (see FIG. 14A). Note that a perspective view of a portable information terminal 730 including the leakage detection circuit is similar to that of the portable information terminal 700.

[0247]

The band 735A includes a power storage device 760. The power storage device 760 is embedded in the band 735A, and part of the positive electrode lead 751, part of the negative electrode lead 752, part of a terminal 761, and part of a terminal 762 protrude from the band 735A. The positive electrode lead 751 and the negative electrode lead 752 are electrically connected to the display panel 702. The terminal 761 and the terminal 762 are electrically connected to the above leakage detection circuit, for example.

[0248]

FIG. 15B is a perspective view of the power storage device 760. FIG. 15B is an enlarged view of FIG. 15A for clarification. The power storage device 760 is different from the power storage device 750 in FIG. 14C in including the terminal 761, terminal 762, a wiring 771, and a wiring 772. The terminal 761 is electrically connected to the wiring 771. The terminal 762 is electrically connected to the wiring 772.

[0249]

Although the wiring 771 and the wiring 772 are indicated by different hatch patterns for clarification in FIG. 15B, the wiring 771 and the wiring 772 are preferably formed using the same material to achieve cost reduction. Although the terminal 761 and the wiring 771 are indicated by the same hatching pattern and the terminal 762 and the wiring 772 are indicated by the same hatching pattern, the terminal 761 and the wiring 771 may be formed using different materials and the terminal 762 and the wiring 772 may be formed using different materials.

[0250]

The wiring 771 and the wiring 772 are provided on a surface of the exterior body 753 with a predetermined gap therebetween (see FIG. 15B). If the electrolyte leaks to a surface of the exterior body 753, the wiring 771 and the wiring 772 are electrically connected to each other through the electrolyte, whereby the leakage detection circuit can detect leakage of the electrolyte.

[0251]

Although the wiring 771 and the wiring 772 each having a linear shape are provided in the direction of the long axis of the power storage device 760 in FIG. 15B, one embodiment of the present invention is not limited thereto. For example, as illustrated in FIG. 15C, the wiring

771 and the wiring 772 each having a comb-like shape may be provided with a gap therebetween so as to engage with each other.

[0252]

Although FIG. 15C illustrates the example where the wirings 771 and 772 are provided only on the top surface of the exterior body 753, the wirings 771 and 772 are preferably provided on the entire surface of the exterior body 753 as illustrated in FIG. 16A. FIG. 16B is a perspective view of the back surface of the power storage device 760 illustrated in FIG. 16A.

[0253]

The wirings 771 and 772 each preferably have a small thickness and a small width, in which case the flexibility of the power storage device 760 can be ensured. For example, the power storage device 760 preferably includes a region in which the thickness of each of the wirings 771 and 772 is 5 μm to 500 μm inclusive. Furthermore, it is preferred that the gap between the wiring 771 and the wiring 772 be small and the width of each of the wiring 771 and the wiring 772 be small, in which case even a small amount of electrolyte leakage can be detected. For example, the power storage device 760 preferably includes a region in which the length of the gap between the wirings 771 and 772 is 0.5 mm and 20 mm inclusive. Furthermore, the power storage device 760 preferably includes a region in which the width of each of the wiring 771 and the wiring 772 is 0.5 mm and 5 mm inclusive. When the occupation area of the wirings 771 and 772 in the surface of the exterior body 753 is excessively small, the detection of electrolyte leakage for the entire surface of the exterior body 753 is not possible in some cases, whereas when the occupation area is excessively large, the flexibility of the power storage device 760 is low in some cases. In the power storage device 760, the proportion of the surface area of the wirings 771 and 772 except side surfaces thereof (the surfaces in contact with the exterior body 753) to the surface area of the exterior body 753 is preferably 5 % to 50 % inclusive.

[0254]

The wirings 771 and 772 preferably include a material having high ductility or high malleability. In particular, the use of a material having both high ductility and high malleability can suppress breakage of the wirings 771 and 772 due to curving of the power storage device 760. Examples of the material having both high ductility and high malleability include a metal material such as gold, silver, platinum, iron, nickel, copper, aluminum, zinc, and tin and an alloy containing any of the metal materials.

[0255]

<<Leakage Detecting Method>>

An example of a method for detecting electrolyte leakage in the portable information

terminal 730 will be described below. FIG. 17A is a block diagram of the configuration of the portable information terminal 730 when the electrolyte 736 leaks. In FIG. 17A, lines with arrows indicate the directions in which a wired signal or a wireless signal is transmitted. Thus, components connected by the corresponding line are electrically connected to each other in some cases. Lines without an arrow indicate wirings, and components connected by the corresponding line are electrically connected to each other.

[0256]

The portable information terminal 730 includes a leakage detection circuit 732, a power source 733, an ammeter 734, the wiring 771, and the wiring 772 (see FIG. 17A). The leakage detection circuit 732, the power source 733, and the ammeter 734 are included in the housing 731. The power source 733 and the ammeter 734 may be included in the leakage detection circuit 732. The portable information terminal 730 also includes a functional circuit 739. The functional circuit 739 includes the speaker, the sensor, the microphone, and the like. The functional circuit 739 is included in the housing 731.

[0257]

The wirings 771 and 772 are electrically connected to the power source 733, and a given voltage is applied between the wiring 771 and the wiring 772 (see FIG. 17A). The on/off of the power source 733 is controlled by the leakage detection circuit 732.

[0258]

FIG. 17B is a flow chart showing the flow of detection of electrolyte leakage in the portable information terminal 730. The method for detecting electrolyte leakage in the portable information terminal 730 includes the following four steps, for example.

[0259]

When the electrolyte 736 of the power storage device 760 leaks, the electrolyte 736 is attached to a surface of the exterior body 753 (see FIG. 17A and S1 in FIG. 17B). The electrolyte 736 attached to the surface of the exterior body 753 comes in contact with the wiring 771 and the wiring 772, whereby a current flows through the wiring 771 and the wiring 772 (see S2 in FIG. 17B). On detecting the current, the ammeter 734 connected to be in parallel to the wiring 772 outputs a detection signal to the leakage detection circuit 732 (see S3 in FIG. 17B). The leakage detection circuit 732 terminates the operation of the display panel 702 and/or the functional circuit 739 in response to the detection signal (see S4 in FIG. 17B).

[0260]

Although FIG. 17A illustrates the example where the ammeter 734 is connected to the wiring 772, the ammeter 734 may be connected to the wiring 771. Furthermore, the power source 733 and the ammeter 734 may be included in the leakage detection circuit 732, and the

leakage detection circuit 732 may be electrically connected to the wirings 771 and 772 (see FIG. 17C). In that case, the leakage detection circuit 732 has a function of applying a predetermined voltage to the wirings 771 and 772 and a function of detecting a current flowing through the wirings 771 and 772.

[0261]

This embodiment can be combined with any of the other embodiments as appropriate.

[0262]

(Embodiment 3)

In this embodiment, flexible power storage devices that are embodiments of the present invention will be described with reference to FIGS. 18A and 18B to FIG. 25. The power storage device of one embodiment of the present invention may have a curved shape. The power storage device of one embodiment of the present invention may be flexible and capable of being used while being curved and while being not curved.

[0263]

<Structural Example 1>

FIG. 18A is a perspective view of a secondary battery 200 and FIG. 18B is a top view of the secondary battery 200.

[0264]

FIG. 19A is a cross-sectional view along dashed-dotted line C1-C2 in FIG. 18B, and FIG. 19B is a cross-sectional view along dashed-dotted line C3-C4 in FIG. 18B. Note that FIGS. 19A and 19B do not illustrate all components for clarity of the drawings.

[0265]

The secondary battery 200 includes a positive electrode 211, a negative electrode 215, and a separator 203. The secondary battery 200 further includes a positive electrode lead 221, a negative electrode lead 225, and an exterior body 207.

[0266]

The positive electrode 211 and the negative electrode 215 each include a current collector and an active material layer. The positive electrode 211 and the negative electrode 215 are provided such that the active material layers face each other with the separator 203 provided therebetween.

[0267]

One of the electrodes (the positive electrode 211 and the negative electrode 215) of the secondary battery 200 that is positioned on the outer diameter side of a curved portion is preferably longer than the other electrode that is positioned on the inner diameter side of the curved portion, in the direction in which the electrode is curved. With such a structure, ends of

the positive electrode 211 and those of the negative electrode 215 are aligned when the secondary battery 200 is curved with a certain curvature. That is, the entire region of the positive electrode active material layer included in the positive electrode 211 can face the negative electrode active material layer included in the negative electrode 215. Thus, positive electrode active materials included in the positive electrode 211 can efficiently contribute to a battery reaction. Therefore, the capacity of the secondary battery 200 per volume can be increased. Such a structure is particularly effective in a case where the curvature of the secondary battery 200 is fixed in using the secondary battery 200.

[0268]

The positive electrode lead 221 is electrically connected to a plurality of positive electrodes 211. The negative electrode lead 225 is electrically connected to a plurality of negative electrodes 215. The positive electrode lead 221 and the negative electrode lead 225 each include a sealing layer 220.

[0269]

The exterior body 207 covers a plurality of positive electrodes 211, a plurality of negative electrodes 215, and a plurality of separators 203. The secondary battery 200 includes an electrolyte (not shown) in a region covered with the exterior body 207. Three sides of the exterior body 207 are bonded, whereby the secondary battery 200 is sealed.

[0270]

In FIGS. 21A and 21B, the separators 203 each having a strip-like shape are used and each pair of the positive electrode 211 and the negative electrode 215 sandwich the separator 203; however, one embodiment of the present invention is not limited to this structure. One separator sheet may be folded in zigzag (or into a bellows shape) or wound so that the separator is positioned between the positive electrode and the negative electrode.

[0271]

An example of a method for fabricating the secondary battery 200 is illustrated in FIGS. 21A to 21D. FIG. 20 is a cross-sectional view along dashed-dotted line C1-C2 in FIG. 18B of the case of employing this manufacturing method.

[0272]

First, the negative electrode 215 is positioned over the separator 203 (FIG. 21A) such that the negative electrode active material layer of the negative electrode 215 overlaps with the separator 203.

[0273]

Then, the separator 203 is folded to overlap with the negative electrode 215. Next, the positive electrode 211 overlaps with the separator 203 (FIG. 21B) such that the positive electrode

active material layer of the positive electrode 211 overlaps with the separator 203 and the negative electrode active material layer. Note that in the case of using an electrode in which one surface of a current collector is provided with an active material layer, the positive electrode active material layer of the positive electrode 211 and the negative electrode active material layer of the negative electrode 215 are positioned to face each other with the separator 203 provided therebetween.

[0274]

In the case where the separator 203 is formed using a material that can be thermally welded, such as polypropylene, a region where the separator 203 overlaps with itself is thermally welded and then another electrode overlaps with the separator 203, whereby the slippage of the electrode in the fabrication process can be suppressed. Specifically, a region which does not overlap with the negative electrode 215 or the positive electrode 211 and in which the separator 203 overlaps with itself, e.g., a region denoted as 203a in FIG. 21B, is preferably thermally welded.

[0275]

By repeating the above steps, the positive electrode 211 and the negative electrode 215 can overlap with each other with the separator 203 provided therebetween as illustrated in FIG. 21C.

[0276]

Note that a plurality of positive electrodes 211 and a plurality of negative electrodes 215 may be placed to be alternately sandwiched by the separator 203 that is repeatedly folded in advance.

[0277]

Then, as illustrated in FIG. 21C, a plurality of positive electrodes 211 and a plurality of negative electrodes 215 are covered with the separator 203.

[0278]

Furthermore, the region where the separator 203 overlaps with itself, e.g., a region 203b in FIG. 21D, is thermally welded as illustrated in FIG. 21D, whereby a plurality of positive electrodes 211 and a plurality of negative electrodes 215 are covered with and tied with the separator 203.

[0279]

Note that a plurality of positive electrodes 211, a plurality of negative electrodes 215, and the separator 203 may be tied with a binding material.

[0280]

Since the positive electrodes 211 and the negative electrodes 215 are stacked in the

above process, one separator 203 has a region sandwiched between a plurality of positive electrodes 211 and a plurality of negative electrodes 215 and a region covering a plurality of positive electrodes 211 and a plurality of negative electrodes 215.

[0281]

In other words, the separator 203 included in the secondary battery 200 in FIG. 20 and FIG. 21D is a single separator which is partly folded. In the folded regions of the separator 203, a plurality of positive electrodes 211 and a plurality of negative electrodes 215 are provided.

[0282]

<Structural Example 2>

FIG. 22A is a perspective view of a secondary battery 250 and FIG. 22B is a top view of the secondary battery 250. Furthermore, FIG. 22C1 is a cross-sectional view of a first electrode assembly 230 and FIG. 22C2 is a cross-sectional view of a second electrode assembly 231.

[0283]

The secondary battery 250 includes the first electrode assembly 230, the second electrode assembly 231, and the separator 203. The secondary battery 250 further includes the positive electrode lead 221, the negative electrode lead 225, and the exterior body 207.

[0284]

As illustrated in FIG. 22C1, in the first electrode assembly 230, a positive electrode 211a, the separator 203, a negative electrode 215a, the separator 203, and the positive electrode 211a are stacked in this order. The positive electrode 211a and the negative electrode 215a each include active material layers on opposite surfaces of a current collector.

[0285]

As illustrated in FIG. 22C2, in the second electrode assembly 231, a negative electrode 215a, the separator 203, the positive electrode 211a, the separator 203, and the negative electrode 215a are stacked in this order. The positive electrode 211a and the negative electrode 215a each include active material layers on opposite surfaces of a current collector.

[0286]

In other words, in each of the first electrode assembly 230 and the second electrode assembly 231, the positive electrode and the negative electrode are provided such that the active material layers face each other with the separator 203 provided therebetween.

[0287]

The positive electrode lead 221 is electrically connected to a plurality of positive electrodes 211. The negative electrode lead 225 is electrically connected to a plurality of negative electrodes 215. The positive electrode lead 221 and the negative electrode lead 225 each include the sealing layer 220.

[0288]

FIG. 23 is an example of a cross-sectional view along dashed-dotted line D1-D2 in FIG. 22B. Note that FIG. 23 does not illustrate all components for clarity of the drawings.

[0289]

As illustrated in FIG. 23, the secondary battery 250 has a structure in which a plurality of first electrode assemblies 230 and a plurality of second electrode assemblies 231 are covered with the wound separator 203.

[0290]

The exterior body 207 covers a plurality of first electrode assemblies 230, a plurality of second electrode assemblies 231, and the separator 203. The secondary battery 200 includes an electrolyte (not shown) in a region covered with the exterior body 207. Three sides of the exterior body 207 are bonded, whereby the secondary battery 200 is sealed.

[0291]

An example of a method for fabricating the secondary battery 250 is illustrated in FIGS. 24A to 24D.

[0292]

First, the first electrode assembly 230 is positioned over the separator 203 (FIG. 24A).

[0293]

Then, the separator 203 is folded to overlap with the first electrode assembly 230. After that, two second electrode assemblies 231 are positioned over and under the first electrode assembly 230 with the separator 203 positioned between each of the second electrode assemblies 231 and the first electrode assembly 230 (FIG. 24B).

[0294]

Then, the separator 203 is wound to cover the two second electrode assemblies 231. Moreover, two first electrode assemblies 230 are positioned over and under the two second electrode assemblies 231 with the separator 203 positioned between each of the first electrode assemblies 230 and each of the second electrode assemblies 231 (FIG. 24C).

[0295]

Then, the separator 203 is wound to cover the two first electrode assemblies 230 (FIG. 24D).

[0296]

Since a plurality of first electrode assemblies 230 and a plurality of second electrode assemblies 231 are stacked in the above process, these electrode assemblies are each positioned surrounded with the spirally wound separator 203.

[0297]

Note that the outermost electrode preferably does not include an active material layer on the outer side.

[0298]

Although FIGS. 22C1 and 22C2 each illustrate a structure in which the electrode assembly includes three electrodes and two separators, one embodiment of the present invention is not limited to this structure. The electrode assembly may include four or more electrodes and three or more separators. A larger number of electrodes lead to higher capacity of the secondary battery 250. Alternatively, the electrode assembly may include two electrodes and one separator. A smaller number of electrodes enable higher resistance of the secondary battery against bending. Although FIG. 23 illustrates the structure in which the secondary battery 250 includes three first electrode assemblies 230 and two second electrode assemblies 231, one embodiment of the present invention is not limited to this structure. The number of the electrode assemblies may be increased. A larger number of electrode assemblies lead to higher capacity of the secondary battery 250. The number of the electrode assemblies may be decreased. A smaller number of electrode assemblies enable higher resistance of the secondary battery against bending.

[0299]

FIG. 23 illustrates another example of a cross-sectional view along dashed-dotted line D1-D2 in FIG. 22B. As illustrated in FIG. 23, the separator 203 may be folded into a bellows shape so that the separator 203 is positioned between the first electrode assembly 230 and the second electrode assembly 231.

[0300]

This embodiment can be combined with any of the other embodiments as appropriate.

[0301]

(Embodiment 4)

In this embodiment, application examples of the power storage device of one embodiment of the present invention will be described with reference to FIGS. 26A to 26F to FIGS. 30A and 30B.

[0302]

The power storage device of one embodiment of the present invention can be used for an electronic device or a lighting device, for example. The power storage device of one embodiment of the present invention has excellent charge and discharge characteristics. Therefore, the electronic device or the lighting device can be used for a long time by a single charge. Moreover, since a decrease in capacity with an increasing number of charge and discharge cycles is inhibited, the time between charges is unlikely to be reduced by repetitive

charge. Furthermore, the power storage device of one embodiment of the present invention exhibits excellent charge and discharge characteristics and high long-term reliability and is highly safe at a wide range of temperature including high temperatures, so that the safety and reliability of an electronic device or a lighting device can be improved.

[0303]

Examples of electronic devices include a television set (also referred to as a television or a television receiver), a monitor of a computer or the like, a digital camera, a digital video camera, a digital photo frame, a mobile phone (also referred to as a mobile phone device), a portable game machine, a portable information terminal, an audio reproducing device, a large game machine such as a pinball machine, and the like.

[0304]

Since the power storage device of one embodiment of the present invention is flexible, the power storage device or an electronic device or a lighting device using the power storage device can be incorporated along a curved inside/outside wall surface of a house or a building or a curved interior/exterior surface of a motor vehicle.

[0305]

FIG. 26A illustrates an example of a mobile phone. A mobile phone 7400 is provided with a display portion 7402 incorporated in a housing 7401, an operation button 7403, an external connection port 7404, a speaker 7405, a microphone 7406, and the like. Note that the mobile phone 7400 includes a power storage device 7407.

[0306]

FIG. 26B illustrates the mobile phone 7400 in the state of being bent. When the whole mobile phone 7400 is bent by the external force, the power storage device 7407 included in the mobile phone 7400 is also bent. The power storage device 7407 is a thin power storage device. The power storage device 7407 is fixed in a state of being bent. FIG. 26C illustrates the power storage device 7407 in the state of being bent

[0307]

FIG. 26D illustrates an example of a bangle display device. A portable display device 7100 includes a housing 7101, a display portion 7102, an operation button 7103, and a power storage device 7104. FIG. 26E illustrates the bent power storage device 7104.

[0308]

FIG. 26F illustrates an example of a watch-type portable information terminal. A portable information terminal 7200 includes a housing 7201, a display portion 7202, a band 7203, a buckle 7204, an operation button 7205, an input output terminal 7206, and the like.

[0309]

The portable information terminal 7200 is capable of executing a variety of applications such as mobile phone calls, e-mailing, viewing and editing text, music reproduction, Internet communication, and a computer game.

[0310]

The display surface of the display portion 7202 is curved, and images can be displayed on the curved display surface. In addition, the display portion 7202 includes a touch sensor, and operation can be performed by touching the screen with a finger, a stylus, or the like. For example, by touching an icon 7207 displayed on the display portion 7202, application can be started.

[0311]

With the operation button 7205, a variety of functions such as time setting, power ON/OFF, ON/OFF of wireless communication, setting and cancellation of silent mode, and setting and cancellation of power saving mode can be performed. For example, the functions of the operation button 7205 can be set freely by the operating system incorporated in the portable information terminal 7200.

[0312]

Furthermore, the portable information terminal 7200 can employ near field communication, which is a communication method based on an existing communication standard. In that case, for example, mutual communication between the portable information terminal 7200 and a headset capable of wireless communication can be performed, and thus hands-free calling is possible.

[0313]

Moreover, the portable information terminal 7200 includes the input output terminal 7206, and data can be directly transmitted to and received from another information terminal via a connector. In addition, charging via the input output terminal 7206 is possible. Note that the charging operation may be performed by wireless power feeding without using the input output terminal 7206.

[0314]

The display portion 7202 of the portable information terminal 7200 is provided with the power storage device of one embodiment of the present invention. For example, the power storage device 7104 illustrated in FIG. 26E that is in the state of being curved can be provided in the housing 7201. Alternatively, the power storage device 7104 illustrated in FIG. 26E can be provided in the band 7203 such that it can be curved.

[0315]

FIG. 27A illustrates an example of a wrist-worn activity meter. The activity meter

7250 includes a housing 7251, the band 7203, the buckle 7204, and the like. Furthermore, the housing 7251 incorporates a wireless communication device, a pulse sensor, an acceleration sensor, a temperature sensor, and the like. The activity meter 7250 has a function of acquiring data such as pulse variation and the amount of activity of the user with the pulse sensor and the acceleration sensor and sending the data to an external portable information terminal by the wireless communication device. Furthermore, the activity meter 7250 may have a function of measuring calorie consumption and calorie intake of the user, a function of measuring the number of steps taken, a function of measuring a sleeping condition, or the like. Note that the activity meter 7250 may be provided with a display portion for displaying data acquired by the above function.

[0316]

The activity meter 7250 includes the power storage device of one embodiment of the present invention. For example, the power storage device 7104 illustrated in FIG. 26E that is in the state of being curved can be provided in the housing 7201. Alternatively, the power storage device 7104 illustrated in FIG. 26E can be provided in the band 7203 such that it can be curved.

[0317]

FIG. 27B illustrates an example of an armband display device. A display device 7300 includes a display portion 7304 and the power storage device of one embodiment of the present invention. The display device 7300 can include a touch sensor in the display portion 7304 and can serve as a portable information terminal.

[0318]

The display surface of the display portion 7304 is bent, and images can be displayed on the bent display surface. A display state of the display device 7300 can be changed by, for example, near field communication, which is a communication method based on an existing communication standard.

[0319]

The display device 7300 includes an input output terminal, and data can be directly transmitted to and received from another information terminal via a connector. In addition, charging via the input output terminal is possible. Note that the charging operation may be performed by wireless power feeding without using the input output terminal.

[0320]

FIG. 27C illustrates an example of a glasses-type display device. A display device 7350 includes lenses 7351, a frame 7352, and the like. Furthermore, a projection portion (not illustrated) that projects an image or video on the lenses 7351 is provided in the frame 7352 or in contact with the frame 7352. The display device 7350 has a function of displaying an image

7351A on the entire lenses 7351 in the direction in which the user can see the image 7351A. Alternatively, the display device 7350 has a function of displaying an image 7351B on part of the lenses 7351 in the direction in which the user can see the image 7351B.

[0321]

The display device 7350 includes the power storage device of one embodiment of the present invention. FIG. 27D is an enlarged view of an edge portion 7355 of the frame 7352. The edge portion 7355 can be formed using a rubber material such as fluorine rubber or silicone rubber. The power storage device 7360 of one embodiment of the present invention is embedded in the edge portion 7355, and the positive electrode lead 7361 and the negative electrode lead 7362 protrude from the edge portion 7355. The positive electrode lead 7361 and the negative electrode lead 7362 are electrically connected to a wiring provided in the frame 7352 and connected to a projection portion or the like. Note that the edge portion 7355 can be formed so as to incorporate the power storage device 7360 as in Embodiment 2.

[0322]

The edge portion 7355 and the power storage device 7360 have flexibility. Thus, the display device 7350 can be worn so as to be in close contact with the user along with the shape of the head of the user.

[0323]

FIGS. 28A and 28B illustrate an example of a tablet terminal that can be folded in half. A tablet terminal 9600 illustrated in FIGS. 28A and 28B includes a pair of housings 9630, a movable portion 9640 connecting the pair of housings 9630, a display portion 9631a, a display portion 9631b, a display mode changing switch 9626, a power switch 9627, a power saving mode changing switch 9625, a fastener 9629, and an operation switch 9628. FIG. 28A illustrates the tablet terminal 9600 that is opened, and FIG. 28B illustrates the tablet terminal 9600 that is closed.

[0324]

The tablet terminal 9600 includes a power storage unit 9635 inside the housings 9630. The power storage unit 9635 is provided across the housings 9630, passing through the movable portion 9640.

[0325]

Part of the display portion 9631a can be a touch panel region 9632a, and data can be input by touching operation keys 9638 that are displayed. Note that FIG. 28A shows, as an example, that half of the area of the display portion 9631a has only a display function and the other half of the area has a touch panel function. However, the structure of the display portion 9631a is not limited to this, and all the area of the display portion 9631a may have a touch panel

function. For example, all the area of the display portion 9631a can display a keyboard and serve as a touch panel while the display portion 9631b can be used as a display screen.

[0326]

As in the display portion 9631a, part of the display portion 9631b can be a touch panel region 9632b. When a keyboard display switching button 9639 displayed on the touch panel is touched with a finger, a stylus, or the like, a keyboard can be displayed on the display portion 9631b.

[0327]

Touch input can be performed in the touch panel region 9632a and the touch panel region 9632b at the same time.

[0328]

The display mode changing switch 9626 allows switching between a landscape mode and a portrait mode, color display and black-and-white display, and the like. The power saving mode changing switch 9625 can control display luminance in accordance with the amount of external light in use of the tablet terminal 9600, which is measured with an optical sensor incorporated in the tablet terminal 9600. In addition to the optical sensor, other detecting devices such as sensors for determining inclination, such as a gyroscope or an acceleration sensor, may be incorporated in the tablet terminal.

[0329]

Although the display portion 9631a and the display portion 9631b have the same area in FIG. 28A, one embodiment of the present invention is not limited to this example. The display portion 9631a and the display portion 9631b may have different areas or different display quality. For example, one of the display portions 9631a and 9631b may display higher definition images than the other.

[0330]

The tablet terminal is closed in FIG. 28B. The tablet terminal includes the housings 9630, a solar cell 9633, and a charge and discharge control circuit 9634 including a DCDC converter 9636. The power storage device of one embodiment of the present invention is used as the power storage unit 9635.

[0331]

The tablet terminal 9600 can be folded such that the housings 9630 overlap with each other when not in use. Thus, the display portions 9631a and 9631b can be protected, which increases the durability of the tablet terminal 9600. In addition, the power storage unit 9635 of one embodiment of the present invention has flexibility and can be repeatedly bent without a significant decrease in charge and discharge capacity. Thus, a highly reliable tablet terminal

can be provided.

[0332]

The tablet terminal illustrated in FIGS. 28A and 28B can also have a function of displaying various kinds of data (e.g., a still image, a moving image, and a text image) on the display portion, a function of displaying a calendar, a date, or the time on the display portion, a touch-input function of operating or editing data displayed on the display portion by touch input, a function of controlling processing by various kinds of software (programs), and the like.

[0333]

The solar cell 9633, which is attached on the surface of the tablet terminal, supplies electric power to a touch panel, a display portion, an image signal processing portion, and the like. Note that the solar cell 9633 can be provided on one surface or opposite surfaces of the housing 9630 and the power storage unit 9635 can be charged efficiently. The use of a lithium-ion battery as the power storage unit 9635 brings an advantage such as reduction in size.

[0334]

The structure and operation of the charge and discharge control circuit 9634 illustrated in FIG. 28B will be described with reference to a block diagram in FIG. 28C. The solar cell 9633, the power storage unit 9635, the DCDC converter 9636, a converter 9637, switches SW1 to SW3, and the display portion 9631 are illustrated in FIG. 28C, and the power storage unit 9635, the DCDC converter 9636, the converter 9637, and the switches SW1 to SW3 correspond to the charge and discharge control circuit 9634 in FIG. 28B.

[0335]

First, an example of operation when electric power is generated by the solar cell 9633 using external light will be described. The voltage of electric power generated by the solar cell is raised or lowered by the DCDC converter 9636 to a voltage for charging the power storage unit 9635. When the display portion 9631 is operated with the electric power from the solar cell 9633, the switch SW1 is turned on and the voltage of the electric power is raised or lowered by the converter 9637 to a voltage needed for operating the display portion 9631. When display on the display portion 9631 is not performed, the switch SW1 is turned off and the switch SW2 is turned on, so that the power storage unit 9635 can be charged.

[0336]

Note that the solar cell 9633 is described as an example of a power generation means; however, one embodiment of the present invention is not limited to this example. The power storage unit 9635 may be charged using another power generation means such as a piezoelectric element or a thermoelectric conversion element (Peltier element). For example, the power storage unit 9635 may be charged with a non-contact power transmission module capable of

performing charging by transmitting and receiving electric power wirelessly (without contact), or any of the other charge means used in combination.

[0337]

FIG. 29 illustrates other examples of electronic devices. In FIG. 29, a display device 8000 is an example of an electronic device including a power storage device 8004 of one embodiment of the present invention. Specifically, the display device 8000 corresponds to a display device for TV broadcast reception and includes a housing 8001, a display portion 8002, speaker portions 8003, and the power storage device 8004. The power storage device 8004 of one embodiment of the present invention is provided in the housing 8001. The display device 8000 can receive electric power from a commercial power supply. Alternatively, the display device 8000 can use electric power stored in the power storage device 8004. Thus, the display device 8000 can be operated with the use of the power storage device 8004 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0338]

A semiconductor 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 the display portion 8002.

[0339]

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

[0340]

In FIG. 29, an installation lighting device 8100 is an example of an electronic device including a power storage device 8103 of one embodiment of the present invention. Specifically, the lighting device 8100 includes a housing 8101, a light source 8102, and the power storage device 8103. Although FIG. 29 illustrates the case where the power storage device 8103 is provided in a ceiling 8104 on which the housing 8101 and the light source 8102 are installed, the power storage device 8103 may be provided in the housing 8101. The lighting device 8100 can receive electric power from a commercial power supply. Alternatively, the lighting device 8100 can use electric power stored in the power storage device 8103. Thus, the lighting device 8100 can be operated with the use of power storage device 8103 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0341]

Note that although the installation lighting device 8100 provided in the ceiling 8104 is illustrated in FIG. 29 as an example, the power storage device of one embodiment of the present invention can be used in an installation lighting device provided in, for example, a wall 8105, a floor 8106, a window 8107, or the like other than the ceiling 8104. Alternatively, the power storage device of one embodiment of the present invention can be used in a tabletop lighting device or the like.

[0342]

As the light source 8102, an artificial light source which emits light artificially by using electric power can be used. Specifically, an incandescent lamp, a discharge lamp such as a fluorescent lamp, and light-emitting elements such as an LED and an organic EL element are given as examples of the artificial light source.

[0343]

In FIG. 29, an air conditioner including an indoor unit 8200 and an outdoor unit 8204 is an example of an electronic device including a power storage device 8203 of one embodiment of the present invention. Specifically, the indoor unit 8200 includes a housing 8201, an air outlet 8202, and the power storage device 8203. Although FIG. 29 illustrates the case where the power storage device 8203 is provided in the indoor unit 8200, the power storage device 8203 may be provided in the outdoor unit 8204. Alternatively, the power storage devices 8203 may be provided in both the indoor unit 8200 and the outdoor unit 8204. The air conditioner can receive electric power from a commercial power supply. Alternatively, the air conditioner can use electric power stored in the power storage device 8203. Particularly in the case where the power storage devices 8203 are provided in both the indoor unit 8200 and the outdoor unit 8204, the air conditioner can be operated with the use of the power storage device 8203 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0344]

Note that although the split-type air conditioner including the indoor unit and the outdoor unit is illustrated in FIG. 29 as an example, the power storage device of one embodiment of the present invention can be used in an air conditioner in which the functions of an indoor unit and an outdoor unit are integrated in one housing.

[0345]

In FIG. 29, an electric refrigerator-freezer 8300 is an example of an electronic device including a power storage device 8304 of one embodiment of the present invention. Specifically, the electric refrigerator-freezer 8300 includes a housing 8301, a door for a refrigerator 8302, a door for a freezer 8303, and the power storage device 8304. The power

storage device 8304 is provided in the housing 8301 in FIG. 29. The electric refrigerator-freezer 8300 can receive electric power from a commercial power supply. Alternatively, the electric refrigerator-freezer 8300 can use electric power stored in the power storage device 8304. Thus, the electric refrigerator-freezer 8300 can be operated with the use of the power storage device 8304 of one embodiment of the present invention as an uninterruptible power supply even when electric power cannot be supplied from a commercial power supply due to power failure or the like.

[0346]

Note that a high-frequency heating apparatus such as a microwave oven and an electronic device such as an electric rice cooker require high power in a short time. The tripping of a breaker of a commercial power supply in use of an electronic device can be prevented by using the power storage device of one embodiment of the present invention as an auxiliary power supply for supplying electric power which cannot be supplied enough by a commercial power supply.

[0347]

In addition, in a time period when electronic devices are not used, particularly when the proportion of the amount of electric power which is actually used to the total amount of electric power which can be supplied from a commercial power supply source (such a proportion referred to as a usage rate of electric power) is low, electric power can be stored in the power storage device, whereby the usage rate of electric power can be reduced in a time period when the electronic devices are used. For example, in the case of the electric refrigerator-freezer 8300, electric power can be stored in the power storage device 8304 in night time when the temperature is low and the door for a refrigerator 8302 and the door for a freezer 8303 are not often opened or closed. On the other hand, in daytime when the temperature is high and the door for a refrigerator 8302 and the door for a freezer 8303 are frequently opened and closed, the power storage device 8304 is used as an auxiliary power supply; thus, the usage rate of electric power in daytime can be reduced.

[0348]

Furthermore, the power storage device of one embodiment of the present invention can be provided in a vehicle.

[0349]

The use of power storage devices in vehicles enables production of next-generation clean energy vehicles such as hybrid electric vehicles (HEVs), electric vehicles (EVs), and plug-in hybrid electric vehicles (PHEVs).

[0350]

FIGS. 30A and 30B each illustrate an example of a vehicle using one embodiment of the present invention. An automobile 8400 illustrated in FIG. 30A is an electric vehicle that runs on the power of an electric motor. Alternatively, the automobile 8400 is a hybrid electric vehicle capable of driving appropriately using either the electric motor or the engine. One embodiment of the present invention can provide a high-mileage vehicle. The automobile 8400 includes the power storage device. The power storage device is used not only for driving the electric motor, but also for supplying electric power to a light-emitting device such as a headlight 8401 or a room light (not illustrated).

[0351]

The power storage device can also supply electric power to a display device of a speedometer, a tachometer, or the like included in the automobile 8400. Furthermore, the power storage device can supply electric power to a semiconductor device included in the automobile 8400, such as a navigation system.

[0352]

FIG. 30B illustrates an automobile 8500 including the power storage device. The automobile 8500 can be charged when the power storage device is supplied with electric power through external charging equipment by a plug-in system, a contactless power feeding system, or the like. In FIG. 30B, a power storage device included in the automobile 8500 is charged with the use of a ground-based charging apparatus 8021 through a cable 8022. In charging, a given method such as CHAdeMO (registered trademark) or Combined Charging System may be employed as a charging method, the standard of a connector, or the like as appropriate. The ground-based charging apparatus 8021 may be a charging station provided in a commerce facility or a power source in a house. For example, with the use of a plug-in technique, the power storage device included in the automobile 8500 can be charged by being supplied with electric power from outside. The charging can be performed by converting AC electric power into DC electric power through a converter such as an ACDC converter.

[0353]

Furthermore, although not illustrated, the vehicle may include a power receiving device so that it can be charged by being supplied with electric power from an above-ground power transmitting device in a contactless manner. In the case of the contactless power feeding system, by fitting a power transmitting device in a road or an exterior wall, charging can be performed not only when the electric vehicle is stopped but also when driven. In addition, the contactless power feeding system may be utilized to perform transmission and reception of electric power between vehicles. Furthermore, a solar cell may be provided in the exterior of the automobile to charge the power storage device when the automobile stops or moves. To

supply electric power in such a contactless manner, an electromagnetic induction method or a magnetic resonance method can be used.

[0354]

According to one embodiment of the present invention, the power storage device can have improved cycle characteristics and reliability. Furthermore, according to one embodiment of the present invention, the power storage device itself can be made more compact and lightweight as a result of improved characteristics of the power storage device. The compact and lightweight power storage device contributes to a reduction in the weight of a vehicle, and thus increases the driving distance. Furthermore, the power storage device included in the vehicle can be used as a power source for supplying electric power to products other than the vehicle. In such a case, the use of a commercial power source can be avoided at peak time of electric power demand.

[0355]

This embodiment can be combined with any of the other embodiments as appropriate.

[Example 1]

[0356]

In this example, a power storage device of one embodiment of the present invention was fabricated according to Embodiment 1, and subjected to a cycle life test at 25 °C together with power storage devices for comparison.

[0357]

<Fabrication methods for samples>

In this example, the power storage device 500 illustrated in FIG. 1A was fabricated. Fabrication methods for samples will be described below.

[0358]

The one embodiment of the present invention was applied to 14 samples, A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4. For comparison, 2 comparison samples, a1 and a2 were fabricated.

[0359]

Lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were used as solutes for the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4. The concentration of lithium hexafluorophosphate in the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4 differs from one another. Lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was used as a solute for the comparison samples a1 and a2, and lithium hexafluorophosphate was not used.

[0360]

Cellulosic fiber was used for a separator in the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, and F2 and the comparison samples a1 and a2. Polyphenylene sulfide (PPS) was used for the samples B3 and B4.

[0361]

After the power storage device 500 was manufactured, the samples A2, B2, C2, D2, E2, F2, and B4 and the comparison sample a2 were subjected to heat treatment at 170 °C for 15 minutes. The heat treatment is performed assuming that the samples and fluorine rubber are integrated as in Embodiment 2. Note that the samples A1, B1, C1, D1, E1, F1, and B3 and the comparison sample a1 were not subjected to heat treatment.

[0362]

Table 1 shows the electrolyte, the separator, and conditions of heat treatment for each sample.

[0363]

[Table 1]

Sample	Electrolyte		Separator	Heat treatment
	Condition	$LiPF_6$ [wt%]		
Comparison sample a1	Electrolyte a	0.0	Cellulosic fiber	-
Comparison sample a2				170°C 15min
Sample A1	Electrolyte A	0.18	Cellulosic fiber	-
Sample A2				170°C 15min
Sample B1	Electrolyte B	0.27	Cellulosic fiber	-
Sample B2				170°C 15min
Sample C1	Electrolyte C	0.51	Cellulosic fiber	-
Sample C2				170°C 15min
Sample D1	Electrolyte D	1.1	Cellulosic fiber	-
Sample D2				170°C 15min
Sample E1	Electrolyte E	2.0	Cellulosic fiber	-
Sample E2				170°C 15min
Sample F1	Electrolyte F	3.0	Cellulosic fiber	-
Sample F2				170°C 15min
Sample B3	Electrolyte B	0.27	Polyphenylene sulfide	-
Sample B4				170°C 15min

[0364]

Manufacturing methods of the electrolyte are described.

[0365]

The electrolyte a used for the comparison samples a1 and a2 is described. The

electrolyte a was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte a was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte a was 1 mol/L in the molecular concentration.

[0366]

The electrolyte A used for the samples A1 and A2 is described. The electrolyte A was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte A was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte A was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte A was 0.18 wt% in the weight ratio.

[0367]

The electrolyte B used for the samples B1, B2, B3, and B4 is described. The electrolyte B was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte B was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte B was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte B was 0.27 wt% in the weight ratio.

[0368]

The electrolyte C used for the samples C1 and C2 is described. The electrolyte C was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte C was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte C was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte C was 0.51 wt% in the

weight ratio.

[0369]

The electrolyte D used for the samples D1 and D2 is described. The electrolyte D was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte D was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte D was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte D was 1.1 wt% in the weight ratio.

[0370]

The electrolyte E used for the samples E1 and E2 is described. The electrolyte E was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte E was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte E was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte A was 2.0 wt% in the weight ratio.

[0371]

The electrolyte F used for the samples F1 and F2 is described. The electrolyte F was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte F was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte F was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte F was 3.0 wt% in the weight ratio.

[0372]

Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-00798) was used for the mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1. Lithium battery grade produced by

Kishida Chemical Co., Ltd. (product code number LBG-84923) was used for vinylene carbonate (VC). A product by IoLiTec Ionic Liquids Technologies Inc. (product number KI-0016-HP) was used for lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-45860) was used for lithium hexafluorophosphate ($LiPF_6$).

[0373]

Next, a method for forming a negative electrode is described. The method for forming a negative electrode is common to all the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4 and the comparison samples a1 and a2.

[0374]

Spherical natural graphite having a specific surface area of 6.3 m^2/g and an average particle size of 15 μm (CGB-15 manufactured by Nippon Graphite Industries, Co.,Ltd.) was used as a negative electrode active material. For a binder, sodium carboxymethyl cellulose (CMC-Na) and SBR were used. The polymerization degree of CMC-Na that was used was higher than or equal to 600 and lower than or equal to 800, and the viscosity of a 1 wt% CMC-Na aqueous solution was in the range from 300 mPa·s to 500 mPa·s. The compounding ratio of graphite: CMC-Na: SBR was set to 97:1:1.5 (wt%).

[0375]

First, CMC-Na powder and an active material were mixed and then kneaded with a mixer, so that a first mixture was obtained.

[0376]

Subsequently, a small amount of water was added to the first mixture and kneading was performed, so that a second mixture was obtained. Here, "kneading" means "mixing something with a high viscosity".

[0377]

Then, water was further added and the mixture was kneaded with a mixer, so that a third mixture was obtained.

[0378]

Then, a 50 wt% SBR aqueous dispersion liquid was added, and mixing was performed with a mixer. After that, the obtained mixture was degassed under a reduced pressure, so that a slurry was obtained.

[0379]

Subsequently, the slurry was applied to a negative electrode current collector with the use of a continuous coater. An 18-μm-thick rolled copper foil was used as the negative electrode current collector. The coating speed was set to 0.75 m/min.

[0380]

Then, the solvent in the slurry applied to the negative electrode current collector was vaporized in a drying furnace. Vaporization treatment was performed at 50 °C in an air atmosphere for 120 seconds and then further performed at 80 °C in the air atmosphere for 120 seconds. After that, further vaporization treatment was performed at 100 °C under a reduced pressure (−100 kPa) for 10 hours.

[0381]

Through the above steps, the negative electrode active material layer was formed on one surface of the negative electrode current collector, so that the negative electrode was fabricated.

