



US 20030198588A1

(19) **United States**

(12) **Patent Application Publication**
Muramaki et al.

(10) **Pub. No.: US 2003/0198588 A1**

(43) **Pub. Date: Oct. 23, 2003**

(54) **VAPOR GROWN CARBON FIBER AND METHOD FOR PRODUCING THE SAME**

(75) Inventors: **Kazuo Muramaki, Kanagawa (JP);
Atsuo Nishimura, Kanagawa (JP);
Kotaro Yano, Kanagawa (JP)**

Correspondence Address:
**SUGHRUE MION, PLLC
2100 PENNSYLVANIA AVENUE, N.W.
WASHINGTON, DC 20037 (US)**

(73) Assignee: **SHOWA DENKO K.K.**

(21) Appl. No.: **10/414,024**

(22) Filed: **Apr. 16, 2003**

Related U.S. Application Data

(60) Provisional application No. 60/380,286, filed on May 15, 2002.

(30) **Foreign Application Priority Data**

Apr. 17, 2002 (JP)..... P2002-114235

Publication Classification

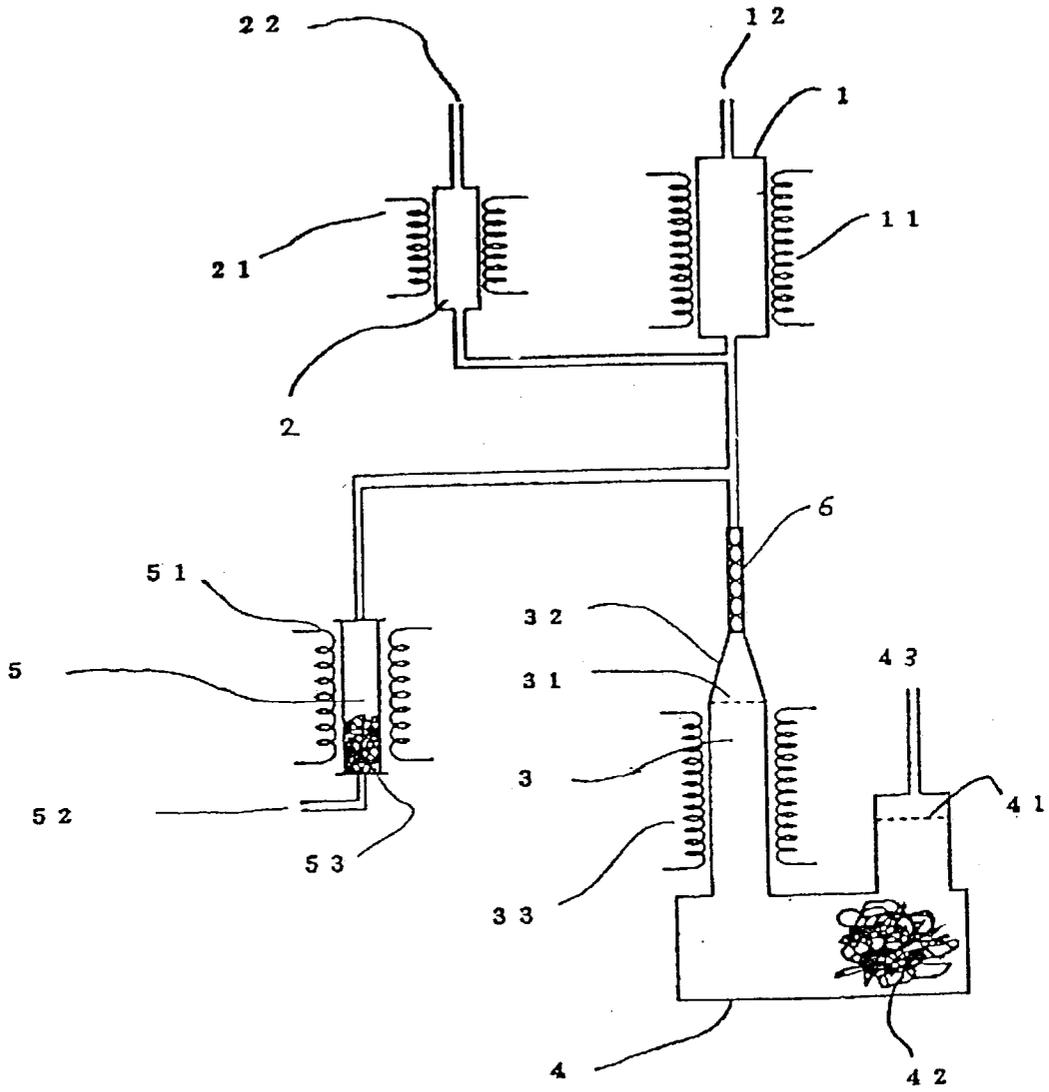
(51) **Int. Cl.⁷** **D01F 9/12**

(52) **U.S. Cl.** **423/447.3**

(57) **ABSTRACT**

A method for producing vapor grown carbon fiber including the step of thermally decomposing an organic compound and an inorganic transition metallic compound, serving as main raw materials, is disclosed. The inorganic transition metallic compound is a transition metal chloride, and the amount of transition metal chloride 0.01 to 20 mass % is based on the entire amount of the organic compound. The carbon fiber, a resin composition and a battery containing the carbon fiber are also disclosed.

Fig. 1



VAPOR GROWN CARBON FIBER AND METHOD FOR PRODUCING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of Provisional Application No. 60/380,286, filed May 15, 2002, incorporated herein by reference, under 35 U.S.C. §111(b) pursuant to 35 U.S.C. §119(e) (1).

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a method for producing vapor grown carbon fiber through thermal decomposition of an organic compound serving as a carbon source and an inorganic transition metallic compound serving as a catalyst. In addition, the present invention relates to vapor grown carbon fiber produced through the method; and to the use of the vapor grown carbon fiber, such as in a resin composition or battery.

[0004] 2. Description of the Related Art

[0005] Conventionally known production methods for fine carbon fiber include a method in which an organic compound such as benzene, serving as a raw material, and an organo-transition metallic compound such as ferrocene, serving as a metallic catalyst, are introduced into a high-temperature reaction furnace together with a carrier gas, to thereby produce fine carbon fiber on a substrate (Japanese Patent Application Laid-Open (kokai) No. 60-27700); a method in which carbon fiber is produced in a dispersed state (Japanese Patent Application Laid-Open (kokai) No. 60-54998); and a method in which carbon fiber is grown on a reaction furnace wall (Japanese Patent No. 2778434). Carbon fiber produced through any of these methods is called "vapor grown carbon fiber".

