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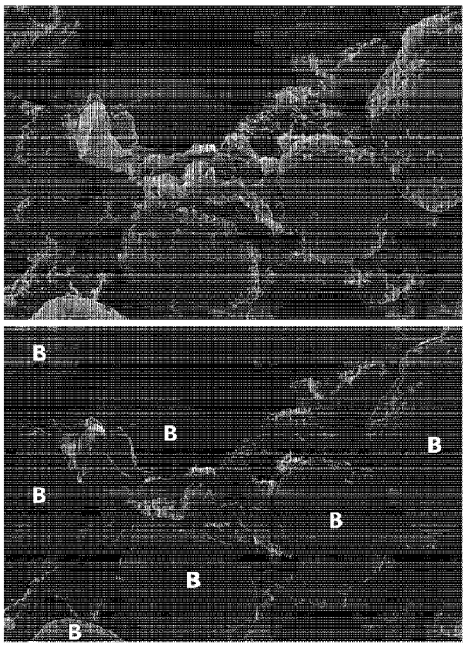
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(54) **Titre : MATERIAU DE CATHODE POUR BATTERIE AU LITHIUM-SOUFRE ET BATTERIE AU LITHIUM-SOUFRE LE CONTENANT**
(54) **Title: POSITIVE ELECTRODE MATERIAL FOR LITHIUM-SULFUR BATTERY AND LITHIUM-SULFUR BATTERY COMPRISING THE SAME**



(57) **Abrégé/Abstract:**
Disclosed is a novel form of cathode active material for use in a cathode for a lithium-sulfur battery. The cathode active material of the present invention comprises: a) a particle (A) comprising a first porous carbon material, of which at least a portion is crystalline, and catalyst particles deposited on the first porous material; and b) a particle (B) comprising a second porous carbon material, of which at least a portion is crystalline, and sulfur supported on the second porous carbon material, wherein the particle (A) and the particle (B) have different morphologies.

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Abstract:

Disclosed is a novel form of cathode active material for use in a cathode for a lithium-sulfur battery. The cathode active material of the present invention comprises: a) a particle (A) comprising a first porous carbon material, of which at least a portion is crystalline, and catalyst particles deposited on the first porous material; and b) a particle (B) comprising a second porous carbon material, of which at least a portion is crystalline, and sulfur supported on the second porous carbon material, wherein the particle (A) and the particle (B) have different morphologies.

DESCRIPTION

TITLE OF INVENTION: POSITIVE ELECTRODE MATERIAL FOR LITHIUM-SULFUR BATTERY AND LITHIUM-SULFUR BATTERY COMPRISING THE SAME

TECHNICAL FIELD

The present disclosure relates to a positive electrode material for a lithium-sulfur battery and a lithium-sulfur battery comprising the same.

The present application claims priority to Korean Patent Application No. 10-2022-0110413 filed on August 31, 2022, Korean Patent Application No. 10-2022-0110385 filed on August 31, 2022, Korean Patent Application No. 10-2022-0187899 filed on December 28, 2022, Korean Patent Application No. 10-2023-0025408 filed on February 24, 2023, and Korean Patent Application No.10-2023-0042283 filed on March 30, 2023 in the Republic of Korea, the disclosures of which are incorporated herein by reference.

BACKGROUND ART

A lithium-sulfur battery is a battery system using a sulfur-based material having a sulfur-sulfur (S-S) bond for a positive electrode active material and a lithium metal for a negative electrode active material. Sulfur, a main component of the positive electrode active material, is abundant in nature and can be found around the world, is non-toxic, and has low atomic weight.

As secondary batteries are used in a wide range of applications including electric vehicles (EVs) and energy storage systems (ESSs), attention is drawn to lithium-sulfur

batteries theoretically having higher energy storage density by weight (~2,600 Wh/kg) than lithium-ion secondary batteries having lower energy storage density by weight (~250 Wh/kg).

During discharging, lithium-sulfur batteries undergo oxidation at the negative electrode active material, lithium, by releasing electrons into lithium cation, and reduction at the positive electrode active material, the sulfur-based material, by accepting electrons. Through the reduction reaction, the sulfur-based material is converted to sulfur anion by the S-S bond accepting two electrons. The lithium cation produced by the oxidation reaction of lithium migrates to the positive electrode via an electrolyte, and bonds with the sulfur anion produced by the reduction reaction of the sulfur-based compound to form a salt. Specifically, sulfur before the discharge has a cyclic S_8 structure, and it is converted to lithium polysulfide (Li_2Sx) by the reduction reaction and is completely reduced to lithium sulfide (Li_2S).

Since sulfur used in the positive electrode active material is nonconductive, electrons generated by electrochemical reaction cannot move, and elusion of poly sulfide (LiSx) occurs during charging·discharging and low electrical conductivity of sulfur and lithium sulfide slows down the dynamics of electrochemical reaction, which degrades the battery life characteristics and rate characteristics.

In these circumstances, recently, studies have been made to use platinum (Pt) that has been primarily used as an electrochemical catalyst to improve the dynamics of oxidation and reduction reactions of sulfur during charging·discharging of lithium-sulfur secondary batteries so as to improve the performance of the lithium-sulfur secondary batteries. However, since noble metal catalysts such as platinum are expensive, the high cost is the

obstacle to the commercialization, and there are poisoning risks by oxidation and reduction reactions of sulfur during charging and discharging, so it is not easy to use as a positive electrode material of lithium-sulfur secondary batteries.

Accordingly, there is a need for technology development of positive electrode materials that improve the dynamics of electrochemical reaction during charging and discharging of lithium-sulfur secondary batteries and can be commercialized with cost efficiency.

SUMMARY

Technical Problem

The present disclosure is directed to providing a new type of positive electrode active material for use in positive electrodes of lithium-sulfur batteries.

Technical Solution

To solve the above-described problem, according to an aspect of the present disclosure, there is provided a positive electrode active material of the following embodiments.

A positive electrode active material according to a first embodiment comprises a) particles A comprising a first porous carbon material, at least part of which is crystalline, and catalyst particles deposited on the first porous carbon material; and b) particles B comprising a second porous carbon material, at least part of which is crystalline, and sulfur loaded in the second porous carbon material, wherein the particles A and the particles B have different morphologies.

According to a second embodiment, in the first embodiment, a sphericity of the particles B may be larger than a sphericity of the particles A, and the sphericity may be defined according to the following equation 1:

[Equation 1]

$$\Psi = \frac{\pi^{\frac{1}{3}}(6V_p)^{\frac{2}{3}}}{A_p}$$

where Ψ denotes the sphericity, V_p denotes a volume of the particle, and A_p denotes a surface area of the particle.

According to a third embodiment, in the first or second embodiment, 50% or more of the particles A may be present on a surface of the particles B.

According to a fourth embodiment, in any one of the first to third embodiments, a surface of at least some of the particles B may be covered by the particles A, and a coverage area of the particles B by the particles A may be 20% to 50% of an entire outer area of the particles B.

According to a fifth embodiment, in any one of the first to fourth embodiments, a porosity of the particles A may be larger than a porosity of the particles B.

According to a sixth embodiment, in any one of the first to fifth embodiments, a specific surface area of the particles A may be larger than a specific surface area of the particles B.

According to a seventh embodiment, in any one of the first to sixth embodiments, the particles A and the particles B may be in contact with each other in at least one location at which the catalyst particles included in the particles A are present.

According to an eighth embodiment, in any one of the first to seventh embodiments, a weight of the sulfur (S_8) may be 60 weight% to 90 weight% based on a total weight of the

first porous carbon material and the second porous carbon material.

According to a ninth embodiment, in any one of the first to eighth embodiments, the first porous carbon material and the second porous carbon material may be different materials.

According to a tenth embodiment, in any one of the first to ninth embodiments, the first porous carbon material and the second porous carbon material may be a same material.

According to an eleventh embodiment, in any one of the first to tenth embodiments, each of the first porous carbon material and the second porous carbon material may independently comprise at least one of bundled carbon nanotubes (CNT), entangled CNT or reduced graphene oxide (rGO).

According to a twelfth embodiment, in any one of the first to eleventh embodiments, the catalyst particles may comprise vanadium nitride.

According to a thirteenth embodiment, in any one of the first to twelfth embodiments, the catalyst particles may comprise at least one of cobalt (Co) or iron (Fe).

According to a fourteenth embodiment, in any one of the first to thirteenth embodiments, an elasticity of each of the first porous carbon material and the second porous carbon material may be larger than an elasticity of an amorphous carbon material.

According to a fifteenth embodiment, in any one of the first to fourteenth embodiments, an electrical conductivity of each of the first porous carbon material and the second porous carbon material may be larger than an electrical conductivity of an amorphous carbon material.

According to a sixteenth embodiment, in any one of the first to fifteenth embodiments, an I_D/I_G value of the positive electrode active material may be equal to or less

than 2.0.

According to another aspect of the present disclosure, there is provided a lithium-sulfur battery of the following embodiment.

The lithium-sulfur battery according to a seventeenth embodiment comprises the positive electrode active material according to any one of the first to sixteenth embodiments.

Advantageous Effects

The positive electrode active material according to an embodiment of the present disclosure is a new type for used in secondary batteries, especially lithium-sulfur batteries.

Specifically, the positive electrode active material according to an embodiment of the present invention is a new type of positive electrode active material suitable to significantly improve the loading amount and catalytic activity of sulfur. It is, therefore, possible to improve the performance of a secondary battery, especially a lithium-sulfur battery, using the same, but the effect of the present disclosure is not limited thereto.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate exemplary embodiments of the present disclosure and together with the foregoing description, serve to provide a further understanding of the technical aspect of the present disclosure, and thus the present disclosure should not be construed as being limited to the accompanying drawings.

FIG. 1 shows a scanning electron microscopy (SEM) image of a positive electrode active material according to an embodiment of the present disclosure. In FIG. 1, section 'A' represents a particle A, and section 'B' represents a particle B. The SEM image of FIG.

1 is an image obtained by taking an area of 10 μm X 10 μm at 2,000x magnification.

FIG. 2 shows an SEM image of a positive electrode active material in which vanadium nitride particles as catalyst particles are loaded in the particles A according to an embodiment of the present invention. The SEM image of FIG. 2 is an image obtained by taking an area of 10 μm X 10 μm at 15,000x magnification.

FIG. 3 shows an SEM image of bundled CNT used in an embodiment of the present disclosure. The image of FIG. 3 is an image obtained by taking an area of 10 μm X 10 μm at 500x magnification.

FIG. 4 shows an SEM image of entangled CNT used in an embodiment of the present disclosure. The image of FIG. 4 is an image obtained by taking an area of 10 μm X 10 μm at 500x magnification.

