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**Chung**

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[54] **PARTICULATE CARBON COMPLEX**

5,445,327 8/1995 Creehan .

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[73] **Assignee:** **The Research Foundation of State University of New York at Buffalo**, Buffalo, N.Y.

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[52] **U.S. Cl.** ..... **428/367; 428/376; 428/418; 428/408; 428/398; 427/115; 427/122; 427/255.1; 427/376.6**

[58] **Field of Search** ..... **428/408, 367, 428/409, 376, 418, 398; 427/115, 122, 376.6, 249, 255.1, 216**

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[57] **ABSTRACT**

The present invention relates to a particulate carbon complex made from a porous, particulate carbon substrate and a plurality of carbon filaments each having a first end attached to the porous, particulate carbon substrate and a second end distal from substrate. The complex is capable of transferring electrical current at a density of 350 to 10,000 mA/cm<sup>2</sup> for a Fe<sup>+2</sup>/Fe<sup>+3</sup> oxidation/reduction electrochemical reaction couple carried out in an aqueous electrolyte solution containing 6 mM potassium ferrocyanide and 1M potassium nitrate. The complex is prepared by providing a porous, particulate carbon substrate with impregnated metal catalyst and contacting the substrate with a gaseous carbonaceous material under conditions effective to form a plurality of carbon filaments on the substrate. Generally, the complex includes particles of metal catalyst material at the end of the filaments distal from the substrate. The carbon complex is useful in electrochemical applications as well as in structural composites.

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**12 Claims, 8 Drawing Sheets**



