reserach

ttl/Electrode and ttl/carbon and ttl/battery and spec/graphitized and spec/manufacture

Electrode carbon battery process manufacture
Carbonaceous Material
Carbonized graphitized crystalline synthetic graphite graphitized carbon

The fourth manufacturing method of a carbon material for a negative electrode comprises the steps of applying a heat treatment to a carbonaceous material containing at least one material selected from the group consisting essentially of the carbonized material and the graphitized material under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO.sub.2, a second gaseous atmosphere containing at least 1% by volume of H.sub.2 O and a third gaseous atmosphere containing at least 10% by volume of CO.sub.2 and at least 1% by volume of H.sub.2 O, and bringing the carbonaceous material into contact with a gaseous acid.

It is desirable to apply a heat treatment to the carbonaceous material in order to maintain a gaseous state of the acid when the gaseous acid is brought into contact with the carbonaceous material having the heat treatment applied thereto. It is desirable for the heat treating temperature to fall within a range of between the vaporizing temperature of the inorganic acid or organic acid and 800.degree. C. If the heat treating temperature exceeds 800.degree. C., the reaction proceeds rapidly, with the result that it is possibly difficult to apply a uniform acid treatment to the surface of the carbonaceous material. It is more desirable for the heat treating temperature to fall within a range of between the vaporizing temperature of the inorganic acid or the organic acid and 500.degree. C. Where, for example, nitric acid is used as the inorganic acid, it is desirable for the heat treating temperature to fall within a range of between 130.degree. C. and 500.degree. C.

One of 30 sample methods was prepared by spinning a petroleum pitch used as a carbon precursor, followed by applying a heat treatment to the spun sample at 300.degree. C. for one hour so as to make the spun sample infusible. Then, a heat treatment was applied to the carbon precursor at 900.degree. C. for 3 hours in the presence of an atmosphere gas consisting of 100% by volume of a carbon dioxide gas so as to obtain a carbonized material. The carbonized material thus obtained belonged to an amorphous carbon or a soft carbon. Further, a heat treatment was applied to the carbonized material at 2800.degree. C. for 3 hours in the presence of an atmosphere

gas consisting of 100% by volume of a carbon dioxide gas so as to obtain a fibrous carbon material. Before the heat treatment, an atmosphere gas was introduced into the furnace so as to completely substitute the gas within the furnace, followed by stopping the gas supply and subsequently starting the heat treatment.

The average particle diameter, the interplanar spacing d.sub.002 derived from (002) reflection, which was determined by the X-ray diffractometry, the specific surface area determined by the BET method, and the immersion heat ratio .DELTA.H.sub.i.sup.n /.DELTA.H.sub.i.sup.h of the carbon material were measured under the conditions equal to those employed in Example 24 in respect of the carbon material thus obtained. Table 8 shows the results.
6,623,889 23 Sep 2003
Various processes have been developed over the years for the production of high performance carbon fiber materials. One of the leading processes for producing high performance carbon fibers is the so-called PAN process wherein polyacrylonitrile is used as a precursor fiber. The PAN process typically starts with a highly prestretched PAN fiber and involves three steps. First is a stabilization treatment wherein the PAN fiber is heat treated in air at a temperature from about 200.degree. to 300.degree. C. for one or more hours. In the second step, the fiber is carbonized at a temperature above about 1100.degree. C. in a non-oxidizing atmosphere. Last is a post heat treatment at temperatures up to about 2500.degree. C. to graphitize the fiber and give it high performance properties. It is in this post heat treatment step that the chemical composition, the crystalline structure, and the mechanical properties are strongly influenced.

There has been an intense effort to develop methods of spinning and carbonizing hydrocarbon pitch fiber to reduce precursor filament cost and weight loss. However, such processes require pitch pretreatment, spinning conditions, and post-treatments to insure correct orientation of carbon atoms in the final products. As a result, use of spun and carbonized hydrocarbon pitch has been nearly as expensive as using the previously noted methods involving organic polymers. Both methods require use of continuous filaments to achieve high orientation and good properties. There is a practical fiber diameter lower limit of 6 to 8 micrometers. Thinner fibers break during spinning and require excessive post-treatment. 5,643,670
July 1, 1997

This fine carbon power is required to have properties comparable to normal graphite powder, more specifically, good electrical conductivity as an electrode and in the case of a battery, electrical or chemical properties such that the carbonaceous member is resistant against a corrosion by an acid.