FIG. 5 shows an SEM image of reduced graphene oxide (rGO) used in an embodiment of the present disclosure. The image of FIG. 5 is an image obtained by taking an area of 10 μm X 10 μm at 1,000x magnification.

FIG. 6 shows an SEM image of a positive electrode active material in which iron particles as catalyst particles are loaded in the particles A according to an embodiment of the present invention. The SEM image of FIG. 6 is an image obtained by taking an area of 10 μm X 10 μm at 2,000x magnification.

FIG. 7 shows a capacity-voltage curve graph showing performance evaluation results of a battery using each of the positive electrode active material of example 1 and the positive electrode active material of comparative example 1 according to an embodiment of the present disclosure.

FIG. 8 shows a capacity-voltage curve graph showing performance evaluation results of a battery using each of a positive electrode active material of comparative example 1 and a positive electrode active material of comparative example 2 according to an embodiment of the present disclosure.

FIG. 9 shows a discharge capacity-cycle-coulombic efficiency curve graph showing performance evaluation results of a battery using each of a positive electrode active material of example 1 and a positive electrode active material of comparative example 1 according to an embodiment of the present disclosure.

FIG. 10 shows a discharge capacity-cycle-coulombic efficiency curve graph showing performance evaluation results of a battery using each of a positive electrode active material of comparative example 1 and a positive electrode active material of comparative example 2 according to an embodiment of the present disclosure.

DETAILED DESCRIPTION

Hereinafter, the present disclosure will be described in detail. However, the present disclosure is not limited to the following description and each element may be variously modified or selectively used together, if necessary. Accordingly, it should be understood that the present disclosure encompasses all modifications, equivalents or substitutes included in the aspect and technical scope of the present disclosure.

The term "comprise" when used in this specification, specifies the presence of stated elements, but does not preclude the presence or addition of one or more other elements, unless the context clearly indicates otherwise.

"A and/or B" when used in this specification, specifies either A or B or both.

The terms as used in the specification are for the purpose of convenience, but not intended to being limiting. For example, the terms indicating positions such as 'up', 'down', 'left', 'right', 'front', 'rear', 'inner' and 'outer' are not absolute, and may refer to positions or directions in the drawings used or referenced to describe the relative position or direction between the elements. These terms include themselves as well as words including them and their derivatives and synonyms.

The term "composite" as used herein refers to a combination of two or more materials that have physically and/or chemically different phases and exert more effective functions.

The term "polysulfide" as used herein is the concept including "polysulfide ion (S_x^{2-}, x = 8, 6, 4, 2))" and "lithium polysulfide (Li_2S_x or LiS_x, x = 8, 6, 4, 2)".

Regarding the properties described herein, in case that measurement conditions and methods are not described in detail, the properties are measured by the measurement conditions and methods commonly used by those having ordinary skill in the corresponding technical field.

According to an aspect of the present disclosure, there is provided a positive electrode active material for use in secondary batteries, specifically in lithium-sulfur batteries.

The positive electrode active material comprises a porous carbon material, catalyst particles and sulfur (S). Specifically, the positive electrode active material may comprise two porous carbon materials, catalyst particles and sulfur (S).

The positive electrode active material comprises a) particles A comprising a first

porous carbon material, at least part of which is crystalline, and catalyst particles deposited on the first porous carbon material; and b) particles B comprising a second porous carbon material, at least part of which is crystalline, and sulfur loaded in the second porous carbon material, wherein the particles A and the particles B have different morphologies.

In an embodiment of the present disclosure, it may be provided that the sulfur is not infiltrated into the pores of the first porous carbon material. According to an embodiment of the present disclosure, it may be provided that the first porous carbon material and/or the particles A are substantially free of (or free of) sulfur. The term "free of" in this regard does not exclude impurities. The impurities may be included without hindering the objective achieved by the present disclosure.

In an embodiment of the present disclosure, it may be provided that the catalyst particles are not deposited on the second porous carbon material. According to an embodiment of the present disclosure, it may be provided that the second porous carbon material and/or the particles B are substantially free of (or free of) the catalyst particles. The term "free of" in this regard does not exclude impurities. The impurities may be included without hindering the objective achieved by the present disclosure.

In an embodiment of the present disclosure, the porous carbon material is a material comprising micropores, and comprises the catalyst particles and/or the sulfur on at least one of the outer surface of the porous carbon material or the surface inside the pores.

In an embodiment of the present disclosure, the first porous carbon material and the second porous carbon material may be the same or different from each other. In an embodiment of the present disclosure, the first porous carbon material is a material comprising micropores, and comprises the catalyst particles on at least one of the outer

surface of the porous carbon material or a surface inside the micropores. In an embodiment of the present disclosure, the second porous carbon material is a material comprising micropores, and comprises the sulfur on at least one of the outer surface of the porous carbon material or the surface inside the micropores.

In an embodiment of the present disclosure, the catalyst particles may be chemically and/or physically bonded to at least one of the outer surface of the first porous carbon material or the surface inside the pores. In an embodiment of the present disclosure, the pores may be micropores.

In an embodiment of the present disclosure, the catalyst particles may be physically adsorbed onto the outer surface of the first porous carbon material and/or the surface inside the pores of the first porous carbon material. Alternatively, the catalyst particles may be chemically bonded to the outer surface of the first porous carbon material and/or the surface inside the pores of the first porous carbon material by the C-C covalent bond and/or pi-pi interaction between an element present in the catalyst particles and carbon of the first porous carbon material. Additionally, the physical adsorption and the chemical bond may co-exist between the catalyst particles and the first porous carbon material.

In an embodiment of the present disclosure, the catalyst particles may be physically adsorbed on the outer surface of the first porous carbon material.

In an embodiment of the present disclosure, the sulfur (S, such as S_8) may be chemically and/or physically bonded to at least one of the outer surface of the second porous carbon material or the surface inside the pores.

In an embodiment of the present disclosure, a weight ratio of second porous carbon material and the sulfur may be from 10:90 to 90:10; 10:90 to 50:50, or 25:75.

In an embodiment of the present disclosure, the sulfur included in the particles B is derived from a sulfur-based compound, for example, S_8, that is mixed with the porous carbon material when manufacturing the positive electrode active material, and the sulfur may be included in at least one location of the outer surface of the second porous carbon material or the surface inside the pores. The sulfur containing compound may include, for example, inorganic sulfur (S_8), lithium sulfide (Li_2S), lithium polysulfide (Li_2Sx, $2 \leq x \leq 8$), disulfide compounds or a mixture thereof, but is not limited thereto.

In this disclosure, the 'morphology' of the particle represents a form, a shape and a physiochemical or biochemical structure of the particle. For example, the particles A and the particles B may have different morphologies by having different shapes. For example, the particles A may have a shape with an uneven or rough surface, such as a broccoli-like shape, a cauliflower-like shape, a spiky-shape, etc, and the particles B may have shape with a relatively smooth surface, or a smooth surface, such as a potato-like shape (roughly oval or oblong in shape, with a somewhat smooth surface not excluding minor unevenesses), a spherical shape, an elliptoidic shape, etc. The morphology of the particle may be determined, for example, through a scanning electron microscope (SEM) image.

Accordingly, the particles A and the particles B having different morphologies represent that the particles A and the particles B are different in at least one of the form, the shape, the physiochemical structure or the biochemical structure of the particle.

In an embodiment of the present disclosure, the particles A and the particles B having different morphologies may be determined through the measurement of at least one material property of the specific surface area, the porosity, the particle size and the particle shape seen through an optical microscope, for each of the particles A and the particles B.

In an embodiment of the present disclosure, since the particles A comprise the catalyst particles, the particles A may promote the dynamics of electrochemical reaction of the positive electrode active material, but the function is not limited thereto. Additionally, since the particles B comprise the sulfur (S), the particles B may provide sites at which the electrochemical reaction of the positive electrode active material takes place, but the function is not limited thereto. Accordingly, it is possible that the positive electrode active material has the improved performance when the particles A, especially the catalyst particles present in or on the particles A have the similar morphology to the particles B, especially the sulfur present in (infiltrated in) the particles B.

In this context, according to an embodiment of the present disclosure, the sphericity of the particles B may be preferably larger than the sphericity of the particles A. When the sphericity of the particles B is larger than sphericity of the particles A, the positive electrode active material may be provided such that the particles B are surrounded by the particles A. Through this, it is possible to provide the positive electrode active material with the outstanding performance in which the sulfur (S)-loaded particles B are electrically connected in non-contact (no direct surface-to-surface contact) with each other by the physiochemical contact between the porous carbon material of the particles B and the porous carbon material of the particles A. Here, two or more particles B may be present in contact or non-contact with each other in the positive electrode active material, and it is obvious to those skilled in the art that this mechanism is not intended to limit the non-contact between the particles B.

In an embodiment of the present disclosure, the 'sphericity' may be defined according to the following equation 1.

[Equation 1]

$$\Psi = \frac{\pi^{\frac{1}{3}}(6V_p)^{\frac{2}{3}}}{A_p}$$

where Ψ denotes the sphericity,

V_p denotes the volume of the particle, and

A_p denotes the surface area of the particle.

In an embodiment of the present disclosure, 'Vp' may represent the apparent volume of the particle. The apparent volume of the particle can be measured according to a conventional method for measuring the apparent volume. In an embodiment of the present invention, the apparent volume may be measured through the (mass/apparent density) value of the particle, and the apparent density may be measured by the value of [dry weight/(dry weight-weight in water)] of the particle, but the method of measuring the volume of the particle is not limited thereto. In addition, it may be measured according to a method for measuring the particle volume of the porous material.

In an embodiment of the present disclosure, 'Ap' may represent the apparent area of the particle. The apparent area of the particle may be calculated as, for example, $\pi^{1/3}(6Vp)^{2/3}$, but may also be measured according to a method for measuring the apparent area of the porous material.

In an embodiment of the present disclosure, in the positive electrode active material, the particles A may be present on the surface of the particles B. Specifically, in the positive electrode active material, at least part of the surface of the particles B having larger sphericity may be covered with the particles A having smaller sphericity.

FIG. 1 shows a scanning electron microscopy (SEM) image of the positive electrode active material according to an embodiment of the present disclosure. In FIG. 1, sections

'A' represents the particles A, and sections 'B' represents the particles B.

Referring to FIG. 1, it can be seen that the positive electrode active material comprises the particles B having larger sphericity and the particles A having smaller sphericity, such that the particles A are present on the surface of the particles B, and specifically, the particles A cover at least part of the surface of the particles B.

In an embodiment of the present disclosure, the size of the particles A may be, for example, from 10 to 100 μm, from 15 to 50 μm, or from 20 to 40 μm, for example, 35 μm.

In an embodiment of the present disclosure, the size of the particles B may be, for example, from 10 to 100 μm, or from 20 to 80 μm.

