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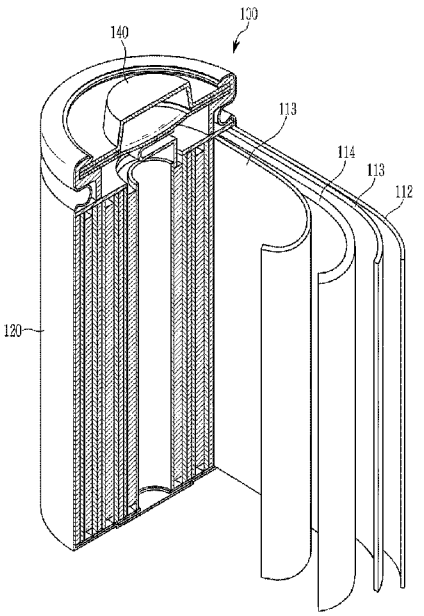
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(54) Titre : MATIERE ACTIVE POSITIVE POUR BATTERIES RECHARGEABLES AU LITHIUM, METHODE DE PREPARATION ET BATTERIES RECHARGEABLES AU LITHIUM COMPRENANT LADITE MATIERE

(54) Title: POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERIES, PREPARATION METHOD THEREOF AND RECHARGEABLE LITHIUM BATTERIES INCLUDING THE SAME



(57) Abrégé/Abstract:
Disclosed are a positive active material for a rechargeable lithium battery, a preparation method thereof, and a rechargeable lithium battery including the same. The positive active material for a rechargeable lithium battery includes a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated, and a second positive active material in a form of a single particle, wherein each of the first positive active material and the second positive active material includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, the first positive active material includes a coating portion in a form of a film on the surface of the secondary particle, the second positive active material includes a coating portion in a form of a film on the surface of the single particle, the coating portion of the first positive active material and the coating portion of the second positive active material includes lithium cobalt oxide and cobalt oxyhydroxide, respectively.

ABSTRACT

Disclosed are a positive active material for a rechargeable lithium battery, a preparation method thereof, and a rechargeable lithium battery including the same. The positive active material for a rechargeable lithium battery includes a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated, and a second positive active material in a form of a single particle, wherein each of the first positive active material and the second positive active material includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, the first positive active material includes a coating portion in a form of a film on the surface of the secondary particle, the second positive active material includes a coating portion in a form of a film on the surface of the single particle, the coating portion of the first positive active material and the coating portion of the second positive active material includes lithium cobalt oxide and cobalt oxyhydroxide, respectively.

Date Reçue/Date Received 2023-11-15

POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERIES, PREPARATION METHOD THEREOF AND RECHARGEABLE LITHIUM BATTERIES INCLUDING THE SAME

BACKGROUND OF THE INVENTION

(a) Field of the Invention

A positive active material for rechargeable lithium batteries, a preparation method thereof, and rechargeable lithium batteries including the same are disclosed.

(b) Description of the Related Art

A portable information device such as a cell phone, a laptop, smart phone, and the like or an electric vehicle has used a rechargeable lithium battery having high energy density and easy portability as a driving power source. Recently, research has been actively conducted to use a rechargeable lithium battery with high energy density as a driving power source or power storage power source for hybrid or electric vehicles.

Various positive active materials have been investigated to realize rechargeable lithium batteries for applications to the uses. Among them, lithium nickel-based oxide, lithium nickel manganese cobalt composite oxide, lithium nickel cobalt aluminum composite oxide, and lithium cobalt oxide are mainly used as positive active materials. However, these positive active materials have structure collapses or cracks during the repeated charges and discharges and thus problems of deteriorating a long-term cycle-life of a rechargeable lithium battery and increasing resistance and thus exhibiting no satisfactory capacity characteristics. Accordingly, development of a novel positive active material securing long-term cycle-life characteristics as well as realizing high capacity and

Date Reçue/Date Received 2023-11-15

high energy density is required.

SUMMARY OF THE INVENTION

While increasing the energy density of the high-nickel-based positive active material, long-term cycle-life characteristics and thermal stability characteristics may be improved.

In an embodiment, a positive active material for a rechargeable lithium battery includes a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated, and a second positive active material in a form of a single particle, wherein each of the first positive active material and the second positive active material includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, the first positive active material includes a coating portion in a form of a film on the surface of the secondary particle, the second positive active material includes a coating portion in a form of a film on the surface of the single particle, the coating portion of the first positive active material and the coating portion of the second positive active material includes lithium cobalt oxide and cobalt oxyhydroxide, respectively.

In another embodiment, a method of preparing a positive active material for a rechargeable lithium battery includes adding a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated and which includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, a second positive active material in a form of a single particle which includes lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol%

Date Reçue/Date Received 2023-11-15

relative to the total elements excluding lithium and oxygen, cobalt sulfate, and sodium hydroxide, to a solvent, followed by mixing the resultant; removing the solvent; adding a lithium raw material to the obtained product; and performing heat treatment to obtain the aforementioned positive active material.

In another embodiment, a rechargeable lithium battery includes a positive electrode including the positive active material, a negative electrode, and an electrolyte.

The positive active material for a rechargeable lithium battery according to an embodiment has enhanced stability while implementing high capacity and high energy density, and a rechargeable lithium battery including the positive active material has improved high-temperature long-term cycle-life characteristics and thermal stability.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view illustrating a rechargeable lithium battery according to an embodiment.

FIG. 2 is an X-ray diffraction (XRD) analysis graph of the positive active material prepared in Example 1, the positive electrode plate before cycle-life, and the positive electrode plate after cycle-life.

FIG. 3 is an enlarged view of the graph in the vicinity of 20 ° in FIG. 2.

FIG. 4 is an enlarged view of a graph near 40 ° in FIG. 2.

FIG. 5 is an graph showing X-ray diffraction analysis for $Co(OH)_2$, CoOOH, and Co_3O_4.

FIG. 6 is an image in which cobalt elements are highlighted by SEM-EDS analysis of a fracture surface of the first positive active material of Example 1.

FIG. 7 is an image in which cobalt elements are highlighted by SEM-EDS analysis

Date Reçue/Date Received 2023-11-15

of a fracture surface of the second positive active material of Example 1.

FIG. 8 is a graph showing cycle-life characteristic evaluation for half-cells manufactured in Example 1, Comparative Example 1, and Comparative Example 2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, specific embodiments will be described in detail so that those of ordinary skill in the art can easily implement them. However, this disclosure may be embodied in many different forms and is not construed as limited to the example embodiments set forth herein.

The terminology used herein is used to describe embodiments only, and is not intended to limit the present invention. The singular expression includes the plural expression unless the context clearly dictates otherwise.

As used herein, "combination thereof" means a mixture, laminate, composite, copolymer, alloy, blend, reaction product, and the like of the constituents.

Herein, it should be understood that terms such as "comprises," "includes," or "have" are intended to designate the presence of an embodied feature, number, step, element, or a combination thereof, but it does not preclude the possibility of the presence or addition of one or more other features, number, step, element, or a combination thereof.

In the drawings, the thickness of layers, films, panels, regions, etc., are exaggerated for clarity and like reference numerals designate like elements throughout the specification. It will be understood that when an element such as a layer, film, region, or substrate is referred to as being “on” another element, it can be directly on the other element or intervening elements may also be present. In contrast, when an element is referred to as being “directly on” another element, there are no intervening elements

Date Reçue/Date Received 2023-11-15

present.

In addition, "layer" herein includes not only a shape formed on the whole surface when viewed from a plan view, but also a shape formed on a partial surface.

In addition, the average particle diameter may be measured by a method well known to those skilled in the art, for example, may be measured by a particle size analyzer, or may be measured by a transmission electron micrograph or a scanning electron micrograph. Alternatively, it is possible to obtain an average particle diameter value by measuring using a dynamic light scattering method, performing data analysis, counting the number of particles for each particle size range, and calculating from this. Unless otherwise defined, the average particle diameter may mean the diameter (D50) of particles having a cumulative volume of 50 volume% in the particle size distribution.

Herein, “or” is not to be construed as an exclusive meaning, for example, “A or B” is construed to include A, B, A+B, and the like.

Positive Active Material

In an embodiment, a positive active material for a rechargeable lithium battery includes a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated, and a second positive active material in a form of a single particle.

Each of the first positive active material and the second positive active material includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen. That is, the first positive active material and the second positive active material may be referred to as high nickel-based positive active materials.

Date Reçue/Date Received 2023-11-15

In addition, the first positive active material includes a coating portion on the surface of the secondary particle in a form of a film, and the second positive active material includes a coating portion on the surface of the single particle in a form of a film. Herein, the coating portion of the first positive active material and the coating portion of the second positive active material may include lithium cobalt oxide ($LiCoO_2$) and cobalt oxyhydroxide (CoOOH), respectively.

In the coating portion, the cobalt oxyhydroxide has an R-3m crystal structure and has little structural heterogeneity with the lithium nickel-based composite oxide, thereby facilitating lithium movement and thus improving the performance of the rechargeable lithium battery.

The coating portion may include a composite phase of lithium cobalt oxide and cobalt oxyhydroxide. Through this composite phase, the surface structure of the positive active material may be strengthened, and thus side reactions between the positive active material and the electrolyte may be suppressed, and cycle-life characteristics, overcharge characteristics, and high-temperature storage characteristics of the rechargeable lithium battery may be improved. Through the composite phase, it is possible to overcome the unstable structure of the high-nickel-based positive active material and secure stable characteristics comparable to that of the low-nickel-based positive active material.

The composite phase may be confirmed through X-ray diffraction analysis of the positive active material or the positive electrode plate. For example, the positive active material may exhibit peaks at about 19.5 ° to about 20.5 ° and about 39 ° to about 40 ° in X-ray diffraction analysis, and these peaks may indicate the presence of cobalt oxyhydroxide.

Date Reçue/Date Received 2023-11-15

The coating portion exists in the form of a film, and may be in a form of a continuous coating layer or in a form of an island, which is different from existing in a form of particles.

Each of the coating portion of the first positive active material and the coating portion of the second positive active material may have a thickness of about 1 nm to about 500 nm, for example, about 1 nm to about 400 nm, about 1 nm to about 300 nm, about 1 nm to about 200 nm, about 1 nm to about 100 nm, about 5 nm to about 50 nm, or about 5 nm to about 40 nm. Since the coating portion is formed within these thickness ranges, the performance of the rechargeable lithium battery may be improved by stabilizing the structure of the positive active material and suppressing a side reaction with the electrolyte without acting as resistance or deteriorating battery performance. The thickness of the coating portion may be measured by TOF-SIMS, XPS, or EDS, and may be measured, for example, by TEM-EDS line profile.