Carbon black is a material having properties satisfying these requirements to a certain extent and is used over a

wide range. In general, carbon commonly obtained from coke is graphitized, for example, by heating at a high temperature with an attempt to stabilize chemically and improve the corrosion resistance. However, carbon black is a material difficult to graphitize and can be hardly graphitized by mere heating.

Therefore, for example, JP-A-62-246813 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a technique of adding boric acid to carbon black and heating the obtained slurry at a temperature of 1,000 to 2,000.degree. C. to reduce the d.sub.002 of carbon crystal, which is an index of showing the graphitization, even to 3.41 .ANG. (0.341 nm), thereby attaining the graphitization. However, according to the study by the present inventors, d.sub.002 of carbon black cannot be lowered to less than 3.40 .ANG. which is by far larger than the theoretical value for complete graphite (i.e. 3.354 A). Furthermore, mere heating for the graphitization fails in elevating the electrical conductivity as demanded.

Therefore the first object of the present invention is to obtain graphitized fine carbon powder having excellent crystallinity and thereby increased in the resistance against chemical corrosion and at the same time, improved in the electrical conductivity, and to provide a high performance catalyst for polymer electrolyte fuel battery and polymer electrolyte fuel battery using the catalyst.

As a result of extensive investigations by taking account of the above-described problems, the present inventors have found that by using carbon black that was considered to be hardly graphitized, submicron fine graphitized carbon powder having an X-ray plane spacing C.sub.0 value (double of d.sub.002) of less than 0.680 nm (namely, d.sub.002 is less than 3.40 .ANG.) can be obtained. Futhermore the present inventors succeeded to obtain a high-performance fuel battery by using the powder as a catalyst support for fuel battery.

12. The electrically conducting carbon composite powder for supporting a catalyst as described in 11 above, wherein from 1 to 7% by mass of vapor grown carbon fiber is mixed with carbon powder.

13. The electrically conducting carbon composite powder for supporting a catalyst as described in any one of 10 to 12 above, wherein the carbon powder is heat-treated at a temperature of 2,500.degree. C. or more.

14. The electrically conducting carbon composite powder for supporting a catalyst as described in any one of 11 to 13 above, wherein the vapor grown carbon fiber is graphitized at a temperature of 2,500.degree. C. or more and boron content in the fiber is in a range of 0.001 to 5% by mass.

DETAILED DESCRIPTION OF THE INVENTION

To begin with, the first group of the present invention: fine graphitized carbon powder having good crystallinity, production method thereof, an electrically conducting carbon composite powder for supporting a catalyst using the carbon powder, a catalyst for polymer electrolyte fuel battery, polymer electrolyte fuel battery cell, and polymer electrolyte fuel battery, will be described in detail below.

The raw material used for obtaining the carbon powder of the present invention is a submicron fine particle comprising an amorphous carbonaceous material called carbon black. Examples of the carbon black include oil furnace black (e.g., Ketjen Black, Valcan, both are trade names) obtained by incompletely combusting aromatic hydrocarbon oil such as creosote oil; acetylene black (e.g., Denka-Black, trade name) obtained by complete combusting method using acetylene as a raw material; thermal black obtained by complete combusting method using natural gas as a raw material; and channel black obtained by incomplete combusting method using natural gas as a raw material. Any of these can be used.

Among these carbon blacks, oil furnace black and acetylene black are preferred.