The size of the particles may refer to D50 size, and the D50 size may be measured by a method commonly used in the art without particular limitation. For example, the size of the particles, for example, D50 size, may be measured by scanning electron microscopy (SEM), laser diffraction or field-emission electron microscopy. The particle size measurement using the laser diffraction method may be performed using, for example, a commercially available laser diffraction particle size analyzer, for example, Microtrac MT 3000, but is not limited thereto. The particle size D50 refers to a particle diameter at 50% of the particles in a cumulative particle size distribution.

In an embodiment of the present disclosure, the particles A included in the positive electrode active material may not be present on the surface of the particles B, but the above-described effect may work better when 50% or more of the total number of particles A included in the positive electrode active material are present on the surface of the particles B. Accordingly, 50% or more of the particles A may be present on the surface of the particles B. That is, 50% or more of the particles A may be in direct contact with the

surface of at least one of the particles B. Specifically, the number of particles A present on the surface of the particles B may be 50% to 100%, for example, 55% to 90%, 60% to 85% or 70% to 80% of the total number of particles A included in the positive electrode active material, but is not limited thereto.

In this disclosure, the particles A may be present on the surface of the particles B, for example, such that the surface of the particles B surrounded by the particles A is 20% or more of the total area of the outer surface of the particles B. Here, the area of the surface of the particles B surrounded by the particles A may be measured, for example, through SEM image analysis of the positive electrode active material. Specifically, the measurement may be made on the area of 10 μm X 10 μm at 2,000x magnification.

In an embodiment of the present disclosure, in the positive electrode active material, the surface of at least part of the particles B may be surrounded and/or covered by the particles A.

Specifically, since the particles B are particles of sulfur (S)-loaded porous carbon material, the particles B may have one of the features of the porous carbon material, the outer surface and the specific surface area. The particles B may have an outer surface and/or a specific surface area corresponding to that of the second porous carbon material. In this instance, the area of the outer surface of the particles B may be measured through SEM image analysis as described above, and the specific surface area of the particles B may have the similar value to the inner area, and for example, may be measured by the BET specific surface area measurement method known in the corresponding technical field, for example, the method in accordance with ISO 9277:2010.

In this instance, according to an embodiment of the present disclosure, the coverage

area of the particles B by the particles A may be, for example, 20% or more with respect to the entire outer area of the particles B, specifically 20% to 90%, preferably 20% to 80%, 30% to 70% or 40% to 50%. In an embodiment of the present disclosure, when the entire outer area of the particles B is covered by the particles A, for example, the coverage area of the particles B by the particles A is 100%, an electrolyte cannot easily move in and out of the positive electrode active material during the assembly of batteries using the same, and it may slow down the dynamics of electrochemical reaction during the operation of batteries. In an aspect, when the coverage area of the particles B by the particles A is within the above-described range, it may be advantageous in providing the new type of positive electrode active material with significantly improved loading amount and catalytic activity of sulfur, but the present disclosure is not limited thereto.

According to an embodiment of the present disclosure, a weight ratio of the particles A and the particles B in the positive electrode active material may be, for example, 50:50 to 1:99, 40:60 to 5:95, 30:70 to 5:95, 20:80 to 5:95, or 7.5:92.5, but is not limited thereto. When the weight ratio of the particles A and the particles B is within the above-described range, the coverage area of the particles B by the particles A satisfies the above-described range and it may be advantageous in improving the activation of the positive electrode active material and the performance of batteries using the same, but the present disclosure is not limited thereto.

In an embodiment of the present disclosure, the porosity of the particles A may be larger than the porosity of the particles B. In other words, the total pore volume of the particles A may be larger than the total pore volume of the particles B. Since the particles A and the particles B comprise the porous carbon material having outer pores and inner pores,

it is possible to ensure the predefined porosity. As described above, the pores of the particles B may be surrounded by sulfur (S) and/or sulfur may be loaded in the pores of the particles B, while the particles A may have open pores, and thus the porosity of the particles A may be larger than the porosity of the particles B. The porosity and/or pore volume of the particles A and/or the particles B may be measured through the method in accordance with ISO 15901:2019 known in the corresponding technical field, but the measurement method is not limited thereto.

In an embodiment of the present disclosure, the specific surface area of the particles A may be larger than the specific surface area of the particles B. As described above, at least part of the outer surface of the particles B may be covered by the particles A, and the pores of the particles B may be surrounded by sulfur (S) and/or sulfur may be loaded in the pores of the particles B, while the particles A may have open pores, and thus the specific surface area of the particles A may be larger than the specific surface area of the particles B. Since the specific surface area of the particles A that surround the particles B is larger than the specific surface area of the particles B, lithium polysulfide that may migrate from the particles B may be adsorbed onto the particles A, and it may be advantageous in prompting the reactivity due to the large specific surface area of the particles A.

In this disclosure, the specific surface area may be measured, for example, by the BET method, and specifically, may be a value calculated from the amount of adsorbed nitrogen gas under liquid nitrogen temperature (77K) using BEL Japan BELSORP-mini II, but the measurement method is not limited thereto.

In an embodiment of the present disclosure, as described above, the particles A comprise the catalyst particles in or on at least one of the outer surface of the first porous

carbon material or the surface inside the pores of the first porous carbon material. Specifically, the catalyst particles may be adsorbed onto the outer surface of the particles A.

In this instance, according to an embodiment of the present disclosure, the particles A and the particles B may be in contact with each other in at least one location at which the catalyst particles included in the particles A are present. In other words, the particles A and the particles B may be anchored to each other by the catalyst particles. Alternatively, the particles A may be anchored on the surface of the particles B by the catalyst particles. That is, a connection between the particles A and the particles B may be made via the catalyst particles. At least one particle A and at least one particle B may be anchored to each other by at least one catalyst particle.

In an embodiment of the present disclosure, in the positive electrode active material, the particles A may be merged with the particles B. For example, as described above, in the positive electrode active material, the particles A may be merged with the particles B such that the particles A cover at least part of the surface of the particles B. In an embodiment of the present disclosure, the particles A may be merged with the particles B such that the particles A are, at least in part, arranged between the particles B.

In an embodiment of the present disclosure, in the positive electrode active material, the particles A may fill the gaps between the particles B. For example, in the positive electrode active material, the particles A may fill the gaps between the particles B while covering the surface of at least two particles B spaced a predetermined distance apart. In an embodiment of the present disclosure, the gap may refer to a distance of at least 10% of the diameter of the smaller particle B, and the distance may refer to, for example, the shortest distance between two opposite surfaces of the particle B.

The above-described type of positive electrode active material may increase the loading amount of sulfur and improve the catalytic activity of the loaded catalyst particles, thereby improving the performance of batteries, especially of lithium-sulfur batteries, using the same.

In an embodiment of the present disclosure, the positive electrode active material may be in a fully charged state. In this disclosure, the 'fully charged state' indicates a state of charge of at least 90%, for example, at least 99% or 100%. Specifically, a lithium-sulfur battery comprising the positive electrode active material involves oxidation/reduction reactions of sulfur according to the state of charge·discharge, and has the loss of sulfur content relative to the initial sulfur content during repeated charging·discharging. Accordingly, the positive electrode active material according to an embodiment of the present disclosure having the above-described morphology can be seen in the fully charged state of the positive electrode active material, and the fully charged state of the positive electrode active material may refer to a state in which the sulfur content is at least 90%, for example, at least 99% or 100% based on the initial amount of sulfur loaded in the positive electrode active material or the amount of sulfur in at least reversible state, but the present disclosure is not limited thereto.

In an embodiment of the present disclosure, the positive electrode active material may comprise sulfur (S_8), for example, in an amount of 60 weight% to 90 weight% based on the total weight of the first porous carbon material and the second porous carbon material. Specifically, the weight of the sulfur (S_8) may be 65 weight% to 90 weight%, 70 weight% to 85 weight%, 75 weight% to 80 weight% or 65 weight% to 75 weight% based the total weight of the first porous carbon material and the second porous carbon material.

In an embodiment of the present disclosure, the first porous carbon material, at least part of which is crystalline, and the second porous carbon material, at least part of which is crystalline, may be different from each other.

In an embodiment of the present disclosure, the first porous carbon material, at least part of which is crystalline, and the second porous carbon material, at least part of which is crystalline, may be the same.

In an embodiment of the present disclosure, each of the first porous carbon material and the second porous carbon material may be, for example, independently selected from at least one of carbon nanotubes (CNT), graphene, graphene oxide (GO), reduced graphene oxide (rGO), carbon black, graphite, graphite nanofiber (GNF), carbon nanofiber (CNF), activated carbon fiber (ACF), natural graphite, artificial graphite, expanded graphite, activated carbon or fullerene.

In an embodiment of the present disclosure, each of the first porous carbon material and the second porous carbon material may be independently selected from carbon nanotubes and reduced graphene oxide. In an embodiment of the present disclosure, the first porous carbon material may be independently selected from carbon nanotubes and reduced graphene oxide and the second porous carbon material may be carbon nanotubes.

In an embodiment of the present disclosure, the carbon nanotubes may be classified into single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) according to the number of carbon atom layers in their structure. In an embodiment of the present disclosure, when each of the first porous carbon material and the second porous carbon material optionally comprises carbon nanotubes, the carbon nanotubes may comprise at least one of single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes

(MWCNT).

In another embodiment of the present disclosure, the carbon nanotubes may exist such that two or more carbon nanotubes come into close contact and get entangled with each other by their cohesion strength. In particular, in an embodiment of the present disclosure, the carbon nanotubes may be provided in the form of a carbon nanotube dispersion in which carbon nanotubes are dispersed as a single strand in a dispersion medium, but may be provided in the form of secondary structure or an agglomerate of carbon nanotubes of primary structure.

In this aspect, when each of the first porous carbon material and the second porous carbon material optionally comprises carbon nanotubes, the carbon nanotubes may comprise at least one of a bundled secondary structure or an entangled secondary structure, respectively. In an embodiment of the present disclosure, the first porous carbon material may be selected from bundled carbon nanotubes and reduced graphene oxide and the second porous carbon material may be entangled carbon nanotubes.

The bundled secondary structure of the carbon nanotubes is an agglomerate of primary structures oriented in the lengthwise direction of the carbon nanotubes by the cohesion strength between carbon, each primary structure being single-stranded carbon nanotubes, and may be referred to as bundled carbon nanotubes (bundled CNT).

FIG. 3 shows an SEM image of an example of the bundled CNT.

The entangled secondary structure of the carbon nanotubes is a randomly entangled and agglomerated form of primary structures in a spherical shape, each primary structure being single-stranded carbon nanotubes, and may be referred to as entangled carbon nanotubes (entangled CNT). The entangled CNT may have the improved porosity by

interstitial volume formed by the entanglement of the carbon nanotubes of primary structure, compared to the carbon nanotubes of primary structure.