[0006] A carbon fiber production method employing, as a catalyst, an inorganic transition metallic compound which is relatively readily evaporated has also been disclosed (Japanese Patent Publication (kokoku) No. 4-13449). However, this method requires a large amount of a catalyst (although the amount varies depending on the type of catalyst to be employed) and involves productivity problems attributed to poor efficiency of catalyst utilization.

[0007] When a large amount of a catalyst is employed, the resultant carbon fiber is contaminated with a large amount of a metal. Since the metal is not completely removed from the carbon fiber even when subjected to heat treatment performed subsequent to a fiber growth process, when the carbon fiber is employed in, for example, an electronic material, the quality of the material may be deteriorated.

[0008] When the carbon fiber containing a large amount of a metal is thermally treated at high temperature, the metal (i.e., an impurity) precipitates in a heat treatment apparatus and inflicts damage on the apparatus, thereby lowering productivity.

[0009] In order to generate fine particles of a transition metallic catalyst employed for producing carbon fiber through vapor-phase thermal decomposition, in general, ferrocene, an organo-transition metallic compound, is used as a catalyst raw material. For example, in one known

method, ferrocene, which characteristically vaporizes by sublimation, is evaporated under heating, and the thus-evaporated ferrocene is fed to a reaction apparatus (production zone) together with a carrier gas, to thereby generate fine iron catalyst particles in the apparatus through thermal decomposition of ferrocene. In another method, ferrocene is dissolved in advance in a raw material (an organic compound serving as a carbon source), and the resultant solution is vaporized and fed to a reaction apparatus, to thereby generate fine iron catalyst particles in the apparatus through thermal decomposition of ferrocene. Such a method is advantageous in that the method enables uniform distribution of catalyst particles in a reaction apparatus through gasification of sublimable ferrocene, and thus is widely employed in the industry. However, ferrocene employed in such a method is expensive. Therefore, in order to mass-produce carbon fiber on an industrial scale at low cost, demand has arisen for a method employing an inexpensive catalyst raw material.

[0010] In addition to ferrocene, transition-metal-containing carbonyl compounds or transition-metal-containing carboxylic acid compounds may be employed as a catalyst raw material. However, since such a compound has a low thermal decomposition temperature and is easily decomposed in a reaction apparatus, difficulty is encountered in generating fine transition metal particles from the compound. Therefore, such a compound is not suitable for use as a catalyst for producing carbon fiber.

[0011] Meanwhile, known inorganic transition metallic compounds, including transition metal oxides, transition metal nitrates, transition metal sulfides, transition metal fluorides, and transition metal bromides, are difficult to gasify. When an inorganic transition metallic compound whose thermal decomposition temperature is equal to or lower than its evaporation temperature is heated to a high temperature, the compound is thermally decomposed before being gasified. Therefore, such a compound cannot be fed to a reaction apparatus in the form of gas, and thus is unsuitable for use as a catalyst for producing carbon fiber.

SUMMARY OF THE INVENTION

[0012] An object of the present invention is to produce carbon fiber at low cost and high productivity by using a small amount of an inexpensive catalyst.

[0013] In order to solve the aforementioned problems, the present inventors have conducted extensive studies on the type of catalyst to be employed and a feeding method of the catalyst, and have found that, when an inorganic transition metal chloride (e.g., iron chloride) is employed as a catalyst, the incorporation amount of the catalyst can be reduced, and carbon fiber can be produced at high productivity. The present invention has been accomplished on the basis of this finding.

[0014] Accordingly, the present invention provides the following embodiments.

[0015] 1) A method for producing vapor grown carbon fiber comprising thermally decomposing an organic compound and an inorganic transition metallic compound, wherein the inorganic transition metallic compound is a transition metal chloride, and the amount of the transition metal chloride is about 0.01 to about 20 mass % based on the entire amount of the organic compound.

[0016] 2) A method for producing vapor grown carbon fiber according to 1) above, further comprising dissolving the transition metal chloride in the organic compound, vaporizing the resultant solution to form a gas mixture containing the organic compound and the transition metal chloride; mixing the gas mixture with a carrier gas, and feeding the resultant gas mixture to a carbon fiber production zone.

[0017] 3) A method for producing vapor grown carbon fiber according to 1) above, further comprising forming a gas mixture of a carrier gas and a gas of the organic compound; mixing the gas mixture with a gas of the transition metal chloride, and feeding the resultant gas mixture to a carbon fiber production zone.

[0018] 4) A method for producing vapor grown carbon fiber according to 1) above, further comprising forming fine transition metal chloride particles by spraying a solution of the transition metal chloride; forming a gas mixture of a carrier gas and a gas of the organic compound; feeding the fine transition metal chloride particles, the carrier gas, and the organic compound gas to a carbon fiber production zone.

[0019] 5) A method for producing vapor grown carbon fiber according to any one of 1) through 4) above, wherein the transition metal chloride is a chloride of at least one transition metal selected from the group consisting of iron, nickel, cobalt, molybdenum, and vanadium.

[0020] 6) A method for producing vapor grown carbon fiber according to 5) above, wherein the transition metal chloride is at least one chloride selected from the group consisting of iron chloride, nickel chloride, and cobalt chloride.

[0021] 7) A method for producing vapor grown carbon fiber according to any one of 1) through 5) above, wherein the organic compound is an aromatic compound, acetylene, ethylene, butadiene, or a mixture thereof.

[0022] 8) A method for producing vapor grown carbon fiber according to 7) above, wherein the aromatic compound is benzene, toluene, xylene, or naphthalene.

[0023] 9) A method for producing vapor grown carbon fiber according to 2) above, wherein said dissolving comprises adding at least one dissolution aid selected from the group consisting of methanol, ethanol or acetone to the organic compound.

[0024] 10) A vapor grown carbon fiber produced through a production method as recited in any one of 1) through 9) above.

