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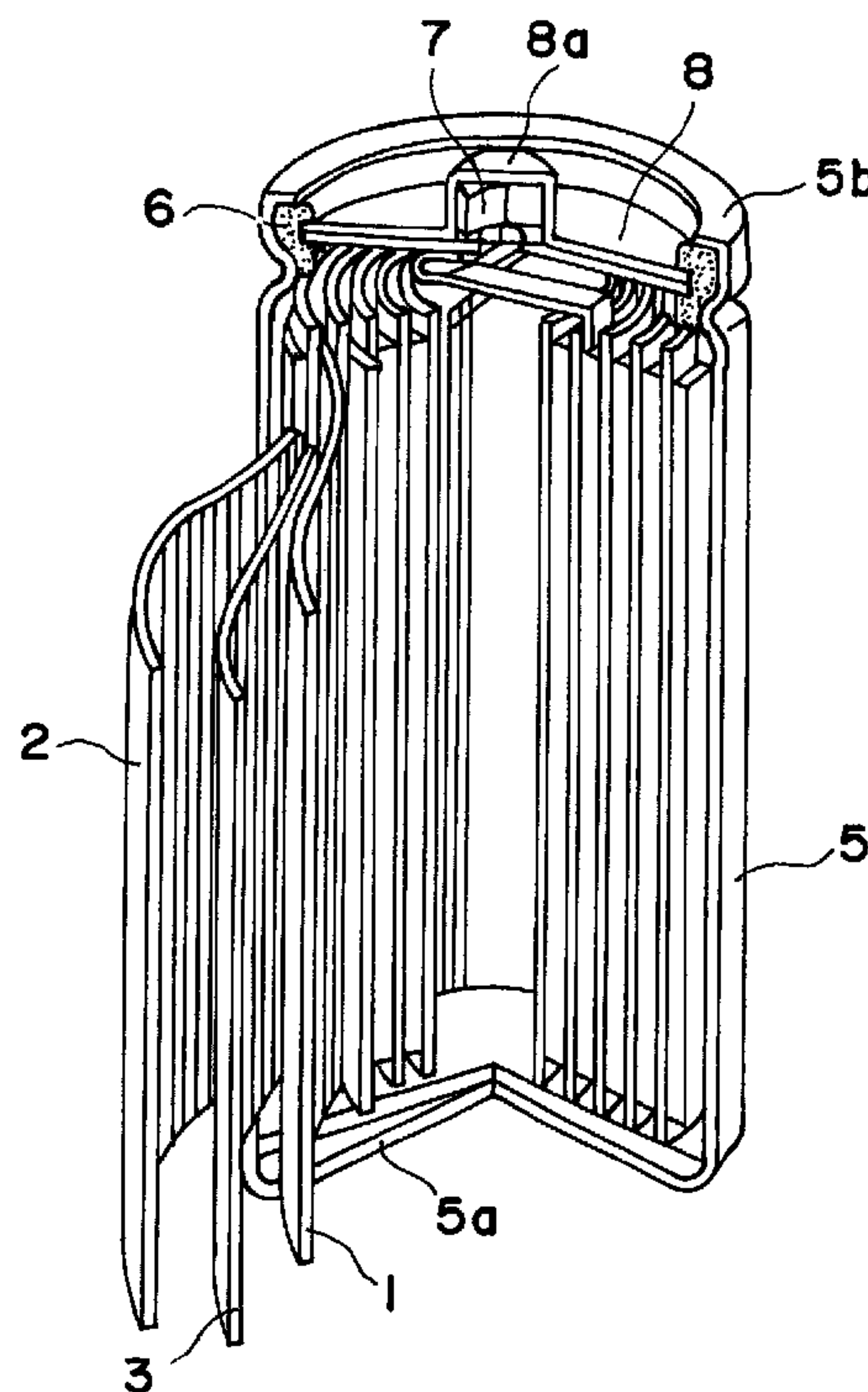
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(54) Titre : MATERIAU CARBONE POUR LA FABRICATION D'ELECTRODES POUR ACCUMULATEURS ET PROCEDE DE PRODUCTION

(54) Title: CARBONACEOUS ELECTRODE MATERIAL FOR SECONDARY BATTERY AND PROCESS FOR PRODUCTION THEREOF



(57) Abrégé/Abstract:

A carbonaceous electrode having improved capacities for doping and dedoping of a cell active substance, such as lithium, and suitable for a non-aqueous solvent-type secondary battery, is constituted by a carbonaceous material obtained by carbonizing an organic material of plant origin, and having a pore volume of at least 0.55 ml/g of pores having a pore diameter of at most 5 μm as measured by mercury injection method and a specific surface area of at most 100 m^2/g as measured by the nitrogen adsorption BET method. The carbonaceous material may preferably be produced by carbonizing an organic material of plant origin in contact with a flowing inert gas at a temperature of 700 - 1500 $^{\circ}\text{C}$ under a pressure exceeding 10 kPa.

ABSTRACT OF THE DISCLOSURE

A carbonaceous electrode having improved capacities for doping and dedoping of a cell active substance, such as lithium, and suitable for a non-
5 aqueous solvent-type secondary battery, is constituted by a carbonaceous material obtained by carbonizing an organic material of plant origin, and having a pore volume of at least 0.55 ml/g of pores having a pore diameter of at most 5 μm as measured by mercury
10 injection method and a specific surface area of at most 100 m^2/g as measured by the nitrogen adsorption BET method. The carbonaceous material may preferably be produced by carbonizing an organic material of plant origin in contact with a flowing inert gas at a
15 temperature of 700 - 1500 $^{\circ}\text{C}$ under a pressure exceeding 10 kPa.

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CARBONACEOUS ELECTRODE MATERIAL FOR SECONDARY BATTERY
AND PROCESS FOR PRODUCTION THEREOF

FIELD OF THE INVENTION AND RELATED ART

5 The present invention relates to a
carbonaceous material obtained by carbonizing an
organic material of plant origin and suitable as an
electrode material for a non-aqueous solvent-type
secondary battery, and a process for production
10 thereof. The present invention also relates to an
electrode structure comprising such a carbonaceous
electrode material, and a non-aqueous solvent-type
secondary battery having such an electrode structure.