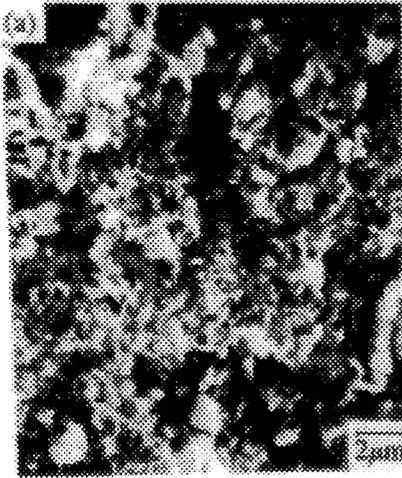


FIG. 1A

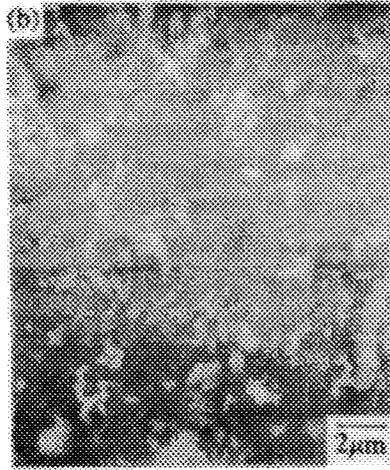


FIG. 1B



FIG. 1C

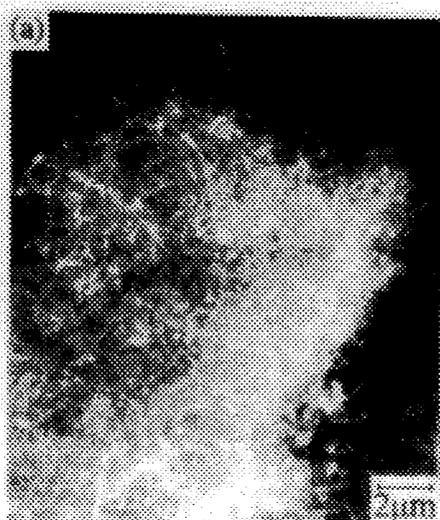


FIG. 2A

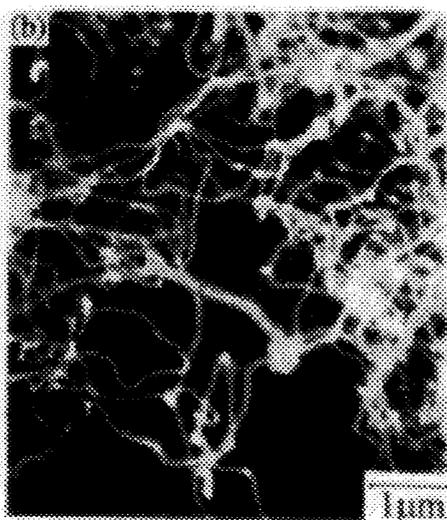


FIG. 2B

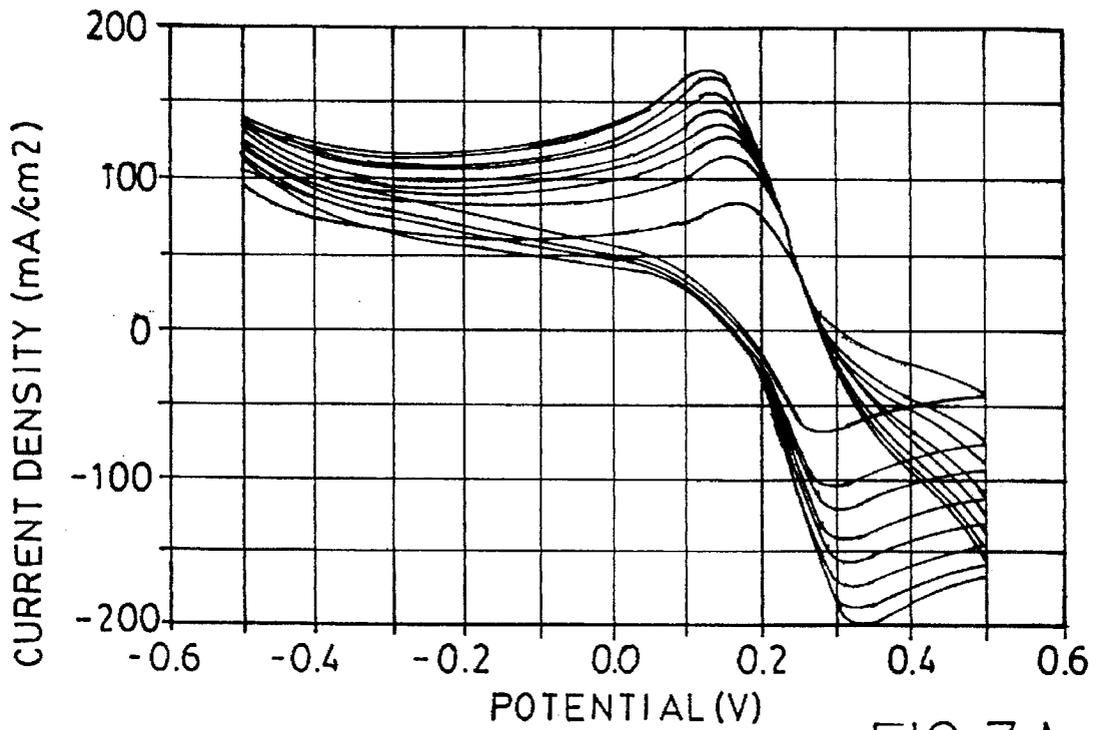


FIG. 3A

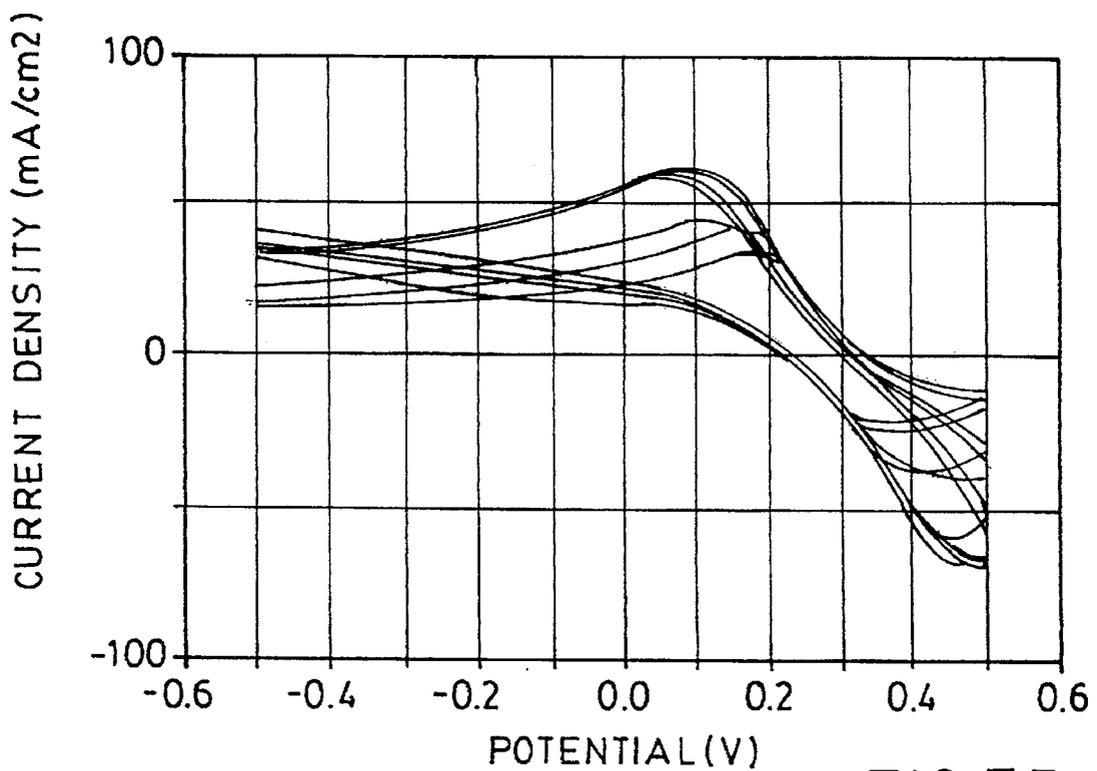


FIG. 3B

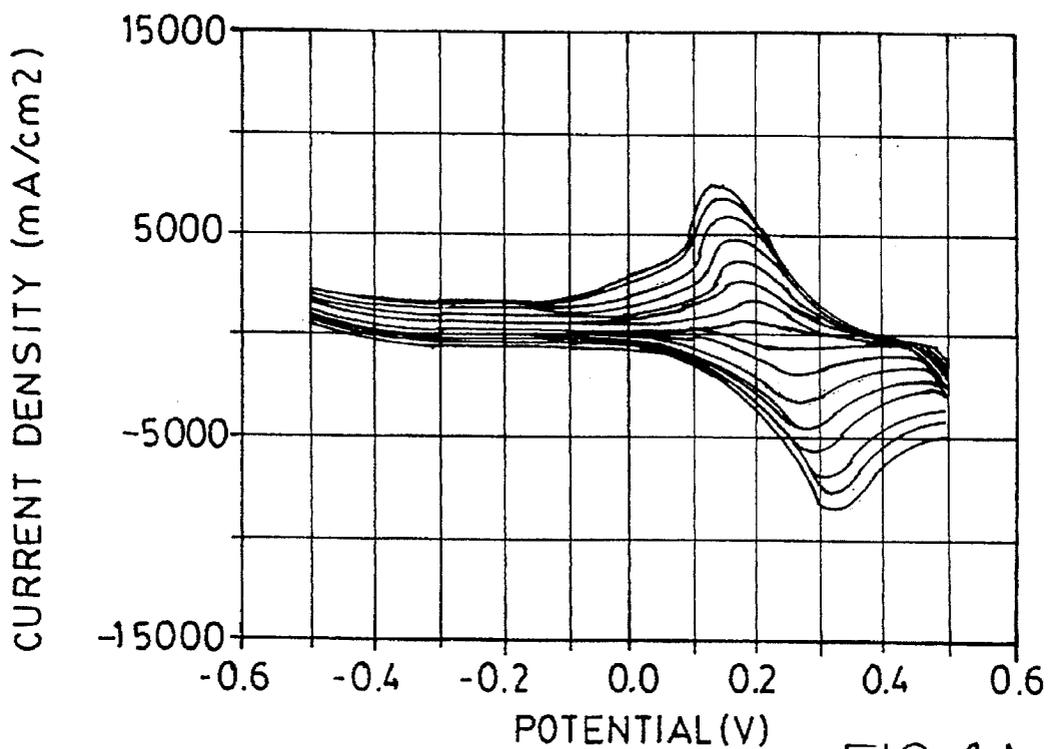


FIG. 4A

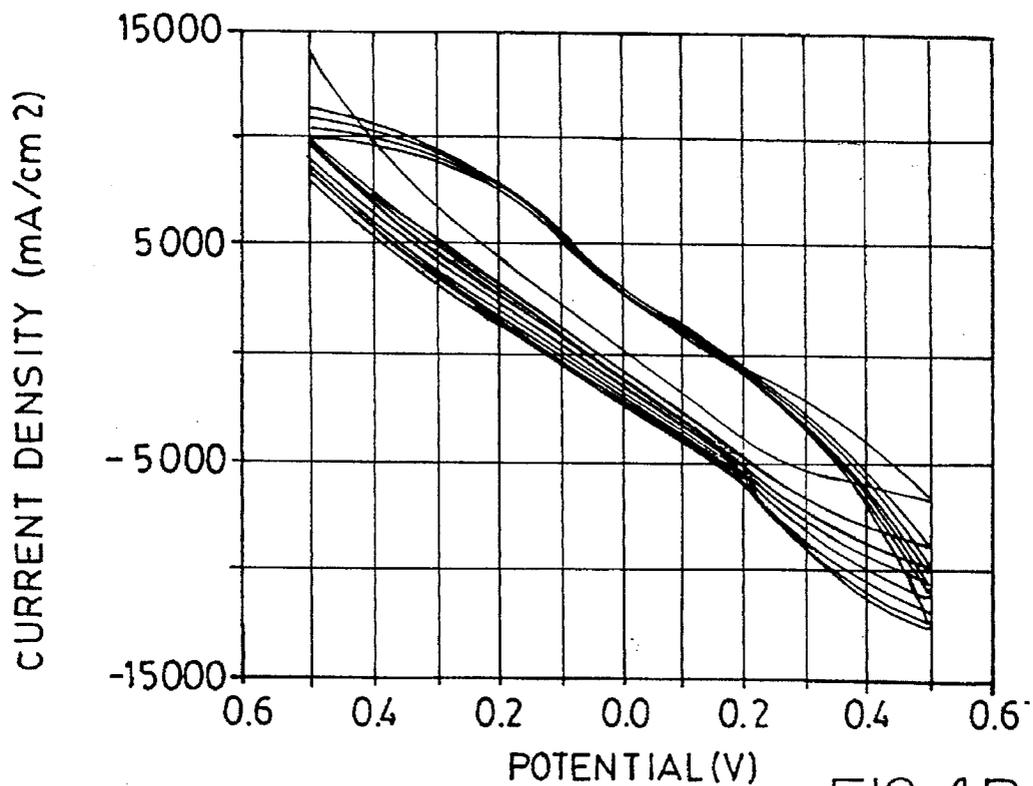


FIG. 4B

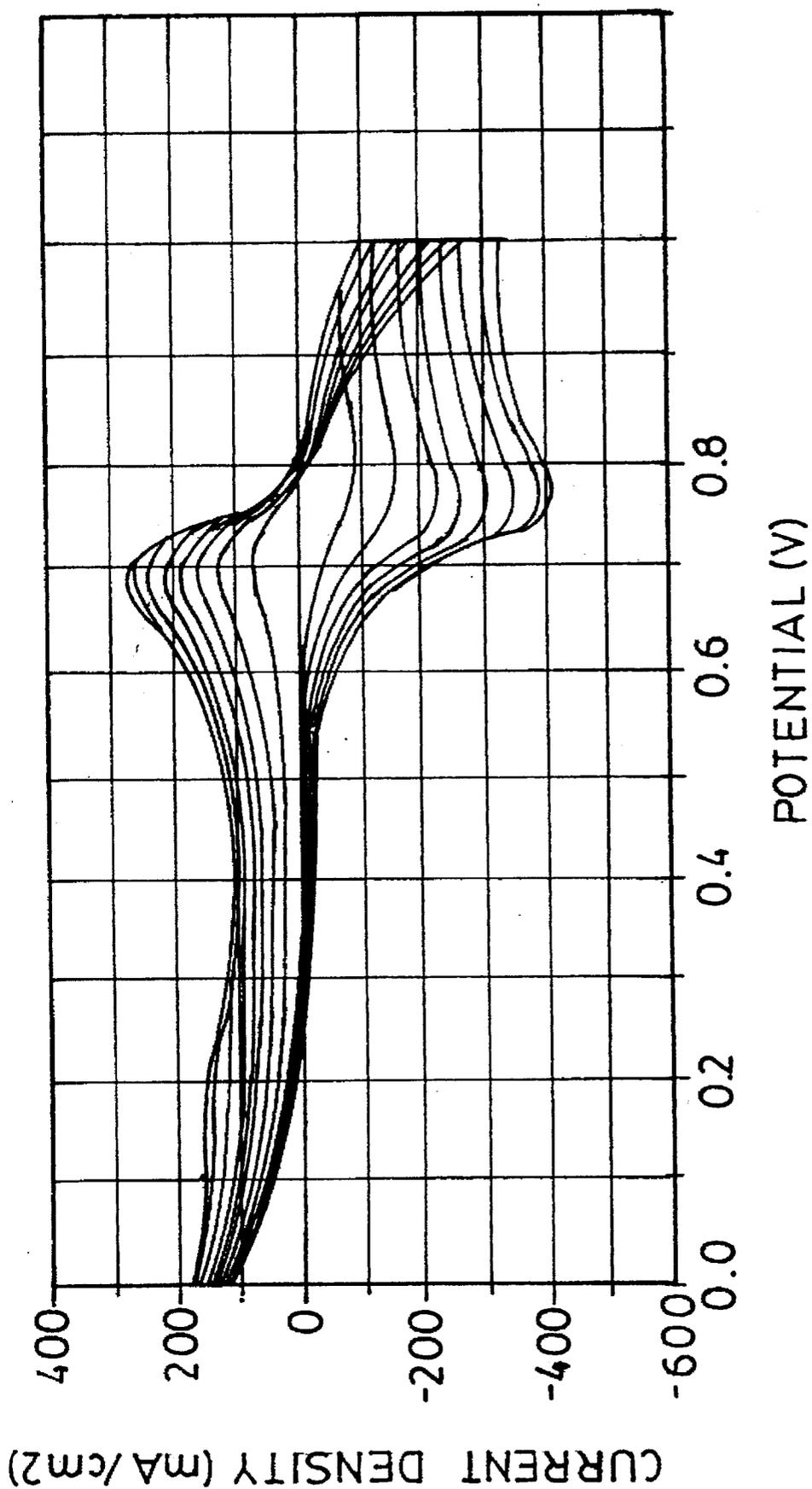


FIG. 5A

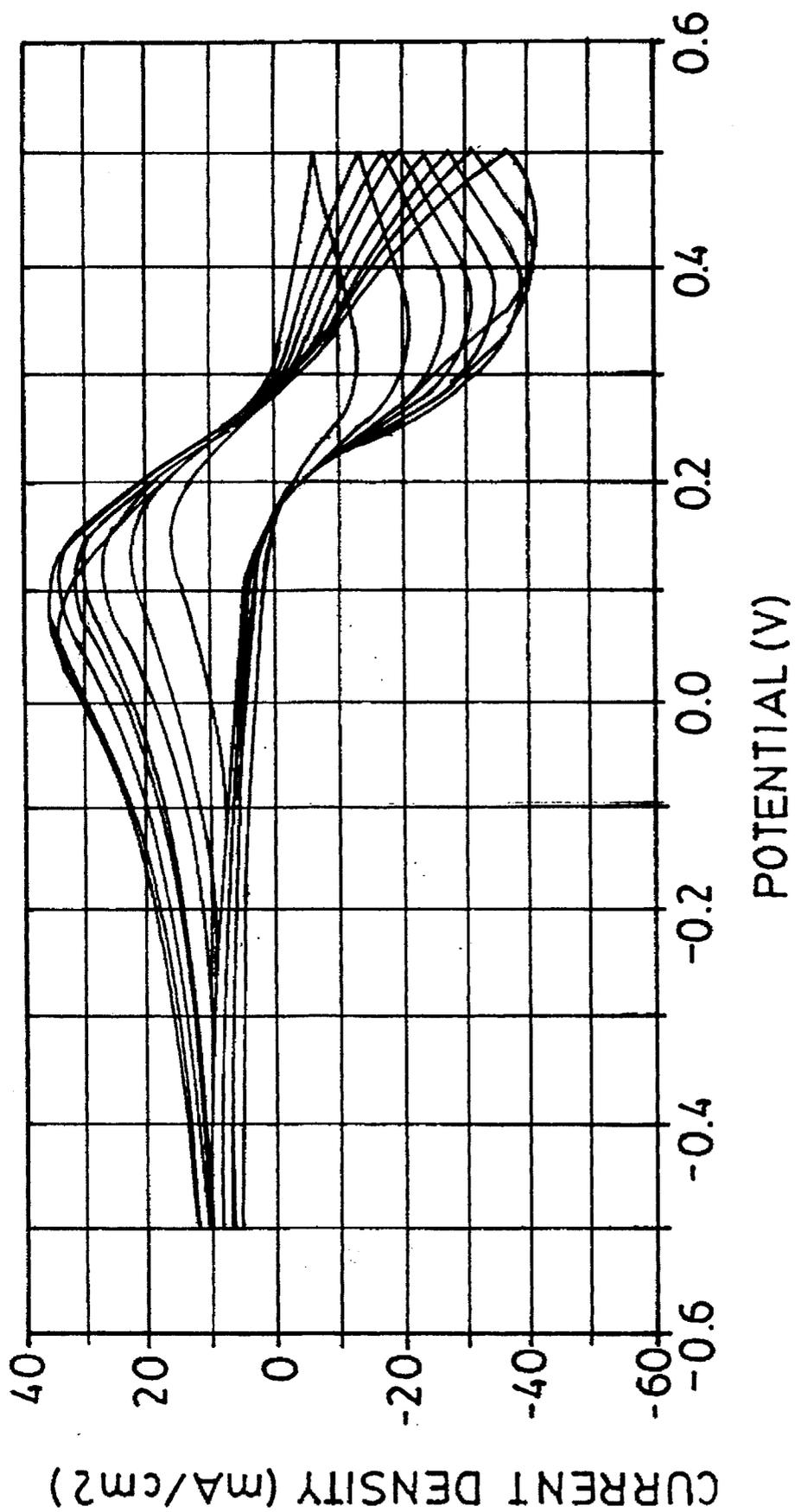


FIG. 5B

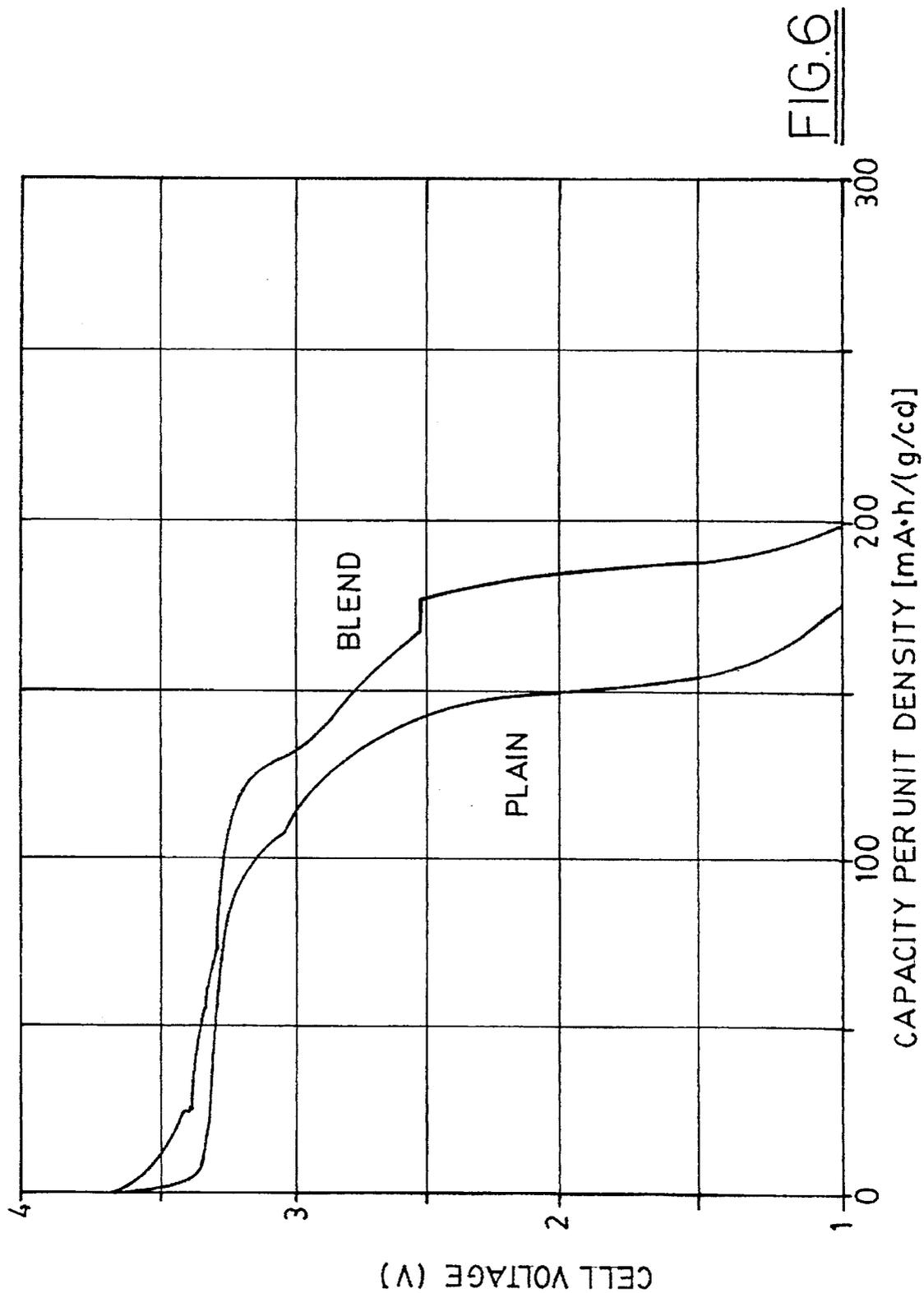


FIG. 6

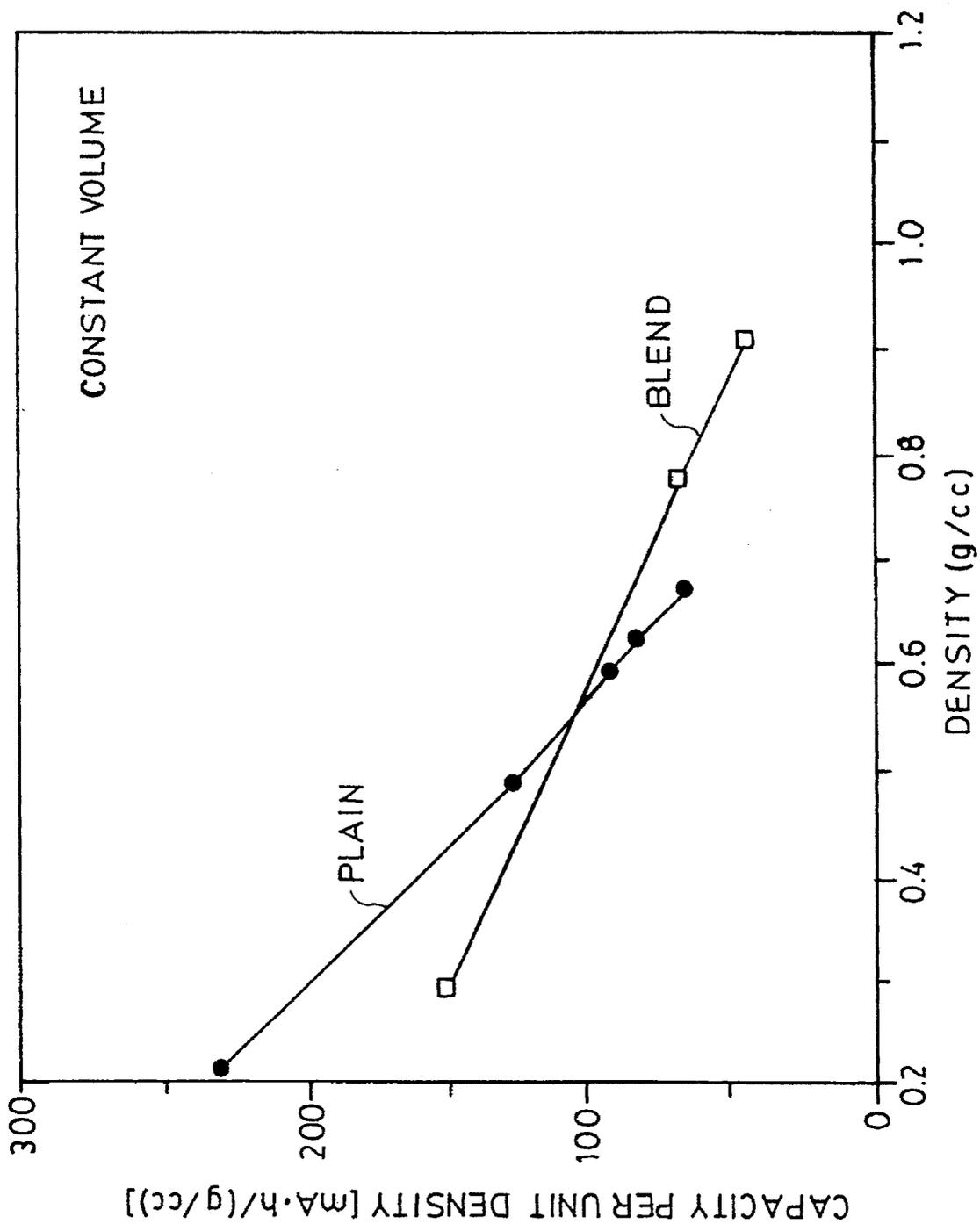


FIG. 7

## PARTICULATE CARBON COMPLEX

## FIELD OF THE INVENTION

The present invention relates to a carbon complex and its process of manufacture.

## BACKGROUND OF THE INVENTION

The superior mechanical and strength-to-weight properties of carbon fibers has led to an important class of high performance fiber/matrix composites. These high performance composites are particularly useful for the production of aircraft and automobile body parts for which both strength and light weight are critical. Such composites enable manufacturers to produce relatively light weight structures without sacrificing strength. Consequently, much research has been directed to producing carbon fiber materials with ever increasing high performance properties and physical features that make them more valuable in commercial products and processes.

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° to 300° C. for one or more hours. In the second step, the fiber is carbonized at a temperature above about 1100° C. in a non-oxidizing atmosphere. Last is a post heat treatment at temperatures up to about 2500° 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.

An entirely different approach for carbon fiber formation involves the preparation of carbon filaments through the catalytic decomposition at metal surfaces of a variety of carbon containing gases, e.g., CO/H<sub>2</sub>, hydrocarbons, and acetone. These filaments are found in a wide variety of morphologies (e.g., straight, twisted, helical, branched) and diameters (e.g., ranging from tens of angstroms to tens of microns). Usually, a mixture of filament morphologies is obtained, frequently admixed with other, non-filamentous carbon (cf. Baker and Harris, *Chemistry and Physics of Carbon*, Vol. 14, 1978). Frequently, the originally-formed carbon filaments are coated with poorly organized thermal carbon.

The vapor decomposition technique for forming carbon filaments has been extensively studied. U.S. Pat. No. 4,855,091 to Geus prepares carbon filaments by exposing a thermostable substrate covered with reduced metal particles to a carbon-containing gas at 200° to 700° C. U.S. Pat. No.

5,149,584 to Baker et al. deposits a catalyst comprising a group IB element and a second metal which is either iron, nickel, cobalt, or zinc on a carbon fiber substrate and contacts it with carbonaceous material at 500° to 700° C. U.S. Pat. No. 4,565,684 to Tibbetts et al. discloses growing graphite fibers on a suitably nucleated ceramic surface by passing methane gas over the substrate at elevated temperatures, and thickening the initially-formed microscopic carbon filaments by increasing the concentration of methane. Endo et al., "Structural Improvement Of Carbon Fibers Prepared From Benzene," *Japanese Journal of Applied Physics*, Vol. 15, No. 11, pp. 2073-76 (November, 1976) discloses the preparation of carbon fibers by thermal decomposition of benzene at 1050° to 1080° C. Kato et al., "Formation Of Vapor-Grown Carbon Fibers On A Substrate," *Carbon*, Vol. 31, No. 7, pp. 989-94 (1992) relates to growing fibers on activated carbon pellets by impregnating the pellets with an iron catalyst and introducing hydrogen sulfide and benzene in a gaseous state with "[n]o carbon fibers . . . produced without the feed of sulfur". U.S. Pat. Nos. 4,663,230, 5,165,909, and 5,171,560 to Tennent disclose the formation of substantially cylindrical carbon fibrils with an outer region of multiple layers of ordered carbon atoms and a distinct inner core region by contacting a metal particle (preferably supported on a refractory material) with a gaseous carbon-containing compound. M. Egashira et al., "Whiskerization of Carbon Beads by Vapor Phase Growth of Carbon Fibers to Obtain Sea Urchin-Type Particles," *Carbon*, vol. 21, no. 1., pp. 89-92 (1983) produces carbon filaments on hard, non-porous, sulfur-containing carbon beads.

In many cases, these vapor decomposition processes form filaments which can be utilized in high strength applications. There is also some mention that such filaments can be utilized as an electrical conductor or in electrochemical applications, such as for electrodes. See U.S. Pat. No. 4,855,091 to Geus et al. and U.S. Pat. Nos. 4,663,230, 5,165,909, and 5,171,560 to Tennent et al. Unfortunately, the art has been unable to produce carbon filament materials which are commercially useful in such electrical applications. This is due to the low electron transfer rates for such materials. The need, therefore, remains for vapor decomposition products which can be effectively utilized in electrical and electrochemical applications.

## SUMMARY OF THE INVENTION

The present invention relates to a particulate carbon complex having a porous, particulate carbon substrate and a plurality of carbon filaments each with a first end attached to the substrate and a second end distal from the substrate. The particulate carbon complex is capable of transferring electrical current at a density of 350 to 10,000 mA/cm<sup>2</sup> for a Fe<sup>+2</sup>/Fe<sup>+3</sup> oxidation/reduction electrochemical reaction couple carried out in an aqueous electrolyte solution containing 6 mM potassium ferrocyanide and 1M potassium nitrate. The complex will usually further include a particulate metal catalyst material at the second end of each carbon filament selected from the group consisting of iron, nickel, cobalt, zinc, platinum, and mixtures thereof. The particulate substrate desirably has pores less than 5000 Angstroms, while the particulate metal catalyst is similarly sized.

The carbon complex of the present invention is prepared by providing a porous, particulate carbon substrate impregnated with a metal catalyst material. The impregnated substrate is then contacted with a gaseous carbonaceous material under conditions effective to form the particulate carbon complex.

The carbon complex of the present invention is particularly useful in conjunction with electrochemical devices. Such devices include an electrode formed from the carbon complex having a porous particulate carbon substrate and a plurality of carbon filaments each having a first end attached to the substrate and a second end distal from the substrate.

The complex of the present invention is also useful as a composite in admixture with a dissimilar material. Suitable dissimilar materials include metals, polymers, glasses, ceramics, and mixture thereof.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a scanning electron micrograph showing the morphology of an iron catalyst on acetylene carbon black.

FIG. 1B is a scanning electron micrograph showing the back scattering of the image of FIG. 1A.

FIG. 1C is a scanning electron micrograph showing the carbon complex of the present invention with carbon filaments grown on acetylene carbon black, using ferric nitrate as the catalyst.

FIG. 2A is a scanning electron micrograph showing the carbon complex of the present invention with carbon filaments grown on acetylene carbon black, using nickel nitrate as the catalyst.

FIG. 2B is a scanning electron micrograph showing the carbon complex of FIG. 2A at a higher magnification.

FIG. 3A is a voltammetric response plot of current density versus potential for the carbon complex of the present invention with a graphite substrate.

FIG. 3B is a voltammetric response plot of current density versus potential for plain graphite.

FIG. 4A is a voltammetric response plot of current density versus potential for the carbon complex of the present invention with a carbon black substrate.

FIG. 4B is a voltammetric response plot of current density versus potential for plain carbon black.

FIG. 5A is a voltammetric response plot of current density versus potential for the carbon complex of the present invention with a carbon fiber substrate.

FIG. 5B is a voltammetric response plot of current density versus potential for the plain carbon fibers.

FIG. 6 is a graph showing plots of cell voltage versus capacity per unit density for a blend of 50 wt % of the carbon complex (made from a carbon black substrate) and 50 wt % plain carbon black, identified as the "blend" plot, and for plain carbon black alone, identified as the "plain" plot.

FIG. 7 is a graph showing capacity per unit density versus density plots for both a blend of 50 wt % of the carbon complex of the present invention (made from a carbon black substrate) and 50 wt % plain carbon black, identified as the "blend" plot, and plain carbon black alone, identified as the "plain" plot.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a particulate carbon complex which includes a porous particulate carbon substrate and a plurality of carbon filaments each having a first end attached to the substrate and a second end distal from the substrate. The particulate carbon complex is capable of transferring electrical current at a high charge density.