FIG. 4 shows an SEM image of an example of the entangled CNT.

When comparing the morphology of the example of bundled CNT and the morphology of the example of entangled CNT with reference to FIGS. 3 and 4, it can be seen that the bundled CNT is close to a planar shape while the entangled CNT is close to a spherical shape. Accordingly, the sphericity of the example of entangled CNT may be higher than the sphericity of the example of bundled CNT.

In an embodiment of the present disclosure, the first porous carbon material that hosts the catalyst particles may comprise a planar carbon material to improve the specific surface area of the particles A. For example, in case that the first porous carbon material comprises carbon nanotubes, the first porous carbon material may preferably comprise bundled carbon nanotubes, but the present disclosure is not limited thereto. Additionally, in case that the first porous carbon material comprises a graphene-based material, the first porous carbon material may preferably comprise reduced graphene oxide, but the present disclosure is not limited thereto.

In an embodiment of the present disclosure, the second porous carbon material that hosts sulfur may comprise carbon nanotubes to improve the sulfur content in the positive electrode active material. For example, in case that the second porous carbon material comprises carbon nanotubes, specifically the second porous carbon material may comprise at least one of bundled CNT or entangled CNT, and more specifically may comprise entangled CNT to improve the coverage area by the particles A, but the present disclosure is not limited thereto.

In an embodiment of the present disclosure, each of the first porous carbon material and the second porous carbon material may comprise the micropores in the outer surface and inside, and the average diameter of the micropores may range, for example, from 1 nm to 200 nm, for example, from 1 nm to 100 nm, from 10 nm to 80 nm or from 20 nm to 50 nm. The average diameter of the pores may be measured by in accordance with ISO 15901:2019 known in the corresponding technical field, but is not limited thereto. The average diameter may be a D50 diameter, and the D50 diameter refers to a diameter at 50% of the particles in a cumulative particle size distribution.

Additionally, in an embodiment of the present disclosure, the porosity (or void fraction) of each of the first porous carbon material and the second porous carbon material may range from 10% to 90% of the total volume of each porous carbon material. The porosity of the porous carbon material may be measured by the method in accordance with ISO 15901:2019 known in the corresponding technical field, but the measurement method is not limited thereto.

In an embodiment of the present disclosure, the pore volume of the porous carbon material may be, for example, 1 cm^3/g to 20 cm^3/g or 1 cm^3/g to 10 cm^3/g. The pore volume may be, for example, a value calculated and measured through N2 isotherm analysis obtained based on adsorption of liquid nitrogen.

In an embodiment of the present disclosure, for example, each of the first porous carbon material and the second porous carbon material may have the specific surface area of 100 to 2000 m^2/g, 300 to 2000 m^2/g, 400 to 1800 m^2/g, 450 to 1500 m^2/g or 500 to 1200 m^2/g. The specific surface area may be measured by the BET method in accordance with ISO 15901:2019 known in the corresponding technical field, but is not limited thereto.

In an embodiment of the present disclosure, the catalyst particles are not limited to a particular type and may include any catalyst particles that promote the dynamics of lithium-sulfur batteries.

In an embodiment of the present disclosure, the catalyst particles may have catalytic activity on oxidation and reduction reactions of sulfur (S_8) included in the particles B, and at least one of lithium sulfide (Li_2S), lithium polysulfide (Li_2Sx, $2 \leq x \leq 8$) or disulfide compounds produced by the oxidation/reduction of sulfur during the operation of lithium-sulfur batteries.

In another embodiment of the present disclosure, the catalyst particles may comprise vanadium nitride.

In an embodiment of the present disclosure, the catalyst particles may comprise cobalt (Co) or iron (Fe).

In an embodiment of the present disclosure, the catalyst particles in the particles A may be present in an amount of 10 to 30 wt.-%, for example, 20 wt.-%, based on the total weight of the particles A. The amount of the catalyst particles may be measured using a thermogravimetric analyzer (TGA).

In an embodiment of the present disclosure, the catalyst particles may be metal composite particles. The metal composite particles may comprise a core comprising a metal and a carbon coating layer coated on at least part of the surface of the core, and the carbon coating layer may be, for example, a crystalline carbon coating layer. In the catalyst particles, a ratio of the thickness of the carbon coating layer to the average particle size D50 of the core may be 10 to 20%, for example, 15%, but the present disclosure is not limited

thereto.

In an embodiment of the present disclosure, the particles A may be doped with a heteroelement. Specifically, the first porous carbon material and/or the carbon coating layer may be doped with the heteroelement. The heteroelement may independently include one or more element selected from nitrogen, sulfur and oxygen, and for example, may include nitrogen. Specifically, the heteroelement used in the doping may be derived from a precursor used when the carbon coating layer is introduced, but the present disclosure is not limited thereto.

In an embodiment of the present disclosure, the catalyst particles may, for example, have the average particle size (D_{50}) of 1 nm to 200 nm, but the present disclosure is not limited thereto. In this disclosure, the particle size may be measured by the known measurement method and the measurement method is not limited to a particular method. For example, the particle size may be measured by scanning electron microscopy (SEM), field emission scanning electron microscopy or a laser diffraction method. The measurement using the laser diffraction method may be performed, for example, using a commercially available laser diffraction particle size measurement device (for example Microtrac MT 3000). The average particle size (D_{50}) refers to a particle size at 50% of the particles in a cumulative volume particle size distribution.

In an embodiment of the present disclosure, at least part of each of the first porous carbon material and the second porous carbon material may be crystalline by the thermal treatment process when manufacturing the positive electrode active material. Specifically, each of the first porous carbon material and the second porous carbon material may be

crystalline in whole.

In this disclosure, when a material such as the porous carbon material is at least partially crystalline, it can be seen through at least one peak in an XRD spectrum of the material. In the XRD spectrum of the material, for example, when a signal-to-noise ratio is greater than 1, for example, 1.5:1, 2:1, 5:1 or 10:1, it may be said that the material is at least partially crystalline.

Accordingly, in an embodiment of the present disclosure, the elasticity of each of the first porous carbon material and the second porous carbon material may be higher than the elasticity of amorphous carbon materials.

Additionally, in an embodiment of the present disclosure, the electrical conductivity of each of the first porous carbon material and the second porous carbon material may be higher than the electrical conductivity of amorphous carbon materials.

In this disclosure, the amorphous carbon materials may be, for example, the carbon material disclosed by Liu at al. *Nanoscale*, 2018, 10, 5246-5253.

In this disclosure, the degree of crystallinity of the porous carbon material may be measured, for example, by X-Ray Diffraction (XRD) analysis. 'XRD' is the analysis of diffraction (Bragg condition: $2d\sin\theta=n\lambda$: a distance between 2 planes is d, an angle at which a plane is formed with X-ray is θ, an arbitrary integer is n, and the wavelength of X-ray is λ) resulting by scattering and interference of X-ray by electrons around atoms when a sample is irradiated with X-ray, and is used to determine the phase, quantity, crystal size or crystallinity of the components. For example, when at least one independent peak appears in XRD spectrum, it can be seen that at least part is crystalline. In this instance, in the independent peak, a signal is measured 1 time or more, 1.5 times or more, 2 times or more,

5 times or more or 10 times or more, compared to noise.

In an embodiment of the present disclosure, an I_D/I_G value of the positive electrode active material may be equal to or less than 2.0. For example, a Raman peak intensity ratio (I_D/I_G) <2.0.

The Raman peak intensity ratio may be measured through I_G and I_D values obtained in the spectrum of the positive electrode active material obtained through Raman spectroscopy. In the obtained spectrum, I_G refers to peak (G-peak, 1573/cm) of crystalline region, and I_D refers to peak (D-peak, 1309/cm) of amorphous region. Accordingly, in this instance, the smaller I_G/I_D ratio value, the lower crystallinity.

In an embodiment of the present disclosure, the positive electrode active material may be formed by mixing the first porous carbon material, the second porous carbon material, the catalyst particles and the sulfur-based compound in a sequential order or at the same time, and performing thermal treatment. The positive electrode active material manufactured by the thermal treatment may comprise the first and second porous carbon materials, at least part of which is crystalline as described above, but the present disclosure is not limited thereto.

According to another aspect of the present disclosure, there is provided a positive electrode for a lithium-sulfur battery comprising the positive electrode active material.

In addition to the positive electrode active material, the positive electrode for a lithium-sulfur battery may further comprise a binder. The binder is not limited to a particular type and may include any binder that may be used in positive electrodes of lithium-sulfur batteries.

The binder is the component that helps to bind the positive electrode active material

and the conductive material and bind to the current collector, and may include, for example, at least one of polyvinylidene fluoride (PVdF), a polyvinylidene fluoride-polyhexafluoropropylene copolymer (PVdF/HFP), polyvinylacetate, polyvinylalcohol, polyvinylether, polyethylene, polyethyleneoxide, alkylated polyethylene oxide, polypropylene, polymethyl(meth)acrylate, polyethyl(meth)acrylate, polytetrafluoroethylene (PTFE), polyvinylchloride, polyacrylonitrile, polyvinylpyridine, polyvinylpyrrolidone, styrene-butadiene rubber, acrylonitrile-butadiene rubber, ethylene-propylene-diene monomer (EPDM) rubber, sulfonated EPDM rubber, styrene-butylene rubber, fluoro rubber, carboxyl methyl cellulose (CMC), starch, hydroxypropyl cellulose or regenerated cellulose, but is not necessarily limited thereto.

In an embodiment of the present disclosure, the binder may comprise, for example, polyvinylidene fluoride (PVDF), and specifically may comprise PVDF dispersed in N-methyl-2-pyrrolidone (NMP).

In another embodiment of the present disclosure, the binder may comprise an aqueous binder, for example, styrene butadiene rubber (SBR), and specifically may comprise an aqueous binder dispersed in an aqueous solvent such as water.

In an embodiment of the present disclosure, the positive electrode for a lithium-sulfur battery may comprise a positive electrode current collector, and a positive electrode active material layer coated on one or two surfaces of the current collector and comprising the positive electrode active material and the binder. In this instance, the positive electrode current collector is not limited to a particular type and may include those having high conductivity without causing any chemical change to the corresponding battery.

In another embodiment of the present disclosure, in addition to the positive electrode

active material and the binder, the positive electrode for a lithium-sulfur battery may further comprise a conductive material and an additive. In this instance, the binder, the conductive material and the additive may include common types, and their detailed description is omitted.

A lithium-sulfur battery according to still another aspect of the present disclosure is a lithium-sulfur battery comprising the above-described positive electrode active material.