Non-aqueous solvent-type lithium secondary
15 batteries having a negative electrode comprising
a carbonaceous material have been proposed (Japanese
Laid-Open Patent Application (JP-A) 62-90863, JP-A 62-
122066, etc.). Such a secondary battery utilizes a
phenomenon that a carbon intercalation compound of
20 lithium as a (cell) active substance is easily formed
electrochemically. When the battery is charged,
lithium in a positive electrode comprising a
chalcogenide, such as LiCoO_2 , is introduced between
layers of negative electrode carbon (i.e., dopes the
25 carbon) electrochemically. The carbon thus doped with
lithium functions as a lithium electrode, from which
the lithium is released (i.e., de-doped) during

discharge to return to the positive electrode. Thus, a secondary battery capable of repetitive charge-discharge is formed.

As carbonaceous materials capable of
5 providing non-aqueous solvent-type lithium secondary batteries of high energy density, there have been known so-called "hard carbon" obtained by calcining phenolic resin or furan resin at a relatively low temperature (e.g., ca. 800 - 1500 °C), so-called "soft
10 carbon" obtained by carbonizing pitch or tar; and activated carbon having a large specific surface area on the order of 900 - 2000 m²/g.

However, the above-mentioned known carbonaceous materials are accompanied with a problem
15 that a large amount of active substance, such as lithium, remains in the carbon (i.e., the carbon shows a large non-dedoping capacity) during the dedoping step, so that the active substance is wasted uselessly, and also a problem that the dedoping
20 capacity per se determining the battery performance (discharge capacity) is relatively small.

SUMMARY OF THE INVENTION

In the course of our study for obtaining
25 high-performance carbonaceous electrode materials more suitably used for non-aqueous solvent-type secondary batteries, we have examined organic materials of plant

origin characterized by the presence of vessel, sieve
tube, plant fiber, etc., as new carbon sources. As a
result, it has been unexpectedly found that the
carbonization of such an organic material of plant
5 origin under appropriate conditions provides an
excellent carbonaceous electrode material having well-
balanced performances including a small non-dedoping
capacity and a large dedoping capacity in combination,
and the resultant carbonaceous material has a large
10 pore volume suitable for doping with a cell active
substance not found in conventional carbonaceous
electrode materials.

Thus, a principal object of the present
invention is to provide such a carbonaceous electrode
15 material having well-balanced high performances as
described above, a process for producing such a
carbonaceous material, and also a non-aqueous solvent-
type secondary battery having an electrode comprising
such a carbonaceous material.

20 Another object of the present invention is to
provide a carbonaceous material having advantageous
features in production thereof, such as easy
pulverization by means of a jet mill, etc., and easy
handling of feedstock for calcination.

25 According to the present invention, there is
provided a carbonaceous electrode material for a non-
aqueous solvent-type secondary battery, obtained by

carbonizing an organic material of plant origin, and having a pore volume of at least 0.55 ml/g of pores having a pore diameter of at most 5 μm as measured by mercury injection and a specific surface area of at
5 most 100 m^2/g as measured by the nitrogen adsorption BET method.

The carbonaceous material may preferably be a non-graphitic material as represented by an average (002)-plane spacing of at least 0.365 nm as measured
10 by X-ray diffraction method.

According to another aspect of the present invention, there is provided a process for producing a carbonaceous electrode material for a non-aqueous solvent-type secondary battery, comprising:
15 carbonizing an organic material of plant origin in contact with a flowing inert gas at a temperature of 700 - 1500 $^{\circ}\text{C}$ under a pressure exceeding 10 kPa (ca. 0.1 atm), or carbonizing an organic material of plant origin except for coconut shell at a temperature of
20 700 - 1500 $^{\circ}\text{C}$ under a reduced pressure of at most 10 kPa (ca. 0.1 atm).

According to another aspect of the present invention, there is provided an electrode structure for a non-aqueous solvent-type secondary battery,
25 comprising: an electroconductive substrate and a composite electrode layer disposed on at least one surface of the electroconductive substrate; the

composite electrode layer comprising a carbonaceous electrode material as described above in a particulate form, and a binder.

According to a further aspect of the present invention, there is provided a non-aqueous solvent-type secondary battery, comprising, a positive electrode, a negative electrode, and a separator and a non-aqueous electrolytic solution disposed between the positive and negative electrodes; at least one of the positive and negative electrodes comprising an electrode structure as described above.

The carbonaceous material according to the present invention is practically so-called non-graphitizable carbon capable of storing a large amount of active substance and accordingly has an essentially large capacity for doping with an active substance. In addition, the carbonaceous material according to the present invention has many pores of a relatively large diameter represented by a pore volume of at least 0.55 ml/g of pores having a pore diameter of at most 5 μm as measured by mercury injection method and is characterized by relatively large penetrating or open pores originated from structures, such as vessel, sieve tube and plant fiber, attributable to the starting material.

Accordingly, the electrolytic solution is allowed to easily penetrate into the interior of the

carbon through pores, and the active substance is allowed to easily move between the inside and outside of the carbon. As a result, it is possible to provide a carbonaceous electrode material having a small non-
5 dedoping capacity and capable of effectively utilizing an active substance.

Incidentally, we have already proposed a carbonaceous electrode material for a non-aqueous solvent-type secondary battery obtained by carbonizing
10 coconut shell at a temperature of 900 - 1500 °C under a reduced pressure of at most 10 kPa (EP-A 0,700,105). The present invention provides a further development of the proposal based on a knowledge that even an organic material of plant origin other than coconut
15 shell can provide an excellent carbonaceous electrode material for a non-aqueous solvent-type secondary battery if treated under appropriate carbonization conditions, and the excellent performance thereof is attributable to its pore structure originated from
20 natural plant materials.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the
25 present invention taken in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a partially exploded perspective view of a non-aqueous solvent-type secondary battery which can be constituted according to the invention.

Figure 2 is a partial sectional view of an electrode structure adopted in the secondary battery.

DETAILED DESCRIPTION OF THE INVENTION

10 The carbonaceous material according to the present invention is characterized by a specific surface area of at most $100 \text{ m}^2/\text{g}$ as measured by the BET method using nitrogen as adsorbate gas, and a pore volume of at least 0.55 ml/g of pores having a
15 diameter of at most $5 \mu\text{m}$ as measured by mercury injection method. A carbonaceous material having a specific surface area in excess of $100 \text{ m}^2/\text{g}$ as represented by activated carbon or a carbonaceous material having a pore volume below 0.55 ml/g provides
20 a large non-dedoping capacity, i.e., a large amount of active substance left within the carbonaceous material without dedoping. The specific surface area may preferably be $0.5 - 10 \text{ m}^2/\text{g}$, more preferably $0.5 - 5 \text{ m}^2/\text{g}$.

