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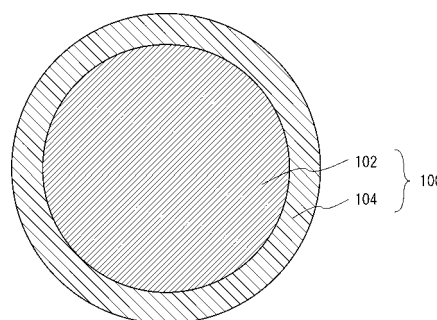
(54) [Title of the invention] Power storage device

(57) [Abstract]

[Problems] One of the issues is to obtain a power storage device with a large capacity, high discharge voltage, and high energy density.

[Means for solving] A power storage device having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron. The formation of the surface layer of the positive electrode active material in a second region comprising iron can reduce the energy barrier in insertion and removal of lithium at the positive electrode active material surface.

[Representative drawing] Figure 1



[Scope of patent claims]

[Claim 1]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

[Claim 2]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

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A power storage device characterized by a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

[Claim 3]

In Claim 2, a power storage device characterized in that the phosphate compound comprising lithium and one or more of manganese, cobalt, and nickel comprises a region having an olivine structure.

[Claim 4]

In Claim 2 or 3, a power storage device characterized in that the phosphate compound comprising the lithium and iron comprises a region having an olivine structure.

[Claim 5]

In any one of Claims 1 to 4, a power storage device characterized in that the first region and the second region of the positive electrode active material coincide in the axial direction of the crystal lattice.

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[Claim 6]

In any one of Claims 1 to 5, a power storage device characterized in that the positive electrode active material is a particulate.

[Claim 7]

In any one of Claims 1 to 5, a power storage device characterized in that the first region and the second region are membrane-like.

[Claim 8]

In Claim 7, a power storage device characterized in that the first region has a plurality of regions in the positive electrode active material.

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[Claim 9]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

A power storage device characterized by the positive electrode material being in particulate form, being formed of a compound containing lithium, iron, and one or more of manganese, cobalt, and nickel, and the concentration of iron being higher in the surface layer than in the center of the positive electrode active material.

[Claim 10]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

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A power storage device characterized by the positive electrode material being in particulate form, being formed of a compound containing lithium, iron, and one or more of manganese, cobalt, and nickel, and the concentration of iron being higher in the surface layer than in the center of the positive electrode active material.

A power storage device, wherein the second part of the positive electrode active material has a higher concentration of iron than the first part, and the first part is closer to the center than the second part.

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[Claim 11]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

A power storage device characterized by the positive electrode material being in membrane form, being formed of a compound containing lithium, iron, and one or more of manganese, cobalt, and nickel, and the concentration of iron being higher in the surface layer than in the center of the positive electrode active material.

and the surface layer part of the positive electrode active material having a higher iron concentration than the side closer to the positive electrode current collector.

[Claim 12]

A power storage device characterized by having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel, and a second region formed of a compound covering the first region and comprising lithium and iron.

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A power storage device characterized by the positive electrode material being in membrane form, being formed of a compound containing lithium, iron, and one or more of manganese, cobalt, and nickel, and the concentration of iron being higher in the surface layer than in the center of the positive electrode active material.

A power storage device, wherein the second part of the positive electrode active material has a higher concentration of iron than the first part, and the first part is closer to the center than the second part.

A power storage device characterized by the second part second closer to the surface than the first part.

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[Claim 13]

In any one of Claims 9 through 12, a power storage device characterized in that the compound comprising of lithium and iron and one or more of manganese, cobalt, and nickel is a phosphate compound.

[Claim 14]

In Claim 13, a power storage device characterized in that the phosphate compound comprising lithium and one or more of manganese, cobalt, and nickel comprises a region having an olivine structure.

[Detailed description of the invention]

[Technical field]

[0001]

One aspect of the disclosed invention relates to a power storage device.

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[Background technology]

[0002]

The field of portable electronic devices, such as personal computers and mobile phones, is making significant progress. Portable electronic devices require compact, lightweight, reliable, high energy density and chargeable power storage devices. Such power storage devices are known, for example, as lithium ion secondary batteries. The development of electric propulsion vehicles equipped with secondary batteries is also rapidly progressing due to the increasing awareness of environmental and energy problems.

[0003]

In lithium ion secondary batteries, phosphate compounds having olivine structures including lithium (Li), such as lithium iron phosphate (LiFePO_4), lithium manganese phosphate (LiMnPO_4), lithium cobalt phosphate (LiCoPO_4), lithium nickel phosphate (LiNiPO_4), and iron (Fe), manganese (Mn), and cobalt (Co) or nickel (Ni) are known as positive electrode active materials (see Patent document 1, Non-Patent document 1, and Non-Patent document 2).

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[0004]

Since lithium iron phosphate is represented by the formula LiFePO_4 , and the FePO_4 with all lithium removed is stable, this realizes safe high capacity.

(Prior art literature)

(Patent literature)

[0005]

[Patent literature 1] Japanese Unexamined Patent Application Publication H11-25983

[Non-patent literature]

[0006]

[Non-patent literature 1] Byoungwoo Kang, Gerbrand Ceder, Nature, (UK), March 2009, Vol. 458, p. 190-193

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[Non-patent literature 2] F. Zhou et al. Electrochemistry Communications, (Netherlands), November 2004, Volume 6, Issue 11, p.

1144-1148

[Outline of the invention]

[Problem to be solved by the invention]

[0007]

The positive electrode active material formed of a phosphate compound having an olivine structure comprising lithium and manganese as described above having a higher discharge potential compared to the positive electrode active material formed of a phosphate compound having an olivine structure comprising lithium and iron has been realized. Also, phosphate compounds having an olivine structure comprising lithium and manganese (e.g., the general formula LiMnPO_4) and phosphate compounds having an olivine structure comprising lithium and iron (e.g., the general formula LiFePO_4) have approximately the same theoretical capacity. Based on these results, it is expected that positive electrode active materials formed of phosphate compounds having an olivine structure including lithium and manganese have high energy density.

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[0008]

However, even if the positive electrode active material formed from phosphate compounds having an olivine structure including lithium and manganese is used, the expected capacity has not been realized. One cause of this may be the presence of an energy barrier when inserting and removing lithium at the active material surface.

[0009]

In view of the above-mentioned issues, in one of the aspects of the disclosed invention, the problem is to obtain a power storage device with a large capacity, high discharge voltage, and high energy density.

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[Means for solving the problem]

[0010]

One aspect of the Present Invention is a power storage device having a positive electrode having a positive electrode active material on a positive electrode current collector, and a positive electrode and a negative electrode facing each other with an electrolyte interposed between, the positive electrode active material having a first region formed of a compound comprising lithium (Li) and one or more of manganese (Mn), cobalt (Co), and nickel (Ni), and a second region formed of a compound covering the first region and comprising lithium (Li) and iron (Fe).

[0011]

An aspect of the Present Invention is also a positive electrode active material for a power storage device having a first region formed of a compound comprising lithium and one or more of manganese, cobalt and nickel, and a second region covering the first region and formed of a compound comprising lithium and iron.

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[0012]

The positive electrode active material is in particulate form and the positive electrode active material layer described below may comprise a plurality of particles.

[0013]

Also, the first region and the second region are membrane-like, and the positive electrode active material layer described below may be formed of a membrane-like positive electrode active material.

[0014]

In particulate positive electrode active material or membrane positive electrode active material, the first region may employ a phosphate compound comprising of lithium and one or more of manganese, cobalt, and nickel. The second region may also use a phosphate compound comprising lithium and iron. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, and the phosphate compounds comprising one or more of lithium and manganese, cobalt, and nickel forming the first region may include regions having an olivine structure. The phosphate compound comprising lithium and iron forming the second region may also include a region having an olivine structure. In addition, both the first region and the second region may include a phosphate compound having an olivine structure. Also, the first region may be monocrystalline, polycrystalline, microcrystalline, or may contain amorphous. The second region may be monocrystalline, polycrystalline, microcrystalline, or may contain amorphous.

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[0015]

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In particulate positive electrode active material or membrane active material, the second region may be membrane-like and may cover at least a part of the first region. The second region preferably covers 30% or more of the surface of the first region, and more preferably 100% of the surface of the first region.

[0016]

Phosphate compounds containing lithium and one or more of manganese, cobalt, and nickel may also contain substances represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (y_1 is 0 to less than 1). Phosphate compounds containing lithium and iron may also contain substances represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) (y_2 is 0 to 1 or less). M, Me and Mn may take a single element or multiple elements of Mn, Co, and Ni. In the case of multiple elements, the ratio of the constituent elements can be arbitrary.

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[0017]

For substances represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (x_1 is 0 to less than 1), each case where M is a single element or a plurality of elements is shown below.

[0018]

If M is a single element of Mn, Co, and Ni, then the material forming the first region is represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_a(\text{M}_1)_b\text{PO}_4$ (x_1 is 0 to 1 or less) (M_1 is either Mn, Co, or Ni) ($a + b = 1$, a is 0 to less than 1, and b is 0 to 1).

[0019]

If M is two elements of Mn, Co, and Ni, the material forming the first region is represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_a(\text{M}_1)_b(\text{M}_2)_c\text{PO}_4$ (x_1 is 0 to 1) ($\text{M}_1 \neq \text{M}_2$, M_1 , and M_2 are either Mn, Co, and Ni, respectively) ($a + b + c = 1$, a is 0 to less than 1, b is 0 to less than 1, and c is 0 to less than 1).

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[0020]

If M is the three elements of Mn, Co, and Ni, the material forming the first region is represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_a(\text{M}_1)_b(\text{M}_2)_c(\text{M}_3)_d\text{PO}_4$ (x_1 is 0 to 1) ($\text{M}_1 \neq \text{M}_2$, $\text{M}_1 \neq \text{M}_3$, $\text{M}_2 \neq \text{M}_3$, and M_1 , M_2 and M_3 are each one of Mn, Co and Ni) ($a + b + c + d = 1$, a is 0 to less than 1, b is 0 to less than 1, c is 0 to less than 1, and d is 0 to less than 1).

[0021]

For substances represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) (y_2 is 0 to less than 1), each case where Me is a single element or a plurality of elements is shown below.

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[0022]

If Me is a single element of Mn, Co, and Ni, then the material forming the second region is represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_a(\text{Me}_1)_b\text{PO}_4$ (x_2 is 0 to 1 or less) (Me_1 is either Mn, Co, or Ni) ($a + b = 1$, a is 0 to less than 1, and b is 0 to less than 1).

[0023]

If Me is two elements of Mn, Co, and Ni, the material forming the second region is represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_a(\text{Me}_1)_b(\text{Me}_2)_c\text{PO}_4$ (x_2 is 0 to 1) ($\text{Me}_1 \neq \text{Me}_2$, Me_1 and Me_2 are either Mn, Co, and Ni, respectively) ($a + b + c = 1$, a is 0 to less than 1, b is 0 to less than 1, and c is 0 to less than 1).

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[0024]

If Me is the three elements of Mn, Co, and Ni, the material forming the second region is represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_a(\text{Me}_1)_b(\text{Me}_2)_c(\text{Me}_3)_d\text{PO}_4$ (x_2 is 0 to 1 or less) ($\text{Me}_1 \neq \text{Me}_2$, $\text{Me}_1 \neq \text{Me}_3$, $\text{Me}_2 \neq \text{Me}_3$, and Me_1 , Me_2 and Me_3 are each one of Mn, Co and Ni) ($a + b + c = 1$, a is 0 to less than 1, b is 0 to less than 1, c is 0 to less than 1, and d is 0 to less than 1).

[0025]

Substances represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is from 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (y_1 is from 0 to less than 1) may be olivine structures.

[0026]

Substances represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) (y_2 is from 0 to 1 or less) may be olivine structures.