[0382]

Next, a method for forming the positive electrode is described. The method for forming a negative electrode is common to all the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4 and the comparison samples a1 and a2.

[0383]

$LiCoO_2$, polyvinylidene fluoride (PVDF), and acetylene black were used as a positive electrode active material, a binder, and a conductive additive. $LiCoO_2$ with a specific surface area of 0.55 m^2/g and an average particle size of 6.3 μm produced by NIPPON CHEMICAL INDUSTRIAL CO., LTD. (C-5hV) was used. The compounding ratio of $LiCoO_2$: acetylene black: PVDF was 95:3:2 (wt%).

[0384]

Note that the average particle size in this specification and the like is a cumulative sum value of 50 % (D50) on the basis of volume.

[0385]

First, acetylene black and PVDF were mixed in a mixer, so that a third mixture was obtained.

[0386]

Next, the active material was added to the third mixture, so that a fourth mixture was obtained.

[0387]

After that, a solvent *N*-methyl-2-pyrrolidone (NMP) was added to the fourth mixture and mixing was performed with a mixer. Through the above steps, a slurry was formed.

[0388]

Then, mixing was performed with a large-sized mixer.

[0389]

Subsequently, the slurry was applied to a positive electrode current collector with the

use of a continuous coater. A 20-μm-thick aluminum current collector was used as the positive electrode current collector. The coating speed was set to 0.2 m/min.

[0390]

Then, the solvent in the slurry applied to the positive electrode current collector was vaporized in a drying furnace. Solvent vaporization treatment was performed at 70 °C in an air atmosphere for 7.5 minutes and then further performed at 90 °C in the air atmosphere for 7.5 minutes.

[0391]

After that, heat treatment was performed in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa) at 170 °C for 10 hours. Subsequently, the positive electrode active material layer was pressed by a roll press method so as to be consolidated.

[0392]

Through the above steps, the positive electrode active material layer was formed on one surface of the positive electrode current collector, so that the positive electrode was fabricated.

[0393]

Table 2 lists the averages of the active material loadings, the thicknesses, and the densities of each of the positive electrode active material layers, and Table 3 lists those for the negative electrode active material layers. The values shown in this specification are the averages of measurement values of each of the electrodes used in fabricating the samples. Note that when the active material layers were formed on opposite surfaces of the current collector, the values are the averages of the active material loadings, the thicknesses, and the densities of the active material layer on one surface of the current collector.

[0394]

The content was calculated from the area and weight of electrodes weighed by an electronic balance. The density was calculated from the thickness measured by a micrometer.

[0395]

[Table 2]

Sample	Positive electrode		
	Loading [mg/cm^2]	Thickness [μm]	Density [g/cm^3]
Comparison sample a1	21.1	66	3.20
Comparison sample a2	21.2	67	3.16
Sample A1	21.4	66	3.25
Sample A2	21.5	66	3.25
Sample B1	21.3	70	3.05
Sample B2	21.3	67	3.18
Sample C1	21.3	66	3.22
Sample C2	21.3	66	3.22
Sample D1	21.3	66	3.23
Sample D2	21.3	66	3.23
Sample E1	21.6	67	3.23
Sample E2	21.6	68	3.18
Sample F1	21.3	65	3.28
Sample F2	21.4	67	3.19
Sample B3	24.4	72	3.39
Sample B4	24.4	71	3.44

[0396]

[Table 3]

Sample	Negative electrode		
	Loading [mg/cm^2]	Thickness [mm]	Density [g/cm^3]
Comparison sample a1	9.5	107	0.89
Comparison sample a2	9.7	101	0.96
Sample A1	10.2	106	0.96
Sample A2	10.2	103	0.99
Sample B1	9.7	99	0.98
Sample B2	9.8	105	0.93
Sample C1	10.1	103	0.98
Sample C2	10.1	102	0.99
Sample D1	10.1	107	0.95
Sample D2	10.2	102	1.00
Sample E1	10.3	109	0.95
Sample E2	10.4	103	1.01
Sample F1	10.2	106	0.96
Sample F2	10.2	108	0.94
Sample B3	9.7	101	0.96
Sample B4	9.7	103	0.95

[0397]

Next, the method for manufacturing the power storage device is described. The samples fabricated in this example each include one positive electrode in which a positive electrode active material layer is provided on one surface of a positive electrode current collector and one negative electrode in which a negative electrode active material layer is provided on one surface of a negative electrode current collector. In other words, the samples in this example each include one positive electrode active material layer and one negative electrode active material layer.

[0398]

First, a positive electrode, a negative electrode, and a first separator were cut. The size of the positive electrode, negative electrode, and first separator were respectively 20.49 cm^2, 23.84 cm^2, and 24.75 cm^2.

[0399]

Cellulosic fiber was used for a separator in the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, and F2 and the comparison samples a1 and a2. Specifically, 30-μm-thick solvent-spun regenerated cellulosic fiber (product number TF40) produced by NIPPON KODOSHI CORPORATION was used. Polyphenylene sulfide was used for the samples B3 and B4. Specifically, a stack of two 46-μm-thick polyphenylene sulfide paper (product number PS0020) produced by Toray Industries, Inc. was used.

[0400]

Then, the positive electrode active material and the negative electrode active material in tab regions were removed to expose the current collectors.

[0401]

After that, the positive electrode and the negative electrode were stacked with the first separator therebetween. At this time, the positive electrode and the negative electrode were stacked such that the positive electrode active material layer and the negative electrode active material layer faced each other.

[0402]

Then, leads were bonded to the positive electrode and the negative electrode by ultrasonic welding.

[0403]

Next, the region where the electrodes are stacked and the lead is bonded was wrapped with a second separator. This can prevent dissolution of the resin layer of the exterior body by heat treatment performed later and contact of aluminum of the exterior body with the electrodes. The size of the second separator was 104 cm^2.

[0404]

Then, facing parts of two of four sides of the exterior body were bonded to each other by heating.

[0405]

As an exterior body, an aluminum film with opposite surfaces covered with a resin layer was used.

[0406]

After that, sealing layers provided for the leads were positioned so as to overlap with a sealing layer of the exterior body, and bonding was performed by heating. At this time, facing parts of a side of the exterior body except a side used for introduction of an electrolyte solution were bonded to each other.

[0407]

Next, heat treatment for drying the exterior body and the positive electrode, the separator, and the negative electrode wrapped by the exterior body was performed in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa) at 80 °C for 10 hours.

[0408]

Next, in an argon gas atmosphere, an approximately 600 μL of electrolyte was introduced from one side of the exterior body that was not sealed. The electrolyte a was introduced to the comparison samples a1 and a2. The electrolyte A was introduced to the samples A1 and A2. The electrolyte B was introduced to the samples B1 to B4. The electrolyte C was introduced to the samples C1 and C2. The electrolyte D was introduced to the samples D1 and D2. The electrolyte E was introduced to the samples E1 and E2. The electrolyte F was introduced to the samples F1 and F2.

[0409]

After that, the one side of the exterior body was sealed by heating in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa). Through the above steps, each thin storage battery was fabricated.

[0410]

Next, the samples A2, B2, C2, D2, E2, F2, and B4 and the comparison sample a2 were subjected to heat treatment. Assuming that each sample and fluorine rubber are integrally formed as in Embodiment 2, heat treatment was performed in an atmospheric pressure atmosphere at 170 °C for 15 minutes. Specifically, the temperature of a thermostatic bath was raised to approximately 170 °C, each sample was put in the thermostatic bath, and after 15 minutes, the sample was taken out. Expansion accompanying the heat treatment did not occur in the exterior body of each sample.

[0411]

Through the above, the samples A1, A2, B1, B2, C1, C2, D1, D2, E1, E2, F1, F2, B3, and B4 and the comparison samples a1 and a2 were fabricated.

[0412]

<Measurement of charge and discharge characteristics>

Next, the charge and discharge characteristics at 25 °C of the samples in this example were measured. The measurement was performed with a charge-discharge measuring instrument (produced by TOYO SYSTEM Co., LTD.). Constant current−constant voltage charging was performed until the voltage reached an upper voltage limit of 4.3 V, and constant current discharging was performed until the voltage reached a lower voltage limit of 2.5 V. The charging and discharging were performed 3 cycles at a rate of 0.1 C, and then, a long-term cycle test was performed at a rate of 0.3 C. A 10-minute break was taken after the charging and

discharging.

[0413]

Note that the rates were calculated using 170 mAh/g, which is capacity obtained when the upper charging voltage limit of $LiCoO_2$ serving as the positive electrode active material, is 4.3 V, as a reference.

[0414]

FIG. 31A shows charge-discharge curves of the comparison sample a1, FIG. 31B for the comparison sample a2, FIG. 31C for the sample A1, FIG. 31D for the sample A2, FIG. 32A for the sample B1, FIG. 32B for the sample B2, FIG. 32C for the sample C1, FIG. 32D for the sample C2, FIG. 33A for the sample D1, FIG. 33B for the sample D2, FIG. 33C for the sample E1, FIG. 33D for the sample E2, FIG. 34A for the sample F1, FIG. 34B for the sample F2, FIG. 34C for the sample B3, and FIG. 34D for the sample B4. In FIGS. 31A to 34D, the horizontal axis and the vertical axis represent capacity [mAh/g] and voltage [V], respectively. Charge and discharge characteristics at the 1st cycle and the 300th cycle are shown for each sample. The capacity is per weight of the positive electrode active material.

[0415]

It was found that in the samples subjected to heat treatment at 170 °C for 15 minutes, repetitive charge and discharge resulted in a decrease in capacity. It was shown that a reduction in capacity after repetitive charge and discharge of the samples A2, B2, C2, D2, and B4 containing lithium hexafluorophosphate, which were embodiments of the present invention, was suppressed as compared to the comparison sample a2 containing no lithium hexafluorophosphate.

[0416]

FIG. 35A shows cycle characteristics of the discharge capacity of the comparison samples a1 and a2, FIG. 35B for the samples A1 and A2, FIG. 35C for the samples B1 and B2, FIG. 35D for the samples C1 and C2, FIG. 36A for the samples D1 and D2, FIG. 36B for the samples E1 and E2, FIG. 36C for the samples F1 and F2, and FIG. 36D for the samples B3 and B4. In FIGS. 35A to 35D and FIGS. 36A to 36D, the horizontal axis and the vertical axis represent cycles [times] and capacity [mAh/g], respectively.

[0417]

FIG. 37A shows cycle characteristics of discharge capacity retention rate of the comparison samples a1 and a2, FIG. 37B for the samples A1 and A2, FIG. 37C for the samples B1 and B2, FIG. 37D for the samples C1 and C2, FIG. 38A for the samples D1 and D2, FIG. 38B for the samples E1 and E2, FIG. 38C for the samples F1 and F2, and FIG. 38D for the samples B3 and B4. In FIGS. 37A to 37D and FIGS. 38A to 38D, the horizontal axis and the

vertical axis represent cycles [times] and capacity retention rate [%], respectively. The capacity retention rate is percentage of discharge capacity for each cycle time with respect to the maximum value of the discharge capacity of each sample.

[0418]

It was found that in the samples subjected to heat treatment at 170 °C for 15 minutes, repetitive charge and discharge resulted in a decrease in capacity. It was shown that a reduction in capacity after repetitive charge and discharge of the samples A2, B2, C2, D2, and B4 containing lithium hexafluorophosphate, which were embodiments of the present invention, was suppressed as compared to the comparison sample a2 containing no lithium hexafluorophosphate.

[0419]

In this embodiment, it was found that lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) with high thermal resistance mainly supplies lithium ions which serve as carrier ions, which can prevent a reduction in capacity after repetitive charge and discharge even when heat treatment was performed. In addition, owing to lithium hexafluorophosphate, a passivation film was formed on the surface aluminum used for a positive electrode current collector in heat treatment at 170 °C or charging and discharging, so that favorable cycle characteristics were kept. Note that the capacity of the samples E2 and F2 was much reduced as compared to the comparison sample a2. Since the concentration of lithium hexafluorophosphate in each of the samples E2 and F2 was high, lithium hexafluorophosphate was decomposed into LiF and PF_5 by the heat treatment at 170 °C, and PF_5 decomposed the solvent, which probably caused degradation of battery characteristics such as a reduction in capacity. In other words, it was found that lithium hexafluorophosphate ($LiPF_6$) was desirably used at an amount enough to form a passivation film on the current collector surface.

[0420]

In one embodiment of the present invention, since lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate ($LiPF_6$) were used as solutes, the capacity is less likely to be reduced after repetitive charging and discharging even when the power storage battery was subjected to heat treatment.

[0421]

FIG. 39A shows cycle characteristics of the energy density of the comparison samples a1 and a2, FIG. 39B for the samples A1 and A2, FIG. 39C for the samples B1 and B2, FIG. 39D for the samples C1 and C2, FIG. 40A for the samples D1 and D2, FIG. 40B for the samples E1 and E2, FIG. 40C for the samples F1 and F2, and FIG. 40D for the samples B3 and B4. In FIGS. 39A to 39D and FIGS. 40A to 40D, the horizontal axis and the vertical axis represent

cycles [times] and energy density [mWh/g], respectively. The energy density is the product of discharge capacity and voltage shown in the discharge curves in FIGS. 31A to 31D, FIGS. 32A to 32D, FIGS. 33A to 33D, and FIGS. 34A to 34D.

[0422]

FIG. 41A shows cycle characteristics of the energy density of the comparison samples a1 and a2, FIG. 41B for the samples A1 and A2, FIG. 41C for the samples B1 and B2, FIG. 41D for the samples C1 and C2, FIG. 42A for the samples D1 and D2, FIG. 42B for the samples E1 and E2, FIG. 42C for the samples F1 and F2, and FIG. 42D for the samples B3 and B4. In FIGS. 41A to 41D and FIGS. 42A to 42D, the horizontal axis and the vertical axis represent cycles [times] and energy density retention rate [%], respectively. The energy density retention rate is percentage of energy density for each cycle time with respect to the maximum value of the energy density of each sample.

[0423]

It was found that in the samples subjected to heat treatment at 170 °C for 15 minutes, repetitive charge and discharge resulted in a decrease in energy density. It was shown that a reduction in energy density after repetitive charge and discharge of the samples A2, B2, C2, D2, and B4 containing lithium hexafluorophosphate, which were embodiments of the present invention, was suppressed as compared to the comparison sample a2 containing no lithium hexafluorophosphate.

[0424]

In this embodiment, it was found that lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) with high thermal resistance mainly supplies lithium ions which serve as carrier ions, which can prevent a reduction in energy density after repetitive charge and discharge even when heat treatment was performed. In addition, owing to lithium hexafluorophosphate, a passivation film was formed on the surface aluminum used for a positive electrode current collector in heat treatment at 170 °C or charging and discharging, so that favorable cycle characteristics were kept. Note that the energy density of the samples E2 and F2 was much reduced as compared to the comparison sample a2. Since the concentration of lithium hexafluorophosphate in each of the samples E2 and F2 was high, lithium hexafluorophosphate was decomposed into LiF and PF_5 by the heat treatment at 170 °C, and PF_5 decomposed the solvent, which probably caused degradation of battery characteristics such as a reduction in energy density. In other words, it was found that lithium hexafluorophosphate ($LiPF_6$) was desirably used at an amount enough to form a passivation film on the current collector surface.

[0425]

In one embodiment of the present invention, since lithium

bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate ($LiPF_6$) were used as solutes, the energy density is less likely to be reduced after repetitive charging and discharging even when the power storage battery was subjected to heat treatment.

[0426]

Table 3 and FIG. 43A show the relationship between the concentration of $LiPF_6$ with respect to the electrolyte and the capacity retention rate for each of the comparison sample a1 and the samples A2, B2, C2, D2, E2, F2, and B4 which were subjected to heat treatment at 170 °C. In FIG. 43A, the horizontal axis and the vertical axis represent the $LiPf_6$ concentration [wt%] and capacity retention [%], respectively. In FIG. 43A, black circles indicate data of the comparison sample a2 and the samples A2, B2, C2, D2, E2, and F2 in which cellulosic fiber was used for the separator, and crosses indicate data of the sample B4 in which polyphenylene sulfide was used as the separator. The capacity retention rate is a value at the 300th cycle for each sample shown in FIGS. 37A to 37D and FIGS. 38A to 38D.

[0427]

Table 4 and FIG. 43B show the relationship between the concentration of $LiPF_6$ with respect to the electrolyte and the energy density for each of the comparison sample a2 and the samples A2, B2, C2, D2, E2, F2, and B4 which were subjected to heat treatment at 170 °C for 15 minutes. In FIG. 43B, the horizontal axis and the vertical axis represent the $LiPf_6$ concentration [wt%] and energy density [%], respectively. In FIG. 43B, black circles indicate data of the comparison sample a2 and the samples A2, B2, C2, D2, E2, and F2 in which cellulosic fiber was used for the separator, and crosses indicate data of the sample B4 in which polyphenylene sulfide was used as the separator. The energy density retention rate is a value at the 300th cycle for each sample shown in FIGS. 41A to 41D and FIGS. 42A to 42D.

[0428]

[Table 4]

Sample	Electrolyte		Separator	Capacity retention rate [%]	Energy retention rate [%]
	Condition	$LiPF_6$ [wt%]			
Comparison sample a1	Electrolyte a	0.0	Cellulosic fiber	89.8	87.9
Comparison sample a2				84.3	81.8
Sample A1	Electrolyte A	0.18	Cellulosic fiber	87.9	86.6
Sample A2				89.0	88.3
Sample B1	Electrolyte B	0.27	Cellulosic fiber	88.7	87.3
Sample B2				88.9	88.0
Sample C1	Electrolyte C	0.51	Cellulosic fiber	89.3	88.6
Sample C2				85.8	84.1
Sample D1	Electrolyte D	1.1	Cellulosic fiber	89.4	88.8
Sample D2				84.9	82.3
Sample E1	Electrolyte E	2.0	Cellulosic fiber	89.6	89.0
Sample E2				79.0	73.8
Sample F1	Electrolyte F	3.0	Cellulosic fiber	88.5	87.9
Sample F2				71.4	59.9
Sample B3	Electrolyte B	0.27	Polyphenylene sulfide	85.0	82.7
Sample B4				86.0	84.7

[0429]

As shown in Table 4 and FIGS. 43A and 43B, the capacity retention rate and energy retention rate after repetitive charge and discharge of the samples A2, B2, C2, D2, and B4 which were embodiments of the present invention were higher than those of the comparison sample a2 containing no lithium hexafluorophosphate. In contrast, the capacity retention rate and energy retention rate of the samples E2 and F2 having high $LiPF_6$ concentrations were decreased.

[0430]

These results show that the electrolyte preferably contains ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC), lithium bis(pentafluoroethanesulfonyl)amide (LiBETA), and lithium hexafluorophosphate. It was also shown that the amount of lithium hexafluorophosphate dissolved in the electrolyte is preferably more than or equal to 0.01 wt% and less than or equal to 1.9 wt%, further preferably more than or equal to 0.05 wt% and less than or equal to 1.2 wt%, still further more than or equal to 0.1 wt% and less than or equal to 0.8 wt%.

[0431]

It was shown that the use of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and

lithium hexafluorophosphate as electrolyte solutes can produce a power storage battery with high thermal resistance.

[Example 2]

[0432]

In this example, a power storage device of one embodiment of the present invention was fabricated on the basis of Embodiment 1, and subjected to a cycle life test at 45 °C together with power storage devices for comparison.

[0433]

<Fabrication methods for samples>

In this example, the power storage device 500 illustrated in FIG. 1A was fabricated. Fabrication methods for samples will be described below.

[0434]

The one embodiment of the present invention was applied to 4 samples, G1, G2, H1, and H2. For comparison, 2 comparison samples, a3 and a4 were fabricated.

[0435]

Lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were used as solutes for the samples G1, G2, H1, and H2. The concentration of lithium hexafluorophosphate in the samples G1, G2, H1, and H2 differs from one another. Lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was used as a solute for the comparison samples a3 and a4, and lithium hexafluorophosphate was not used.

[0436]

Cellulosic fiber was used for a separator in the samples G1, G2, H1, and H2 and the comparison samples a3 and a4.

[0437]

After the power storage device 500 was manufactured, the samples G2 and H2 and the comparison sample a4 were subjected to heat treatment at 170 °C for 15 minutes. The heat treatment was performed assuming that the samples and fluorine rubber are integrated as in Embodiment 2. Note that the samples G1 and H1 and the comparison sample a3 were not subjected to heat treatment.

[0438]

Table 5 shows the electrolyte, the separator, and conditions of heat treatment for each sample.

[0439]

[Table 5]

Sample	Electrolyte		Separator	Heat treatment
	Condition	$LiPF_6$ [wt%]		
Comparison sample a3	Electrolyte a	0.0	Cellulosic fiber	-
Comparison sample a4				170°C 15min
Sample G1	Electrolyte G	0.26	Cellulosic fiber	-
Sample G2				170°C 15min
Sample H1	Electrolyte H	0.51	Cellulosic fiber	-
Sample H2				170°C 15min

[0440]

Manufacturing methods of the electrolyte are described.

[0441]

The electrolyte a was used as an electrolyte of the comparison samples a3 and a4. The description of the electrolyte a is omitted here because Example 1 can be referred to.

[0442]

The electrolyte G used for the samples G1 and G2 is described. The electrolyte G was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte G was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte G was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte G was 0.26 wt% in the weight ratio.

[0443]

The electrolyte H used for the samples H1 and H2 is described. The electrolyte H was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte H was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte H was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte H was 0.51 wt% in the weight ratio.

[0444]

Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-00798) was used for the mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1. Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-84923) was used for vinylene carbonate (VC). A product by IoLiTec Ionic Liquids Technologies Inc. (product number KI-0016-HP) was used for lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-45860) was used for lithium hexafluorophosphate.

[0445]

Next, a negative electrode was formed. Since Example 1 can be referred to for the formation method of the negative electrode, the description is omitted here.

[0446]

Next, a positive electrode was formed. Since Example 1 can be referred to for the formation method of the negative electrode, the description is omitted here.

[0447]

Table 6 lists the averages of the active material loadings, the thicknesses, and the densities of each of the positive electrode active material layers, and Table 7 lists those for the negative electrode active material layers.

[0448]

[Table 6]

Sample	Positive electrode		
	Loading [mg/cm^2]	Thickness [μm]	Density [g/cm^3]
Comparison sample a3	21.2	67	3.16
Comparison sample a4	21.2	66	3.21
Sample G1	21.3	66	3.23
Sample G2	21.3	66	3.23
Sample H1	21.5	67	3.20
Sample H2	21.5	66	3.26

[0449]

[Table 7]

Sample	Negative electrode		
	Loading [mg/cm^2]	Thickness [mm]	Density [g/cm^3]
Comparison sample a3	9.7	106	0.91
Comparison sample a4	9.7	99	0.98
Sample G1	9.9	101	0.98
Sample G2	9.9	105	0.95
Sample H1	10.3	106	0.97
Sample H2	10.3	110	0.93

[0450]

Next, the method for manufacturing the power storage device is described. The samples fabricated in this example each include one positive electrode in which a positive electrode active material layer is provided on one surface of a positive electrode current collector and one negative electrode in which a negative electrode active material layer is provided on one surface of a negative electrode current collector. In other words, the samples in this example each include one positive electrode active material layer and one negative electrode active material layer.

[0451]

First, a positive electrode, a negative electrode, and a first separator were cut. The size of the positive electrode, negative electrode, and first separator were respectively 20.49 cm^2, 23.84 cm^2, and 24.75 cm^2.

[0452]

Cellulosic fiber was used for a separator in the samples G1, G2, H1, and H2 and the comparison samples a3 and a4. Specifically, 30-μm-thick solvent-spun regenerated cellulosic fiber (product number TF40) produced by NIPPON KODOSHI CORPORATION was used.

[0453]

Then, the positive electrode active material and the negative electrode active material in tab regions were removed to expose the current collectors.

[0454]

After that, the positive electrode and the negative electrode were stacked with the first separator therebetween. At this time, the positive electrode and the negative electrode were stacked such that the positive electrode active material layer and the negative electrode active material layer faced each other.

[0455]

Then, leads were bonded to the positive electrode and the negative electrode by ultrasonic welding.

[0456]

Next, the region where the electrodes are stacked and the lead is bonded was wrapped with a second separator. This can prevent dissolution of the resin layer of the exterior body by heat treatment performed later and contact of aluminum of the exterior body with the electrodes. The size of the second separator was 104 cm^2.

[0457]

Then, facing parts of two of four sides of the exterior body were bonded to each other by heating.

[0458]

As an exterior body, an aluminum film with opposite surfaces covered with a resin layer was used.

[0459]

After that, sealing layers provided for the leads were positioned so as to overlap with a sealing layer of the exterior body, and bonding was performed by heating. At this time, facing parts of a side of the exterior body except a side used for introduction of an electrolyte solution were bonded to each other.

[0460]

Next, heat treatment for drying the exterior body and the positive electrode, the separator, and the negative electrode wrapped by the exterior body was performed in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa) at 80 °C for 10 hours.

[0461]

Next, in an argon gas atmosphere, an approximately 600 μL of electrolyte was introduced from one side of the exterior body that was not sealed. The electrolyte a was introduced to the comparison samples a3 and a4. The electrolyte G was introduced to the samples G1 and G2. The electrolyte H was introduced to the samples H1 and H2.

[0462]

After that, the one side of the exterior body was sealed by heating in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa). Through the above steps, each thin storage battery was fabricated.

[0463]

Next, the samples G2 and H2 and the comparison sample a4 were subjected to heat treatment. Assuming that each sample and fluorine rubber are integrally formed as in

Embodiment 2, heat treatment was performed in an atmospheric pressure atmosphere at 170 °C for 15 minutes. Specifically, the temperature of a thermostatic bath was raised to approximately 170 °C, each sample was put in the thermostatic bath, and after 15 minutes, the sample was taken out. Expansion accompanying the heat treatment did not occur in the exterior body of each sample.

[0464]

Through the above, the samples G1, G2, H1, and H2 and the comparison samples a3 and a4 were fabricated.

[0465]

<Measurement of charge and discharge characteristics>

Next, the charge and discharge characteristics at 45 °C of the samples in this example were measured. The measurement was performed with a charge-discharge measuring instrument (produced by TOYO SYSTEM Co., LTD.). Constant current–constant voltage charging was performed until the voltage reached an upper voltage limit of 4.3 V, and constant voltage discharging was performed until the voltage reached a lower voltage limit of 2.5 V. The charging and discharging were performed at a rate of 0.1 C, and a 10-minute break was taken after the charging. The charging and discharging were performed 2 cycles.

[0466]

Note that the rates were calculated using 170 mAh/g, which is capacity obtained when the upper charging voltage limit of $LiCoO_2$ serving as the positive electrode active material, is 4.3 V, as a reference.

[0467]

FIG. 44A shows charge-discharge curves of the comparison sample a3, FIG. 44B for the comparison sample a4, FIG. 44C for the sample G1, FIG. 44D for the sample G2, FIG. 45A for the sample H1, and FIG. 45B for the sample H2. In FIGS. 44A to 44D and FIGS. 45A and 45B, the horizontal axis and the vertical axis represent capacity [mAh/g] and voltage [V], respectively. Charge and discharge characteristics at the 1st cycle and the 300th cycle are shown for each sample. The capacity is per weight of the positive electrode active material.

[0468]

Note that the 300th-cycle capacity of the comparison samples a3 and a4 containing no lithium hexafluorophosphate was close to zero.

[0469]

FIG. 46A shows cycle characteristics of discharge capacity of the comparison samples a3 and a4, FIG. 46B for the samples G1 and G2, and FIG. 46C for the samples H1 and H2. In FIGS. 46A to 46C, the horizontal axis and the vertical axis represent cycles [times] and capacity

[mAh/g], respectively.

[0470]

FIG. 47A shows cycle characteristics of discharge capacity retention rate of the comparison samples a3 and a4, FIG. 47B for the samples G1 and G2, and FIG. 47C for the samples H1 and H2. In FIGS. 47A to 47C, the horizontal axis and the vertical axis represent cycles [times] and capacity retention rate [%], respectively. The capacity retention rate is percentage of discharge capacity for each cycle time with respect to the maximum value of the discharge capacity of each sample.

[0471]

About-150th-cycle capacity of the comparison samples a3 and a4 containing no lithium hexafluorophosphate was close to zero. It seems that repetitive charge and discharge at 45 °C causes corrosion of aluminum used as the positive electrode current collector by lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). Capacity decrease of the samples G1, G2, H1, and H2, which were embodiments of the present invention, was suppressed even after repetitive charge and discharge cycle, as compared to the comparison samples a3 and a4. In particular, although the sample H2 was subjected to the heat treatment at 170 °C for 15 minutes, it showed high capacity retention rate. This is probably because a passivation film was formed on the aluminum surface by lithium hexafluorophosphate, resulting in suppressing corrosion of aluminum even when the heat treatment was performed.

[0472]

FIG. 48A shows cycle characteristics of energy density of the comparison samples a3 and a4, FIG. 48B for the samples G1 and G2, and FIG. 48C for the samples H1 and H2. In FIGS. 48A to 48C, the horizontal axis and the vertical axis represent cycles [times] and energy density [mWh/g], respectively. The energy density is the product of discharge capacity and voltage shown in the discharge curves in FIGS. 44A to 44D and FIGS. 45A and 45B.

[0473]

FIG. 49A shows cycle characteristics of energy density retention rate of the comparison samples a3 and a4, FIG. 49B for the samples G1 and G2, and FIG. 49C for the samples H1 and H2. In FIGS. 49A to 49C, the horizontal axis and the vertical axis represent cycles [times] and energy density retention rate [%], respectively. The energy density retention rate is percentage of energy density for each cycle time with respect to the maximum value of the energy density of each sample.

[0474]

About-150th-cycle energy density of the comparison samples a3 and a4 containing no lithium hexafluorophosphate was close to zero. Capacity decrease of the samples G1, G2, H1,

and H2, which were embodiments of the present invention, was suppressed even after repetitive charge and discharge cycle, as compared to the comparison samples a3 and a4. In particular, although the sample H2 was subjected to the heat treatment at 170 °C for 15 minutes, it showed high energy density retention rate.

[0475]

Table 5 and FIG. 50A show the relationship between the concentration of $LiPF_6$ with respect to the electrolyte and the capacity retention rate for each of the comparison sample a3 and the samples G2 and H2 which were subjected to heat treatment at 170 °C. In FIG. 50A, the horizontal axis and the vertical axis represent the $LiPf_6$ concentration [wt%] and capacity retention [%], respectively. The capacity retention rate is a value at the 300th cycle for each sample shown in FIGS. 47A to 47C.

[0476]

Table 8 and FIG. 50B show the relationship between the concentration of $LiPF_6$ with respect to the electrolyte and the energy density for each of the comparison sample a4 and the samples G2 and H4 which were subjected to heat treatment at 170 °C for 15 minutes. In FIG. 50B, the horizontal axis and the vertical axis represent the $LiPf_6$ concentration [wt%] and energy density [%], respectively. The energy density retention rate is a value at the 300th cycle for each sample shown in FIGS. 49A to 49C.

[0477]

[Table 8]

Sample	Electrolyte		Separator	Capacity retention rate [%]	Energy retention rate [%]
	Condition	$LiPF_6$ [wt%]			
Comparison sample a3	Electrolyte a	0.0	Cellulosic fiber	0.105	0.081
Comparison sample a4				0.051	0.041
Sample G1	Electrolyte G	0.26	Cellulosic fiber	87.0	85.7
Sample G2				76.0	67.3
Sample H1	Electrolyte H	0.51	Cellulosic fiber	88.1	87.5
Sample H2				87.6	85.2

[0478]

As shown in Table 8 and FIGS. 50A and 50B, the capacity retention rate and energy retention rate after repetitive charge and discharge of the samples G2 and H2 which were embodiments of the present invention were higher than those of the comparison sample a4 containing no lithium hexafluorophosphate.

[0479]

These results show that the electrolyte preferably contains ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC), lithium bis(pentafluoroethanesulfonyl)amide (LiBETA), and lithium hexafluorophosphate. It was also shown that the amount of lithium hexafluorophosphate dissolved in the electrolyte is preferably more than or equal to 0.01 wt% and less than or equal to 1.9 wt%, further preferably more than or equal to 0.05 wt% and less than or equal to 1.2 wt%, still further more than or equal to 0.1 wt% and less than or equal to 0.8 wt%.

[0480]

It was shown that the use of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate as electrolyte solutions can produce a power storage battery with high thermal resistance and favorable charge and discharge characteristics even in high temperature environment (45 °C).

[Example 3]

[0481]

In this example, reaction of an electrolyte and aluminum used as the positive electrode current collector will be described.

[0482]

<Methods of fabricating samples>

In this example, a power storage battery which was one embodiment of the present invention was formed and subjected to heat treatment at 170 °C for 15 minutes. After that, the positive electrode was taken out of the power storage battery, and the aluminum surface of the positive electrode was subjected to composition analysis by XPS measurement. The power storage battery subjected to heat treatment at 170 °C for 15 minutes is referred to as a power storage battery 1. The positive electrode taken out of the power storage battery 1 is referred to as a positive electrode 1. For comparison, a sample (a comparison positive electrode 1) in which assembly of a power storage battery and heat treatment were not performed after a positive electrode is formed was subjected to XPS analysis.

[0483]

A fabrication method of the positive electrode is described. The same fabrication method was used to fabricate the comparison positive electrode 1 and the power storage battery 1 (positive electrode 1).

[0484]

As each positive electrode active material, $LiCoO_2$ with a specific surface area of 0.21 m^2/g and an average particle size of 10 μm was used. As each binder, polyvinylidene fluoride (PVDF) was used. As each conductive additive, acetylene black was used. The compounding

ratio of $LiCoO_2$: acetylene black: PVDF was set to 95:3:2 (wt%).

[0485]

First, acetylene black and PVDF were mixed in a mixer, so that a fifth mixture was obtained.

[0486]

Next, the active material was added to the fifth mixture, so that a sixth mixture was obtained.

[0487]

After that, a solvent *N*-methyl-2-pyrrolidone (NMP) was added to the fourth mixture and mixing was performed with a mixer. Through the above steps, a slurry was formed.

[0488]

Then, mixing was performed with a large-sized mixer.

[0489]

Subsequently, the slurry was applied to a positive electrode current collector with the use of a continuous coater. A 20-μm-thick aluminum current collector was used as the positive electrode current collector. The coating speed was set to 0.2 m/min.

[0490]

Then, the solvent in the slurry applied to the positive electrode current collector was vaporized in a drying furnace. Solvent vaporization treatment was performed at 70 °C in an air atmosphere for 7.5 minutes and then further performed at 90 °C in the air atmosphere for 7.5 minutes.

[0491]

After that, heat treatment was performed in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa) at 170 °C for 10 hours. Subsequently, the positive electrode active material layer was pressed by a roll press method so as to be consolidated.

[0492]

Through the above steps, the positive electrode active material layer was formed on one surface of the positive electrode current collector.

[0493]

A sample fabricated in the above manner was used as the comparative positive electrode 1.

[0494]

Next, a fabrication method of the power storage battery 1 is described.

[0495]

A fabrication method of the negative electrode is described.

[0496]

Spherical natural graphite having a specific surface area of 6.3 m^2/g and an average particle size of 15 μm (CGB-15 manufactured by Nippon Graphite Industries, Co.,Ltd.) was used as a negative electrode active material. For a binder, sodium carboxymethyl cellulose (CMC-Na) and SBR were used. The polymerization degree of CMC-Na that was used was higher than or equal to 600 and lower than or equal to 800, and the viscosity of a 1 wt% CMC-Na aqueous solution was in the range from 300 mPa·s to 500 mPa·s. The compounding ratio of graphite: CMC-Na: SBR was set to 97:1.5:1.5 (wt%).

[0497]

First, CMC-Na powder and an active material were mixed and then kneaded with a mixer, so that a seventh mixture was obtained.

[0498]

Subsequently, a small amount of water was added to the seventh mixture and kneading was performed, so that an eighth mixture was obtained. Here, "kneading" means "mixing something with a high viscosity".

[0499]

Then, water was further added and the mixture was kneaded with a mixer, so that an eighth mixture was obtained.

[0500]

Then, a 50 wt% SBR aqueous dispersion liquid was added to the third mixture, and mixing was performed with a mixer. After that, the obtained mixture was degassed under a reduced pressure, so that a slurry was obtained.

[0501]

Subsequently, the slurry was applied to a negative electrode current collector with the use of a continuous coater. An 18-μm-thick rolled copper foil was used as the negative electrode current collector. The coating speed was set to 0.75 m/min.

[0502]

Then, the solvent in the slurry applied to the negative electrode current collector was vaporized in a drying furnace. Vaporization treatment was performed at 50 °C in an air atmosphere for 120 seconds and then further performed at 80 °C in the air atmosphere for 120 seconds. After that, further vaporization treatment was performed at 100 °C under a reduced pressure (−100 kPa) for 10 hours.

[0503]

Through the above steps, the negative electrode active material layer was formed over

one surface of the negative electrode current collector, so that the negative electrode was fabricated.

[0504]

A fabrication method of the electrolyte of the power storage battery 1 is described.

[0505]

The electrolyte B2 was formed as follows: vinylene carbonate (VC) was mixed with a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) and lithium hexafluorophosphate were dissolved in the solution. The amount of vinylene carbonate (VC) dissolved in the electrolyte A was 1 wt% in the weight ratio. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the electrolyte B2 was 1 mol/L in the molecular concentration. The amount of lithium hexafluorophosphate dissolved in the electrolyte B2 was 0.27 wt% in the weight ratio. The electrolyte B2 used in this example was formed in the same manner as the electrolyte B shown in Example 1.

[0506]

Next, a positive electrode, a negative electrode, and a first separator were cut. The size of the positive electrode, negative electrode, and first separator were respectively 20.49 cm^2, 23.84 cm^2, and 24.75 cm^2.

[0507]

Cellulosic fiber was used for a separator. Specifically, 30-μm-thick solvent-spun regenerated cellulosic fiber (product number TF40) produced by NIPPON KODOSHI CORPORATION was used.

[0508]

Then, the positive electrode active material and the negative electrode active material in tab regions were removed to expose the current collectors.

[0509]

After that, the positive electrode and the negative electrode were stacked with the first separator therebetween. At this time, the positive electrode and the negative electrode were stacked such that the positive electrode active material layer and the negative electrode active material layer faced each other.

[0510]

Then, leads were bonded to the positive electrode and the negative electrode by ultrasonic welding.

[0511]

Next, the region where the electrodes are stacked and the lead is bonded was wrapped

with a separator. This can prevent dissolution of the resin layer of the exterior body by heat treatment performed later and contact of aluminum of the exterior body with the electrodes. The size of the second separator was 104 cm^2.

[0512]

Then, facing parts of two of four sides of the exterior body were bonded to each other by heating.

[0513]

As an exterior body, an aluminum film with opposite surfaces covered with a resin layer was used.

[0514]

After that, sealing layers provided for the leads were positioned so as to overlap with a sealing layer of the exterior body, and bonding was performed by heating. At this time, facing parts of a side of the exterior body except a side used for introduction of an electrolyte solution were bonded to each other.

[0515]

Next, heat treatment for drying the exterior body and the positive electrode, the separator, and the negative electrode wrapped by the exterior body was performed in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa) at 80 °C for 10 hours.

[0516]

Next, in an argon gas atmosphere, an approximately 600 μL of electrolyte B2 was introduced from one side of the exterior body that was not sealed.

[0517]

After that, the one side of the exterior body was sealed by heating in a reduced-pressure atmosphere (at a gauge pressure of −100 kPa). Through the above steps, each thin storage battery was fabricated.

[0518]

Through the above steps, the power storage battery 1 was fabricated.

[0519]

Then, heat treatment was performed on the power storage battery 1. Assuming that each sample and fluorine rubber are integrally formed as in Embodiment 2, heat treatment was performed in an atmospheric pressure atmosphere at 170 °C for 15 minutes. Specifically, the temperature of a thermostatic bath was raised to approximately 170 °C, each sample was put in the thermostatic bath, and after 15 minutes, the power storage battery 1 was taken out.

[0520]

Next, the power storage battery 1 was disassembled in a glove box in a nitrogen

atmosphere, and a positive electrode 1, which was the positive electrode of the power storage battery 1, was taken out. The positive electrode 1 was washed with dimethyl carbonate (DMC) and dried.

[0521]

In this manner, the positive electrode 1 was fabricated.

[0522]

<X-ray photoelectron spectroscopy measurement>

Next, the comparison positive electrode 1 and the positive electrode 1 were subjected to X-ray photoelectron spectroscopy (XPS). The aluminum surface to which a positive electrode active material was not applied was irradiated with X-ray. FIG. 51 shows the position where the XPS measurement was performed. The arrow in FIG. 51 indicates the X-ray irradiation direction.

[0523]

Quantera SXM produced by PHYSICAL ELECTRONICS, INC. was used for the XPS measurement. Monochromatic Al Kα ray (1486.6 eV) was used as an X-ray source. A detection area was set to 100 μmϕ. An extraction angle was set to 45°. The detection depth was estimated to be about 4 nm to 5 nm.

[0524]

FIG. 52A shows spectra of Al2q obtained by XPS measurement, FIG. 52B for C1s, FIG. 52C for O1s, FIG. 53A for S2p, FIG. 53B for Li1s, FIG. 53C for F1s, FIG. 54A for P2s, FIG. 54B for N1s, FIG. 54C for Si2s, FIG. 55A for Na1s, and FIG. 55B for Ca2p. In FIGS. 52A to 52C, FIGS. 53A to 53C, FIGS. 54A to 54C, and FIGS. 55A and 55B, the horizontal axis and the vertical axis represent the binding energy [eV] and photoelectron intensity (arbitrary unit), respectively.

[0525]

Al, O, C, a trace of F, and a trace of Si were detected from the comparison positive electrode 1 not subjected to heat treatment. Al, F, O, Li, C, a trace of P, a trace of N, a trace of Na, and a trace of Ca were detected from the positive electrode 1 subjected to heat treatment.

[0526]

Table 9 shows quantitative values of the elements obtained from XPS spectra. Note that the quantitative accuracy is about ±1 atomic%. Although the lower limit of detection is different from the elements, it is about 1 atomic%.

[0527]

[Table 9]

	Quantitative value [atomic%]	
	Comparison positive electrode 1	Positive electrode 1
Al	26.8	17.9
C	25.5	15.7
O	40.4	9.3
S	Lower limit of detection or less	Lower limit of detection or less
Li	Lower limit of detection or less	5.3
F	3.3	48.3
P	Lower limit of detection or less	1.9
N	Lower limit of detection or less	0.5
Si	4.0	Lower limit of detection or less
Na	Lower limit of detection or less	0.6
Ca	Lower limit of detection or less	0.5

[0528]

The positive electrode 1 contained less O and more F than the comparison positive electrode 1 did. Al of the comparison positive electrode 1 was present in the oxidation state and the metal state, whereas Al of the positive electrode 1 was present in the fluoridation state and metal state. In addition, Li detected from the positive electrode 1 was present mainly in the state of LiPF*x*, LiF, and like. Note that it seems that Si detected from the positive electrode 1 is present mainly in the oxidation state and C is present manly in C-C or C-H state.