The reasons that the two are preferred are explained as follows. One of important factors determining the performance of carbon black as an electrically conducting material is a primary particle chain structure (aggregation structure) called structure. The structure of carbon black have generally this aggregation structure where fine spherical primary particles are gathered and form irregular chained branches. As the number of primary particles is larger and as the chained branches are more complicated (called high structure state), the effect of imparting electrical conductivity is higher. This high structure state can be easily formed in the oil furnace black and acetylene furnace black and therefore, these carbon blacks are preferred.

The carbon powder of the present inveniton can preferably contain boron. This carbon powder containg boron can be produced, for example, carbon black and boron compound such as boron carbide (B.sub.4 C), boron oxide and boron nitride are mixed, and the mixture is heat-treated at 2,500.degree. C. or more in a non-oxidative atmosphere.

Among these methods, one preferable method where the carbon black is mixed with boron carbide (B.sub.4 C) and heated at a high temperature, that is not described in a literature, is explained below.

The boron carbide is ground to a particle size of 40 .mu.m or less and then mixed with carbon black. The average particle size of boron carbide is preferably 20 .mu.m or less. If the average particle size exceeds this range, the effect by the addition is small and also the yield and productivity decrease.

In the grinding, a commercially available general impact-type grinder (e.g., roller mill, ball mill, pulverizer) can be used. The boron carbide is difficult to grind and therefore, is preferably ground in advance to the mixing with carbon black.

The amount of boron carbide added is suitably from 0.01 to 7% by mass, preferably from 0.5 to 7% by mass as calculated in terms of boron. If the amount added is less than this range, the graphitization barely proceeds, whereas even if the amount added exceeds 7% by mass, the graphitization does not proceed any more and this is useless. The boron added in this range comes to be present in the carbon powder in an amount of 0.001 to 5% by mass, preferably 0.1 to 5% by mass and by virtue of this, the above-described graphitization effect can be brought out.

The boron carbide and carbon black may be mixed by any method without using any special machine as long as these are uniformly mixed.

The mixture of carbon black and boron carbide is preferably placed in a graphitic container and heat-treated in a non-oxidative atmosphere by passing an inert gas such as argon. The heat-treatment temperature must be 2,500.degree. C. or more. If the temperature is less than this range, the graphitization does not proceed and the graphitic fine carbon powder having a plane spacing of a unit lattice (C.sub.0 value) of less than 0.680 nm, furthermore 0.6730 nm or less for use in the present invention cannot be obtained.

The heat-treatment furnace for the graphitization may be any furnace as long as the heat-treatment can be performed at a desired temperature in a non-oxidative atmosphere and for example, an Acheson furnace utilizing carbon powder particles for the heat generation, a high frequency furnace and a furnace using a solid graphite heating element may be used. The non-oxidative atmosphere can be obtained by burying the material to be graphitized in the carbon powder or purging the inside of the furnace with an inert gas such as nitrogen gas or argon gas.

In the heating, after the entire material to be heated reaches a predetermined temperature, holding for a certain time is not particularly necessary. The heat-treated material is allowed to cool in the same non-oxidative atmosphere and ground by lightly stirring it.

If a boric acid which is in general easily available is mixed and heat-treated, instead of using boron carbide as the raw material of boron, enough reduction in the C.sub.0 value cannot be attained by the graphitization, and it

is difficult to make the C.sub.0 value of less than 0.680 nm.

By the above-described method of the present invention, carbon black which is said usually non-graphitizable and difficult to graphitize, can be graphitized.

When the carbon fine powder of the present invention is measured by an X ray, the C.sub.0 crystallite plane spacing (double of d.sub.002) generally used as an index for showing the graphitization degree is less than 0.680 nm, furthermore 0.6730 nm or less. C.sub.0 value as low as this level can not be attained using the submicron carbon powder.

The fine carbon powder of the present invention uses carbon black having a primary particle size of about several nm to about 100 nm as the raw material and is obtained by the partial aggregation of the carbons and therefore, after the graphitization, the particles having this primary particle size are aggregated as they are.

Even after the heat-treatment and grinding, the aggregated particles are estimated to have almost the same average particle size and distribution as those before the heat-treatment.