[0027]

In addition, the axial alignment of the crystal lattice of the first region and the second region makes it easy to charge and discharge because the diffusion path (channel) of lithium is aligned one-dimensionally without bending. It should be noted that the specifications include cases where the difference in the axial direction of the crystal lattice between the first region and the second region is generally equal to or less than 10 degrees.

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[0028]

Furthermore, it is more desirable that there is a concentration gradient of the transition metal between the first region and the second region such that the lattice constant varies continuously between the first region and the second region. Continuous changes in lattice constants reduce stress and strain, making it easier for lithium to diffuse.

[0029]

For particulate positive electrode active materials, the particle size is from 10 nm to 200 nm, preferably from 20 nm to 80 nm. Since the particle size of the positive electrode active material is within the above range, the positive electrode active material particles are small, making it easier to insert and detach the lithium ion, improving the rate characteristics of the secondary battery, and enabling charging and discharging in a short time.

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[0030]

In addition, in the case of particulate positive electrode active material, the second region is membrane-like, so even if the particles of the positive electrode active material are small, it is possible to make a thin film. By making it a thin coating, the percentage occupied by the second area can be reduced, and the decrease in energy density can be suppressed.

[0031]

In addition, for particulate positive electrode active material or membrane active material, the film thickness of the second region is preferably 1 nm to 8 nm, and the percentage occupied by the second region of the positive electrode active material is low, so it is possible to suppress the decrease in energy density per unit weight.

[0032]

One aspect of the Present Invention is a particulate positive electrode active material formed of a compound comprising lithium (Li) and iron (Fe) and one or more of manganese (Mn), cobalt (Co), and nickel (Ni), with a higher concentration of iron in the surface than in the center of the positive electrode active material.

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[0033]

One aspect of the Present Invention is a particulate positive electrode active material formed of a compound including lithium and iron and one or more of manganese, cobalt and nickel, where the second part has a higher iron concentration than the first part, and first part is closer to the center than the second part.

[0034]

The positive electrode active material is in particulate form and the positive electrode active material layer described below may comprise a plurality of particles.

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[0035]

One aspect of the Present Invention is a power storage device having a positive electrode having a positive electrode active material on the positive electrode current collector, and a positive electrode active material having a positive electrode and an opposing negative electrode via an electrolyte, wherein the positive electrode active material is membrane-like, wherein the positive electrode active material is formed of a compound comprising lithium (Li) and iron (Fe), and one or more of manganese (Mn), cobalt (Co), nickel (Ni), wherein the surface layer has a higher iron concentration than the side close to the positive electrode current collector of the positive electrode active material.

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[0036]

One aspect of the Present Invention has a positive electrode having a positive electrode active material on the positive electrode current collector and a positive electrode active material having a positive electrode and an opposing negative electrode via an electrolyte, wherein the positive electrode active material is membrane-like, wherein the positive electrode active material is formed of a compound comprising one or more of lithium, iron, manganese, cobalt, nickel, wherein the second part of the positive electrode active material has a higher concentration of iron than the first part, and wherein the second part is a power storage device closer to the surface than the first part.

[0037]

The positive electrode active material layer described below may be formed of a membrane-like positive electrode active material.

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[0038]

The particulate positive electrode active material or membrane positive electrode active material may employ a phosphate compound comprising of lithium and iron and one or more of manganese, cobalt, and nickel. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, and the phosphate compounds comprising lithium and iron and one or more of manganese, cobalt, and nickel may include regions having an olivine structure. Compounds containing lithium and iron and one or more of manganese, cobalt, and nickel may be monocrystalline, polycrystalline, microcrystalline, or may contain amorphous.

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[0039]

Phosphate compounds containing lithium and iron and one or more of manganese, cobalt, and nickel may also contain substances represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (y is 0 to less than 1). M may take a single element or multiple elements of Mn, Co, and Ni. In the case of multiple elements, the ratio of the constituent elements can be arbitrary.

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[0040]

For substances represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (y is 0 to less than 1), each case where M is a single element or a plurality of elements is shown below.

[0041]

If M is a single element of Mn, Co, and Ni, then the material forming the positive electrode active material is represented by the general formula $\text{Li}_{1-x}\text{Fe}_a(\text{M1})_b\text{PO}_4$ (x is 0 to 1 or less) (M1 is either Mn, Co, or Ni) ($a + b = 1$, a is 0 to less than 1, and b is 0 to less than 1).

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[0042]

If M is two elements of Mn, Co, and Ni, the material forming the positive electrode active material is represented by the general formula $\text{Li}_{1-x}\text{Fe}_a(\text{M1})_b(\text{M2})_c\text{PO}_4$ (x is 0 to 1) ($\text{M1} \neq \text{M2}$, M1 , and M2 are either Mn, Co, and Ni, respectively) ($a + b + c = 1$, a is 0 to less than 1, b is 0 to less than 1, and c is 0 to less than 1).

[0043]

If M is the three elements of Mn, Co, and Ni, the material forming the positive electrode active material is represented by the general formula $\text{Li}_{1-x}\text{Fe}_a(\text{M1})_b(\text{M2})_c(\text{M3})_d\text{PO}_4$ (x is 0 to 1) ($\text{M1} \neq \text{M2}$, $\text{M1} \neq \text{M3}$, $\text{M2} \neq \text{M3}$, and M1 , M2 and M3 are each one of Mn, Co and Ni) ($a + b + c + d = 1$, a is 0 to less than 1, b is 0 to less than 1, c is 0 to less than 1, and d is 0 to less than 1).

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[0044]

Substances represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1) (M is one or more of Mn, Co, and Ni) (y is greater than 0 and less than 1) may be olivine structures.

[Effect of the invention]

[0045]

According to one embodiment of the disclosed invention, a power storage device with a large capacity, high discharge voltage, and a large energy density can be obtained.

[Brief description of the drawings]

[0046]

[Figure 1] An example of a cross-sectional view of positive electrode active material (particle)

[Figure 2] An example of a cross-sectional view of positive electrode active material (particle)

[Figure 3] An example of a cross-sectional view of a power storage device

[Figure 4] An example of a cross-sectional view of a positive electrode including a positive electrode active material

[Figure 5] An example of a cross-sectional view of a positive electrode including a positive electrode active material 10

[Figure 6] An example of a cross-sectional view of a positive electrode including a positive electrode active material

[Figure 7] An example of a cross-sectional view of a positive electrode including a positive electrode active material

[Figure 8] An example of a cross-sectional view of a positive electrode including a positive electrode active material

[Figure 9] A diagram showing an example of a method of making a positive electrode comprising a positive electrode active material

[Figure 10] A diagram to illustrate an example of application of a power storage device

[Figure 11] A perspective view to illustrate an example of an application of a power storage device

[Figure 12] A diagram to illustrate an example of an application of a power storage device

[Figure 13] A diagram showing an example of the configuration of a wireless power supply system

[Figure 14] A diagram showing an example of the configuration of a wireless power supply system 20

[Mode For carrying out the invention]

[0047]

Embodiments of the invention will be described below with reference to the drawings. However, the Present Invention is not limited to the following description. It will be readily understood by those skilled in the art that various changes in form and details may be made without departing from the spirit and scope of the invention. Accordingly, the Present Invention is not to be construed solely as described in the following embodiments. In explaining the construction of the invention using drawings, the symbols that refer to the same are used in common between different drawings.

[0048]

It should be noted that the size, layer thickness, or region of each configuration shown in the drawings, etc. of each embodiment may be exaggerated and denoted for clarity. Therefore, it is not necessarily limited to its scale. 30

[0049]

It should be noted that terms using ordinals such as first, second, and third used in the specifications are provided for convenience in identifying components and are not limited in number.

[0050]

(Embodiment 1)

In the present embodiment, the structure of a particulate positive electrode active material, which is a form of the Present Invention, is described using Figure 1.

[0051]

Figure 1 corresponds to a cross-sectional schematic view of a particulate positive electrode active material, which is one form of the Present Invention. 40

[0052]

As shown in Figure 1, in the present embodiment, the positive electrode active material 100 has a first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel (hereinafter referred to as the first region 102). a second region (hereinafter referred to as second region 104) that covers the surface of first region 102 and is formed of a compound comprising lithium and iron.

[0053]

The positive electrode active material is particulate, and the positive electrode active material layer described below may be formed using a plurality of the particulate positive electrode active material. 50

[0054]

That is, the positive electrode active material 100 is a positive electrode active material particle located on the central side and having a first region 102 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel, and a second region 104 covering the surface of the first region 102 and formed of a compound comprising lithium and iron. The second region 104 is membrane-like, and the second region 104 may cover at least a part of the first region 102. The second region 104 preferably covers 30% or more of the surface of the first region 102, and more preferably 100% of the surface of the first region 102. The surface layer of the positive electrode active material particles is formed in a membrane-like second region 104 comprising iron, which can reduce the energy barrier in insertion and removal of lithium at the positive electrode active material surface. As a result, the positive electrode active material 100 can bring the available capacity closer to the theoretical capacity and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0055]

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The first region 102 may use a phosphate compound containing lithium and one or more of manganese, cobalt, and nickel. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, wherein a phosphate compound comprising lithium and one or more manganese, cobalt, and nickel forming a first region 102 may comprise a region having an olivine structure.

[0056]

In the case of a phosphate compound comprising a region in which the first region 102 has an olivine structure, it is composed of lithium, a transition metal, and phosphoric acid (PO_4). Transition metals in the first region 102 include one or more of iron, manganese, cobalt, nickel and one or more of manganese, cobalt, nickel. High discharge potential is achieved by including one or more of manganese, cobalt, and nickel with high redox potential. Furthermore, higher ratios of one or more of manganese, cobalt and nickel in positive electrode active materials result in higher energy density due to higher ratios of discharge capacity due to redox of one or more of manganese, cobalt and nickel.

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[0057]

Phosphate compounds containing lithium and one or more of manganese, cobalt, and nickel and forming first region 102 may also contain substances represented by the general formula $\text{Li}_{1-x1}\text{Fe}_{y1}\text{M}_{1-y1}\text{PO}_4$ ($x1$ is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) ($y1$ is 0 to less than 1). The material represented by the general formula may be an olivine structure. The value of $y1$ is 0 to less than 1, preferably 0. A higher energy density can be achieved by making it 1 or less, more preferably 0.

[0058]

The second region 104 may also employ a phosphate compound comprising lithium and iron. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, wherein a phosphate compound comprising lithium and iron forming the second region 104 may comprise a region having an olivine structure.

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[0059]

If the second region 104 is a phosphate compound comprising a region having an olivine structure, it is composed of lithium, a transition metal, and phosphoric acid (PO_4). Transition metals of the second region 104 include one or more of iron, manganese, cobalt, and nickel, as well as iron.

[0060]

Phosphate compounds containing lithium and iron that form the second region 104 may also contain substances represented by the general formula $\text{Li}_{1-x2}\text{Fe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ ($x2$ is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) ($y2$ is 0 to 1 or less). The material represented by the general formula may be an olivine structure.

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[0061]

If the second region 104 is a compound that can be a positive electrode active material that contributes to charge and discharge, it may not lead to a decrease in capacity. If a phosphate compound having an olivine structure is used in the second region 104, high capacity can be achieved in charge and discharge.

[0062]

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On the other hand, since the second region 104 includes iron, the discharge potential is lower and the energy density is therefore lower. Thus, the lower the ratio c ($c=d/r$) of the film thickness d of the second region 104, relative to the particle size r of the positive electrode active material 100, the more preferred. The value of the ratio c is preferably 0.005 or more to 0.25 or less, more preferably 0.01 or more to 0.1 or less. Specifically, the film thickness of the second region is preferably about 1 nm to 8 nm. Also, changing the ratio c can produce a positive electrode active material having the desired energy density. Also, in the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni), the value of y_2 is greater than 0 and less than 1, preferably 0. A higher energy density can be achieved by setting this to 15 or more to 0.5 or less, more preferably 0.2 or more to 0.3 or less.