25 The large pore volume is a characteristic of the carbonaceous material. A smaller pore volume makes it difficult for the electrolytic solution to

penetrate into the inside of the carbon and hinders
free movement of the active substance within the
carbonaceous material, thereby resulting in a
remarkable increase in non-dedoping capacity defined
5 as a difference (A-B) between a doping capacity (A)
and a dedoping capacity (B) and a lowering in rate of
effective utilization of active substance. On the
other hand, an extremely large pore volume results in
a lowering in packing density of the carbonaceous
10 material for preparing a secondary battery.
Accordingly, the pore volume may preferably be 0.55 -
1.00 ml/g, further preferably 0.55 - 0.70 ml/g.

The carbonaceous material according to the
present invention having a developed pore structure
15 has a characteristic that it is readily pulverized and
causes little wearing of a pulverizer, such as a jet
mill. Further, as for micropores relating to the
production process described hereinafter, the
characteristic micropore and fibrous structures of an
20 organic material of plant origin are believed to allow
easy dissipation or removal of a decomposition by-
product formed during the carbonization, and
contribute to an increased pore volume in the finally
obtained carbonaceous material.

25 In the present invention, the carbonaceous
material should be construed as a term covering a
graphitic material having a developed graphite

structure as obtained through heat treatment at a temperature of 2000 °C or higher. However, a high-temperature heat treatment causes a shrinkage of carbon structure and is liable to deprive the pore structures, such as vessel, sieve tube and plant fiber, originated from the starting material.

Accordingly, the carbonaceous material according to the present invention is practically advantageously realized as a non-graphitic carbonaceous material having an average (002)-plane spacing as measured by X-ray diffraction method (hereinafter sometimes denoted by " d_{002} ") of at least 0.365 nm. d_{002} is more preferably 0.365 - 0.390 nm, further preferably 0.370 - 0.390 nm. If d_{002} is below 0.365 nm, the carbonaceous material is liable to exhibit a small capacity for doping with active substance.

The carbonaceous material may preferably have a hydrogen-to-carbon atomic ratio H/C of at most 0.1. A carbonaceous material having an H/C exceeding 0.1 is insufficient in carbonization and is not suitable as a carbonaceous electrode material for a non-aqueous solvent-type secondary battery.

Now, the process for producing a carbonaceous material according to the present invention will be described.

The production process according to the present invention comprises: carbonizing an organic

material of plant origin in contact with a flowing inert gas at a temperature of 700 - 1500 °C under a pressure exceeding 10 kPa (first process), or carbonizing an organic material of plant origin other
5 than coconut shell at a temperature of 700 - 1500 °C under a reduced pressure of at most 10 kPa (ca. 0.1 atm) (second process).

Preferred examples of the organic material of plant origin used in the present invention as carbon
10 sources of the carbonaceous material may generally include: coconut shell, coffee bean, chaffs, broad-leaf tree wood, conifer wood, and bamboo.

The carbonization may preferably be performed while taking care so that tar or decomposition
15 products, such as hydrogen and methane, will not hinder the pore formation in the organic material. In case where the organic material is carbonized in an environment rich or dense in decomposition product, the formation of minute pores is liable to be
20 insufficient, thus resulting in a carbonaceous material having a lower capacity for doping with active substance.

As the organic material of plant origin is inherently porous because of the presence of vessel,
25 sieve tube, etc., the dissipation or removal of decomposition products during the carbonization is facilitated to result in a large volume of pores

having a relatively large diameter.

According to the first production process of the present invention, the organic material is carbonized while flowing an inert gas in contact with the organic material under a pressure of atmospheric pressure (1 atm = ca. 100 kPa) or higher, or a sub-atmospheric pressure exceeding 10 kPa (ca. 0.1 atm). In this instance, the material to be carbonized (organic material as it is or after pre-calcination as desired) may be disposed in a piled layer within a reactor and is carbonized while flowing the inert gas in a space outside but in contact with the layer (outside-layer flow scheme), or the material to be carbonized (organic material) is disposed in a layer or bed and is carbonized while flowing the inert gas through within the layer or bed (intra-layer flow scheme).

In a batch-wise outside-layer flow scheme, it is preferred to suppress the piled layer thickness of the material to be carbonized as thin as possible so as to increase the area of contact of the material layer with the inert gas and allow quick removal of the decomposition product from the material out of the system. The piled layer thickness of the material to be carbonized may preferably be at most 50 mm, more preferably at most 30 mm. The inert gas may be supplied or flowed at a vacant reactor-basis speed of

at least 1 mm/sec, more preferably at least 5 mm/sec.

It is preferred to adopt an intra-layer flow scheme of a continuous-type or a batch-type using a fluidized bed, a fixed bed, etc. In this case, the
5 inert gas may preferably be supplied or flowed at a rate of at least 10 ml/min., more preferably at least 50 ml/min., further preferably at least 100 ml/min., per gram of the material to be carbonized, while it can depend on the amount of the material to be
10 carbonized per unit time. A higher inert gas supply rate may be preferred in view of the properties of the product carbonaceous material, but practically the supply rate may be at most 500 ml/min. per gram of the material to be carbonized.

15 In the first production process, the inert gas may preferably be nitrogen or argon, and the above-mentioned inert gas supply rate is calculated based on the volume of the inert gas under the standard state (0 °C and 1 atm). The inert gas can
20 contain up to 40 mol. % of halogen gas, such as chlorine.

In the second production process, the carbonization is performed at a reduced pressure of at most 10 kPa, preferably at most 1 kPa, further
25 preferably at most 0.1 kPa. If the pressure at the time of carbonization exceeds 10 kPa in the absence of a flowing inert gas, the withdrawal of decomposition

products from the material to be carbonized becomes insufficient. The whole course of carbonization can be performed under a reduced pressure of at most 10 kPa, but the object of the present invention may be
5 sufficiently achieved if the carbonization in a temperature range of 700 °C or higher is performed under the reduced pressure.

The carbonization may be performed at a temperature of 700 - 1500 °C in either of the first
10 and second processes. Carbonization at a temperature below 700 °C results in an increased non-dedoping active substance capacity of the product carbonaceous material. Carbonization at a temperature higher than 1500 °C results in a decrease in capacity for doping
15 with active substance. The carbonization temperature is 700 - 1500 °C, preferably 1000 - 1400 °C, further preferably 1100 - 1400 °C.

In either of the first and second production processes, the organic material of plant origin may
20 preferably be subjected to pre-calcination at 300 - 1000 °C in an inert gas atmosphere or under a reduced pressure so as to remove tar and other volatile matters in advance. Further, it is preferred to pulverize the pre-calcined organic material into fine
25 particles of at most 100 µm in average diameter so as to promote the dissipation of decomposition products generated from the material to be carbonized during

the carbonization.