[0529]

The above results show that a film containing aluminum fluoride was formed on the surface of aluminum heated with the electrolyte, which is one embodiment of the present invention. In other words, it was suggested that a secondary battery including an electrolytic solution containing lithium hexafluorophosphate which was subjected to heat treatment in the fabrication process forms a film on a positive electrode current collector, which contributes to prevention of degradation of charging and discharging cycle.

[Example 4]

[0530]

In this example, examination results of thermal resistance of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) will be described.

[0531]

<Methods of fabricating samples>

Three samples of samples 1, 2, and 3 were used in this example.

[0532]

The sample 1 is described. The sample 1 was lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). A product by IoLiTec Ionic Liquids Technologies Inc. (product number KI-0016-HP) was used for lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). The product in a power state was measured.

[0533]

The sample 2 is described. As the sample 2, a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1 was used. Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-00798) was used for the mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1.

[0534]

Next, the sample 3 is described. As the sample 3, a mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1 was formed, and lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was dissolved in the solution. The amount of lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) dissolved in the sample 3 a was 1 mol/L in the molecular concentration. In this manner, the sample 3 was formed. Lithium battery grade produced by Kishida Chemical Co., Ltd. (product code number LBG-00798) was used for the mixed solution in which ethylene carbonate (EC) and propylene carbonate (PC) were mixed at a volume ratio of 1:1. A product by IoLiTec Ionic Liquids Technologies Inc. (product number KI-0016-HP) was used for lithium bis(pentafluoroethanesulfonyl)amide (LiBETA).

[0535]

<Thermogravimetry-differential thermal analysis>

Then, thermogravimetry-differential thermal analysis (TG-DTA) was performed. TG-DTA was performed with Thermo Mass Photo (manufactured by Rigaku Corporation) at a temperature increase rate of 10 °C/min under helium stream (the flow rate: 300 ml/min) from room temperature to 600 °C.

[0536]

TG-DTA results of the samples 1, 2, and 3 are shown in FIG. 56A, FIG. 56B, and FIG. 57, respectively. In FIG. 56A, FIG. 56B, and FIG. 57, the horizontal axis represents temperature [°C], the left vertical axis represents weight change rate ΔW [%], and the right vertical axis represents heat flow [μV]. The weight change rate ΔW is weight change rate

during heating with respect to the initial weight (before heating). The negative value means the weight decreased by heating.

[0537]

The weight of the sample 1 started to decrease from around 330 °C, and the weight at around 420 °C was about −95% with respect to the initial weight. In addition, endothermic reaction was observed at around 327.4 °C and around 416.7 °C. The endothermic reaction at around 327.4 °C was probably caused by lithium bis(pentafluoroethanesulfonyl)amide (LiBETA). Thus, it was found that lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was stable at room temperature to around 300 °C.

[0538]

The weight of the sample 2 started to decrease from around 150 °C, and the weight at around 235 °C was about −96% with respect to the initial weight. In addition, endothermic reaction was observed at around 232.5 °C. The endothermic reaction at around 232.5 °C was estimated to be caused by evaporation of ethylene carbonate (EC) and propylene carbonate (PC).

[0539]

The weight of the sample 3 started to decrease from around 150 °C, and the weight at around 300 °C was about −78% and at around 450 °C was about −100% with respect to the initial weight. The change in weight from room temperature to around 300 °C is almost in agreement with behavior of the sample 2 described above. The change within this temperature range is thought to be derived from ethylene carbonate (EC) and propylene carbonate (PC). Thus, it was shown that lithium bis(pentafluoroethanesulfonyl)amide (LiBETA) was thermally stable even in the solvent at 300 °C or lower.

REFERENCE NUMERALS

[0540]

50: film, 51: film, 52: film, 53: embossing roll, 54: roll, 55: embossing roll, 56: embossing roll, 57: embossing roll, 58: embossing roll, 60: direction, 115: sealing layer , 118: bonding portion, 119: inlet, 200: secondary battery, 203: separator, 203a: region, 203b: region, 207: exterior body, 211: positive electrode, 211a: positive electrode, 215: negative electrode, 215a: negative electrode, 220: sealing layer , 221: positive electrode lead, 225: negative electrode lead, 230: electrode assembly, 231: electrode assembly, 250: secondary battery, 281: tab region , 282: tab region , 500: power storage device, 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: electrolyte, 509: exterior body, 510: positive electrode lead, 511: negative

electrode lead, 512: bonding portion, 513: curved portion, 514: bonding portion, 518: bonding portion, 520: separator, 521: bonding portion, 529: exterior body, 700: personal digital assistant , 701: housing , 702: display panel , 703: clasp, 705A: band, 705B: band, 711: operation button , 712: operation button , 730: personal digital assistant , 731: housing , 732: leakage detection circuit , 733: power source , 734: ammeter, 735A: band, 736: electrolyte, 739: functional circuit , 750: power storage device, 751: positive electrode lead, 752: negative electrode lead, 753: exterior body, 760: power storage device, 761: terminal , 762: terminal , 771: wiring , 772: wiring , 7100: portable display device , 7101: housing , 7102: display area , 7103: operation button , 7104: power storage device, 7200: personal digital assistant , 7201: housing , 7202: display area , 7203: band, 7204: buckle, 7205: operation button , 7206: input output terminal , 7207: icon, 7250: activity meter, 7251: housing , 7300: display device , 7304: display area , 7350: display device , 7351: lens, 7351A: image, 7351B: image, 7352: frame, 7355: edge portion, 7360: power storage device, 7361: positive electrode lead, 7362: negative electrode lead, 7400: cellular phone , 7401: housing , 7402: display area , 7403: operation button , 7404: external connection port , 7405: speaker , 7406: microphone, 7407: power storage device, 8000: display device , 8001: housing , 8002: display area , 8003: speaker portion, 8004: power storage device, 8021: charging apparatus, 8022: cable, 8024: power storage device, 8100: lighting device, 8101: housing , 8102: light source, 8103: power storage device, 8104: ceiling, 8105: wall, 8106: floor, 8107: window, 8200: indoor unit, 8201: housing , 8202: air outlet, 8203: power storage device, 8204: outdoor unit, 8300: electric refrigerator-freezer, 8301: housing , 8302: refrigerator, 8303: freezer, 8304: power storage device, 8400: automobile, 8401: headlight, 8500: automobile, 9600: tablet terminal, 9625: switch , 9626: switch , 9627: power source switch , 9628: operation switch, 9629: fastener, 9630: housing , 9631: display area , 9631a: display area , 9631b: display area , 9632a: region , 9632b: region , 9633: solar cell, 9634: charging and discharging control circuit , 9635: power storage unit, 9636: DCDC converter , 9637: converter , 9638: control key , 9639: button, 9640: movable portion.

This application is based on Japanese Patent Application Serial No. 2016-234674 filed with Japan Patent Office on December 2, 2016, the entire contents of which are hereby incorporated by reference.

CLAIMS

1. A power storage device comprising:

a positive electrode;

a negative electrode;

a first separator;

an electrolyte; and

an exterior body,

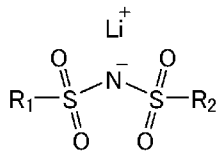
wherein the positive electrode includes a positive electrode active material layer and a positive electrode current collector,

wherein the negative electrode includes a negative electrode material layer and a negative electrode current collector,

wherein the first separator is positioned between the positive electrode and the negative electrode,

wherein the first separator includes polyphenylene sulfide or cellulosic fiber,

wherein the electrolyte includes propylene carbonate, ethylene carbonate, and vinylene carbonate, lithium hexafluorophosphate, and lithium salt expressed by General Formula (G1):



(G1)

, and

wherein, R^1 and R^2 independently represent fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 10 carbon atoms.

2. The power storage device according to claim 1 further comprising:

a second separator,

wherein the second separator is positioned between one or both of the positive electrode and negative electrode and the exterior body, and

wherein the second separator includes polyphenylene sulfide or cellulosic fiber.

3. The power storage device according to claim 1,

wherein a concentration of lithium hexafluorophosphate with respect to the electrolyte is more than or equal to 0.01 wt% and less than or equal to 1.9 wt% in a weight ratio.

4. The power storage device according to claim 1,

wherein the lithium salt represented by General Formula (G1) is lithium bis(pentafluoroethanesulfonyl)amide.

5. The power storage device according to claim 1,
wherein the positive electrode current collector includes aluminum or stainless steel.

6. An electronic device comprising:
the power storage device according to claim 1;
a band;
a display panel; and
a housing,
wherein the power storage device includes a positive electrode lead and a negative electrode lead,
wherein the positive electrode lead is electrically connected to the positive electrode,
wherein the negative electrode lead is electrically connected to the negative electrode,
wherein the power storage device is embedded in the band,
wherein part of the positive electrode lead and part of the negative electrode lead protrude from the band,
wherein the power storage device has flexibility,
wherein the power storage device is electrically connected to the display panel,
wherein the display panel is included in the housing,
wherein the band is connected to the housing, and
wherein the band includes a rubber material.

7. The electronic device according to claim 6,
wherein the rubber material is fluorine rubber or silicone rubber.

8. A power storage device comprising:
a positive electrode;
a negative electrode;
a first separator;
a second separator,
an electrolyte; and
an exterior body,
wherein the positive electrode includes a positive electrode active material layer and a

positive electrode current collector,

wherein the negative electrode includes a negative electrode material layer and a negative electrode current collector,

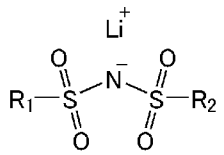
wherein the first separator is positioned between the positive electrode and the negative electrode,

wherein each of the first separator and the second separator includes polyphenylene sulfide or cellulosic fiber,

wherein the second separator is positioned between one or both of the positive electrode and negative electrode and the exterior body,

wherein the positive electrode current collector includes aluminum or stainless steel,

wherein the electrolyte includes propylene carbonate, ethylene carbonate, and vinylene carbonate, lithium hexafluorophosphate, and lithium salt expressed by General Formula (G1):



(G1)

, and

wherein, R^1 and R^2 independently represent fluorine or a straight-chain, branched-chain, or cyclic fluoroalkyl group having 1 to 10 carbon atoms.

9. The power storage device according to claim 8,

wherein a concentration of lithium hexafluorophosphate with respect to the electrolyte is more than or equal to 0.01 wt% and less than or equal to 1.9 wt% in a weight ratio.

10. The power storage device according to claim 8,

wherein the lithium salt represented by General Formula (G1) is lithium bis(pentafluoroethanesulfonyl)amide.

11. An electronic device comprising:

the power storage device according to claim 8;

a band;

a display panel; and

a housing,

wherein the power storage device includes a positive electrode lead and a negative electrode lead,

wherein the positive electrode lead is electrically connected to the positive electrode,

wherein the negative electrode lead is electrically connected to the negative electrode,

wherein the power storage device is embedded in the band,

wherein part of the positive electrode lead and part of the negative electrode lead protrude from the band,

wherein the power storage device has flexibility,

wherein the power storage device is electrically connected to the display panel,

wherein the display panel is included in the housing,

wherein the band is connected to the housing, and

wherein the band includes a rubber material.

12. The electronic device according to claim 11,

wherein the rubber material is fluorine rubber or silicone rubber.