In large part, the substrate utilized in prior art vapor decomposition processes are merely surfaces to grow carbon filaments on. Once filament growth is completed, the fila-

ments are harvested and the substrate disposed of. As a result, conductive and non-conductive materials (e.g., refractory supports like alumina, carbon, quartz, or silicate) have been disclosed as useful even where electrical applications are suggested for filament production. See U.S. Pat. Nos. 4,663,230, 5,165,909, and 5,171,560 to Tennent et al. Even where a carbon substrate (e.g., carbon fibers) are suggested in the prior art, the complex of that substrate with a plurality of filaments extending from it have insufficient electron transfer rates to function satisfactorily in electrochemical applications. Such smooth carbon substrates lack the porosity and pore size needed to make the complex suitable for such uses.

Applicant has found that, in order for the carbon complex of the present invention to be useful in electrochemical applications, the substrate must be a porous carbonaceous material, preferably with pores less than 5000 Angstroms in diameter. A particularly preferred porous carbon substrate is carbon black, such as acetylene carbon black. Another carbonaceous material with a porosity and pore size suitable for forming carbon complexes useful in electrochemical applications is activated carbon. With such materials, the carbon complex of the present invention is capable of transferring current at a high charge density of 350 to 10,000 mA/cm<sup>2</sup>, preferably 2000 to 9000 mA/cm<sup>2</sup>, most preferably 7000 to 8000 mA/cm<sup>2</sup>, for a Fe<sup>+2</sup>/Fe<sup>+3</sup> oxidation/reduction electrochemical reaction couple carried out in an aqueous electrolyte solution containing 6 mM potassium ferrocyanide and 1M potassium nitrate. The Fe<sup>+2</sup>/Fe<sup>+3</sup> oxidation/reduction electrochemical couple is a well known couple used to test the electrochemical behavior of materials. It refers to a pair of oxidation and reduction reactions. The oxidation reaction is Fe<sup>+2</sup>+e<sup>-</sup>→Fe<sup>+3</sup>, while the reduction reaction is Fe<sup>+3</sup>→Fe<sup>+2</sup>+e<sup>-</sup>. Use of this test system is not intended to limit the scope of the present invention; it is simply the standard used to define the electrochemical current density of the carbon complex of the present invention as well as that of other test materials.

It is also believed that the use of substrates with pores having diameters below 5000 Angstroms enhances the adhesion of filaments to the substrate compared to substrates with larger pores.

The plurality of filaments each have a diameter of less than 5000 Angstroms, preferably 0.05 to 0.2 μm. The carbon filaments can range in length from very short nodules (having an aspect ratio of as low as 1) to very long strands (having aspect ratios approaching infinity). Generally, however, their length is at least five times their diameter.

The carbon filaments each comprise a hollow core surrounded by a substantially continuous layer of carbon. The carbon layer preferably comprises layers of ordered carbon atoms oriented in a curved configuration, like a fish rib bone (i.e. graphitic domains having their c-axis at an oblique angle to the cylindrical axis of the filament and are in crystalline form).

It is contemplated that a wide variety of transition metals, in particulate form, can be utilized as catalysts to form the carbon complex of the present invention. In its final form, the carbon complex will usually be utilized with the particulate catalyst material on the ends of the filaments distal from the substrate. However, such catalyst materials can be removed from the complex by selective chemical etching. Suitable particulate metal catalyst materials are formed from metals, like iron, nickel, cobalt, zinc, platinum, and mixtures thereof. These catalyst materials do not need to be activated with sulfur, as in Kato et al., "Formation Of Vapor-Grown

Carbon Fibers On A Substrate," *Carbon*, Vol. 30, No. 7, pp. 989-94 (1992), in order to produce carbon filaments. In the carbon complex of the present invention, the metal catalyst material is at the ends of the filaments distal from the substrate, because, as the filaments grow, the particles of metal catalyst material are lifted off the substrate by the filaments. A minor amount of metal catalyst material, which has not catalyzed carbon filament formation remains on the surface of the particulate carbon substrate. The presence of such unutilized catalyst is minimized when the metal particles are sufficiently small to fit into the pores of the carbon substrate. Generally, particles having a diameter below 5000 Angstroms, preferably below 1000 Angstroms, are suitable.

In the process of the present invention, any number of well known procedures can be utilized to impregnate the porous carbon substrate with metal catalyst material. One procedure involves impregnating the porous particulate carbon substrate with a metal salt solution and drying the impregnated material at a low temperature (such as 70° C.) in a vacuum in order to prevent oxidation of the catalyst. Suitable metal salts include carbonates, bicarbonates, nitrates, citrates, and oxalates of the above-described metal catalyst materials. The salts can be hydrated (e.g.,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ).

To produce the carbon complex of the present invention, the porous carbon substrate impregnated with metal catalyst material is contacted with gaseous carbonaceous material under conditions effective to form a plurality of carbon filaments each having a first end attached to the substrate. While not wishing to be bound by theory, it is believed that the gaseous carbonaceous material reacts with the catalyst material to form an active catalyst phase, probably a metal carbide. Generally, such contact is at a temperature of 500° to 1200° C., for a time period of 10 minutes to 8 hours, and at a pressure of 0.1 to 10 atmospheres. In this process, the gaseous carbonaceous material is mixed with an inert, non-carbonaceous carrier gas (e.g., nitrogen). The gaseous carbonaceous material is contacted with the substrate such that the flow rate ratio of the carbonaceous gas to the carrier gas ranges from 10:100 to 25:100. At a ratio of more than 25:100, the catalyst tends to be "poisoned" due to carbon deposition on it. Once the catalyst is poisoned, filament growth stops.

It is contemplated that a variety of carbon-containing compounds are suitable as the gaseous carbonaceous material of the present invention. Suitable materials include carbon monoxide, saturated aliphatic hydrocarbons, olefinic hydrocarbons, aromatics, oxygen-containing organics, and mixtures thereof. Suitable aromatic include benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene, or mixtures thereof. Methane, ethane, propane, and mixtures thereof are useful saturated aliphatic hydrocarbons, while suitable olefinic hydrocarbons include ethylene, propylene, acetylene, or mixtures thereof. Useful hydrocarbons containing oxygen include, e.g., alcohols such as methanol or ethanol, ketones such as acetone, and aldehydes such as formaldehyde or acetaldehyde or mixtures thereof. Methane is preferred due to its availability, thermal stability, and lack of toxicity.

In some cases, it may be desirable to impart porosity to the filaments after forming the carbon complex of the present invention. This can be achieved by subjecting the complex to an activation step. Any conventional procedure used to activate carbon can be employed. Such procedures involve an oxidation treatment, such as thermal, chemical, electrochemical, or electromagnetic radiation oxidation. A particularly preferred activation technique involves heating

the carbon complex and subjecting the plurality of carbon filaments to partial oxidation with a sub-stoichiometric amount of air or oxygen.

An important use of the carbon complex of the present invention is in electrochemical applications. It is particularly useful in forming electrodes for batteries, biomedical sensing devices, pH meters, chemical analytical equipment, and electrical conductors. Such electrodes can be formed purely from the carbon complex of the present invention which has been compacted into the shape of an electrode. No binders, which are potentially incompatible with certain electrolytes, are necessary. Electrodes, can also be formed from blends of the carbon complex of the present invention with carbonaceous materials conventionally used in electrodes. Alternatively, the carbon complex of the present invention can be blended as a composite with other materials conventionally utilized in electrodes which are either non-conductive or have low conductivity. For example, the carbon complex of the present invention can be mixed with manganese dioxide ( $\text{MnO}_2$ ) or carbon monofluoride ( $\text{CF}_x$ ) to form battery electrodes.

Manganese dioxide ( $\text{MnO}_2$ ), for example, is known to be a good cathode material for aqueous batteries and has recently been commercialized for cathode use in lithium batteries.  $\text{MnO}_2$  can be either chemically or electrolytically produced. The physical, chemical, and electrical properties of  $\text{MnO}_2$  are dependent upon its manufacturing process. Electrolytic production results in good porosity and high depolarizing characteristics, while chemically produced  $\text{MnO}_2$  has a high activity. During discharge,  $\text{MnO}_2$  is reduced from the tetravalent to the trivalent species. Performance is dependent upon the crystalline state, the level of hydration, and the activity of the  $\text{MnO}_2$ . Both aqueous and organic electrolytes can be used with  $\text{MnO}_2$  cathodes. The aqueous electrolyte/ $\text{MnO}_2$  cell, in existence for more than 100 years, commonly utilizes a zinc anode while organic electrolyte/ $\text{MnO}_2$  cells, only recently developed (since 1970), are constructed with lithium anodes. Two primary aqueous electrolyte/ $\text{MnO}_2$  cells have dominated the market, the zinc-carbon or Leclanche cell and, with increasing popularity since 1940, the alkaline zinc/ $\text{MnO}_2$  cell. The increased popularity of the alkaline zinc/ $\text{MnO}_2$  cell is due to its superior performance at high current drains, continuous discharge, and low temperatures as well as its better shelf life over the Leclanche cell under the same operating conditions. Energy densities of around 100 W-h/kg are typically achieved. Lithium (Li) anode cells are gradually replacing these conventional battery systems because they offer still improved energy densities and operate over a wider temperature range while maintaining shelf life. The Li/ $\text{MnO}_2$  cells achieve energy densities of just over 200 W-h/kg.

Carbon monofluoride ( $\text{CF}_x$ ) is another cathode material used in high energy density, high voltage batteries. It is an intercalation compound which, while being electrochemically active, is chemically stable in organic electrolytes and does not thermally decompose at temperatures up to 400° C. The end result is a battery with an even wider temperature range and longer storage life capability.  $\text{CF}_x$  is a nonconductive material which produces conductive carbon during discharge. As discharge progresses, the cell's conductivity increases which improves the regulation of the cell discharge voltage and increases discharge efficiency. Lithium fluoride, the discharge product, precipitates in the cathode structure. Energy densities up to 300 W-h/kg have been obtained from Li/ $\text{CF}_x$  cells.

The carbon complex of the present invention can also be utilized to form composites with other dissimilar materials.

Suitable dissimilar materials include metals, ceramics, glasses, polymers, and mixtures thereof. Such composites are prepared by blending the particulate carbon complex of the present invention with these dissimilar materials in solid particulate form or in liquid form. When utilizing a solid blending technique, the carbon complex of the present invention is advantageous, because it is in a particulate form and can be much more easily dispersed than conventional carbon fibers or carbon filaments harvested from substrates in prior processes.

A variety of polymers can be utilized to form composites with the carbon complex of the present invention. Such polymers include, for example, polyamides, polyesters, polyethers, polyphenylenes, polysulfones, polyurethanes, or epoxy resins. Preferred embodiments include elastomers, thermoplastics, and thermosets.

In another embodiment, the composite contains an inorganic material, e.g., a ceramic material or a glass. Preferred embodiments include plate glass and other molded glass, silicate ceramics, and other refractory ceramics such as aluminum oxide, silicon carbide, silicon nitride, and boron nitride.

In still another embodiment, the composite includes a metal. Suitable metals include aluminum, magnesium, lead, zinc, copper, tungsten, titanium, niobium, hafnium, vanadium, and alloys thereof.

Due to the present carbon complex's ability to transfer electrons at a high density, smaller quantities of it can be utilized (compared to conventional forms of carbon) to deliver a given quantity of power. As a result, the size of electrodes, and therefore, the battery can be reduced. Alternatively, the electrode and battery sizes can be maintained to produce a battery with more power than a battery of the same size with a conventional carbon electrode. The carbon complex of the present invention is advantageously utilized in battery applications, because, compared to similar substrates without filaments, such complexes have a higher capacity per unit density at at least certain electrode densities.

The carbon complex of the present invention can also be advantageously utilized in mechanical applications to improve thermal and electrical conductivity, to retard crack propagation by providing multiple channels for crack growth, and to decrease the coefficient of thermal expansion of composites containing the carbon complex of the present invention. In addition, the complex's improved thermal and electrical conductivity can be useful in electrical applications.

## EXAMPLES

### Example 1

#### Catalyst Preparation

Ferric nitrate was selected as the catalyst in the process. The ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was first dissolved in methanol to form a 20% (by weight) solution. Then the substrate (i.e., acetylene carbon black (Grade AB50P from Chevron Chemical Company)) was mixed with the solution and dried in a vacuum furnace at 60° to 70° C. overnight. The catalyst loading for different substrates corresponds to a ferric nitrate:substrate ratio of 1:1 to 5:1 in weight.

#### Apparatus

A three-zone furnace made by Lindberg, Watertown, Wisconsin was used. It was programmable to give a constant temperature. The growth reactor was a quartz tube with a 2 inch inner diameter.

#### Process

A layer of substrate was placed in an alumina boat. The reactor was first purged with  $\text{N}_2$  for about 1 hour to eliminate oxygen in the reactor. Then, the temperature was raised to 500° C., at which hydrogen was introduced in order to reduce the catalyst. After 2 hours, the  $\text{H}_2$  flow was ceased and the temperature was raised to 670° C. Acetylene gas was introduced when the reactor reached 670° C. The furnace was held at 670° C. for 5 hours.

#### Results

FIG. 1A shows the morphology of the iron catalyst on the surface of acetylene carbon black. The catalyst particles had an irregular shape, and their size ranged from 1 to 2  $\mu\text{m}$ . FIG. 1B is the back-scattered electron image of FIG. 1A, showing the catalyst particles as bright regions. FIG. 1C shows the result of filament growth. A mixture of entangled filaments (about 1  $\mu\text{m}$  in diameter) and carbon nodules (0.1 to 1  $\mu\text{m}$  in size) were obtained. However, the proportion of nodules was lower than when graphite flakes were used as the substrate. The graphite filaments can provide good electrical conductivity, while carbon nodules provide a higher surface area. The presence of both is ideal for the electrode application.

Since acetylene black is a porous material, the catalyst solution was absorbed into the interconnected micropores of the acetylene black by capillary action. During drying, the outer surface of the acetylene black dried first. Then, the catalyst solution inside the acetylene black diffused outward and deposited catalyst particles in the surface region of the acetylene black. The porous nature of the acetylene black confined the catalyst particles and prevented them from coagulation. This process resulted in fine catalyst particles. Their size may depend on the size of the micropores and the concentration of the catalyst solution. Since the pore size of the acetylene black was mostly ten to several hundred Angstroms, the catalyst particle size was also mostly in that range. This particle size range is suitable for catalytic growth of carbon filaments. Therefore, it is easier to grow filaments on acetylene black than on graphite flakes, carbon fibers, or glassy carbon, which are much less porous. The large catalyst particles, though relatively few, were inactive in the catalyzed growth of carbon filaments. Instead, carbon deposited from the vapor phase and formed carbon filaments on the acetylene carbon black.

### Example 2

Carbon complexes were prepared as in Example 1, except that (i) nickel nitrate instead of ferric nitrate was used as the catalyst, (ii) no hydrogen was used, so that the 500° C. heating step was eliminated, (iii) the furnace was held at 670° C. for 30 min, and (iv) graphite powder, carbon black, and carbon fibers were used as substrates. In other words, the process involved (i) purging the reactor containing one of the substrates with  $\text{N}_2$  at a flow rate of 100 cc/min, (ii) raising the temperature to 670° C., (iii) introducing acetylene gas at a flow rate of 20 cc/min while maintaining the  $\text{N}_2$  low, (iv) after 30 min at 670° C. in the presence of acetylene, stopping the acetylene gas flow and allowing the reactor temperature to fall, and (v) stopping the  $\text{N}_2$  flow when the reactor had cooled to room temperature. This process was repeated for each of the different substrates. FIG. 2A is a scanning electron microscope photograph showing the resulting carbon complex with carbon black as the substrate. FIG. 2B also shows this complex but at a higher magnification than FIG. 2A.

### Example 3

The electrochemical behavior of the carbon complexes prepared in Example 2 were compared. The study was

carried out using cyclic voltammetry (CV). A Bioanalytical Systems CV cell was used in conjunction with the Headstart Electrochemistry program (developed by EG&G Princeton Applied Research), a potentiostat, and an IBM personal computer. A saturated calomel electrode served as reference with a platinum wire used as the auxiliary electrode. The working electrode was a holder typically used for carbon paste electrodes. The carbon complex was used to fill the cavity in the same manner as carbon paste, but without the conventional paraffin oil binder. Testing was conducted in 6 mM potassium ferrocyanide ( $K_3Fe(CN)_6$ ) as the electroactive species and in 1M potassium nitrate ( $KNO_3$ ) in water as the supporting electrolyte. This solution allowed study of the  $Fe^{+2}/Fe^{+3}$  oxidation/reduction couple.

The voltammetric responses for the complex made from plain graphite powder (FIG. 3A versus FIG. 3B, respectively) the complex made from carbon black versus plain carbon black (FIG. 4A versus FIG. 4B, respectively), and the complex made from carbon fibers versus plain carbon fibers (FIG. 5A versus FIG. 5B, respectively) were all evaluated.

As shown in these figures, the presence of filaments dramatically improves the electrochemical performance of the plain substrate. This is demonstrated by the increase in electron transfer rate and enhanced reversibility of the redox reactions of the carbon complexes of carbon substrates with a plurality of filaments. This improvement is attributed to increased surface area and particulate connectivity which translates into improved conductivity.

Particularly noteworthy is the high voltammetric response achieved with carbon complexes using carbon black as the substrate compared to that achieved with complexes made from other carbon substrates. More particularly, FIG. 4A shows that a complex with a carbon black substrate has a peak current density of about 7500 mA/cm<sup>2</sup>. Even platinum, commonly used in research and considered an ideal electrode, only achieves a peak current density of about 1,700 mA/cm<sup>2</sup>. Furthermore, graphite powder and carbon fibers only achieve peak current densities of 175 mA/cm<sup>2</sup> (FIG. 3B) and 300 mA/cm<sup>2</sup> (FIG. 5B), respectively. This over 20-fold increase in electron transport capability for such complexes formed from the microporous carbon black substrate imparts dramatic advantages. In batteries, electrodes made from such complexes can decrease size and/or increase power.

#### Example 4

To assess discharge capability, constant current plate-to-plate discharge testing was conducted. A cut-down AA battery case was used as the positive electrode current collector. The carbon was placed inside the case and separated from the lithium by a nonconductive glass fiber paper. Insulative polymer disks were placed on top of the assembly and held in place with a metal clip. The assembly was immersed in a bromine chloride complex electrolyte. The discharge mechanism comprised reduction of complexed thionyl chloride at the carbon electrode. A Keithley power source was used to apply current. Data was collected on a Tandy computer.