[0025] 11) A vapor grown carbon fiber according to 10) above, wherein the carbon fiber comprises fiber filaments each having an outer diameter of about 1 to about 500 nm and a length of about 0.5 to about 100 μm .

[0026] 12) A vapor grown carbon fiber produced through a production method as recited in 1) above wherein the transition metal chloride is iron chloride, and the carbon fiber comprises fiber filaments each having an outer diameter of about 1 to about 500 nm and a length of about 0.5 to about 100 μm , and contains iron in an amount of about 5 mass % or less.

[0027] 13) A resin composition comprising a resin and a vapor grown carbon fiber as recited in any one of 10) through 12) above contained therein.

[0028] 14) A secondary battery comprising, as an electrode material, a vapor grown carbon fiber as recited in any one of 10) through 12) above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. 1 shows an example of an apparatus employed for performing the production method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0030] The present invention will next be described in detail.

[0031] Main raw materials employed for producing the carbon fiber of the present invention are an organic compound serving as a carbon source, and a transition metal chloride.

[0032] No particular limitations are imposed on the organic compound serving as a carbon source, so long as the organic compound has a vaporization temperature lower than its decomposition temperature and contains carbon. Specific examples of such an organic compound which may be employed include aromatic compounds such as benzene, toluene, and xylene; linear-chain hydrocarbons such as acetylene, ethylene, methane, ethane, propane, butane, and butadiene; alicyclic hydrocarbons; and alcohols such as methanol and ethanol. Of these, aromatic compounds are preferred, and benzene and xylene are more preferred. These carbon sources may be employed singly or in combination of two or more species.

[0033] A transition metal chloride is effectively employed as a catalyst raw material. A chloride of a transition metal such as iron, nickel, cobalt, molybdenum, or vanadium exhibits sublimation and has a boiling point lower than that of an oxide, nitrate, sulfate, fluoride, or bromide of such a transition metal, and thus the transition metal chloride can be readily gasified. In addition, the thermal decomposition temperature or hydrogen reduction temperature of such a transition metal chloride is higher than the thermal decomposition temperature of an organo-transition metallic compound. Therefore, when such a transition metal chloride is employed, fine transition metal particles (an outer diameter of about 0.1 to about 50 nm) are generated in a reaction furnace, and the particles effectively function as a catalyst for producing carbon fiber.

[0034] For example, in the case where benzene, ferric chloride, and hydrogen gas are employed as a carbon cluster source (a carbon source), a catalyst source, and a carrier gas, respectively, when a gas mixture containing these materials is fed to a reaction apparatus, the ferric chloride is reduced by the hydrogen gas at about 350° C., to thereby release iron atoms. The thus-released iron atoms undergo repeated collision and aggregation to thereby form fine particles, and the particles gradually increase in size. When the fine particles are grown to a size of 0.1 to 50 nm, preferably 1 to 20 nm, more preferably 2 to 10 nm in diameter, the particles function as a catalyst for producing carbon fiber. Simultaneous with growth of the particles, generation of carbon clusters proceeds through thermal decomposition of the benzene. The clusters are grown around the fine iron particles serving as nuclei, to thereby form carbon fiber.

[0035] Examples of the iron chloride which may be employed include ferrous chloride (FeCl_2) and ferric chloride (FeCl_3), and these chlorides may be employed singly or in combination. The iron chloride may be a hydrate or an anhydride.

[0036] Productivity of carbon fiber can be further enhanced through addition of a sulfur source to the aforementioned raw materials. Examples of the sulfur source which may be employed include elemental sulfur, organic sulfur compounds such as thiophene, and inorganic sulfur compounds such as hydrogen sulfide. Elemental sulfur or thiophene is preferred. From the viewpoint of handling, elemental sulfur is more preferred. These sulfur sources (elemental sulfur and sulfur compounds) may be employed singly or in combination of two or more species.

[0037] Examples of the method for feeding a transition metal chloride to a reaction apparatus include (1) a method in which a transition metal chloride is dissolved in an organic compound, the resultant solution is vaporized to thereby form a gas mixture containing the transition metal chloride and the organic compound, and the gas mixture is mixed with hydrogen serving as a carrier gas, followed by feeding the resultant gas mixture to a carbon fiber production furnace; (2) a method in which a transition metal chloride is gasified, and the thus-gasified chloride is mixed with hydrogen serving as a carrier gas, followed by feeding the resultant gas mixture to a carbon fiber production furnace; and (3) a method in which fine particles obtained through spraying of a transition metal chloride solution are fed to a carbon fiber production furnace together with a carrier gas and a gas of an organic compound.

[0038] Method for Feeding a Transition Metal Chloride After Dissolution in an Organic Compound

[0039] One method for producing carbon fiber includes the following procedure: a transition metal chloride is dissolved in an organic compound serving as a raw material; the resultant solution is fed to a vaporization apparatus; and a gas mixture obtained through vaporization of the solution in the apparatus is fed to a reaction apparatus. This method is advantageous in that an apparatus for feeding a transition metal chloride is not required, and a transition metal chloride can be fed to a reaction apparatus while being uniformly distributed in an organic compound serving as a raw material.

[0040] A transition metal chloride exhibits somewhat low solubility with respect to an organic compound serving as a raw material. Therefore, in the case where a transition metal chloride is dissolved in an organic compound, the solubility of the transition metal chloride with respect to the organic compound can be enhanced by adding, for example, methanol, ethanol, or acetone, serving as a dissolution aid, to the organic compound. For example, in the case where ferric chloride is dissolved in benzene, when ethanol (1 mass %) is added to the benzene, the solubility of the ferric chloride can be increased to about 0.9 mass %.

[0041] When a liquid mixture containing a transition metal chloride and an organic compound is fed to a vaporization apparatus, and then heated under ambient pressure and at about 80°C ., the liquid mixture can be vaporized. In this case, the liquid mixture is effectively heated in the vaporization apparatus when a portion of a carrier gas (hydrogen

gas) is fed into the apparatus. A gas mixture obtained through vaporization in the apparatus is mixed with the remainder of the carrier gas in a line mixer, and the resultant gas mixture is fed to a reaction apparatus. The carrier gas may be preliminarily heated so as to suppress variation in the temperature profile of the gas mixture in the reaction apparatus.