[0063]

For the compounds in the first region 102 and the second region 104, lithium is disengaged and inserted upon charge and discharge. Thus, in the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is 0 to 1) (M is one or more of Mn, Co, and Ni) (y_1 is 0 to less than 1) and in the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to less than 1) (Me is one or more of Mn, Co, and Ni) (y_2 is greater than 0 to less than 1), the values of x_1 , x_2 are any value in the range of 0 to 1 or less. Also, the concentration of lithium in each region may have a gradient.

[0064]

In the first region 102, the concentration of transition metal contained in the compound may not be constant. Also, within the second region 104, the concentration of the transition metal contained in the compound may not be constant.

[0065]

Compounds in the first region 102 and the second region 104 can also use alkali metals (e.g., sodium (Na), potassium (K)) and alkaline earth metals (e.g., calcium (Ca), strontium (Sr), barium (Ba)), beryllium (Be) and magnesium (Mg) instead of lithium. Alternatively, compounds in the first region 102 and the second region 104 may employ compounds comprising lithium and one or more of an alkali metal or an alkali earth metal.

[0066]

Since the second region 104 is membrane-like, a thin film can be formed even if the particles of the positive electrode active material 100 are small. By making it a thin coating, the percentage occupied by the second area 104 can be reduced, and the decrease in energy density can be suppressed. Also, because the second region 104 is membrane-like, the ratio of the interface with the first region 102 to the volume of the second region 104 is large, the coverage can be increased without increasing the volume of the second region 104.

[0067]

That is, the positive electrode active material 100 in the present embodiment is a positive electrode active material particle located on the central side and having a first region 102 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel, and a second region 104 covering the surface of the first region 102 and formed of a compound comprising lithium and iron. The second region 104 is membrane-like, and the second region 104 may cover at least a part of the first region 102. The second region 104 preferably covers 30% or more of the surface of the first region 102, and more preferably 100% of the surface of the first region 102. The surface layer of the positive electrode active material particles is formed in a membrane-like second region 104 comprising iron, which can reduce the energy barrier in insertion and removal of lithium at the positive electrode active material surface. As a result, the positive electrode active material 100 can bring the available capacity closer to the theoretical capacity and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0068]

(Embodiment 2)

In the present embodiment, a positive electrode active material with a higher discharge capacity and energy density is described as compared to Embodiment 1.

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[0069]

In the present embodiment, the first region 102 and the second region 104 together describe a positive electrode active material formed of a phosphate compound having an olivine structure.

[0070]

The material forming the first region 102 is an olivine structure, consisting of lithium, transition metal, and phosphoric acid (PO₄). Transition metals of the first region 102 include one or more of iron, manganese, cobalt, nickel and one or more of manganese, cobalt, nickel. Substances forming the first region 102 are represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is from 0 to 1 or less) (M is one or more of Mn, Co, and Ni) (y_1 is from 0 to less than 1).

[0071]

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The material forming the second region 104 is an olivine structure and consists of lithium, transition metals, and phosphoric acid (PO₄). Transition metals of the second region 104 include one or more of iron, manganese, cobalt, and nickel, as well as iron. Substances forming the second region 104 are represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) (y_2 is from 0 to 1 or less).

[0072]

For the compounds in the first region 102 and the second region 104, lithium is disengaged and inserted upon charge and discharge. Thus, in the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is 0 to 1) (M is one or more of Mn, Co, and Ni) (y_1 is 0 to less than 1) and in the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is 0 to 1) (Me is one or more of Mn, Co, and Ni) (y_2 is 0 to 1), the values of x_1 , x_2 are any value in the range of 0 to 1. Also, the concentration of lithium in each region may have a gradient.

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[0073]

In the olivine structure, the lithium diffusion path (channel) is one-dimensional in the <010> direction. If the first region 102 and the second region 104 are both phosphate compounds having an olivine structure, when the axial directions of the crystal lattices are aligned between the first region 102 and the second region 104, the diffusion path (channel) of lithium is aligned without bending, making charging and discharging easier. It is desirable that the axial direction difference of the crystal lattice between the first region 102 and the second region 104 is generally equal to or less than 10 degrees.

[0074]

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Furthermore, since constituent elements and their ratios differ for the first region 102 and the second region 104, the lattice constants of crystals in each region are different. The lattice constants may interfere with the spread of lithium, such as through stress, lattice strain, and lattice misalignment at the interface due to contact with regions with different lattice constants. More preferably, there is a concentration gradient of the transition metal between the first region 102 and the second region 104 such that the lattice constant varies continuously between the first region 102 and the second region 104. Continuous changes in lattice constants reduce stress and strain, making it easier for lithium to diffuse.

[0075]

The positive electrode active material shown in the present embodiment can reduce the energy barrier in insertion and detachment of lithium at the positive electrode active material surface because the first region 102 and the second region 104 both have a phosphate compound having an olivine structure. As a result, the positive electrode active material 100 can bring the available capacity closer to the theoretical capacity and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

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[0076]

(Embodiment 3)

In the present embodiment, the structure of a positive electrode active material, a form of the Present Invention, is described using Figure 2.

[0077]

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Figure 2 corresponds to a cross-sectional schematic view of a particulate positive electrode active material, which is one form of the Present Invention.

[0078]

As shown in Figure 2, one aspect of the present embodiment is a particulate positive electrode active material (hereinafter, the positive electrode active material is referred to as “positive electrode active material 106”) formed of a compound comprising lithium (Li) and iron (Fe) and a transition metal (one or more of manganese (Mn), cobalt (Co), and nickel (Ni)), with a higher concentration of iron in the surface than in the center of the positive electrode active material. Alternatively, it is formed of a compound comprising lithium, iron, and a transition metal (one or more of manganese, cobalt, and nickel), wherein the second part has a higher iron concentration than the first part of the positive electrode active material, and the first part is a particulate positive electrode active material closer to the center than the second part. The surface part of the positive electrode active material particle is formed of a compound comprising iron, which can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface. As a result, the positive electrode active material 106 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

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[0079]

The positive electrode active material is in particulate form, and a positive electrode active material layer, which will be described later, is formed including a plurality of particles.

[0080]

The positive electrode active material 106 may use a phosphate compound containing lithium and one or more of manganese, cobalt, and nickel. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, and the phosphate compounds comprising lithium and iron and one or more of manganese, cobalt, and nickel may include regions having an olivine structure.

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[0081]

A phosphate compound comprising a region in which the positive electrode active material 106 has an olivine structure is composed of lithium, a transition metal, and phosphoric acid (PO_4). Transition metals include one or more of iron, manganese, cobalt, nickel and one or more of iron and manganese, cobalt, nickel. High discharge potential is achieved by including one or more of manganese, cobalt, and nickel with high redox potential. Furthermore, higher ratios of one or more of manganese, cobalt and nickel in positive electrode active materials result in higher energy density due to higher ratios of discharge capacity due to redox of one or more of manganese, cobalt and nickel.

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[0082]

Phosphate compounds containing lithium and iron and one or more of manganese, cobalt, and nickel that form positive electrode active material 106 may also contain substances represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1) (M is one or more of Mn, Co, and Ni) (y is 0 to less than 1). The material represented by the general formula may be an olivine structure. Also, the value of y is greater than 0 and less than 1 on the surface, preferably 0. A higher energy density can be achieved by setting this to 15 or more to 0.5 or less, more preferably 0.2 or more to 0.3 or less.

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[0083]

For the compound forming the positive electrode active material 106, lithium is disengaged and inserted upon charging and discharging. Thus, in the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1) (M is 1 or more of Mn, Co, and Ni) (y is greater than 0 and less than 1), the value of x is any value in the range 0 to 1. The concentration of lithium may also have a gradient.

[0084]

Compounds in the positive electrode active material 106 can also use alkali metals (e.g., sodium (Na), potassium (K)) and alkaline earth metals (e.g., calcium (Ca), strontium (Sr), barium (Ba)), beryllium (Be) and magnesium (Mg) instead of lithium. Alternatively, the compounds in the positive electrode active material 106 may employ compounds comprising lithium and one or more of an alkali metal or an alkali earth metal.

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[0085]

The positive electrode active material 106 shown in the present embodiment can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface by having the surface layer of the positive electrode active material particles formed of a compound comprising iron. As a result, the positive electrode active material 106 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0086]

(Embodiment 4)

In the present embodiment, methods of making a positive electrode active material, which is a form of the Present Invention, are described below.

[0087]

First, a first region 102 is created.

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[0088]

In accordance with the general stoichiometric ratio of compounds comprising lithium and one or more of manganese, cobalt and nickel as shown in Embodiments 1 and 2, the desired molar ratio for each raw material is weighed. For example, in the case of the phosphoric acid compound having the above olivine structure, the general formula shown in Embodiments 1 and 2 is lithium: iron: M: phosphoric group=1:y1:(1-y1): 1 (where y1 is 0 or more to less than 1, preferably 0.1 or less, more preferably 0), and the weight of each raw material is accurately weighed according to this molar ratio.

[0089]

The raw materials of lithium include lithium carbonate (LiCO_3), lithium hydroxide (Li(OH)), lithium hydroxide hydrate ($\text{Li(OH)/H}_2\text{O}$), and lithium nitrate (LiNO_3). Iron raw materials include iron oxalate dihydrate ($\text{Fe (COO)}_2 \cdot 2\text{H}_2\text{O}$) and iron chloride (FeCl_2). In addition, the raw materials of phosphoric acid include ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), and diphosphate pentoxide (P_2O_5).

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[0090]

In addition, the raw materials for manganese include manganese carbonate (MnCO_3) and manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$). Nickel sources include nickel oxide (NiO) and nickel hydroxide (Ni(OH)_2). Cobalt raw materials include cobalt carbonate (CoCO_3) and cobalt chloride (CoCl_2).

[0091]

However, other oxides, carbonates, oxalates, chlorides, sulfates, and the like may be used if the raw materials include any of the metals, such as lithium, iron, manganese, nickel, cobalt, and the like, but this is not limited to the raw materials described.

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[0092]

In addition, as raw materials for phosphoric acid, other raw materials containing phosphoric acid can be used, not limited to raw materials.

[0093]

Place each of the weighed raw materials in a pulverizer and pulverize until a fine powder is obtained (first pulverization process). At that time, it is better to use a pulverizer made of materials (e.g. agate) where there is consideration not to contaminate the raw material with other metals. If a trace amount of acetone, alcohol, etc. is added at this time, the raw material becomes easier to coalesce and it can be suppressed from scattering as powder.

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[0094]

The powder is then pressurized at a first pressure and molded into pellets. Place this in a firing furnace and heat to perform the first firing process. Degassing and pyrolysis of the raw materials are mostly carried out in the process. Also, in the process, a compound comprising lithium and one or more of manganese, cobalt, and nickel is formed. This is a phosphate compound having an olivine structure including, for example, lithium and one or more of manganese, cobalt, and nickel.

[0095]

Then, the pellet is placed in a pulverizer with a solvent such as acetone and pulverized again (second pulverization process). First region 102 is therefore formed.

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[0096]

The membrane-like second region 104 is then formed.

[0097]

In accordance with the general formula stoichiometric ratio of compounds comprising lithium and iron as shown in Embodiments 1 and 2, the desired molar ratio for each raw material is weighed. For example, in the case of a phosphate compound having an olivine structure, the above general formula is lithium: iron: Me: Phosphate group = 1: y₂: (1-y₂): 1 (however, the value of y₂ is greater than 0 and 1 or less, preferably 0.3 or less) and the weight of each raw material is accurately weighed according to this molar ratio.

[0098]

Place each of the weighed raw materials in a pulverizer and pulverize until a fine powder is obtained (third pulverization process). At that time, it is better to use a pulverizer made of materials (e.g. agate) where there is consideration not to contaminate the raw material with other metals. If a trace amount of acetone, alcohol, etc. is added at this time, the raw material becomes easier to coalesce and it can be suppressed from scattering as powder.