The pre-calcined organic material before carbonization shows a lower hardness than the carbonaceous material after the final carbonization, thus being easily pulverized. Accordingly, in case of requiring a powder carbonaceous electrode material, pulverization after the pre-calcination is accompanied with less abrasion of the pulverizer, and is advantageous from the viewpoint of production process.

Next, the non-aqueous solvent-type secondary battery of the present invention will be described.

Figure 1 is a partially exploded perspective view of a lithium secondary battery as an embodiment of a non-aqueous solvent-type secondary battery according to the present invention.

More specifically, the secondary battery basically includes a laminate structure including a positive electrode 1, a negative electrode 2 and a separator 3 disposed between the positive and negative electrodes 1 and 2 and comprising a fine porous film of a polymeric material, such as polyethylene or polypropylene, impregnated with an electrolytic solution. The laminate structure is wound in a vortex shape to form an electricity-generating element which is housed within a metal casing 5 having a bottom constituting a negative electrode terminal 5a. In the secondary battery, the negative electrode 2 is

electrically connected to the negative electrode terminal 5a, and the uppermost portion of the battery is constituted by disposing a gasket 6 and a safety valve 7 covered with a top plate 8 having a projection 5 constituting a positive electrode terminal 8a electrically connected to the positive electrode. Further, the uppermost rim 5b of the casing 5 is crimped toward the inner side to form an entirely sealed cell structure enclosing the electricity-
10 generating element.

Herein, the positive electrode 1 or negative electrode 2 may be constituted by an electrode structure 10 having a sectional structure as partially shown in Figure 2. More specifically, the electrode
15 structure 10 includes an electroconductive substrate 11 comprising a foil or wire net of a metal, such as iron, stainless steel, copper, aluminum, nickel or titanium and having a thickness of, e.g., 5 - 100 μm , or 5 - 20 μm for a small-sized battery, and a composite
20 electrode layer (12a, 12b) of, e.g., 10 - 1000 μm , preferably 10 - 200 μm , in thickness for a small-sized battery, on at least one surface, preferably on both surfaces as shown in Figure 2, of the electroconductive substrate 11.

25 The composite electrode layers 12a and 12b are respectively a layer comprising a particulate carbonaceous material according to the present

invention, an electroconductive material such as electroconductive carbon, optionally included, and a binder such as a vinylidene fluoride resin.

More specifically, in case of using the
5 carbonaceous material according to the present invention for producing an electrode 10 (1 or 2) of a non-aqueous solvent-type secondary battery as described above, the carbonaceous material may be optionally formed into fine particles having an
10 average particle size of 5 - 100 μm and then mixed with a binder stable against a non-aqueous solvent, such as polyvinylidene fluoride, polytetrafluoroethylene or polyethylene, to be applied onto an electroconductive substrate 11, such as a circular or
15 rectangular metal plate, to form, e.g., a 10 - 200 μm -thick layer. The binder may preferably be added in a proportion of 1 - 20 wt. % of the carbonaceous material. If the amount of the binder is excessive, the resultant electrode is liable to have too large an
20 electric resistance and provide the battery with a large internal resistance. On the other hand, if the amount of the binder is too small, the adhesion of the carbonaceous material particles with each other and with the electroconductive substrate 11 is liable to
25 be insufficient. The above described formulation and values have been set forth with respect to production of a secondary battery of a relatively small size,

whereas, for production of a secondary battery of a larger size, it is also possible to form the above-mentioned mixture of the carbonaceous material fine particles and the binder into a thicker shaped
5 product, e.g., by press-forming, and electrically connect the shaped product to the electroconductive substrate.

The carbonaceous material of the present invention can also be used as a positive electrode
10 material for a non-aqueous solvent-type secondary battery by utilizing its good doping characteristic but may preferably be used as a negative electrode material of a non-aqueous solvent-type secondary battery, particularly for constituting a negative
15 electrode to be doped with lithium as an active substance of a lithium secondary battery.

In the latter case, the positive electrode material may comprise a complex metal chalcogenide, particularly a complex metal oxide, such as LiCoO_2 ,
20 LiNiO_2 or LiMn_2O_4 . Such a positive electrode material may be formed alone or in combination with an appropriate binder into a layer on an electroconductive substrate.

The non-aqueous solvent-type electrolytic
25 solution used in combination with the positive electrode and the negative electrode described above may generally be formed by dissolving an electrolyte

in a non-aqueous solvent. The non-aqueous solvent may comprise one or two or more species of organic solvents, such as propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, 5 dimethoxyethane, diethoxyethane, γ -butyrolactone, tetrahydrofuran, 2-methyl-tetrahydrofuran, sulfolane, and 1,3-dioxolane. Examples of the electrolyte may include LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , LiAsF_6 , LiCl , LiBr , $\text{LiB}(\text{C}_6\text{H}_5)_4$, and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$.

10 As described above, a secondary battery of the present invention may generally be formed by disposing the above-formed positive electrode 1 and negative electrode 2 opposite to each other, optionally with a liquid-permeable separator 3 15 composed of, e.g., unwoven cloth or other porous materials, disposed therebetween, and dipping the positive and negative electrodes together with an intermediate permeable separator in an electrolytic solution as described above.

20 In the above, a cylindrical battery has been described as an embodiment of the non-aqueous solvent-type secondary battery according to the present invention. However, the non-aqueous solvent-type secondary battery according to the present invention can basi- 25 cally have any other shapes, such as those of a coin, a rectangular parallelepiped, or a paper or sheet.

Incidentally, the measurement of various

parameters of carbonaceous materials described herein,
i.e., the pore volume by mercury injection method, the
specific surface area by nitrogen adsorption, d_{002} and
the hydrogen/carbon atomic ratio (H/C), was performed
5 in the following manner.

[Pore volume by mercury injection method]

In case where mercury is injected
(pressurized) into a cylindrical pore having a
diameter D under a pressure P , the following equation
10 is given based on a balance between a surface tension
and a pressure acting on a sectional area of the pore:

$$-\pi D \gamma \cdot \cos \theta = \pi (D/2)^2 P,$$

wherein γ represents a surface tension of the mercury,
and θ denotes a contact angle between the mercury and
15 the pore well. Accordingly,

$$D = (-4\gamma \cdot \cos \theta) / P.$$

Herein, the surface tension (γ) of mercury
was assumed to be 484 dyn/cm, the contact angle (θ)
between mercury and carbon was assumed to be 130 deg;
20 and the pressure P and the diameter D were expressed
in the units of MPa and μm , respectively, whereby the
above equation was reduced to

$$D = 1.27 / P.$$

Based on the formula, a relationship between
25 the pore diameter (D) and the mercury pressure P was
derived.