In the positive active material, a cobalt content of the coating portion may be about 0.5 mol% to about 5 mol%. Specifically, in the entire positive active material, the cobalt content of the surface based on 100 mol% of the elements excluding lithium and oxygen in the lithium nickel-based composite oxide may be about 0.5 mol% to about 5 mol%, for example, about 0.5 mol% to about 4 mol%, or about 1 mol% to about 3 mol%. By coating with the cobalt content, the structure of the positive active material may be stabilized and the efficiency and cycle-life characteristics of the battery may be improved without reducing the capacity.

Meanwhile, according to an embodiment, a ratio of a cobalt content (at%) based on the total amount of nickel and cobalt in the coating portion of the first positive active

Date Reçue/Date Received 2023-11-15

material relative to a cobalt content (at%) based on the total amount of nickel and cobalt in the coating portion of the second positive active material may be about 1.45 to about 1.60. In the positive active material in which the first positive active material in the form of secondary particles is mixed with the second positive active material in the form of single particles, when each coating portion in both of the positive active materials is formed, there may be coating imbalance between two types of the particles. For example, when cobalt-coating is simultaneously carried out in a wet manner after mixing two types of the particles, the single particles having a relatively large specific surface area tend to be more reacted and coated with the coating material. As a result, the secondary particle does not obtain sufficient coating effect, causing structural collapse or side reactions on the surface to accelerate degradation, and coating particles are non-uniformly present on the surface, causing gas generation. In the single particle, excessive coating acts as resistance, which adversely affects battery performance. On the other hand, according to an embodiment, the performance of the rechargeable lithium battery, such as high-temperature long-term cycle-life characteristics, is improved by reinforcing the coating of the secondary particles while suppressing excessive coating on single particles, that is, by appropriately adjusting a relationship between the coating contents of the two types of particles. For example, when a ratio of the cobalt coating content of the first positive active material to the cobalt coating content of the second positive active material satisfies about 1.45 to about 1.60, it is possible to improve high-temperature long-term cycle-life characteristics, suppress gas generation during high-temperature storage, and improve initial charge and discharge efficiency while realizing high capacity and high energy density. The ratio may be, for example, about 1.45 to about 1.55, or about 1.50 to about

Date Reçue/Date Received 2023-11-15

1.60.

First Positive Active Material

The first positive active material is in a polycrystal form and includes secondary particles in which at least two or more primary particles are aggregated. The first positive active material according to an embodiment includes a coating portion in a form of a film along the surface of the secondary particle, and includes a composite phase of lithium cobalt oxide and cobalt oxyhydroxide.

The cobalt content based on the total amount of nickel and cobalt in the cobalt coating portion of the first positive active material may be about 55 at% to about 70 at%, for example, about 55 at% to about 68 at%, about 55 at% to about 65 at%, about 55 at% to about 63 at%, about 57 at% to about 70 at%, about 59 at% to about 70 at%, about 60 at% to about 70 at%, about 60 at% to about 65 at%, or about 61 at% to about 63 at%. When the cobalt coating content of the first positive active material satisfies the above range and is about 1.45 times to about 1.60 times the cobalt coating content of the second positive active material, non-uniform coating between particles is eliminated, and a uniform coating is formed on the surface of the first positive active material to suppress gas generation and to improve initial charge/discharge efficiency and long-term cycle-life characteristics.

The first positive active material according to an embodiment may further include a grain boundary cobalt coating portion on the surface of the primary particles inside the secondary particles. The grain boundary coating portion may include lithium cobalt oxide and cobalt oxyhydroxide. The grain boundary cobalt coating portion exists inside the secondary particle, not on the surface, and may be said to be coated along the interface

Date Reçue/Date Received 2023-11-15

of the primary particles inside the secondary particle, and thus may be expressed as being coated on the grain boundary. Herein, the inside of the secondary particle means the entire inside except for the surface, and for example, it may mean the entire inside from a depth of about 10 nm from the outer surface, or a region from a depth of about 10 nm to a depth of about 2 μm. The first positive active material according to an embodiment further includes a grain boundary cobalt coating portion, thereby enhancing structural stability, inducing a uniform and even coating on the surface, and properly adjusting the coating content on the surface to obtain initial charge/discharge efficiency and cycle-life characteristics without increasing resistance.

An average particle diameter of the first positive active material, that is, the average particle diameter of the secondary particles may be about 5 μm to about 20 μm. For example, it may be about 7 μm to about 20 μm, about 10 μm to about 20 μm, or about 12 μm to about 18 μm. The average particle diameter of the secondary particles of the first positive active material may be greater than the average particle diameter of the second positive active material of single particles, which will be described later. The positive active material according to an embodiment may be a mixture of a first positive active material that is polycrystalline and large particles and a second positive active material that is single and small particles, thereby improving the mixture density and implementing high capacity and high energy density. Herein, the average particle diameter of the first positive active material may be obtained by measuring the particle diameter of about 20 active materials in the form of the secondary particle randomly in an electron microscope photograph of the positive active material, and taking the diameter (D50) of the particle having a cumulative volume of 50 volume% in the particle size

Date Reçue/Date Received 2023-11-15

distribution as the average particle diameter.

The first positive active material may be a high-nickel-based positive active material having a high nickel content. The nickel content in the lithium nickel-based composite oxide may be greater than or equal to about 70 mol%, for example, greater than or equal to about 75 mol%, greater than or equal to about 80 mol%, greater than or equal to about 85 mol%, or greater than or equal to about 90 mol% and less than or equal to about 99.9 mol%, or less than or equal to about 99 mol% based on the total amount of elements other than lithium and oxygen. Such a high-nickel-based first positive active material may realize high capacity and high performance.

Second Positive Active Material

The second positive active material is in the form of a single particle, exists alone without a grain boundary within the particle, is composed of one particle, and has a monolith structure, an one body structure, or a non-aggregated particle, in which particles are not aggregated with each other but exist as an independent phase in terms of morphology, and may be expressed as a single particle (one body particle, single grain), for example, as a single crystal. The positive active material according to an embodiment may exhibit improved cycle-life characteristics while realizing high capacity and high energy density by including the second positive active material in the form of a single particle.

The second positive active material according to an embodiment includes a film-shaped coating portion formed along the surface of a single particle, and the coating portion includes a composite phase of lithium cobalt oxide and cobalt oxyhydroxide.

The cobalt content based on the total amount of nickel and cobalt in the coating

Date Reçue/Date Received 2023-11-15

portion of the second positive active material may be about 39 at% to about 45 at%, for example, about 39 at% to about 44 at%, about 39 at% to about 43 at%, about 39 at% to about 42 at%, about 40 at% to about 45 at%, or about 41 at% to about 45 at%. When the cobalt coating content of the second positive active material satisfies the above range and the ratio of the cobalt coating content of the first positive active material to the cobalt coating content of the second positive active material satisfies about 1.45 to about 1.60, non-uniform coating between particles is eliminated, excessive coating of the second positive active material is suppressed, and uniform coating is induced, thereby reducing resistance and improving initial charge/discharge efficiency and long-term cycle-life characteristics.

On the other hand, in an embodiment, a method for measuring the cobalt content relative to the total amount of nickel and cobalt on the surface of the positive active material may include performing scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) on the surface of the positive active material, obtaining respective contents of nickel and cobalt through quantitative analysis, and then calculating a ratio of the cobalt contents to the sum. In addition to SEM-EDS, methods for measuring cobalt content may include Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), etc.

An average particle diameter of the second positive active material, that is, the average particle diameter of a single particle may be about 0.1 μm to about 10 μm, for example, about 0.1 μm to about 7 μm, about 0.5 μm to about 6 μm, or about 1 μm to about 5 μm. The particle diameter of the second positive active material may be smaller

Date Reçue/Date Received 2023-11-15

than that of the first positive active material, and thus, the density of the positive active material may be further increased. Herein, the average particle diameter of the second positive active material may be obtained by measuring the particle diameter of about 20 active materials in the form of the single particle randomly in an electron microscope photograph of the positive active material, and taking the diameter (D50) of the particle having a cumulative volume of 50 volume% in the particle size distribution as the average particle diameter.

The second positive active material may be a high-nickel-based positive active material having a high nickel content. The nickel content in the lithium nickel-based composite oxide may be greater than or equal to about 70 mol%, for example, greater than or equal to about 75 mol%, greater than or equal to about 80 mol%, greater than or equal to about 85 mol%, or greater than or equal to about 90 mol% and less than or equal to about 99.9 mol%, or less than or equal to about 99 mol% based on the total amount of elements other than lithium and oxygen. Such a high-nickel-based second positive active material may realize high capacity and high performance.

Specifically, the first positive active material and the second positive active material may each independently include a lithium nickel-based composite oxide represented by Chemical Formula 1.

[Chemical Formula 1]

$Li_{a1}Ni_{x1}M^1_{y1}M^2_{z1}O_{2-b1}X_{b1}$

In Chemical Formula 1, $0.9 \leq a1 \leq 1.8$, $0.7 \leq x1 \leq 1$, $0 \leq y1 \leq 0.3$, $0 \leq z1 \leq 0.2$, $0.9 \leq x1+y1+z1 \leq 1.1$, $0 \leq b1 \leq 0.1$, M^1 and M^2 are each independently at least one element selected from Al, B, Ba, Ca, Ce, Co, Cr, Cu, Fe, Mg, Mn, Mo, Nb, Si, Sr, Ti, V,

Date Reçue/Date Received 2023-11-15

W, and Zr, and X is at least one element selected from F, P, and S.

In Chemical Formula 1, $0.8 \leq x1 \leq 1$, $0 \leq y1 \leq 0.2$, and $0 \leq z1 \leq 0.15$, or $0.9 \leq x1 \leq 1$, $0 \leq y1 \leq 0.1$, and $0 \leq z1 \leq 0.1$.

For example, the first positive active material and the second positive active material may each independently include a lithium nickel-based composite oxide represented by Chemical Formula 2. The compound represented by Chemical Formula 2 may be referred to as a lithium nickel cobalt-based composite oxide.