To maintain good electrode pore size and distribution, and yet assess the effect of increased electrode conductivity, discharge testing of acetylene carbon black electrodes employed electrodes made from plain carbon black alone and blended with the carbon complex of the present invention having carbon filaments grown on a carbon black substrate. In the blend, the plain carbon black provided

retention of good pore size and distribution, while the carbon complex helped the connectivity. FIG. 6 compares the discharge performance of plain carbon black, identified as the "plain" plot, having a density of 0.39 g/cm<sup>3</sup> (not pressed), with that of a blend of 50 wt. % carbon complex (with carbon filaments grown on carbon black) and 50 wt. % plain carbon black, identified as the "blend" plot, having a density of 0.29 g/cm<sup>3</sup> (not pressed). Since the experiment was conducted at a constant current of 3 mA, the capacity (in units of mA-h) is directly proportional to the time of discharge. In other words, the horizontal axis is related to the lifetime of the cell during constant current discharge. The electrodes for both cases were prepared identically, except for the difference in material. An improvement of approximately 40 mA-h per unit density was achieved when discharged to 2 volts.

With a carbon reduction electrode of fixed volume, the cell capacity decreased with increasing density of the carbon reduction electrode, such that the plot of the capacity per unit density versus the density was a straight line of negative slope. This is due to the filling of pores in the reduction electrode by the reduction reaction product. FIG. 7 shows plots for plain acetylene carbon black, identified as the "plain" plot, and a blend of 50 wt. % carbon complex (with carbon filaments grown on carbon black) and 50 wt. % plain carbon black, identified as the "blend" plot. The plot for plain carbon black had a more negative slope, such that the blend gave a higher capacity per unit density than the plain carbon black at densities above 0.55 g/cm<sup>3</sup>. The different densities were obtained by compression of the carbon particles at different pressures. To attain the same density, the plain carbon black required a much higher pressure than the blend. This is due to the resilient nature of carbon black compact. Thus, the electrode with the blend is easier to fabricate than that with plain carbon black, if a high density is desired. A high density corresponds to a greater energy density which is a desirable property in batteries.

#### Example 5

The adhesion of the carbon filaments to the acetylene carbon black in the carbon complex was tested by shaking about 0.5 cm<sup>3</sup> of the complex in ethanol contained in a 10 ml beaker, which was placed in water in an ultrasonic cleaner for 15 minutes. Subsequent scanning electron microscope examination revealed no sign of filaments coming off.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is made solely for that purpose and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

What is claimed:

1. A particulate carbon complex comprising:

a carbon black substrate and

a plurality of carbon filaments each having a first end attached to said carbon black substrate and a second end distal from said carbon black substrate, wherein said particulate carbon complex transfers electrical current at a density of 7000 to 8000 mA/cm<sup>2</sup> for a  $Fe^{+2}/Fe^{+3}$  oxidation/reduction electrochemical reaction couple carried out in an aqueous electrolyte solution containing 6 mM potassium ferrocyanide and 1M aqueous potassium nitrate.

2. A particulate carbon complex according to claim 1, wherein said carbon black substrate has pores less than 5000 Angstroms in diameter.

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3. A particulate carbon complex according to claim 1, wherein said plurality of carbon filaments each have a diameter of less than 5000 Angstroms.

4. A particulate carbon complex according to claim 1, wherein said plurality of carbon filaments are activated. 5

5. A particulate carbon complex according to claim 1 further comprising:

a particulate metal catalyst material at the second end of each carbon filament, wherein the metal in said particulate metal catalyst material is selected from the group consisting of iron, nickel, cobalt, zinc, platinum, and mixtures thereof. 10

6. A particulate carbon complex according to claim 5, wherein said particulate metal catalyst has a diameter of less than 5000 Angstroms. 15

7. A particulate carbon complex according to claim 1, wherein said plurality of carbon filaments each comprise a hollow core surrounded by an outer substantially continuous layer of carbon atoms.

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8. A composite comprising:

a particulate carbon complex according to claim 1 and a dissimilar material in admixture with said particulate carbon complex, wherein said dissimilar material is selected from the group consisting of metal, ceramic, glass, polymer, and mixtures thereof.

9. A composite according to claim 8, wherein said carbon complex lowers the coefficient of thermal expansion of said composite.

10. A composite according to claim 8, wherein said carbon complex enhances electrical and thermal conductivity.

11. A particulate carbon complex according to claim 1, wherein the carbon black substrate is acetylene black. 15

12. A composite according to claim 8, wherein the carbon black substrate is acetylene black.

\* \* \* \* \*



US005851504A

**United States Patent** [19]  
**Barker et al.**

[11] **Patent Number:** **5,851,504**  
[45] **Date of Patent:** **\*Dec. 22, 1998**

[54] **CARBON BASED ELECTRODES**  
[75] Inventors: **Jeremy Barker**, Henderson, Nev.; **Ib I. Olsen**, Cockeysville, Md.  
[73] Assignee: **Valence Technology, Inc.**, Henderson, Nev.  
[ \* ] Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).  
[21] Appl. No.: **716,741**  
[22] Filed: **Sep. 23, 1996**  
[51] **Int. Cl.**<sup>6</sup> ..... **D01F 9/12**  
[52] **U.S. Cl.** ..... **423/447.2**; 204/290 R; 204/294; 204/291; 429/218; 429/217

[58] **Field of Search** ..... 204/291, 294, 204/290 R; 429/217, 218, 232; 423/445 R, 447.2, 447.9

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[57] **ABSTRACT**  
Provided by the present invention is a new anode material comprised of a carbon obtained by pyrolyzing a polymer of a conjugated vinyl monomer. The carbon is suitable for a lithium intercalated anode as it offers potential advantages of high capacity. The economics of manufacturing such anodes are also beneficial.

**20 Claims, No Drawings**

## CARBON BASED ELECTRODES

### BACKGROUND OF THE INVENTION

The present invention relates to electrochemical devices and, more particularly, relates to non-aqueous lithium cells. The present invention also relates to novel carbon based electrodes useful in such cells.

Non-aqueous lithium electrochemical cells typically include an anode, a lithium electrolyte prepared from a lithium salt dissolved in one or more organic solvents and a cathode of an electrochemically active material, typically a chalcogenide of a transition metal. During discharge, lithium ions from the anode pass through the liquid electrolyte to the electrochemically active material of the cathode where the ions are taken up with the simultaneous release of electrical energy. During charging, the flow of ions is reversed so that lithium ions pass from the electrochemically active cathode material through the electrolyte and are plated back onto the lithium anode.

Recently, the lithium metal anode has been replaced with a carbon anode such as coke or graphite intercalated with lithium ions to form  $\text{Li}_x\text{C}_6$ . In the operation of the cell, lithium passes from the carbon through the electrolyte to the cathode where it is taken up just as in a cell with a metallic lithium anode. During recharge, the lithium is transferred back to the anode where it reintercalates into the carbon. Because no metallic lithium is present in the cell, melting of the anode does not occur even under abusive conditions. Also, because lithium is reincorporated into the anode by intercalation rather than by plating, dendritic and spongy lithium growth does not occur. Such non-aqueous lithium electrochemical cells are well known and are often referred to as "rocking chair" batteries because lithium ions move back and forth between the intercalation compounds during charge/discharge cycles.

U.S. Pat. No. 5,028,500 discusses such rocking chair batteries which use a carbon anode intercalated with lithium metal when graphite is used as the carbon material, intercalation with lithium metal generally forms  $\text{Li}_x\text{C}_6$ . Coke is another carbon material useful in preparing the carbon anode, with intercalation with lithium metal forming  $\text{Li}_x\text{C}_{12}$ . In U.S. Pat. No. 5,028,500, a carbon anode is used wherein every particle of the carbon includes a first carbonaceous phase and a second carbonaceous phase intimately admixed with the first carbonaceous phase, and with the first phase having a higher degree of graphitization than said second phase.

Conjugated backbone polymers, e.g., polyacetylene, polyphenylene, polyacenes, polythiophene, poly(phenylene vinylene), polyazulene, poly(phenylene sulfide), polyaniline and polypyrrole, have been suggested for use in a variety of applications based upon their characteristic of becoming conductive when oxidized or reduced either chemically or electrochemically. U.S. Pat. No. 4,321,114 employs one or more electrodes having conjugated backbone polymers as the electroactive material in secondary battery applications. U.S. Pat. No. 4,472,487 describes the use of polymeric electrodes having conjugated backbone polymers as the electroactive material in rocking chair batteries as well.

The use of carbon derived from poly(p-phenylene) in an electrode of a secondary electrochemical cell is also known. Such use is described, for example, in "The Behavior of Carbon Electrodes Derived from Poly(p-phenylene) in Polyacrylonitrile-based Polymer Electrolyte Cells", by M. Alamgir et al, *J. Electrochem. Soc.*, Vol. 141, No. 11, November 1994, pp. L143-144. The article discusses the

discovery of disordered carbons derived from poly(p-phenylene) and phenylformaldehyde resin as being able to electrochemically and reversibly store as high as 680 mAh of lithium per gram of carbon. Such material is suggested for use in high capacity intercalation anodes in lithium ion batteries. The carbon is generally prepared by pyrrolization of the poly(p-phenylene) at temperatures from 700° to 1000° C.

While use of carbon derived from poly(p-phenylene) gives very high discharge capacities when used as lithium anodes in lithium ion batteries, the preparation of the material is quite expensive, and can involve toxic compounds such as benzene. The industry, therefore, would benefit greatly from useful carbons which can be derived from materials more economically and safely, while still providing a high capacity anode material useful in lithium ion batteries.

It is therefore an object of the present invention to provide a novel carbon anode material which can provide high capacity when used as the lithium intercalated anode material in a lithium ion battery.

Another object of the present invention is to provide a method of preparing such a carbon material which is economical and safe.

Still another object of the present invention is to provide high capacity batteries using such carbon material.

These and other objects of the present invention will become apparent upon a review of the following specification and the claims appended thereto.

### SUMMARY OF THE INVENTION

In accordance with the foregoing objectives, there is provided a high capacity carbon anode material which is derived from the pyrolyzed polymer of a conjugated vinyl monomer. The carbon material can be safely and economically made by polymerizing, either chemically or electrochemically, vinyl monomers which are conjugated. The resultant polymers, which are generally non conductive, are then pyrolyzed by heating to a temperature of preferably around 1000° C. The result is a carbon which offers a high conductive capacity upon the intercalation of an alkaline metal salt such as lithium. The polymer which is pyrolyzed is generally easy to prepare from the vinyl monomers, thereby lending the manufacturing costs to a process which is very economical. The process is also generally safe in regard to the chemicals involved when compared to the preparation and pyrrolization of poly(p-phenylene).

Among other factors, therefore, the present invention is based at least in part on the recognition that the polymers readily prepared from vinyl compounds having appropriate conjugation can be pyrolyzed to provide a carbon with a structure capable of high capacity potential as an electrode, preferably as an anode. This is particularly true when lithium is intercalated with the carbon material. The high capacity and economics make the carbon anode of the present invention potentially extremely attractive to the battery industry.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

The electrochemical cells of the present invention generally include a cathode and the intercalation based carbon anode of the present invention. Each electrode, the cathode as well as the anode, is capable of reversibly incorporating (e.g., intercalating) an alkali metal ion. The cell further

comprises a polymeric matrix containing an electrolyte solution comprising an organic electrolyte solvent and a salt of the alkali metal. Each electrode in the cell preferably has a current collector. The electrochemical cells and batteries employing the carbon based anodes of the present invention preferably use lithium and salts thereof.

The anode used in the electrochemical devices of the present invention generally comprises an anode film that is laminated onto one or both sides of a current collector which is a thin metal foil or grid. Typically, each anode film is from about 100  $\mu\text{m}$  to about 250  $\mu\text{m}$  in thickness, preferably about 110  $\mu\text{m}$  to about 200  $\mu\text{m}$ , and more preferably about 125  $\mu\text{m}$  to about 175  $\mu\text{m}$ .

The preferred anodes of the present invention are lithium intercalation anodes employing the carbon material of the present invention. The carbon material is obtained by polymerizing, either chemically or electrochemically, a vinyl monomer having a conjugated matrix. It is preferred that the conjugated matrix is comprised of an aromatic matrix. For example, such vinyl monomers can include 4-vinyl anisole, 9-vinyl anthracene, 4-vinyl biphenyl, vinyl toluene, 2-vinyl naphthalene, as well as styrene. Cyclohexalene ethylene is another appropriate vinyl monomer. In general, the vinyl monomers are very advantageous as they are easily polymerized due to the vinyl substituent. Such vinyl monomer polymerization is well known in the art. The process used to polymerize the monomers can be any of those that are well known in the art for vinyl monomer polymerization. A catalyst/oxidizing agent such as  $\text{FeCl}_3$ , for example, can be used to aid in the polymerization of the monomers.

Once the polymers have been obtained, the polymers are pyrolyzed to carbonize, at least partially, the polymer. The pyrolysis is generally conducted at a temperature in the range of from about 700° to 1100° C. more preferably 800° to 1000° C., and generally about 1000° C. The time required for the pyrolysis will depend upon the particular polymer being pyrolyzed and the degree of carbonization desired. In general, however, the length of time will range from 1 to 10 hrs. The amount of time used for the pyrolysis will generally be sufficient to achieve a partial carbonization of the polymer to form a carbon material which still exhibits some of the conjugated matrix as well as a high capacity (and conductivity).

In general, the vinyl monomer and polymer used to prepare the carbon of the present invention are non-conductive, which is directly contrary to the use of a conductive polymer such as poly-p-phenylene. Nonetheless, the pyrolyzed carbon material does exhibit conductivity. It is preferred, however, to add a conductive carbon such as carbon black or finely divided graphite to enhance the conductivity of the carbon material used to prepare the anode.

Once the carbon material has been obtained, the material can be formulated into an anode electrode as by any technique well known to the art. The carbon can be mixed with a binder and a plasticizer, for example, suitable for forming a bound porous composite having a molecular weight of from 1,000 to 5,000,000. Examples of suitable polymeric binders include EPDM (ethylene propylene diamene termonomer), PVDF (polyvinylidene difluoride), EAA (ethylene acrylic acid copolymer), EVA (ethylene vinyl acetate copolymer), EAA/EVA copolymers, a copolymer of PVDF and hexafluoropropylene, and the like. The anode preferably also includes an electron conducting material such as carbon black or graphite. This carbon mixture is then

coated onto a suitable current collector, such as a copper foil. The lithium can be intercalated into the carbon anode using techniques known to the art. For example, the technique described in U.S. Pat. No. 5,028,500 can be employed, which patent is herein specifically incorporated by reference. An example of such a technique can be described as follows.

A sheet of lithium metal is placed between a cathode and a separator so that the lithium sheet lies adjacent to, and in contact with, the anode. Preferably, the size of the lithium metal sheet is chosen so that the surface of the sheet is co-extensive with the surface of the anode, and the thickness of the sheet is chosen so that the correct amount of lithium is present for the intercalation reaction as discussed below.

The sandwich structure may further include an additional separator disposed on a cathode current collector. This sandwich structure may be wound around a metallic center post, thus forming the sandwich structure into a convoluted, spiral configuration. In this spiral configuration, the additional separator lies between the anode current collector of the sandwich structure on one turn of the spiral and the cathode current collector on the next adjacent turn, thus maintaining the anode and cathode electrically insulated from one another. The sandwich structure may be wound onto the center post under some tension, where tension facilitates the winding process. This tension may produce a compressive load between neighboring turns of the spiral structure. Compressive load between components in a cell is also referred to as "stack pressure". However, there is no need to apply any particular degree of stack pressure, and the winding tension may be entirely omitted.

The spiral assembly is then fitted into a cell casing and the cell casing is closed by a cell cap. The anode and cathode current collector are electrically connected by conventional means with cell casing and cap, respectively. Casing and cap are insulated from each other and serve as terminals for the finished cell.

An electrolyte, preferably including a lithium salt or other lithium-containing compound dispersed in a suitable organic solvent and comparable with both the cathode and anode materials, is added to the cell, typically through an opening in the cap which is subsequently sealed. Desirably, the electrolyte solvent is capable of wetting the separators and particulate materials. The electrolyte solvent preferably includes ester solvents, such as propylene carbonate (PC), ethylene carbonate (EC), or mixtures thereof. When the solvent comprises both PC and EC, the ratio of PC to EC, by volume is preferably about 1:3 to about 3:1, more preferably about 1:2 to 2:1, and even more preferably, about 1:1. Other solvents may be used such as 2-methyl tetrahydrofuran (2-MTHF), tetrahydrofuran, sulfolane, dimethylsulfite, monoglyme (1,2-dimethoxyethane), diglyme, triglyme, tetraglyme, p-dioxane, 1,3-dioxane, dimethoxymethane, diethylether and trimethoxyethane. Of the lower viscosity solvents, 2-MTHF is preferred. One useful electrolyte solvent includes about 75% 2-MTHF, 12.5% PC and 12.5% EC, all by volume. References in this disclosure to percentages of solvent ingredients by volume should be understood as referring to the volume of the individual ingredients prior to mixing. Suitable electrolyte salts include  $\text{LiAsF}_6$ ;  $\text{LiPF}_6$ ;  $\text{LiClO}_4$ ;  $\text{LiB}(\text{C}_6\text{H}_5)_4$ ;  $\text{LiCF}_3\text{F}$ ;  $\text{LiAlCl}_4$ ;  $\text{LiBr}$ ; and mixtures thereof. The less toxic salts are more preferred.

The addition of the electrolyte to the cell causes the lithium metal in the sheet to intercalate into the carbonaceous composition of the anode, as the lithium metal has a higher electrochemical potential than the anode. In effect,

the lithium sheet and anode constitute a temporary cell having a lithium electrode and a carbonaceous electrode. Because the sheet is electrically connected to the anode by the physical contact between these elements, this temporary cell is short-circuited. Accordingly, the temporary cell discharges, with lithium passing from the high-potential electrode (the sheet) to the lower potential electrode (anode). This lithiation process desirably is conducted at about room temperature (20° C.) or below. This initial lithiation process continues until the lithium metal in sheet is totally consumed by the carbon of anode in the formation of  $\text{Li}_x\text{C}_6$ , or until the anode has become saturated with lithium, whichever occurs first. Desirably, the amount of lithium in the sheet is equal to the amount of lithium required to saturate the anode, so that the lithium sheet is entirely consumed and the anode is fully saturated with lithium. Typical isotropic graphite compositions will take up between 0.5 and 1 mole of lithium for each 6 moles of carbon in the composition, i.e., isotropic graphite typically will intercalate Li up to a value of  $x$  between 0.5 and 1.0 in the formula  $\text{Li}_x\text{C}_6$ . The carbon black incorporated in the anode also will take up some lithium, typically up to about  $x=0.5$  in the formula  $\text{Li}_x\text{C}_6$ , i.e., 1 mole of Li for each 12 moles of carbon black.