More specifically, the pore volume was

measured by "AUTOPORE 9200" (available from Micromeritics Instrument Corp.) in the following manner.

A sample carbonaceous material in the form of 5 particles having an average diameter of 10 - 30 μm was placed in a sample vessel, which was then evacuated for 30 min. at room temperature and a pressure of at most 2.67 Pa. Then, mercury was introduced into the sample vessel and gradually injected into pores under 10 a gradually increasing pressure (up to a maximum pressure of 414 MPa). From the measurement, a relationship between pressure P and injected volume of mercury was derived and converted into a relationship between pore diameter D and the injected volume. From 15 the relationship, a pore volume distribution was derived versus pore diameter as a variant. Thus, the volume of mercury injected from a pressure (0.25 MPa) corresponding to a pore diameter of 5 μm to the maximum pressure (414 MPa; corresponding to a pore 20 diameter of 3 nm) was measured as a pore volume of pores having a diameter of at most 5 μm .

[Specific surface area by nitrogen adsorption]

An approximate equation

$$v_m = 1/(v \cdot (1-x))$$

25 derived from the BET equation was used to obtain v_m (amount ($\text{cm}^3/\text{g-sample}$)) of adsorbed nitrogen required to form a mono-molecular layer of nitrogen on the

sample surface) from a measured nitrogen volume v at a relative pressure x ($= 0.3$) according to the BET single-point method using nitrogen adsorption. From the thus-obtained v_m -value, a specific surface area S_{BET} was calculated based on the following equation:

$$S_{BET} = 4.35 \times v_m \text{ (m}^2\text{/g)}.$$

More specifically, the nitrogen adsorption onto a carbonaceous material was performed at liquid nitrogen temperature by using "Flow Sorb II 2300" (available from Micromeritics Instrument Corp.) in the following manner.

A sample carbonaceous material pulverized into an average diameter of 5 - 50 μm was packed in a sample tube, and the sample tube was cooled to -196°C while flowing helium gas containing nitrogen at a concentration of 30 mol. %, thereby to cause the carbonaceous material to adsorb nitrogen. Then, the sample tube was restored to room temperature to measure the amount of nitrogen desorbed from the sample by a thermal conductivity-type detector, thereby to obtain the adsorbed nitrogen amount v ($\text{cm}^3\text{/g-sample}$).

[d_{002} of carbonaceous material]

A powdery sample of a carbonaceous material was packed in an aluminum-made sample cell and irradiated with monochromatic $\text{CuK}\alpha$ rays (wavelength $\lambda = 0.15418 \text{ nm}$) through a graphite monochromator to

obtain an X-ray diffraction pattern. The peak position of the diffraction pattern is determined by the center of gravity method (i.e., a method wherein the position of a gravity center of diffraction lines is obtained to determine a peak position as a 2θ value corresponding to the gravity center) and calibrated by the diffraction peak of (111) plane of high-purity silicon powder as the standard substance. The d_{002} value is calculated from the Bragg's formula shown below.

$$d_{002} = \lambda / (2 \cdot \sin\theta) \quad (\text{Bragg's formula})$$

[Hydrogen/carbon (H/C) atomic ratio]

A sample of carbonaceous material was subjected to elementary analysis by using a CNH analyzer, and a hydrogen/carbon(H/C) atomic ratio was calculated as a ratio of numbers of atoms of hydrogen/carbon based on the weight proportions of hydrogen and carbon in the sample.

[Examples]

Hereinbelow, the present invention will be described more specifically based on Examples and Comparative Examples. All the volumes or flow rates of inert gases described hereinafter are values calculated under the standard state (0°C , 1 atm).

25 Example 1

Coconut shell char (available from M.C. Carbon K.K.) was heated to 600°C and held at 600°C

for 1 hour in a nitrogen gas atmosphere (normal pressure) to be pre-calcined, whereby a carbon precursor having a volatile content of at most 2 %. The carbon precursor was pulverized into a powdery carbon precursor having an average particle size (diameter) of 25 μm . Then, 20 g of the carbon precursor was piled in a ca. 2 mm-thick layer in an alumina-made boat and then placed in a horizontal tubular furnace of 100 mm in diameter to be heated to 1200 $^{\circ}\text{C}$ at a temperature-raising rate of 250 $^{\circ}\text{C/hr}$ and held for 1 hour at 1200 $^{\circ}\text{C}$ for carbonization while flowing nitrogen gas at a rate of 10 liter/min.

The properties of the resultant carbonaceous material are shown in Table 1 appearing hereinafter together with those of other Examples and Comparative Examples.

Example 2

A carbonaceous material was prepared in the same manner as in Example 1 except that the carbonization temperature was changed to 1300 $^{\circ}\text{C}$.

Example 3

A carbonaceous material was prepared in the same manner as in Example 1 except that the nitrogen flow rate during the carbonization was decreased to 1 liter/min.

Example 4

Milled and extracted coffee bean (produce of

Brazil) in particle size of 2 - 3 mm was dried at 120 °C for 1 hour and then pre-calcined by heating up to 600 °C and holding at 600 °C for 1 hour in a nitrogen atmosphere (normal pressure), followed by

5 pulverization into a powdery carbon precursor having an average particle size of 25 µm. The carbon precursor was carbonized in the same manner as in Example 1.

Example 5

10 Mohsoh bamboo trunk (produce of Fukushima-ken, Japan; age: 3, diameter: ca. 70 mm) was dried at 120 °C for 3 hours and pre-calcined by heating up to 600 °C and holding at 600 °C for 1 hour in a nitrogen atmosphere (normal pressure), followed by
15 pulverization into a powdery carbon precursor having an average particle size of 25 µm. Then, 20 g of the carbon precursor was placed on an alumina-made boat and charged in a vacuum furnace, which was then sucked by a vacuum pump to an internal pressure of 0.01 -
20 0.03 Pa. While keeping the internal pressure, the vacuum furnace was heated up to 1200 °C and held at 1200 °C to effect carbonization, thereby obtaining a carbonaceous material.

Example 6

25 A carbonaceous material was prepared by carbonization of cherry wood (produce of Fukushima-ken, Japan, age: 10, diameter: ca. 50 mm), otherwise

in the same manner as in Example 5.