FIG. 1A

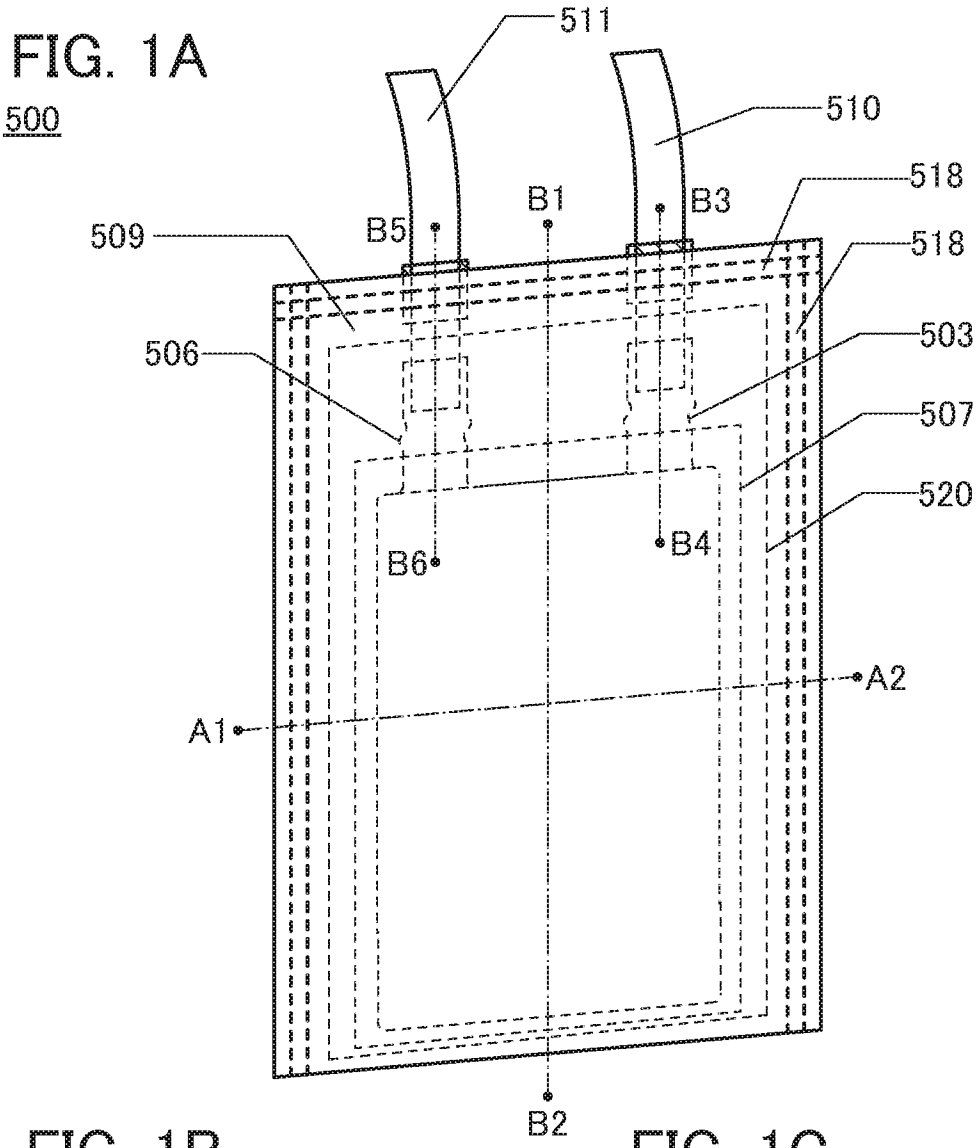


FIG. 1B

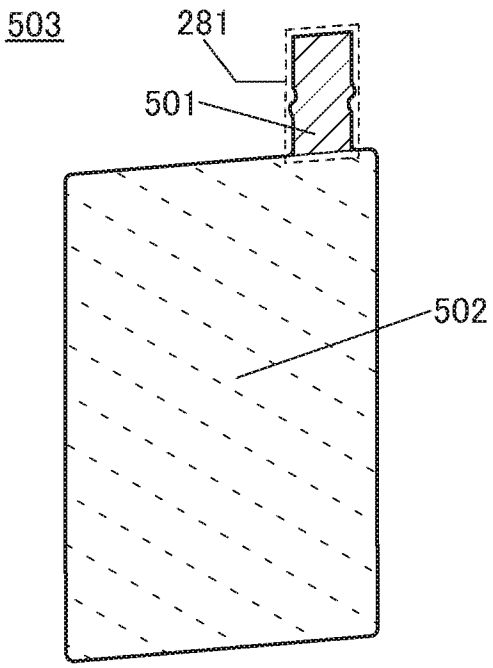


FIG. 1C

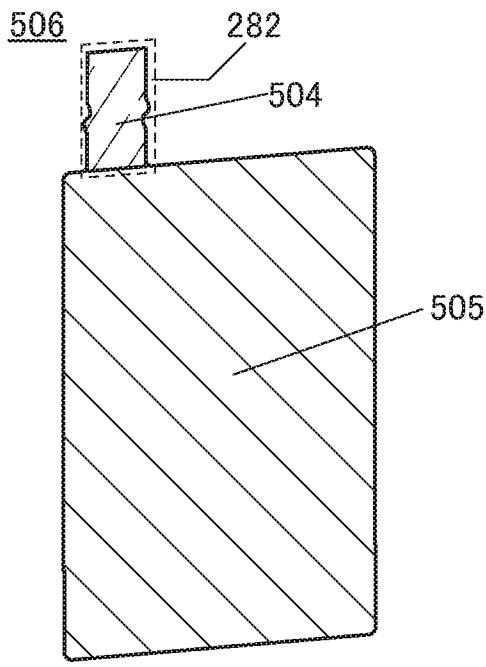


FIG. 2A

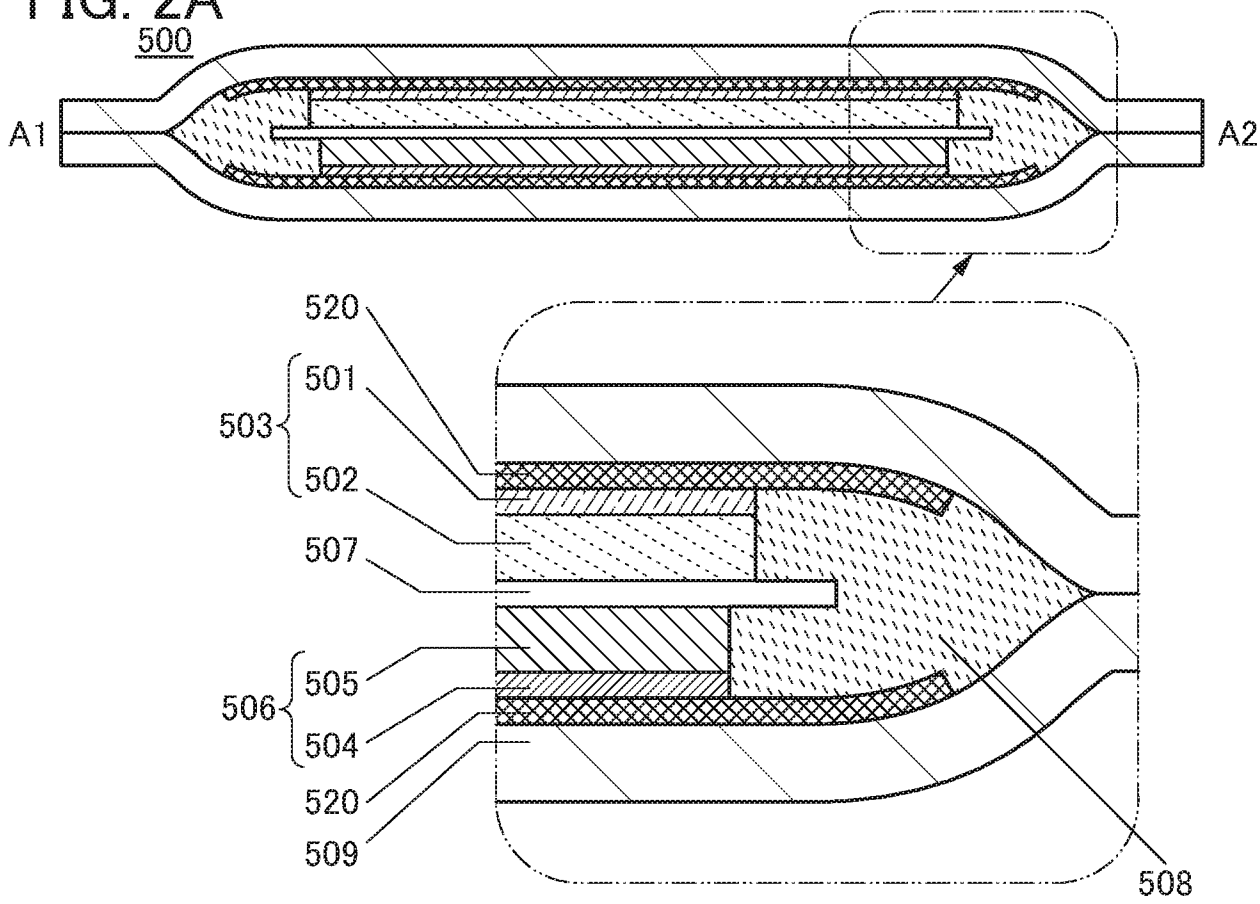

500
A1
A2
520
501
503
502
507
505
506
504
520
509
508

FIG. 2B

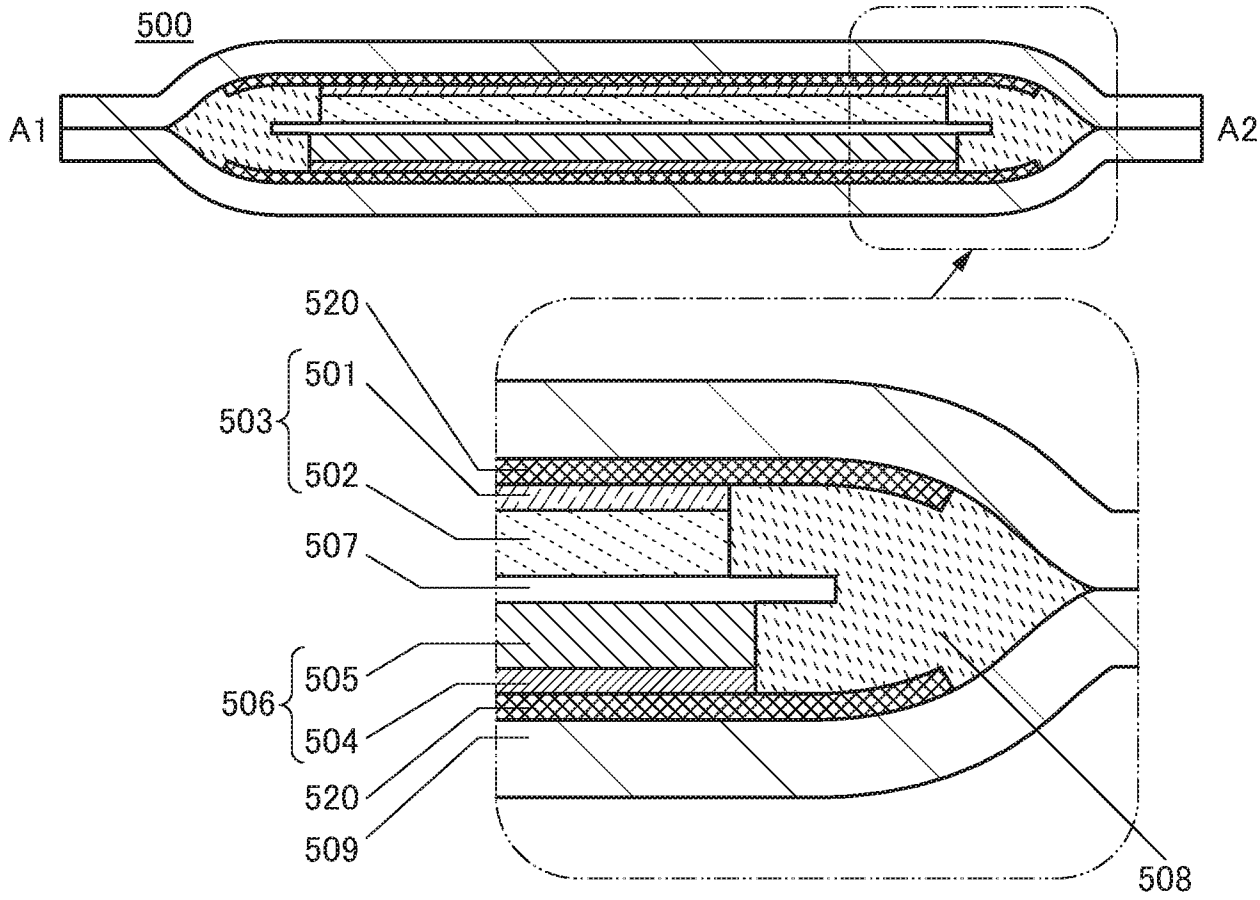

500
A1
A2
520
501
503
502
507
505
506
504
520
509
508

FIG. 3A

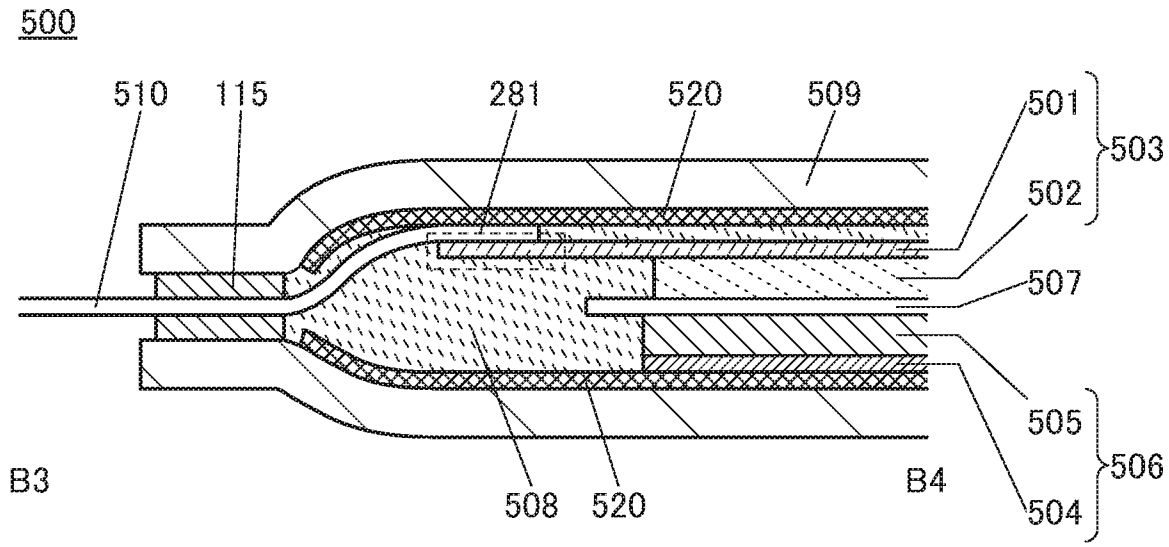

500
510
115
281
520
509
501
503
502
507
505
506
504
B3
B4
508
520

FIG. 3B

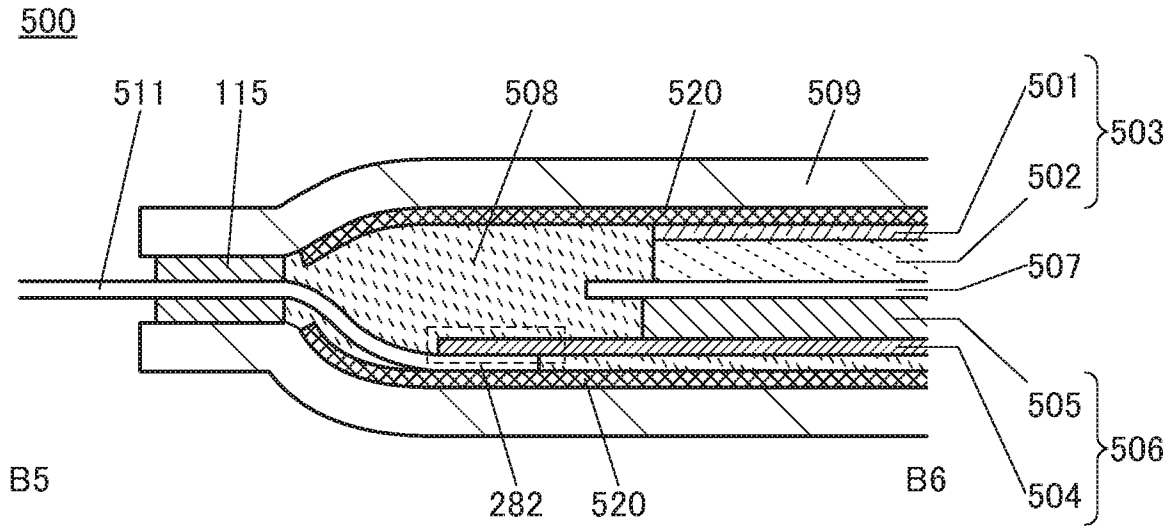

500
511
115
508
520
509
501
503
502
507
505
506
504
B5
B6
282
520

FIG. 4A

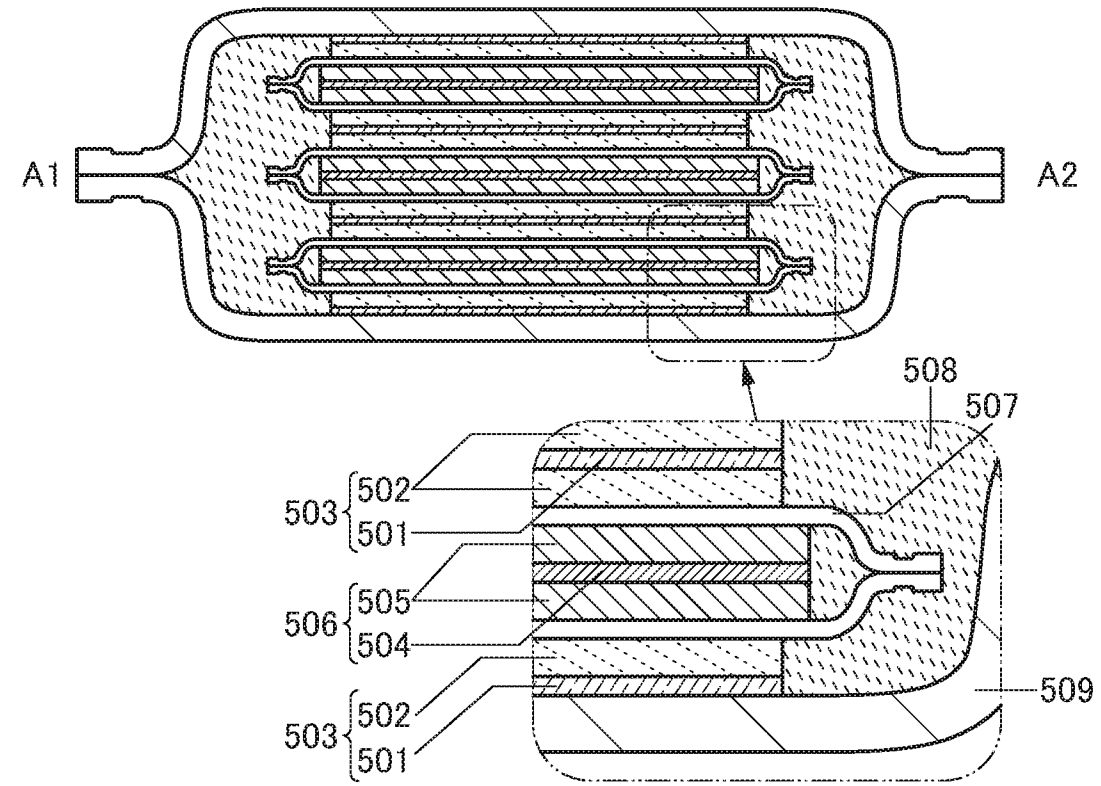

A1
A2
508
507
503
502
501
506
505
504
503
502
501
509

FIG. 4B

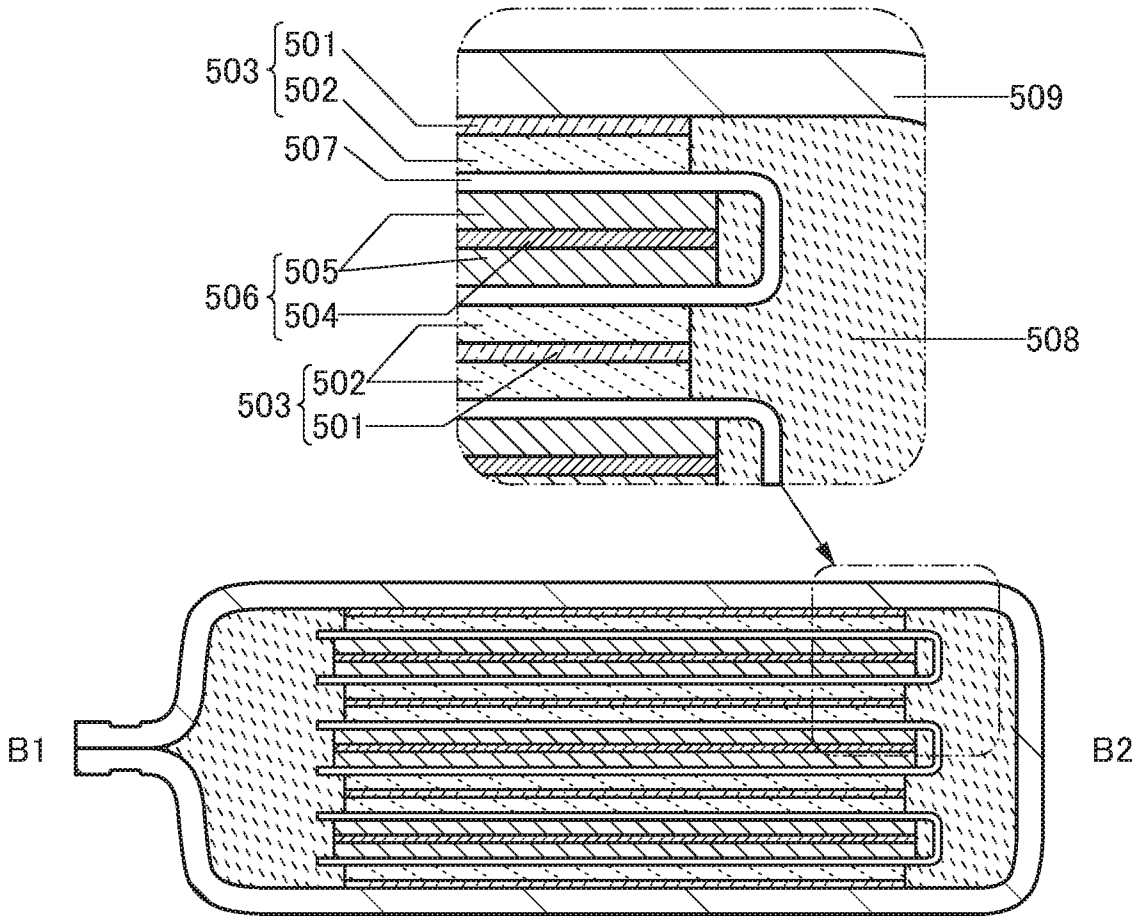

503
501
502
509
507
506
505
504
508
503
502
501
B1
B2

FIG. 5A

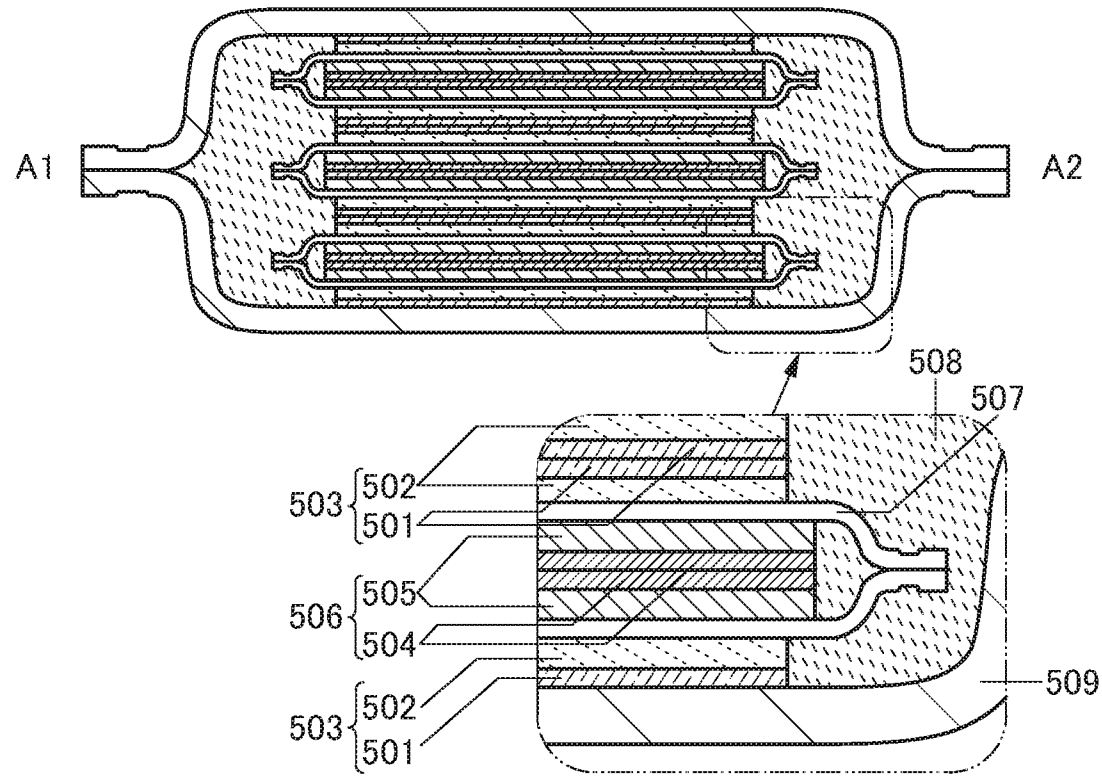

A1
A2
508
507
503
502
501
506
505
504
503
502
501
509

FIG. 5B

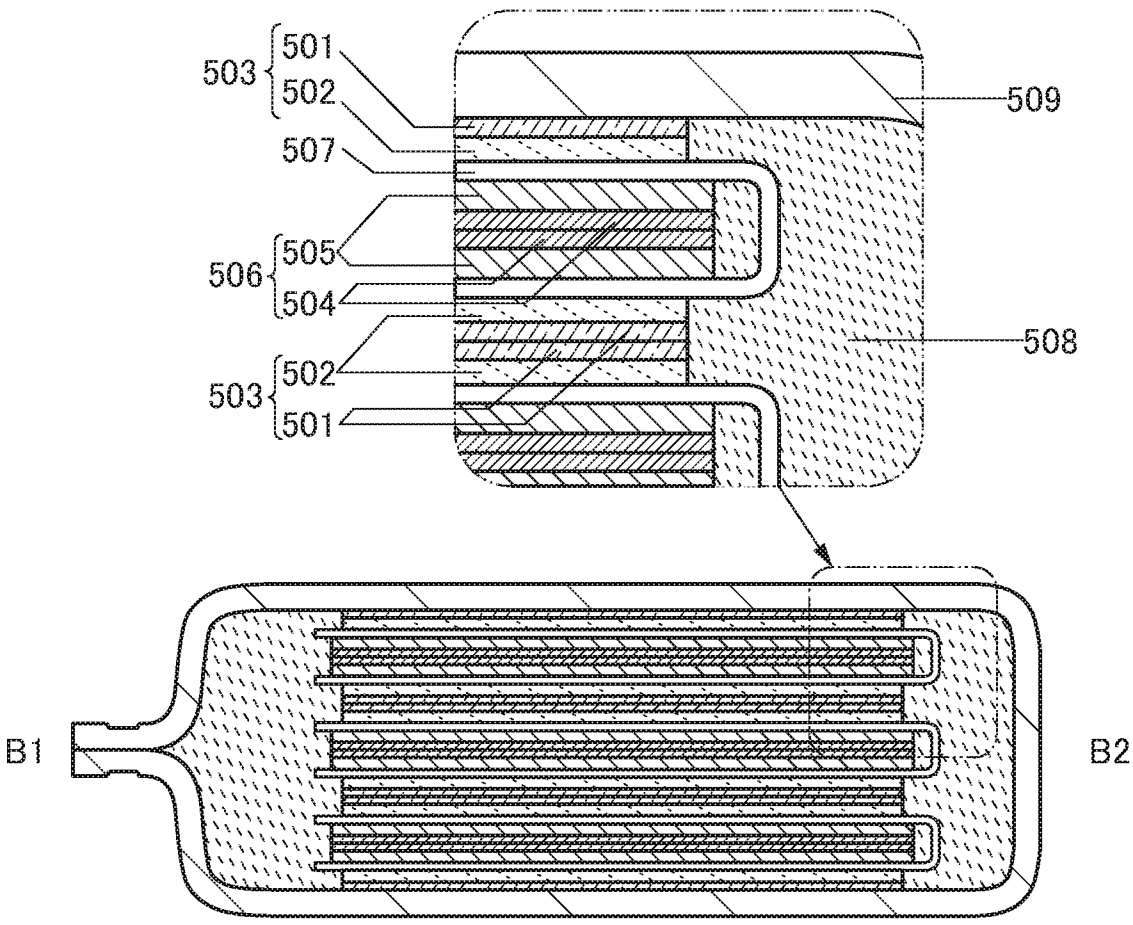

503
501
502
509
507
506
505
504
508
503
502
501
B1
B2

FIG. 6A

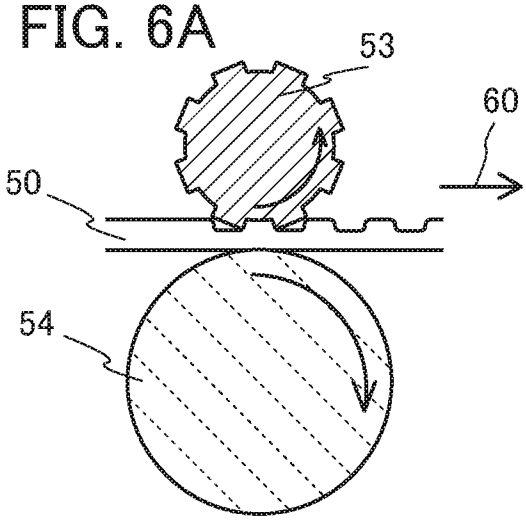


FIG. 6B

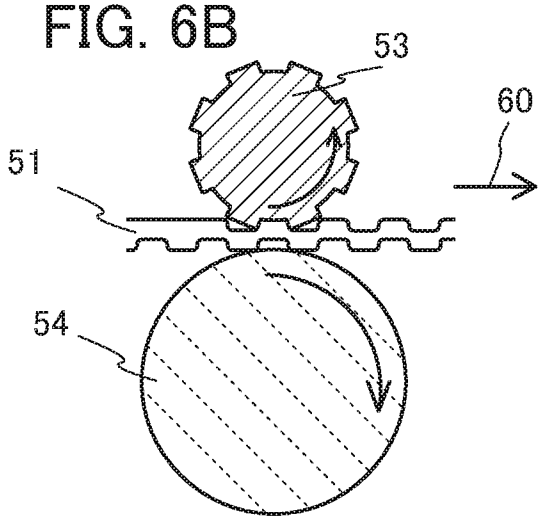


FIG. 6C

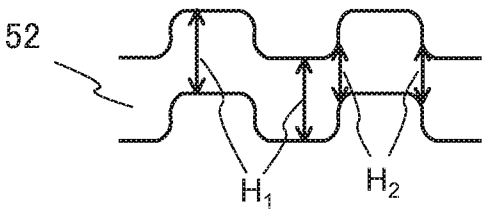


FIG. 6D

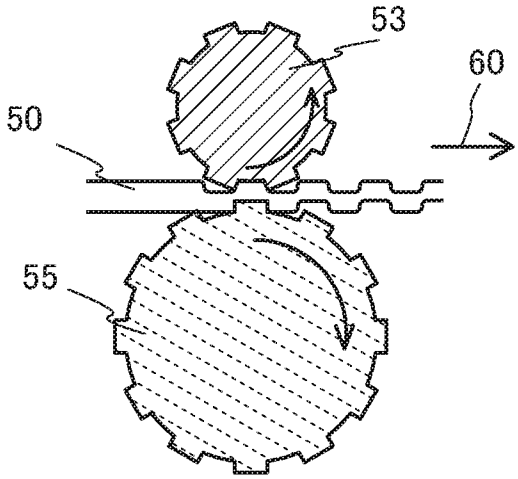


FIG. 6E

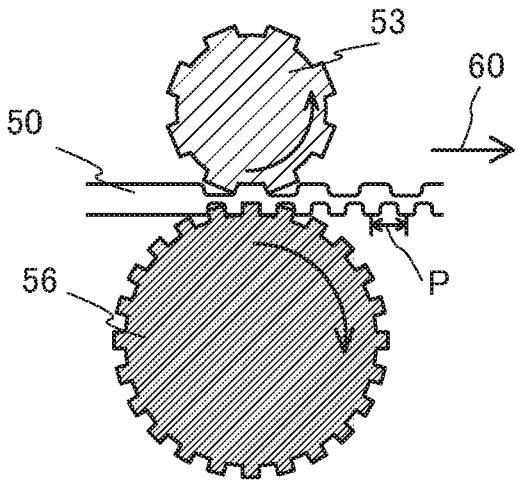


FIG. 6F

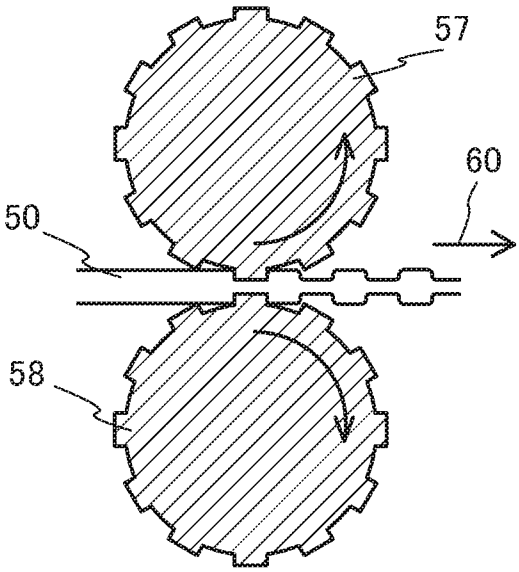


FIG. 7A

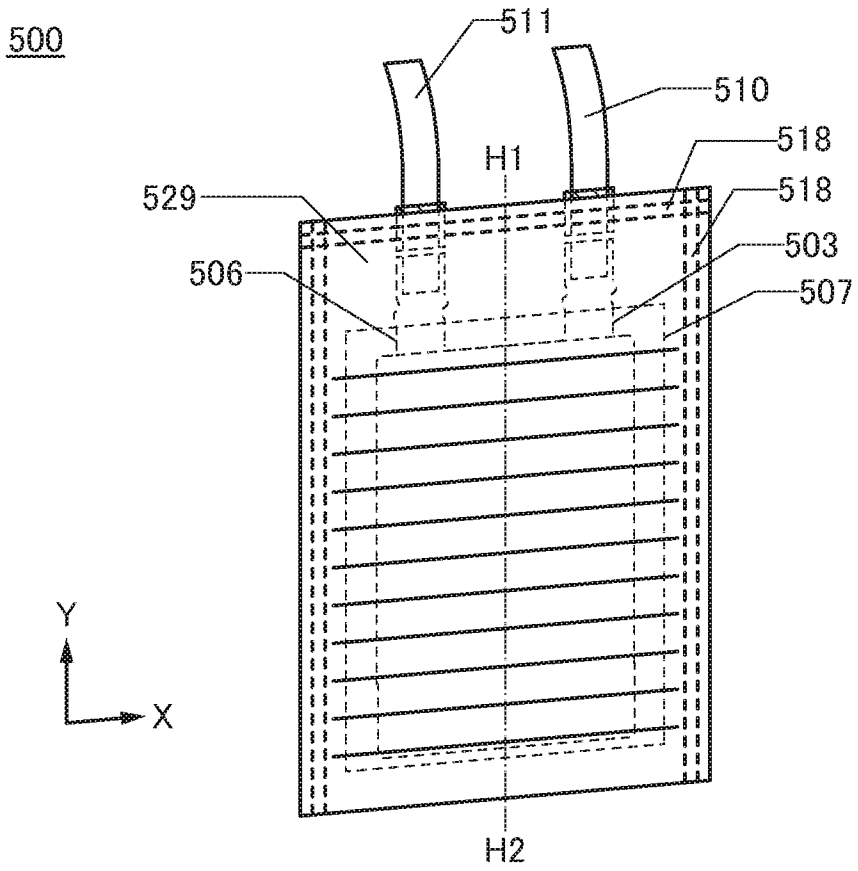

500
511
510
518
H1
529
518
506
503
507
Y
X
H2

FIG. 7B

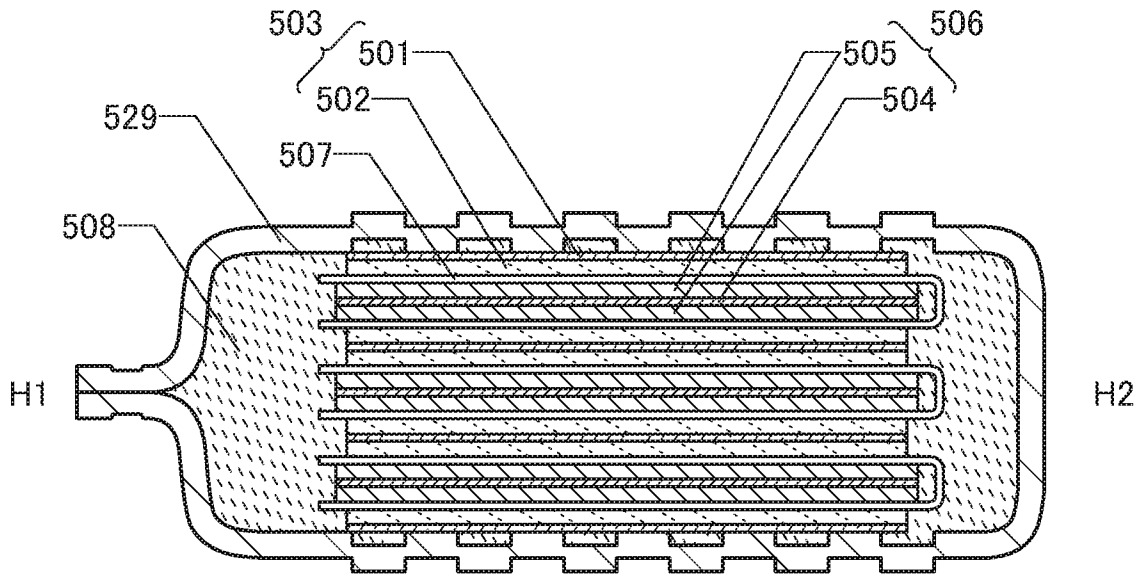

503
501
506
505
502
504
529
507
508
H1
H2

FIG. 8

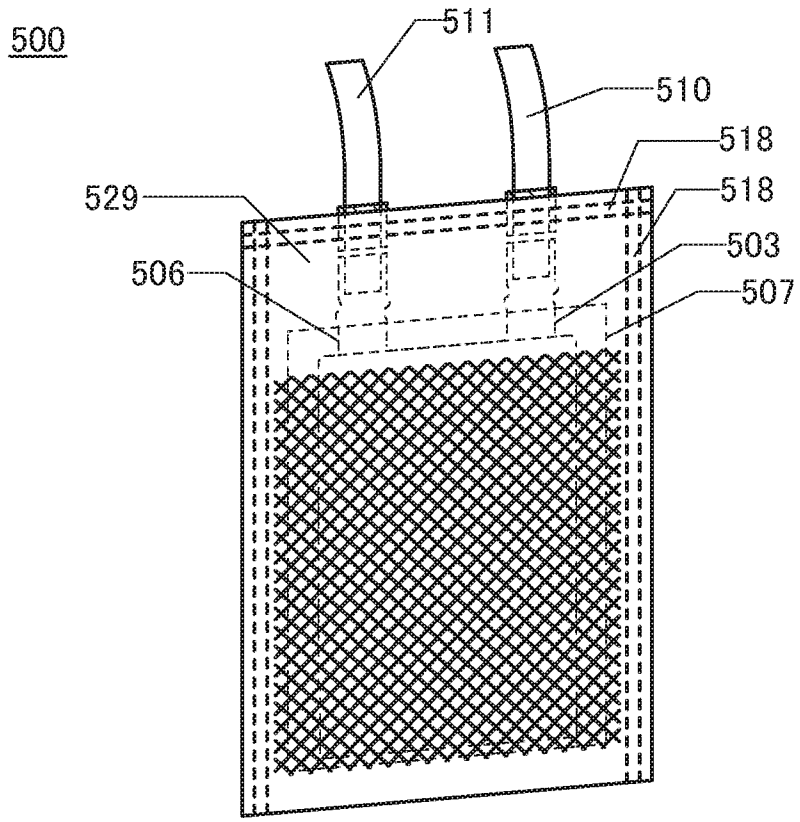


FIG. 9

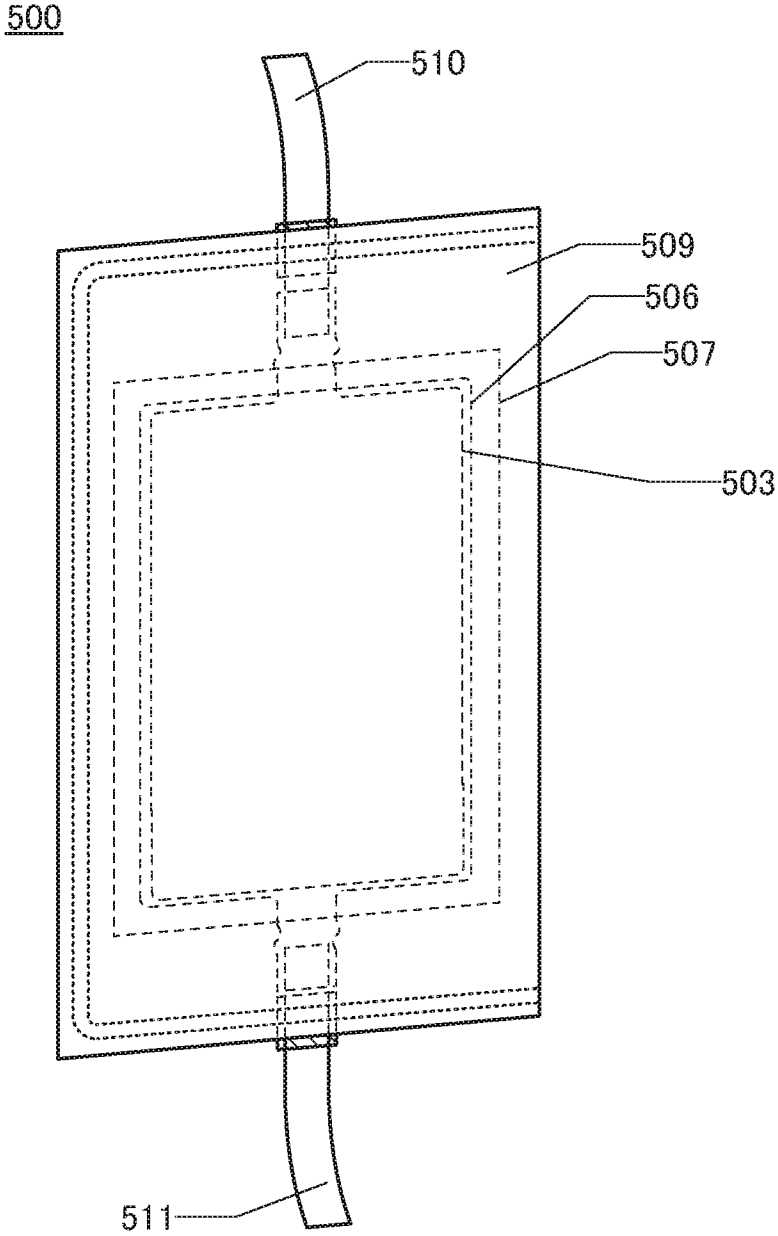


FIG. 10A

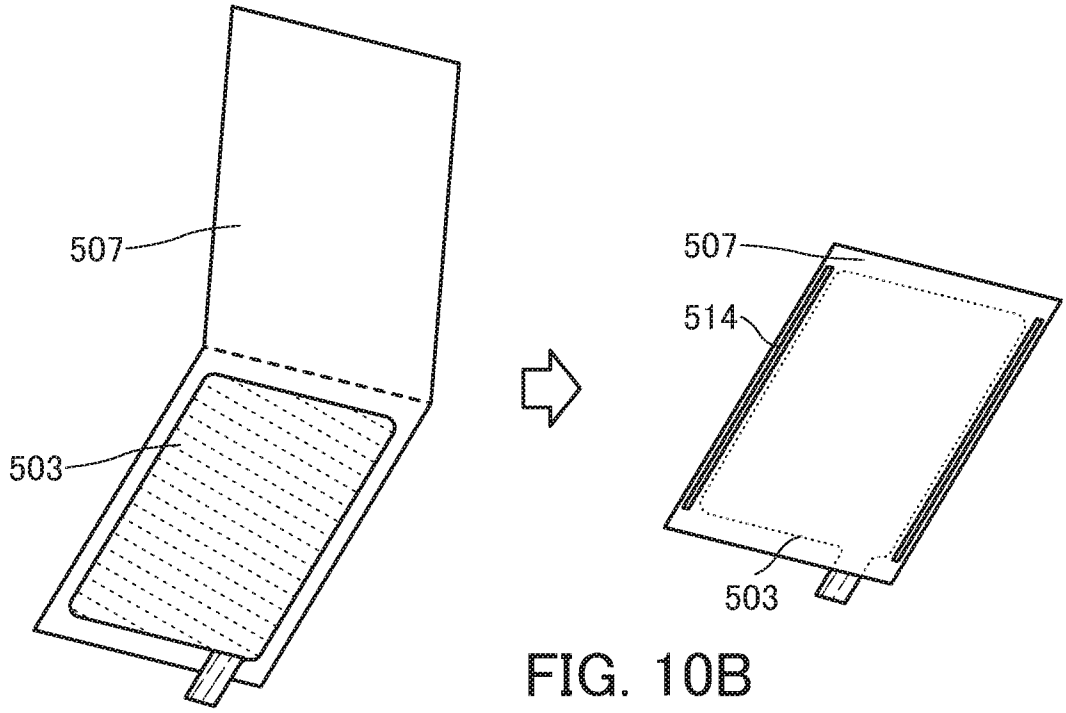


FIG. 10B

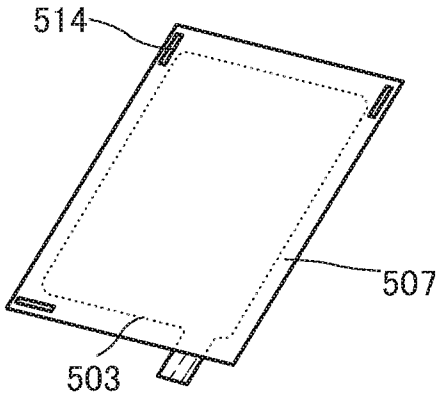


FIG. 10C

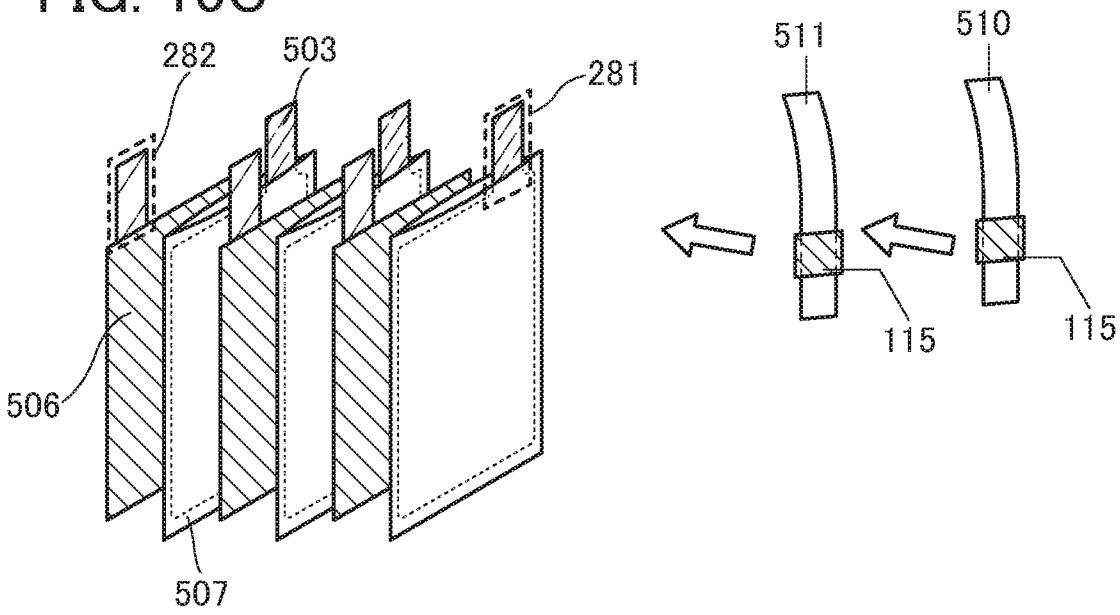


FIG. 11A

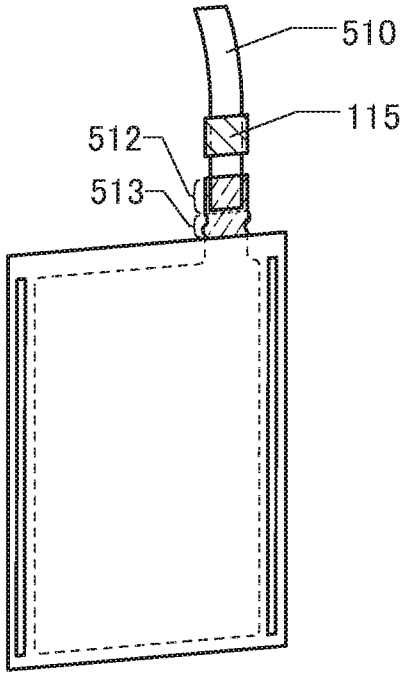


FIG. 11B

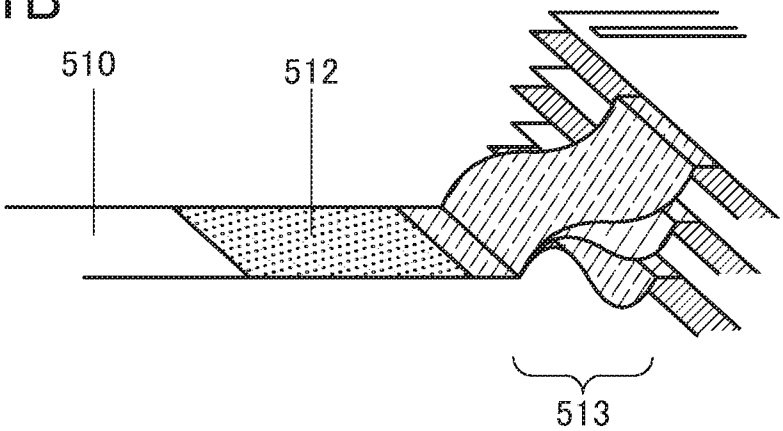


FIG. 11C

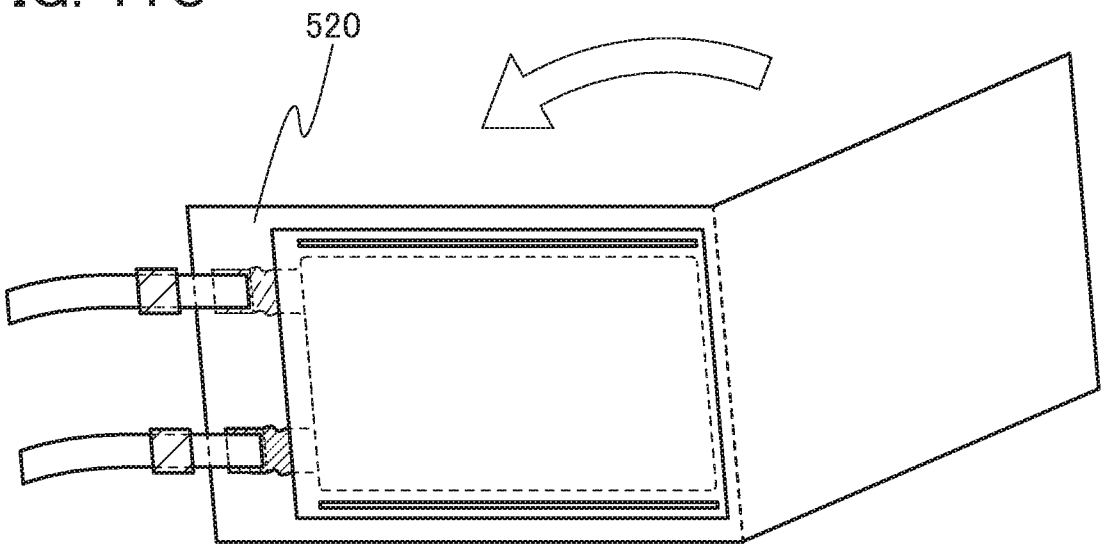


FIG. 12A

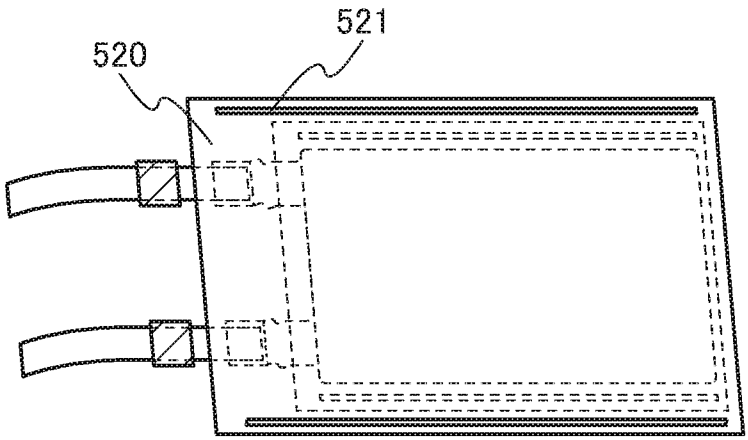


FIG. 12B

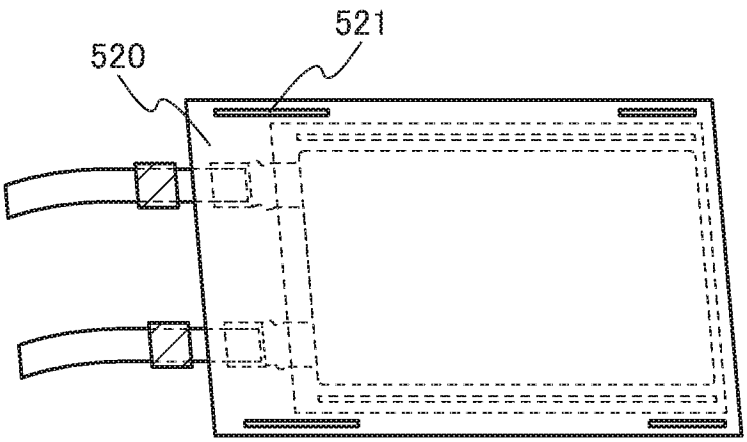


FIG. 12C

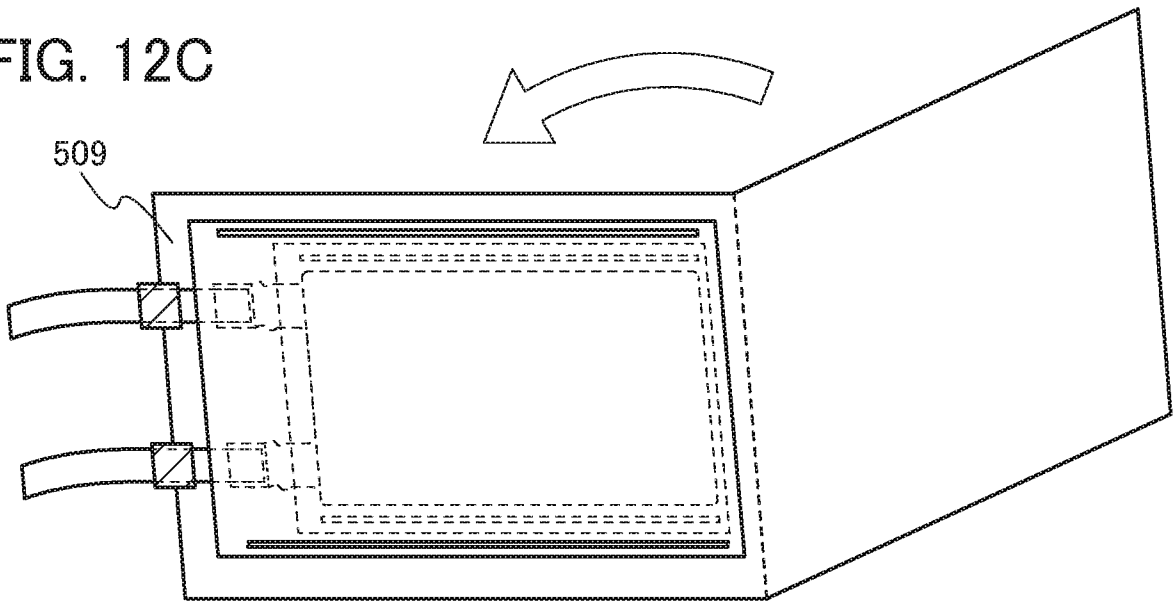


FIG. 13

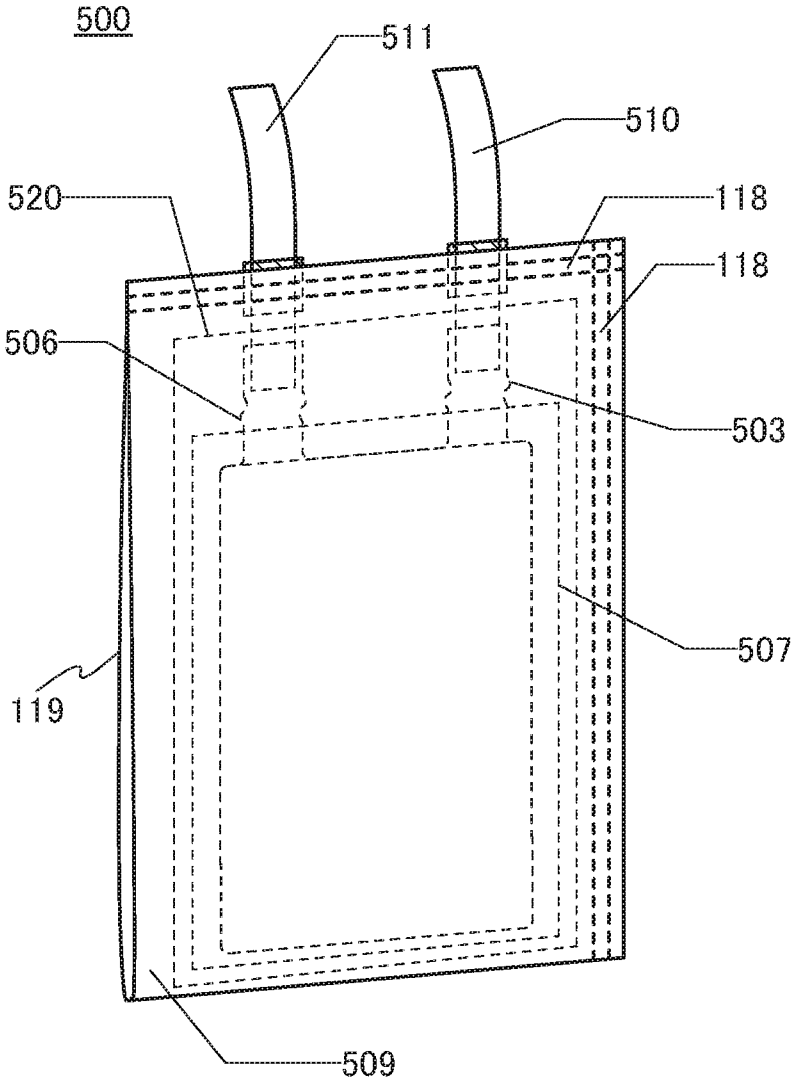


FIG. 14A

700,730

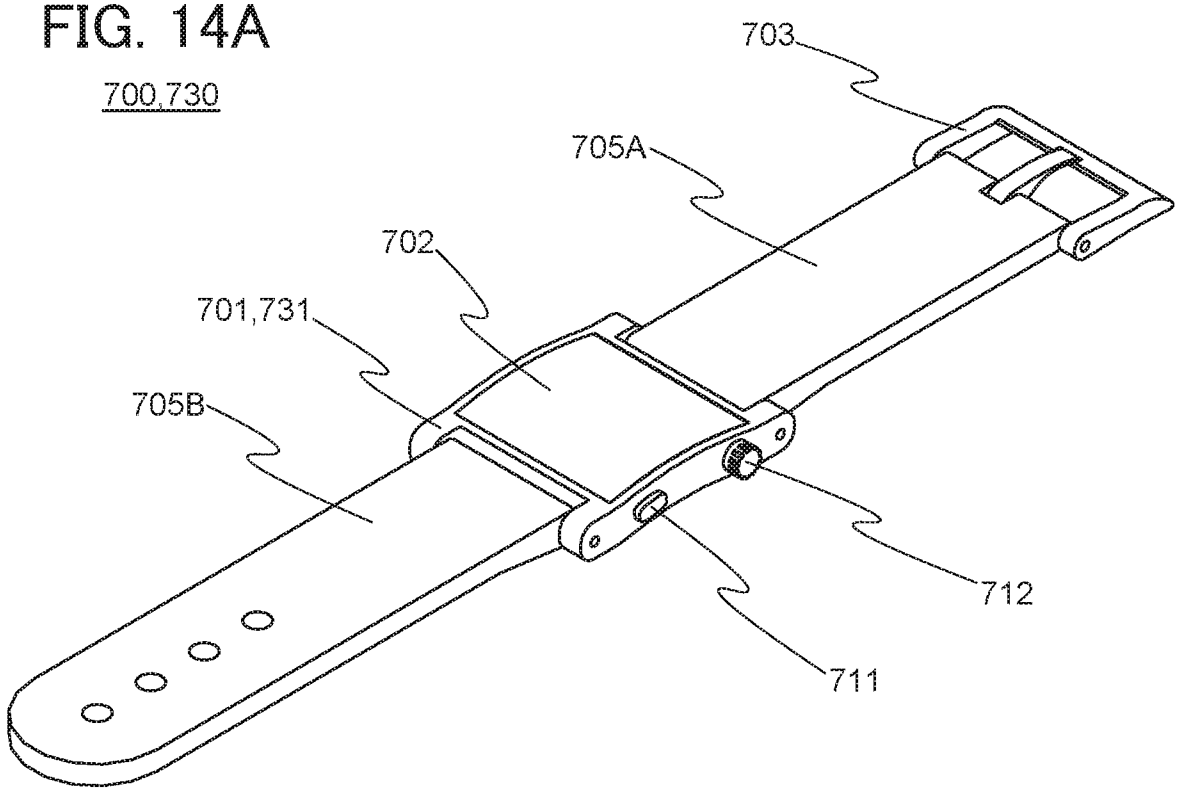


FIG. 14B

705A

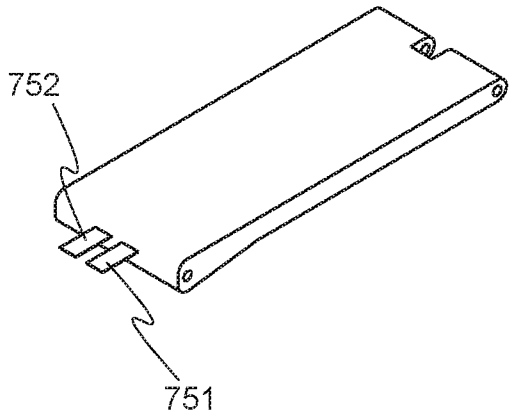


FIG. 14C

750