[0042] In the reaction apparatus, the transition metal chloride is reduced by hydrogen gas, to thereby release transition metal atoms. Through repeated collision and aggregation of the transition metal atoms, fine transition metal particles are formed. Simultaneous with formation of the fine transition metal particles, generation of carbon clusters proceeds through thermal decomposition of the organic compound. The clusters are grown around the fine transition metal particles serving as nuclei, to thereby form carbon fiber.

[0043] Method for Feeding a Transition Metal Chloride After Gasification

[0044] The aforementioned method for feeding a transition metal chloride after dissolution in an organic compound serving as a raw material is not preferable where large amounts of fine transition metal particles must be formed, since a limitation is imposed on the solubility of a transition metal chloride with respect to an organic compound serving as a raw material. In such a case, a method utilizing physical properties (specifically, boiling point) of a transition metal chloride is advantageously employed. In general, a transition metal chloride has a lower boiling point than do other transition metallic compounds.

[0045] The boiling points of ferric chloride, nickel dichloride, and cobalt dichloride as measured under ambient pressure are 319°C ., 987°C ., and $1,049^\circ\text{C}$., respectively. When a transition metal chloride is fed to a reaction apparatus in gaseous form, the transition metal chloride is not necessarily heated to its boiling point. When a transition metal chloride is fed to a reaction apparatus together with a carrier gas while the transition metal chloride is heated at a predetermined temperature, the transition metal chloride can be fed in gaseous form at a temperature lower than its boiling point. An amount of a transition metal chloride fed to a reaction apparatus can be appropriately regulated by controlling the operation pressure and operation temperature of a heating apparatus to which the transition metal chloride is supplied, or by varying the amount of a carrier gas to be fed. The operation temperature is preferably 0 to 200°C ., the operation pressure is preferably 0.001 to 1 MPa.

[0046] For example, in the case where ferric chloride is supplied to a heating apparatus and argon is employed as a carrier gas, when the ferric chloride is heated to 260°C ., while the operation pressure of the heating apparatus is regulated at 0.15 MPa, the ferric chloride can be fed to a reaction apparatus at a rate of 0.37 g/min. When reduction of a transition metal chloride by hydrogen gas may raise some problems, an inert gas such as nitrogen, argon, or helium may be added to a carrier gas (hydrogen gas). Then, reduction of a transition metal chloride decreases.

[0047] A transition metal chloride which has been gasified in a heating apparatus is mixed with hydrogen serving as a carrier gas in, for example, a line mixer, and the resultant gas mixture is fed to a reaction apparatus. The carrier gas may be preliminarily heated so as to suppress variation in the temperature profile of the gas mixture in the reaction apparatus.

[0048] In the reaction apparatus, the transition metal chloride is reduced by hydrogen gas, to thereby release transition metal atoms. Through repeated collision and aggregation of the transition metal atoms, fine transition metal particles are formed. Simultaneous with formation of the fine transition metal particles, generation of carbon clusters proceeds through thermal decomposition of the organic compound. The clusters are grown around the fine transition metal particles serving as nuclei, to thereby form carbon fiber.

[0049] Method for Feeding Fine Particles Obtained Through Spraying of a Transition Metal Chloride Solution

[0050] When the aforementioned method for feeding a transition metal chloride after being gasified is employed, difficulty may be encountered in regulating the size of fine transition metal particles. In order to enhance the efficiency of catalyst utilization, the lifetime of transition metal particles of predetermined size serving as a catalyst must be lengthened.

[0051] Through spraying of a transition metal chloride solution (preferably a transition metal chloride aqueous solution), fine transition metal chloride particles are generated. When the thus-formed fine transition metal chloride particles are fed to a reaction apparatus, transition metal particles are generated from the surfaces of the fine transition metal chloride particles through reduction of the fine transition metal chloride particles by hydrogen gas. The thus-generated transition metal particles, serving as a catalyst, exhibit a lifetime longer than that of the transition metal particles produced through any of the aforementioned methods.

[0052] Crude carbon fiber as produced through reaction may be employed as, for example, an electrode material. However, in order to reduce the amount of impurities contained in the carbon fiber for enhancing its quality, or to enhance crystallinity of the carbon fiber, the carbon fiber may be subjected to firing at 100 to 1,500° C., preferably at 500 to 1,400° C., more preferably at 1,000 to 1,300° C., and subsequently graphitized through heat treatment at 2,000° C. or higher, preferably 2,400° C. or higher, more preferably 2,700° C. or higher, much more preferably 2,900° C. or higher. Furthermore, the thus-graphitized carbon fiber may be subjected to classification, to thereby remove impurities such as granular graphite therefrom.

[0053] In the production methods of the present invention, since an inorganic transition metal chloride is employed as a catalyst, the feed amount of the catalyst can be reduced.

[0054] The feed amount of an inorganic transition metal chloride to be employed is about 0.01 to about 20 mass %, preferably about 0.1 to about 10 mass %, more preferably about 0.2 to about 5 mass %, on the basis of the entire amount of an organic compound serving as a raw material.

[0055] When a small amount of an inorganic transition metal chloride is employed, the resultant carbon fiber contains a small amount of a transition metal (i.e., impurity). For example, when iron chloride is employed as a transition metal chloride, and the resultant carbon fiber is subjected to heat treatment (firing) at about 1,000° C., the thus-heated carbon fiber contains iron in an amount of about 3 mass % or less.

[0056] In the case where the carbon fiber is subjected to heat treatment by using a known heating apparatus, when the

rate of temperature increase falls within a range defined by a rate of minimum temperature increase and a rate of maximum temperature increase in the apparatus, the performance of the carbon fiber is not considerably affected. However, from the viewpoint of production cost, the rate of temperature increase is preferably high. The time elapsed when the carbon fiber is heated from ambient temperature to the maximum temperature is preferably 12 hours or less, more preferably six hours or less, and even more preferably two hours or less.

[0057] Any known heat treatment apparatus, such as an Acheson furnace or a direct electrical heating furnace, may be employed for firing. Such an apparatus is advantageous from the viewpoint of production cost. However, preferably, a furnace having a structure such that the interior of the furnace can be filled with an inert gas such as argon or helium is employed, since the resistance of carbonaceous powder may be lowered in the presence of nitrogen gas, and the strength of the carbon fiber may be lowered through oxidation by oxygen. Preferred examples of such a furnace include a batch furnace whose interior enables evacuation and gas substitution, a batch furnace in which the interior atmosphere can be controlled by means of a tubular furnace, and a continuous furnace.