The lithium-sulfur battery comprises, for example, a positive electrode, a negative electrode, a separator between the positive electrode and the negative electrode and an electrolyte solution, and the positive electrode comprises the above-described positive electrode active material.

In an embodiment of the present disclosure, the negative electrode and the separator are not limited to a particular type and may include those used in lithium-sulfur batteries without hindering the objective achieved by the present disclosure. The negative electrode may include, for example, a lithium metal.

In an embodiment of the present disclosure, the separator is not limited to a particular type and may include the commonly used separators of lithium-sulfur batteries.

In an embodiment of the present disclosure, the separator may comprise a porous polyolefin substrate, and if necessary, may further comprise inorganic particles on at least one surface of the porous polyolefin substrate. Additionally, the separator may further comprise a binder to bind the inorganic particles, if necessary.

In another embodiment of the present disclosure, the separator may be an electrolyte membrane of a film shape comprising a solid electrolyte, and may further comprise a binder

to bind the solid electrolyte, if necessary. The solid electrolyte is not limited to a particular type and may include those commonly used in lithium-sulfur batteries, for example, at least one of a polymer-based solid electrolyte or an inorganic solid electrolyte.

In an embodiment of the present disclosure, the electrolyte solution comprises those commonly used in lithium-sulfur batteries. The electrolyte solution may comprise a lithium salt and a nonaqueous solvent.

The lithium salt is not limited to a particular type and may include those commonly used in electrolyte solutions of lithium-sulfur batteries. The lithium salt may comprise, for example, at least one of LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, LiC_4BO_8, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2NLi$, $(C_2F_5SO_2)_2NLi$, $(SO_2F)_2NLi$, $(CF_3SO_2)_3CLi$, chloro borane lithium, lower aliphatic carboxylic acid lithium, lithium tetraphenyl borate or lithium imide, but is not limited thereto.

The nonaqueous solvent is not limited to a particular type and may include those commonly used in electrolyte solutions of lithium-sulfur batteries. The nonaqueous solvent may comprise, for example, at least one of a cyclic carbonate solvent, a linear carbonate solvent, an ester solvent or a ketone solvent, but is not limited thereto.

In an embodiment of the present disclosure, the electrolyte solution may comprise $(CF_3SO_2)_2NLi$ as the lithium salt and a 2-component system of dioxolane (DOL)/dimethoxyethane (DME) as the nonaqueous solvent. For example, the electrolyte solution may further comprise the common additives such as $LiNO_3$.

In an embodiment of the present disclosure, the shape of the lithium-sulfur battery is not limited to a particular shape and may include, for example, coin-type, cylindrical, pouch-type or prismatic. Additionally, the lithium-sulfur battery may be used as a battery

cell used as a power source of a small device and a unit cell of a medium- and large-scale battery module comprising a plurality of battery cells, and the use is not limited to a particular range of application.

Hereinafter, a method for manufacturing the positive electrode active material according to an embodiment of the present disclosure will be described in detail through examples. However, the following embodiment is provided by way of illustration, and the scope of the present disclosure is not limited thereto.

[Manufacture of positive electrode active material]

A positive electrode active material was manufactured by the following method, the positive electrode active material comprising a) particles A comprising a first porous carbon material, at least part of which is crystalline, and catalyst particles deposited on the first porous carbon material; and b) particles B comprising a second porous carbon material, at least part of which is crystalline, and sulfur loaded in the second porous carbon material, wherein the particles A and the particles B have different morphologies have been prepared.

FIG. 3 shows an SEM image of bundled CNT used as a raw material.

FIG. 4 shows an SEM image of entangled CNT used as a raw material.

FIG. 5 shows an SEM image of reduced graphene oxide (rGO) used as a raw material.

Example 1

142 mg of iron chloride hexahydrate ($FeCl_2 \cdot 6H_2O$) and 100 mg of dopamine

hydrochloride (98 wt%) were added to 500 mL of distilled water at a mole ratio of 1:1 and stirred at 230 rpm for 30 min at room temperature (23℃). 300 mg of bundled CNT (FIG. 3) was added and stirred at room temperature for 30 min to prepare a dispersion. Subsequently, 960 ppm of Trizma base (tris(hydroxymethyl)aminomethane (TRIS)) was added to the prepared dispersion to maintain a pH of 8.5. The obtained dispersion was stirred at room temperature for 24 hours, followed by filtration, washing with distilled water three times and then ethanol once, and drying at 60℃. Subsequently, the reaction product was put into a tube electric furnace under an argon atmosphere and thermally treated at 800℃ for 2 hours (temperature increase rate 1℃/min) to obtain particles A having the average particle size (D_{50}) of 35 ㎛.

The obtained particles A comprise bundled CNT as a porous carbon substrate; transition metal composite particles disposed in at least one of the outer surface of the bundled CNT or the surface inside the pores and comprising a core comprising iron particles and a crystalline carbon coating layer coated on at least part of the surface of the core; and doped nitrogen. In this instance, a ratio of the thickness of the carbon coating layer to the average particle size D_{50} of the transition metal composite particles was 15%.

Subsequently, entangled CNT (FIG. 4) and sulfur (S_8) were mixed at a weight ratio of 25:75 and thermally treated at 155℃ for 1 hour by a melt-diffusion method to prepare a sulfur-carbon composite (particles B).

The particles A and the particles B were mixed at a weight ratio of 7.5:92.5, dispersed in water and dried to obtain a positive electrode active material having a structure in which the particles A and the particles B having different morphologies were in contact with each other.

Example 2

1.6g of reduced graphene oxide (rGO, FIG. 5); 24g of dicyanodiamide and 0.8g of ammonium metavanadate; and 0.2g of glucose were mixed in a 500 mL of solvent in which ethanol and water were mixed at a 1:1 volume ratio, and dissolved and dispersed through sonication and magnetic stirring. Subsequently, the solvent except the vanadium nitride precursor adsorbed on the carbon nanotubes surface was removed through vacuum filtration. Subsequently, drying was performed in a 80℃ oven for 12 hours. Subsequently, thermal treatment was performed in a tube furnace of an inert atmosphere at 600℃ for 3 hours and at 800℃ for 2 hours to obtain a carbon composite (particles A) in which vanadium nitride particles as catalyst particles are deposited on the surface of the reduced graphene oxide. FIG. 2 shows an SEM image of the obtained particles A. In this instance, the vanadium nitride particles were present in an amount of 20 parts by weight based on 100 parts by weight of the obtained particles A. The amount of the vanadium nitride particles was measured using a thermogravimetric analyzer (TGA).

Subsequently, entangled CNT (FIG. 4) and sulfur (S_8) were mixed at a weight ratio of 25:75 to prepare a sulfur-carbon composite (particles B).

The particles A and the particles B were mixed at a weight ratio of 7.5:92.5, dispersed in water and dried to obtain a positive electrode active material having a structure in which the particles A and the particles B having different morphologies were in contact with each other.

FIG. 1 shows an SEM image of the obtained positive electrode active material, and in FIG. 1, each area in which the particles A and the particles B are disposed is represented

through an image analysis method based on Energy Dispersive X-Ray Spectrometer (EDS) analysis.

Example 3

Particles A were obtained using the same amount of bundled CNT (FIG. 3) instead of reduced graphene oxide when manufacturing the particles A. FIG. 6 shows an SEM image of the obtained particles A.

Subsequently, a positive electrode active material were obtained by the same method as example 2.

Comparative example 1

A positive electrode active material was manufactured by the same method as example 1 except that particles A were replaced with the same amount of bundled CNT (FIG. 3).

Specifically, entangled CNT (FIG. 4) and sulfur (S_8) were mixed at a weight ratio of 25:75 to prepare a sulfur-carbon composite (particles B).

Subsequently, the bundled CNT and the particles B were mixed at a weight ratio of 7.5:92.5, dispersed in water and dried to obtain a positive electrode active material having a structure in which the bundled CNT and the particles B were in contact with each other.

Comparative example 2

Particles A were prepared by the same method as example 1.

The prepared particles A, entangled CNT and sulfur (S_8) were mixed at a weight

ratio of 5:20:75 and thermally treated at 155℃ for 1 hour by a melt-diffusion method to obtain a positive electrode active material in which sulfur was loaded in the particles A and the entangled CNT.

[Battery performance evaluation]

To evaluate the performance of lithium-sulfur batteries using the positive electrode active materials manufactured in example 1 and comparative examples 1 and 2, a lithium-sulfur coin-type battery was prepared as follows.

Manufacture of battery

First, to manufacture a working electrode, each positive electrode active material manufactured as described above and polyvinylidene fluoride (PVDF) as a binder were mixed at a weight ratio of 9:1 using an N-methyl-2-pyrrolidone (NMP) solvent to prepare a positive electrode slurry. The prepared positive electrode slurry was coated on a carbon-coated Al foil and dried at 60℃ for 8 hours. Subsequently, the electrode was rolled and cut into a coin shape to manufacture a positive electrode.

Subsequently, the positive electrode and a negative electrode were placed in a case together with an electrolyte solution with a separator interposed between the positive electrode and the negative electrode to manufacture a battery. For the positive electrode, the positive electrode manufactured as described above was prepared, and for the separator, a porous polypropylene membrane (Celgard 2400, Welcos Ltd) was prepared. For each of a reference electrode and a counter electrode, a lithium metal (200 ㎛ thick) was prepared. The electrolyte solution had a mixed solvent (PANAX E-TEC Co., Korea) of 1,3-dioxolane and dimethoxymethane (DOL/DME) at a 1:1 volume ratio, 1.0 M bis(trifluoromethane)

sulfonamide lithium salt (LiTFSI) as an electrolyte and 2.0 wt% of $LiNO_3$ (99.99% metal basis, Sigma-Aldrich) as an additive.

The loading amount of sulfur in each positive electrode was 2.25 mg/cm^2, and the El/S ratio of the battery was 10 μL/mg.

Discharge capacity and life evaluation

Each of the batteries manufactured as described above was charged and discharged at the current density of 0.1 C and the voltage of 1.8 V to 2.5 V for 3 cycles, the current density of 0.2C for 3 cycles, and then the current density of 0.5C for 20 cycles. The evaluation was all conducted in a constant temperature chamber of 25°C using PESCO5-0.1 equipment from PNE Solution.

In this instance, graphs (FIGS. 7 and 8) show the result of measuring capacity-voltage after 3 charge/discharge cycles at the current density of 0.1C, and graphs (FIGS. 9 and 10) show the result of measuring discharge capacity after 20 charge/discharge cycles.

First, referring to the graphs of FIGS. 7 and 9, it was confirmed that the battery using the positive electrode active material according to example 1 had better discharge capacity and life characteristics than the battery using the positive electrode active material according to comparative example 1 in which Fe catalyst particles were not loaded.