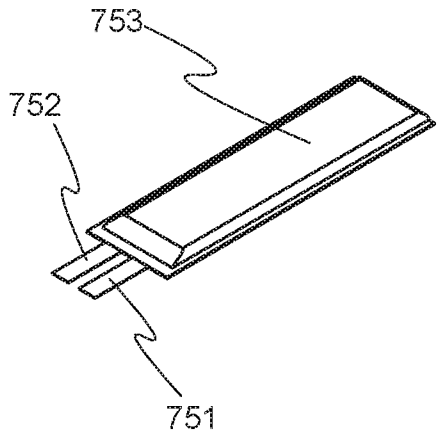


FIG. 15A

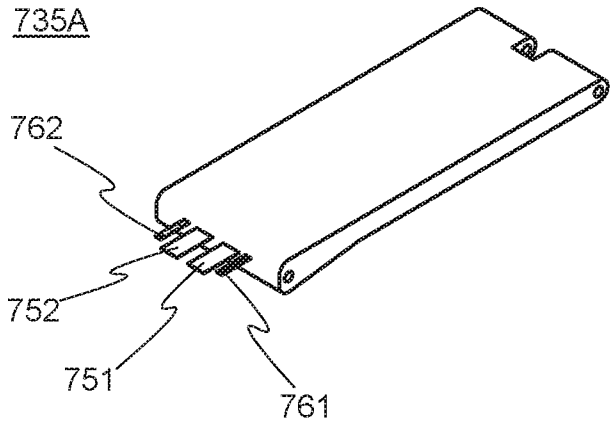


FIG. 15B

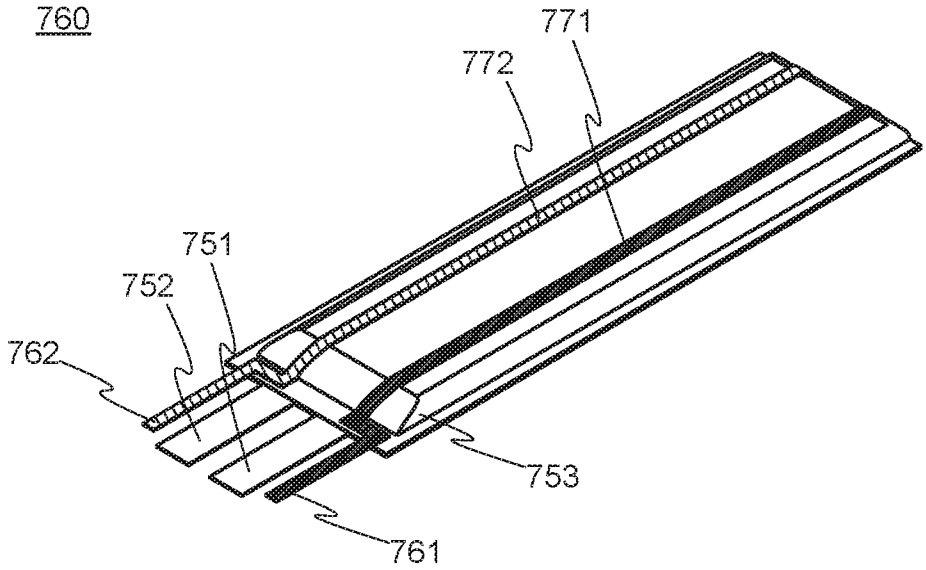


FIG. 15C

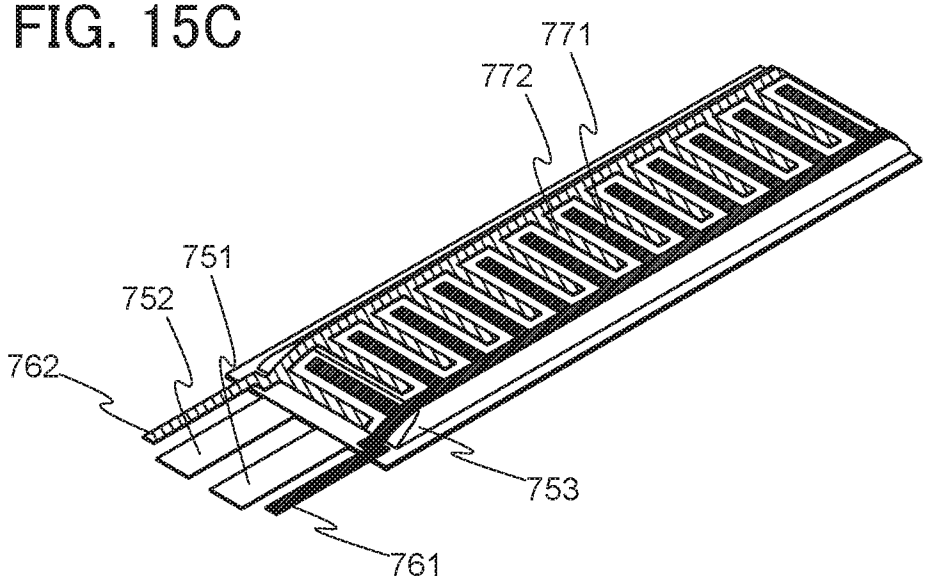


FIG. 16A

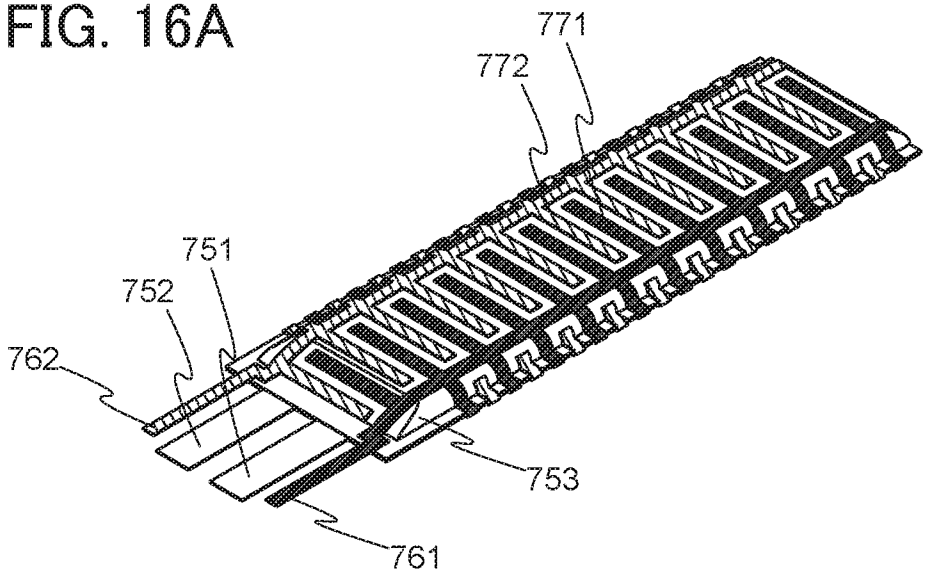


FIG. 16B

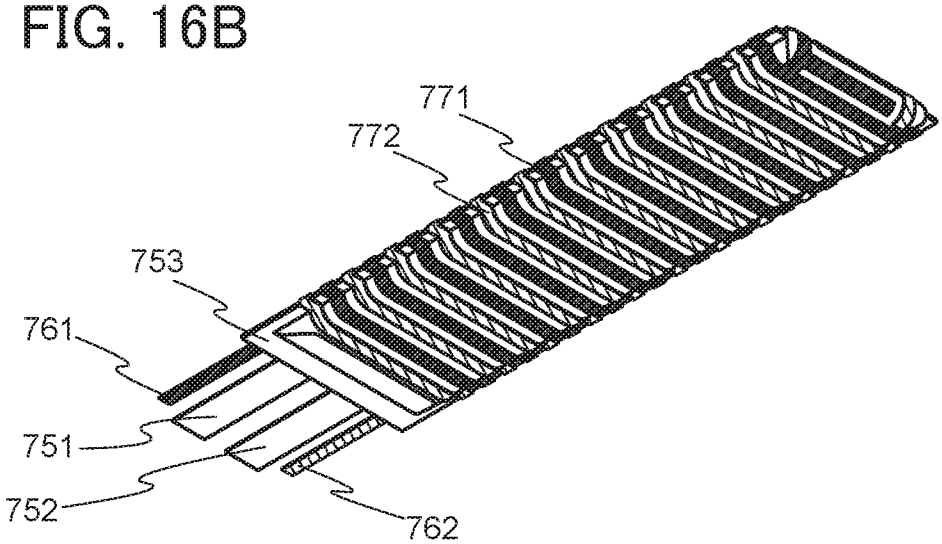


FIG. 17A

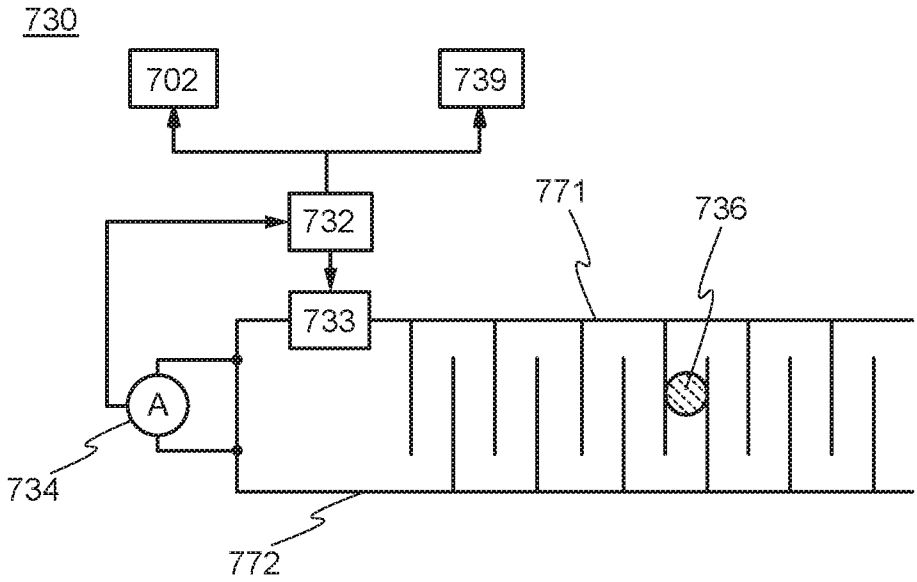


FIG. 17B

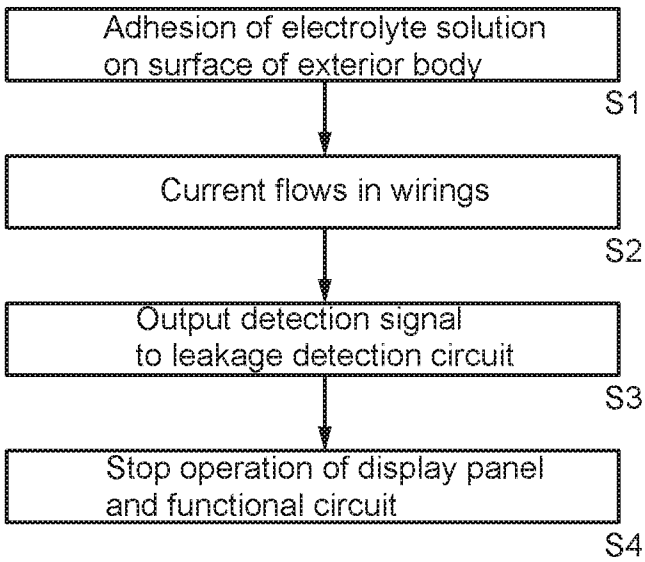


FIG. 17C

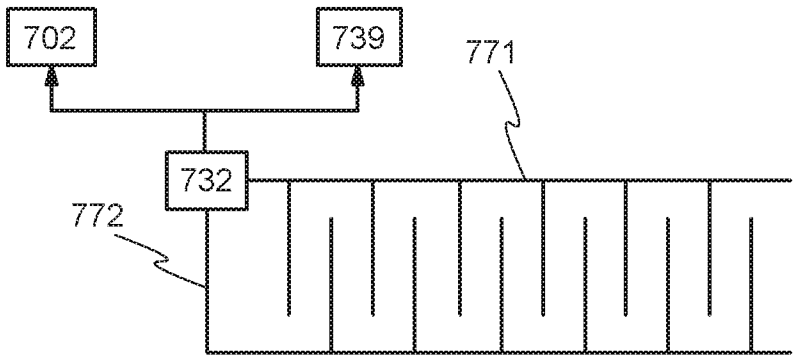


FIG. 18A

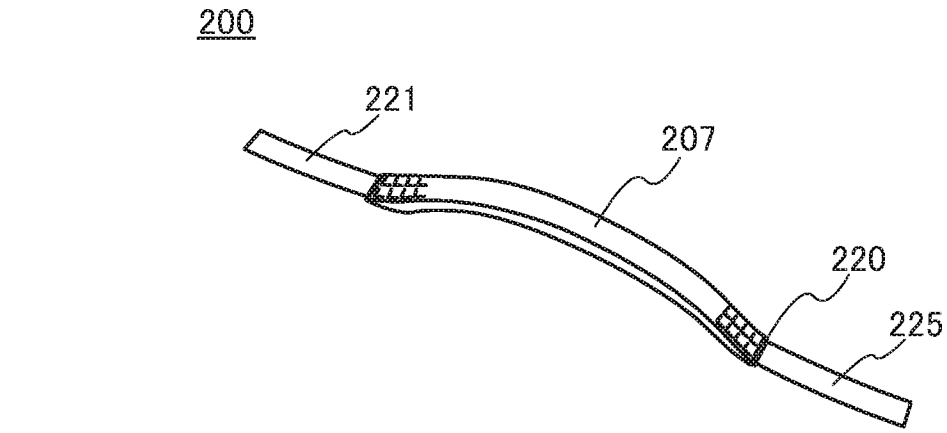


FIG. 18B

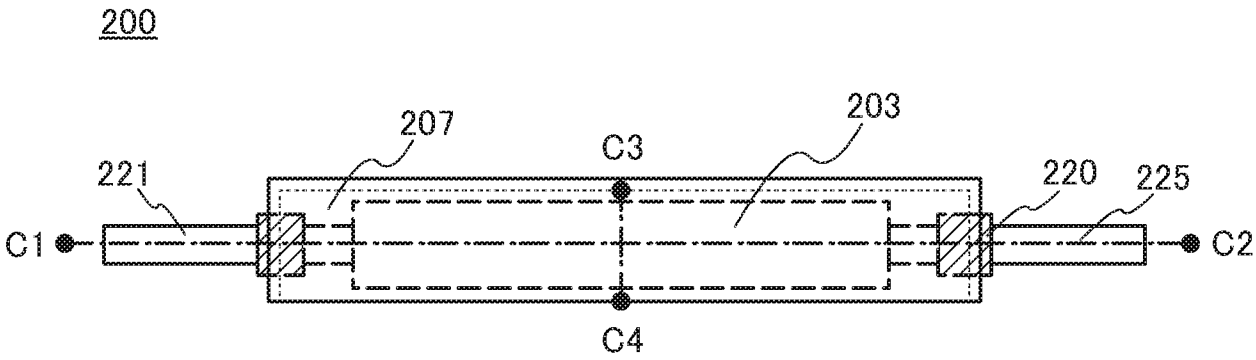


FIG. 19A

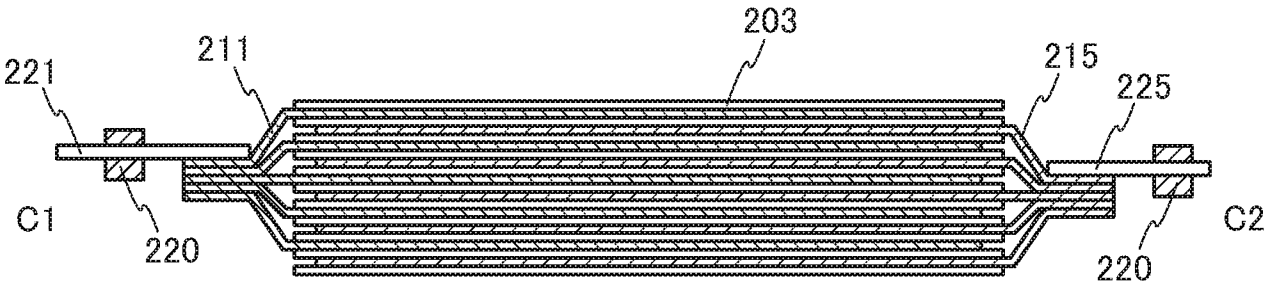


FIG. 19B

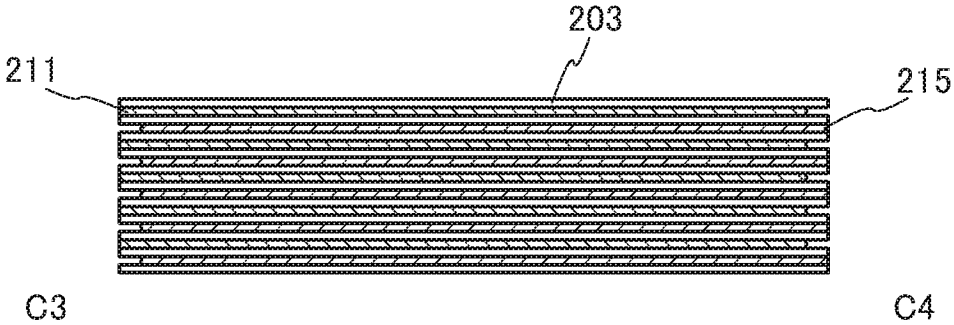


FIG. 20

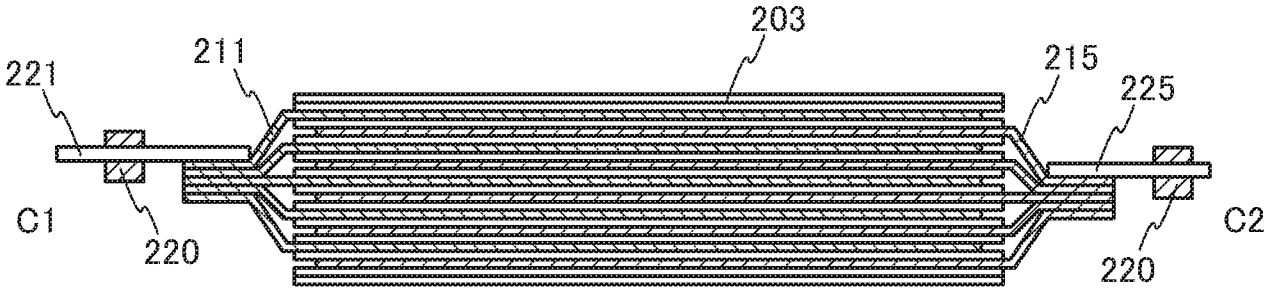


FIG. 21A

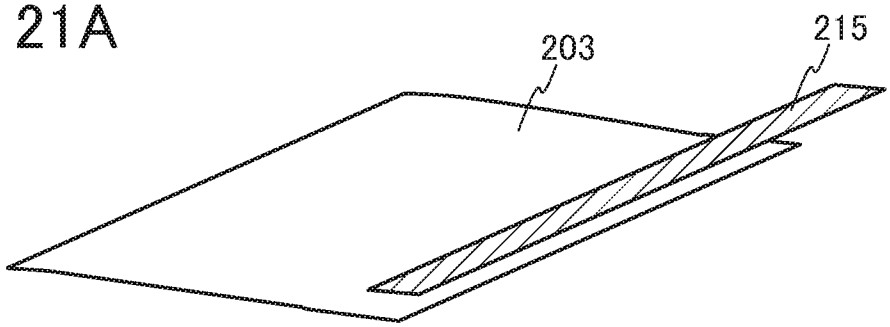


FIG. 21B

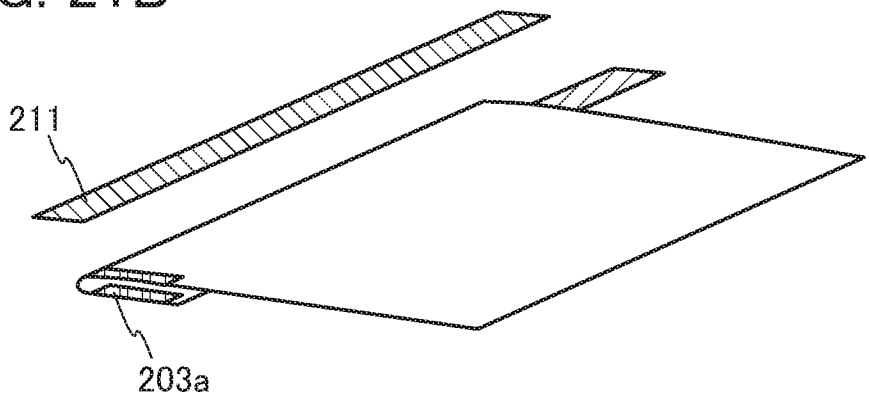


FIG. 21C

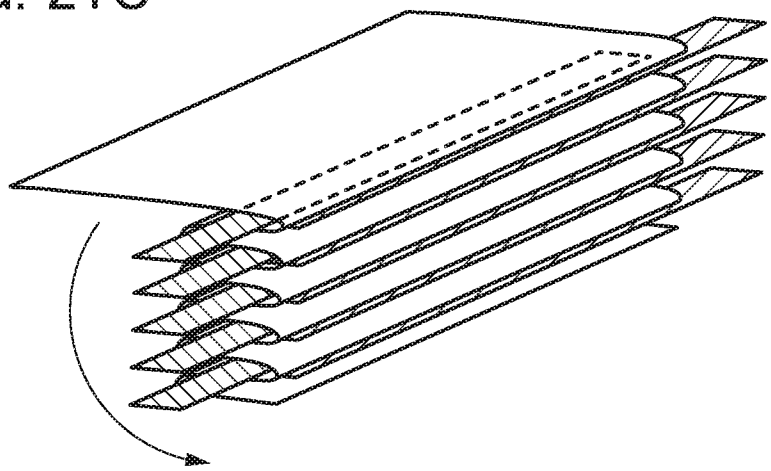


FIG. 21D

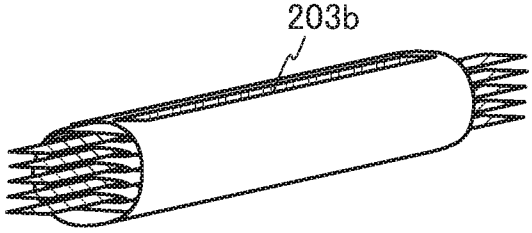


FIG. 22A

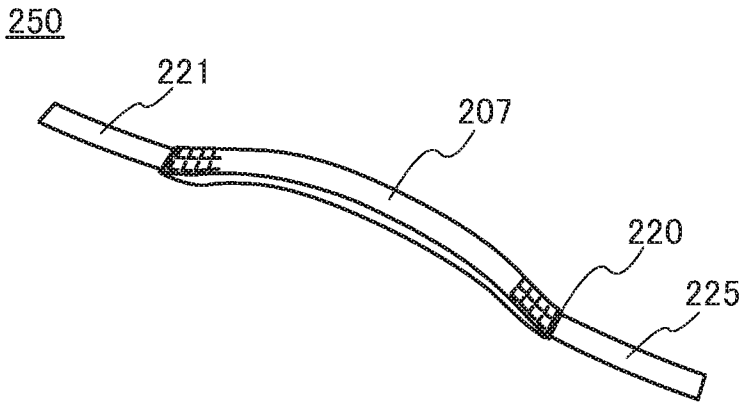


FIG. 22B

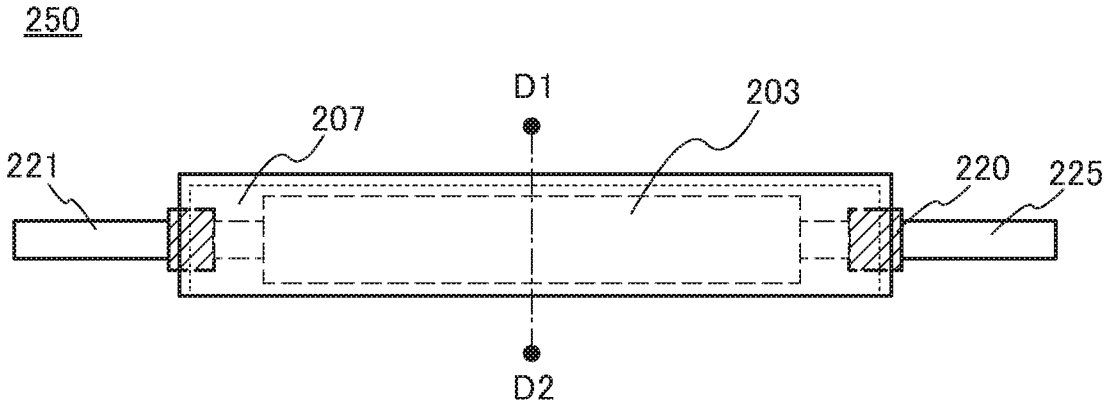


FIG. 22C1

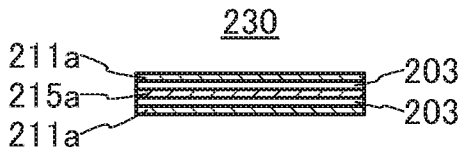


FIG. 22C2

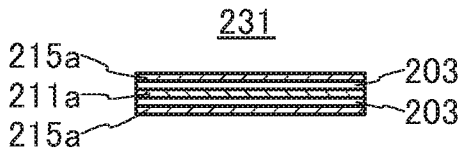


FIG. 23

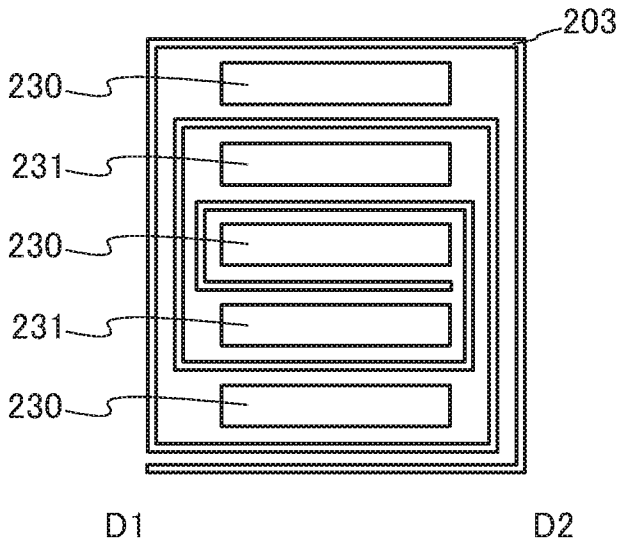


FIG. 24A

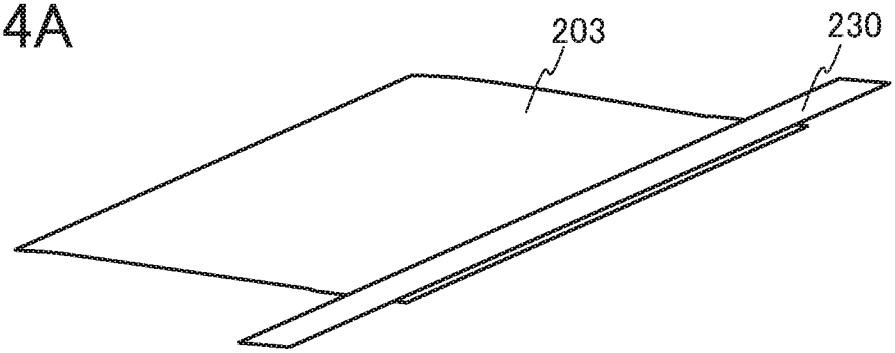


FIG. 24B

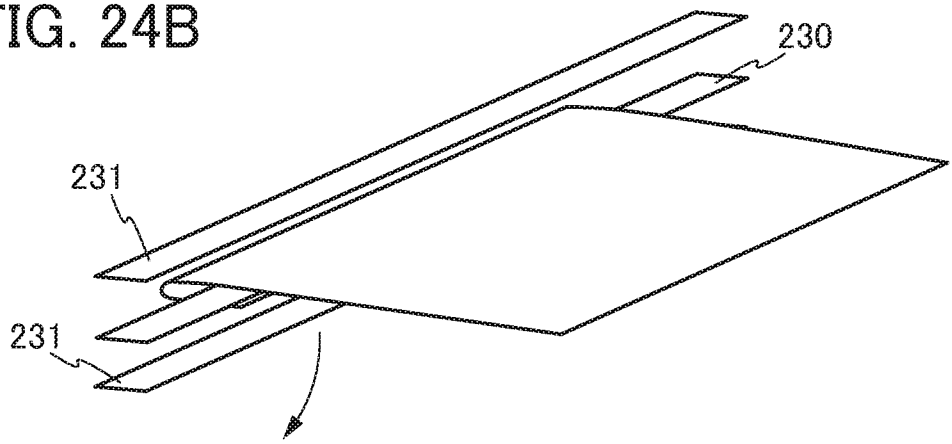


FIG. 24C

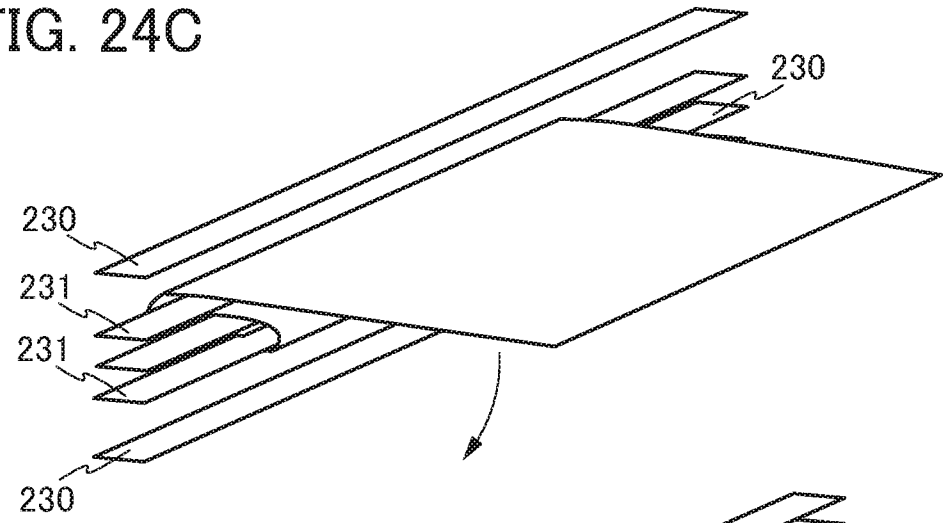


FIG. 24D

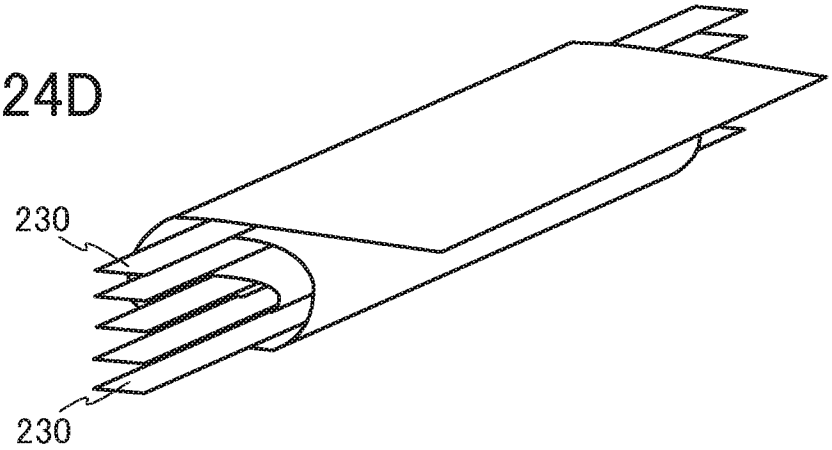


FIG. 25

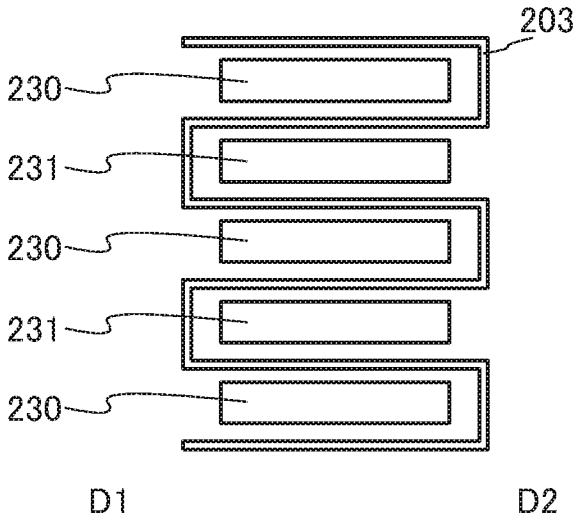


FIG. 26A

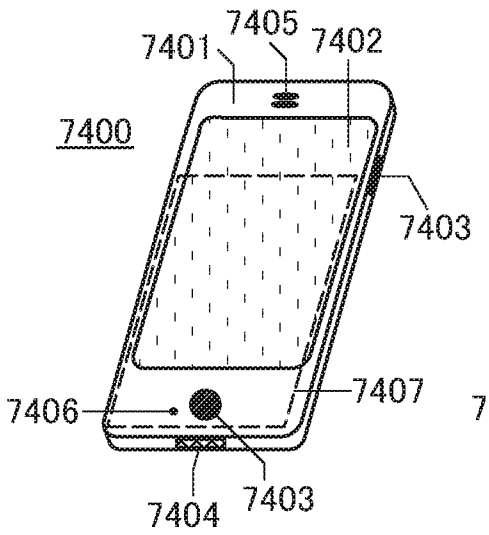


FIG. 26B

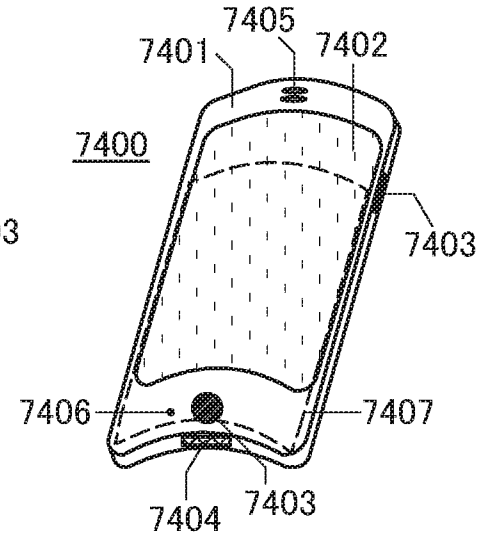


FIG. 26C

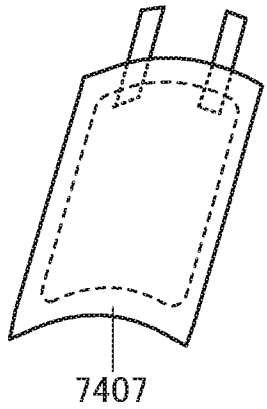


FIG. 26D

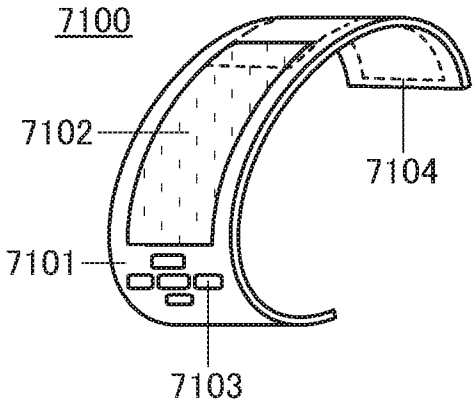


FIG. 26E

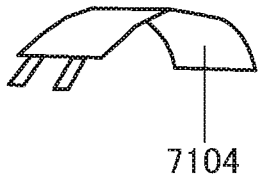


FIG. 26F

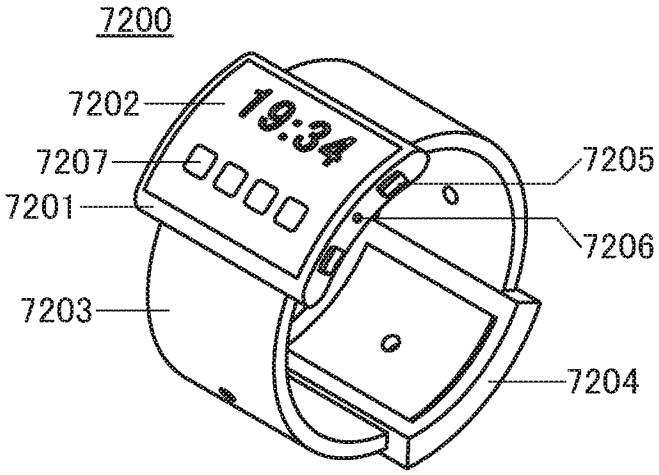


FIG. 27A

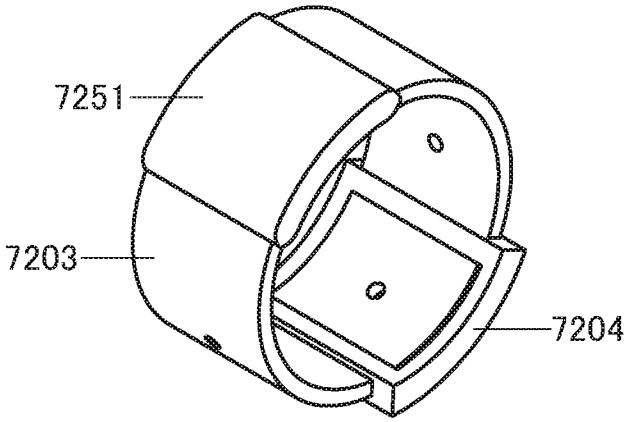


FIG. 27B

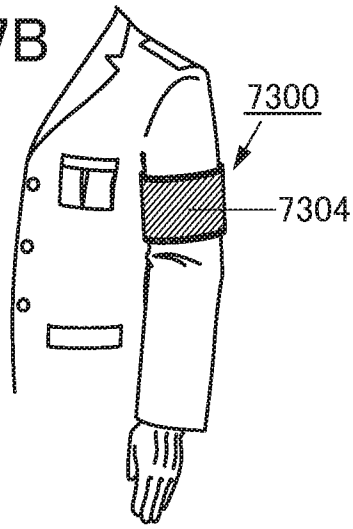


FIG. 27C

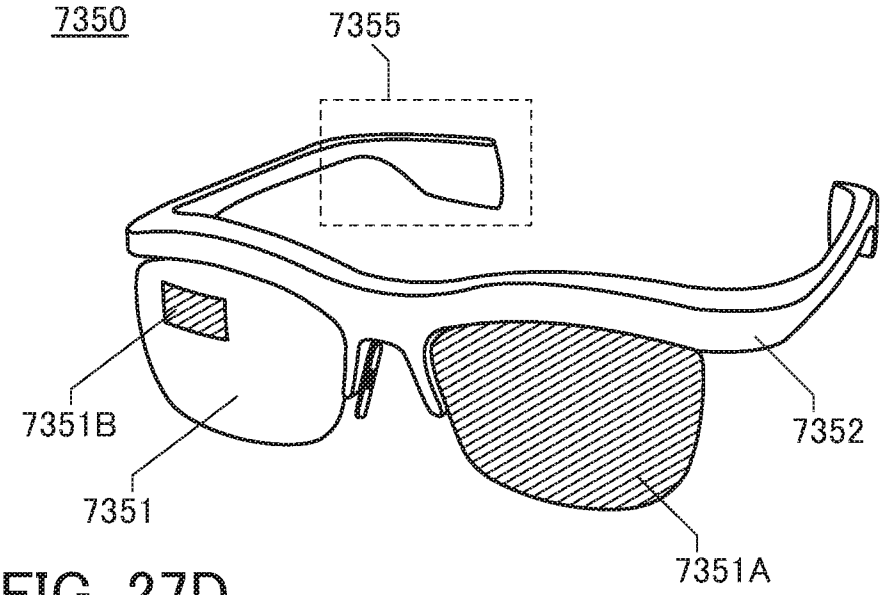


FIG. 27D

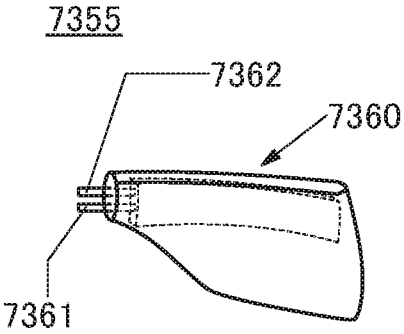


FIG. 28A

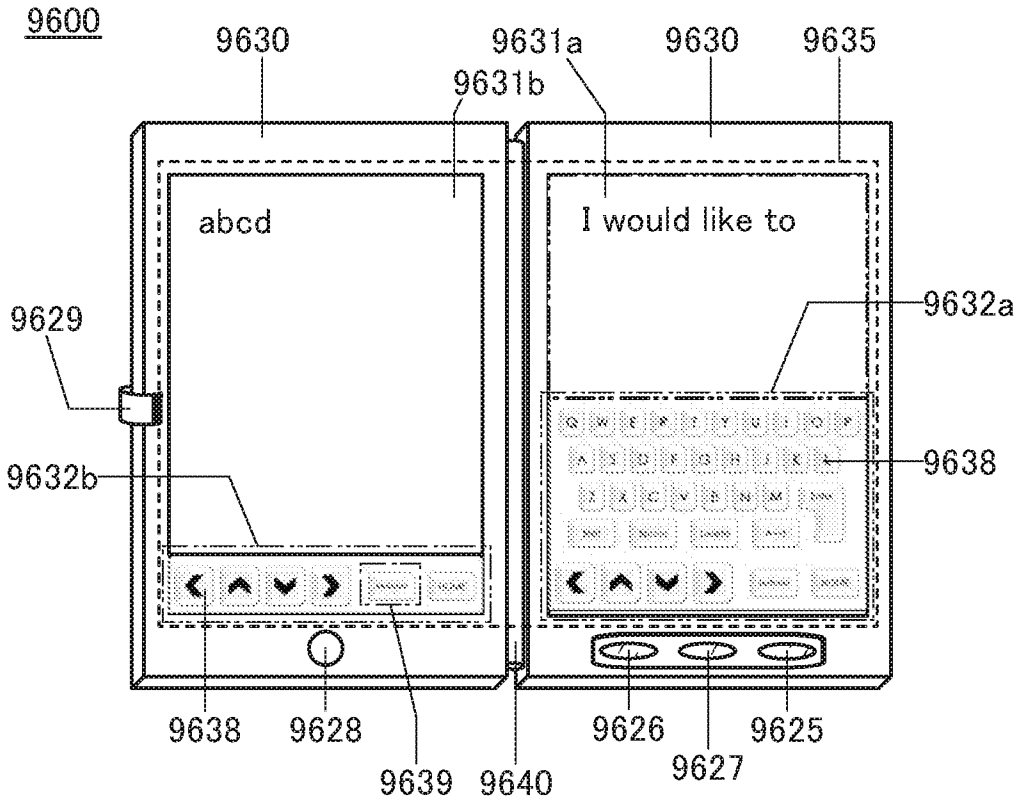


FIG. 28B

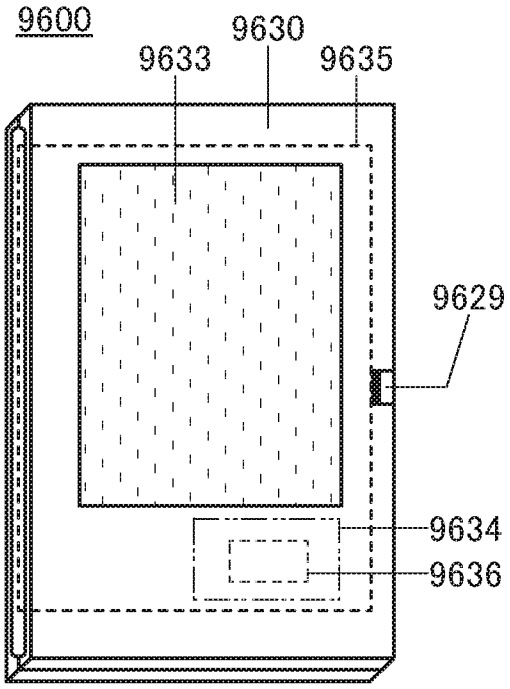
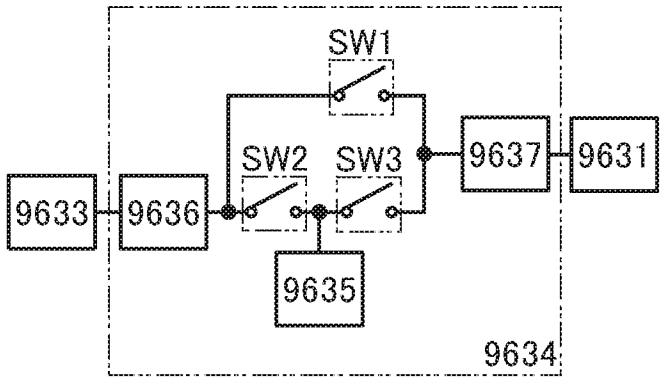


FIG. 28C



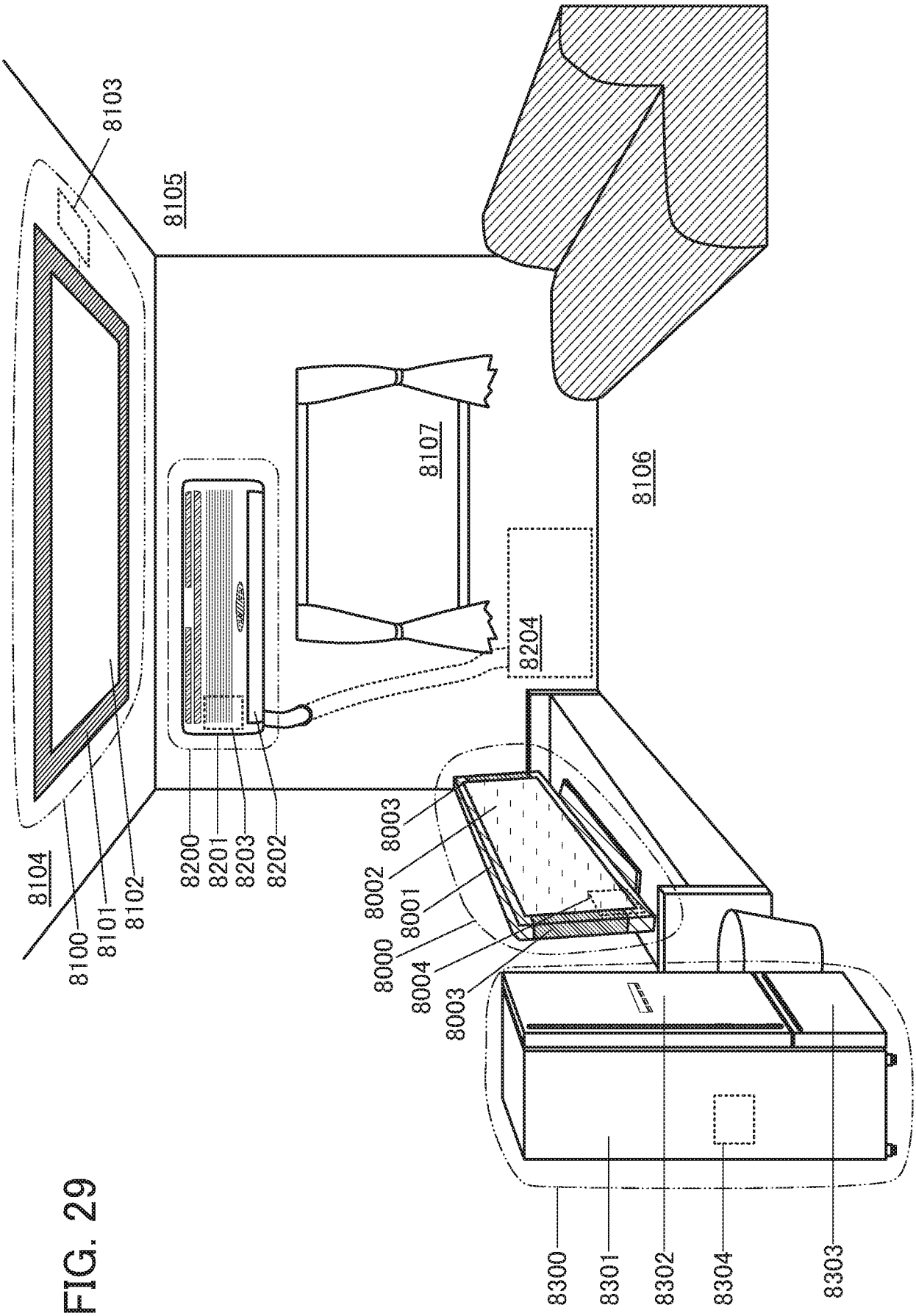

8103
8105
8107
8106
8204
8104
8100
8101
8102
8200
8201
8203
8202
8003
8002
8001
8000
8004
8003
8300
8301
8302
8304
8303