Once the lithium sheet has been substantially consumed and the carbonaceous composition of the anode has been saturated by lithium, the cell is in a charged condition and ready for use. The cell can then be employed in a normal fashion. During discharge, the anode is electrically connected to the cathode via an external electrical load. During discharge, lithium passes from the anode through the electrolyte into the electrochemically active material of the cathode, where the lithium is then intercalated into the cathode material. During recharge, the process is reversed under the influence of an externally applied potential so that lithium is withdrawn from the cathode material and reintercalated into the carbonaceous composition of the anode.

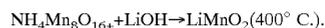
The anode of the present invention, using a carbon obtained from the pyrolyzation of a conjugated vinyl monomer polymer, provides advantages with regard to economics and high capacity. The economic advantages are realized due to the ease of polymerization of the vinyl monomer. Advantages are also realized due to the less toxic compounds involved in the preparation of the carbon material as compared to the carbon material obtained from the pyrolyzation of, for example, poly(*p*-phenylene). The potential capacity of the carbon based anodes of the present invention are also believed to be quite high, as high as 600 mAh/g or greater.

The cathode used in the electrochemical devices of the present invention generally comprises a cathode film that is laminated onto one or both sides of a cathode current collector, which is a thin metal foil or grid. Typically, each cathode film is from about 100  $\mu\text{m}$  to about 200  $\mu\text{m}$  in thickness, preferably about 130  $\mu\text{m}$  to about 175  $\mu\text{m}$ , and more preferably about 140  $\mu\text{m}$  to about 165  $\mu\text{m}$ .

The cathode typically comprises a compatible cathodic material (i.e., insertion compounds) which is any material which functions as a positive pole in a solid electrolytic cell. The cathode can include a mixture of cathodic material(s). Suitable cathodic materials may include, by way of example, transition metal oxides, sulfides, and solenides, including lithiated compounds thereof. Representative materials include cobalt oxides, manganese oxides, molybdenum oxides, vanadium oxides, sulfides of titanium, molybdenum and niobium, the various chromium oxides, copper oxides, lithiated cobalt oxides, e.g.,  $\text{LiCoO}_2$  and  $\text{LiCoVO}_4$ , lithiated manganese oxides, e.g.,  $\text{LiMn}_2\text{O}_4$ , lithiated nickel oxides,

e.g.,  $\text{LiNiO}_2$  and  $\text{LiNiVO}_4$ , and mixtures thereof. Cathode-active material blends of  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) is described in U.S. Pat. 5,429,890 which is incorporated herein. The blends can include  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) and at least one lithiated metal oxide selected from  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  wherein  $0 < x \leq 2$ . Blends can also include  $\text{Li}_y\alpha\text{-MnO}_2$  ( $0 \leq y < 1$ ) which is  $\text{Li}_y\text{NH}_4\text{Mn}_8\text{O}_{16}$  ( $0 \leq y < 1$ ) which has a hollandite-type structure.  $\text{Li}_y\alpha\text{-MnO}_2$  where  $0 \leq y < 0.5$  is preferred.  $\alpha\text{MnO}_2$  can be synthesized by precipitation from a reaction between a  $\text{MnSO}_4$  solution and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidizing agent.

Lithiation (also referred to as "prelithiation") of  $\alpha\text{MnO}_2$  can be accomplished via a solid state reaction:



$\text{Li}\alpha\text{-MnO}_2$  retains the same structure as Hollandite. See, Botkovitz et. al., J. of Power Sources, 4344 (1993) 657-665, which is incorporated herein, for a discussion of the structure and electrochemical characteristics of  $\text{Li}\alpha\text{-MnO}_2$ .  $\text{Li}_y\alpha\text{-MnO}_2$   $0 \leq y < 0.5$  is commercially available from SEDEMA, Tertre, Belgium.

In a preferred embodiment, a cathodic material is mixed with an electroconductive material including, by way of example, graphite, powdered carbon, powdered nickel, metal particles, conductive polymers (i.e., characterized by a conjugate network of double bonds like polypyrrole and polyacetylene), and the like, and a polymeric binder to form under pressure a positive cathodic plate. Suitable binders for use in the cathode have a molecular weight of from about 1,000 to 5,000,000.

In one preferred embodiment, the cathode is prepared from a cathode paste which comprises from about 35 to 65 weight percent of a compatible cathodic material; from about 1 to 20 weight percent of an electroconductive agent; from about 1 to 20 weight percent of suitable polymeric binders that may include EPDM (ethylene propylene diene termonomer), PVDF (polyvinylidene difluoride), EAA (ethylene acrylic acid copolymer), EVA (ethylene vinyl acetate copolymer), EAA/EVA copolymers, and the like; from about 0 to about 20 weight percent of polyethylene oxide having a number average molecular weight of at least 100,000; from about 10 to 50 weight percent of solvent comprising a 10:1 to 1:4 (w/w) mixture of an organic carbonate and a glyme; and from about 5 weight percent to about 25 weight percent of a solid matrix forming monomer or partial polymer thereof. Also included is an ion conducting amount of an inorganic ion salt. Generally, the amount of the salt is from about 1 to about 25 weight percent. (All weight percents are based on the total weight of the cathode.)

The current collector used in the anode of the present invention and the cathode preferably comprises, for example, a screen, grid, expanded metal, woven or non-woven fabric, or knitted wire formed from an electron conductive material such as metals or alloys. Particularly preferred current collectors comprise perforated metal foils or sheets. Preferably, the current collector has a thickness from about 25  $\mu\text{m}$  to about 75  $\mu\text{m}$ , preferably about 35  $\mu\text{m}$  to about 65  $\mu\text{m}$ , and more preferably about 45  $\mu\text{m}$  to about 55  $\mu\text{m}$ . In order to minimize the weight of the electrochemical cell, thin current collectors are preferred. It is expected that a current collector having a thickness of about 12.5  $\mu\text{m}$  can be employed. Each current collector is also connected to a current collector tab which extends from the edge of the current collector. The current collector tab is integral to the current collector. By integral is meant that the body of the current collector and tab form a unit, that is, they are not separate members that are attached (e.g., welded) together.

In batteries comprising multiple electrochemical cells, the anode tabs are preferably welded together and connected to a nickel lead. The cathode tabs are similarly welded and connected to a lead. External loads can be electrically connected to the leads. Current collectors and tabs are described in U.S. Pat. Nos. 4,925,752, 5,011,501, and 5,326,653, which are incorporated herein.

In further describing the present invention, particularly as it relates to electrochemical cells, the following terms are defined for purposes of the subject invention.

The term "plasticizer" refers to an organic solvent, with limited solubility of polymers, that facilitates the formation of porous polymeric structures. By "porous structure" is meant that upon extraction of the plasticizer the polymer remains as a porous mass. Suitable plasticizers have high boiling points typically from about 100° C. to about 350° C. A number of criteria are important in the choice of a plasticizer including compatibility with the components of the electrochemical cell precursor, processability, low polymer solubility and extractability, liquid solvents, e.g., diethyl ether, or dense gases for example. Preferred plasticizers include, for example, dibutyl phthalate, dioctylphthalate, and acetates, glymes, and low molecular weight polymers.

In operation, the plasticizer is first well mixed with a polymer. Thereafter the plasticizer is removed by extraction and in the process the porous structure is formed. Preferably the weight ratio of plasticizer to polymer is from about 1 to about 50, more preferably about 10 to about 30, and most preferably about 20 to about 25.

The term "electrochemical cell precursor" or "electrolytic cell precursor" refers to the structure of the electrochemical cell prior to the addition of the inorganic salt and electrolyte solution. The precursor typically comprises (each in precursor form) an anode, a cathode, and a polymeric matrix, which can be a solid polymeric matrix. The anode and/or cathode may each include a current collector. The polymeric matrix can function as a separator between the anode and cathode.

The term "activation" refers to the placement of an inorganic salt and electrolyte solvent into the porous portions of an electrochemical cell precursor. After activation, the electrochemical cell is charged by an external energy source prior to use.

The term "electrolytic cell" or "electrochemical cell" refers to a composite containing an anode, a cathode and polymeric layer comprising an electrolyte solution interposed therebetween.

The term "battery" refers to two or more electrochemical cells electrically interconnected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels.

The term "solid polymeric matrix" refers to an electrolyte compatible material formed by polymerizing an inorganic or organic monomer (or partial polymer thereof) and which, when used in combination with the other components of the electrolyte, renders the electrolyte solid. Suitable solid polymeric matrices are well known in the art and include solid matrices formed from inorganic polymers, organic polymers or a mixture of organic polymers with inorganic non-polymeric materials. Preferably, the solid polymeric matrix is an organic matrix derived from a solid matrix forming monomer and from partial polymers of a solid matrix forming monomer. See, for example, U.S. Pat. 4,925,751, which is incorporated herein.

Alternatively, the solid polymeric matrix can be used in combination with a non-polymeric inorganic matrix. See, for example, U.S. Pat. No. 4,990,413, which is incorporated

herein by reference in its entirety. Suitable non-polymeric inorganic materials for use in conjunction with the solid polymeric matrix include, by way of example,  $\beta$ -alumina, silver oxide, lithium iodide, and the like. Suitable inorganic monomers are also disclosed in U.S. Pat. Nos. 4,247,499, 4,388,385, 4,414,607, 4,394,280, 4,432,891, 4,539,276, and 4,557,985, each of which is incorporated herein by reference.

The term "a solid matrix forming monomer" refers to inorganic or organic materials which in monomeric form can be polymerized, preferably the presence of an inorganic ion salt, and a solvent mixture of an organic carbonate and a glyme compound, to form solid matrices which are suitable for use as solid electrolytes in electrolytic cells. Suitable solid matrix forming monomers are well known in the art and the particular monomer employed is not critical. The solid matrix forming monomers may also comprise heteroatoms capable of forming donor acceptor bonds with inorganic cations (e.g., alkali ions).

Examples of suitable organic solid matrix forming monomers include, by way of example, propylene oxide, ethyleneimine, ethylene oxide, epichlorohydrin, acryloyl-derivatized polyalkylene oxides (as disclosed in U.S. Pat. No. 4,908,283), urethane acrylate, vinyl sulfonate polyalkylene oxides (as disclosed in U.S. Pat. No. 5,262,253, which patent is incorporated herein by reference in its entirety), and the like as well as mixtures thereof. Examples of suitable inorganic solid matrix forming monomers include, by way of example, phosphazenes and siloxanes. Phosphazene monomers and the resulting polyphosphazene solid matrix are disclosed, for example, by Abraham et al., Proc. Int. Power Sources Symp., 34th. pp. 81-83 (1990) and by Abraham et al., J. Electrochemical Society, Vol. 138, No. 4, pp. 921-927 (1991).

The term "a partial polymer of a solid matrix forming monomer" refers to solid matrix forming monomers which have been partially polymerized to form reactive oligomers. Partial polymerization may be conducted for the purpose of enhancing the viscosity of the monomer, decreasing the volatility of the monomer, and the like. Partial polymerization is generally permitted so long as the resulting partial polymer can be further polymerized, preferably in the presence of a solvent, such as, a mixture of organic carbonate(s) to form solid polymeric matrices which are suitable for use as solid electrolytes in electrolytic cells.

The term "cured" or "cured product" refers to the treatment of the solid matrix forming monomer or partial polymer thereof under polymerization conditions (including cross-linking) so as to form a solid polymeric matrix. Suitable polymerization conditions are well known in the art and include by way of example, heating the monomer, irradiating the monomer with UV light, electron beams, and the like. The resulting cured product preferably contains repeating units containing at least one heteroatom such as oxygen or nitrogen which is capable of forming donor acceptor bonds with inorganic cations (alkali ions). Examples of suitable cured products suitable for use in this invention are set forth in U.S. Pat. Nos. 4,830,939 and 4,990,413 which are incorporated herein by reference in their entirety.

The solid matrix forming monomer or partial polymer can be cured or further cured prior to or after addition of the salt, solvent and, optionally, a viscosifier. For example, a composition comprising requisite amounts of the monomer or partial polymer, salt, organic carbonate solvent and viscosifier can be applied to a substrate and then cured. Alternatively, the monomer or partial polymer can be first

cured and then dissolved in a suitable volatile solvent. Requisite amounts of the salt, organic carbonate solvent and viscosifier can be added. The mixture is then placed on a substrate and cured; removal of the volatile solvent would result in the formation of a solid electrolyte. In either case, the resulting solid electrolyte would be a homogeneous, single phase product which is maintained upon curing, and does not readily separate upon cooling to temperatures below room temperature.

Alternatively, the solid polymeric matrix can be formed by a casting process which does not require the use of monomers or prepolymers, that is, no curing is required. A preferred method employs a copolymer of polyvinylidene difluoride and hexafluoropropylene dissolved in acetone or other suitable solvent(s). Upon casting the solution, the solvent is evaporated to form the solid polymeric matrix. The solution may be casted directly onto a current collector. Alternatively, the solution is cast onto a substrate, such as a carrier web, and after the solvent (e.g., acetone) is removed, an electrode film is formed thereon.

The term "salt" refers to any salt, for example, an inorganic salt, which is suitable for use in a non-aqueous electrolyte. Representative examples of suitable inorganic ion salts are alkali metal salts of less mobile anions of weak bases having a large anionic radius. Examples of such anions are  $\Gamma^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{CF}_3\text{COO}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ , and the like. Specific examples of suitable inorganic ion salts include  $\text{LiClO}_4$ ,  $\text{LiSCN}$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiPF}_6$ ,  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ ,  $(\text{CF}_3\text{SO}_2)_3\text{CLi}$ ,  $\text{NaSCN}$ , and the like. The inorganic ion salt preferably contains at least one cation selected from the group consisting of Li, Na, Cs, Rb, Ag, Cu, Mg and K.

The electrolyte typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte, preferably, from about 10 to 20 weight percent, and even more preferably about 10 to about 15 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed.

The term "compatible electrolyte solvent" or "electrolytic solvent," or in the context of components of the non-aqueous electrolyte, just "solvent," is a low molecular weight organic solvent added to the electrolyte and/or the cathode composition, which may also serve the purpose of solvating the inorganic ion salt. The solvent is any compatible, relatively non-volatile, aprotic, relatively polar, solvent. Preferably, these materials have boiling points greater than about 85° C. to simplify manufacture and increase the life of the electrolyte/battery. Organic carbonates are preferred solvents. Typical examples of suitable solvents are mixtures of such materials as dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, methyl ethyl carbonate, gamma-butyrolactone, triglyme, tetraglyme, dimethylsulfoxide, dioxolane, sulfolane, and the like. When using propylene carbonate based electrolytes in an electrolytic cell with graphite anodes, a sequestering agent, such as a crown ether, is added in the electrolyte.

The term "organic carbonates" refers to hydrocarbon carbonate compounds of no more than about 12 carbon atoms and which do not contain any hydroxyl groups. Preferably, the organic carbonate is an aliphatic carbonate and more preferably a cyclic aliphatic carbonate.

Suitable cyclic aliphatic carbonates for use in this invention include 1,3-dioxolan-2-one (ethylene carbonate); 4-methyl-1,3-dioxolan-2-one (propylene carbonate); 4,5-dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one; 4-methyl-5-ethyl-1,3-dioxolan-2-one; 4,5-diethyl-1,3-dioxolan-2-one; 4,4-

diethyl-1,3-dioxolan-2-one- 1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one; 5,5-dimethyl-1,3-dioxolan-2-one; 5-methyl-1,3-dioxolan-2-one; 4-methyl-1,3-dioxolan-2-one; 5,5-diethyl-1,3-dioxolan-2-one; 4,6-dimethyl-1,3-dioxolan-2-one; 4,4,6-trimethyl-1,3-dioxolan-2-one; and spiro (1,3-oxa-2-cyclohexanone-5',5',1',3'-oxa-2'-cyclohexanone).

Several of these cyclic aliphatic carbonates are commercially available such as propylene carbonate and ethylene carbonate. Alternatively, the cyclic aliphatic carbonates can be readily prepared by well known reactions. For example, reaction of phosgene with a suitable alkane- $\alpha,\beta$ -diol (dihydroxy alkanes having hydroxyl substituents on adjacent carbon atoms) or an alkane- $\alpha,\gamma$ -diol (dihydroxy alkanes having hydroxyl substituents on carbon atoms in a 1,3 relationship) yields a cyclic aliphatic carbonate for use within the scope of this invention. See, for instance, U.S. Pat. No. 4,115,206, which is incorporated herein by reference in its entirety.

Likewise, the cyclic aliphatic carbonates useful for this invention may be prepared by transesterification of a suitable alkane- $\alpha,\beta$ -diol or an alkane- $\alpha,\gamma$ -diol with, e.g., diethyl carbonate under transesterification conditions. See, for instance, U.S. Pat. Nos. 4,384,115 and 4,423,205 which are incorporated herein by reference in their entirety. Additional suitable cyclic aliphatic carbonates are disclosed in U.S. Pat. No. 4,747,850 which is also incorporated herein by reference in its entirety.

The term "viscosifier" refers to a suitable viscosifier for solid electrolytes. Viscosifiers include conventional viscosifiers such as those known to one of ordinary skill in the art. Suitable viscosifiers include film forming agents well known in the art which include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a number average molecular weight of at least about 100,000, polyvinylpyrrolidone, carboxymethylcellulose, and the like. Preferably, the viscosifier is employed in an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

The electrolyte composition typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably from about 10 to about 1.5 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed.

The electrolyte composition typically comprises from 0 to about 80 weight percent electrolyte solvent based on the total weight of the electrolyte; preferably from about 60 to about 80 weight percent; and even more preferably about 70 weight percent.

The electrolyte composition typically comprises from about 5 to about 30 weight percent of the solid polymeric matrix based on the total weight of the electrolyte; preferably from about 15 to about 25 weight percent.

In a preferred embodiment, the electrolyte composition further comprises a small amount of a film forming agent. Suitable film forming agents are well known in the art and include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a number average molecular weight of at least about 100,000. Preferably, the film forming agent is employed in an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

Electrochemical cells are known in the art. See, for example, U.S. Pat. Nos. 5,300,373, 5,316,556, 5,346,385, 5,262,253, 4,472,487, 4,668,595, and 5,028,500, all of which are incorporated herein. The inventive anode active material can be adapted to form anode structures in prior art electrochemical cells.

The invention will be described using anode and cathode structures wherein films (i.e., electrode materials) are laminated on both surfaces of the current collectors, however, it is understood that the invention is applicable to other configurations, for instance, where only one surface of the anode and/or cathode current collector is laminated.