In contrast, referring to the graphs of FIGS. 8 and 10, it was confirmed that the battery using the positive electrode active material according to comparative example 2 in which sulfur was loaded in the Fe catalyst particle-loaded particles A had lower performance in 0.1C charge/discharge, 0.2C charge/discharge and 0.5C charge/discharge than the battery using the positive electrode active material according to comparative example 1 in which

catalyst particles are not loaded.

Through this, it is found that it is possible to improve the performance of the lithium-sulfur batteries by the positive electrode active material containing the particles A and the particles B having different morphologies according to the present disclosure.

5

WHAT IS CLAIMED IS:

1. A positive electrode active material, comprising:

a) particles A comprising a first porous carbon material, at least part of the first porous carbon material is crystalline, and catalyst particles deposited on the first porous carbon material; and

b) particles B comprising a second porous carbon material, at least part of the second porous carbon material is crystalline, and sulfur loaded in the second porous carbon material,

wherein the particles A and the particles B have different morphologies.

2. The positive electrode active material according to claim 1, wherein a sphericity of the particles B is larger than a sphericity of the particles A;

wherein the sphericity is defined according to the following equation 1:

[Equation 1]

$$\Psi = \frac{\pi^{\frac{1}{3}}(6V_p)^{\frac{2}{3}}}{A_p}$$

where Ψ denotes the sphericity,

V_p denotes a volume of the particle, and

A_p denotes a surface area of the particle.

3. The positive electrode active material according to claim 1, wherein 50% or more of the particles A are present on a surface of the particles B.

4. The positive electrode active material according to claim 1, wherein a surface

of at least some of the particles B is covered by the particles A, and

wherein a coverage area of the particles B by the particles A is 20% to 50% of an entire outer area of the particles B.

5. The positive electrode active material according to claim 1, wherein a porosity of the particles A is larger than a porosity of the particles B.

6. The positive electrode active material according to claim 1, wherein a specific surface area of the particles A is larger than a specific surface area of the particles B.

7. The positive electrode active material according to claim 1, wherein the particles A and the particles B are in contact with each other in at least one location at which the catalyst particles included in the particles A are present.

8. The positive electrode active material according to claim 1, wherein a weight of the sulfur is from 60 weight% to 90 weight% based on a total weight of the first porous carbon material and the second porous carbon material.

9. The positive electrode active material according to claim 1, wherein the first porous carbon material and the second porous carbon material are different materials.

10. The positive electrode active material according to claim 1, wherein the first

porous carbon material and the second porous carbon material are the same material.

11. The positive electrode active material according to claim 1, wherein each of the first porous carbon material and the second porous carbon material independently comprises at least one of bundled carbon nanotubes (CNT), entangled CNT or reduced graphene oxide (rGO).

12. The positive electrode active material according to claim 1, wherein the catalyst particles comprise vanadium nitride.

13. The positive electrode active material according to claim 1, wherein the catalyst particles comprise at least one of cobalt (Co) or iron (Fe).

14. The positive electrode active material according to claim 1, wherein an elasticity of each of the first porous carbon material and the second porous carbon material is larger than an elasticity of an amorphous carbon material.

15. The positive electrode active material according to claim 1, wherein an electrical conductivity of each of the first porous carbon material and the second porous carbon material is larger than an electrical conductivity of an amorphous carbon material.

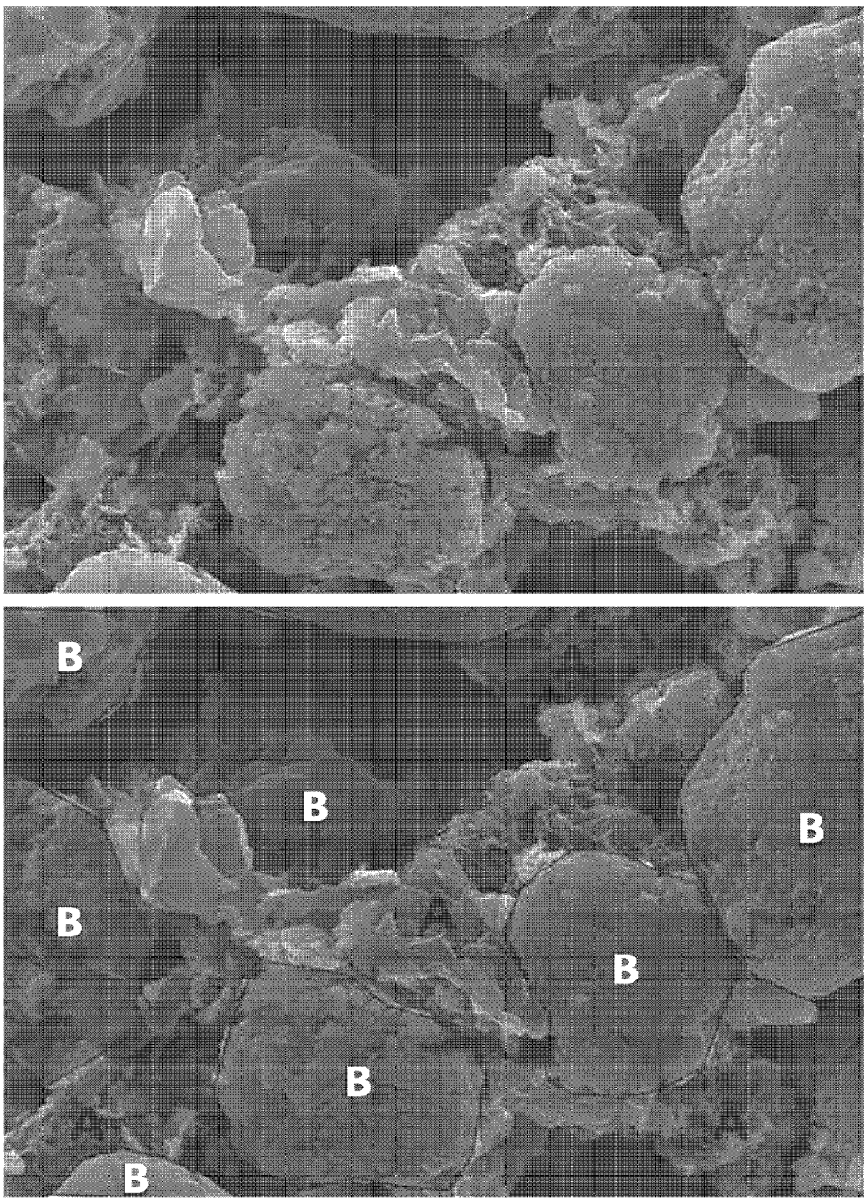
16. The positive electrode active material according to claim 1, wherein an I_D/I_G value of the positive electrode active material is equal to or less than 2.0.

17. A lithium-sulfur battery, comprising:

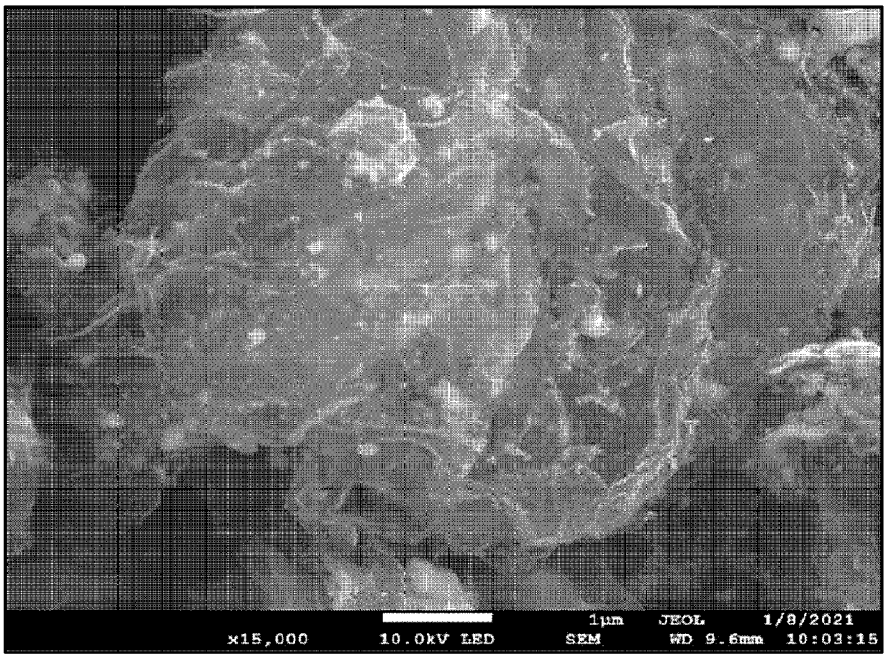
a positive electrode, a negative electrode, a separator between the positive electrode and the negative electrode; and a nonaqueous electrolyte solution,

wherein the positive electrode comprises the positive electrode active material according to any one of claims 1 to 16.

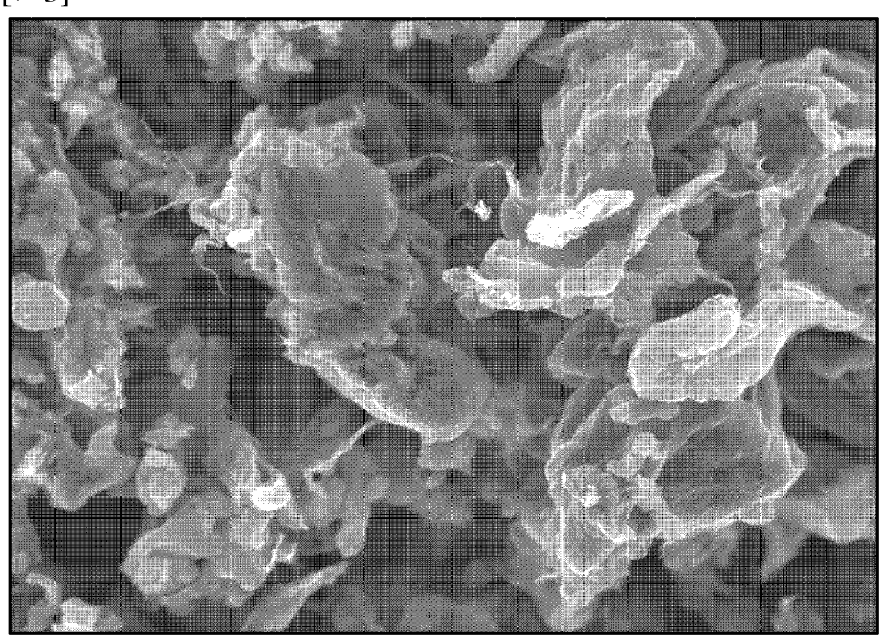
[도1]