[Chemical Formula 2]

$Li_{a2}Ni_{x2}Co_{y2}M^3_{z2}O_{2-b2}X_{b2}$

In Chemical Formula 2, $0.9 \leq a2 \leq 1.8$, $0.7 \leq x2 < 1$, $0 < y2 \leq 0.3$, $0 \leq z2 \leq 0.2$, $0.9 \leq x2+y2+z2 \leq 1.1$, $0 \leq b2 \leq 0.1$, M^3 at least one element selected from Al, B, Ba, Ca, Ce, Cr, Cu, Fe, Mg, Mn, Mo, Nb, Si, Sr, Ti, V, W, and Zr, and X is at least one element selected from F, P, and S.

In Chemical Formula 2, $0.8 \leq x2 \leq 0.99$, $0.01 \leq y2 \leq 0.2$, and $0.01 \leq z2 \leq 0.15$, or $0.9 \leq x2 \leq 0.99$, $0.01 \leq y2 \leq 0.1$, and $0.01 \leq z2 \leq 0.1$.

For example, the first positive active material and the second positive active material may each independently include a lithium nickel-based composite oxide represented by Chemical Formula 3. The compound represented by Chemical Formula 3 may be referred to as lithium nickel-cobalt-aluminum oxide or lithium nickel-cobalt-manganese oxide.

[Chemical Formula 3]

$Li_{a3}Ni_{x3}Co_{y3}M^4_{z3}M^5_{w3}O_{2-b3}X_{b3}$

In Chemical Formula 3, $0.9 \leq a3 \leq 1.8$, $0.7 \leq x3 \leq 0.98$, $0.01 \leq y3 \leq 0.29$,

Date Reçue/Date Received 2023-11-15

$0.01 \leq z3 \leq 0.29$, $0 \leq w3 \leq 0.19$, $0.9 \leq x3+y3+z3+w3 \leq 1.1$, $0 \leq b3 \leq 0.1$, M^4 is at least one element selected from Al and Mn, M^5 is at least one element selected from B, Ba, Ca, Ce, Cr, Cu, Fe, Mg, Mo, Nb, Si, Sr, Ti, V, W, and Zr, and X is at least one element selected from F, P, and S.

In Chemical Formula 3, $0.85 \leq x3 \leq 0.98$, $0.01 \leq y3 \leq 0.14$, $0.01 \leq z3 \leq 0.14$, and $0 \leq w3 \leq 0.14$, or $0.9 \leq x3 \leq 0.98$, $0.01 \leq y3 \leq 0.09$, $0.01 \leq z3 \leq 0.09$, and $0 \leq w3 \leq 0.09$.

In the positive active material according to an embodiment, the first positive active material may be included in an amount of about 50 wt% to about 90 wt%, and the second positive active material may be included in an amount of about 10 wt% to about 50 wt% based on the total amount of the first positive active material and the second positive active material. The first positive active material may be for example included in an amount of about 60 wt% to about 90 wt%, or about 70 wt% to about 90 wt% and the second positive active material may be for example included in an amount of about 10 wt% to about 40 wt%, or about 10 wt% to about 30 wt%. When the content ratio of the first positive active material and the second positive active material is as described above, the positive active material including the same may realize high capacity, improve a mixture density, and exhibit high energy density.

Method of Preparing Positive Active Material

In an embodiment, a method of preparing a positive active material for a rechargeable lithium battery includes adding a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated and which includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, a

Date Reçue/Date Received 2023-11-15

second positive active material in a form of a single particle which includes lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, cobalt sulfate, and sodium hydroxide, to a solvent, followed by mixing the resultant; removing the solvent; adding a lithium raw material to the obtained product; and performing heat treatment to obtain the aforementioned positive active material.

Through the preparing method, obtained is a positive active material in which the first positive active material including a coating portion on the surface of the secondary particles as a film and the second positive active material including a coating portion on the surface of the single particles as a film are mixed. The coating portion includes a composite phase of lithium cobalt oxide and cobalt oxyhydroxide.

A description of the lithium nickel-based composite oxide is omitted since it is the same as described above. The solvent may be an aqueous solvent such as water or an alcohol-based solvent.

The first positive active material and the second positive active material may be mixed in a weight ratio of about 9:1 to about 5:5, for example, about 8:2 to about 6:4. In this case, it is advantageous to implement high capacity and high energy density.

The cobalt sulfate may be referred to as a coating raw material introduced to prepare the positive active material according to an embodiment. The cobalt sulfate may be mixed so that the cobalt content based on 100 parts by mole of total elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material may be is about 0.5 parts by mole to about 5 parts by mole, for example about

Date Reçue/Date Received 2023-11-15

0.5 parts by mole to about 4 parts by mole, or about 1 part by mole to about 3 parts by mole.

The sodium hydroxide may be referred to as a precipitant and/or a pH regulator. If the sodium hydroxide is not added, the coating portion may not form or the designed amount of cobalt may not be coated, and the CoOOH phase may not appear in the coating portion of the final positive active material.

The sodium hydroxide may be mixed so that a sodium content based on 100 parts by mole of total elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material may be about 1 parts by mole to about 10 parts by mole, for example, about 3 parts by mole to about 9 parts by mole, or about 5 part by mole to about 8 parts by mole. When the content of sodium satisfies the above range, the coating portion in the form of a film containing $LiCoO_2$ and CoOOH may be effectively formed.

The ratio of the molar content of cobalt in cobalt sulfate to the molar content of sodium in sodium hydroxide may be 1:1.1 to 1:5, for example, 1:1.5 to 1:4, or 1:2 to 1:3. When the molar ratio of cobalt to sodium satisfies the above range, it is advantageous to form a film-like coating portion containing $LiCoO_2$ and CoOOH.

Then, after removing the solvent, a lithium raw material is added to the obtained product, wherein the lithium raw material may be, for example, Li_2CO_3, LiOH, a hydrate thereof, or a combination thereof. The lithium raw material may be added so that a lithium content based on elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite

Date Reçue/Date Received 2023-11-15

oxide of the second positive active material may be about 0.1 parts by mole to about 10 parts by mole, for example about 0.1 parts by mole to about 8 parts by mole, or about 1 part by mole to about 6 parts by mole. In the process of washing and coating the positive active material in the solvent, there may be a problem of deteriorating capacity and rate capability due to generation of damage on the surface of the lithium nickel-based composite oxide particles and increasing resistance at the high temperature storage, but the surface damages may be recovered in addition to improvement of capacity, rate capability, and the like by putting the lithium raw material during the heat treatment, as aforementioned.

The heat treatment may be performed in an oxidizing gas atmosphere such as oxygen or air atmosphere, and may be performed at about 650 °C to about 900 °C, or about 650 °C to about 800 °C. The heat treatment may be performed during variable time depending on a heat-treatment temperature and the like, for example, for about 5 hours to about 30 hours or about 10 hours to about 24 hours. By performing heat treatment under the above conditions, a coating portion having a composite phase of lithium cobalt oxide and cobalt oxyhydroxide may be formed.

According to an embodiment, the mixing of the first positive active material, the second positive active material, cobalt sulfate, and sodium hydroxide in a solvent may include a first process of adding the second positive active material, cobalt sulfate, and sodium hydroxide in a solvent followed by mixing, and a second process of adding the first positive active material, cobalt sulfate, and sodium hydroxide followed by mixing. According to this method, the coating of the secondary particles is strengthened, while suppressed from excessive coating for single particles, that is, the coating contents of two

Date Reçue/Date Received 2023-11-15

types of particles are appropriately adjusted, resulting in improving performance of a rechargeable lithium battery such as high-temperature long-term cycle-life characteristics, initial charge/discharge efficiency, high temperature storage performance, and the like. For example, according to the sequential process, prepared is a positive active material satisfying that a ratio of the cobalt content (at%) based on the total amount of nickel and cobalt in the cobalt coating portion of the first positive active material, relative to the cobalt content (at%) based on the total amount of nickel and cobalt in the cobalt coating portion of the second positive active material is about 1.45 to about 1.60.

Herein, a ratio between the time (minutes) required for the first process and the time required (minutes) for the second process may be about 50:50 to about 75:25, or about 65:35 to about 75:25. By designing at such a time ratio, it is possible to optimize the coating content of each of the first positive active material and the second positive active material. The time required for the first process may be about 10 minutes to about 100 minutes and the time required for the second process may be about 10 to about 100 minutes.

Positive Electrode

The positive electrode for a rechargeable lithium battery may include a current collector and a positive active material layer on the current collector. The positive active material layer may include a positive active material, and may further include a binder and/or a conductive material.

The binder improves binding properties of positive active material particles with one another and with a current collector. Examples thereof may be polyvinyl alcohol, carboxylmethyl cellulose, hydroxypropyl cellulose, diacetyl cellulose, polyvinylchloride,

Date Reçue/Date Received 2023-11-15

carboxylated polyvinylchloride, polyvinylfluoride, an ethylene oxide-containing polymer, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, a styrene-butadiene rubber, an acrylated styrene-butadiene rubber, an epoxy resin, nylon, and the like, but are not limited thereto.

The content of the binder in the positive active material layer may be about 1 wt% to about 5 wt% based on the total weight of the positive active material layer.

The conductive material is included to provide electrode conductivity and any electrically conductive material may be used as a conductive material unless it causes a chemical change. Examples of the conductive material may include a carbon-based material such as natural graphite, artificial graphite, carbon black, acetylene black, ketjen black, a carbon fiber, a carbon nanofiber, a carbon nanotube, and the like; a metal-based material of a metal powder or a metal fiber including copper, nickel, aluminum, silver, and the like; a conductive polymer such as a polyphenylene derivative; or a mixture thereof.

The content of the conductive material in the positive active material layer may be about 1 wt% to about 5 wt% based on the total weight of the positive active material layer.

An aluminum foil may be used as the positive electrode current collector, but is not limited thereto.

Negative Electrode

A negative electrode for a rechargeable lithium battery includes a current collector and a negative active material layer on the current collector. The negative active material layer may include a negative active material, and may further include a binder and/or a conductive material.

The negative active material may include a material that reversibly

Date Reçue/Date Received 2023-11-15

intercalates/deintercalates lithium ions, a lithium metal, a lithium metal alloy, a material capable of doping/dedoping lithium, or transition metal oxide.

The material that reversibly intercalates/deintercalates lithium ions may include, for example crystalline carbon, amorphous carbon, or a combination thereof as a carbon-based negative active material. The crystalline carbon may be irregular, or sheet, flake, spherical, or fiber shaped natural graphite or artificial graphite. The amorphous carbon may be a soft carbon, a hard carbon, a mesophase pitch carbonization product, calcined coke, and the like.