#### EXAMPLE 1

An anode current collector can be employed which is a sheet of expanded copper metal that is about 50  $\mu\text{m}$  thick. It is available under the designation 2Cu5-125 (flatten) from Delker, Corp. in Branford, Conn. The anode slurry can be prepared as follows:

A polymer mixture comprising a copolymer of polyvinylidene difluoride (PVDF) and hexafluoropropylene (HFP) may be prepared by mixing 6.8 grams of the copolymer in 20 grams of acetone. The copolymer (ave. MW 125K) can be Kynar Flex 2801<sup>TM</sup> from Elf Atochem North America, in Philadelphia, Pa. The mixture may be stirred for about 24 hours in a milling jar available from VWR Scientific, in San Francisco, Calif., model H-04172-00. The copolymer can function as a binder for the carbon in the anode.

A mixture of carbon obtained by pyrolyzing at 1000° C. polymerized 4-vinyl biphenyl can be prepared separately. For example, 23.4 grams of the carbon can be mixed with 0.9 grams of carbon black into a solution containing 60 grams acetone, and 10.5 grams dibutyl phthalate. A preferred carbon black is available under the designation Super P<sup>TM</sup> from M.M.M. Carbon, Willebroek, Belgium. The carbon mixture is then vigorously mixed in a high shear mixer until a substantially homogeneous blend is formed. A suitable mixer is available from Ross Model ME100DLX, Hauppauge, N.Y., operating at its highest setting (about 10,000 RPM) for 30 minutes. Optionally, a surfactant can be added to the carbon mixture to facilitate dispersion of the carbon. Preferred surfactants include Pluronic FC68<sup>TM</sup> from BASF, Mt. Olive, N.J. and Flurad 430<sup>TM</sup> from 3M Co., St. Paul, Minn.

The anode slurry can then be prepared by mixing the polymer mixture and the carbon mixture together under low shear conditions to form the anode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it was laminated onto the current collector. Anode films form when the remaining portion of the acetone evaporates.

#### EXAMPLE 2

A cathode current collector can be employed which is a sheet of expanded aluminum that is about 50  $\mu\text{m}$  thick. The aluminum grid is available under the designation 2AL5-077 from Delker. The cathode slurry can be prepared as follows:

A polymer mixture comprising a copolymer of polyvinylidene difluoride (PVDF) and hexafluoropropylene (HFP) can be prepared by mixing 4.4 grams of the copolymer in 15 ml of acetone. The copolymer may be Kynar Flex 280<sup>TM</sup>. The mixture can be stirred for about 24 hours in a milling jar.

A cathode mixture can be prepared separately by first adding 28.9 grams of LiMnO<sub>2</sub> or an appropriate amount of some other lithated cathodic material), and 2-4 grams of

carbon black (Super P) into a solution containing 60 grams acetone, and 8.7 grams dibutyl phthalate. The mixture may then be vigorously mixed in the a high shear mixer until a substantially homogeneous blend is formed. Optionally, a surfactant can be added to facilitate dispersion.

The cathode slurry may be prepared by mixing the polymer mixture and the cathode mixture together under low shear conditions to form the cathode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it is laminated onto the current collector. Cathode films form when the remaining portion of the acetone evaporates.

The above anode and cathode films can be formed directly on the current collector by laminating the slurry mixtures onto the current collector surfaces. Alternatively, each film can be prepared by first casting a slurry onto a substrate or carrier web and allowing the solvent to evaporate, thus leaving the film. Thereafter, the films can be laminated onto each side of the metal sheet.

#### EXAMPLE 3

A solid electrochemical cell may be prepared by first positioning a polymeric matrix between the anode and cathode and thereafter fusing the structures under moderate pressure and temperature (e.g., 130° C.) to form an electrochemical cell precursor. The pressure and temperature will depend on the polymer(s) forming the polymer matrix. The polymeric matrix may be formed by casting a polymeric slurry comprising acetone, dibutyl phthalate, silanized fumed SiO<sub>2</sub>, and the PVDF/HFP copolymer on a suitable substrate or carrier web and allowing the acetone to evaporate. No curing by radiation is required. The SiO<sub>2</sub> is a filler which imparts toughness and strength to the film. In addition, it is believed that the SiO<sub>2</sub> assists the activation process by creating physico-chemical conditions such that the electrolyte solution quickly and completely fills the pores created by the extraction of the dibutyl phthalate. Preferably, the polymeric slurry is mixed under low shear conditions as not to degrade the copolymer.

It is preferred that in preparing the polymer mixture for both the anode and cathode slurries the polymer (or copolymer) not be subject to high shear so as to be degraded. Furthermore, it is preferred the polymer or copolymer employed has a high average molecular weight. Preferably the average molecular weight is between 50K to 750K, more preferably 50K to 200K, and most preferably 50K to 120K. Furthermore, it is preferred that the polymer or copolymer has a narrow molecular weight range; preferably

$$\frac{M_n}{M_w} = 1.0$$

Next the dibutyl phthalate plasticizer is extracted from the precursor. Extraction can be accomplished using conventional organic liquid solvents such as diethyl ether or by supercritical fluids which includes, for example, a gas compressed and heated to either supercritical or supercritical conditions to achieve liquid-like densities. Supercritical fluids are known in the art. See, for example, U.S. Pat. Nos. 5,013,366, 5,267,455, 4,219,333, 4,012,194, and 3,969,196, which are incorporated herein. A preferred supercritical fluid is carbon dioxide. The precursor is than pre-packaged in moisture-impermeable material which is described, for example, in U.S. Pat. No. 5,326,653 which is incorporated herein, before being activated. Activation preferably occurs in an inert (e.g., argon) atmosphere. Finally, the packaging of the electrochemical cell is sealed.

This example demonstrates electrochemically polymerizing 4-vinyl biphenyl, with subsequent pyrolysis to form a carbon useful as an anode in accordance with the present invention. A solution of 0.2 molar 4-vinyl biphenyl, 0.1 molar tetrabutylammonium PF<sub>6</sub> (an electrolyte salt) in acetonitrile (an electrolyte solvent) is prepared and placed in a cell. The cell also contains positive and negative nickel electrodes. Ten mA/cm<sup>2</sup> current is applied with rapid polymerization of the monomer occurring at the positive electrode (the cathode). The mechanism relies upon anodic extraction of a hydrogen from the monomer.

After the polymerization is complete, the polymer is removed from the solution by means of filtration. The polymer can then be pyrolyzed at a temperature of about 1,000° C. to carbonize (partially) the polymer. The carbon product can then be formulated into an anode electrode by mixing the carbon with a conductive carbon such as carbon black and a binder, forming a slurry and coating the slurry on a current collector such as a copper foil. The anode can then be intercalated with a lithium.

While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate the various modifications, substitutions, and changes which may be made without departing from the spirit hereof. The descriptions of the subject matter in this disclosure are illustrative of the invention and are not intended to be construed as limitations upon the scope of the invention.

What is claimed is:

1. A process for preparing a composite anode comprising mixing a binder with a carbon material which is obtained by pyrolyzing a polymer of a conjugated vinyl monomer.

2. The process of claim 1, wherein the composite anode comprises a conductive carbon.

3. The process of claim 2, wherein the polymer is non-conductive.

4. The process of claim 2, wherein the binder comprises ethylene propylene diamine termonomer, polyvinylidene difluoride, ethylene acrylic acid copolymer, ethylene vinyl acetate copolymer, ethylene acrylic acid/ethylene vinyl acetate copolymers, a copolymer of polyvinylidene difluoride and hexafluoropropylene or mixtures thereof.

5. The process of claim 1, wherein pyrolyzing the polymer comprises heating the polymer to a temperature in the range of about 700° C. to 1100° C.

6. The process of claim 1, wherein composite anode has a specific capacity of at least 600 mAh/g.

7. The process of claim 1, wherein the polymer of the conjugated vinyl monomer is a polymer comprised of polymerized 4-vinyl anisole, 9-vinyl anthracene, 4-vinyl biphenyl, vinyl toluene, 2-vinyl naphthalene, or styrene.

8. The process of claim 7, wherein the polymer from which the carbon material is obtained is polymerized 4-vinyl biphenyl.

9. A process for preparing a secondary electrochemical cell which comprises the steps of:

providing a cathode;

providing an anode which comprises a carbon material obtained by pyrolyzing a polymer of a conjugated vinyl monomer; and

positioning an electrolyte comprising a solvent, inorganic salt, and polymeric matrix between the cathode and anode.

10. The process of claim 9, wherein the anode comprises a conductive carbon and a binder.

11. The process of claim 10, wherein the conductive carbon is carbon black.

12. The process of claim 10, wherein the binder of the anodic material is comprised of ethylene propylene diamine termonomer, polyvinylidene difluoride, ethylene acrylic acid copolymer, ethylene vinyl acetate copolymer, ethylene acrylic acid/ethylene vinyl acetate copolymers, a copolymer of polyvinylidene difluoride and hexafluoropropylene or mixtures thereof.

13. The process of claim 9, wherein pyrolyzing the polymer comprises heating the polymer to a temperature in the range of about 700° C. to 1100° C.

14. The process of claim 9, wherein the anode has specific capacity of at least 600 mAh/g.

15. The process of claim 9, wherein the polymer from which the carbon is obtained comprises a polymer of 4-vinyl anisole, 9-vinyl anthracene, 4-vinyl biphenyl, vinyl toluene, 2-vinyl naphthalene or styrene.

16. The process of claim 9, wherein the anode is intercalated with lithium.

17. The process of claim 9, wherein the polymer is non-conductive.

18. The process of claim 9, wherein the polymer from which the carbon is obtained is 4-vinyl biphenyl.

19. The process of claim 9, wherein the cathode comprises material that is selected from the group consisting of lithiated manganese oxide, lithiated nickel oxide, lithiated cobalt oxide, and mixtures thereof.

20. The process of claim 9, wherein the cathode comprises LiMn<sub>2</sub>O<sub>4</sub>.

\* \* \* \* \*



US005882621A

**United States Patent** [19]  
**Doddapaneni et al.**

[11] **Patent Number:** **5,882,621**  
[45] **Date of Patent:** **Mar. 16, 1999**

[54] **METHOD OF PREPARATION OF CARBON MATERIALS FOR USE AS ELECTRODES IN RECHARGEABLE BATTERIES**

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[73] Assignee: **Sandia Corporation**, Albuquerque, N. Mex.

[21] Appl. No.: **853,971**

[22] Filed: **May 9, 1997**

**Related U.S. Application Data**

[63] Continuation of Ser. No. 568,844, Dec. 7, 1995, abandoned.

[51] **Int. Cl.**<sup>6</sup> ..... **H01M 4/04**

[52] **U.S. Cl.** ..... **423/445 R**; 264/29.7; 423/447.6; 429/218

[58] **Field of Search** ..... 264/29.7; 423/445 R, 423/447.6; 429/218

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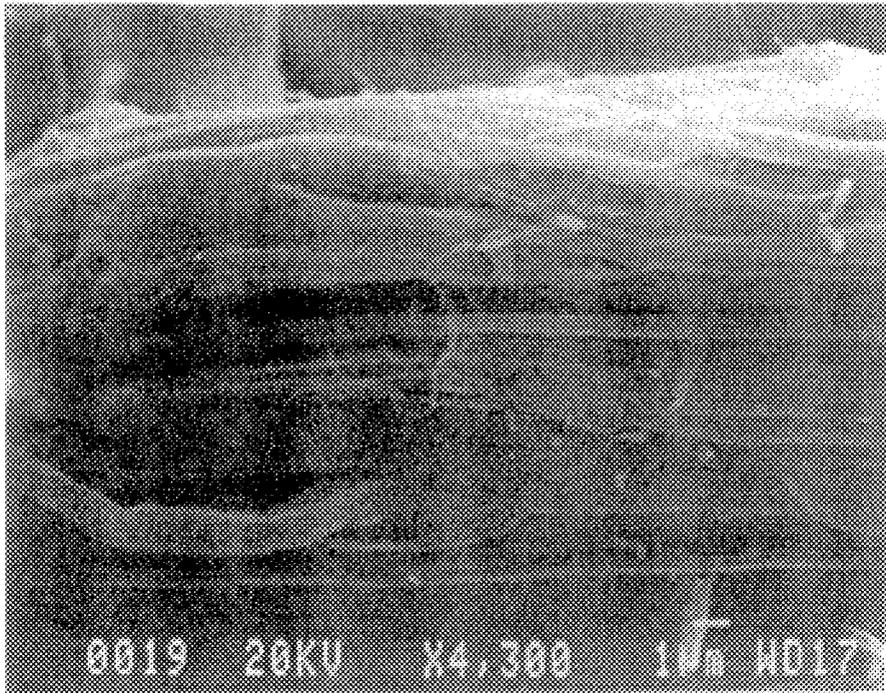
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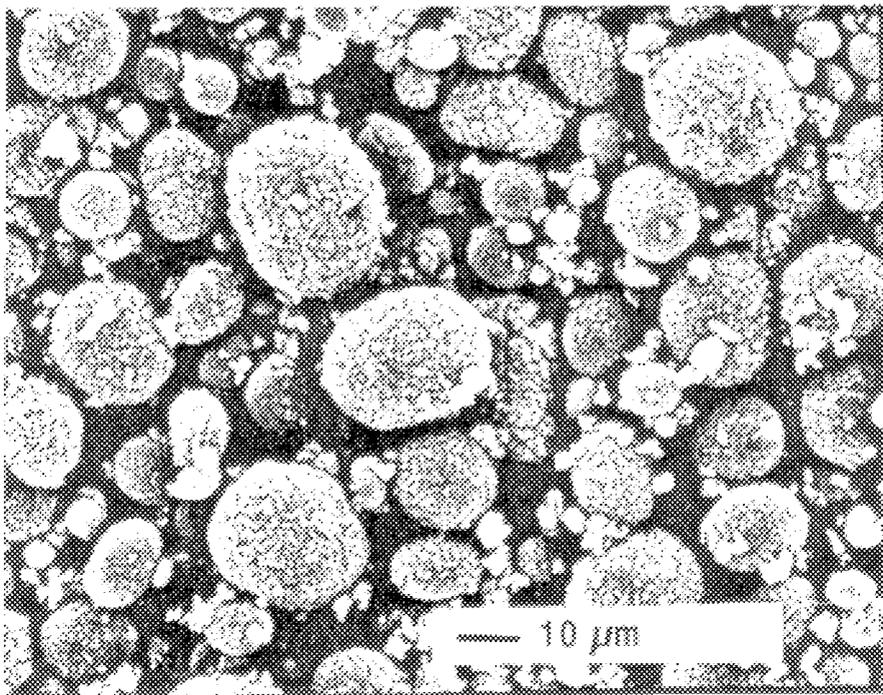
[57] **ABSTRACT**

A method of producing carbon materials for use as electrodes in rechargeable batteries. Electrodes prepared from these carbon materials exhibit intercalation efficiencies of ≈80% for lithium, low irreversible loss of lithium, long cycle life, are capable of sustaining a high rates of discharge and are cheap and easy to manufacture. The method comprises a novel two-step stabilization process in which polymeric precursor materials are stabilized by first heating in an inert atmosphere and subsequently heating in air. During the stabilization process, the polymeric precursor material can be agitated to reduce particle fusion and promote mass transfer of oxygen and water vapor. The stabilized, polymeric precursor materials can then be converted to a synthetic carbon, suitable for fabricating electrodes for use in rechargeable batteries, by heating to a high temperature in a flowing inert atmosphere.

**16 Claims, 2 Drawing Sheets**



*FIG. 1*



*FIG. 2*

FIG. 3

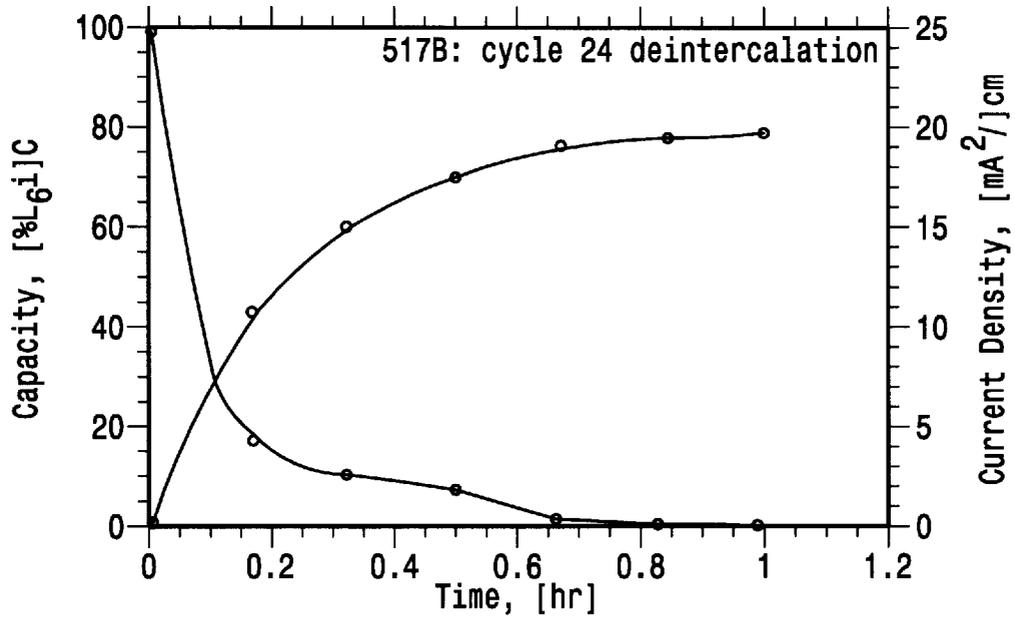
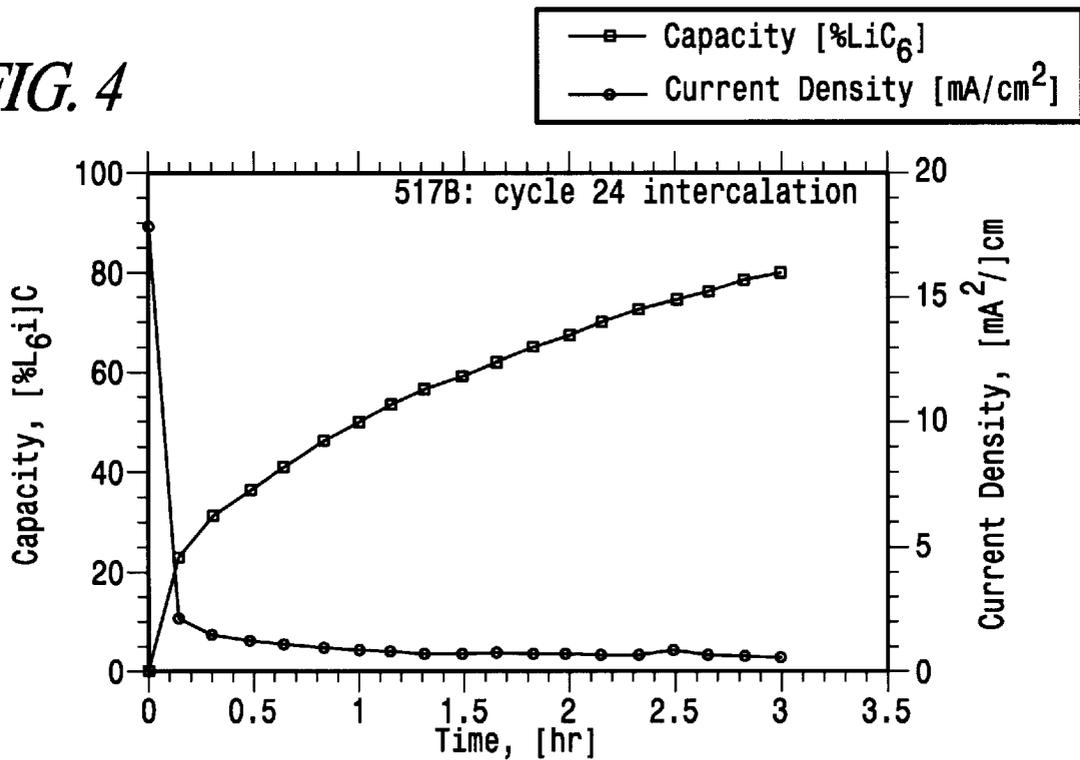


FIG. 4



## METHOD OF PREPARATION OF CARBON MATERIALS FOR USE AS ELECTRODES IN RECHARGEABLE BATTERIES

This application is a continuation of application Ser. No. 08/568,844, filed Dec. 7, 1995, now abandoned.