FIG. 29

FIG. 30A

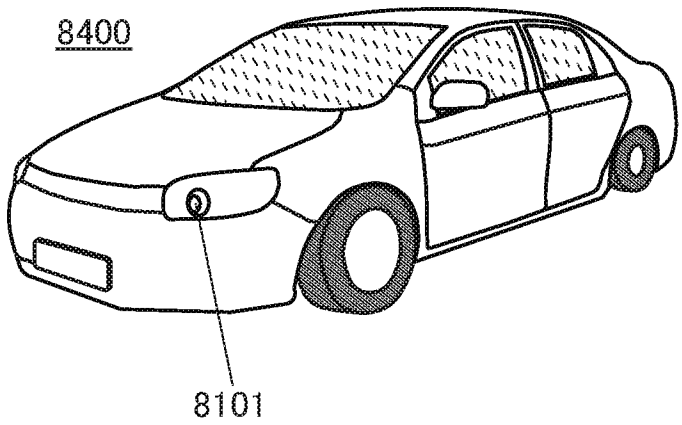


FIG. 30B

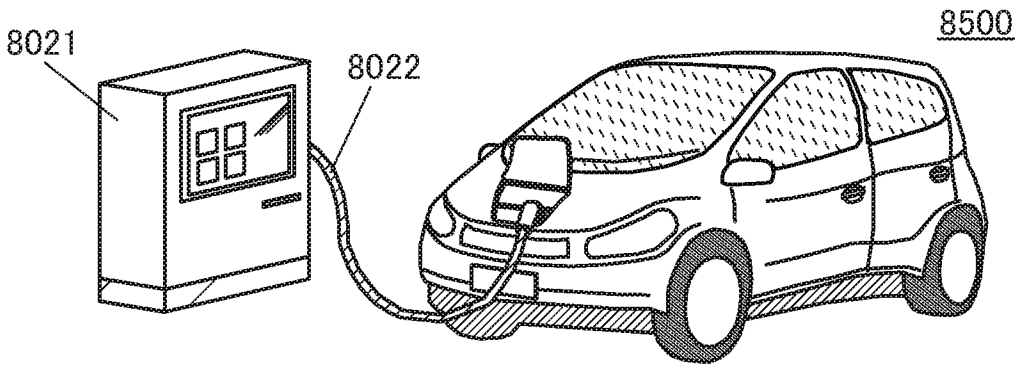


FIG. 31A

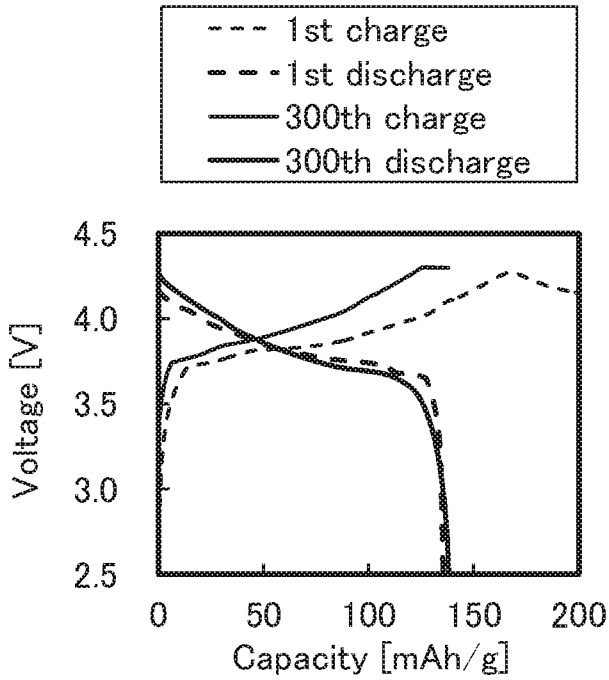


FIG. 31B

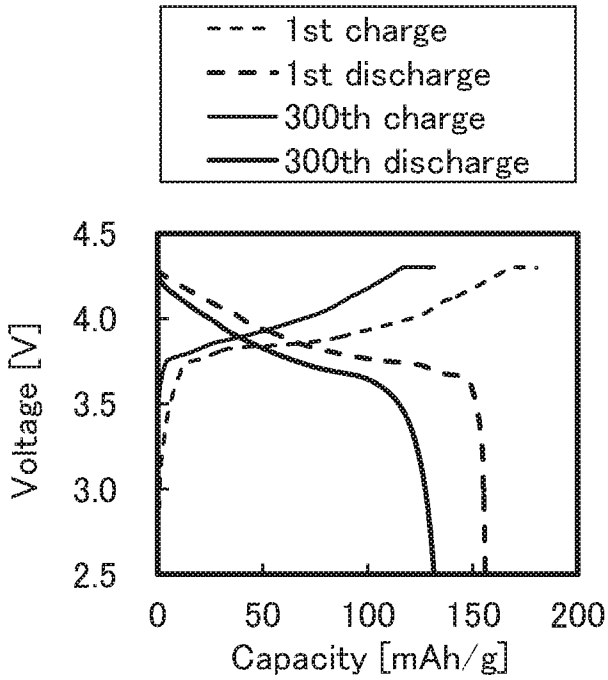


FIG. 31C

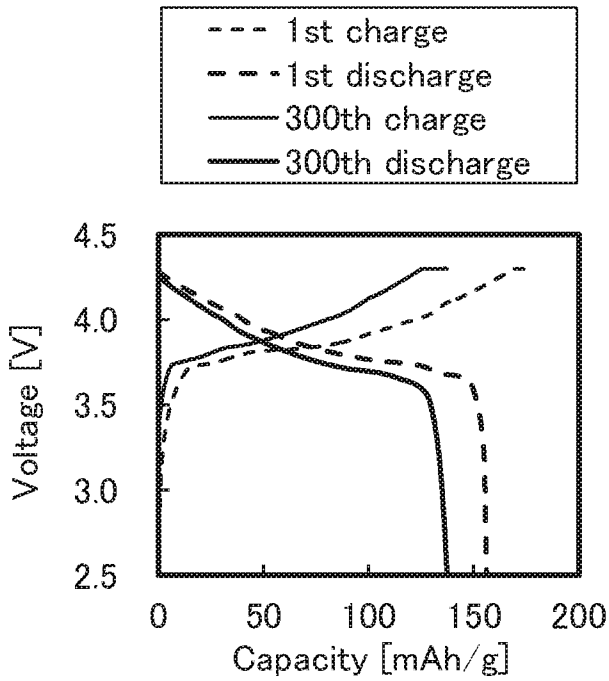


FIG. 31D

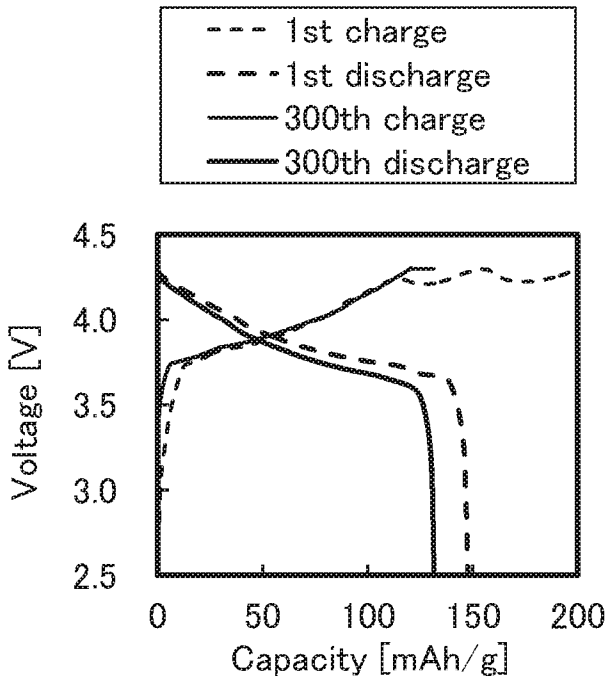


FIG. 32A

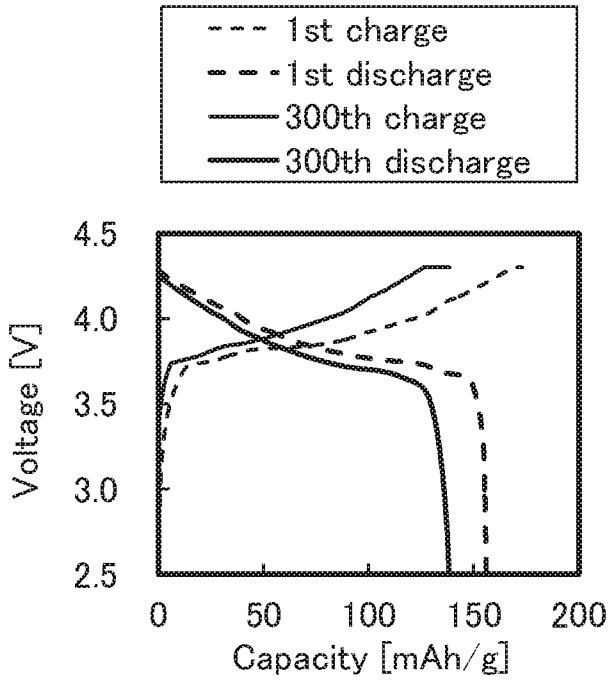


FIG. 32B

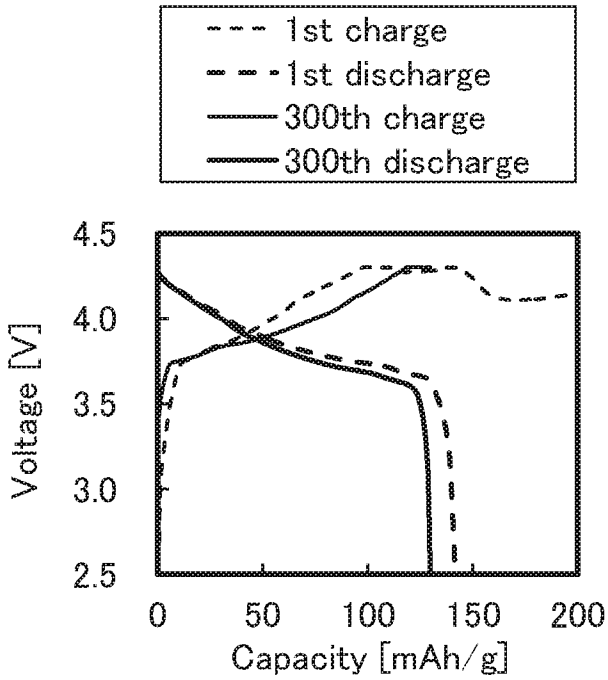


FIG. 32C

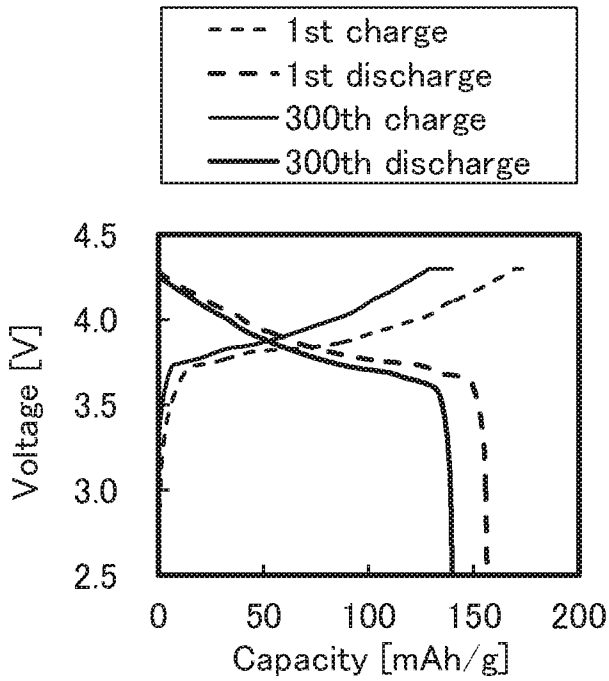


FIG. 32D

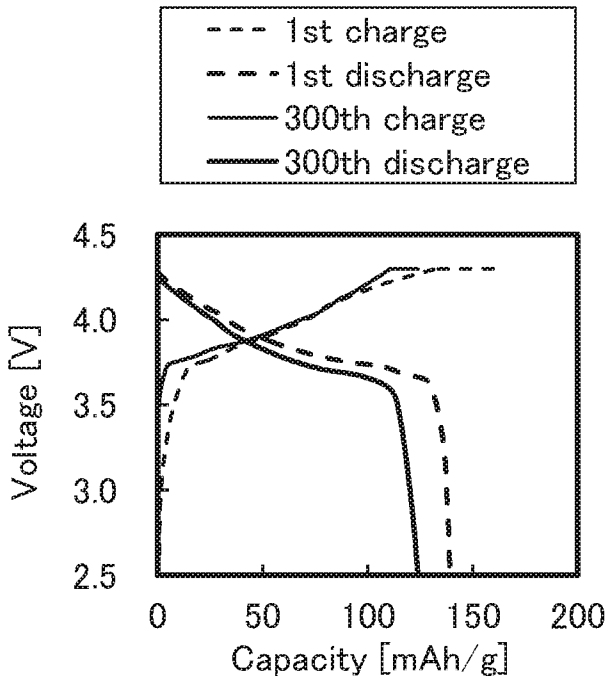


FIG. 33A

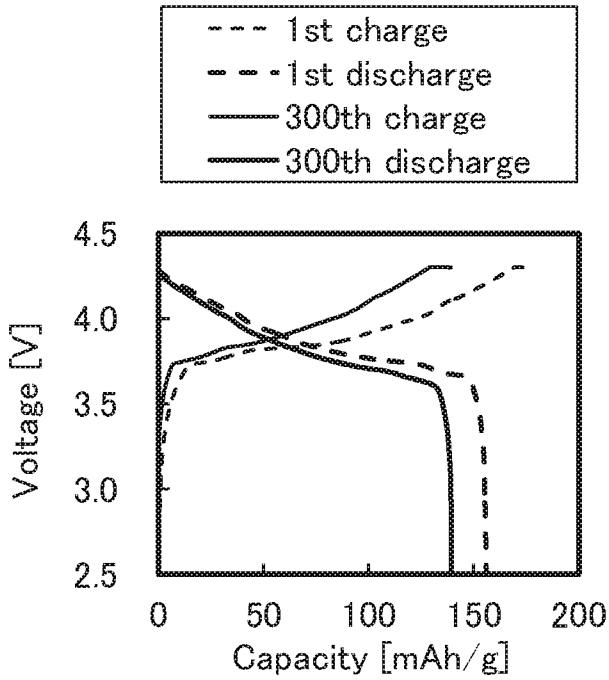


FIG. 33B

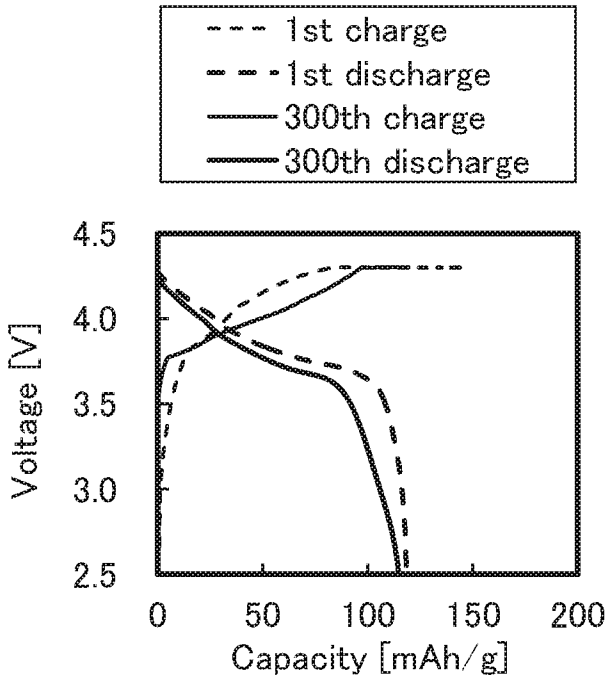


FIG. 33C

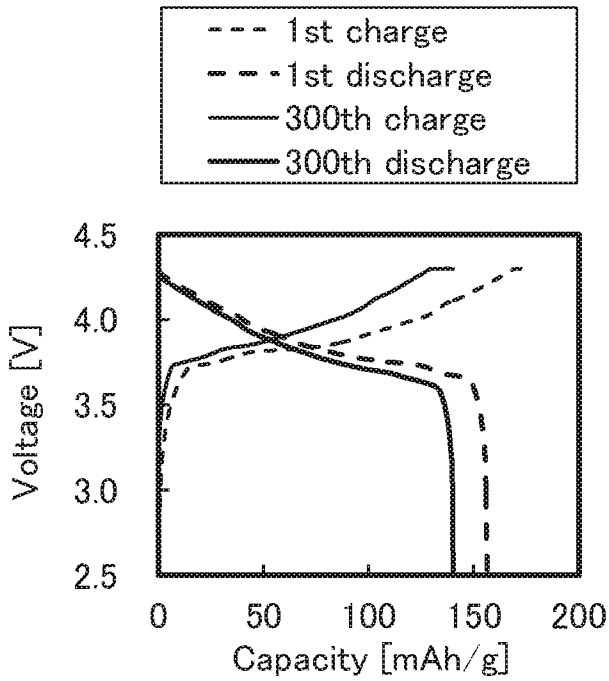


FIG. 33D

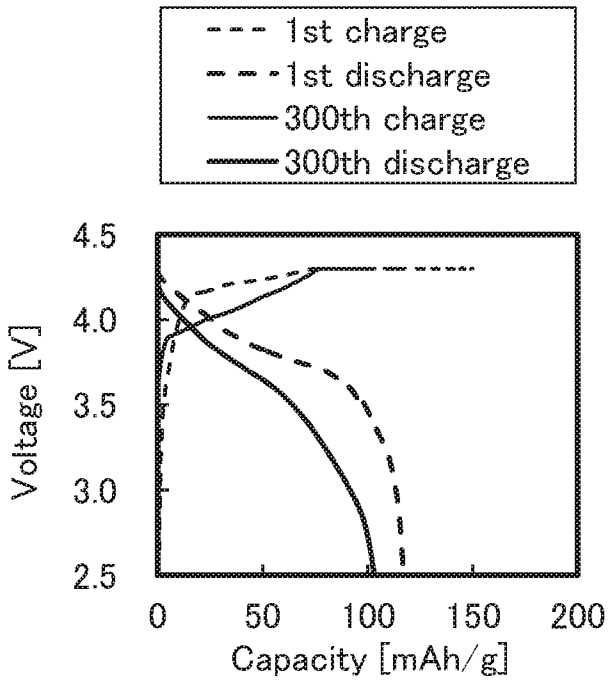


FIG. 34A

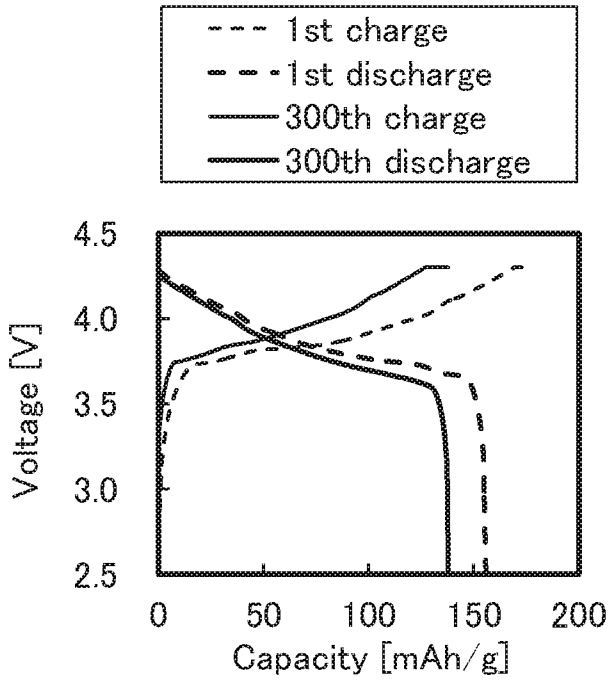


FIG. 34B

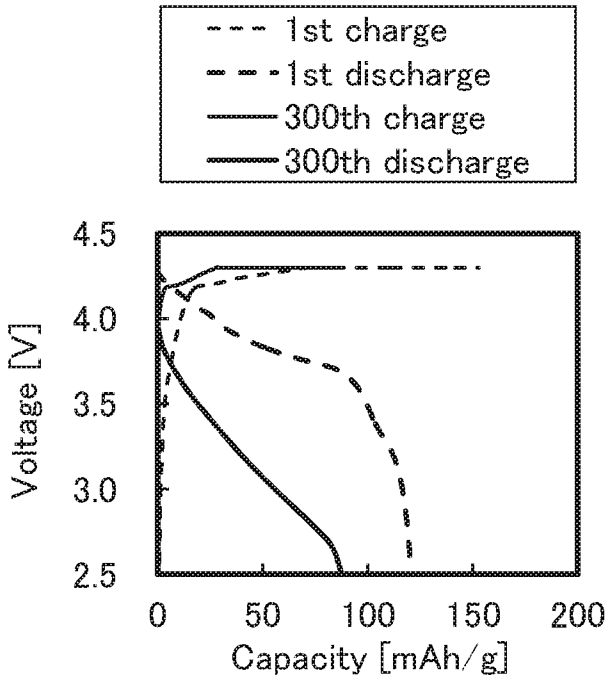


FIG. 34C

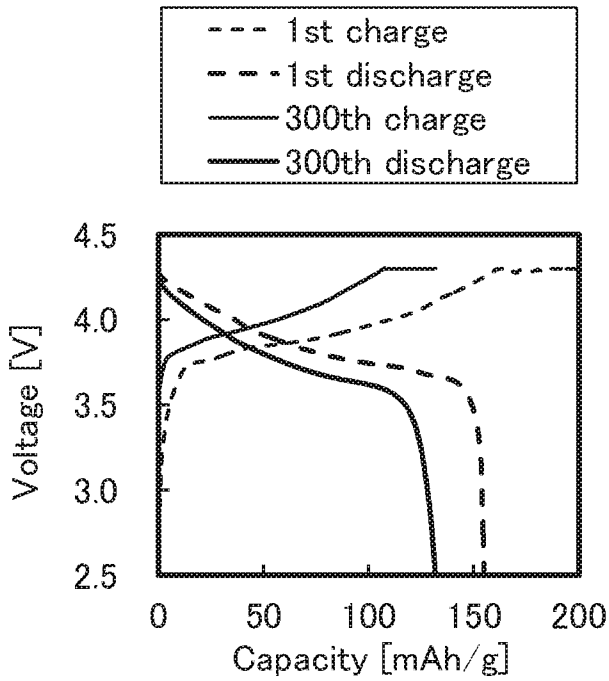


FIG. 34D

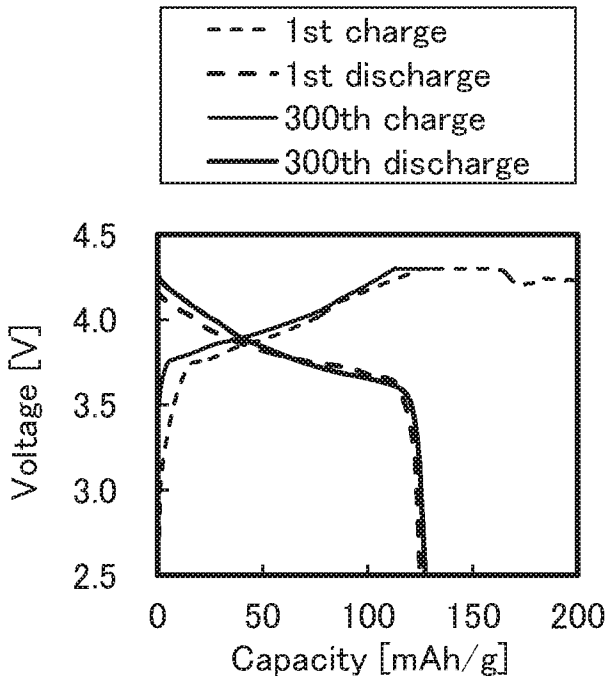


FIG. 35A

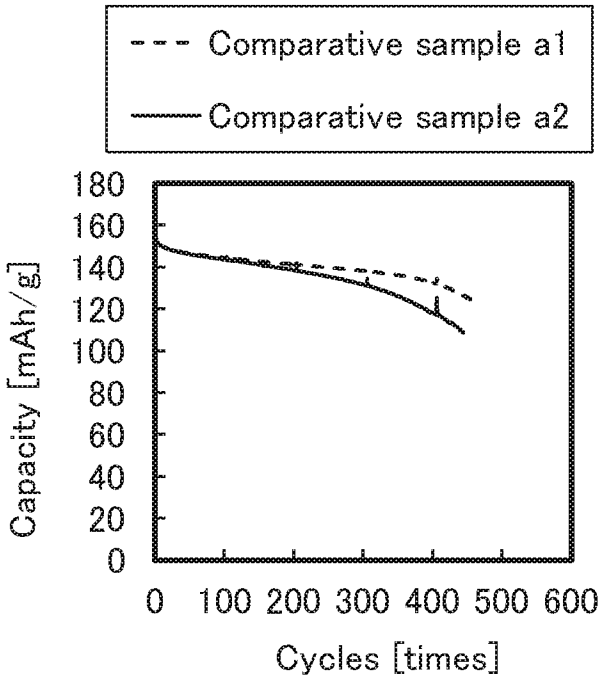


FIG. 35B

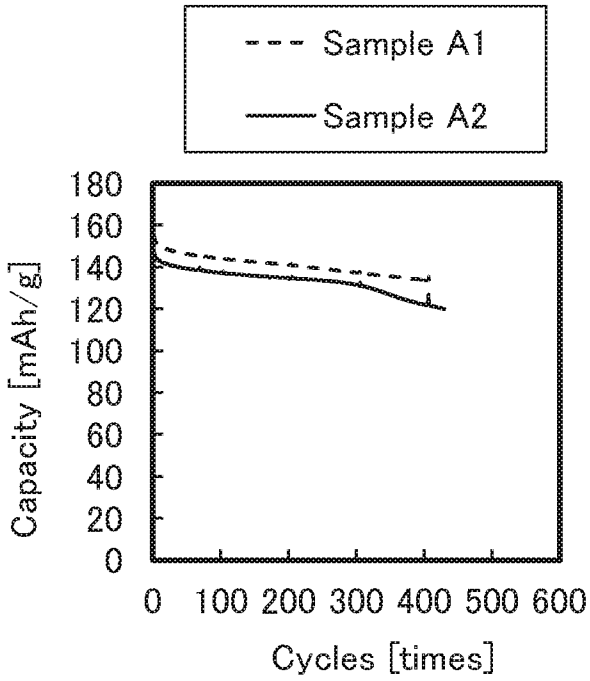


FIG. 35C

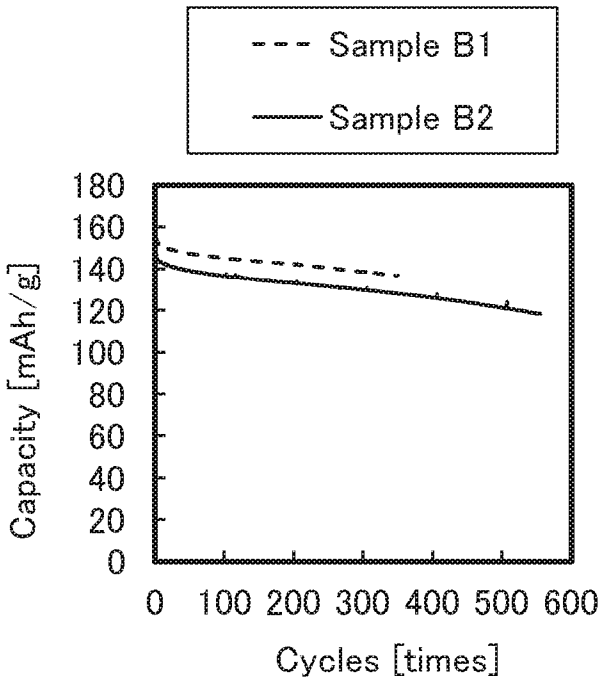


FIG. 35D

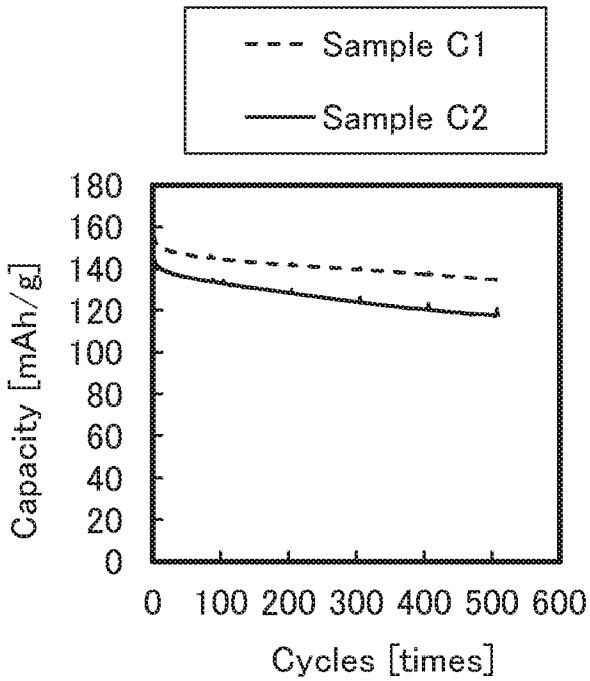


FIG. 36A

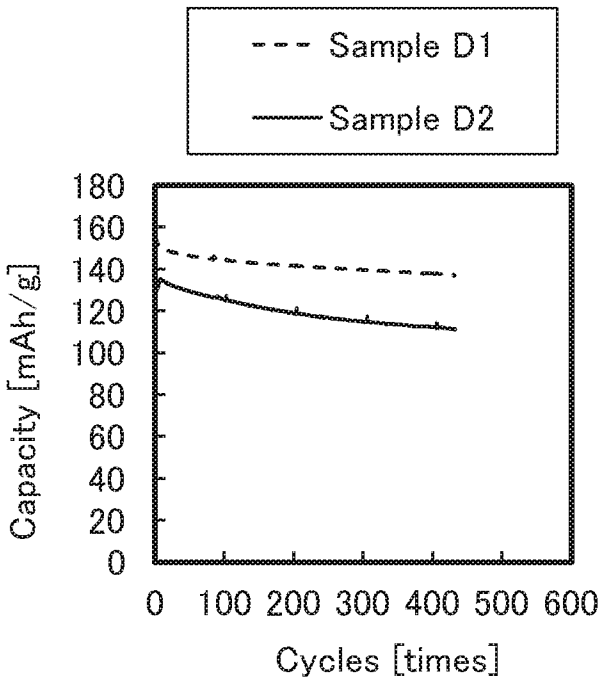


FIG. 36B

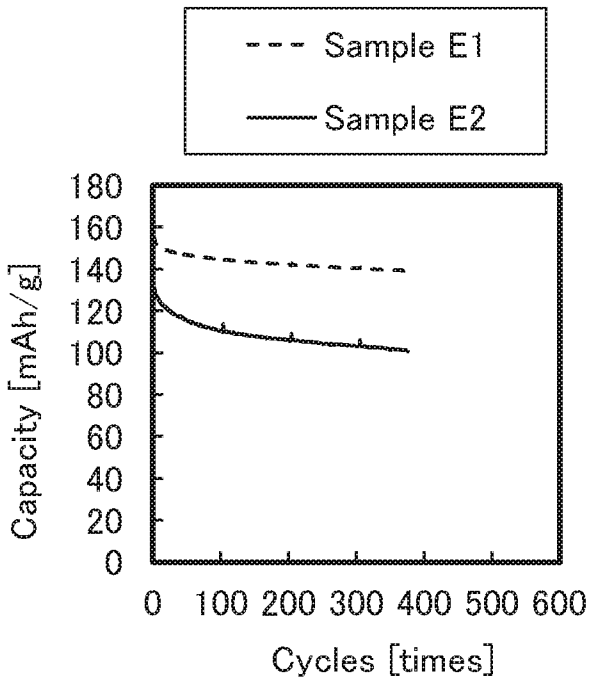


FIG. 36C

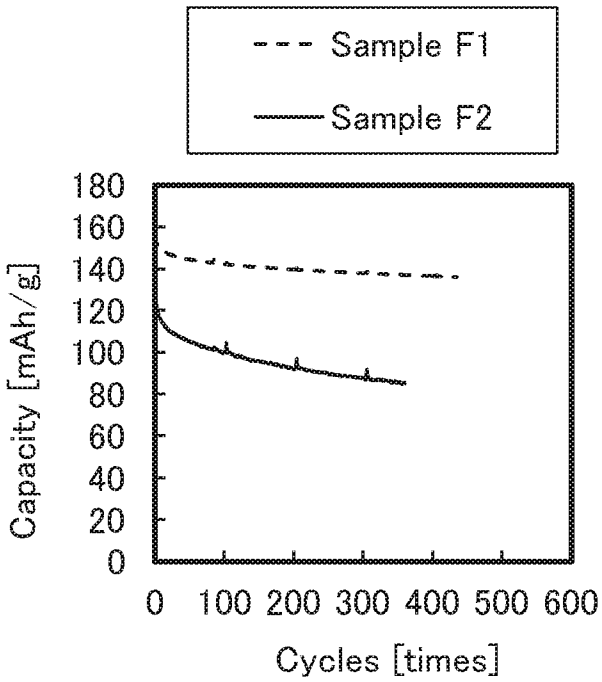


FIG. 36D

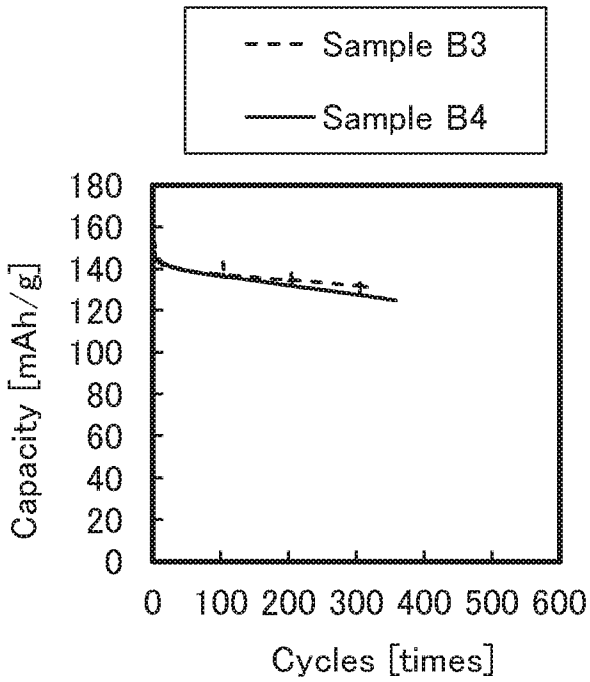


FIG. 37A

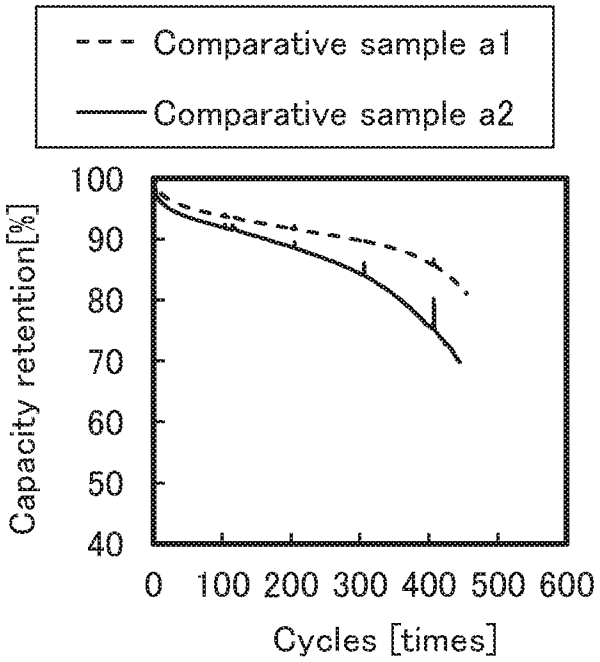


FIG. 37B

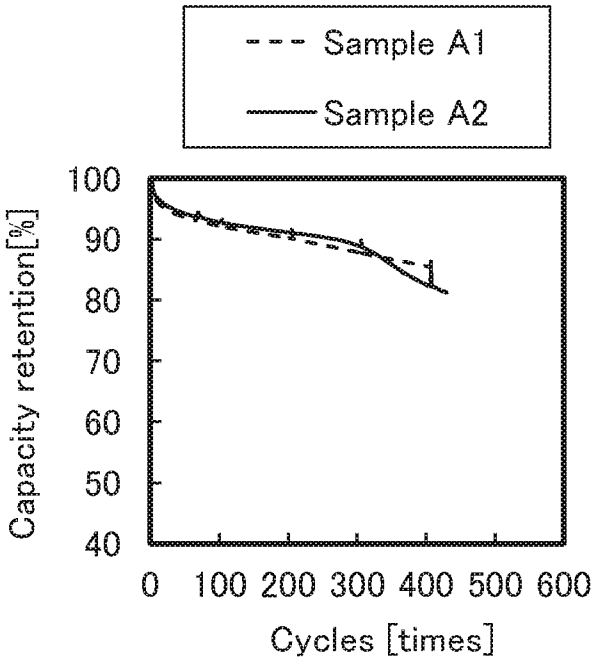


FIG. 37C

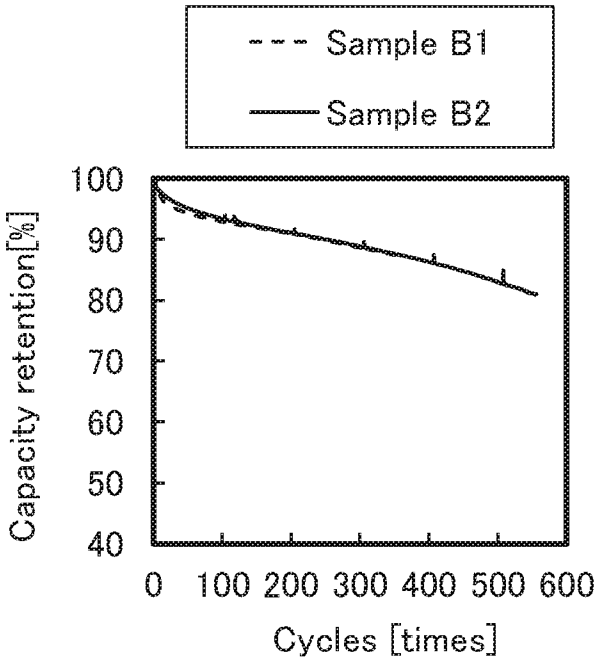


FIG. 37D

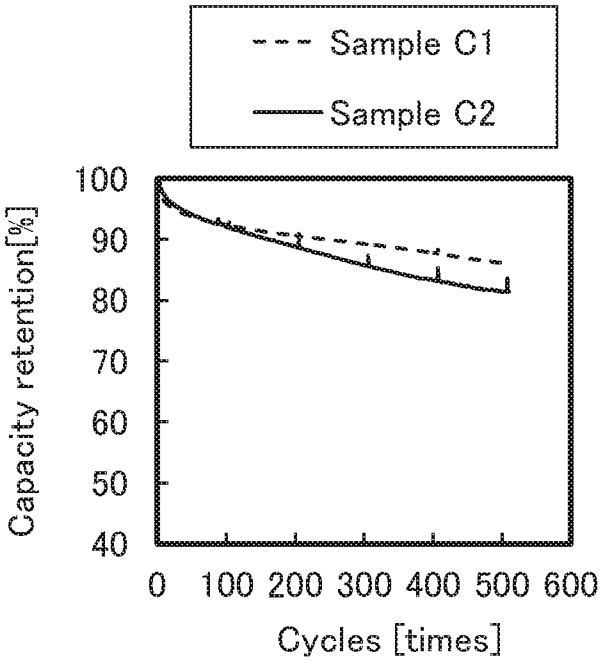


FIG. 38A

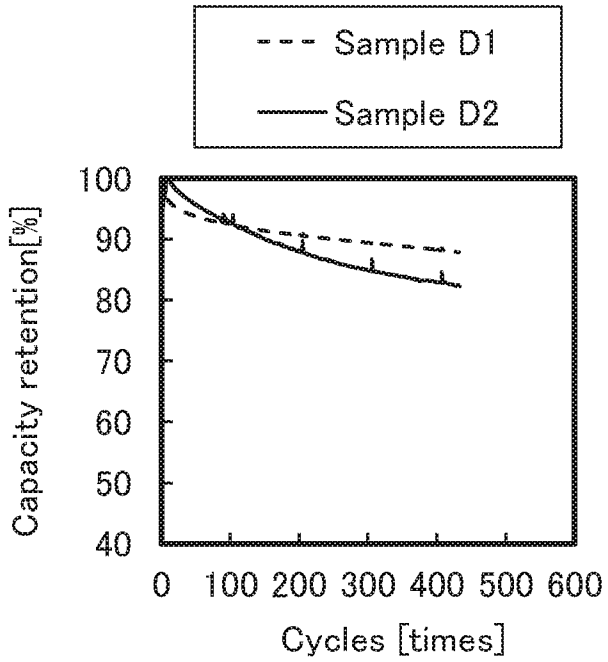


FIG. 38B

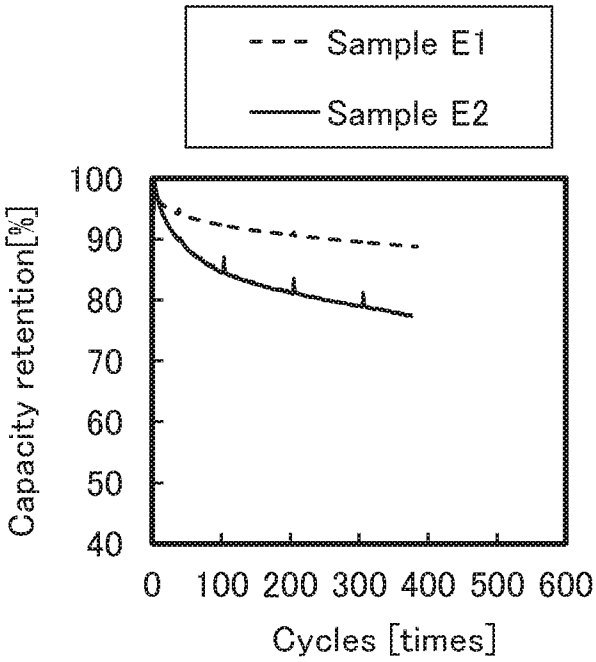


FIG. 38C

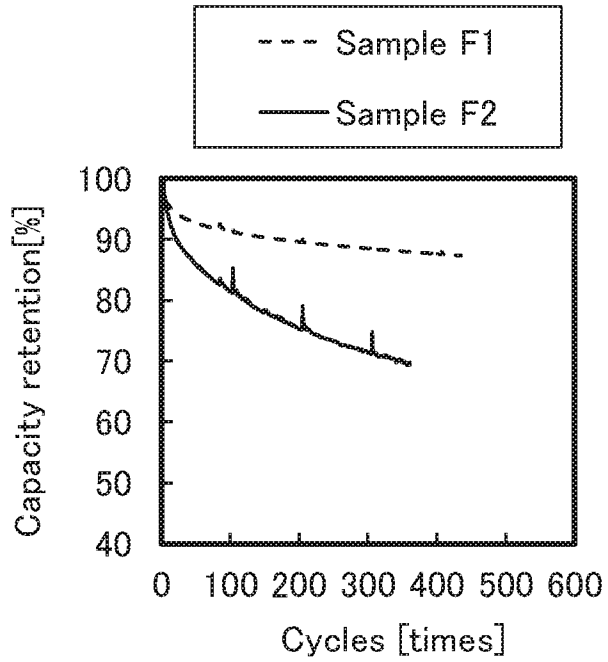


FIG. 38D

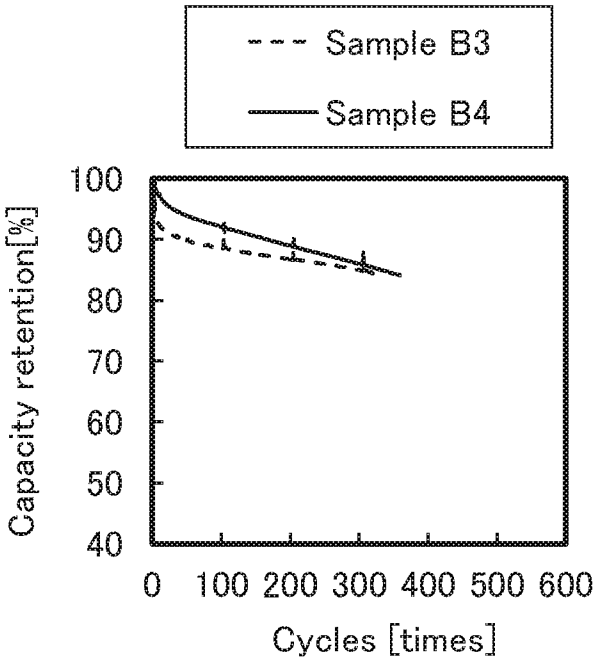


FIG. 39A