The lithium metal alloy includes an alloy of lithium and a metal selected from Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Si, Sb, Pb, In, Zn, Ba, Ra, Ge, Al, and Sn.

The material capable of doping/dedoping lithium may be a Si-based negative active material or a Sn-based negative active material. The Si-based negative active material may include silicon, a silicon-carbon composite, SiO_x ($0 < x < 2$), a Si-Q alloy (wherein Q is an alkali metal, an alkaline-earth metal, a Group 13 element, a Group 14 element, a Group 15 element, a Group 16 element, a transition metal, a rare earth element, and a combination thereof, but not Si) and the Sn-based negative active material may include Sn, SnO_2, an Sn-R alloy (wherein R is an alkali metal, an alkaline-earth metal, a Group 13 element, a Group 14 element, a Group 15 element, a Group 16 element, a transition metal, a rare earth element, and a combination thereof, but not Sn). At least one of these materials may be mixed with SiO_2. The elements Q and R may be selected from Mg, Ca, Sr, Ba, Ra, Sc, Y, Ti, Zr, Hf, Rf, V, Nb, Ta, Db, Cr, Mo, W, Sg, Tc, Re, Bh, Fe, Pb, Ru, Os, Hs, Rh, Ir, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, Sn, In, Tl, Ge, P, As, Sb, Bi, S, Se, Te, Po, and a combination thereof.

Date Reçue/Date Received 2023-11-15

The silicon-carbon composite may be, for example, a silicon-carbon composite including a core including crystalline carbon and silicon particles and an amorphous carbon coating layer disposed on the surface of the core. The crystalline carbon may be artificial graphite, natural graphite, or a combination thereof. The amorphous carbon precursor may be a coal-based pitch, mesophase pitch, petroleum-based pitch, coal-based oil, petroleum-based heavy oil, or a polymer resin such as a phenol resin, a furan resin, or a polyimide resin. In this case, the content of silicon may be about 10 wt% to about 50 wt% based on the total weight of the silicon-carbon composite. In addition, the content of the crystalline carbon may be about 10 wt% to about 70 wt% based on the total weight of the silicon-carbon composite, and the content of the amorphous carbon may be about 20 wt% to about 40 wt% based on the total weight of the silicon-carbon composite. In addition, a thickness of the amorphous carbon coating layer may be about 5 nm to about 100 nm. An average particle diameter (D50) of the silicon particles may be about 10 nm to about 20 μm. The average particle diameter (D50) of the silicon particles may be preferably about 10 nm to about 200 nm. The silicon particles may exist in an oxidized form, and in this case, an atomic content ratio of Si:O in the silicon particles indicating a degree of oxidation may be a weight ratio of about 99:1 to about 33:67. The silicon particles may be SiO_x particles, and in this case, the range of x in SiO_x may be greater than about 0 and less than about 2. In the present specification, unless otherwise defined, an average particle diameter (D50) indicates a particle where an accumulated volume is about 50 volume% in a particle distribution.

The Si-based negative active material or Sn-based negative active material may be mixed with the carbon-based negative active material. When the Si-based negative

Date Reçue/Date Received 2023-11-15

active material or Sn-based negative active material and the carbon-based negative active material are mixed and used, the mixing ratio may be a weight ratio of about 1:99 to about 90:10.

In the negative active material layer, the negative active material may be included in an amount of about 95 wt% to about 99 wt% based on the total weight of the negative active material layer.

In an embodiment, the negative active material layer further includes a binder, and may optionally further include a conductive material. The content of the binder in the negative active material layer may be about 1 wt% to about 5 wt% based on the total weight of the negative active material layer. In addition, when the conductive material is further included, the negative active material layer may include about 90 wt% to about 98 wt% of the negative active material, about 1 wt% to about 5 wt% of the binder, and about 1 wt% to about 5 wt% of the conductive material.

The binder serves to well adhere the negative active material particles to each other and also to adhere the negative active material to the current collector. The binder may be a water-insoluble binder, a water-soluble binder, or a combination thereof.

Examples of the water-insoluble binder include polyvinyl chloride, carboxylated polyvinyl chloride, polyvinyl fluoride, an ethylene oxide-containing polymer, an ethylene propylene copolymer, polystyrene, polyvinylpyrrolidone, polyurethane, polytetrafluoro ethylene, polyvinylidene fluoride, polyethylene, polypropylene, polyamideimide, polyimide, or a combination thereof.

The water-soluble binder may include a rubber binder or a polymer resin binder. The rubber binder may be selected from a styrene-butadiene rubber, an acrylated

Date Reçue/Date Received 2023-11-15

styrene-butadiene rubber, an acrylonitrile-butadiene rubber, an acrylic rubber, a butyl rubber, a fluororubber, and a combination thereof. The polymer resin binder may be selected from polyethylene oxide, polyvinylpyrrolidone, polyepichlorohydrin, polyphosphazene, polyacrylonitrile, an ethylene propylene diene copolymer, polyvinylpyridine, chlorosulfonated polyethylene, latex, a polyester resin, an acrylic resin, a phenol resin, an epoxy resin, polyvinyl alcohol, and a combination thereof.

When a water-soluble binder is used as the negative electrode binder, a cellulose-based compound capable of imparting viscosity may be further included. As the cellulose-based compound, one or more of carboxymethyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, or alkali metal salts thereof may be mixed and used. The alkali metal may be Na, K, or Li. The amount of the thickener used may be about 0.1 parts by weight to about 3 parts by weight based on 100 parts by weight of the negative active material.

The conductive material is included to provide electrode conductivity and any electrically conductive material may be used as a conductive material unless it causes a chemical change. Examples of the conductive material include a carbon-based material such as natural graphite, artificial graphite, carbon black, acetylene black, ketjen black, a carbon fiber, a carbon nanofiber, a carbon nanotube, and the like; a metal-based material of a metal powder or a metal fiber including copper, nickel, aluminum silver, and the like; a conductive polymer such as a polyphenylene derivative; or a mixture thereof.

The negative electrode current collector may include one selected from a copper foil, a nickel foil, a stainless steel foil, a titanium foil, a nickel foam, a copper foam, a polymer substrate coated with a conductive metal, and a combination thereof.

Date Reçue/Date Received 2023-11-15

Rechargeable Lithium Battery

Another embodiment provides a rechargeable lithium battery including a positive electrode, a negative electrode, a separator between the positive electrode and the negative electrode, and an electrolyte.

FIG. 1 is a schematic view illustrating a rechargeable lithium battery according to an embodiment. Referring to FIG. 1, a rechargeable lithium battery 100 according to an embodiment includes a battery cell including a positive electrode 114, a negative electrode 112 facing the positive electrode 114, a separator 113 between the positive electrode 114 and the negative electrode 112, and an electrolyte for a rechargeable lithium battery impregnating the positive electrode 114, negative electrode 112, and separator 113, a battery case 120 housing the battery cell, and a sealing member 140 sealing the battery case 120.

The electrolyte includes a non-aqueous organic solvent and a lithium salt.

The non-aqueous organic solvent serves as a medium for transmitting ions taking part in the electrochemical reaction of a battery. The non-aqueous organic solvent may be a carbonate-based, ester-based, ether-based, ketone-based, or alcohol-based solvent, or aprotic solvent. Examples of the carbonate-based solvent include dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate (DPC), methylpropyl carbonate (MPC), ethylpropyl carbonate (EPC), methylethyl carbonate (MEC), ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and the like. Examples of the ester-based solvent include methyl acetate, ethyl acetate, n-propyl acetate, dimethyl acetate, methyl propionate, ethyl propionate, γ-butyrolactone, decanolide, valerolactone, mevalonolactone, caprolactone, and the like. The ether-based solvent may be dibutyl

Date Reçue/Date Received 2023-11-15

ether, tetraglyme, diglyme, dimethoxyethane, 2-methyltetrahydrofuran, tetrahydrofuran, and the like and the ketone-based solvent may be cyclohexanone, and the like. In addition, the alcohol-based solvent may be ethyl alcohol, isopropyl alcohol, etc. and the aprotic solvent may be nitriles such as R-CN (where R is a C2 to C20 linear, branched, or cyclic hydrocarbon group and may include a double bond, an aromatic ring, or an ether bond), amides such as dimethylformamide, dioxolanes such as 1,3-dioxolane, sulfolanes, and the like.

The non-aqueous organic solvent may be used alone or in a mixture. When the organic solvent is used in a mixture, the mixture ratio may be controlled in accordance with a desirable battery performance.

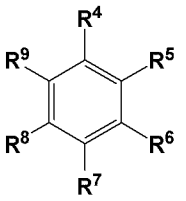
In addition, in the case of the carbonate-based solvent, a mixture of a cyclic carbonate and a chain carbonate may be used. In this case, when the cyclic carbonate and the chain carbonate are mixed in a volume ratio of about 1:1 to about 1:9, the electrolyte may exhibit excellent performance.

The non-aqueous organic solvent may further include an aromatic hydrocarbon-based organic solvent in addition to the carbonate-based solvent. In this case, the carbonate-based solvent and the aromatic hydrocarbon-based organic solvent may be mixed in a volume ratio of about 1:1 to about 30:1.

The aromatic hydrocarbon-based solvent may be an aromatic hydrocarbon-based compound represented by Chemical Formula I.

[Chemical Formula I]

Date Reçue/Date Received 2023-11-15



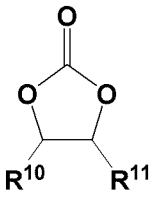
In Chemical Formula I, R^4 to R^9 are the same or different and are selected from hydrogen, a halogen, a C1 to C10 alkyl group, a C1 to C10 haloalkyl group, and a combination thereof.

Specific examples of the aromatic hydrocarbon-based solvent may be selected from benzene, fluorobenzene, 1,2-difluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene, 1,2,3-trifluorobenzene, 1,2,4-trifluorobenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, iodobenzene, 1,2-diiodobenzene, 1,3-diiodobenzene, 1,4-diiodobenzene, 1,2,3-triiodobenzene, 1,2,4-triiodobenzene, toluene, fluorotoluene, 2,3-difluorotoluene, 2,4-difluorotoluene, 2,5-difluorotoluene, 2,3,4-trifluorotoluene, 2,3,5-trifluorotoluene, chlorotoluene, 2,3-dichlorotoluene, 2,4-dichlorotoluene, 2,5-dichlorotoluene, 2,3,4-trichlorotoluene, 2,3,5-trichlorotoluene, iodotoluene, 2,3-diiodotoluene, 2,4-diiodotoluene, 2,5-diiodotoluene, 2,3,4-triiodotoluene, 2,3,5-triiodotoluene, xylene, and a combination thereof.