### STATEMENT OF GOVERNMENT INTEREST

The government has rights in this invention pursuant to contract no. DE-AC04-94AL8500 between the U.S. Department of Energy and Sandia Corporation.

### BACKGROUND OF THE INVENTION

The present invention relates generally to the preparation of carbon materials for use as electrodes in rechargeable batteries and more particularly to methods of treating polymeric precursor powders and fibers and producing carbon materials for use as anode materials in rechargeable lithium batteries having improved performance.

A majority of the research aimed at development of rechargeable batteries that exhibit improved performance characteristics, such as increased cycle life and energy and power densities, has focused on the development of lithium rechargeable batteries because they provide significant advantages in performance characteristics when compared to other battery systems. Of particular interest, has been the development of lithium anodes for secondary battery applications.

Rechargeable lithium battery cells that utilize lithium metal as an anode material have not gained widespread use due to limitations in cell performance resulting from extensive dendrite formation leading to cell shorting and inefficient electrochemical deposition of lithium on charging, coupled with safety problems inherent in the use of lithium metal, which is highly reactive. As disclosed by Murakami et al. in U.S. Pat. No. 4,749,514, many of these problems can be overcome by incorporating lithium into a graphitic carbon structure. This process, known as intercalation, involves insertion of lithium metal atoms along the c-axis of graphite to form a charge transfer compound, wherein the lithium atom appears to donate an electron to the graphite/carbon host binding the lithium to the graphite/carbon host by electrostatic attraction. By incorporating lithium into a graphite/carbon host in this fashion the chemical reactivity of the lithium is reduced, overcoming problems associated with the use of metallic lithium.

Carbon in various physical forms (foams, powders, fibers) and states of aggregation (films, monolithic pieces, pressed powders/fibers) has been used for many years as an electrode material in batteries. The synthesis of carbonaceous materials for lithium intercalation anodes has been extensively described. These syntheses generally involve the controlled pyrolysis of an organic precursor material such as benzene (Mohri et al., U.S. Pat. No. 4,863,814; Yoshimoto et al., U.S. Pat. No. 4,863,818 and Yoshimoto et al., U.S. Pat. No. 4,968,527), selected furan resins (Nishi et al., U.S. Pat. No. 4,959,281), thin films of poly(phenylene oxadiazole) (Murakami et al., U.S. Pat. No. 4,749,514), various carbonizable organic compounds such as condensed polycyclic hydrocarbons and polycyclic heterocyclic compounds, novalac resins and polyphenylene and poly(substituted) phenylenes (Miyabayashi et al., U.S. Pat. No. 4,725,422; Hirasuka et al., U.S. Pat. No. 4,702,977).

By way of example, Arnold et al., U.S. Pat. No. 4,832,881 and Simandl et al., U.S. Pat. No. 5,208,003, describe carbon materials in the form of foams, aerogels and microcellular

carbons which are useful as anode materials for high energy density batteries. While these carbon materials represent an improvement over conventional carbon powder for use as anodes, they have several disadvantages. Methods used to prepare these carbon materials require elaborate processing steps to prepare their precursor materials; among other things, solvents used to prepare the precursor materials must be completely removed from the precursor materials prior to the carbonization step. In order not to disrupt the microstructure of the precursor material the solvent removal step must be done under carefully controlled conditions using, for example, freeze drying or supercritical extraction. Furthermore, the solvents must either be disposed of or purified if they are to be reused. In addition, before the carbonized product produced by these processes can be used, additional fabrication steps, such as machining, must be employed.

For the reasons set forth above, there has been a particular interest in developing carbon materials that will reversibly intercalate and deintercalate lithium. However, many of the carbon-based systems initially developed were not able to provide high cycle life due to limitations of the graphite/carbon electrode material, e.g., exfoliation during cycling and/or reaction with the solvent. Further work has led to development of carbon materials that are able to cycle well, and battery cells utilizing these materials are commercially available. However, these carbons are typically monolithic materials, having high surface areas, which limit their usefulness, particularly for secondary battery applications. Furthermore, they are difficult and expensive to manufacture.

In addition to new carbon electrode materials that are more compatible with lithium, there have been numerous efforts to improve the intercalation efficiency of carbon materials useful for lithium intercalation electrodes. One solution is described in Yoshino et al, in U.S. Pat. No. 4,668,595, wherein doping of a wide variety of carbons formed from carbon powders, carbon blacks and carbonized polymeric fibers is disclosed. Azuma et al., U.S. Pat. No. 5,093,216 disclose incorporation of phosphorous into carbonized materials to improve intercalation efficiency and Mayer et al., in U.S. Pat. No. 5,358,802, disclose doping carbon foams with dopants such as phosphorous, boron, arsenic and antimony to improve intercalation efficiency. However, these carbon materials showed poor cycle life and one problem that still remains to be overcome is the irreversible loss of lithium that takes place during initial cycling of these carbon material as an electrode in a battery environment. The irreversible losses of lithium from the carbon electrode materials can result in the loss of 30 to 60% of the initial battery capacity.

What is required is a carbon material that can be fabricated into electrodes for lithium secondary batteries that exhibits high intercalation efficiencies for lithium, low irreversible loss of lithium, long cycle life, is capable of sustaining a high rate of discharge and is cheap and easy to manufacture.

Responsive to these needs, novel processing methods have been developed for producing carbon materials for use as electrodes in rechargeable batteries. Polymeric precursor materials processed in accordance with the present invention can yield carbon materials for use as electrodes that exhibit high intercalation efficiencies and in which the irreversible loss of lithium can be reduced to a few percent of the initial capacity. Furthermore, the lengthy and involved extraction procedures for removing solvents can be eliminated thereby reducing the cost of producing the carbon material. In

addition, carbon materials having higher densities can be obtained, thereby making it possible to achieve high energy density batteries. In particular, the present invention can improve the performance of alkali metal secondary batteries by the use of anodes prepared from treated polymeric precursor materials. Additionally, lithium intercalation electrodes prepared from polymeric precursor materials processed in accordance with the present invention exhibit minimal dendritic deposition, have long cycle life and are capable of sustaining the high rate of discharge required for high energy density secondary batteries. Electrodes prepared from such treated polymeric precursor materials can also retain a large fraction of their initial capacity.

#### SUMMARY OF THE INVENTION

The present invention provides methods for processing carbonizable polymeric precursor materials and producing carbon materials which can be used to produce electrodes for use in rechargeable batteries. In particular, a novel two-step stabilization process is described in which the polymeric precursor materials can be stabilized by first heating the polymeric precursor materials in an inert atmosphere and subsequently heating the product of the first heating step in air. During the stabilization steps, the polymeric precursor material can be agitated by tumbling the powder within a rotating container, or fluidized in a fluidized bed or by any other means of imparting relative motion to the particles to reduce particle fusion and enhance heat and mass transfer of water vapor and oxygen between the particles and the gas phase. The stabilized polymeric precursor material can then be converted to a synthetic carbon material, suitable for fabricating lithium intercalation electrodes, by heating to a high temperature in an inert atmosphere. Control of carbon particle morphology can also be achieved by the addition of inert pore formers, such as urea, prior to either the initial stabilization step or the carbonization step.

These and other features will become apparent to those skilled in the art from detailed disclosure of the present invention as described and claimed herein.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a micrograph of a carbon fiber produced from a polymer fiber precursor by the process disclosed herein.

FIG. 2 shows a micrograph of carbon powder produced from a polymer powder precursor by the process disclosed herein.

FIG. 3 show a discharge curve for a carbon anode made from carbon powder produced by the process disclosed herein. Also shown is the variation in battery capacity with time as a function of %  $\text{Li}_6\text{C}$ . The electrolyte was an anhydrous 1.0 molar solution of lithium hexafluoroarsenate in a 70:30 mixture of ethylene carbonate and diethylcarbonate.

FIG. 4 shows a charge curve for incorporation of lithium into a carbon anode made from powder produced by the process disclosed herein. The electrolyte was an anhydrous 1.0 molar solution of lithium hexafluoroarsenate.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates generally to methods for processing carbonizable polymeric precursor materials and producing carbon materials for use as electrodes in rechargeable batteries.

To better understand the present invention, the following introductory comments are provided. It has been recognized by the inventors that the final properties of carbon materials produced by thermal decomposition of polymeric precursor materials, such as polyacrylonitrile (PAN) and co-polymers of (PAN), are strongly determined by the pretreatment process that stabilizes the polymeric precursor material prior to carbonization. The need for pretreating ("preoxidizing" or "stabilizing") certain polymeric precursor materials prior to carbonization in order both to increase the carbon yield as well as ensure that the desired carbon structure is achieved is known. In order, for example, for PAN to pyrolyze it is necessary to crosslink or cyclize the polymeric precursor material prior to carbonization. As disclosed by Arnold, supra, this pretreatment has traditionally be done by slowly heating the precursor material in air to a temperature in the range of 150°–300° C. Without this pretreatment step, carbonization of the precursor material occurs with significant degradation of the polymeric material; low molecular weight fragments are formed in preference to carbon and the carbon yield is low.

The chemistry associated with the aforementioned pretreatment step has been extensively investigated. Although it is a complex system, it is generally accepted that PAN undergoes an intermolecular reaction that leads to fused, conjugated cyclic structures down the chain length (referred to as a "ladder polymer") and that this ladder polymer rapidly reacts with oxygen to form the final brown/black "preoxidized" or "stabilized" material. This pretreated material can be subsequently heated to temperatures in the range 500°–2500° C., in the presence of an inert gas, to form a final carbonized product. The overall pretreatment step is quite exothermic; without careful control of processing conditions the polymeric precursor material can become so hot that it may fuse, decompose or even burn. However, the inventors have found that by appropriate control of the pretreatment process, it is possible not only to produce carbon materials for use as electrodes in rechargeable batteries with improved and reproducible properties without the need for further processing but also to reduce significantly lot-to-lot variability in the produced carbon materials, thereby lowering costs.

The ability to tailor the morphology, i.e. surface area, particle shape and size, of the final carbon materials is also critical for various applications. For example, for capacitors, solid electrolyte batteries and high rate applications, in general, submicron sized carbon particles are required, whereas for lower rates of discharge and/or with liquid electrolytes, carbon particles having a diameter of about 30  $\mu\text{m}$  are necessary in order to reduce self discharge. The inventors have discovered that carbon materials having low surface areas (<10  $\text{m}^2/\text{g}$ ) are advantageous for reducing the irreversible loss of lithium.

More specifically, the instant invention is directed to a method of processing carbonizable, polymeric, precursor materials that can be subsequently pyrolyzed to produce carbon materials for use as lithium intercalation electrodes in rechargeable batteries. The process disclosed herein provides a novel two-step method for stabilizing polymeric precursor materials, such as polyacrylonitrile (PAN) and co-polymers of PAN with monomers including, but not limited to, itaconic acid, acrylic acid, methacrylic acid, vinyl acetate, styrene, divinyl benzene, vinyl chloride and vinylidene chloride, thereby improving the yield and quality of the carbon materials produced by carbonizing these stabilized precursor materials. It will be appreciated that by first heating the precursor material to a range of about 150°

C. to about 250° C. in an inert atmosphere, preferably nitrogen, followed by a second heating step to a range of about 100° C. to about 250° C. in an oxygen containing atmosphere, preferably air, the methods of the instant invention provide a significant improvement over existing pretreatment processes for stabilizing carbonizable, polymeric precursor materials.

Examples of carbon materials, both powder and fiber, which are prepared from acrylonitrile based polymers, such as PAN and PAN co-polymers, by the method of the present invention are shown in FIGS. 1 and 2. They have microcrystalline structures consisting of randomly oriented domains shown by transmission electron microscopy to contain approximately 4 to 10 lattice planes extending approximately 20 to 50 Å in the lateral dimension. X-ray diffraction spectra show  $d_{002}$  lattice spacing on the order of 3.5 to 3.7 Å and Raman spectra show peaks of near equal height at 1360  $\text{cm}^{-1}$  (disordered peak) and 1580  $\text{cm}^{-1}$  (ordered peak). Carbon materials when produced in accordance with the process of the present invention from PAN powder (having an average particle size of 35  $\mu\text{m}$ ), the BET surface area of the carbon material was approximately 5  $\text{m}^2/\text{g}$ . Electrodes constructed from this carbon material are suited for use as the anode in lithium ion secondary batteries and are capable of utilizations in excess of 80%, based on LiC6 as shown in FIGS. 3 and 4.

The product of the first heating step of the stabilization pretreatment procedure comprises a ladder polymer or PAN cyclic imine having a yellow to orange color and the following nominal elemental composition:

- 65.2% Carbon
- 5.14% Hydrogen
- 22% Nitrogen
- 6.9% Oxygen.

The product of the second heating step of the stabilization pretreatment procedure has the following nominal elemental composition:

- 60% Carbon
- 3.23% Hydrogen
- 21.6% Nitrogen
- 13% Oxygen.

These compositions are intended only to be indicative and neither limit nor define the process of this invention.

The material produced by the pretreatment program disclosed herein can be converted to a synthetic carbon by heating to a high temperature in a flowing inert atmosphere, preferably argon flowing at a rate of about 25 standard cubic ft/hr. The pretreated polymeric precursor material is placed in a container or crucible, preferably alumina, that will withstand the carbonization conditions. The following carbonization conditions can be used:

- 1) Place the crucible and its contents in a furnace and adjust the flow rate of an inert gas over the crucible;
- 2) Raise the temperature of the crucible and its contents at a rate of less than about 5° C./min from ambient to about 300° C.;
- 3) Maintain the temperature at about 300° C. for about 2 hours;
- 4) Raise the temperature of the furnace from about 300° C. to about 370° C. at a rate of less than about 5° C./min;
- 5) Maintain that temperature for about 5 hours;
- 6) Raise the temperature from about 370° C. to about 900° C. at a rate of less than about 5° C./min;

7) Maintain that temperature for about 6 hours;

8) Cool to ambient temperature.

The carbon powder resulting from this procedure can be characterized as having a radially symmetric branched fractal morphology similar to the original polymer precursor. It possesses the following characteristics: Tap density: >0.95  $\text{g}/\text{cm}^3$  Particle size distribution: 10 to 90  $\mu\text{m}$  with a mean size of 30  $\mu\text{m}$  Principal Raman peaks: 1300 to 1400  $\text{cm}^{-1}$  and 1550–1600  $\text{cm}^{-1}$  Ratio of principal Raman peaks: 3.2.

Analysis of the elemental composition showed the following (on a weight percent basis except for sulfur):

- >90% carbon
- <3–6% nitrogen
- <1.5% oxygen
- <0.5% hydrogen
- <150 ppm sulfur.

By agitating the particle bed during the two-step stabilization or pretreatment process, for example, tumbling the particle bed in a rotating container in a furnace or fluidized in a fluidized bed reactor, detrimental self-heating effects such as particle agglomeration and fusion can be mitigated. Agitating the particle bed further operates to enhance heat transfer and mass transfer of oxygen and water vapor between particles and the gas phase. This results in better process control and a more highly reproducible product. The carbon material produced from the agitation process exhibits high capacity and improved charge/discharge rates for lithium.

The present invention now will be described more fully hereinafter by way of various examples illustrative of the invention. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth herein.

The following examples illustrate the process of pretreatment of carbonizable, polymeric precursor materials.

#### EXAMPLE 1

1200 g of PAN powder was placed into a 12" diameter rotating drum which was mounted in the interior of a programmable oven. The drum was purged with nitrogen for about an hour and then heated according to the following cycle: from room temperature to about 175° C. at a rate of less than 100° C./hr, 175° C. to about 250° C. at a rate of less than 5° C./hr, hold at about 250° C. for about 6 hours. During the heating cycle the drum was rotated at approximately 10 rpm and a stream of nitrogen was directed into the drum to maintain the inert atmosphere. After cooling to room temperature, the nitrogen purge was exchanged for a flow of compressed air (approximately 275 ml/min) and the drum was again heated using the following cycle: room temperature to about 100° C. at a rate of less than 100° C./hr, 100° C. to about 250° C. at a rate of less than 10° C./hr, hold at about 250° C. for about 18 hours. As before, the drum was rotated during the heating cycle at about 10 rpm.

#### EXAMPLE 2

1200 g of PAN powder was placed into a 12" diameter rotating drum which was mounted in the interior of a programmable oven. The drum was purged with nitrogen for about an hour and then heated according to the following cycle: from room temperature to about 175° C. at a rate of less than 100° C./hr, 175° C. to about 250° C. at a rate of less than 5° C./hr, hold at about 250° C. for about 6 hours. During the heating cycle the drum was rotated at approxi-

mately 10 rpm and a stream of nitrogen was directed into the drum to maintain the inert atmosphere. After cooling to room temperature under the nitrogen purge, the contents of the drum were transferred into a drum of similar dimension made from porous graphite/carbon. This drum was mounted in a programmable oven. A stream of compressed air (approximately 275 ml/min) was directed into the drum and the drum was rotated at approximately 10 rpm while the following heat cycle was applied: room temperature to about 100° C. at a rate of 100° C./hr, 100° C. to about 250° C. at a rate of less than 10° C./hr, hold for about 8 hours at about 250° C.