[0058] In order to enhance crystallinity of the carbon fiber, if desired, any known graphitization catalyst, such as boron, beryllium, aluminum, or silicon, may be employed.

[0059] In a graphite network crystal structure, carbon atoms can be substituted by boron atoms. When such substitution occurs, restructuring of a crystal structure is considered to occur; i.e., a carbon-carbon bond is cleaved, and then reconstituted. Therefore, when graphite particles of relatively poor crystallinity are subjected to such restructuring, the resultant particles may exhibit high crystallinity. The expression "carbon coating layer contains boron (elemental boron)" refers to the case where a portion of incorporated boron forms a solid solution and is present in the surface of the carbon layer or between carbon-atom-layers of hexagonal network structure; or the case where carbon atoms are partially substituted by boron atoms.

[0060] No particular limitations are imposed on the boron compound which may be employed, so long as the boron compound generates boron when heated. Examples of the boron compound which may be employed include boron, boron carbide, boron oxide, and organic boron oxide. The boron compound may assume a solid, liquid, or gaseous form. Specific examples include elemental boron, boric acid (H_3BO_3), boric acid salts, boron oxide (B_2O_3), boron carbide (B_4C), and BN.

[0061] No particular limitations are imposed on the amount of a boron compound to be incorporated, which depends on chemical properties and physical properties of the compound. For example, when boron carbide (B_4C) is employed, it is preferably incorporated into carbonaceous powder to be heated, in an amount of B_4C of 0.05 to 10 mass %, more preferably 0.1 to 5 mass % based on the entire amount of the carbonaceous powder.

[0062] The vapor grown carbon fiber of the present invention is preferably a branched carbon fiber. Since each fiber filament of the branched carbon fiber has a hollow structure in which a hollow space extends throughout the interior

length of the filament, including a branched portion thereof, sheath-forming carbon layers of the filament assume the form of uninterrupted layers. As used herein, the term "hollow structure" refers to a structure in which a plurality of carbon layers form a sheath. The hollow cylindrical structure encompasses a structure in which sheath-forming carbon layers form an incomplete sheath; a structure in which the carbon layers are partially broken; and a structure in which two laminated carbon layers are formed into a single carbon layer. The cross section of the sheath does not necessarily assume a round shape, and may assume an elliptical shape or a polygonal shape. No particular limitations are imposed on the interlayer distance (d_{002}) of carbon crystal layers. The interlayer distance (d_{002}) of the carbon layers as measured through X-ray diffraction is preferably 0.339 nm or less, more preferably 0.338 nm or less. The thickness (Lc) of the carbon crystal layer in the C axis direction is 40 nm or less.

[0063] The outer diameter of each fiber filament of the vapor grown carbon fiber of the present invention is 500 nm or less, and the aspect ratio of the filament is at least 10. Preferably, the fiber filament has an outer diameter of 50 to 500 nm and a length of 1 to 100 μm (i.e., an aspect ratio of 2 to 2,000); or an outer diameter of 2 to 50 nm and a length of 0.5 to 50 μm (i.e., an aspect ratio of 10 to 25,000).

[0064] When vapor grown carbon fiber is subjected to heat treatment at 2,000° C. or higher after the carbon fiber has been produced, crystallinity of the carbon fiber is further enhanced, thereby increasing electrical conductivity. In such a case, an effective measure is addition of boron, which promotes graphitization, to the carbon fiber before heat treatment.

[0065] Production of Secondary Battery

[0066] The carbon fiber of the present invention is added to a battery electrode, to thereby enhance performance of the battery. The fiber enhances electric conductivity of an electrode plate of batteries such as a lithium battery, a lead secondary battery, a polymer battery, and a dry battery, or the performance of a battery requiring an intercalating property. In addition to an effect of enhancing conductivity of these batteries, the carbon fiber of the present invention, having excellent crystallinity and conductivity, is added to a lithium battery to thereby enhance the charge-discharge capacity thereof, since the fibers exhibit a great intercalating property as a carbonaceous material for a negative electrode. Particularly, a carbon fiber in which d_{002} is 0.3420 nm or less and Lc is 40 nm or less provides the above effects to a considerable degree. Even in the case of boron-containing carbon fibers in which d_{002} and Lc fall outside the above ranges, crystallinity and conductivity are more excellent than in the case of boron-free fine carbon fibers. Thus, the fiber is also adaptable to the above use.

[0067] The carbon fiber is preferably added to an electrode in an amount of about 0.1 to about 20 mass % based on the mass % of the electrode. Amounts in excess of 20 mass % have an effect of decreasing the filling density of carbon in the electrode to thereby lower the charge-discharge capacity of the produced battery; whereas amounts less than 0.1 mass % provide a poor effect.

[0068] In order to produce a battery with the addition of the carbon fiber, a material for a negative electrode, the fiber,

and a binder are sufficiently kneaded to thereby disperse the fiber as homogeneously as possible. Examples of material for a negative electrode of a lithium battery include graphite powder and meso-phase carbon microbeads (MCMB).

[0069] Any known method may be employed for producing a lithium secondary battery from the carbon fiber of the present invention.

[0070] An electrode can be produced through the following procedure: a binder is diluted with a solvent and then kneaded with a negative electrode material (i.e., the carbon fiber) in a typical manner, and the resultant mixture is applied to a collector (substrate).

[0071] Examples of the binder which may be employed include known binders, such as fluorine-based polymers (e.g., polyvinylidene fluoride and polytetrafluoroethylene), and rubbers (e.g., SBR (styrene-butadiene rubber)). Any known solvent suitable for a binder to be used may be employed. When a fluorine-based polymer is to be employed as a binder, for example, toluene or N-methylpyrrolidone is employed as a solvent. When SBR is to be employed as a binder, for example, water is employed as a solvent.

[0072] The amount of the binder to be employed is preferably 1 to 30 parts by mass, more preferably about 3 to 20 parts by mass, on the basis of 100 parts by mass of the negative electrode carbon material.