[0099]

Thereafter, the powder obtained in the second pulverization process (the part that becomes the first region 102) and the powder obtained in the third pulverization process (the raw material forming the second region 104) are mixed well, and the pressurization process at the second pressure is carried out to form a pellet. Place this in a firing furnace and heat to perform a second firing process. Degassing and pyrolysis in the raw materials of compounds containing lithium and iron are mostly carried out in the process.

Also, in this process, positive electrode active material 100 is formed having a first region 102 formed of a compound containing lithium and one or more of manganese, cobalt and a second region 104 covering the surface of the first region 102 and being formed of a compound including lithium and iron. For example, a positive electrode active material 100 is formed having a first region 102 formed of a phosphate compound having an olivine structure comprising lithium and one or more of manganese, cobalt, and nickel, and a second region 104 that covers the surface of the first region 102 and is formed of a phosphate compound having an olivine structure comprising lithium and iron.

[0100]

Then, the pellet is placed in a pulverizer with a solvent such as acetone and pulverized again (fourth pulverization process). Next, the fine powder is again molded into pellets, and a third firing process is performed in a firing furnace. Through the third firing process, the positive electrode active material 100 having a first region 102 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel and a second region 104 covering the surface of the first region 102 and formed of a compound comprising lithium and iron is created multiple times. For example, a positive electrode active material 100 having a first region 102 formed of a phosphate compound having an olivine structure of good crystallinity comprising lithium and one or more of manganese, cobalt, and nickel, and a second region 104 that covers the surface of the first region 102 and is formed of a phosphate compound having an olivine structure of good crystallinity comprising lithium and iron is created multiple times.

[0101]

By adjusting the conditions of the third firing process, the elements contained in the first region 102 and the second region 104 can diffuse into each other's region, obscuring the boundaries of the first region 102 and the second region 104, and forming the structure (positive electrode active material 106) shown in Embodiment 3.

[0102]

In addition, organic compounds such as glucose may be added during the third firing process. Upon addition of glucose and subsequent processes, the carbon supplied from the glucose is carried on the surface of the positive electrode active material.

[0103]

In addition, in the specifications it is said that the surface of the positive electrode active material is supported by a carbon material, and that the iron phosphate compound is carbon coated.

[0104]

The thickness of the carbon (carbon layer) supported is preferably greater than 0 nm and no greater than 100 nm, preferably 2 nm and no greater than 10 nm.

[0105]

By carrying carbon on the surface of the positive electrode active material, the conductivity of the surface of the positive electrode active material can be increased. In addition, if the positive electrode active materials come into contact with each other via the carbon supported on the surface, the positive electrode active materials can conduct each other, further increasing the conductivity of the positive electrode active materials.

[0106]

Note that in the present embodiment, glucose is used as a source of carbon because glucose readily reacts with phosphate groups, but instead of glucose, cyclic monosaccharides, linear monosaccharides, or polysaccharides that are reactive with phosphate groups may be used.

[0107]

The particle size of the positive electrode active material 100 obtained through the third firing process is 10 nm to 100 nm, preferably 20 nm to 60 nm. Since the particle size of the positive electrode active material is within the above range, the positive electrode active material particles are small, making it easier to insert and detach the lithium ion, improving the rate characteristics of the secondary battery, and enabling charging and discharging in a short time.

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[0108]

As a method of forming a first region, it is also possible to use a sol-gel method, hydrothermal method, co-sedimentation method, spray-drying method, etc., in place of the present embodiment. It is also possible to use a sputtering method, CVD method, sol-gel method, hydrothermal method, co-sedimentation method, etc., in place of the present embodiment as a method of forming a second area of membrane shape.

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[0109]

Through the present embodiment, it is possible to lower the energy barrier in insertion and removal of lithium at the positive electrode active material surface. As a result, the available capacity can be brought closer to the theoretical capacity and a positive electrode active material can be formed that can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0110]

(Embodiment 5)

An example of a power storage device using a positive electrode active material obtained by the above-described manufacturing process is described below. An overview of the lithium ion secondary battery is shown in Figure 3.

[0111]

The lithium ion secondary battery shown in Figure 3 places the positive electrode 202, the negative electrode 207, and the separator 210 in housing 220 isolated from the outside, and housing 220 is filled with electrolyte 211. There is separator 210 between the positive electrode 202 and the negative electrode 207.

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[0112]

A positive electrode active material layer 201 is formed in contact with the positive electrode current collector 200. Positive electrode active material 100 having a first region 102 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel, and a second region 104 covering the surface of the first region 102 and formed of a compound comprising lithium and iron and shown in Embodiments 1, 2 and 4 is included in positive electrode active material layer 201. Alternatively, as shown in Embodiments 3 and 4, particulate positive electrode active material 106, where the surface of the positive electrode active material has a higher iron concentration than the center, and is formed by compounds including lithium, iron and transition metals (one of more of manganese, cobalt and nickel), or particulate positive electrode active material 106, in which the positive electrode active material second part has a higher iron concentration than the first part, and the first part is closer to the center than the second part, is included in positive electrode active material layer 201. Herein, the positive electrode active material layer 201 and the positive electrode current collector 200 from which it is formed are collectively referred to as the positive electrode 202.

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[0113]

On the other hand, a negative electrode active material layer 206 is formed in contact with the negative electrode current collector 205. Herein, the negative electrode active material layer 206 and the negative electrode current collector 205 from which it is formed are referred to as the negative electrode 207.

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[0114]

A first electrode 221 is connected to the positive electrode current collector 200 and a second electrode 222 is connected to the negative electrode current collector 205, and charging and discharging is performed from the first electrode 221 and the second electrode 222.

[0115]

In addition, although the distance between the positive electrode active material layer 201 and the separator 210 and the negative electrode active material layer 206 and the separator 210 are shown at fixed intervals, it is not limited to that, the positive electrode active material layer 201 and the separator 210 and the negative electrode active material layer 206 and the separator 210 may be in contact with each other. In addition, the positive electrode 202 and the negative electrode 207 may be cylindrically rounded with the separator 210 positioned between them.

[0116]

It should be noted that active substances refer to substances involved in the insertion and removal of ions that are carriers, and do not include carbon layers, etc., using glucose. When the positive electrode 202 is made by the application method described below, a mixture of conductive aids, binders, solvents, and other materials together with active materials having a formed carbon layer is formed on the positive electrode current collector 200 as the positive electrode active material layer 201. Thus, the active material and the positive electrode active material layer 201 are distinguished.

[0117]

For the positive electrode current collector 200, highly conductive materials such as aluminum and stainless steel can be used. The positive electrode current collector 200 can use a shape such as a thin film formed on an insulating substrate such as a foil, plate, net or glass as appropriate.

[0118]

Positive electrode active material 100 having a first region 102 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel, and a second region 104 covering the surface of the first region 102 and formed of a compound comprising lithium and iron is used as positive electrode active material. For example, positive active material 100 having a first region 102 formed of a material represented by the general formula $\text{Li}_{1-x_1}\text{Fe}_{y_1}\text{M}_{1-y_1}\text{PO}_4$ (x_1 is between 0 and 1) (M is one or more of 0, Co, and Ni) (y_1 is 0 to less than 1), and a second region 104 that covers the first region 102 and has an olivine structure, and is formed of materials represented by the general formula $\text{Li}_{1-x_2}\text{Fe}_{y_2}\text{Me}_{1-y_2}\text{PO}_4$ (x_2 is between 0 and 1) (Me is one or more of 0, Co, and Ni) (y_2 is between 0 and 1) is used.

[0119]

Alternatively, the positive electrode active material is formed of a compound comprising lithium, iron, and a transition metal (one or more of manganese, cobalt, and nickel), wherein the surface layer is more iron-concentrated particulate positive electrode active material 106 than the center of the positive electrode active material, or a compound comprising lithium, iron, and a transition metal (one or more of manganese, cobalt, and nickel), wherein the second part of the positive electrode active material has a higher iron concentration than the first part, and wherein the first part uses a particulate positive electrode active material 106 closer to the center than the second part. For example, an olivine structure employs a positive electrode active material 106 formed of a material represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is greater than or equal to 0 and less than 1) (M is greater than or equal to Mn, Co, and Ni) (y is greater than or equal to 0 and less than 1).

[0120]

After the third firing process shown in Embodiment 4, the resulting positive electrode active material is pulverized again with a pulverizer (fifth pulverization process) to obtain fine powder. The obtained fine powder is used as a positive electrode active material, and conductive aids, binders, and solvents are added to prepare a paste.

[0121]

The conductive aid may be one whose material is an electron conductor and does not cause chemical changes with other materials in the battery device. Examples include carbon-based materials such as graphite, carbon fibers, carbon black, acetylene black, VGCF®, powders and fibers of metallic materials such as copper, nickel, aluminum or silver or mixtures thereof. Conductive aids are materials that assist conductivity between active materials, are filled between distant active materials and provide continuity between active materials.

[0122]

Binders include starch, polyvinyl alcohol, carboxymethyl cellulose, hydroxypropyl cellulose, regenerated cellulose, diacetyl cellulose, polyvinyl chloride, polyvinylpyrrolidone, polytetrafluorethylene, polyvinylidene fluoride,

polyethylene, polypropylene, Ethylene Propylene Diene Monomer (EPDM), sulfonated EPDM, polysaccharides such as styrene butadiene rubber, butadiene rubber, fluororubber or polyethylene oxide, thermoplastic resin or polymer having rubber elastic.

[0123]

The active substances, conductive aids, and binders are mixed at a ratio of 80 to 96 weight percent, 2 to 10 weight percent, share of 2 to 10 weight percent, respectively, and 100 weight percent overall. In addition, organic solvents of the same volume as the mixture of active materials, conductive co-agents, and binders are mixed and processed into a slurry. It should be noted that the material obtained by processing active substances, conductive aids, binders, and organic solvents into a slurry form is referred to as a slurry. Solvents include Nmethyl-2 pyrrolidone and lactic acid ester. It is good to adjust the ratio of active substances, conductive aids, and binders as appropriate, such as by increasing the binder when the adhesion of active substances and conductive aids is weak when deposition is made, and increasing the conductive aid when the resistance of active substances is high.

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[0124]

Here, aluminum foil is used as the positive electrode current collector 200, and the slurry is dropped onto it and spread thinly by the cast method, then further stretched with a roll press to equalize the thickness, and then vacuum dried (10 Pa or less) or heated dried (150 to 280°C) to form a positive electrode active material layer 201 on the positive electrode current collector 200. The thickness of the positive electrode active material layer 201 selects the desired thickness between 20 and 100 μm . Preferably, the thickness of the positive electrode active material layer 201 is adjusted accordingly to avoid cracking or peeling. Furthermore, depending on the form of the battery, it is preferable to prevent cracking or peeling of the positive electrode active material layer 201 when rounded in a tubular shape as well as a flat plate.

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[0125]

For the negative electrode current collector 205, highly conductive materials such as copper, stainless steel, iron, nickel, etc. can be used.

[0126]

The negative electrode active material layer 206 includes lithium, aluminum, graphite, silicon, and germanium. A negative electrode active material layer 206 may be formed on the negative electrode current collector 205 by application, sputtering, deposition, etc. Each negative electrode active material layer 206 may be used as a single negative electrode without using a negative electrode current collector 205. Compared to graphite, the theoretical lithium capacity of germanium, silicon, lithium and aluminum is large. Large capacity can be sufficiently charged and discharged even in small areas, and can function as a negative electrode, leading to cost savings and miniaturization of secondary batteries. However, the volume of silicon, etc. increases up to about 4 times by absorbing lithium, and the material itself becomes brittle, and the reduction in charge and discharge capacity (cycle degradation) becomes noticeable by repeated charge and discharge, so measures to prevent deterioration are necessary.