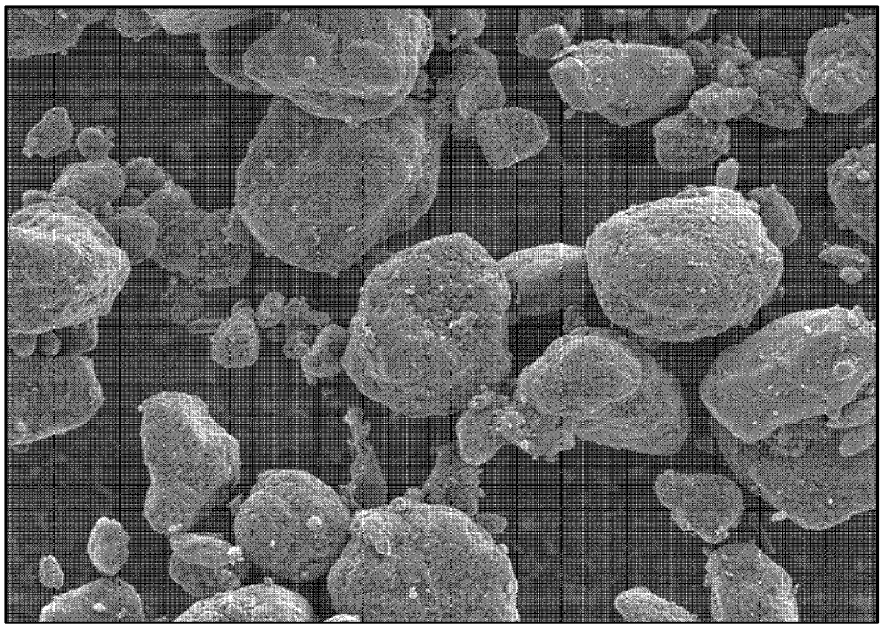
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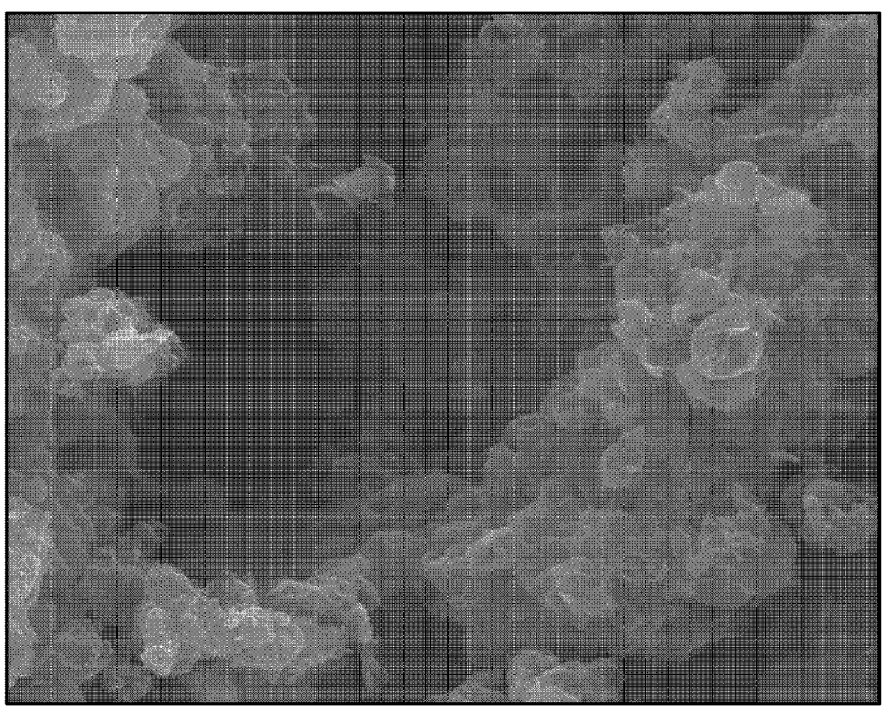
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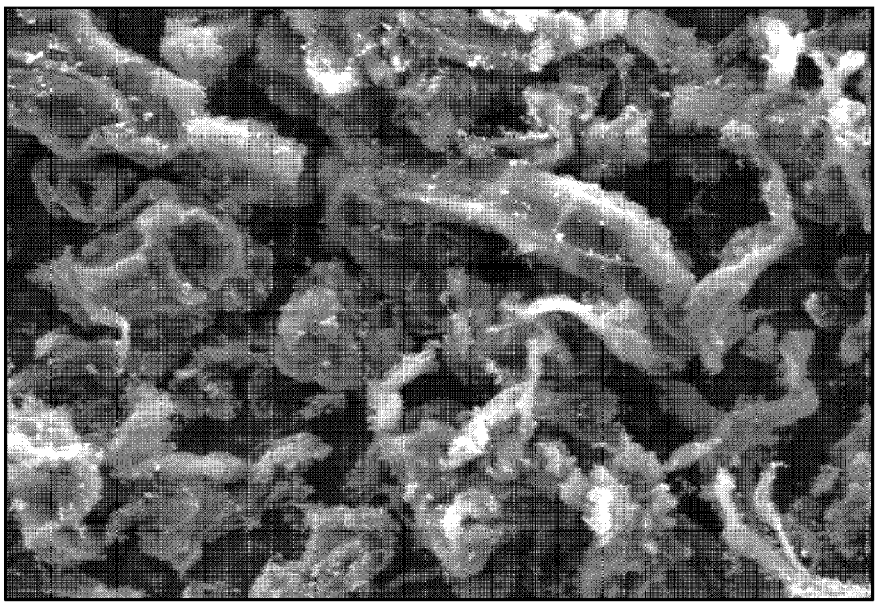
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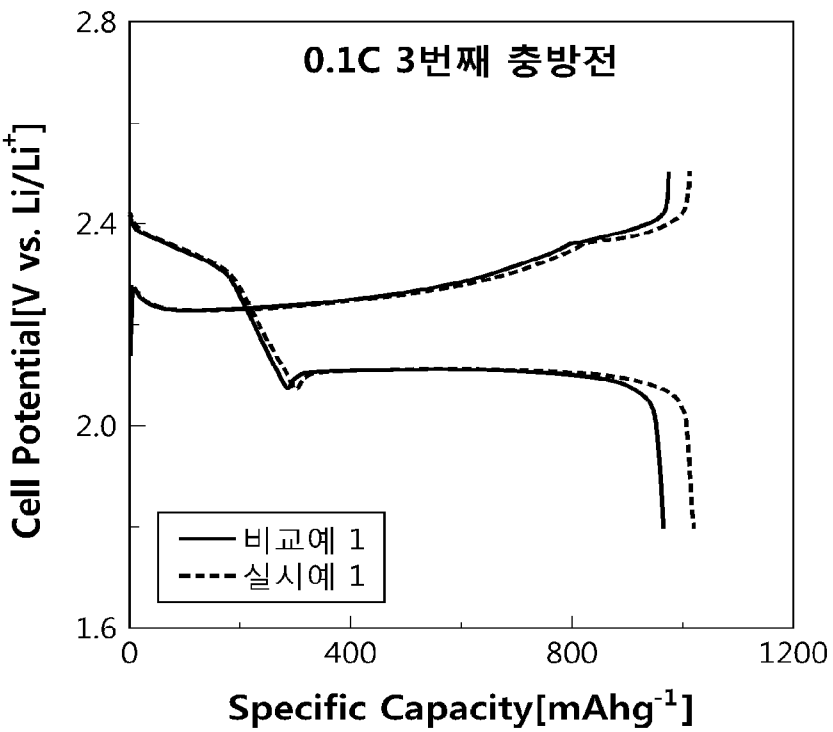
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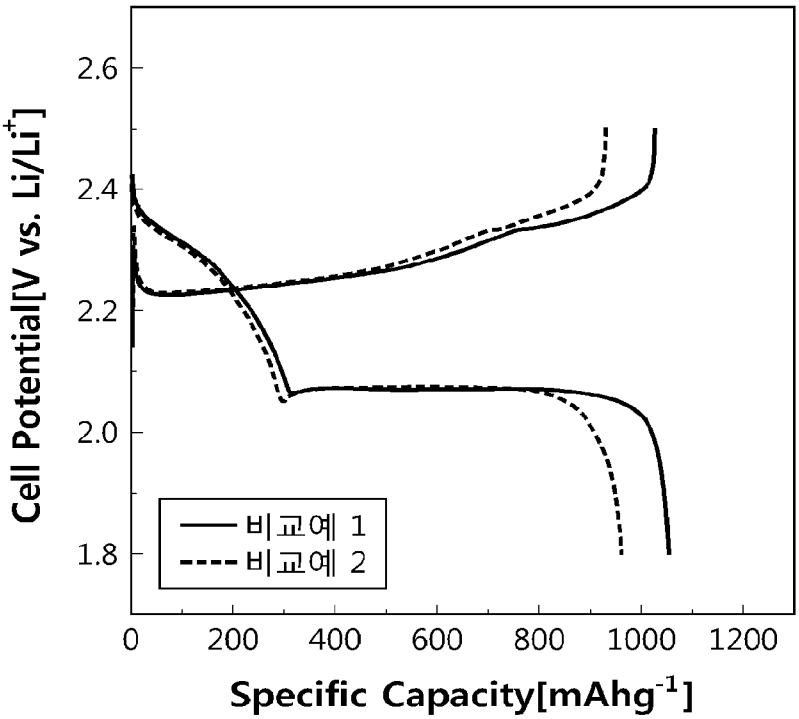
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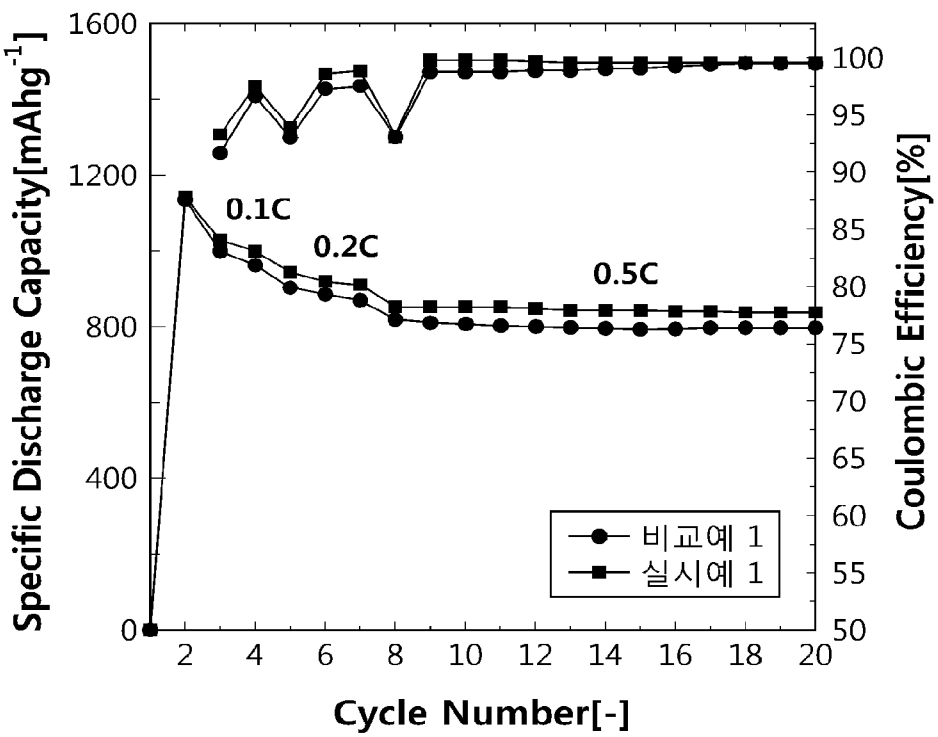
[도7]