[0073] Kneading of the negative electrode material with the binder may be carried out by use of any known apparatus, such as a ribbon mixer, a screw kneader, a Spartan ruzer, a Lodige mixer, a planetary mixer, or a general-purpose mixer.

[0074] The thus-kneaded mixture may be applied to a collector by means of any known method. For example, the mixture is applied to the collector by use of a doctor blade, a bar coater, or a similar apparatus, and then the resultant collector is subjected to molding through, for example, roll pressing.

[0075] Examples of the collector which may be employed include known materials such as copper, aluminum, stainless steel, nickel, and alloys thereof.

[0076] Any known separator may be employed, but polyethylene- or polypropylene-made nonwoven fabric is particularly preferred.

[0077] In the lithium secondary battery of the present invention, the electrolytic solution may be a known organic electrolytic solution, and the electrolyte may be a known inorganic solid electrolyte or polymer solid electrolyte. From the viewpoint of electrical conductivity, an organic electrolytic solution is preferred.

[0078] Preferred examples of the organic solvent employed for preparing the organic electrolytic solution include ethers such as diethyl ether, dibutyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol dimethyl ether, and ethylene glycol phenyl ether; amides such as formamide, N-methylformamide, N,N-dimethylformamide, N-ethylformamide, N,N-diethylformamide, N-methylacetamide, N,N-dimethylacetamide, Nethylacetamide, N,N-di-

ethylacetamide, N,N-dimethylpropionamide, and hexamethylphosphoryl amide; sulfur-containing compounds such as dimethyl sulfoxide and sulfolane; dialkyl ketones such as methyl ethyl ketone and methyl isobutyl ketone; cyclic ethers such as ethylene oxide, propylene oxide, tetrahydrofuran, 2-methoxytetrahydrofuran, 1,2-dimethoxyethane, and 1,3-dioxolan; carbonates such as ethylene carbonate and propylene carbonate; γ -butyrolactone; N-methylpyrrolidone; acetonitrile; and nitromethane. More preferred examples include esters such as ethylene carbonate, butylene carbonate, diethyl carbonate, dimethyl carbonate, propylene carbonate, vinylene carbonate, and γ -butyrolactone; ethers such as dioxolan, diethyl ether, and diethoxyethane; dimethyl sulfoxide; acetonitrile; and tetrahydrofuran. Particularly, carbonate-based non-aqueous solvents such as ethylene carbonate and propylene carbonate are preferred. These solvents may be employed singly or in combination of two or more species.

[0079] A lithium salt is employed as a solute (electrolyte) which is dissolved in the aforementioned solvent. Examples of generally known lithium salts include LiClO_4 , LiBF_4 , LiPF_6 , LiAlCl_4 , LiSbF_6 , LiSCN , LiCl , LiCF_3SO_3 , LiCF_3CO_2 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

[0080] Examples of the polymer solid electrolyte include polyethylene oxide derivatives and polymers containing the derivatives, polypropylene oxide derivatives and polymers containing the derivatives, phosphoric acid ester polymers, and polycarbonate derivatives and polymers containing the derivatives.

[0081] In the lithium secondary battery of the present invention containing the negative electrode material, when a lithium-containing transition metal oxide (chemical formula: Li_xMO_2 , wherein M represents at least one transition metal selected from among Co, Ni, Mn, and Fe, and X falls within the following range: $0 \leq X \leq 1.2$) is employed as a positive electrode active substance, the resultant lithium secondary battery exhibits excellent safety and highly efficient charge/discharge characteristics. The positive electrode active substance is particularly preferably Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, and compounds obtained by partially substituting Co atoms, Ni atoms, and Mn atoms of the above compounds with other elements such as transition metals.

[0082] No particular limitations are imposed on the elements (exclusive of the aforementioned elements) which are required for producing a battery.

EXAMPLES

[0083] The present invention will next be described in more detail by way of Examples, which should not be construed as limiting the invention thereto.

Example 1

[0084] Carbon fiber was produced by use of an apparatus shown in FIG. 1. In FIG. 1, reference numeral 1 denotes a carrier gas heating furnace, 2 an organic compound vaporization apparatus, 3 a reaction tube, 4 a collecting apparatus, and 5 a transition metal chloride heating apparatus. Reference numerals 11, 21, 33, and 51 denote heaters employed for heating the respective furnaces to predetermined temperatures. Benzene serving as a raw material of carbon fiber, and hydrogen gas employed for promoting vaporization of

the benzene were fed through an inlet 22. Hydrogen serving as a carrier gas was fed through an inlet 12. Ferric chloride was employed as a transition metal chloride 53 (i.e., catalyst raw material). The ferric chloride was placed in the transition metal chloride heating apparatus 5, and heated by means of the heater 51. Argon gas was fed to the apparatus S through an inlet 52. After being vaporized in the apparatus 5, the ferric chloride was instantaneously mixed with benzene (raw material) and hydrogen gas in a line mixer 6. The resultant mixture was fed to the reaction tube 3 via a funnel-shaped tube 32 and a distributor 31. Carbon fiber 42 produced in the reaction tube 3 fell into the collecting apparatus 4 and was collected in the apparatus incorporating a filter 41. The carrier gas was discharged from a gas outlet 43.

[0085] Operation conditions and results are as follows.

[0086] (1) Carrier gas heating furnace

[0087] Temperature: 300 to 1,200° C.

[0088] Hydrogen gas feed rate: 150 NL/min (NL/min means normal liter per minute)

[0089] (2) Organic compound heating furnace

[0090] Organic compound: benzene

[0091] Temperature: 200 to 300° C.

[0092] Organic compound feed rate: 10 g/min

[0093] (3) Transition metal chloride heating apparatus

[0094] Heating temperature: 250 to 280° C.

[0095] Operation pressure: 0.15 to 0.25 Mpa

[0096] Transition metal chloride: ferric chloride

[0097] Ferric chloride feed rate: 0.6 g/min

[0098] Argon gas feed rate: 1 to 2 NL/min

[0099] (4) Reaction conditions

[0100] Reaction temperature: 1,000 to 1,300° C.

[0101] Reaction time: 0.5 to 10 sec

[0102] (5) Results

[0103] Amount of produced carbon fiber: 0.92 g/min (* yield: 10%)

[0104] Shape of carbon fiber: diameter: 0.01 μm , length: 10 μm

[0105] (* Carbon fiber yield was obtained on the basis of carbon contained in benzene)

Example 2

[0106] Carbon fiber was produced by use of a reactor formed of sintered silicon carbide (inner diameter: 90 mm, length: 260 mm).