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[0127]

The electrolyte comprises alkali metal ions, which are carrier ions, and alkaline earth metal ions, and the carrier ions carry electrical conduction. Alkaline metal ions include, for example, lithium ions, sodium ions, or potassium ions. Alkaline earth metal ions include, for example, beryllium ions, magnesium ions, calcium ions, strontium ions, or barium ions.

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[0128]

Electrolyte 211, for example, consists of a solvent and a lithium or sodium salt dissolved in the solvent. Lithium salts include, for example, lithium chloride (LiCl), lithium borofluoride (LiF), lithium perchlorate (LiClO_4), lithium fluoride (LiBF_4), LiAsF_6 , LiPF_6 , $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$. Sodium salts include, for example, sodium chloride (NaCl), sodium fluoride (NaF), sodium perchlorate (NaClO_4), and sodium fluoride (NaBF_4).

[0129]

As solvents for electrolyte 211, there are cyclic carbonates (e.g., ethylene carbonate (hereinafter abbreviated as "EC"), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC) etc.), non-cyclic carbonates (dimethyl carbonate (DMC), diethyl carbonate (DEC), Ethyl methyl carbonate (EMC), methyl propyl carbonate (MPC), methyl isobutyl carbonate (MIBC), and dipropyl carbonate (DPC) etc.), aliphatic carboxylic acid esters

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(methyl formate; methyl acetate, methyl propionate, and ethyl propionate, etc.), noncyclic ethers (γ -lactones such as γ -butyrolactone, 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), and ethoxymethoxyethane (EME), etc.), cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran, etc.); cyclic sulfone (such as sulfolane), alkyl phosphate esters (dimethylsulfoxide, 1, 3-dioxolane, etc., trimethyl phosphate, triethyl phosphate) and its fluorides. They are used as one type of a mix of two or more types.

[0130]

For separator 210, paper, nonwoven fabric, glass fibers, or synthetic fibers such as nylon (polyamide), vinylon (also referred to as vinalon) (polyvinyl alcohol based fibers), polyester, acrylic, polyolefin, polyurethane, etc. may be used. However, it is necessary to select a material that will not dissolve in the electrolyte solution 211 described above.

[0131]

More particularly, as materials of separator 210, one or more of the following can be used, alone or in combination, for example: polyethers such as fluorine-based polymers, polyethylene oxide, and polypropylene oxide, polyolefins such as polyethylene and polypropylene, polyacrylonitrile, polyvinylidene chloride, polymethylmethacrylate, polyvinyl alcohol, polymethacrylonitrile, polyvinyl acetate, polyvinylpyrrolidone, polyethyleneimine, polybutadiene, polystyrene, polyisoprene, polyurethane-based polymers and derivatives thereof, cellulose, paper, and nonwoven fabrics.

[0132]

When charging the lithium ion secondary battery shown above, a positive electrode terminal is connected to the first electrode 221 and a negative electrode terminal to the second electrode 222. From the positive electrode 202, the electrons are taken via the first electrode 221 and travel to the negative electrode 207 through the second electrode 222. In addition, from the positive electrode, lithium ion elutes from the positive electrode active material in the positive electrode active material layer 201, passes through the separator 210 to the negative electrode 207, and is incorporated into the negative electrode active material in the negative electrode active material layer 206. At the same time, in the positive electrode active material layer 201, electrons are released from the positive electrode active material, resulting in an oxidation reaction of the transition metals (one or more of iron, manganese, cobalt, nickel) contained in the positive electrode active material.

[0133]

When discharging, at the negative electrode 207, the negative electrode active material layer 206 releases lithium as an ion and sends electrons to the second electrode 222. Lithium ion passes through separator 210 to reach positive electrode active material layer 201 and is incorporated into the positive electrode active material in positive electrode active material layer 201. At that time, electrons from the negative electrode 207 also reach the positive electrode 202, resulting in a reduction reaction of the transition metals (one or more of iron, manganese, cobalt, and nickel) contained in the positive electrode active material.

[0134]

The energy density obtained by the present embodiment increases the lower the ratio c ($c=d/r$) of the film thickness d of the second region 104 to the particle size r of the positive electrode active material 100. The value of the ratio c is preferably 0.005 or more to 0.25 or less, more preferably 0.01 or more to 0.1 or less. 1 or less can be used. Specifically, the film thickness of the second region is preferably about 1 nm to 8 nm. Also, changing the ratio c can produce a positive electrode active material having the desired energy density.

[0135]

Lithium-ion secondary batteries made as described above have compounds containing one or more of manganese, cobalt, and nickel as the first region 102 of the positive electrode active material, or as the positive electrode active material 106. The positive electrode active material contains more than one of manganese, cobalt, and nickel, resulting in a high discharge potential. For example, for positive electrode active materials having an olivine structure, the theoretical capacity per unit weight of active material, although there are some differences depending on the type of transition metal included, exhibits approximately the same theoretical capacity regardless of the type of transition metal included. Therefore, the higher the discharge potential, the higher the energy density is expected.

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[0136]

However, even if the positive electrode active material formed from phosphate compounds having an olivine structure including lithium and one or more of manganese, cobalt and nickel is used, the expected capacity has not been realized. One cause of this may be the presence of an energy barrier when inserting and removing lithium at the active material surface.

[0137]

On the other hand, by using particulate positive electrode active material 106 in which the iron concentration is higher on the surface of the positive electrode active material than the center, and which is formed by positive electrode active material 100, which has first region 102 formed of a compound including lithium and one or more of manganese, cobalt and nickel that was obtained in the present embodiment, and second region 104, which covers the surface of first region 102 and which is formed by a compound including lithium and iron, or which is formed by a compound including lithium, iron and transition metals (one or more of manganese, cobalt, and nickel), or by using particulate positive electrode active material 106 in which positive electrode active material part 2 has a higher iron concentration than part 1, and in which part 1 is closer to the center than part 2, and that is formed by a compound including lithium, iron and transition metals (one or more of manganese, cobalt, and nickel), it is possible to lower the energy barrier in lithium intercalation and deintercalation on the surface of the positive electrode active material. As a result, the positive electrode active material 100, or the positive electrode active material 106, can bring the available capacity closer to the theoretical capacity and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0138]

(Embodiment 6)

The positive electrode active material layer 201 described in Embodiment 5 may be formed of a membrane-like positive electrode active material. When a positive electrode active material layer 201 is formed of a membrane-like positive electrode active material, it is described in the following embodiments.

[0139]

As shown in Figure 4, in the present embodiment, the positive electrode active material layer 201 has a membrane-like first region formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel (hereinafter referred to as the first region 112) and a membrane-like second region (hereinafter referred to as second region 114) that is formed of a compound comprising lithium and iron. The first region 112 is covered by the second region 114.

[0140]

That is, the top or top and side surfaces of the membrane-like first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel are covered by the membrane-like second region 114 formed of a compound comprising lithium and iron. The surface part of the positive electrode active material layer 201 is formed in a second region 114 comprising iron, which can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface. As a result, the positive electrode active material layer 201 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0141]

In addition, by forming a positive electrode active material into a membrane, the ratio of positive electrode active material to the positive electrode active material layer can be increased. Because the positive electrode active material layer 201 is formed only in the membrane-like first region 112 and the membrane-like second region 114, the ratio of the positive electrode active material to the positive electrode active material layer 201 can ideally be 100%. Therefore, the energy density per unit volume can be increased.

[0142]

The first region 112 may use a phosphate compound containing lithium and one or more of manganese, cobalt, and nickel. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, wherein a phosphate compound comprising lithium and one or more of manganese, cobalt, and nickel forming a first

region 112 may comprise a region having an olivine structure. Also, the first region 112 may be monocrystalline, polycrystalline, or microcrystalline, or may contain amorphous.

[0143]

A phosphate compound comprising a region where the first region 112 has an olivine structure is composed of lithium, a transition metal, and phosphoric acid (PO_4). Transition metals include one or more of iron, manganese, cobalt, nickel and one or more of manganese, cobalt, nickel. High discharge potential is achieved by including one or more of manganese, cobalt, and nickel with high redox potential. Furthermore, higher ratios of one or more of manganese, cobalt and nickel in positive electrode active materials result in higher energy density due to higher ratios of discharge capacity due to redox of one or more of manganese, cobalt and nickel.

[0144]

Phosphate compounds containing lithium and one or more of manganese, cobalt, and nickel and forming first region 112 may also contain substances represented by the general formula $\text{Li}_{1-x1}\text{Fe}_{y1}\text{M}_{1-y1}\text{PO}_4$ ($x1$ is 0 to 1 or less) (M is one or more of Mn, Co, and Ni) ($y1$ is 0 to less than 1). The material represented by the general formula may be an olivine structure. The value of $y1$ is 0 to less than 1, preferably 0. A higher energy density can be achieved by making it 1 or less, more preferably 0.

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[0145]

The second region 114 may also use a phosphate compound comprising lithium and iron. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, wherein the phosphate compounds comprising lithium and iron forming a second region 114 may include regions having an olivine structure. Also, the second region 114 may be monocrystalline, polycrystalline, or microcrystalline, or may contain amorphous.

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[0146]

A phosphate compound comprising a region in which the second region 114 has an olivine structure is composed of lithium, a transition metal, and phosphoric acid (PO_4). Transition metals include one or more of iron, manganese, cobalt, and nickel, as well as iron.

[0147]

Phosphate compounds containing lithium and iron that form the second region 114 may also contain substances represented by the general formula $\text{Li}_{1-x2}\text{Fe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ ($x2$ is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni) ($y2$ is 0 to 1 or less). The material represented by the general formula may be an olivine structure.

[0148]

If the second region 114 is a compound that can be a positive electrode active material that contributes to charge and discharge, it does not have to lead to a decrease in capacity. If a phosphate compound comprising a region having an olivine structure in the second region 114 is used, a high capacity can be achieved in charge and discharge.

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[0149]

On the other hand, since the second region 114 includes iron, the discharge potential is lower and the energy density is therefore lower. Thus, the lower the ratio c_f ($c_f = d_f/r_f$) of the film thickness d_f of the second region 114, relative to the film thickness r_f of the positive electrode active material layer 201, the more preferred. The value of the ratio c_f is preferably 0. Specifically, the film thickness of the second region is preferably about 1 nm to 8 nm. Also, changing the ratio c_f can produce a positive electrode active material having the desired energy density. Also, in the general formula $\text{Li}_{1-x2}\text{Fe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ ($x2$ is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni), the value of $y2$ is greater than 0 and less than 1, preferably 0. A higher energy density can be achieved by setting this to 15 or more to 0.5 or less, more preferably 0.2 or more to 0.3 or less.

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[0150]

For the compounds in the first region 112 and the second region 114, lithium is disengaged and inserted upon charge and discharge. Thus, in the general formula $\text{Li}_{1-x1}\text{Fe}_{y1}\text{M}_{1-y1}\text{PO}_4$ ($x1$ is 0 to 1) (M is one or more of Mn, Co, and Ni) ($y1$ is 0 to less than 1) and in the general formula $\text{Li}_{1-x2}\text{Fe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ ($x2$ is 0 to 1) (Me is one or more of Mn, Co, and Ni) ($y2$ is 0 to 1), the values of $x1$, $x2$ are any value in the range of 0 to 1. Also, the concentration of lithium in each region may have a gradient.

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[0151]

Within the first region 112, the concentration of transition metal contained in the compound does not need to be constant. Within the second region 114, the concentration of transition metal contained in the compound does not need to be constant.

[0152]

Compounds in the first region 112 and the second region 114 can also use alkali metals (e.g., sodium (Na), potassium (K)) and alkaline earth metals (e.g., calcium (Ca), strontium (Sr), barium (Ba)), beryllium (Be) and magnesium (Mg) instead of lithium. Alternatively, compounds in the first region 112 and the second region 114 may employ compounds comprising lithium and one or more of an alkali metal or an alkali earth metal.