The electrolyte may further include vinylene carbonate or an ethylene carbonate-based compound represented by Chemical Formula II in order to improve cycle-life of a battery.

[Chemical Formula II]

Date Reçue/Date Received 2023-11-15



In Chemical Formula II, R^{10} and R^{11} are the same or different and selected from hydrogen, a halogen, a cyano group, a nitro group, and fluorinated C1 to C5 alkyl group, provided that at least one of R^{10} and R^{11} is a halogen, a cyano group, a nitro group, and fluorinated C1 to C5 alkyl group, and R^{10} and R^{11} are not simultaneously hydrogen.

Examples of the ethylene carbonate-based compound may be difluoroethylene carbonate, chloroethylene carbonate, dichloroethylene carbonate, bromoethylene carbonate, dibromoethylene carbonate, nitroethylene carbonate, cyanoethylene carbonate, or fluoroethylene carbonate. The amount of the additive for improving cycle-life may be used within an appropriate range.

The lithium salt dissolved in the non-aqueous organic solvent supplies lithium ions in a battery, enables a basic operation of a rechargeable lithium battery, and improves transportation of the lithium ions between positive and negative electrodes.

Examples of the lithium salt include at least one selected from $LiPF_6$, $LiBF_4$, $LiSbF_6$, $LiAsF_6$, $LiN(SO_2C_2F_5)_2$, $Li(CF_3SO_2)_2N$, $LiN(SO_3C_2F_5)_2$, $Li(FSO_2)_2N$ (lithium bis(fluorosulfonyl)imide; LiFSI), $LiC_4F_9SO_3$, $LiClO_4$, $LiAlO_2$, $LiAlCl_4$, $LiPO_2F_2$, $LiN(C_xF_{2x+1}SO_2)(C_yF_{2y+1}SO_2)$, wherein x and y are natural numbers, for example, an integer ranging from 1 to 20, lithium difluoro(bisoxalato) phosphate, LiCl, LiI, $LiB(C_2O_4)_2$ (lithium bis(oxalato) borate, LiBOB), and lithium difluoro(oxalato)borate (LiDFOB).

The lithium salt may be used in a concentration ranging from about 0.1 M to about 2.0 M. When the lithium salt is included at the above concentration range, an electrolyte

Date Reçue/Date Received 2023-11-15

may have excellent performance and lithium ion mobility due to optimal electrolyte conductivity and viscosity.

The separator 113 separates a positive electrode 114 and a negative electrode 112 and provides a transporting passage for lithium ions and may be any generally-used separator in a lithium ion battery. In other words, it may have low resistance to ion transport and excellent impregnation for an electrolyte. For example, the separator 113 may include a glass fiber, polyester, polyethylene, polypropylene, polytetrafluoroethylene, or a combination thereof and may have a form of a non-woven fabric or a woven fabric. For example, in a lithium ion battery, a polyolefin-based polymer separator such as polyethylene and polypropylene is mainly used. In order to ensure the heat resistance or mechanical strength, a coated separator including a ceramic component or a polymer material may be used. Optionally, it may have a mono-layered or multi-layered structure.

Rechargeable lithium batteries may be classified as lithium ion batteries, lithium ion polymer batteries, and lithium polymer batteries according to the presence of a separator and the type of electrolyte used therein. The rechargeable lithium batteries may have a variety of shapes and sizes, and include cylindrical, prismatic, coin, or pouch-type batteries, and may be thin film batteries or may be rather bulky in size. Structures and manufacturing methods for these batteries pertaining to this disclosure are well known in the art.

The rechargeable lithium battery according to an embodiment may be used in an electric vehicle (EV), a hybrid electric vehicle such as a plug-in hybrid electric vehicle (PHEV), and portable electronic device because it implements a high capacity and has excellent storage stability, cycle-life characteristics, and high rate characteristics at high

Date Reçue/Date Received 2023-11-15

temperatures.

Hereinafter, examples of the present invention and comparative examples are described. However, the examples are for the purpose of illustration and are not to be construed as limiting the present invention.

Example 1

1. Preparation of First Lithium Nickel-based Composite oxide in Form of Secondary Particle

Nickel sulfate ($NiSO_4 \cdot 6H_2O$), cobalt sulfate ($CoSO_4 \cdot 7H_2O$), and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) as metal raw materials in a mole ratio of 91:8:1 are dissolved in distilled water as a solvent to prepare a mixed solution, and in order to form a complex compound, ammonia water (NH_4OH) and sodium hydroxide (NaOH) as a precipitant are prepared.

After adding an ammonia water dilution solution to a continuous reactor, the metal raw material mixed solution is added thereto, and the sodium hydroxide is added thereto to maintain pH inside the reactor. When a reaction slowly proceeds for about 80 hours and is stabilized, a product overflowing therefrom is collected, washed, and dried, obtaining a final precursor. Accordingly, a first nickel-based hydroxide ($Ni_{0.91}Co_{0.08}Al_{0.01}(OH)_2$), in which primary particles are aggregated into secondary particles, is obtained.

The first nickel-based hydroxide is mixed with LiOH, so that a content of lithium to a total metal content of the first nickel-based hydroxide may have a mole ratio of 1.0, and then, primarily heat-treated under an oxygen atmosphere at about 750 °C for 15 hours, obtaining a first lithium nickel-based oxide ($LiNi_{0.91}Co_{0.08}Al_{0.01}O_2$). The obtained first

Date Reçue/Date Received 2023-11-15

lithium nickel-based oxide has an average particle diameter of about 15 μm and is the secondary particles in which the primary particles are aggregated.

2. Preparation of Second Lithium Nickel-Based Composite Oxide in a Form of Single Particle

Nickel sulfate, cobalt sulfate, and manganese sulfate ($MnSO_4 \cdot H_2O$) are dissolved in distilled water as a solvent in a mole ratio of 95:4:1 to prepare a mixed solution. In order to form a complex, an ammonia water (NH_4OH) diluent and sodium hydroxide (NaOH) as a precipitant are prepared. Subsequently, the raw metal material mixed solution, the ammonia water, and the sodium hydroxide are each put into a reactor. While stirred, a reaction proceeds for about 20 hours. Subsequently, the slurry solution in the reactor is filtered, washed with distilled water with high purity, and dried for 24 hours, obtaining a second nickel-based hydroxide ($Ni_{0.95}Co_{0.04}Mn_{0.01}(OH)_2$) powder. The obtained second nickel-based hydroxide powder has an average particle diameter of about 4.0 μm and a specific surface area of about 15 m^2/g, which is measured in a BET method.

The obtained second nickel-based hydroxide, and LiOH satisfying Li/(Ni+Co+Mn) = 1.05 are mixed and then, put in a firing furnace and secondarily heat treated under an oxygen atmosphere at 820 °C for 10 hours. Subsequently, a product obtained therefrom is pulverized for about 30 minutes and then, separated/dispersed into a plurality of second lithium nickel-based oxides having a form of a single particle. The obtained second lithium nickel-based oxide having a form of a single particle has an average particle diameter of about 3.7 μm.

3. Preparation of Cobalt Coating and Final Positive Active Material

Date Reçue/Date Received 2023-11-15

A distilled water solvent and cobalt sulfate ($CoSO_4 \cdot 7H_2O$) are put in a mixer, and the prepared second lithium nickel-based composite oxide is added thereto and then, mixed, which is a first process. The cobalt sulfate is added to be 3.0 parts by mole of cobalt based on the total amount of all the elements excluding lithium and oxygen in the second lithium nickel-based composite oxide. In the first process, after adding the second lithium nickel-based composite oxide, the sodium hydroxide as a precipitant and a pH-controlling agent are added thereto and mixed. The sodium hydroxide was added to be 6.0 parts by mole of sodium based on 100 parts by mole of total elements excluding lithium and oxygen in the second lithium nickel-based composite oxide.

After performing the first process for 30 minutes, a second process of adding the first lithium nickel-based composite oxide thereto after adding cobalt sulfate thereto and then, mixing them is carried out. The first lithium nickel-based composite oxide is added to have a weight ratio of 7:3 with the previously introduced second lithium nickel-based composite oxide. The cobalt sulfate is added to have 3.0 parts by mole of a cobalt content based on the total amount of all the elements excluding lithium and oxygen in the first lithium nickel-based composite oxide. In the second process, after adding the first lithium nickel-based composite oxide, the sodium hydroxide is also added thereto and mixed together. The sodium hydroxide was added to have 6.0 parts by mole of a sodium content based on 100 parts by mole of total elements excluding lithium and oxygen in the first lithium nickel-based composite oxide.

After performing the second process for 30 minutes, a product therefrom is filtered and dried at 200 °C for 10 hours. Subsequently, the obtained product is mixed with lithium hydroxide and then, put in a firing furnace and heat-treated under an oxygen atmosphere

Date Reçue/Date Received 2023-11-15

at about 700 °C for 15 hours. Herein, the lithium hydroxide is added to have 6 parts by mole of a lithium content based on the total amount of all elements excluding lithium and oxygen in the obtained product. Then, the firing furnace is cooled to room temperature, obtaining a final positive active material in which a first positive active material having a film coated on the surface of secondary particles formed of the first lithium nickel-based composite oxide and a second positive active material having a film coated on the surface of single particles formed of second lithium nickel-based composite oxide.

4. Manufacture of Positive Electrode

95 wt% of the final positive active material, 3 wt% of a polyvinylidene fluoride binder, and 2 wt% of carbon nanotube conductive material are mixed in an N-methylpyrrolidone solvent to prepare positive active material slurry. The positive active material slurry is coated on an aluminum current collector, dried, and then compressed to manufacture a positive electrode.

5. Manufacture of Rechargeable Lithium Battery Cell

A coin half-cell is manufactured by disposing a separator having a polyethylene polypropylene multilayer structure is disposed between the manufactured positive electrode and lithium metal counter electrode, and injecting an electrolyte in which 1.0 M $LiPF_6$ lithium salt was added to a solvent in which ethylene carbonate and diethyl carbonate are mixed in a volume ratio of 50:50.