[0107] A raw material solution was prepared as follows: ferric chloride (20 g) was dissolved in ethanol (20 g) to thereby prepare solution 1; sulfur (2 g) was dissolved in benzene (2,000 g) to thereby prepare solution 2; and solution 1 and solution 2 were mixed together to thereby prepare the raw material solution. The thus-prepared raw material solution was stored in a raw material container. The raw material

solution had a ferric chloride content of 0.9 mass % and a sulfur content of 0.1 mass %.

[0108] Nitrogen gas was flowed through the reactor so as to purge oxygen gas from the reactor, and subsequently hydrogen gas was flowed through the reactor, to thereby fill the reactor with hydrogen gas. Thereafter, the reactor was heated to 1,200° C.

[0109] The raw material solution was fed to a vaporization apparatus at a flow rate of 10 g/min by use of a pump, and the entire solution was vaporized. The thus-vaporized solution was carried by using hydrogen gas (flow rate: 20 N/min), and then mixed with hydrogen gas which had been heated to 400° C. (flow rate: 60 NL/min) immediately before being fed to the reactor. The resultant gas mixture was fed to the reactor for reaction. The reaction conditions were maintained for three hours, to thereby produce carbon fiber.

[0110] The thus-produced carbon fiber was observed under an electron microscope, and the carbon fiber was found to have an average diameter of 21 nm. The mass of the carbon fiber was measured, and carbonization yield (i.e., mass of the carbon fiber/mass of fed benzene) was calculated to be 3%. Subsequently, the carbon fiber was subjected to heat treatment (firing) at 1,000° C., and the iron content of the thus-treated carbon fiber was measured. The iron content was found to be 3.2 mass %.

Example 3

[0111] Carbon fiber was produced by using a reactor formed of sintered alumina (inner diameter: 90 mm, length: 260 mm).

[0112] A raw material solution was prepared as follows: ferrous chloride (26 g) was dissolved in ethanol (20 g) to thereby prepare solution 1; sulfur (2 g) was dissolved in benzene (2,000 g) to thereby prepare solution 2; and solution 1 and solution 2 were mixed together to thereby prepare the raw material solution. The thus-prepared raw material solution was stored in a raw material container. The raw material solution had a ferrous chloride content of 1.3 mass % and a sulfur content of 0.1 mass %.

[0113] Nitrogen gas was flowed flow through the reactor so as to purge oxygen gas from the reactor, and subsequently hydrogen gas was flowed flow through the reactor, to thereby fill the reactor with hydrogen gas. Thereafter, the reactor was heated to 1,200° C.

[0114] The raw material solution was carried at a flow rate of 10 g/min by using a pump, and then mixed with hydrogen gas which had been heated to 400° C. (flow rate: 60 NL/min) immediately before being fed to the reactor. The resultant gas mixture was fed to the reactor for reaction. The reaction conditions were maintained for three hours, to thereby produce carbon fiber.

[0115] The thus-produced carbon fiber was observed under an electron microscope, and the carbon fiber was found to have an average diameter of 40 nm. The mass of the carbon fiber was measured, and carbonization yield (i.e., mass of the carbon fiber/mass of fed benzene) was calculated to be 4%. Subsequently, the carbon fiber was subjected to heat treatment (firing) at 1,000° C., and the iron content of the thus-treated carbon fiber was measured. The iron content was found to be 3.0 mass %.

Example 4

[0116] Carbon fiber was produced by using a reactor formed of sintered alumina (inner diameter: 90 mm, length: 260 mm).

[0117] A raw material solution was prepared by dissolving sulfur (2 g) in benzene (2,000 g). The thus-prepared raw material solution was stored in a raw material container. The raw material solution had a sulfur content of 0.1 mass %.

[0118] Nitrogen gas was flowed through the reactor so as to purge oxygen gas from the reactor, and subsequently hydrogen gas was flowed through the reactor, to thereby fill the reactor with hydrogen gas. Thereafter, the reactor was heated to 1,200° C.

[0119] The raw material solution was fed to a vaporization apparatus at a flow rate of 10 g/min by using a pump, and the entire solution was vaporized. The thus-vaporized solution was carried by using hydrogen gas (flow rate: 20 NL/min), and then mixed with hydrogen gas which had been heated to 400° C. (flow rate: 60 NL/min) immediately before being fed to the reactor. The resultant gas mixture was fed to the reactor. Ferric chloride (500 g) was placed in a vaporization apparatus and heated to 300° C. The resultant vapor was carried by using hydrogen gas (flow rate: 1 NL/min), and then fed to the reactor for reaction.

[0120] The reaction conditions were maintained for three hours, to thereby produce carbon fiber.

[0121] The thus-produced carbon fiber was observed under an electron microscope, and the carbon fiber was found to have an average diameter of 22 nm. The mass of the carbon fiber was measured, and carbonization yield (i.e., mass of the carbon fiber/mass of fed benzene) was calculated to be 2%. Subsequently, the carbon fiber was subjected to heat treatment (firing) at 1,000° C., and the iron content of the thus-treated carbon fiber was measured. The iron content was found to be 2.5 mass %.

Reference Example 1

[0122] A reactor formed of sintered silicon carbide (inner diameter: 90 mm, length: 260 mm) was employed.

[0123] A raw material solution was prepared by dissolving ferrocene (23 g) and sulfur (2 g) in benzene (2,000 g). The thus-prepared raw material solution was stored in a raw material container. The raw material solution had a ferrocene content of 1.1 mass % and a sulfur content of 0.1 mass %.

[0124] Nitrogen gas was flowed through the reactor so as to purge oxygen gas from the reactor, and subsequently hydrogen gas was flowed through the reactor, to thereby fill the reactor with hydrogen gas. Thereafter, the reactor was heated to 1,200° C.

[0125] The raw material solution was fed to a vaporization apparatus at a flow rate of 10 g/min by using a pump, and the entire solution was vaporized. The thus-vaporized solution was carried by using hydrogen gas (flow rate: 20 NL/min), and then mixed with hydrogen gas which had been heated to 400° C. (flow rate: 60 NL/min) immediately before being fed to the reactor. The resultant gas mixture was fed to the reactor for reaction. The reaction conditions were maintained for three hours, to thereby produce black powder.