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[0153]

For the positive electrode active material layer 201 shown in the present embodiment, the top or top and side surfaces of the membrane-like first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt, nickel are covered by the membrane-like second region 114 formed of a compound comprising lithium and iron. The surface part of the positive electrode active material layer 201 is formed in a second region 114 comprising iron, which can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface. As a result, the positive electrode active material layer 201 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

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[0154]

(Embodiment 7)

In the present embodiment, examples of the structure of a positive electrode having a power storage device, which is a form of the Present Invention, are described using Figures 5, 6 and 7, which are different from Figure 4.

[0155]

Figures 5, 6 and 7 correspond to a cross-sectional schematic diagram of a positive electrode having a power storage device, which is one form of the Present Invention.

[0156]

As shown in Figure 5, in the present embodiment, the positive electrode active material layer 201 has a membrane-like first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel and a membrane-like second region 114 that is formed of a compound comprising lithium and iron, and the first region 112 is covered by second region 114. The top or top and side surfaces of the first region 112 are covered by the second region 114 and there is a second region 114 between the first region 112 and the positive electrode current collector 200.

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[0157]

Figures 6 and 7 show cases having a plurality of the first region 112 in Figures 4 and 5, respectively.

[0158]

Other configurations can be similar to Embodiment 6.

[0159]

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(Embodiment 8)

In the present embodiment, the structure of the positive electrode having a power storage device, which is an embodiment of the Present Invention, is described using Figure 8.

[0160]

Figure 8 corresponds to a cross-sectional schematic diagram of a positive electrode having a power storage device, which is a form of the Present Invention.

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[0161]

As shown in Figure 8, the present embodiment is a positive electrode active material layer (hereinafter, the positive electrode active material layer is referred to as “positive electrode active material 203”) formed of a compound comprising lithium (Li) and iron (Fe) and a transition metal (one or more of manganese (Mn), cobalt (Co), and nickel (Ni)), with a higher concentration of iron in the surface than in the side closer to the positive electrode active material positive electrode current collector. Alternatively, it is positive electrode active material layer 203 formed of a compound comprising lithium, iron, and a transition metal (one or more of manganese, cobalt, and nickel), wherein the second part of the positive electrode active material has a higher iron concentration than the first part, and the second part is closer to the surface than the first part.

[0162]

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The surface part of the positive electrode active material layer 203 is formed of a comprising iron, which can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface. As a result, the positive electrode active material layer 203 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0163]

In addition, by forming a positive electrode active material into a membrane, the ratio of positive electrode active material to the positive electrode active material layer can be increased. Because the positive electrode active material layer 203 is formed by the membrane-like positive electrode active material, the ratio of the positive electrode active material to the positive electrode active material layer 203 can ideally be 100%. Therefore, the energy density per unit volume can be increased.

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[0164]

This may use a phosphate compound containing lithium and iron and one or more of manganese, cobalt, and nickel. Representative examples of phosphate compounds include phosphate compounds having an olivine structure, and the phosphate compounds comprising lithium and iron and one or more of manganese, cobalt, and nickel may include regions having an olivine structure.

[0165]

Phosphate compounds comprising a region in which the positive electrode active material layer 203 has an olivine structure are composed of lithium, transition metals, and phosphoric acid (PO_4). Transition metals include one or more of iron, manganese, cobalt, nickel and one or more of iron and manganese, cobalt, nickel. High discharge potential is achieved by including one or more of manganese, cobalt, and nickel with high redox potential. Furthermore, higher ratios of one or more of manganese, cobalt and nickel in positive electrode active materials result in higher energy density due to higher ratios of discharge capacity due to redox of one or more of manganese, cobalt and nickel.

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[0166]

Phosphate compounds containing lithium and iron and one or more of manganese, cobalt, and nickel that form positive electrode active material layer 203 may also contain substances represented by the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1) (M is one or more of Mn, Co, and Ni). The material represented by the general formula may be an olivine structure. Also, the value of y is greater than 0 and less than 1 on the surface, preferably 0. A higher energy density can be achieved by setting this to 15 or more to 0.5 or less, more preferably 0.2 or more to 0.3 or less.

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[0167]

For the compound forming the positive electrode active material layer 203, lithium is disengaged and inserted upon charging and discharging. Thus, in the general formula $\text{Li}_{1-x}\text{Fe}_y\text{M}_{1-y}\text{PO}_4$ (x is 0 to 1) (M is 1 or more of Mn, Co, and Ni) (y is greater than 0 and less than 1), the value of x is any value in the range 0 to 1. The concentration of lithium may also have a gradient.

[0168]

Compounds in the positive electrode active material layer 203 can also use alkali metals (e.g., sodium (Na), potassium (K)) and alkaline earth metals (e.g., calcium (Ca), strontium (Sr), barium (Ba)), beryllium (Be) and magnesium (Mg) instead of lithium. Alternatively, compounds in the positive electrode active material layer 203 may employ compounds comprising lithium and one or more of an alkali metal or an alkali earth metal.

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[0169]

The surface part of the positive electrode active material for positive electrode active material layer 203 shown in the present embodiment is formed of a compound comprising iron, which can reduce the energy barrier in insertion and desorption of lithium at the positive electrode active material surface. As a result, the positive electrode active material layer 203 can bring the available capacity closer to the theoretical capacity, and can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0170]

(Embodiment 9)

In the present embodiment, a method of making a positive electrode having a power storage device, which is a form of the Present Invention, is described below.

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[0171]

First, a positive electrode current collector 200 is prepared (Figure 9(A)).

[0172]

The materials of the positive electrode current collector 200 are not particularly limited, but highly conductive materials such as platinum, aluminum, copper, titanium, etc. can be used. Titanium is used in this embodiment.

[0173]

Next, a first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel is formed on the positive electrode current collector 200 (Figure 9(B)).

[0174]

Methods of making the first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt, and nickel can use dry methods such as PVD (e.g., sputtering), vacuum vapor deposition, or CVD (e.g., plasma CVD, thermal CVD, LPCVD). By forming a first region 112 formed of a compound comprising lithium and one or more of manganese, cobalt and nickel using a dry method, a first region 112 formed of a homogeneous and thin film compound comprising lithium and one or more of manganese, cobalt, nickel can be obtained. Therefore, the charge/discharge characteristics of the positive electrode can be stabilized.

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[0175]

In the present embodiment, the sputtering method creates a first region 112 formed of, for example, a phosphate compound. For example, a target formed of a material represented by the general formula $\text{LiFe}_{y1}\text{M}_{1-y1}\text{PO}_4$ (M is one or more of Mn, Co, and Ni) ($y1$ is 0 to less than 1) is used to form a phosphate compound film having a film thickness of 10 nm to 3 μm .

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[0176]

It should be noted that heat treatment may be performed after forming the first region 112. For example, the first region 112 can be crystallized by performing a heat treatment. Or it can increase crystallinity.

[0177]

Preferably, the temperature of the heat treatment is between 450 °C and 700 °C. Also, the time of heat treatment may be 30 minutes to 40 hours or less, preferably 2 hours to 10 hours or less. In addition, it is preferable to use a noble gas atmosphere, nitrogen atmosphere, etc. as the atmosphere of the heat treatment. For example, the heating treatment can be performed at 600°C for 4 hours in a nitrogen atmosphere.

[0178]

First region 112 is thus formed.

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[0179]

Next, a second region 114 formed of a compound comprising lithium and iron is formed on the positive electrode current collector 200 by which the first region 112 is formed (Figure 9(C)).

[0180]

Methods of making the first region 114 formed of a compound comprising lithium and iron can use dry methods such as PVD (e.g., sputtering), vacuum vapor deposition, or CVD (e.g., plasma CVD, thermal CVD, LPCVD). By forming a second region 114 formed of a compound comprising lithium and iron using a dry method, a second region 114 formed of a homogeneous and thin film compound comprising lithium and iron can be obtained. Therefore, the charge/discharge characteristics of the positive electrode can be stabilized.

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[0181]

In the present embodiment, a sputtering method creates a second region 114 formed of, for example, a phosphate compound. For example, a target formed of a material represented by the general formula $\text{LiFe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ (Me is one or more of Mn, Co, and Ni) ($y2$ is 0 to 1 or less) is used to form a phosphate compound film having a film thickness of 1 nm to 3 μm .

[0182]

If the second region 114 is a compound that can be a positive electrode active material that contributes to charge and discharge, it does not have to lead to a decrease in capacity. If a phosphate compound comprising a region having an olivine structure in the second region 114 is used, a high capacity can be achieved in charge and discharge.

[0183]

On the other hand, since the second region 114 includes iron, the discharge potential is low and the energy density is therefore lower. Thus, the lower the ratio c_f ($c_f = d_f/r_f$) of the film thickness d_f of the second region 114, relative to the film thickness r_f of the positive electrode active material layer 201, the more preferred. The value of the ratio c_f is preferably 0. Specifically, the film thickness of the second region is preferably about 1 nm to 8 nm. Also, changing the ratio c_f can produce a positive electrode active material having the desired energy density. Also, in the general formula $\text{Li}_{1-x2}\text{Fe}_{y2}\text{Me}_{1-y2}\text{PO}_4$ ($x2$ is 0 to 1 or less) (Me is one or more of Mn, Co, and Ni), the value of $y2$ is greater than 0 and less than 1, preferably 0. A higher energy density can be achieved by setting this to 15 or more to 0.5 or less, more preferably 0.2 or more to 0.3 or less.

[0184]

The first region 112 and the second region 114 are collectively referred to in the specifications as positive electrode active material layer 201. Also, the positive electrode active material layer 201 and the positive electrode current collector 200 formed by it are collectively referred to as the positive electrode 202.

[0185]

It should be noted that heat treatment may be performed after forming the second region 114. For example, a positive electrode active material layer 201 comprising a first region 112 and a second region 114 can be crystallized by performing a heat treatment. Or it can increase crystallinity.

[0186]

Preferably, the temperature of the heat treatment is between 450 °C and 700 °C. Also, the time of heat treatment may be 30 minutes to 40 hours or less, preferably 2 hours to 10 hours or less. In addition, it is preferable to use a noble gas atmosphere, nitrogen atmosphere, etc. as the atmosphere of the heat treatment. For example, the heating treatment can be performed at 600°C for 4 hours in a nitrogen atmosphere.

[0187]

By adjusting the conditions of the heat treatment after the formation of the second region 114, elements contained in the first region 112 and the second region 114 can diffuse into each other's region, obscuring the boundaries of the first region 112 and the second region 114, and forming the structure (positive electrode active material layer 203) shown in Embodiment 6.

[0188]

A coating may be formed on the surface of the positive electrode active material layer 201 using carbon, etc. This can use dry methods such as PVD (e.g., sputtering), vacuum vapor deposition, or CVD (e.g., plasma CVD, thermal CVD, LPCVD). Alternatively, wet methods such as application methods may be used. Heat treatment may also be performed after coating (not shown).

[0189]

It should be noted that active substances refer to substances involved in the insertion and removal of ions that are carriers, and do not include carbon or other coatings.

[0190]

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In this way, a positive electrode 202 comprising a positive electrode active material layer 201 is made.

[0191]

Through the present embodiment, it is possible to lower the energy barrier in insertion and removal of lithium at the positive electrode active material surface. As a result, the available capacity can be brought closer to the theoretical capacity, and a positive electrode 202 can be formed that can take advantage of the high discharge potential of one or more of manganese, cobalt, and nickel.

[0192]

(Embodiment 10)

In the present embodiment, an application of the power storage device described in Embodiment 5 is described.

[0193]

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The power storage device described in Embodiment 5 can be used in electronic devices including cameras such as digital cameras and video cameras, digital photo frames, mobile phones (also referred to as mobile phones and mobile phone devices), portable gaming machines, mobile information terminals, acoustic playback devices, etc. It can also be used for electric vehicles, hybrid vehicles, electric railroad vehicles, work vehicles, carts, wheelchairs, bicycles, etc.