Comparative Example 1

A positive active material, a positive electrode, and a coin half-cell are manufactured in the same manner as in Example 1 except that the sodium hydroxide serving as a precipitant and a pH controlling agent are not added in "3. Preparation of

Date Reçue/Date Received 2023-11-15

Cobalt Coating and Final Positive Active Material."

Comparative Example 2

In "3. Preparation of Cobalt Coating and Final Positive Active Material" of Example 1, the coating is performed not in a wet manner but in a dry manner. In other words, the first lithium nickel-based composite oxide, the second lithium nickel-based composite oxide, cobalt hydroxide, and lithium hydroxide are heat-treated at 700 °C for 15 hours, while stirred in a firing furnace. Herein, the cobalt hydroxide is added to have 3.0 parts by mole of a cobalt content based on the total amount of all the elements excluding lithium and oxygen in the first and second lithium nickel-based composite oxides, and then, the lithium hydroxide is added thereto to have 6.0 parts by mole of a lithium content. Otherwise, a positive active material, a positive electrode, and a coin half-cell are manufactured in the same manner as in Example 1.

Evaluation Example 1: X-ray Diffraction Analysis

An X-ray diffraction analysis is performed with respect to (i) the final positive active material of Example 1, (ii) a positive electrode plate obtained by decomposing the coin half-cell of Example 1 right before driving the coin half-cell, and (iii) the positive electrode plate obtained by decomposing the coin half-cell of Example 1 after 150 cycles, and the results are shown in FIG. 2. Although the (i), (ii), and (iii) curves are all substantially aligned, as illustrated in FIGS. 3 and 4, the (ii) curve is illustrated in FIG. 2 as being shifted to the right by about 2.5 degrees, and the (iii) curve is illustrated in FIG. 2 as being shifted to the right by about 5 degrees, for purposes of clearly illustrating the three curves without the three curves obscuring each other.

In the (iii), the coin half-cell of Example 1 is initially charged under constant current

Date Reçue/Date Received 2023-11-15

(0.2 C) and constant voltage (4.25 V, 0.05 C cut-off) conditions, paused for 10 minutes, and discharged to 3.0 V under a constant current (0.2 C) condition and then, 150 times repeatedly charged and discharged at 0.5 C/0.5 C at 45 °C.

FIG. 3 is an enlarged view of the graph in the vicinity of 20° in FIG. 2 and FIG. 4 is an enlarged view of a graph near 40° in FIG. 2. FIG. 5 is an X-ray diffraction analysis graph of $Co(OH)_2$, CoOOH, and Co_3O_4 for comparison. The (ii) and (iii) curves are illustrated in each of FIGS. 3 and 4 without being shifted to the right (as they are illustrated in FIG. 2).

Referring to FIGS. 2 to 5, the positive active material of Example 1 exhibits a peak at 19.5 ° to 20.5 ° and a peak at 39 ° to 40 °, which confirm that CoOOH is present on the surface. In other words, the positive active material of Example 1 turns out to have a composite phase of a $LiCoO_2$-like structure and CoOOH in the surface coating portion. This composite phase is captured not only in the prepared positive active material but also after manufacturing it into the positive electrode plate and after driving the battery cell.

An X-ray diffraction analysis is performed with respect to Comparative Examples 1 and 2, but quantitative coating is not found in Comparative Example 1, and a CoOOH phase is not found in the X-ray diffraction graph. In Comparative Example 2, continuous coating is not carried out on the surface of the positive active material, and a CoOOH phase is not found in the X-ray diffraction graph.

Evaluation Example 2: SEM-EDS Analysis of Cross-section of Positive Active Material

FIG. 6 is an SEM-EDS analysis image of a cross-section of particles

Date Reçue/Date Received 2023-11-15

corresponding to the first positive active material in the final positive active material prepared in Example 1. FIG. 7 is an SEM-EDS analysis image of a cross-section of particles corresponding to the second positive active material in the final positive active material prepared in Example 1. Highlighted portions in FIGS. 6 and 7 indicate cobalt.

Referring to FIG. 6, a coating portion including cobalt exists on the surface of the secondary particles, and cobalt is coated on grain boundaries, the surface of the primary particles inside the secondary particles. Referring to FIG. 7, on the surface of the single particles, a coating portion including cobalt is formed as a film.

Evaluation Example 3: Analysis of Cobalt Coating Content of Positive Active Material

Each cobalt content (Co/(Ni+Co), at%) on the surfaces of the first positive active material and the second positive active material is measured through the SEM-EDS analysis performed in Evaluation Example 2, and the results are shown in Table 1.

(Table 1)

	Coating content of first positive active material (A)	Coating content of second positive active material (B)	A/B
Example 1	61.8	40.4	1.53

Evaluation Example 4: Evaluation of Battery Performance

Three samples of each rechargeable lithium battery cell of Example 1 and Comparative Examples 1 and 2 are prepared and initially charged under constant current (0.2 C) and constant voltage (4.25 V, 0.05 C cut-off) conditions, paused for 10 minutes, and discharged to 3.0 V under a constant current (0.2 C) condition. Subsequently, the

Date Reçue/Date Received 2023-11-15

cells are 50 times repeatedly charged and discharged at 0.5 C/0.5 C at 45 °C and then, evaluated with respect to cycle-life characteristics, which is used to calculate capacity retention at each cycle relative to initial discharge capacity, and the results are shown in FIG. 8.

Referring to FIG. 8, Example 1 exhibits excellent cycle-life characteristics, compared with Comparative Examples 1 and 2.

While this invention has been described in connection with what is presently considered to be practical example embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, it is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

<Description of Symbols>

100: rechargeable lithium battery 112: negative electrode

113: separator 114: positive electrode

120: battery case 140: sealing member

Date Reçue/Date Received 2023-11-15

WHAT IS CLAIMED IS:

1. A positive active material for a rechargeable lithium battery, comprising

a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated, and

a second positive active material in a form of a single particle,

wherein each of the first positive active material and the second positive active material includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen,

the first positive active material includes a coating portion in a form of a film on the surface of the secondary particle,

the second positive active material includes a coating portion in a form of a film on the surface of the single particle, and

the coating portion of the first positive active material and the coating portion of the second positive active material includes lithium cobalt oxide and cobalt oxyhydroxide, respectively.

2. The positive active material for a rechargeable lithium battery of claim 1, wherein

in the coating portion of the first positive active material and the coating portion of the second positive active material, the lithium cobalt oxide and the cobalt oxyhydroxide are present in a composite phase.

Date Reçue/Date Received 2023-11-15

3. The positive active material for a rechargeable lithium battery of claim 1, wherein

the positive active material exhibits peaks at about 19.5 ° to about 20.5 ° and about 39 ° to about 40 ° in X-ray diffraction analysis.

4. The positive active material for a rechargeable lithium battery of claim 1, wherein

each of the coating portion of the first positive active material and the coating portion of the second positive active material has a thickness of about 1 nm to about 500 nm.

5. The positive active material for a rechargeable lithium battery of claim 1, wherein

in the entire positive active material, a cobalt content of the surface based on 100 mol% of the elements excluding lithium and oxygen in the lithium nickel-based composite oxide is about 0.5 mol% to about 5 mol%.

6. The positive active material for a rechargeable lithium battery of claim 1, wherein

a ratio of a cobalt content (at%) based on the total amount of nickel and cobalt in the coating portion of the first positive active material relative to a cobalt content (at%) based on the total amount of nickel and cobalt in the coating portion of the second positive

Date Reçue/Date Received 2023-11-15

active material is about 1.45 to about 1.60.

7. The positive active material for a rechargeable lithium battery of claim 1, wherein

the coating portion of the first positive active material has a cobalt content of about 55 at% to about 70 at% based on the total amount of nickel and cobalt.

8. The positive active material for a rechargeable lithium battery of claim 1, wherein

a cobalt content relative to the total amount of nickel and cobalt in the coated portion of the second positive active material is about 39 at% to about 45 at%.

9. The positive active material for a rechargeable lithium battery of claim 1, wherein

the first positive active material further includes a grain boundary coating portion on the surface of the primary particles inside the secondary particle, and

the grain boundary coating portion includes lithium cobalt oxide and cobalt oxyhydroxide.

10. The positive active material for a rechargeable lithium battery of claim 1, wherein

an average particle diameter of the first positive active material is about 5 μm to about 20 μm, and

Date Reçue/Date Received 2023-11-15

an average particle diameter of the second positive active material is about 0.1 μm to about 10 μm.

11. The positive active material for a rechargeable lithium battery of claim 1, wherein

the first positive active material is included in an amount of about 50 wt% to about 90 wt%, and the second positive active material is included in an amount of about 10 wt% to about 50 wt% based on the total amount of the first positive active material and the second positive active material.

12. The positive active material for a rechargeable lithium battery of claim 1, wherein

the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material are each independently represented by Chemical Formula 1:

[Chemical Formula 1]

$Li_{a1}Ni_{x1}M^1_{y1}M^2_{z1}O_{2-b1}X_{b1}$

wherein, in Chemical Formula 1, $0.9 \leq a1 \leq 1.8$, $0.7 \leq x1 \leq 1$, $0 \leq y1 \leq 0.3$, $0 \leq z1 \leq 0.2$, $0.9 \leq x1+y1+z1 \leq 1.1$, $0 \leq b1 \leq 0.1$, M^1 and M^2 are each independently at least one element selected from Al, B, Ba, Ca, Ce, Co, Cr, Cu, Fe, Mg, Mn, Mo, Nb, Si, Sr, Ti, V, W, and Zr, and X is at least one element selected from F, P and S.

13. A method of preparing a positive active material for a rechargeable lithium

Date Reçue/Date Received 2023-11-15

battery, comprising

adding a first positive active material in a form of a secondary particle in which a plurality of primary particles are aggregated and which includes a lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, a second positive active material in a form of a single particle which includes lithium nickel-based composite oxide having a nickel content of greater than or equal to about 70 mol% relative to the total elements excluding lithium and oxygen, cobalt sulfate, and sodium hydroxide, to a solvent, followed by mixing the resultant;

removing the solvent;

adding a lithium raw material to the obtained product;

performing heat treatment;

to obtain the positive active material of claim 1.

14. The method of claim 13, wherein

the first positive active material and the second positive active material are mixed in a weight ratio of about 9:1 to about 5:5.