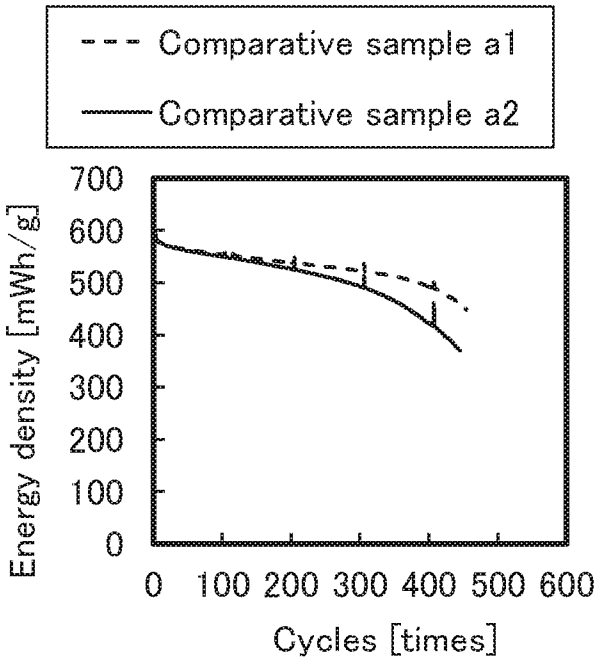


FIG. 39B

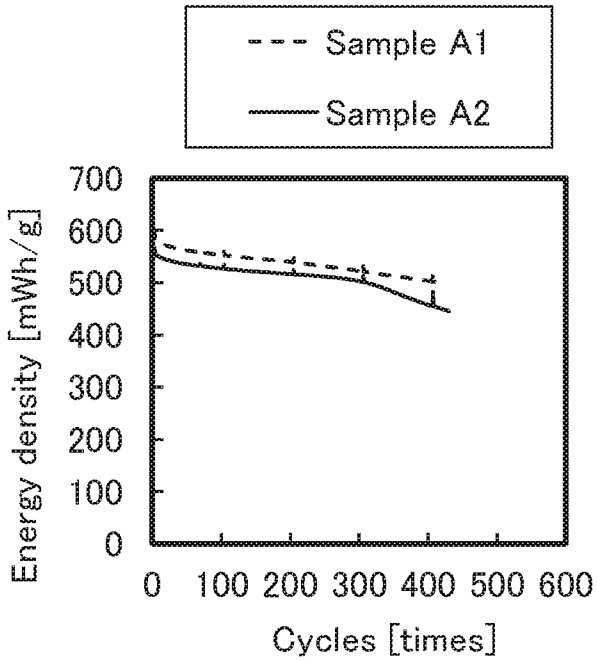


FIG. 39C

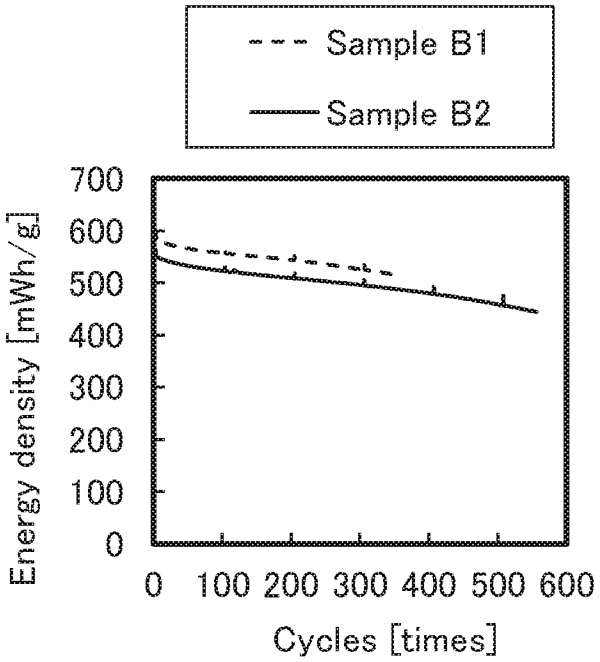


FIG. 39D

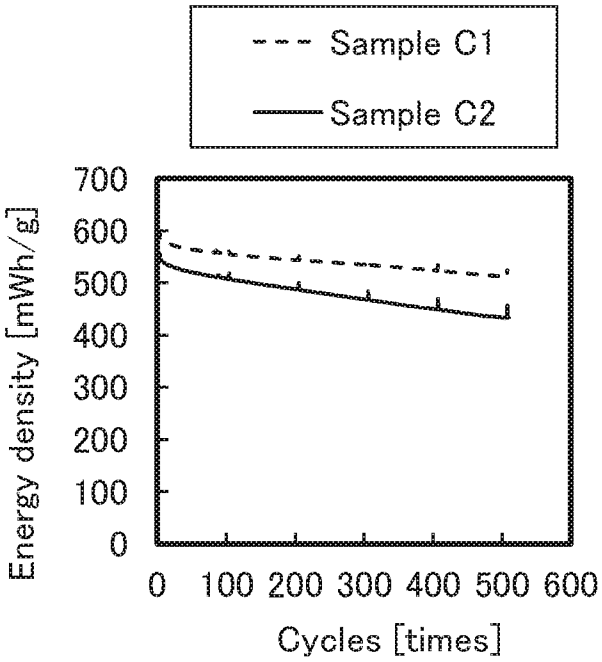


FIG. 40A

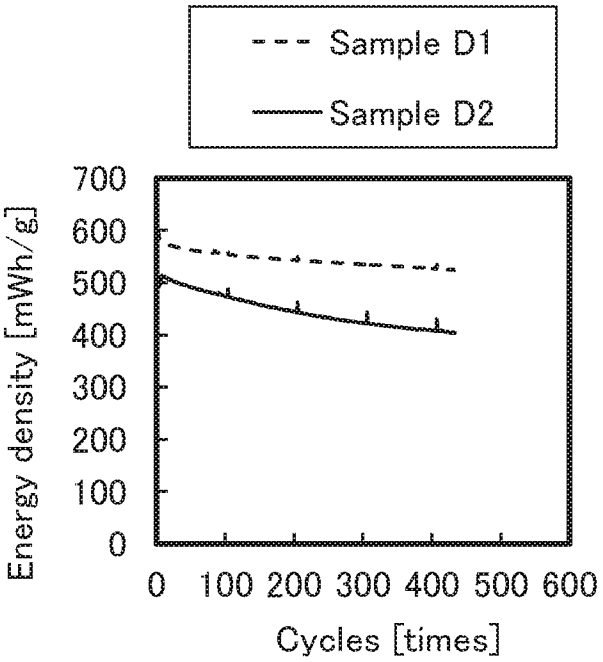


FIG. 40B

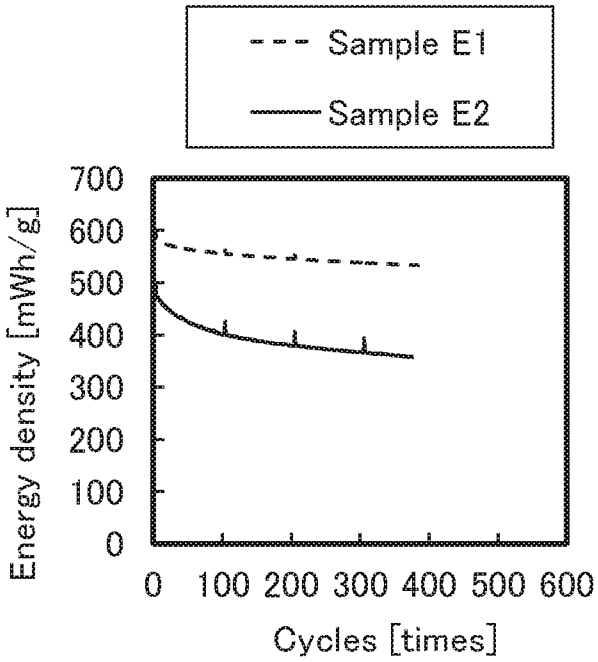


FIG. 40C

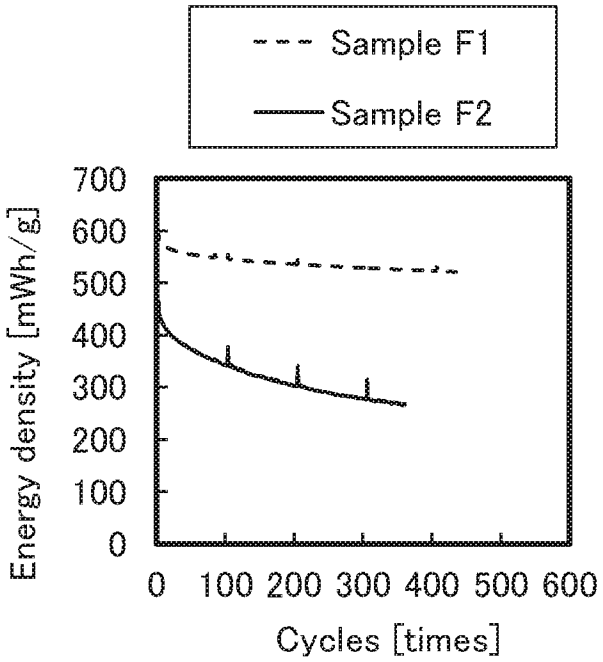


FIG. 40D

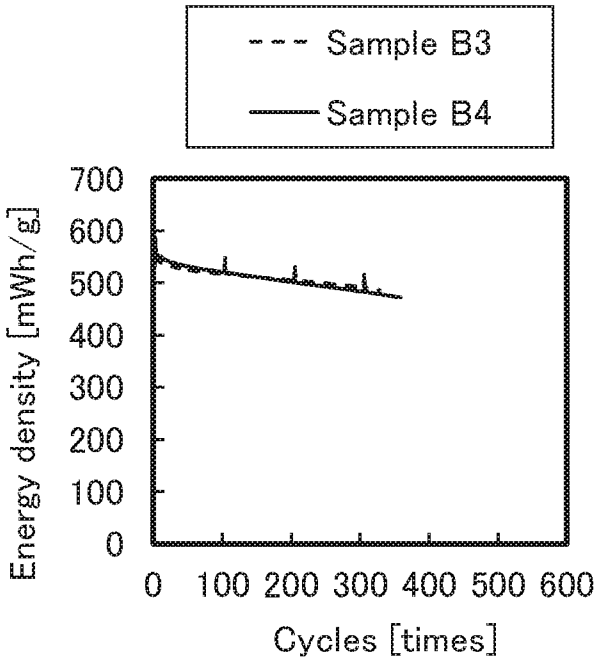


FIG. 41A

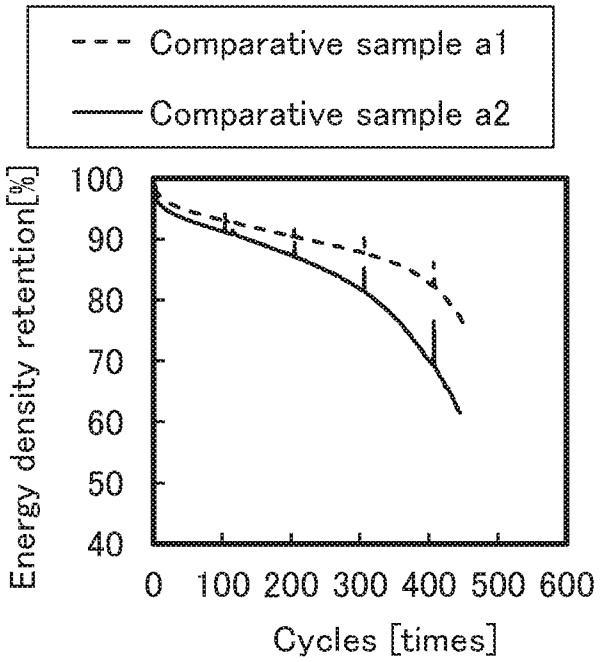


FIG. 41B

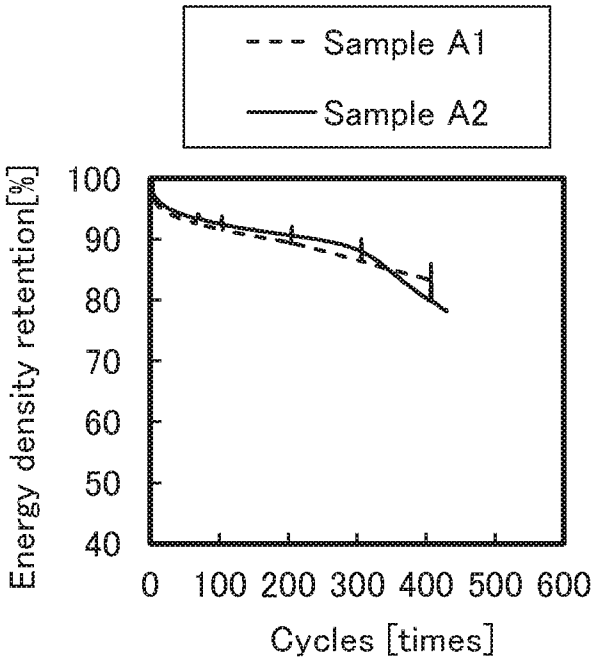


FIG. 41C

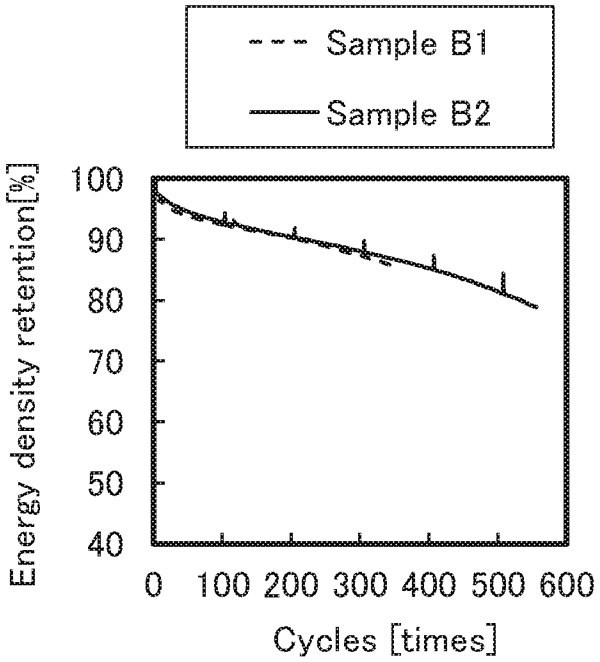


FIG. 41D

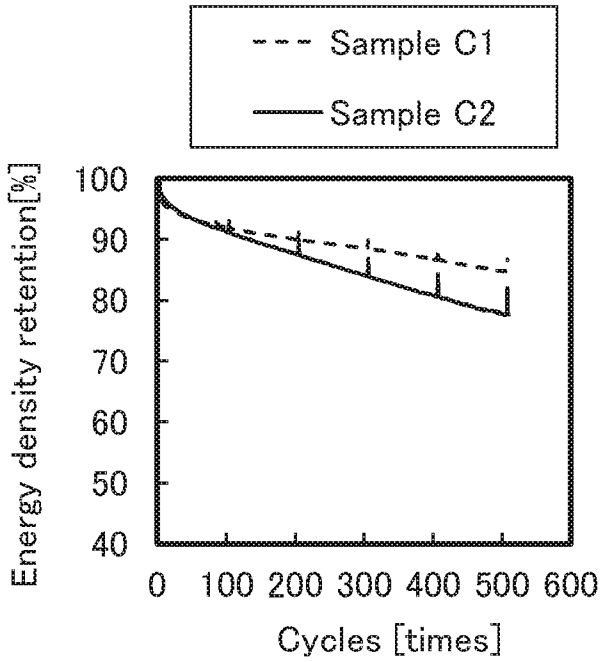


FIG. 42A

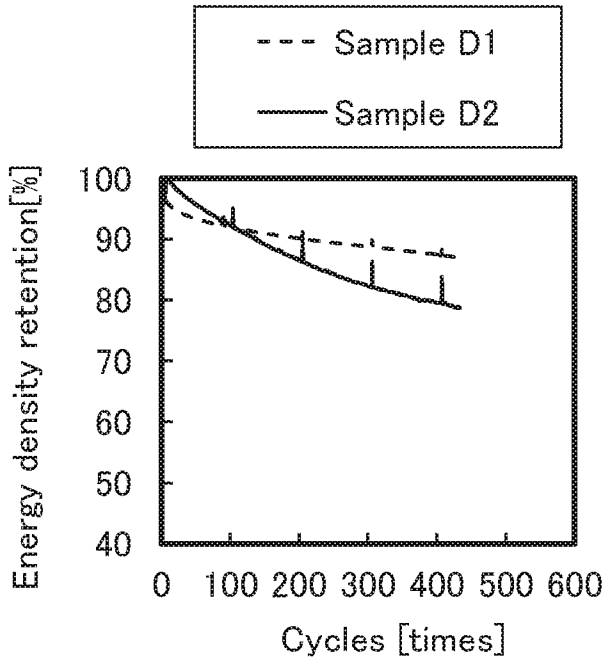


FIG. 42B

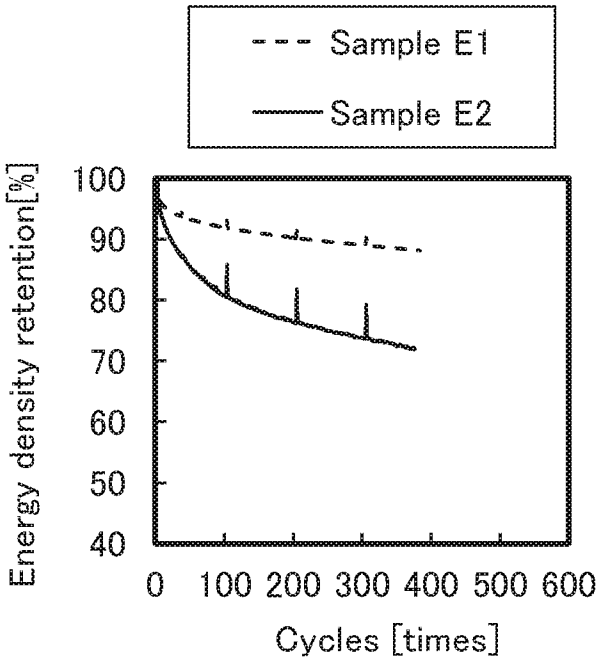


FIG. 42C

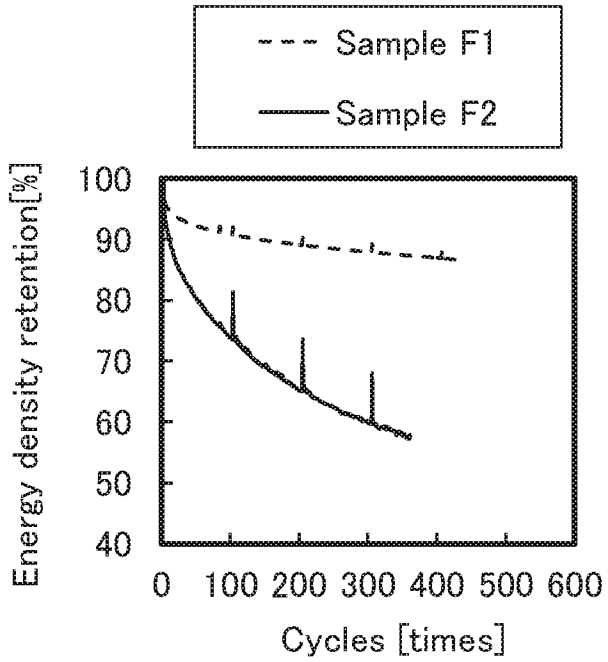


FIG. 42D

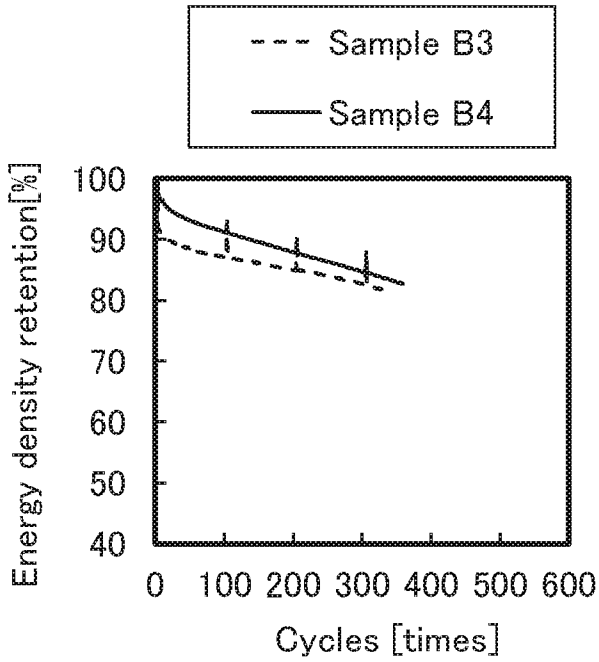


FIG. 43A

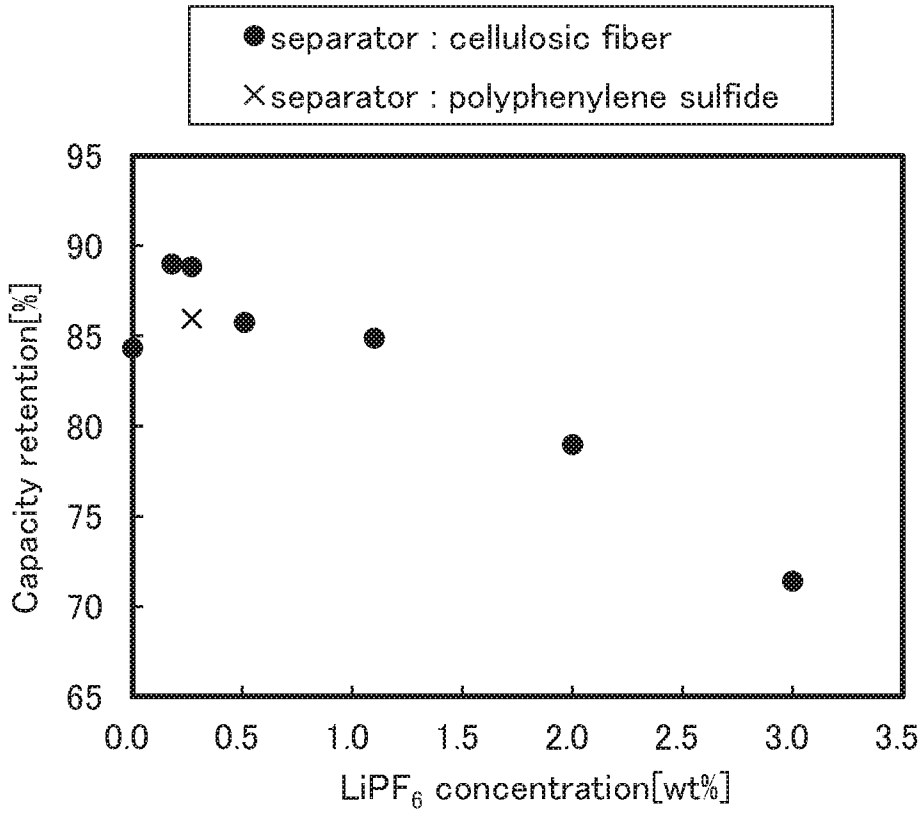


FIG. 43B

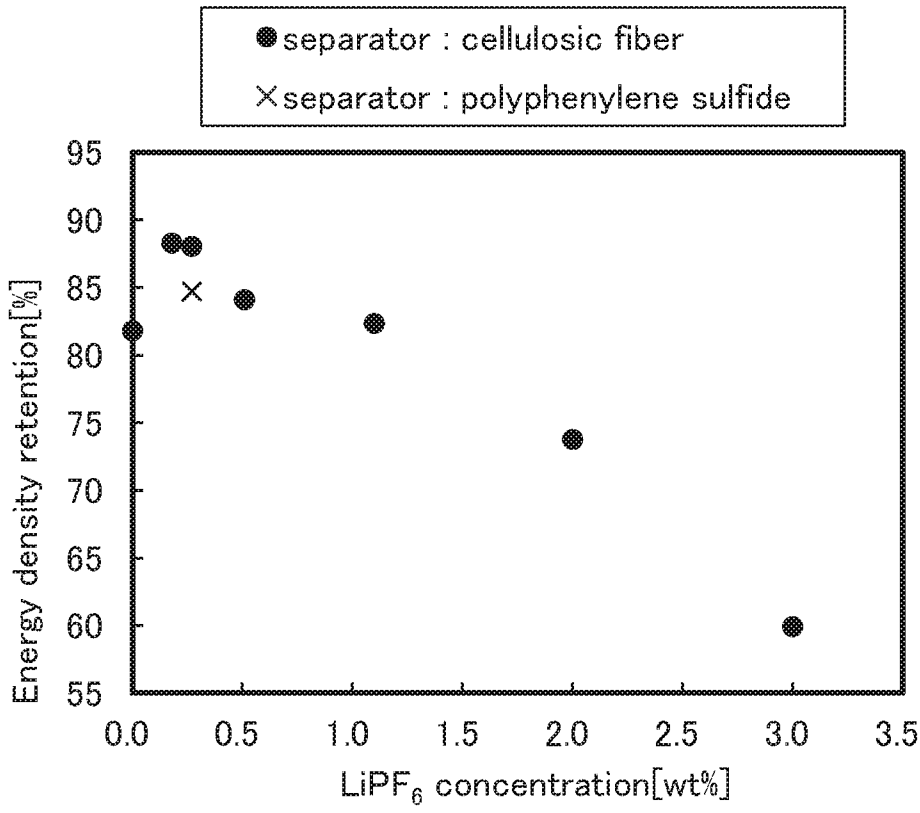


FIG. 44A

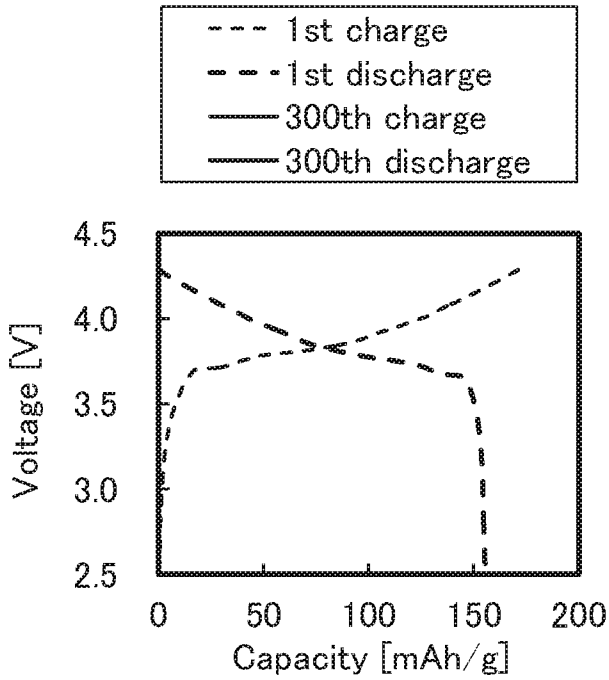


FIG. 44B

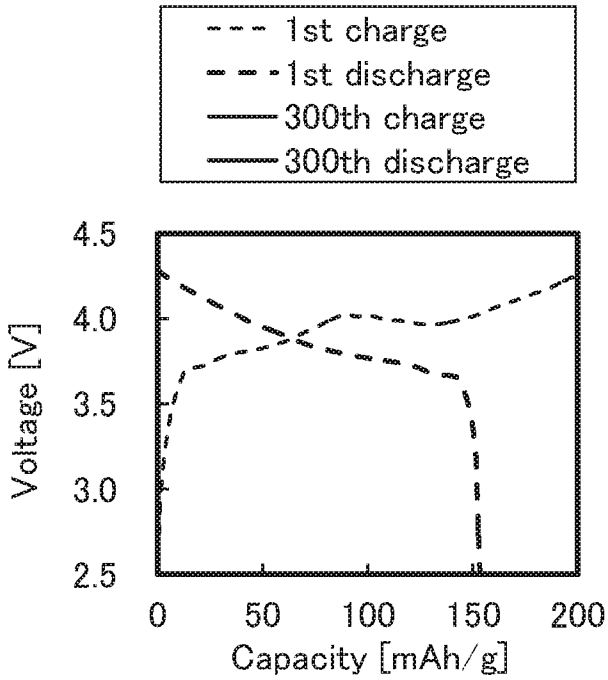


FIG. 44C

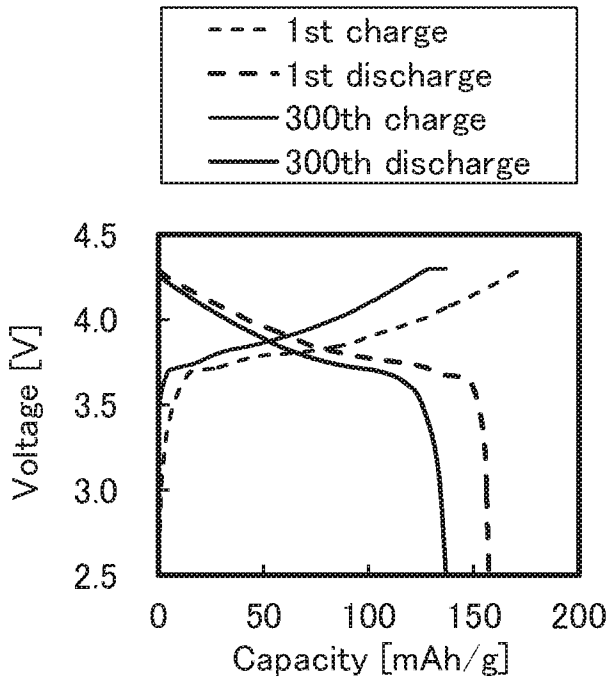


FIG. 44D

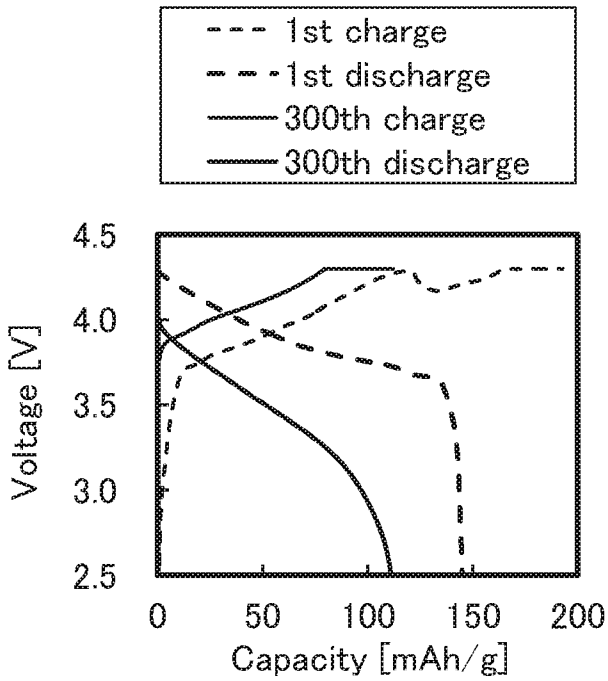


FIG. 45A

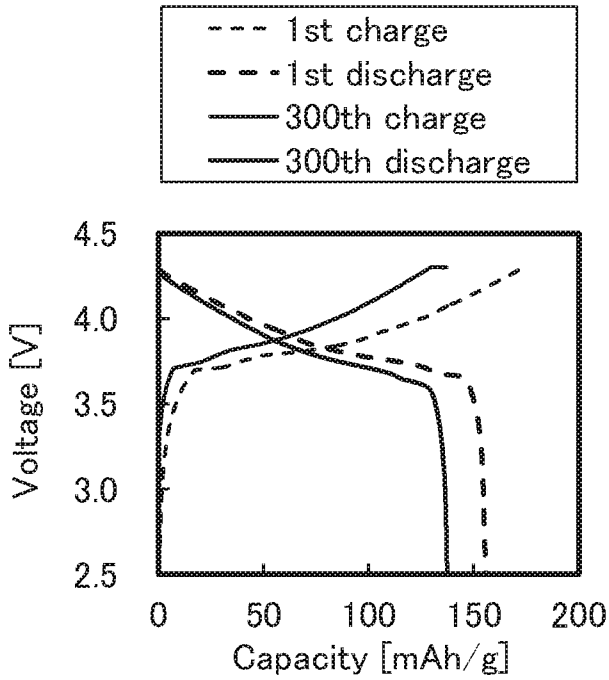


FIG. 45B

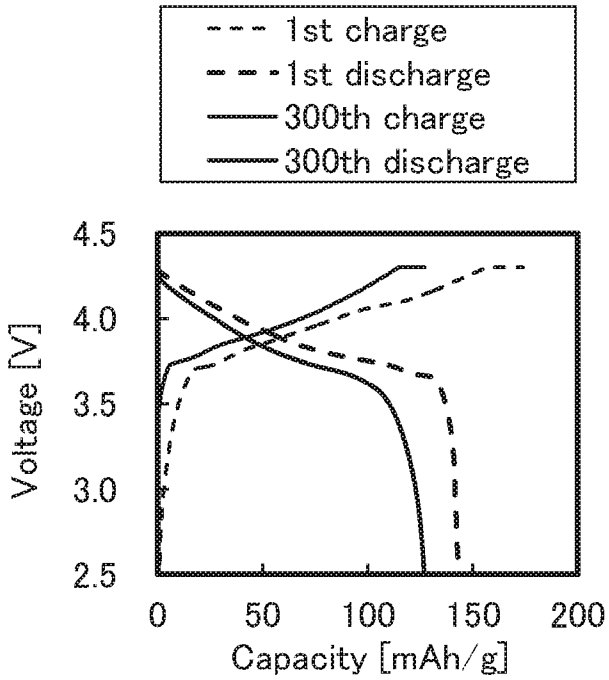


FIG. 46A

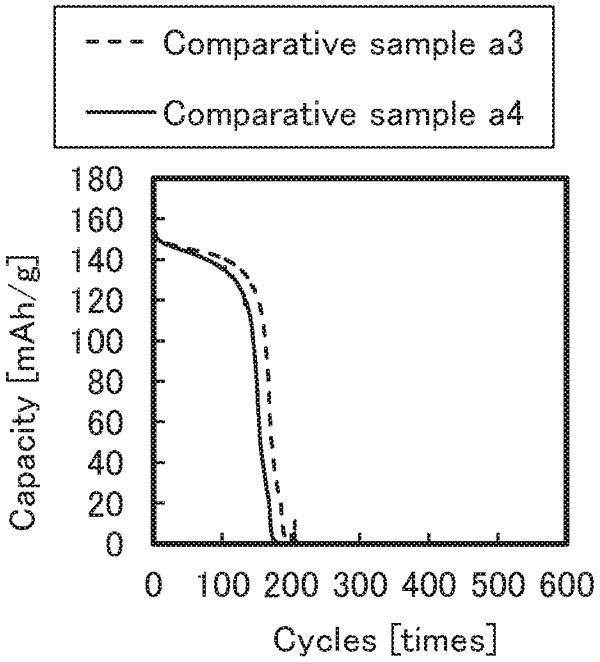


FIG. 46B

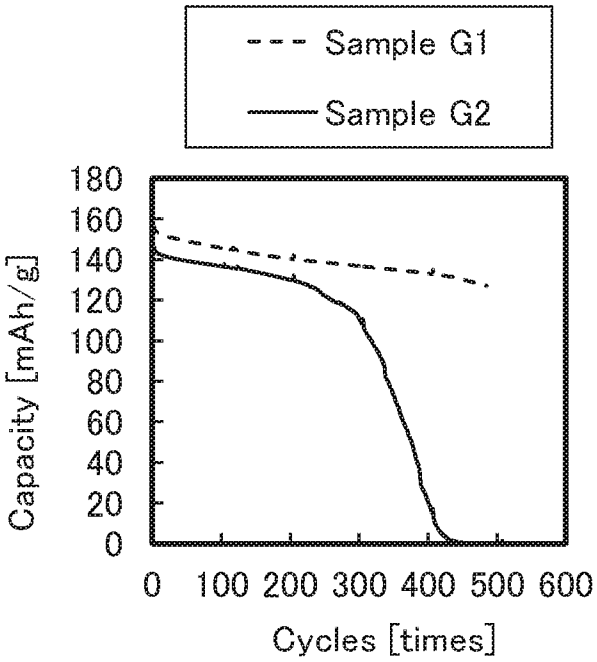


FIG. 46C

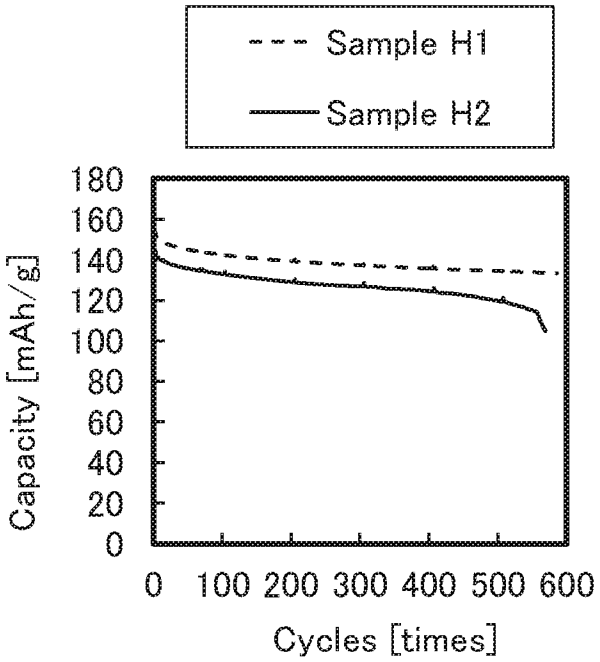


FIG. 47A

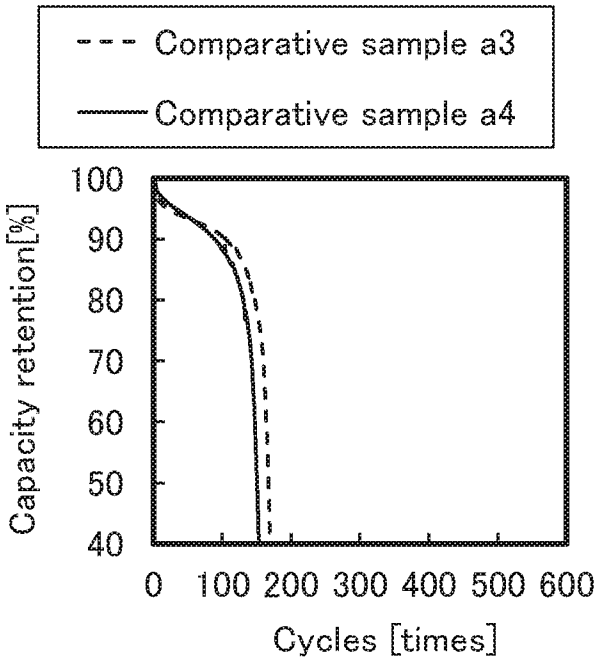


FIG. 47B

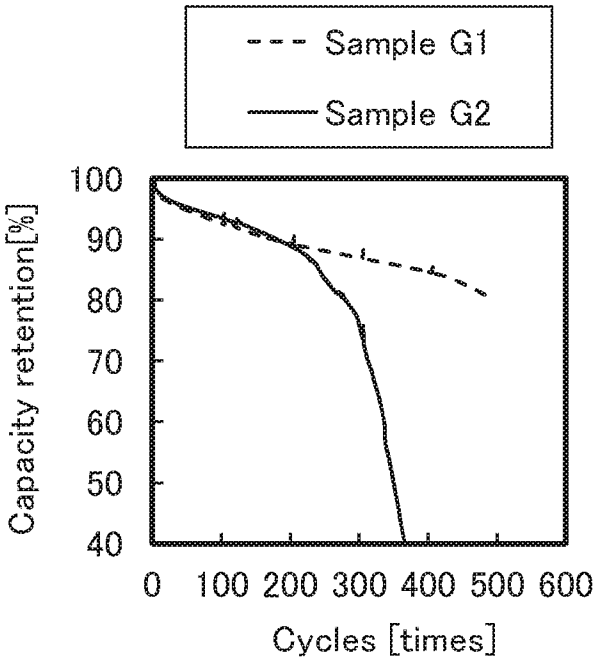


FIG. 47C

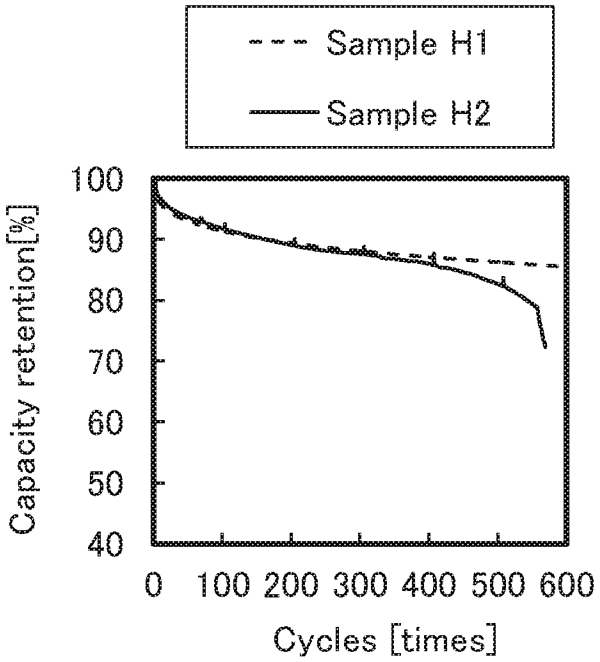


FIG. 48A

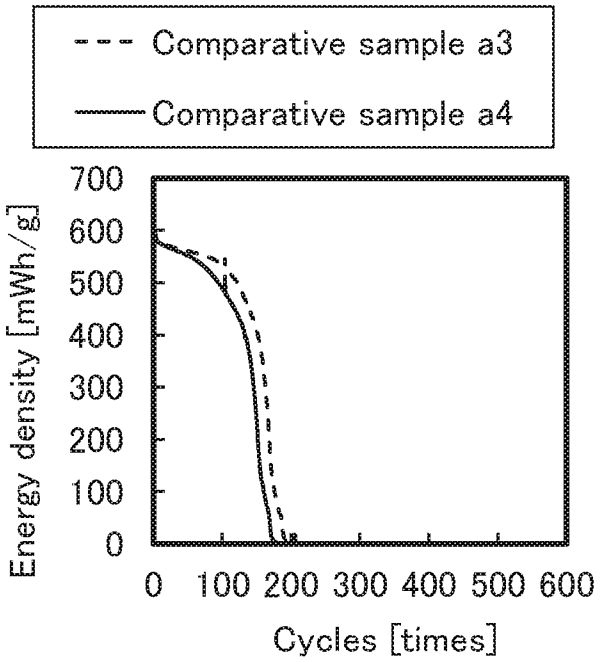


FIG. 48B

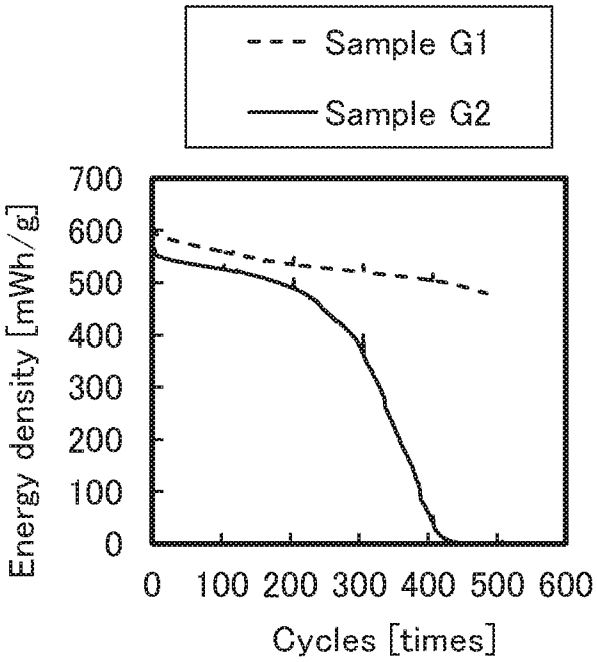


FIG. 48C

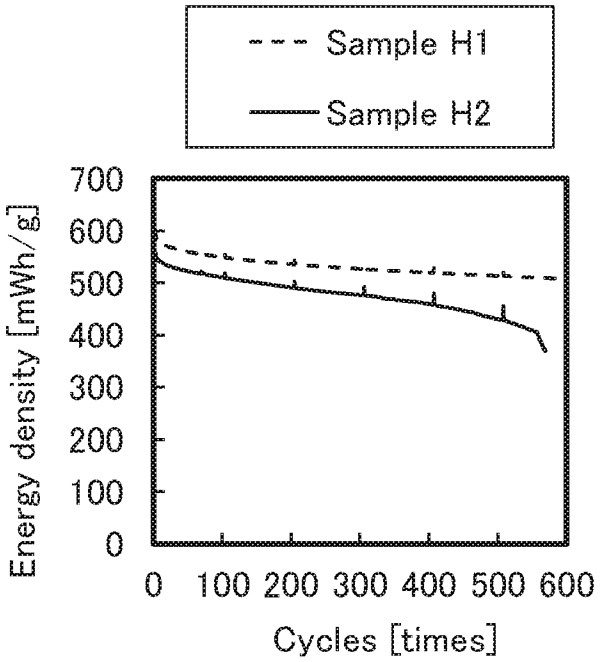


FIG. 49A

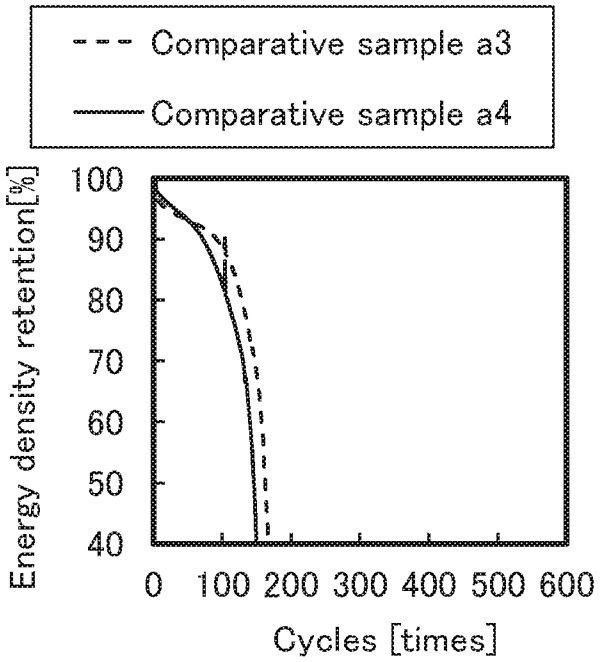


FIG. 49B

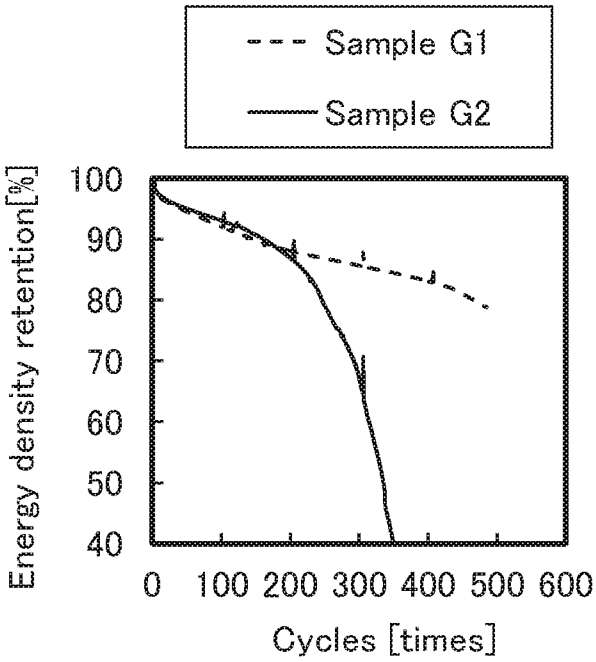


FIG. 49C

(D)