[0194]

Figure 10(A) shows an example of a cell phone. Handset 410 incorporates a display 412 in the housing 411. The housing 411 further includes control button 413, control button 417, external connection port 414, speaker 415, microphone 416, and the like. In addition, the power storage device 418 is located in the housing 411 and can be charged from the external connection port 414. The power storage device described in Embodiment 5 can be used as the power storage device 418 of the handset 410.

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[0195]

Figure 10(B) shows an example of an e-book terminal. The e-book terminal 430 is composed of two housings, a first housing 431 and a second housing 433, with the two housings integrated by the shaft 432. First housing 431 and second housing 433 can open and close on shaft 432. First housing 431 includes a first display 435 and second housing 433 includes a second display 437. The second housing 433 also includes an operation button 439, a power source 443, and a speaker 441, etc. Also, the power storage device 444 is built into the second housing 433 and can be charged from the power supply 443. The power storage device described in Embodiment 5 can be used as the power storage device 444 of the e-book terminal 430.

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[0196]

Figure 11 is a perspective view of an electrically powered wheelchair 501. The electrically powered wheelchair 501 has a seat 503 on which the user sits, a backrest 505 provided behind the seat 503, a footrest 507 provided below and in front of the seat 503, an armrest 509 provided on the left and right sides of the seat 503, and a handle 511 provided on the top rear of the backrest 505. One of the armrests 509 is provided with a controller 513 that controls movement of the wheelchair. A pair of front wheels 517 are provided in front of and below the seat 503 via the frame 515 below the seat 503, and

a pair of rear wheels 519 are provided behind and below the seat 503. Rear wheel 519 is connected to drive 521 having a motor, brake, gear, etc. Below the seat 503 is provided a control unit 523 having a battery, power control unit, control means, etc. The control part 523 is connected to the controller 513 and the drive part 521, and operation of the controller 513 by a user drives the drive part 521 via the control part 523 to control the movement and speed of the electrically powered wheelchair 501, such as moving forward, in reverse, pivoting.

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[0197]

The power storage device described in Embodiment 5 can be used for the battery of the control unit 523. The battery of the control unit 523 can be charged by power supply from the outside by plug-in technology.

[0198]

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Figure 12 shows an example of an electric vehicle. The electric vehicle 650 is equipped with a power storage device 651. The power of the power storage device 651 is adjusted by the control circuitry 653 to supply the power to the drive device 657. The control circuitry 653 is controlled by the computer 655.

[0199]

The drive 657 is configured as a DC or AC motor alone, or as a combination of the motor and the internal combustion engine. The computer 655 outputs a control signal to the control circuit 653 based on input information of the operator of the electric vehicle 650 (acceleration, deceleration, stop, etc.) and information on driving (information on climbing, downhill, etc., load information on the drive wheels, etc.). The control circuitry 653 adjusts the electrical energy supplied from the power storage device 651 to control the output of the drive device 657 by means of a control signal of the computer 655. If an AC motor is installed, an inverter that converts DC to AC is also built in.

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[0200]

The power storage device described in Embodiment 5 can be used for the battery of the power storage device 651. The power storage device 651 can be charged by an external power supply by plug-in technology.

[0201]

If the electric propulsion vehicle is a railway electric vehicle, it can be charged by power supply from overhead wires or conductive tracks.

[0202]

The present embodiments can be suitably combined with other embodiments.

[0203]

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(Embodiment 11)

In this embodiment, an example of the case where the power storage device of one embodiment of the Present Invention is used in a wireless power supply system is described with reference to block diagrams of Figures 13 and 14. Although each block diagram classifies the components of the power receiving device and the power supply device by function and shows them as separate blocks, the actual components are difficult to completely separate by function, as one component may be involved in multiple functions.

[0204]

To begin, an RF powering system is described using Figure 13.

[0205]

The power receiving device 800 is an electronic device or electric propulsion vehicle driven by power supplied by the power supply device 900, which can be applied accordingly to those driven by other power. Representatives of electronic devices include cameras such as digital cameras and video cameras, digital photo frames, mobile phones (also referred to as mobile phones and mobile devices), portable gaming machines, mobile information terminals, acoustic playback devices, display devices, computers, etc. Representative examples of electric propulsion vehicles include electric vehicles, hybrid vehicles, electric railroad vehicles, work vehicles, carts, wheelchairs, etc. The power supply device 900 also has the function of supplying power to the power receiving device 800.

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[0206]

In Figure 13, the power receiving device 800 has a power receiving device part 801 and a power supply load part 810. The power receiving device part 801 has at least an antenna circuit 802 for the power receiving device, a signal processing circuit 803, and a power storage device 804. The power supply 900 also includes an antenna circuit 901 for the power supply and a signal processing circuit 902.

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[0207]

Antenna circuit 802 for the power receiving device has the role of receiving a signal emitted by antenna circuit 901 for the power supply device or transmitting a signal to antenna circuit 901 for the power supply device. The signal processing circuit 803 processes the signals received by the antenna circuit 802 for the power receiving device and controls the charging of the power storage device 804 and the supply of power from the power storage device 804 to the power supply load 810. The power supply load 810 is a drive that receives power from the power storage device 804 and drives the power receiving device 800. Representative examples of power supply load part 810 include motors, drive circuits, etc., but other power supply load parts can be used as appropriate. The antenna circuit 901 for the power supply device is also responsible for sending a signal to the antenna circuit 802 for the power receiving device or for receiving a signal from the antenna circuit 802 for the power receiving device. The signal processing

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circuit 902 controls operation of the antenna circuit 901 for the power supply device. That is, the intensity, frequency, etc. of the signal emitted from the antenna circuit 901 for the power supply device can be controlled.

[0208]

The power storage device related to one aspect of the Present Invention is utilized as a power storage device 804 that the power receiving device 800 has in an RF power supply system.

[0209]

By utilizing the power storage device related to one aspect of the Present Invention in an RF power supply system, the power storage amount can be increased compared to conventional power storage devices. Therefore, the interval between wireless power supplies can be increased (eliminates the need to supply power repeatedly).

[0210]

In addition, by utilizing the power storage device related to one aspect of the Present Invention in the RF power supply system, if the power storage amount that can drive the power supply load part 810 is the same as before, it is possible to miniaturize and lighten the power receiving device 800. Therefore, the total cost can be reduced.

[0211]

Other examples of RF power delivery systems will now be described using Figure 14.

[0212]

In Figure 14, the power receiving device 800 has a power receiving device part 801 and a power supply load part 810. The power receiving device part 801 has at least an antenna circuit 802 for the power receiving device, a signal processing circuit 803, a power storage device 804, a rectification circuit 805, a modulation circuit 806, and a power supply circuit 807. The power supply 900 also has at least an antenna circuit 901 for the power supply device, a signal processing circuit 902, a rectification circuit 903, a modulation circuit 904, a demodulation circuit 905, and an oscillation circuit 906.

[0213]

Antenna circuit 802 for the power receiving device has the role of receiving a signal emitted by antenna circuit 901 for the power supply device or transmitting a signal to antenna circuit 901 for the power supply device. If the antenna circuit 901 for the power supply device receives a signal emitted, the rectification circuit 805 is responsible for generating a DC voltage from the signal received by the antenna circuit 802 for the power receiving device. The signal processing circuit 803 processes the signals received by the antenna circuit 802 for the power receiving device and controls the charging of the power storage device 804 and the supply of power from the power storage device 804 to the power circuit 807. The power supply circuit 807 has the role of converting the voltage stored by the power storage device 804 to the voltage required by the power supply load part 810. Modulation circuit 806 is used to send any response from power receiving device 800 to power supply device 900.

[0214]

Having a power supply circuit 807 can control the power supplied to the power supply load part 810. For this reason, it is possible to reduce the overvoltage applied to the power supply load part 810, and to thereby reduce the deterioration and breakdown of the power receiving device 800.

[0215]

Also, having a modulation circuit 806 allows a signal to be sent from the power receiving device 800 to the power supply device 900. Therefore, the charge amount of the power receiving device 800 can be determined, and if a certain amount of charge is made, a signal can be sent from the power receiving device 800 to the power supply device 900 to stop the power supply from the power supply device 900 to the power receiving device 800. As a result, it is possible to not charge the power storage device 804 100% and to thereby reduce deterioration and destruction due to overcharging and to increase the number of times the power storage device 804 is charged.

[0216]

The antenna circuit 901 for the power supply device also serves to signal the antenna circuit 802 for the power receiving device or to receive signals from the antenna circuit 802 for the power receiving device. When sending a signal to the antenna circuit 802 for the power receiving device, the signal processing circuit 902 is a circuit that generates a signal to be sent to the power receiving device 800. The oscillating circuit 906 is a circuit that generates a signal at a constant frequency. The modulation circuit 904 has the role of applying voltage to the antenna circuit 901 for the power supply device according to the signal generated by the signal processing circuit 902 and a constant frequency signal generated by the oscillation circuit 906. In doing so, a signal is output from the antenna circuit 901 for the power supply device. On the other hand, when receiving a signal from the antenna circuit 802 for the power receiving device, the rectification circuit 903 serves to rectify the received signal. The demodulation circuit 905

extracts the signal sent by the power receiving device 800 to the power supply 900 from the signal that the rectification circuit 903 has rectified. The signal processing circuit 902 serves to analyze the signals extracted by the demodulation circuit 905.

[0217]

If RF power can be supplied, any circuit may exist between each circuit. For example, after the receiving device 800 receives electromagnetic waves and generates a DC voltage at the rectification circuit 805, a circuit such as a DC-DC converter or regulator may be provided to generate a constant voltage. Doing so can inhibit overvoltage from being applied to the interior of the power receiving device 800.

[0218]

The power storage device related to one aspect of the Present Invention is utilized as a power storage device 804 that the power receiving device 800 has in an RF power supply system.

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[0219]

By using the power storage device related to one aspect of the Present Invention in an RF power supply system, the amount of power storage can be increased compared to conventional power storage devices, so the interval between wireless power supply can be extended (eliminates the need to supply power repeatedly).

[0220]

In addition, by utilizing the power storage device related to one aspect of the Present Invention in the RF power supply system, if the power storage amount that can drive the power supply load part 810 is the same as before, it is possible to miniaturize and lighten the power receiving device 800. Therefore, the total cost can be reduced.

[0221]

If the power storage device related to one aspect of the Present Invention is used in the RF power supply system and the antenna circuit 802 for the power receiving device and the power storage device 804 are superimposed, it is preferable that the shape changes as the power storage device 804 is charged and discharged, so that the impedance of the antenna circuit 802 for the power receiving device does not change. This is because if the impedance of the antenna changes, there may be insufficient power supply. For example, the power storage device 804 may be loaded into a metal or ceramic battery pack. At that time, it is desirable that the antenna circuit 802 for the power receiving device and the battery pack are separated by several tens of μm or more.

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[0222]

Also, in the present embodiment, there is no particular limitation on the frequency of the signal for charging, and at any frequency at which power can be transmitted, any band is acceptable. The charging signal may be, for example, a 135 kHz L F band (long wave), the 13.56 MHz HF band, the 900 MHz to 1GHz UHF band, or the 2.45 GHz microwave band.

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[0223]

In addition, there are various types of signal transmission methods, such as electromagnetic coupling method, electromagnetic induction method, resonance method, microwave method, etc., so select this as appropriate. However, in order to suppress the loss of energy due to moisture-containing foreign matter such as rain and mud, it is desirable to use an electromagnetic induction method and resonance method using frequencies in low frequency bands, specifically short waves of 3 MHz to 30 MHz, medium waves of 300 kHz to 3 MHz, long waves of 30 kHz to 300 kHz, and ultra-long waves of 3 kHz to 30 kHz.