Example 7

A carbonaceous material was prepared by carbonization of oak wood (produce of Fukushima-ken, Japan, age: 10, diameter: ca. 50 mm), otherwise in the same manner as in Example 5.

Example 8

Milled and extracted coffee bean (produce of Brazil) in particle size of 2 - 3 mm was dried at 120 °C for 1 hour and then pre-calcined by heating up to 600 °C and holding at 600 °C for 1 hour in a nitrogen atmosphere (normal pressure), followed by pulverization into a powdery carbon precursor having an average particle size of 25 µm.

Then, 30 g of the powdery carbon precursor was placed on a porous filter plate disposed at a middle of a reaction tube of a vertical tubular furnace (diameter = 50 mm) and heated at a rate of 250 °C/hour while supplying nitrogen gas downward at a rate of 2400 ml/min from an upper part of the reaction tube. When the furnace temperature reached 1100 °C, the temperature was retained for 1 hour to effect carbonization while keeping the nitrogen supply rate. After cooling, a carbonaceous material was recovered.

Example 9

A carbonaceous material was prepared in the same manner as in Example 8 except that the nitrogen

gas was supplied upward from a lower part of the reaction tube and the nitrogen gas supply rate was decreased to 100 ml/min.

Comparative Example 1

5 A phenolic resin ("Bellpearl C-800", available from Kanebo K.K.) was pre-cured at 170 °C for 3 min., and then cured at 130 °C for 8 hours, followed by pulverization into an average particle size of 25 µm. Then, 20 g of the pulverizate was
10 placed in a horizontal tubular furnace identical to the one used in Example 1 and carbonized by heating up to 1200 °C at a rate of 250 °C/hr, holding at 1200 °C for 1 hour and cooling, while flowing nitrogen gas at a rate of 10 liter/min., whereby a phenolic resin-
15 calcined carbon was prepared.

Comparative Example 2

 A furan resin ("Hitafuran VF-303", available from Hitachi Kasei K.K.) was cured at 100 °C for 14 hours, followed by pulverization into an average
20 particle size of 25 µm. Then, 20 g of the pulverizate was placed in a horizontal tubular furnace identical to the one used in Example 1 and carbonized by heating up to 1200 °C at a rate of 250 °C/hr, holding at 1200 °C for 1 hour and cooling, while flowing nitrogen gas
25 at a rate of 10 liter/min., whereby a furan resin-calcined carbon was prepared.

Comparative Example 3

A petroleum pitch having a softening point of 210 °C, a quinoline-insoluble content of 1 wt. % and an H/C atomic ratio of 0.63 was pre-calcined by heating up to 600 °C and holding at 600 °C for 1 hour in a nitrogen gas atmosphere (normal pressure), followed by pulverization into a powdery carbon precursor having an average particle size of 20 µm. The carbon precursor was carbonized at 1200 °C for 1 hour under a reduced pressure of 0.01 - 0.03 Pa to prepare a carbonaceous material.

Comparative Example 4

Coconut shell-based activated carbon (available from Kuraray Chemical K.K.) was pulverized to an average particle size of 25 µm and treated at 1200 °C for 1 hour in a nitrogen atmosphere, to prepare a carbonaceous material.

The properties of the carbonaceous materials prepared in the above Examples and Comparative Examples are inclusively shown in Table 1 appearing hereinafter.

[Doping/de-doping capacity for active substance]

The carbonaceous materials obtained in Examples and Comparative Examples were respectively used to prepare a non-aqueous solvent-type secondary battery (cell) and the performances thereof were evaluated in the following manner.

The carbonaceous material is generally suited

for constituting a negative electrode of a non-aqueous solvent secondary battery. However, in order to accurately evaluate the performances of a carbonaceous material inclusive of a doping capacity (A) and a de-
5 doping capacity (B) and also a non-dedoping capacity (A-B) for a cell active substance without being affected by a fluctuation in performance of a counter electrode material, a large excess amount of lithium metal showing a stable performance was used as a
10 negative electrode, and each carbonaceous material prepared above was used to constitute a positive electrode, thereby forming a lithium secondary battery, of which the performances were evaluated.

More specifically, the positive electrode was
15 prepared as follows. That is, 90 wt. parts of the carbonaceous material thus formulated in the form of fine particles and 10 wt. parts of polyvinylidene fluoride were mixed together with N-methyl-2-pyrrolidone to form a paste composite, which was then
20 applied uniformly onto a copper foil. The composite, after being dried, was peeled off the copper foil and stamped into a 21 mm-dia. disk. The disk was then press-bonded onto a 21 mm-dia. circular shaped net of stainless steel to form a positive electrode
25 containing about 40 mg of the carbonaceous material. On the other hand, a negative electrode was prepared by stamping a 1 mm-thick sheet of lithium metal into a

21 mm-dia. disk.

The thus-prepared positive and negative electrodes were disposed opposite to each other with a porous polypropylene film as a separator disposed
5 therebetween, and the resultant structure was dipped in an electrolytic solution comprising a 1:1 (by volume)-mixture solvent of propylene carbonate and dimethoxyethane and LiClO_4 dissolved therein at a rate of 1 mol/liter, thereby forming a non-aqueous solvent-
10 type lithium secondary battery.

In the lithium secondary battery thus constituted, the carbonaceous material in the positive electrode was subjected to doping and dedoping of lithium to evaluate capacities therefor.

15 More specifically, the doping was effected by repeating a cycle including 1 hour of current conduction at a current density of 0.5 mA/cm^2 and 2 hours of pause until the equilibrium potential between the positive and negative electrodes reached 5 mV.
20 The electricity thus flowed was divided by the weight of the carbonaceous material to provide a doping capacity (A) in terms of Ah/kg. Then, in a similar manner, a current was flowed in a reverse direction to dedope the lithium from the doped carbonaceous
25 material. The de-doping was effected by repeating a cycle including 1 hour of current conduction at a current density of 0.5 mA/cm^2 and 2 hours of pause,

down to a cut-off voltage of 1.5 volts. The electricity thus flowed was divided by the weight of the carbonaceous material to provide a dedoping capacity (B) in terms of Ah/kg. Then, a non-dedoping capacity (A-B) was calculated as a difference between the doping capacity (A) and the dedoping capacity (B), and a discharge efficiency (%) was obtained by dividing the dedoping capacity (B) with the doping capacity (A) and multiplying the quotient (B/A) with 100. The discharge efficiency is a measure of effective utilization of the active substance.

The performances of the lithium secondary batteries using positive electrodes of the respective carbonaceous materials measured in the above-described manner are summarized in the following Table 2.