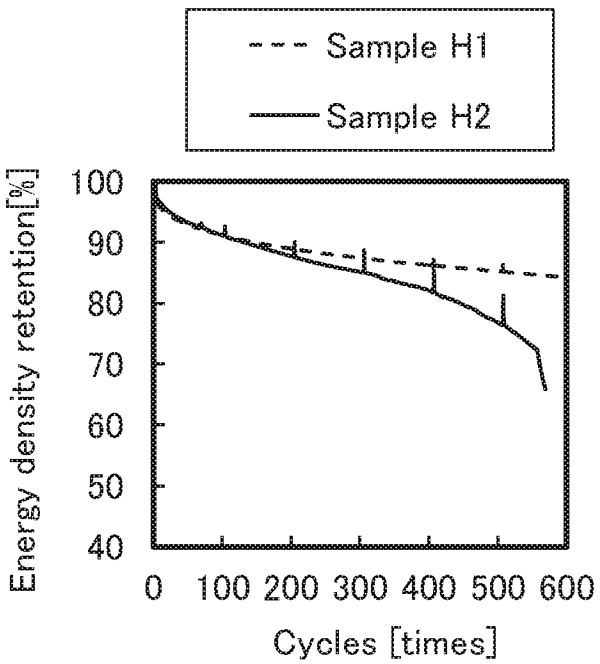


FIG. 50A

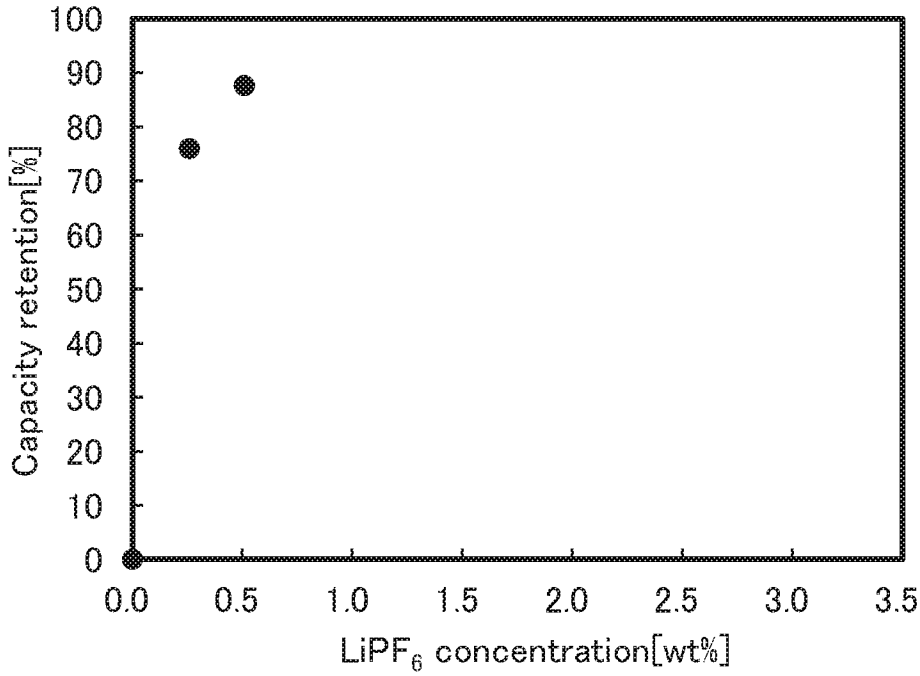


FIG. 50B

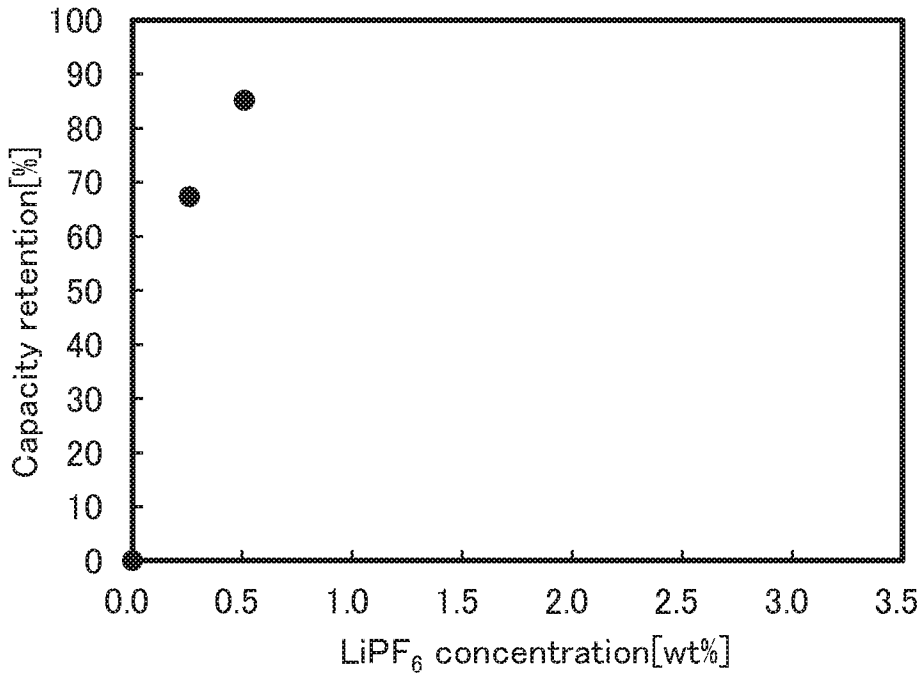


FIG. 51

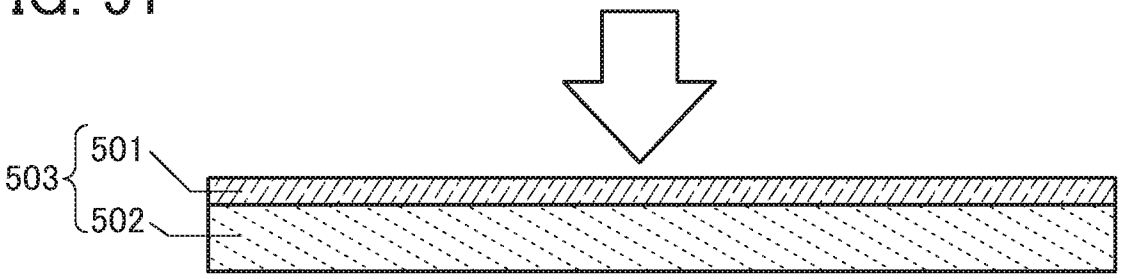


FIG. 52A

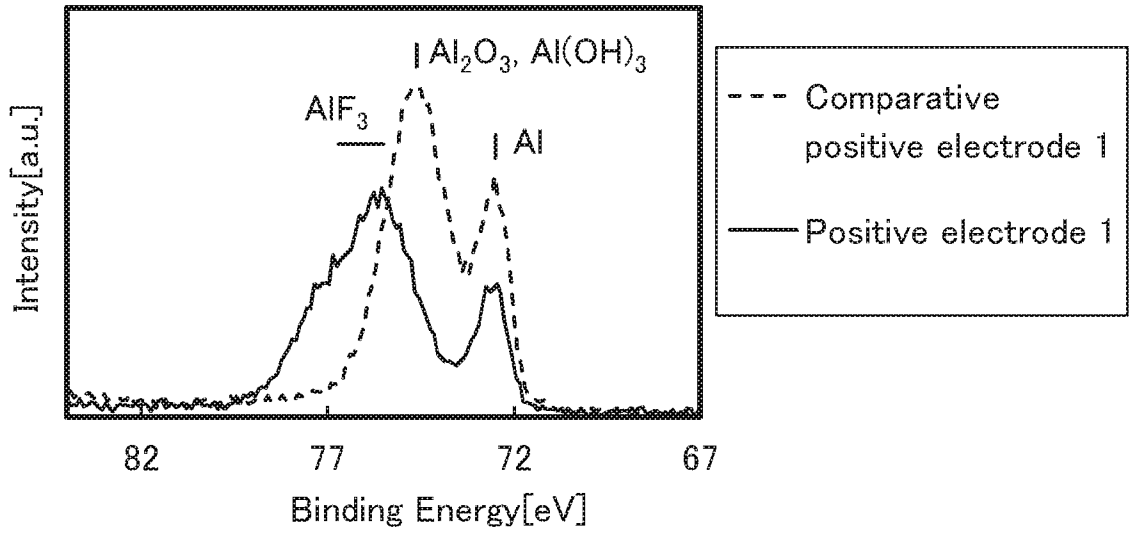


FIG. 52B

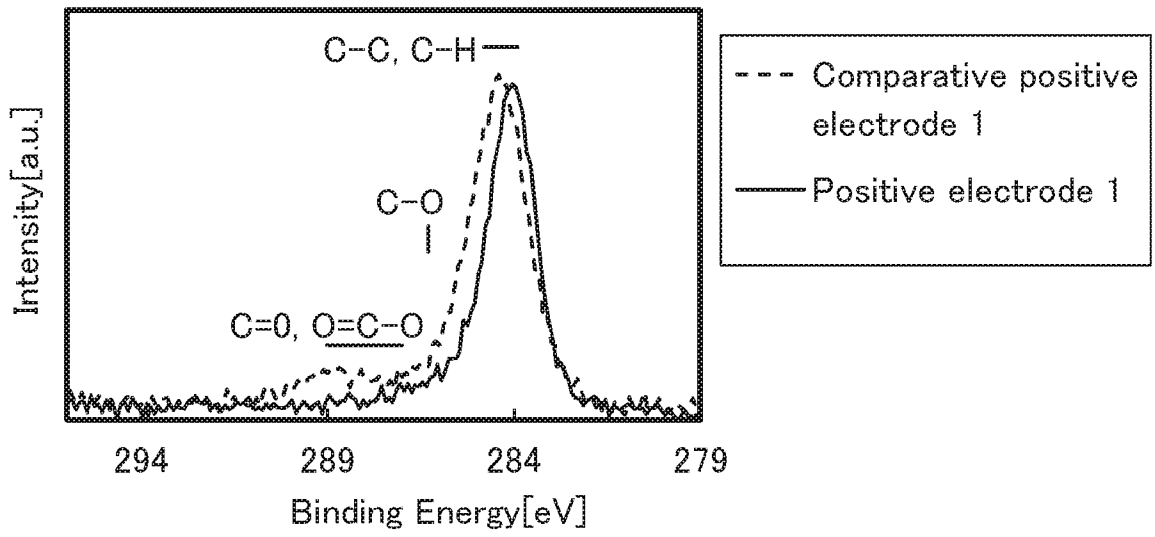


FIG. 52C

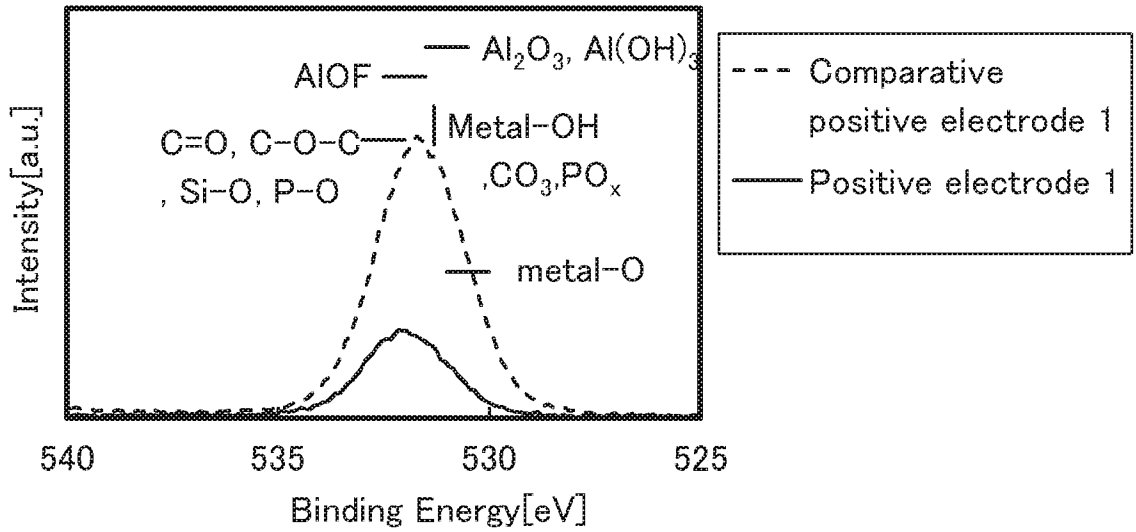


FIG. 53A

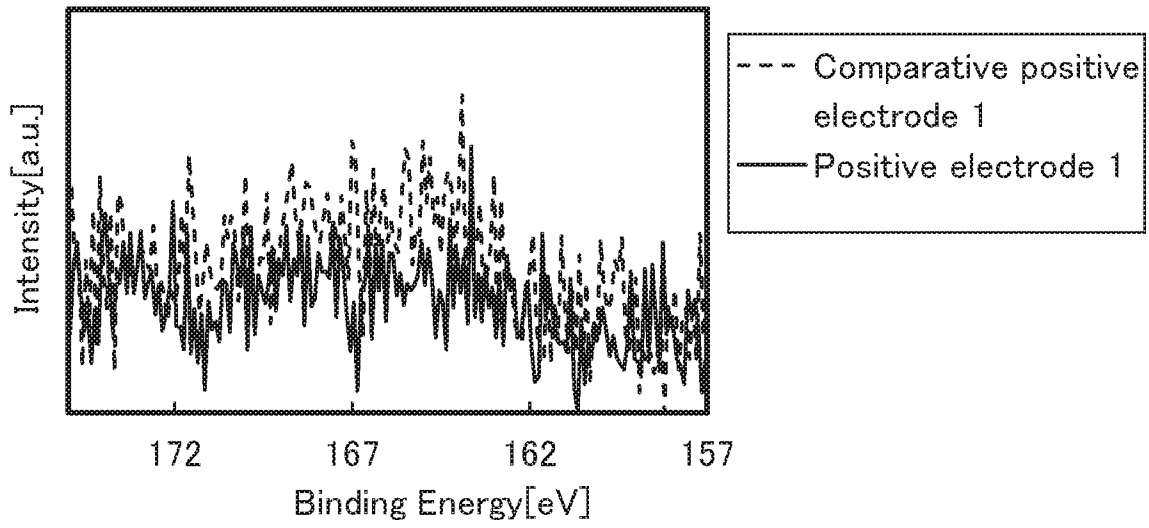


FIG. 53B

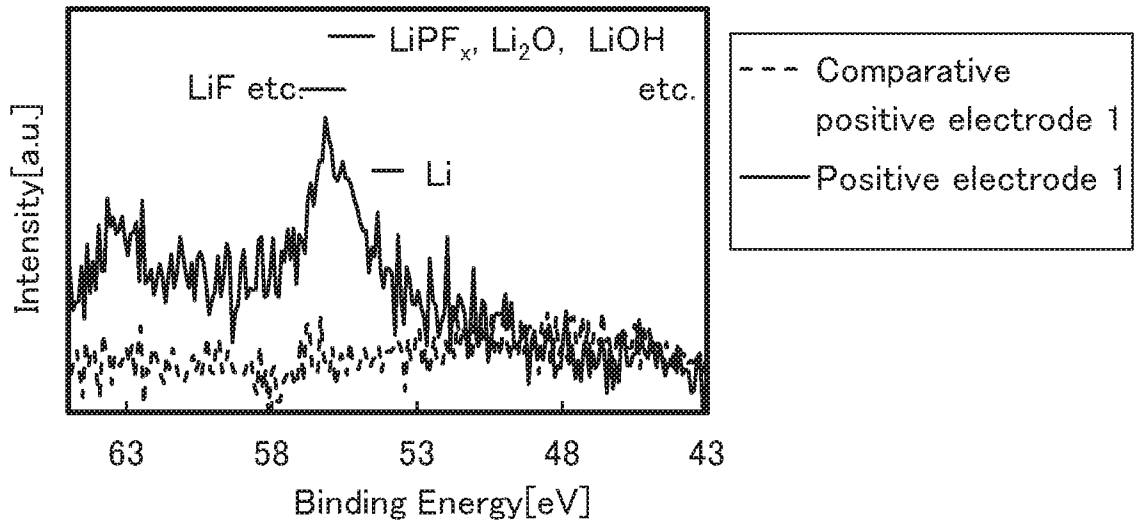


FIG. 53C

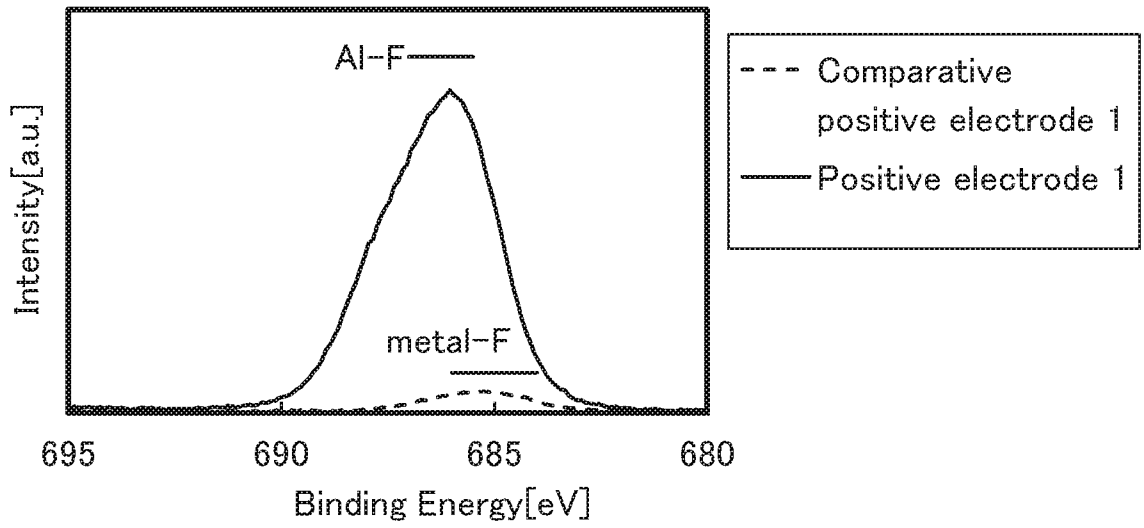


FIG. 54A

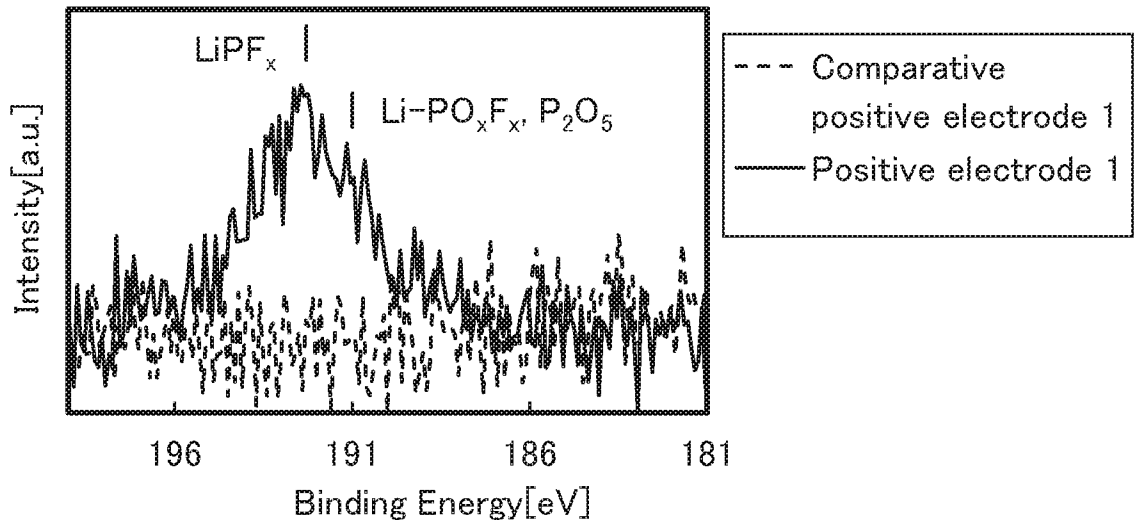


FIG. 54B

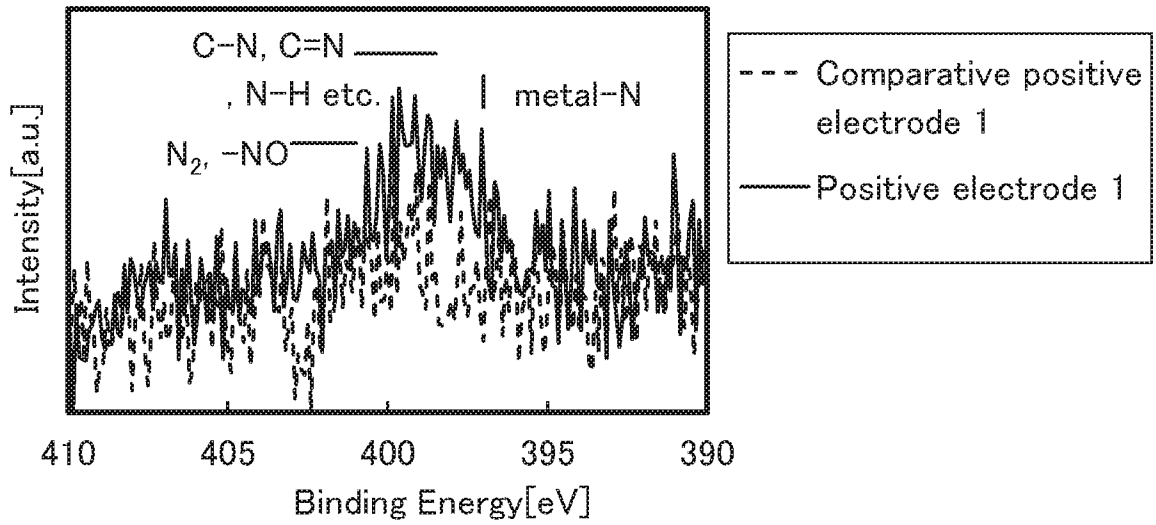


FIG. 54C

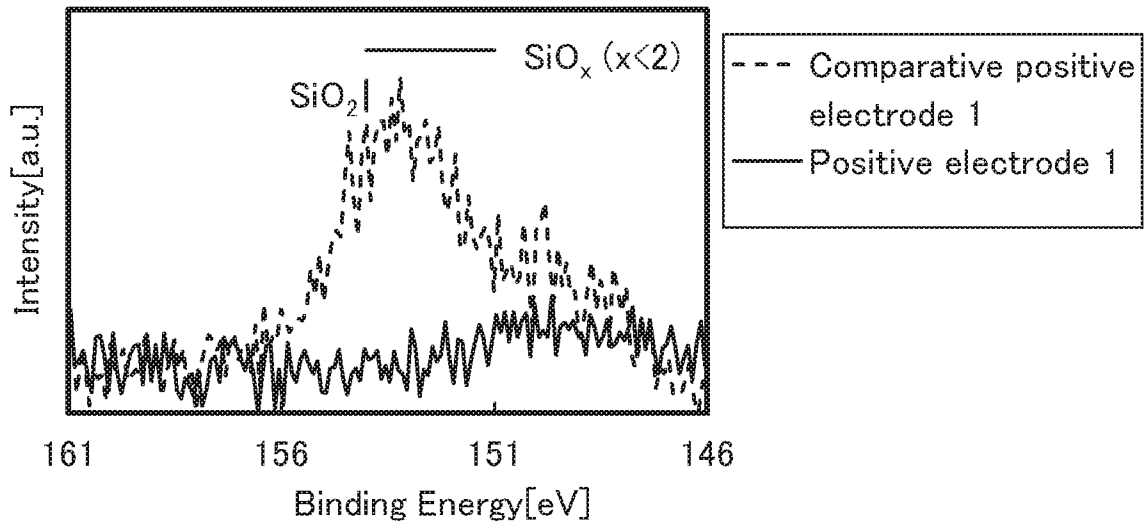


FIG. 55A

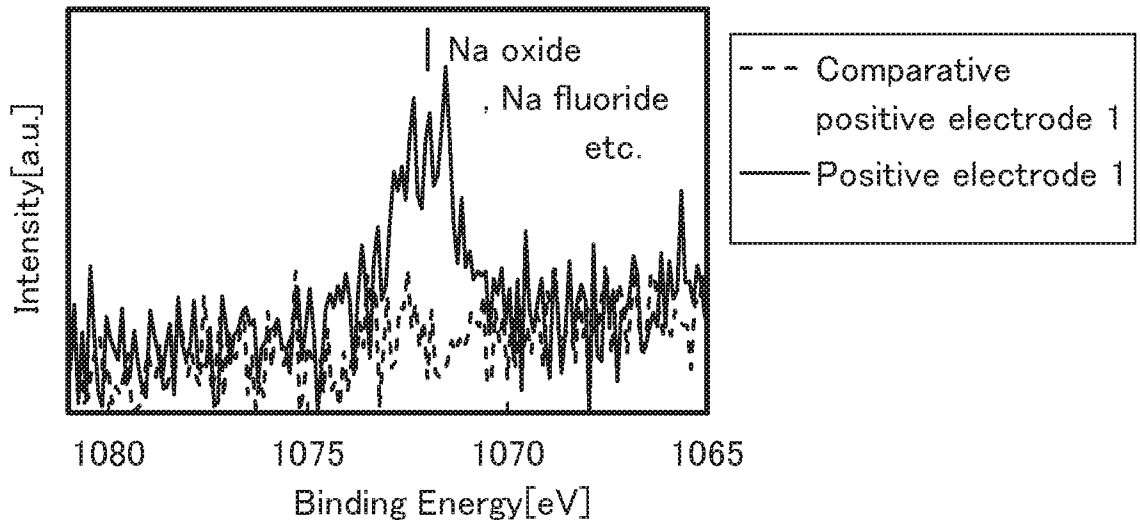


FIG. 55B

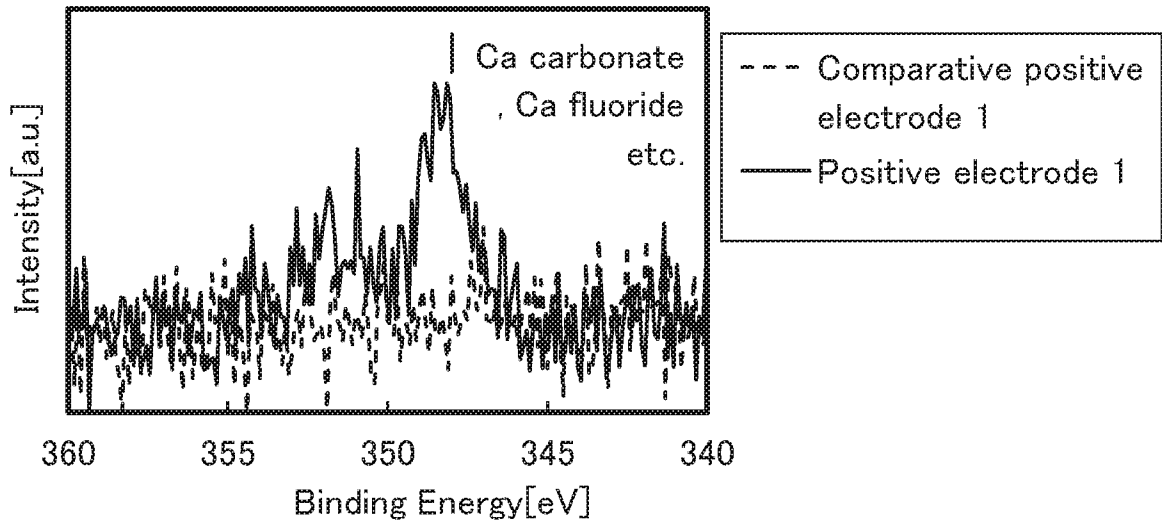


FIG. 56A

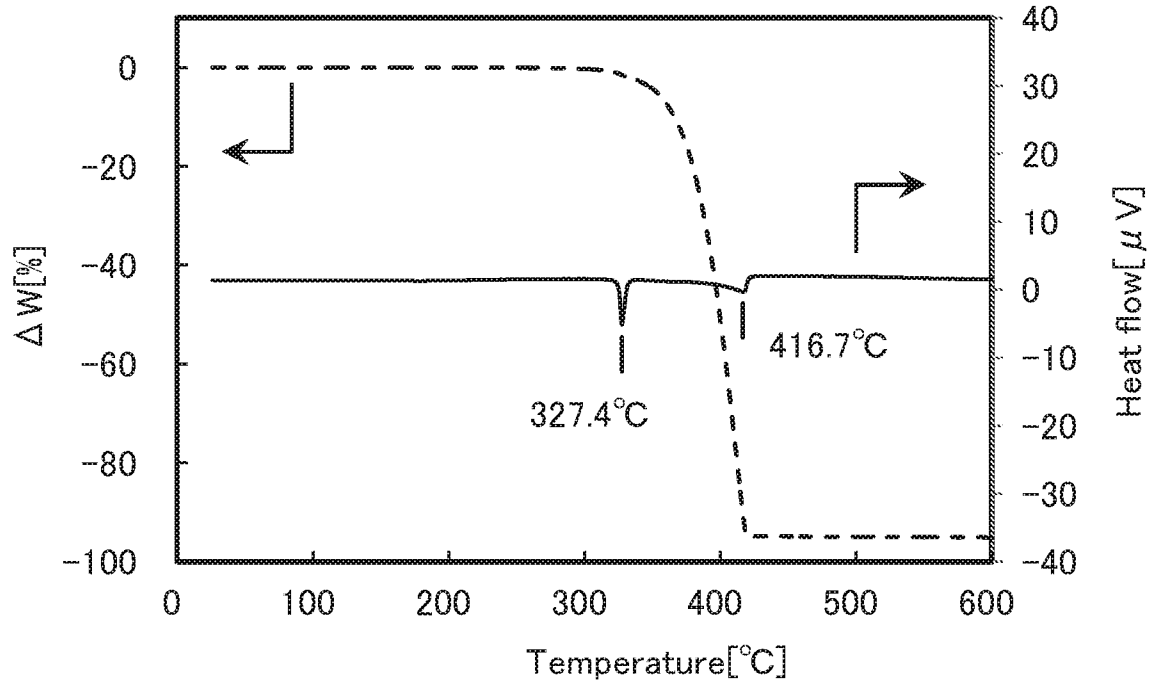


FIG. 56B

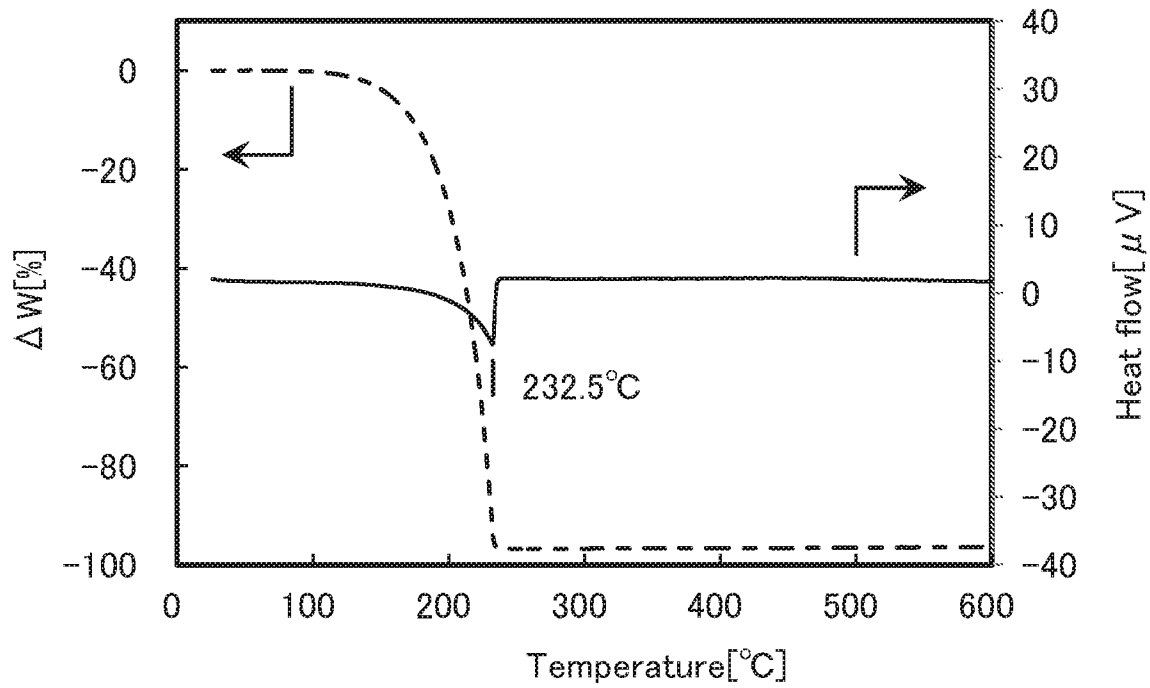
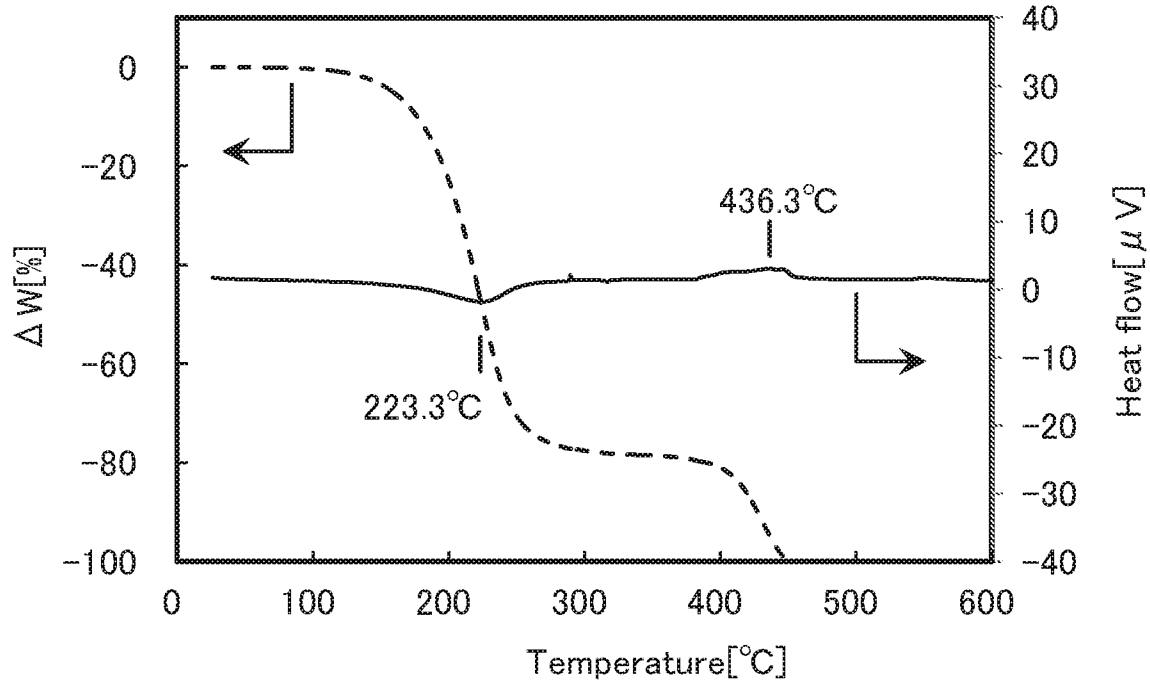


FIG. 57


0
-20
-40
-60
-80
-100
ΔW[%]
40
30
20
10
0
-10
-20
-30
-40
Heat flow[μV]
436.3°C
223.3°C
0
100
200
300
400
500
600
Temperature[°C]

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/057316

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. See extra sheet

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. H01M10/0568, H01G11/52, H01G11/62, H01M2/02, H01M2/10, H01M2/16, H01M4/66, H01M10/0525, H01M10/0569

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 1971-2018
Registered utility model specifications of Japan 1996-2018
Published registered utility model applications of Japan 1994-2018

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.
Y	JP 11-185807 A (SANYO ELECTRIC CO., LTD.) 1999.07.09, Claims, Paragraphs0001-0005,0008, 0014-0021, Examples (No Family)	1-12
Y	JP 2010-97835 A (MITSUBISHI CHEMICAL CORPORATION) 2010.04.30, Paragraph0029 (No Family)	1-12
Y	JP 2015-228359 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 2015.12.17, Claims, Paragraphs0017-0024 & US 2017/0047571 A1, Claims, Paragraphs 0041-0048 & WO 2015/166944 A1 & DE 112015002091 T & KR 10-2016-0146697 A & CN 106463684 A	2,8-12

☑ 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
15.02.2018	27.02.2018

Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	MIYATA, Toru Telephone No. +81-3-3581-1101 Ext. 3477

4X 7878

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/057316

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2015-130331 A (SEMICONDUCTOR ENERGY LABORATORY CO., LTD.) 2015.07.16, Paragraphs0006,0134-0137, Figure15 & US 2015/0155530 A1, Paragraphs0011,0164-0167, Figure15	6-7,11-12
A	JP 2007-207650 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 2007.08.16, Claims, Paragraphs 0002-0014,0030-0036, Examples (No Family)	1-12
A	JP 11-7962 A (JAPAN STORAGE BATTERY CO., LTD.) 1999.01.12, Claims, Paragraphs0002-0006, 0024-0028,0041-0043 (No Family)	1-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/057316

CLASSIFICATION OF SUBJECT MATTER
H01M10/0568(2010.01)i, H01G11/52(2013.01)i, H01G11/62(2013.01)i,
H01M2/02(2006.01)i, H01M2/10(2006.01)i, H01M2/16(2006.01)i,
H01M4/66(2006.01)i, H01M10/0525(2010.01)i, H01M10/0569(2010.01)i