0.1C 3번째 충방전
Cell Potential[V vs. Li/Li+]
2.8
2.4
2.0
1.6
0
400
800
1200
Specific Capacity[mAhg-1]
비교예 1
실시예 1

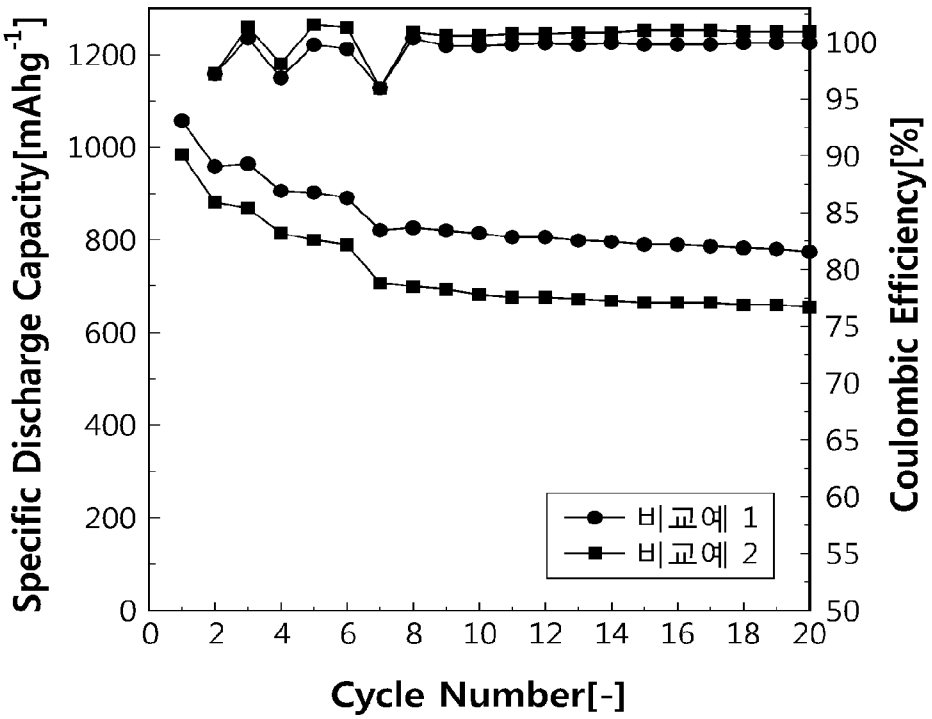
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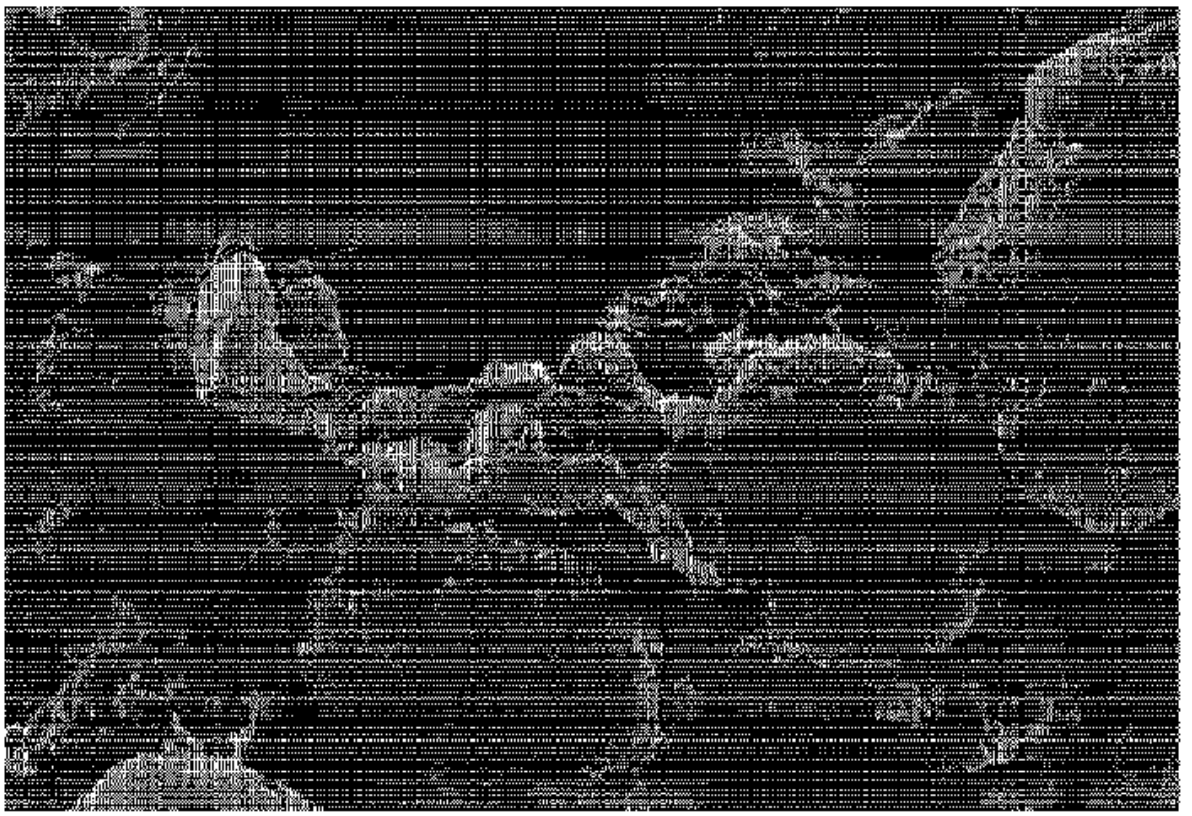

Cell Potential[V vs. Li/Li+]
2.6
2.4
2.2
2.0
1.8
0
200
400
600
800
1000
1200
Specific Capacity[mAhg-1]
비교예 1
비교예 2

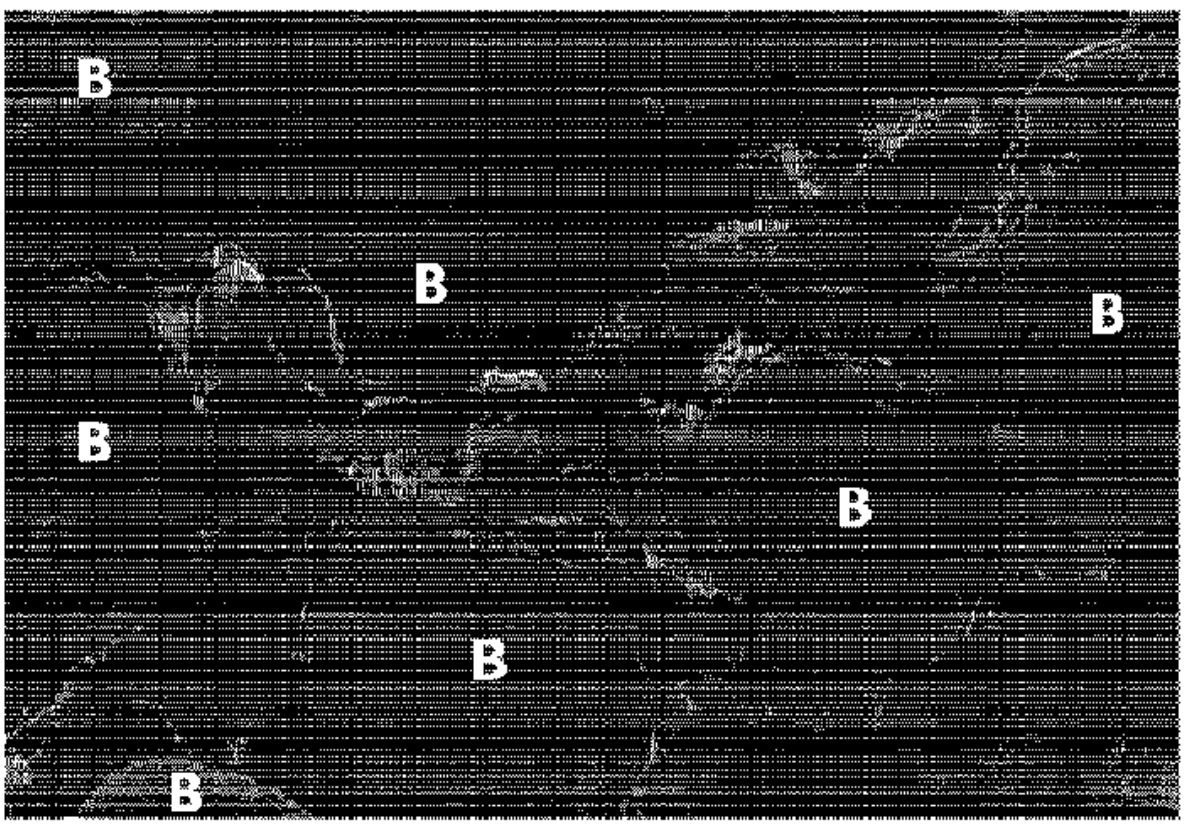
[도9]


Specific Discharge Capacity[mAhg-1]
1600
1200
800
400
0
Coulombic Efficiency[%]
100
95
90
85
80
75
70
65
60
55
50
2
4
6
8
10
12
14
16
18
20
Cycle Number[-]
0.1C
0.2C
0.5C
비교예 1
실시예 1

[도10]


Specific Discharge Capacity[mAhg-1]
Coulombic Efficiency[%]
Cycle Number[-]
비교예 1
비교예 2
0
200
400
600
800
1000
1200
50
55
60
65
70
75
80
85
90
95
100
0
2
4
6
8
10
12
14
16
18
20




B
B
B
B
B
B
B