In view of Table 2, it is understood that the secondary batteries prepared by using the carbonaceous materials according to Examples of the present invention showed larger values in both doping capacity (A) and de-doping capacity (B) and also remarkably small non-dedoping capacities (A-B) determined as differences therebetween, so that the carbonaceous materials of the present invention allow effective utilization of cell active substance.

Secondary batteries obtained by using carbonaceous materials of Comparative Examples 1, 2 and 4 showed large doping capacities but also showed

very large non-dedoping capacities, thus having a disadvantage that lithium as the active substance was not effectively utilized.

A secondary battery obtained by using the
5 carbonaceous material of Comparative Example 3 showed doping capacity and dedoping capacities which were both very small.

As described above, according to the present invention, there is provided a carbonaceous electrode
10 material having well-balanced performances including a small non-dedoping capacity and a large dedoping capacity in combination. Such a carbonaceous material can be easily produced by carbonizing an organic material of plant origin as a starting material under
15 appropriate conditions. By using an electrode, particularly a negative electrode, prepared by using the carbonaceous material according to the present invention, it becomes possible to provide a non-aqueous solvent-type secondary battery having large
20 charge-discharge capacities and a large active substance-utilization efficiency.

Table 1

	Starting material	Carbonization temp. (°C)	d_{002} (nm)	H/C	Pore volume (ml/g)	Specific surface area (m ² /g)
Ex. 1	coconut shell	1200	0.382	0.03	0.63	2.6
2	coconut shell	1300	0.368	0.02	0.59	3.9
3	coconut shell	1200	0.377	0.03	0.62	4.5
4	coffee bean	1200	0.370	0.03	0.60	2.9
5	bamboo	1200	0.374	0.03	0.82	3.5
6	cherry wood	1200	0.383	0.02	0.98	4.5
7	oak wood	1200	0.379	0.02	0.93	1.2
8	coffee bean	1100	0.380	0.04	0.67	3.2
9	coffee bean	1100	0.381	0.04	0.65	3.0
Comp. Ex. 1	phenolic resin	1200	0.377	0.02	0.42	1.0
2	furan resin	1200	0.379	0.02	0.45	1.2
3	petroleum pitch	1200	0.355	0.01	0.38	1.7
4	coconut shell active carbon	1200	0.349	0.03	1.05	1270

Table 2: Secondary battery performances

	Doping capacity (A) (Ah/kg)	Dedoping capacity (B) (Ah/kg)	Non-dedoping capacity (A-B) (Ah/kg)	Discharge efficiency (A-B) /Ax100 (%)
Ex. 1	543	438	105	80.5
2	427	345	82	80.8
3	457	352	105	77.0
4	507	413	94	81.5
5	631	488	143	77.4
6	512	435	77	84.5
7	455	381	74	83.7
8	575	430	145	74.8
9	500	370	130	74.0
Comp. Ex. 1	534	291	243	54.5
2	681	428	253	62.8
3	336	278	58	82.7
4	616	350	266	56.8

WHAT IS CLAIMED IS:

1. A carbonaceous electrode material for a non-aqueous solvent-type secondary battery, obtained by carbonizing an organic material of plant origin, and
5 having a pore volume of at least 0.55 ml/g of pores having a pore diameter of at most 5 μm as measured by mercury injection method and a specific surface area of at most 100 m^2/g as measured by the nitrogen adsorption BET method.
10
2. A carbonaceous electrode material according to Claim 1, wherein the organic material is a member selected from the group consisting of coffee bean, chaffs, broadleaf tree wood, conifer wood, and bamboo.
15
3. A carbonaceous electrode material according to Claim 1 or 2, having an average (002)-plane spacing of at least 0.365 nm as measured by X-ray diffraction method.
20
4. A process for producing a carbonaceous electrode material for a non-aqueous solvent-type secondary battery, comprising: carbonizing an organic material of plant origin in contact with a flowing
25 inert gas at a temperature of 700 - 1500 $^{\circ}\text{C}$ under a pressure exceeding 10 kPa.
5. A process according to Claim 4, wherein the

organic material is piled in a layer and the inert gas is caused to flow in parallel with the layer.

6. A process according to Claim 5, wherein the
5 organic material is caused to form a bed, and the inert gas is caused to flow through the bed.

7. A process according to Claim 6, the organic material forms a fluidized bed under the action of the
10 flowing inert gas.

8. A process according to Claim 6 or 7, wherein the inert gas is caused to flow at a rate of at least 10 ml/min. per gram of the organic material to be
15 carbonized.

9. A process according to any one of Claims 4 - 7, wherein the organic material is pre-calcined and pulverized to an average diameter of at most 100 μm
20 prior to the carbonization.

10. A process for producing a carbonaceous electrode material for a non-aqueous solvent-type secondary battery, comprising: carbonizing an organic
25 material of plant origin except for coconut shell at a temperature of 700 - 1500 $^{\circ}\text{C}$ under a reduced pressure of at most 10 kPa.

11. An electrode structure for a non-aqueous solvent-type secondary battery, comprising: an electroconductive substrate and a composite electrode layer disposed on at least one surface of the electroconductive substrate;

said composite electrode layer comprising a carbonaceous electrode material according to any one of Claims 1 - 3 in a particulate form, and a binder.

12. A non-aqueous solvent-type secondary battery, comprising, a positive electrode, a negative electrode, and a separator and a non-aqueous electrolytic solution disposed between the positive and negative electrodes;

at least one of said positive and negative electrodes comprising an electrode structure according to Claim 11.