[0224]

The present embodiment can be implemented in combination with the above embodiments.

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[Explanation of references]

[0225]

- 100 Positive electrode active materials
- 102 First region
- 104 Second region

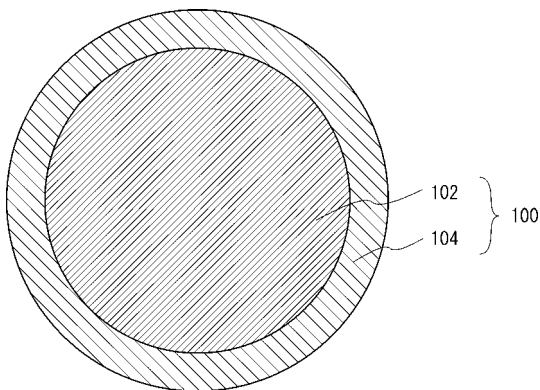
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112	First region	
114	Second region	
200	Positive electrode current collector	
201	Positive electrode active materials	
202	positive electrode	
203	Positive electrode active material layer	
205	Negative electrode current collector	
206	Negative electrode active material layer	
207	Negative electrode	
210	Separator	10
211	Electrolytic solution	
220	Housing	
221	First electrode	
222	Second electrode	
410	Handset	
411	Housing	
412	Display	
413	Control button	
414	External connection port	
415	Speaker	
416	Microphone	20
417	Control button	
418	Power storage equipment	
430	e-book terminal	
431	Housing	
432	Shaft	
433	Housing	
435	Display	
437	Display	
439	Control button	
441	Speaker	
443	Power supply	30
444	Power storage equipment	
501	Electrically powered wheelchair	
503	Seat	
505	Backrest	
507	Footrest	
509	Armrest	
511	Handle	
513	Controller	
515	Frame	
517	Pair of front wheels	
519	Pair of rear wheels	40
521	Drive part	
523	Control unit	
650	Electric vehicle	
651	Power storage equipment	
653	Control circuit	
655	Computer	

- 657 Drive device
- 800 Power receiving device
- 801 Power receiving device part
- 802 Antenna circuit for the power receiving device
- 803 Signal processing circuit
- 804 Power storage equipment
- 805 Rectification circuit
- 806 Modulation circuit
- 807 Power supply circuit
- 810 Power supply load part
- 900 Power supply
- Antenna circuit 901 for the power supply device
- 902 Signal processing circuit
- 903 Rectification circuit
- 904 Modulation circuit
- 905 Demodulation circuit
- 906 Oscillation circuit

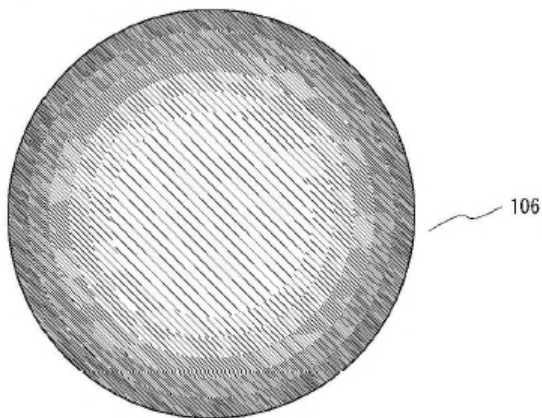
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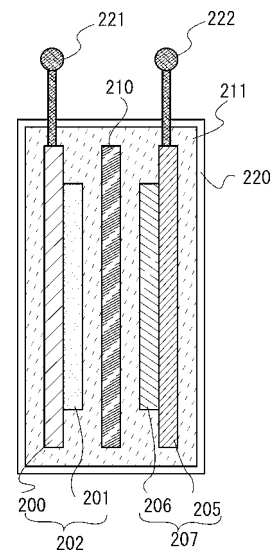
[Figure 1]



[Figure 2]

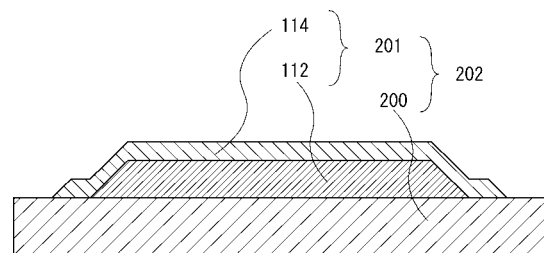


[Figure 3]



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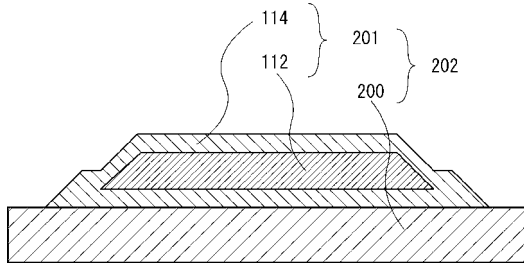
[Figure 4]



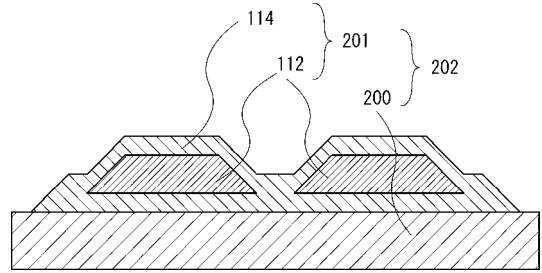
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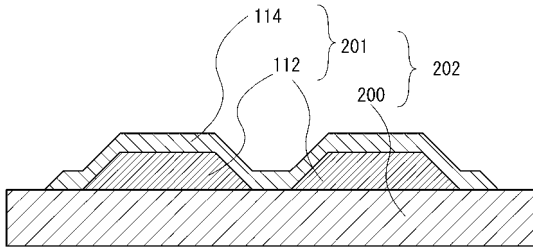
[Figure 5]



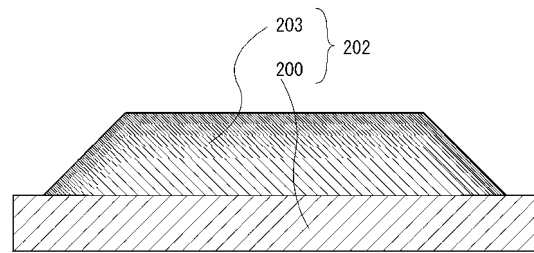
[Figure 7]



[Figure 6]



[Figure 8]

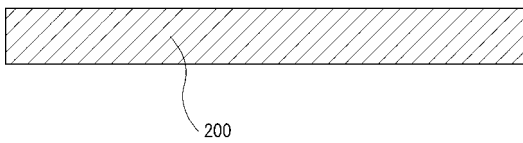


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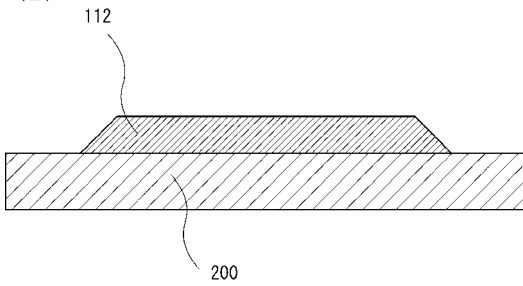
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[Figure 9]

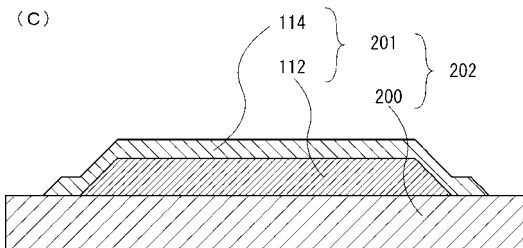
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(B)

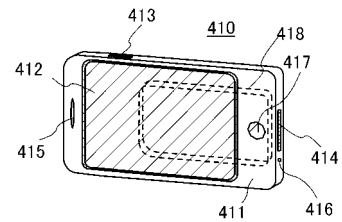


(C)



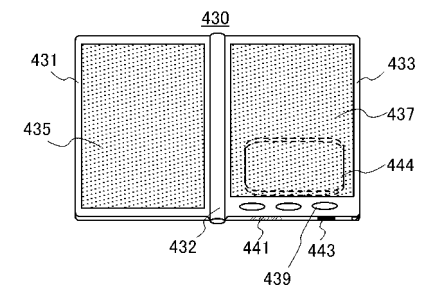
[Figure 10]

(A)



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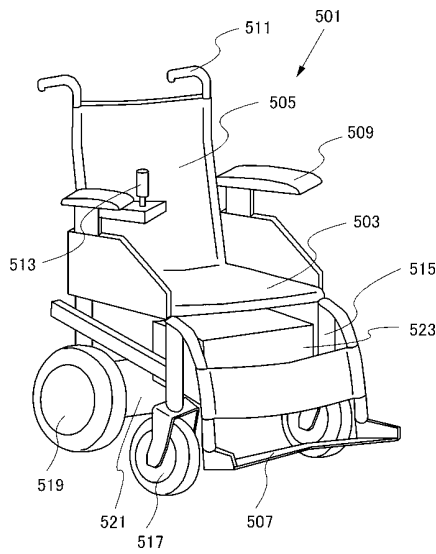
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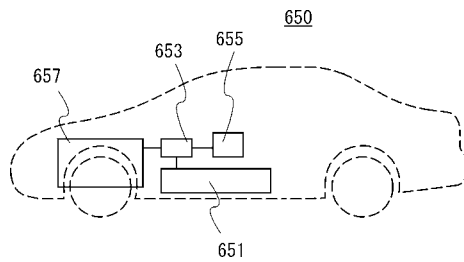
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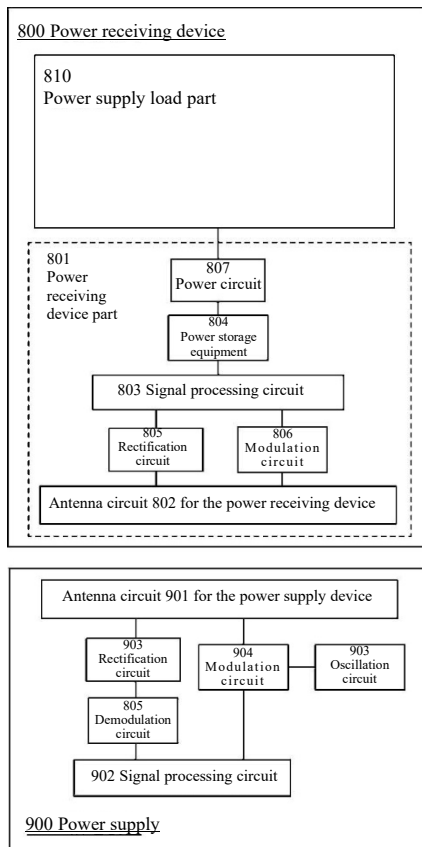
[Figure 11]



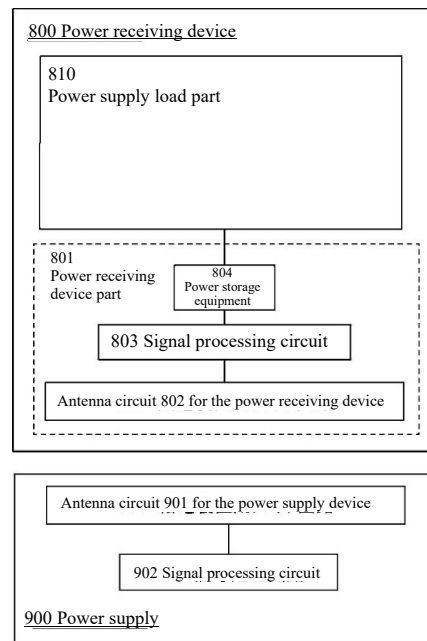
[Figure 12]



[Figure 14]



[Figure 13]



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Daniel McDonald

NAME

4/12/2023
DATE