15. The method of claim 13, wherein

the cobalt sulfate is mixed so that a cobalt content based on 100 parts by mole of total elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material is about 0.5 parts by mole to about 5 parts by mole.

Date Reçue/Date Received 2023-11-15

16. The method of claim 13, wherein the sodium hydroxide is added so that a sodium content, based on 100 parts by mole of total elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material, is about 1 part by mole to about 10 parts by mole.

17. The method of claim 13, wherein a ratio of a molar content of cobalt in cobalt sulfate to a molar content of sodium in sodium hydroxide is about 1:1.1 to about 1:5.

18. The method of claim 13, wherein

the lithium raw material is added so that a lithium content based on elements other than lithium and oxygen in the lithium nickel-based composite oxide of the first positive active material and the lithium nickel-based composite oxide of the second positive active material is about 0.1 parts by mole to about 10 parts by mole.

19. The method of claim 13, wherein

the heat treatment is performed in a temperature range of 650 °C to 900 °C.

20. The method of claim 13, wherein

the mixing of the first positive active material, the second positive active material, cobalt sulfate, and sodium hydroxide in a solvent includes

a first process of adding the second positive active material, cobalt sulfate, and

Date Reçue/Date Received 2023-11-15

sodium hydroxide in a solvent followed by mixing, and a second process of adding the first positive active material, cobalt sulfate, and sodium hydroxide followed by mixing.

21. The method of claim 18, wherein

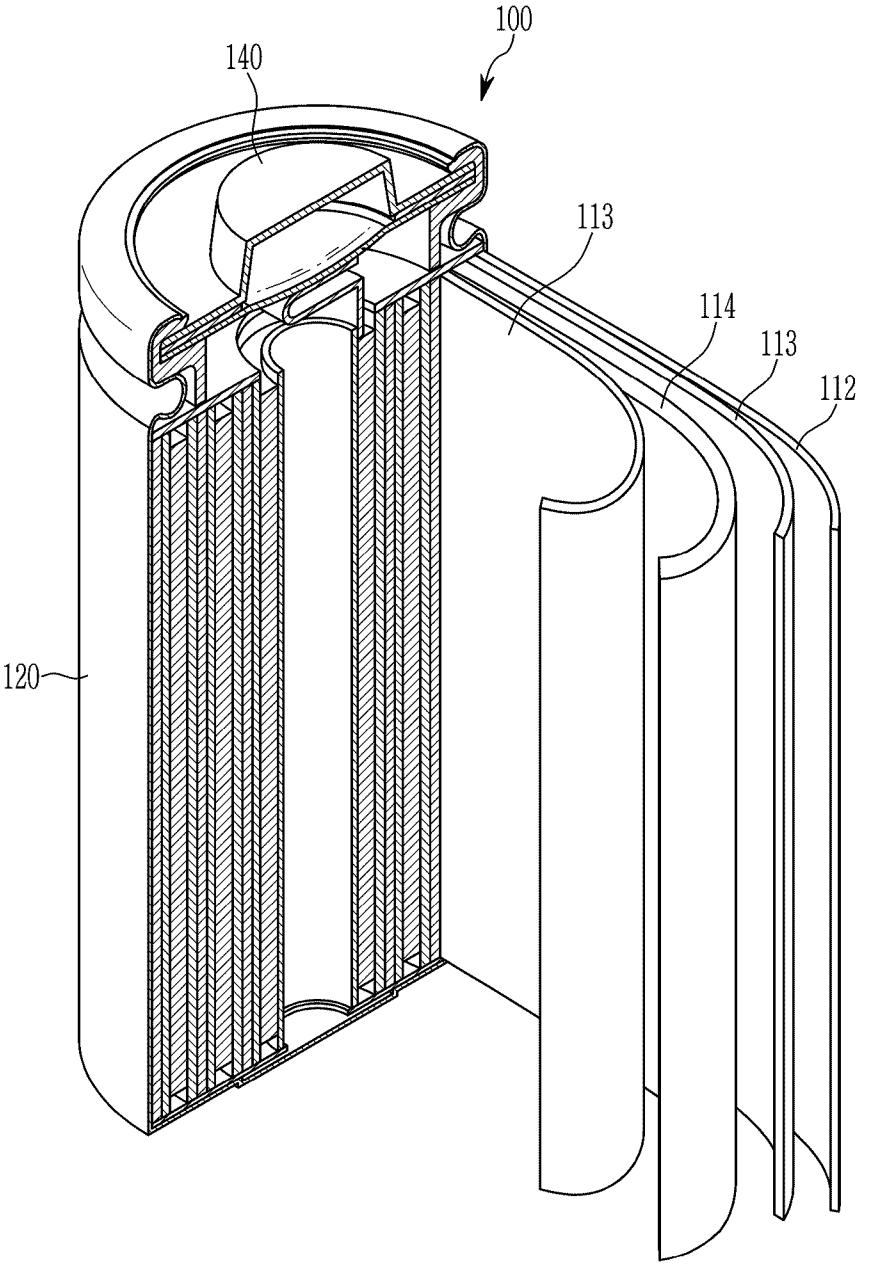
a ratio between the time (minutes) required for the first process and the time required (minutes) for the second process is about 50:50 to about 75:25.

22. A rechargeable lithium battery comprising

a positive electrode including the positive active material of claim 1, a negative electrode, and an electrolyte.