13. A secondary battery according to Claim 12, wherein the electrode structure constitutes the negative electrode.

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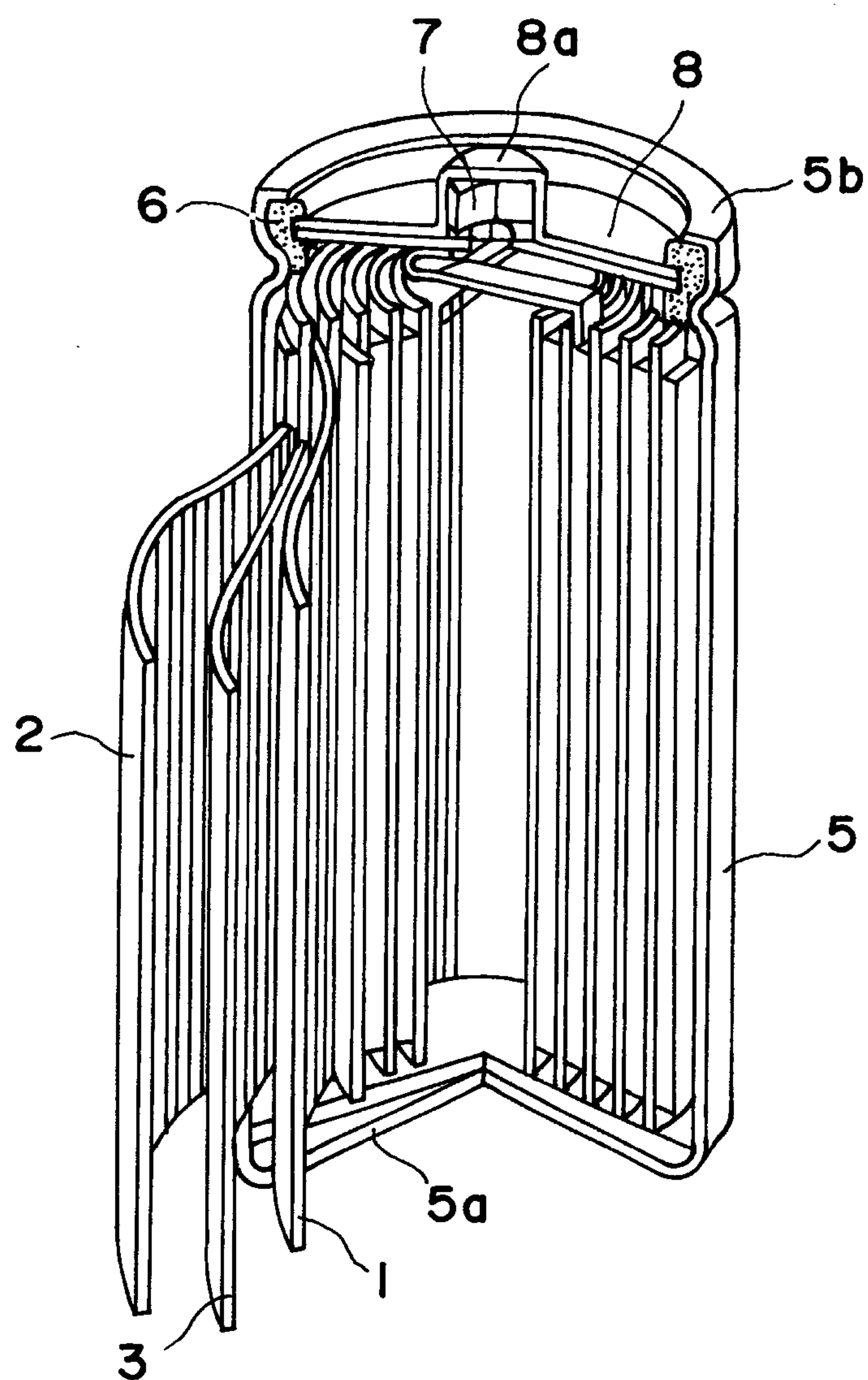


FIG. 1

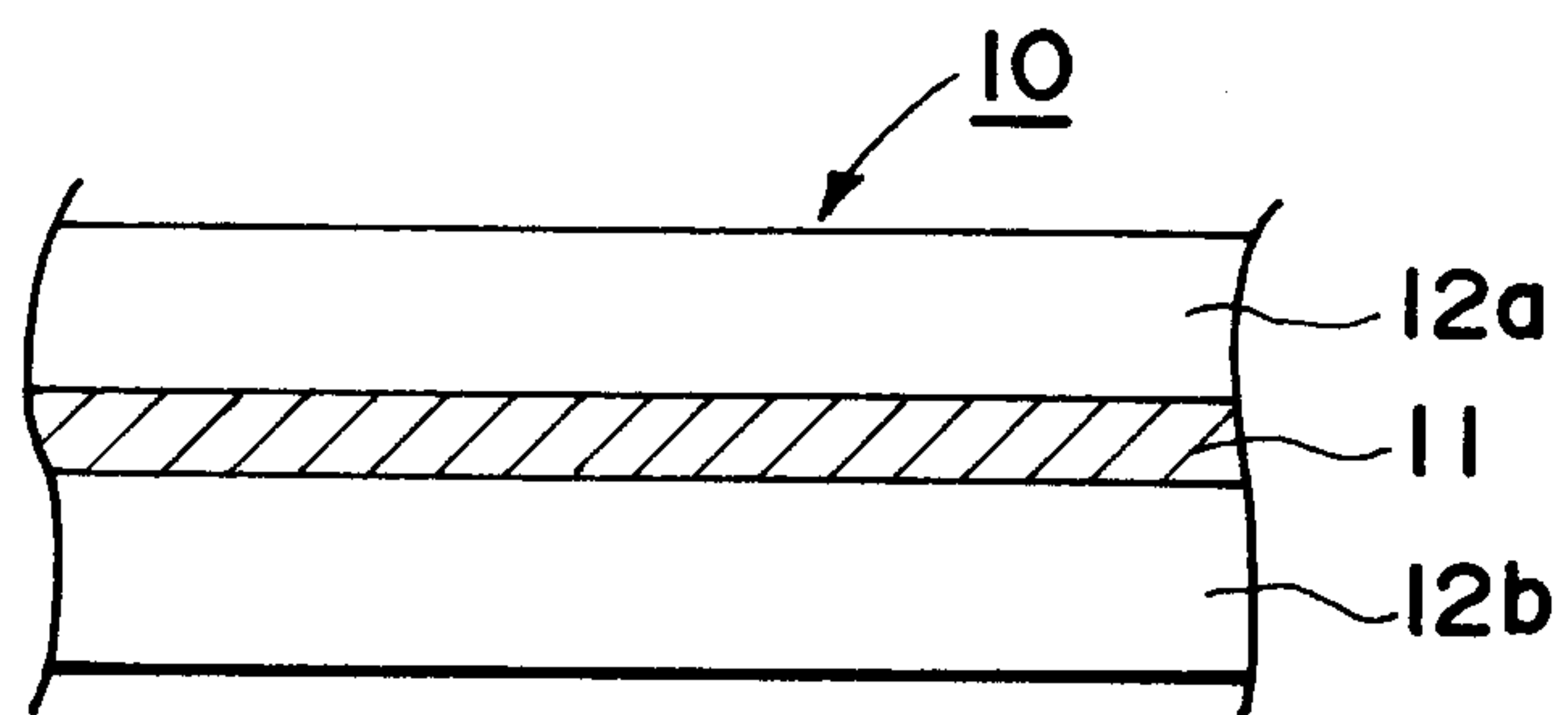


FIG. 2