The primary particle size can be directly measured by the observation through TEM (transmission electron microscope), but the particle size distribution is mostly fixed by the manufacturing standard of carbon black. In the present invention, carbon powder having a primary particle size of 100 nm or less is suitably used and the graphitization product thereof also has a primary particle size within this range. N.sub.2 absorption specific surface area (BET), which is decreased by graphitization, is preferably in a range of 50 to 400 m.sup.2 /g in the present invention.

The particle size of the aggregated particle cannot be precisely measured because of the aggregation form such that primary particles are branched. When the average particle size is measured, for example, by the centrifugal precipitation method, the aggregated particles of the present invention are considered to be submicron particles having an average particle size of less than 1 .mu.m.

Since the fine carbon powder of the present invention is heat-treated together with boron carbide, the graphitization can successfully proceed and the electrical conductivity can be improved as compared with ordinary carbon powder which is not subjected to a heat-treatment or subjected to a heat-treatment by not adding boron carbide.

6,780,388 B2 24 Aug 04

Coating for carbon electrodes can consist of 50% by weight of finely ground graphite and silica. Hardened in a furnace.

Casting electrodes: mix ground coke with coal tar. Pressurize at 60-140 deg C (plastic paste) and using continuous jolts or vibration to increase density. Then baking it for several hours up to a temperature of about 1500 deg C.

A paste mixture of carbon coal particles fired to the point of Graphitizing the Agglomerated Carbon particles.

Heat the carbon particles first to drive off vapors then mix with binder. Inprotant that each partical is coated with the binder. Ground up petroleum coke and pitch coke to about .3mm or smaller then seporated and the larger particles mixed with the pitch (tar) first and the smaller second until it makes a dense paste that still wets the full surface of each practical. See 2,645,583

Bake carbon electrodes used in electric furnaces consist of calcined petroleum coke other cokes, charcoal, certain types of coal and lampblack. They are all amorphous carbon structure. The binders are petroleum pitch which is the residue of the refining of an asphalt-base petroleum, other pitches and various tars. Other binders include molasses, resins, turpentine and various products which are produced by distilling organic substances. The volatile material is largely eliminated by the baking process. The residue left consists of elemental carbon which bonds the particles of the body material. All binders are designated as carbonaceous.

Old method: petroleum coke is crushed and calcined and the resultant carbon body material is ground and this is mixed with the warm binder, which is in the form of small particles. This mixture is cooled crushed and ground to produce the electrode-forming composition. The ground electrode-forming compositon is heated in a mold until it becomes pasty. The mold is then removed from the heating oven, and the material in the mold is subjected to high pressure while still in the mold. The molded shape is then removed from the mold and is baked in a furnace, with the exclusion of air, in order to remove the volatile matter. Due to the low thermal conductivity of the molded

shape, the baking process requires great care, and the finished electrodes are often warped and have low conductivity and lowe mechanical strength due to improper baking. Also, a long baking period of one to two weeks is required, especially if the electrode is large size. Also, a long cooling period of the furnace is required. The maximum temperature of the furnace is about 1050° C. in a gas-fired furnace. 2,764,539

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ttl/pencil and tt/lead and tt/manufacture and tt/process

Pencil lead, for example, black lead, has heretofore been manufactured by blending a coloring material such as natural graphite or artificial graphite, with a clay binder, grinding the blend with water and kneading it, extruding the wet material so obtained into the appropriate form for a lead pencil, and after drying, baking it at elevated temperatures of about 1,000.degree. C and further oil-immersing it. Such a method is complicated for a manufacturing process not only in that it involves a large number of steps but also because close control of the water content at the time of extrusion is required. Moreover, it is necessary to bake the flexible extrudate while maintaining it in a straight line. However, it is almost impossible to bake an endless length of lead continuously. Thus, there is an inherent limitation to the number and types of variations for such a manufacturing process. 4,017,451 April 12, 1977

spec/pencil and ttl/lead and spec/manufacturing and spec/process

Flexible Lead-pencil
Graphite and caoutchouc mixed by titration and mass is subjected to pressure and rolled into sheets and cut.

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