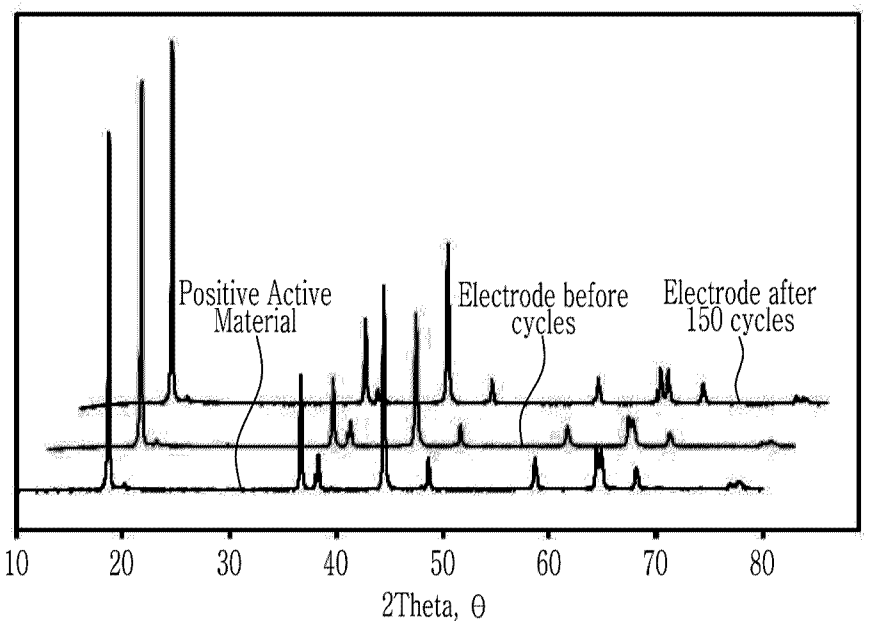
Date Reçue/Date Received 2023-11-15

FIG. 1



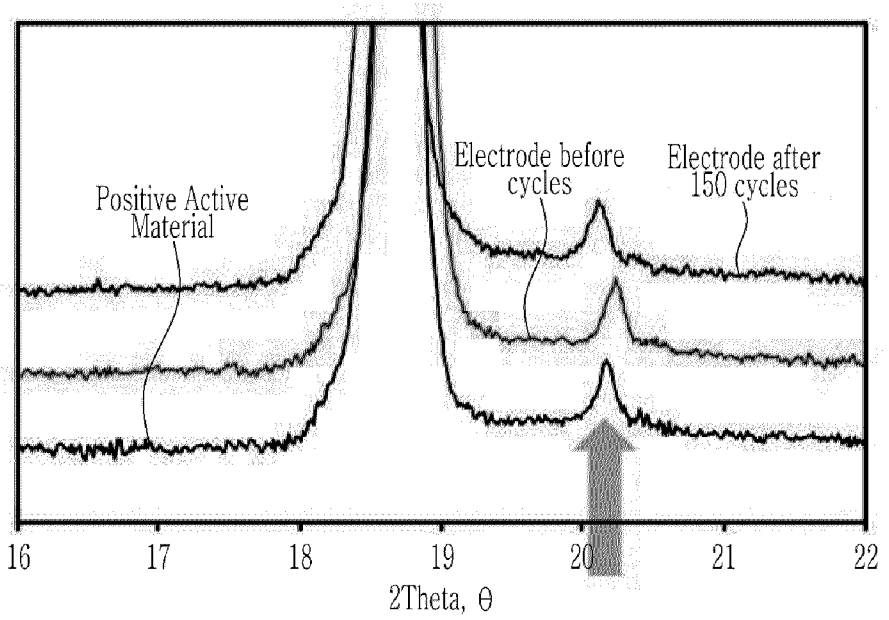
Date Reçue/Date Received 2023-11-15

FIG. 2



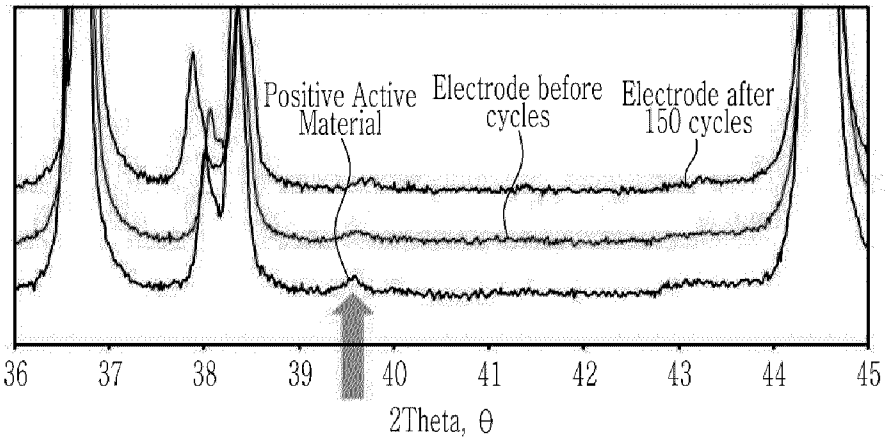
Date Reçue/Date Received 2023-11-15

FIG. 3



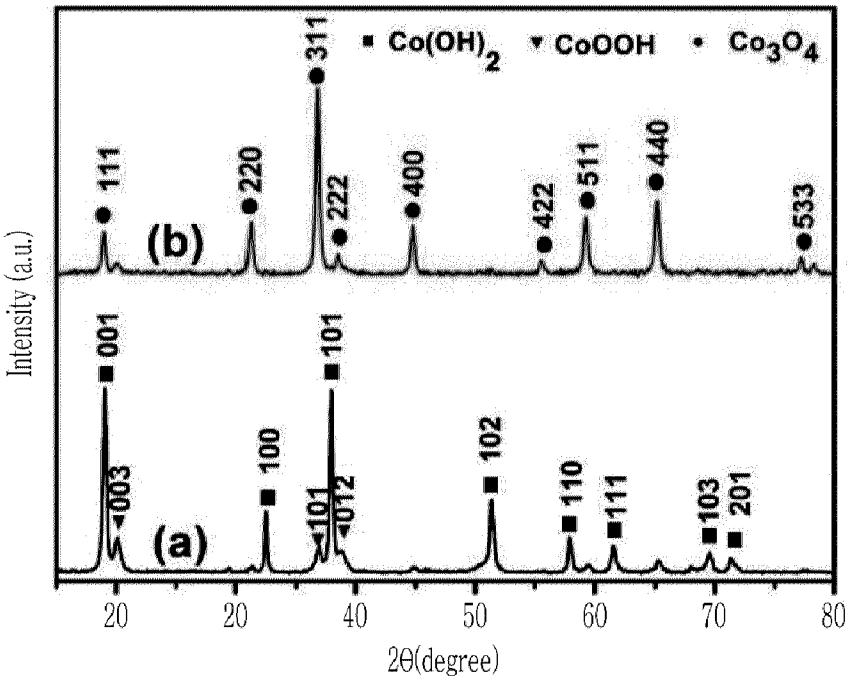
Date Reçue/Date Received 2023-11-15

FIG. 4



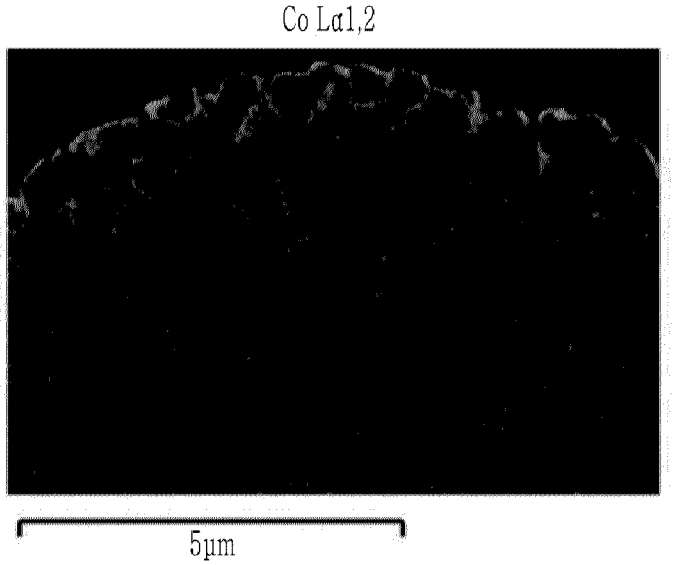
Date Reçue/Date Received 2023-11-15

FIG. 5



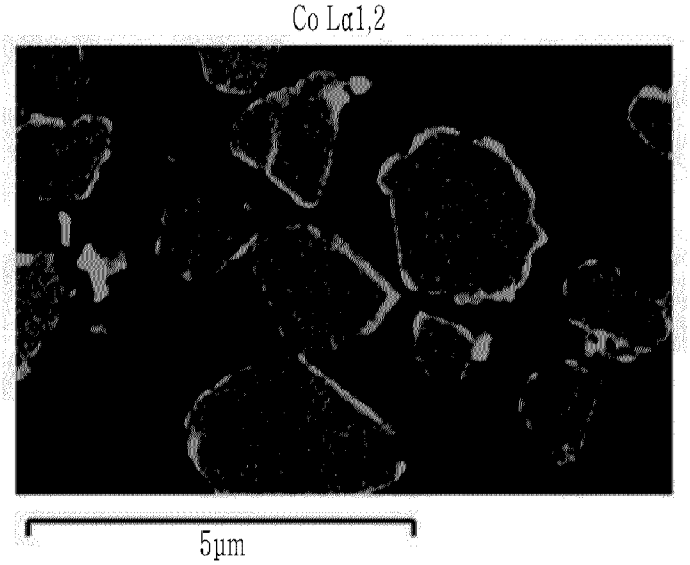
Date Reçue/Date Received 2023-11-15

FIG. 6



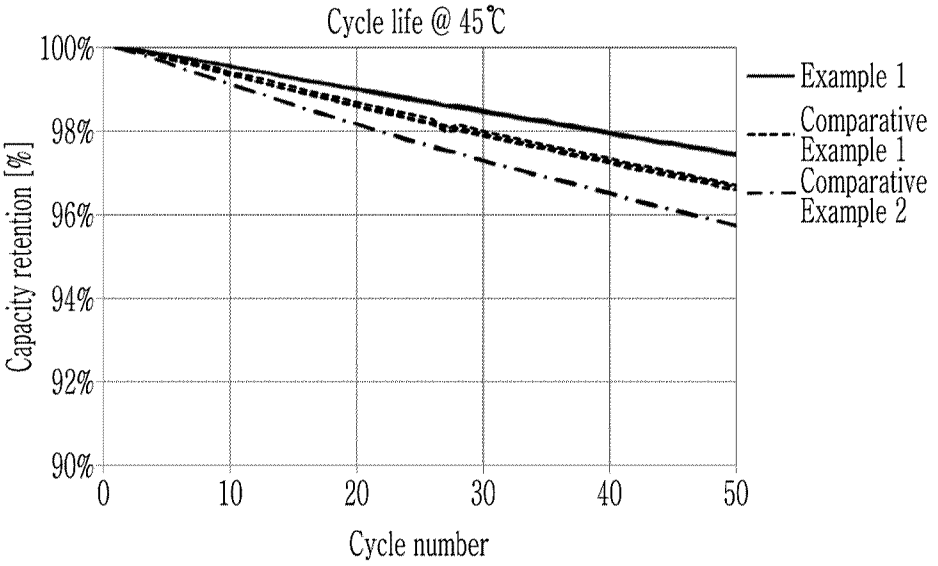
Date Reçue/Date Received 2023-11-15

FIG. 7

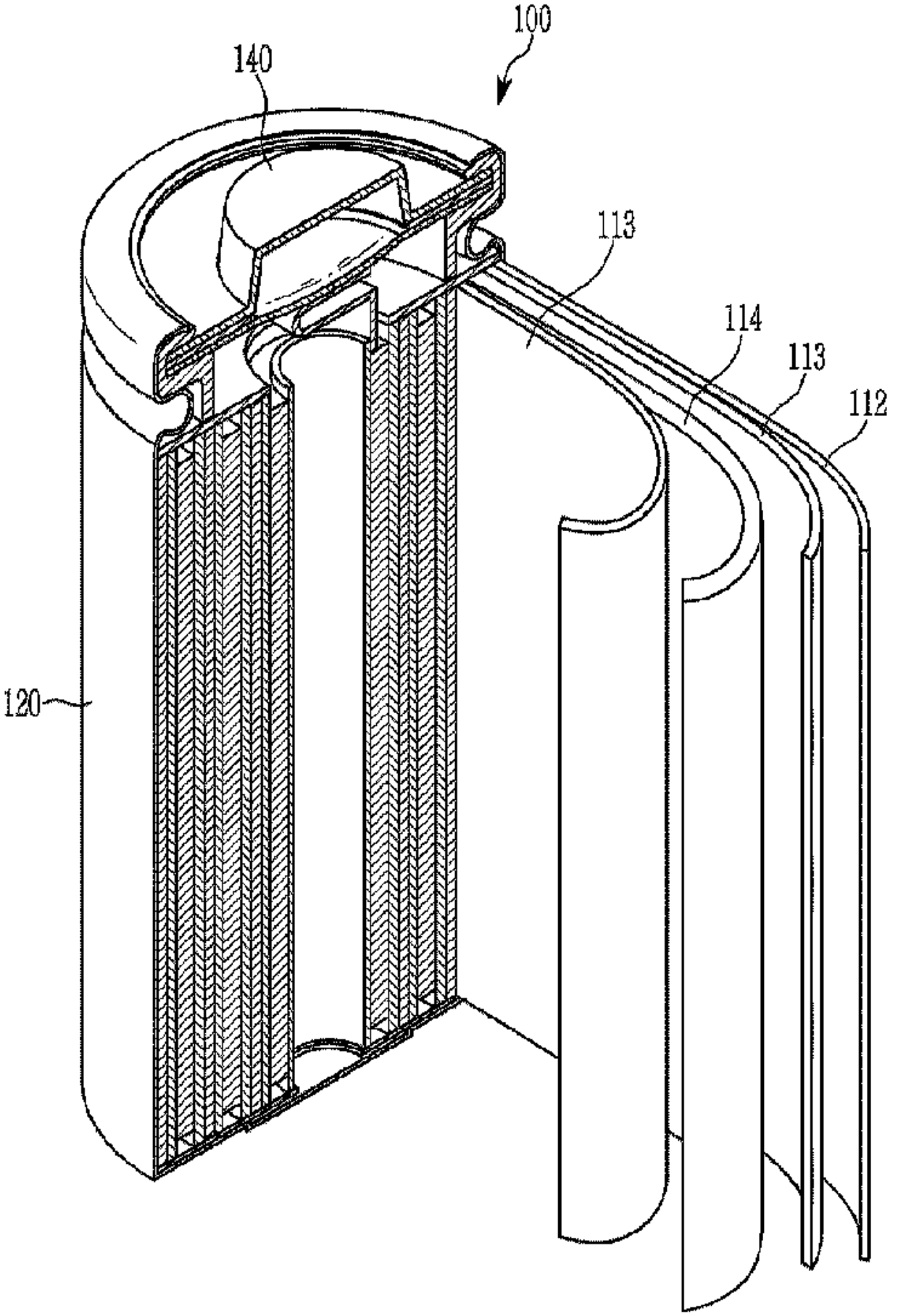


Date Reçue/Date Received 2023-11-15

FIG. 8



Date Reçue/Date Received 2023-11-15


100
140
113
114
113
112
120