[0126] The thus-produced black powder was observed under an electron microscope, and the powder was found to contain few carbon fiber filaments and large amounts of particles. In particular, the number of fiber filaments was 10% or less of the number of particles.

[0127] The results show that the production yield of carbon fiber varies according to the type of catalyst compound to be employed (although the amount of an iron component incorporated into the raw material solution is almost equal to that of an iron component incorporated into the raw material solution of Example 2).

Comparative Example 1

[0128] A reactor formed of sintered silicon carbide (inner diameter: 90 mm, length: 260 mm) was employed.

[0129] A raw material solution was prepared by dissolving $\text{Fe}_2(\text{SO}_4)_3$ (49 g) and sulfur (2 g) in benzene (2,000 g). The thus-prepared raw material solution was stored in a raw material container. The raw material solution had an $\text{Fe}_2(\text{SO}_4)_3$ content of 2.4 mass % and a sulfur content of 0.1 mass %.

[0130] Nitrogen gas was flowed through the reactor so as to purge oxygen gas from the reactor, and subsequently hydrogen gas was flowed through the reactor, to thereby fill the reactor with hydrogen gas. Thereafter, the reactor was heated to 1,200° C.

[0131] The raw material solution was fed to a vaporization apparatus at a flow rate of 10 g/min by using a pump, and the entire solution was vaporized. The thus-vaporized solution was carried by using hydrogen gas (flow rate: 20 NL/min), and then mixed with hydrogen gas which had been heated to 400° C. (flow rate: 60 NL/min) immediately before being fed to the reactor. The resultant gas mixture was fed to the reactor for reaction. The reaction conditions were maintained for three hours, to thereby produce black powder.

[0132] The thus-produced black powder was observed under an electron microscope, and the powder was found to contain few carbon fiber filaments and large amounts of particles. In particular, the number of fiber filaments was 10% or less of the number of the particles.

[0133] The results show that the production yield of carbon fiber varies according to the type of catalyst compound employed (although the amount of an iron component incorporated into the raw material solution is almost equal to that of an iron component incorporated into the raw material solution of Example 2).

Effects of the Invention

[0134] According to the production methods of the present invention, vapor grown carbon fiber having a small, uniform diameter can be produced, and there can be employed, as a catalyst source, an inorganic transition metal chloride (e.g., ferric chloride) that is more inexpensively available than is ferrocene, which is a conventionally employed organo-transition metallic compound.

[0135] According to the production method of the present invention, carbon fiber can be produced at high productivity by using a small amount of catalyst.

[0136] The carbon fiber of the present invention contains a small amount of a transition metal (e.g., iron) serving as a catalyst, and thus is suitable for use as a component of a resin composition or as an electrode material of a secondary battery.

[0137] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0138] This application is based on Japanese Patent Application No. P2002-114235 filed Apr. 17, 2002, incorporated herein by reference in its entirety.

What is claimed is:

1. A method for producing vapor grown carbon fiber comprising thermally decomposing an organic compound and an inorganic transition metallic compound,

wherein the inorganic transition metallic compound is a transition metal chloride, and the amount of transition metal chloride is about 0.01 to about 20 mass % based on the entire amount of the organic compound.

2. The method for producing vapor grown carbon fiber as claimed in claim 1, further comprising dissolving the transition metal chloride in the organic compound, vaporizing the resultant solution to form a gas mixture containing the organic compound and the transition metal chloride; mixing the gas mixture with a carrier gas, and feeding the resultant gas mixture to a carbon fiber production zone.

3. The method for producing vapor grown carbon fiber as claimed in claim 1, further comprising forming a gas mixture of a carrier gas and a gas of the organic compound; mixing the gas mixture with a gas of the transition metal chloride, and feeding the resultant gas mixture to a carbon fiber production zone.

4. The method for producing vapor grown carbon fiber as claimed in claim 1, further comprising forming fine transition metal chloride particles by spraying a solution of the transition metal chloride; forming a gas mixture of a carrier gas and a gas of the organic compound; feeding the fine transition metal chloride particles, the carrier gas, and the organic compound gas to a carbon fiber production zone.

5. The method for producing vapor grown carbon fiber as claimed in claim 1, wherein the transition metal chloride is a chloride of at least one transition metal selected from the group consisting of iron, nickel, cobalt, molybdenum, and vanadium.

6. The method for producing vapor grown carbon fiber as claimed in claim 5, wherein the transition metal chloride is at least one chloride selected from the group consisting of iron chloride, nickel chloride, and cobalt chloride.

7. The method for producing vapor grown carbon fiber as claimed in claim 1, wherein the organic compound is an aromatic compound, acetylene, ethylene, butadiene, or a mixture thereof.

8. The method for producing vapor grown carbon fiber as claimed in claim 7, wherein the aromatic compound is benzene, toluene, xylene, or naphthalene.

9. The method for producing vapor grown carbon fiber as claimed in claim 2, wherein said dissolving comprises adding at least one dissolution aid selected from the from the group consisting of methanol, ethanol and acetone to the organic compound.

10. A vapor grown carbon fiber obtained by a method comprising thermally decomposing an organic compound and an inorganic transition metallic compound, serving as main raw materials, wherein the inorganic transition metallic compound is a transition metal chloride, and the amount of transition metal chloride is 0.01 to 20 mass % based on the entire amount of the organic compound.

11. The vapor grown carbon fiber as claimed in claim 10, wherein the carbon fiber comprises fiber filaments each having an outer diameter of about 1 to about 500 nm and a length of about 0.5 to about 100 μm .

12. The vapor grown carbon fiber as claimed in claim 10, wherein the transition metal chloride is iron chloride, and the carbon fiber comprises fiber filaments each having an outer diameter of about 1 to about 500 nm and a length of about 0.5 to about 100 μm , and containing iron in an amount of about 5 mass % or less.

13. A resin composition comprising a resin and a vapor grown carbon fiber as claimed in claim 10.

14. A secondary battery comprising, as an electrode material, a vapor grown carbon fiber as claimed in claim 10.

* * * * *