The inventors have found that other carbonizable polymer, as described below, can be substituted for PAN and pretreated in the same manner as in the examples given above to produce a carbon powder having the desired properties.

#### EXAMPLE 3

A carbonizable polymer was pretreated in exactly the same manner as described in either Examples 1 or 2 except that polyacrylonitrile homopolymer was substituted for PAN.

#### EXAMPLE 4

A carbonizable polymer was pretreated in exactly the same manner as described in either Examples 1 or 2 except that polyacrylonitrile co-monomer of vinyl acetate (containing from 6-10 wt % vinyl acetate) was substituted for PAN.

#### EXAMPLE 5

A carbonizable polymer was pretreated in exactly the same manner as described in either Examples 1 or 2 except that a co-polymer of polyacrylonitrile and polymethylmethacrylate was substituted for PAN.

As illustrated in the next examples, pore formers, such as urea, can be mixed with the polymer precursor material prior to the pretreatment step or with the stabilized polymer precursor prior to the carbonization step in order to control particle morphology and size distribution.

#### EXAMPLE 6

1200 g of PAN powder and 600 g of urea was placed into a 12" diameter rotating drum which was mounted in the interior of a programmable oven. The drum was purged with nitrogen for about an hour and then heated according to the following cycle: from room temperature to about 175° C. at a rate of less than 100° C./hr., 175° C. to about 250° C. at a rate of less than 5° C./hr, hold at about 250° C. for about 6 hours. During the heating cycle the drum was rotated at approximately 10 rpm and a stream of nitrogen was directed into the drum to maintain the inert atmosphere. After cooling to room temperature, the nitrogen purge was exchanged for a flow of compressed air (approximately 275 ml/min) and the drum was again heated using the following cycle: room temperature to about 100° C. at a rate of less than 100° C./hr, 100° C. to about 250° C. at a rate of less than 10° C./hr, hold at about 250° C. for about 18 hours. As before, the drum was rotated during the heating cycle at about 10 rpm. The addition of urea to the PAN powder prior to the pretreatment process creates reduced particle size and an inert atmosphere.

#### EXAMPLE 7

1200 g of PAN powder and 600 g of urea was placed into a 12" diameter rotating drum which was mounted in the

interior of a programmable oven. The drum was purged with nitrogen for an hour and then heated according to the following cycle: from room temperature to about 175° C. at a rate of less than 100° C./hr., 175° C. to about 250° C. at a rate of less than 5° C./hr, hold at about 250° C. for about 6 hours. During the heating cycle the drum was rotated at approximately 10 rpm and a stream of nitrogen was directed into the drum to maintain the inert atmosphere. After cooling to room temperature, the nitrogen purge was exchanged for a flow of compressed air (approximately 275 ml/min) and the drum was again heated using the following cycle: room temperature to about 100° C. at a rate of less than 100° C./hr, 100° C. to about 250° C. at a rate of less than 10° C./hr, hold at about 250° C. for about 18 hours. As before, the drum was rotated during the heating cycle at 10 rpm. The addition of urea creates reduced particle size and an inert atmosphere.

#### EXAMPLE 8

PAN powder was pretreated exactly as described in either of Examples 1 or 2. The stabilized PAN material was treated with an aqueous solution containing about 600 g of urea. This mixture was then dried and placed into a crucible, preferably alumina, that will withstand the carbonization conditions. The following carbonization conditions may be used:

- 1) Place the crucible and its contents in a furnace and adjust the flow rate of an inert gas over the crucible;
- 2) Raise the temperature of the crucible and its contents at a rate of less than 5° C./min from ambient to about 300° C.;
- 3) Maintain the temperature at about 300° C. for about 2 hours;
- 4) Raise the temperature of the furnace from about 300° C. to about 370° C. at a rate of less than 5° C./min;
- 5) Maintain that temperature for about 5 hours;
- 6) Raise the temperature from 370° C. to about 800° C. at a rate of less than 5° C./min;
- 7) Maintain that temperature for about 6 hours;
- 8) Cool to ambient temperature.

While the illustrative Examples have employed PAN powder, the process of the present invention also works equally well for PAN fibers and for many battery applications PAN fibers are the preferred form for the carbon electrode material.

From the foregoing description and examples, one skilled in the art can readily ascertain the essential characteristics of the present invention. The description and examples are intended to be illustrative of the present invention and are not to be construed as limitations or restrictions thereon, the invention being delineated in the following claims.

We claim:

1. A method of producing carbon materials for use as electrodes in rechargeable batteries, comprising the steps of:
  - a) heating a carbonizable polymer material selected from the group consisting of polyacrylonitrile, co-polymers of polyacrylonitrile and mixtures thereof in a step-wise manner at a fixed rate of heating to a temperature in an inert atmosphere while simultaneously agitating the polymer material to form a pretreated product;
  - b) cooling the pretreated product;
  - c) heating the pretreated product in an oxygen containing atmosphere in a step-wise manner at a fixed rate of heating to a temperature while simultaneously agitating the pretreated product to form a stabilized polymer product;

d) carbonizing the stabilized polymer product by heating in a step-wise manner to a temperature in an inert atmosphere, thereby forming a carbon material having a surface area of less than  $10 \text{ m}^2/\text{g}$  wherein the step-wise heating comprises:

- i. heating the stabilized polymer product in an inert atmosphere to about  $300^\circ \text{ C.}$  at a rate of less than  $5^\circ \text{ C./min.}$
- ii. maintaining the temperature at about  $300^\circ \text{ C.}$  for about 2 hours;
- iii. raising the temperature to about  $370^\circ \text{ C.}$  at a rate of less than  $5^\circ \text{ C./min.}$
- iv. maintaining the temperature at about  $370^\circ \text{ C.}$  for about 5 hours;
- v. raising the temperature from about  $370^\circ \text{ C.}$  to at least  $800^\circ \text{ C.}$  at a rate less than  $5^\circ \text{ C./min.}$
- vi. maintaining the temperature at least  $800^\circ \text{ C.}$  for about 6 hours.

2. The method of claim 1, wherein co-polymers of (PAN) are selected from the group consisting of itaconic acid, acrylic acid, methacrylic acid, vinyl acetate, styrene, divinyl benzene, vinyl chloride and vinylidene chloride and combinations thereof.

3. The method of claim 1, further including the step of adding a pore former material consisting of urea.

4. The method of claim 1 wherein said step of carbonizing produces a powder having a symmetric branched morphology with randomly oriented domains shown by transmission electron microscopy to contain approximately 4 to 10 lattice planes extending approximately 20 to 50 Å in the lateral dimension,  $d_{002}$  lattice spacing on the order of 3.5 to 3.7 Å, a Raman spectrum showing peaks of near equal height at  $1360 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$ , and a BET surface area of less than about  $10 \text{ m}^2/\text{g}$  and an average particle size of less than  $35 \mu\text{m.}$

5. A method for producing carbon materials capable of intercalating lithium for lithium ion rechargeable batteries, comprising the steps of:

- a) heating and agitating a carbonizable polymer in an inert atmosphere with a pore forming material consisting of urea to form a pretreated product, wherein the carbonizable polymer is selected from the group consisting of homopolymers and co-polymers of polyacrylonitrile, and mixtures and blends thereof;
- b) heating and agitating the pretreated product in an oxygen-containing atmosphere to form a stabilized polymer product; and
- c) carbonizing the stabilized polymer product in an inert atmosphere to form a carbon material having BET surface area of less than  $10 \text{ m}^2/\text{g}$  and capable of intercalating lithium for lithium ion rechargeable batteries.

6. The method according to claim 5, wherein the carbonizable polymer is a copolymer of polyacrylonitrile formed by copolymerizing acrylonitrile and at least one monomer selected from the group consisting of itaconic acid, acrylic acid, methacrylic acid, vinyl acetate, styrene, divinyl benzene, vinyl chloride, and vinylidene chloride.

7. The method according to claim 5, wherein step (a) and step (b) further comprise heating in a step-wise manner.

8. The method according to claim 7, wherein step (a) further comprises:

- a) heating the carbonizable polymer to a first temperature of about  $175^\circ \text{ C.}$  at a first rate of less than  $100^\circ \text{ C./hr.}$  and
- b) heating the carbonizable polymer to a second temperature of about  $250^\circ \text{ C.}$  at a second rate of less than  $5^\circ \text{ C./hr}$  and maintaining the product at  $250^\circ \text{ C.}$  for about 6 hours.

9. The method of claim 7, wherein step (b) further comprises:

- a) heating the pretreated product to about  $100^\circ \text{ C.}$  at a rate of less than  $100^\circ \text{ C./hr.}$  and
- b) further heating the pretreated product to a temperature of about  $250^\circ \text{ C.}$  at a rate of less than  $10^\circ \text{ C./min}$  and maintaining the pretreated product at about  $250^\circ \text{ C.}$  for about 6 hours.

10. The method of claim 5, wherein step (c) further comprises:

- d) heating the stabilized polymer product to a temperature of about  $300^\circ \text{ C.}$  at a rate of less than about  $5^\circ \text{ C./min}$  and maintaining it at  $300^\circ \text{ C.}$  for about 2 hours;
- e) further heating the stabilized polymer product to a temperature of about  $370^\circ \text{ C.}$  at a rate of less than about  $5^\circ \text{ C./min}$  and maintaining it at  $370^\circ \text{ C.}$  for 5 hours; and
- f) further heating the stabilized polymer product to a temperature of at least  $800^\circ \text{ C.}$ , and maintaining it at that temperature for about 6 hours to produce a carbon material capable of intercalating lithium for lithium ion rechargeable batteries.

11. A method for producing carbon materials capable of intercalating lithium for lithium-ion rechargeable batteries, consisting essentially of the steps of:

- a) heating and agitating a carbonizable polymer with a pore forming material consisting of urea in an inert atmosphere to form a pretreated product;
- b) heating and agitating the pretreated product in an oxygen-containing atmosphere to form a stabilized polymer product; and
- c) carbonizing the stabilized polymer product in an inert atmosphere to form a carbon material capable of intercalating lithium for use in lithium ion rechargeable batteries.

12. The method according to claim 11, wherein the carbon material is capable of a lithium intercalation capacity of at least 50%  $\text{LiC}_6$  after intercalation with lithium.

13. A carbon powder material capable of intercalating lithium for use in lithium ion rechargeable batteries and having a symmetric branched morphology having randomly oriented domains shown by transmission electron microscopy to contain approximately 4 to 10 lattice planes extending approximately 20 to 50 Å in the lateral dimension,  $d_{002}$  lattice spacing of about 3.5 to 3.7 Å, a Raman spectrum showing peaks of near equal height at  $1360 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$ , a BET surface area of less than  $10 \text{ m}^2/\text{g}$  an average particle size of less than  $35 \mu\text{m}$  and a lithium intercalation capacity of at least 50%  $\text{LiC}_6$  after intercalation with lithium.

14. The carbon material according to claim 13, wherein the material has a lithium intercalation capacity of at least 80%  $\text{LiC}_6$  after intercalation with lithium.

15. The carbon material according to claim 13, wherein the material is formed by a method comprising heating and agitating a carbonizable polymer in an inert atmosphere with a pore forming material to form a pretreated product, heating and agitating the pretreated product in an oxygen-containing atmosphere to form a stabilized polymer product, and carbonizing the stabilized polymer product in an inert atmosphere.

## 11

16. A method for producing carbon materials capable of intercalating lithium for use in lithium ion rechargeable batteries, comprising the steps of:

- a) heating and agitating a carbonizable polymer in a step-wise manner in an inert atmosphere to form a pretreated product, wherein the carbonizable polymer is in powder form and selected from the group consisting of homopolymers and co-polymers of polyacrylonitrile, and mixtures and blends thereof;

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- b) heating and agitating the pretreated product in a step-wise manner in an oxygen containing atmosphere to form a stabilized polymer product; and
- c) carbonizing the stabilized polymer product in an inert atmosphere with a pore forming material to form a carbon material capable of intercalating lithium for use in lithium ion rechargeable batteries and having a BET surface area of less than 10 m<sup>2</sup>/g.

\* \* \* \* \*



US005944980A

# United States Patent [19]

[11] **Patent Number:** **5,944,980**

**Yoshimura et al.**

[45] **Date of Patent:** **Aug. 31, 1999**

[54] **METHOD FOR PRODUCING ISOTROPIC PITCH, ACTIVATED CARBON FIBERS AND CARBON MATERIALS FOR NON-AQUEOUS SECONDARY BATTERY ANODES**

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[73] Assignee: **Mitsubishi Gas Chemical Company Co., Inc.**, Japan

[21] Appl. No.: **08/924,864**

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### [30] Foreign Application Priority Data

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May 9, 1997	[JP]	Japan	9-119635

### [57] ABSTRACT

[51] **Int. Cl.<sup>6</sup>** ..... **C10C 1/20**

[52] **U.S. Cl.** ..... **208/39; 208/22; 208/44; 423/44.4**

[58] **Field of Search** ..... **208/39, 22, 44**

A method for preparing a modified optically isotropic pitch comprising, preparing a synthetic pitch by reacting a member selected from the group consisting of a conjugated polycyclic hydrocarbon containing a low molecular weight alkyl group or a material containing such a substituted hydrocarbon in the presence of hydrofluoric acid/boron trifluoride, and treating the synthetic pitch by passing an oxidizing gas through the synthetic pitch at elevated temperatures.

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#### U.S. PATENT DOCUMENTS

4,663,708	5/1987	Seo	208/44
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**4 Claims, No Drawings**

**METHOD FOR PRODUCING ISOTROPIC PITCH, ACTIVATED CARBON FIBERS AND CARBON MATERIALS FOR NON-AQUEOUS SECONDARY BATTERY ANODES**

**FIELD OF THE INVENTION**

The present invention relates to a method for preparing modified optically isotropic pitch exhibiting superior stabilization characteristics and activated carbon fibers and anode materials for secondary batteries using said modified optically isotropic pitch.

**BACKGROUND OF THE INVENTION**

Heretofore, optical isotropic pitch has been prepared from coal pitch or petroleum pitch. Japanese Laid Open Patent Applications 1994-256767 and 1995-18058 teach methods for obtaining superior optical isotropic pitch having excellent stabilization characteristics by particularization of low pressure distillation of and blowing gas into raw materials, such as coal tars. However, the pitch fibers obtained by spinning the optical isotropic pitch obtained from these methods require some protection where high temperatures were applied over long periods in order to stabilize the fibers, and the methods are therefore not entirely satisfactory.

In addition, U.S. Pat. No. 4,789,455 discloses that it is possible to prepare a pitch that may be suitably applied as a high performance carbon material for carbon fibers or other applications by polymerizing conjugated polycyclic hydrocarbons or materials containing them in the presence of an HF/BF<sub>3</sub> catalyst. When the isotropic pitch thus obtained is used for the manufacture of carbon fibers and the like, melt adhesion of the fibers occurs easily during spinning because of a low softening point, and it takes an extremely long time to stabilize the fibers. Where the softening point of the pitch is raised to decrease the time required to stabilize the fibers, then, as taught by U.S. Pat. No. 4,891,126, the pitch obtained has anisotropic properties and fundamentally has ceased to be an isotropic pitch.

The fact that the time required for stabilization when carbon fibers are prepared from either of the aforementioned coal type or petroleum type pitches is so long is an important problem from the standpoint of produceability. In particular, pitch fibers obtained using optically isotropic pitch as raw material require a long period of time for stabilization compared with pitch fibers obtained using optically anisotropic pitch as the raw material, and the stabilization process is difficult.

With respect to various carbon material applications, such as for use as carbon fibers, activated carbon fibers and anode materials for secondary batteries using a non-aqueous solvent, an optically isotropic pitch that can easily be

stabilized as pitch fiber or pitch granules ground to various particle sizes is desired.

Accordingly, it is an object of the present invention to provide a method for making optical isotropic pitch with superior stabilization characteristics for various carbon material applications. It is a further object of the invention to provide a method for producing activated carbon fibers and amorphous type secondary battery material having superior characteristics.

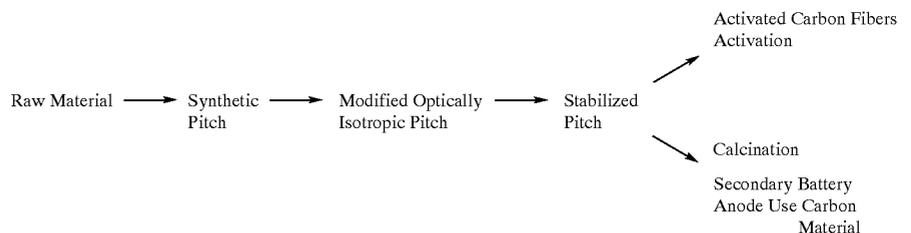
**SUMMARY OF THE INVENTION**

The present invention is predicated on the discovery that an optically isotropic pitch with clearly superior stabilization characteristics can be obtained by polymerizing conjugated polycyclic hydrocarbons substituted with one or more low molecular weight alkyl groups, or a material containing such a conjugated polycyclic hydrocarbon, in the presence of an HF/BF<sub>3</sub> catalyst and treating the resulting polymerized material at elevated temperature with a flow of oxidizing gas.

In one embodiment, the present invention thus provides a method of preparing modified optically isotropic pitch characterized by the polymerization of a conjugated polycyclic hydrocarbon containing at least one low molecular weight alkyl group, or materials containing such conjugated polycyclic hydrocarbons, using an HF/BF<sub>3</sub> catalyst and, at elevated temperatures, passing an oxidizing gas through the pitch thus obtained. In another embodiment, the invention provides a method of preparing activated carbon fibers characterized by melt spinning the modified optically isotropic pitch obtained in accordance with the invention, and after stabilization of said modified pitch, conducting activation treatment. In yet another embodiment, the invention provides a method of preparing anode material for secondary batteries using a non-aqueous solvent characterized by conducting stabilization treatment on the said modified pitch and then calcining.

Using the modified optically isotropic pitch obtained by the method of the present invention, it has been found that activated carbons having high absorption capacity can be obtained. The activated carbon can be applied effectively to gas separation or water treatment and formed for use in secondary battery anodes in which minimization of capacity loss in the initial cycle together with large discharge capacity as compared with materials used to lithium secondary batteries heretofore is achieved.

The flow diagram for preparing the modified optically isotropic pitch, the activated carbon fiber and the anode material for a secondary battery that uses a non-aqueous solvent is as follows:



-continued  
 Polymerization → Modification → Stabilization

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A conjugated polycyclic hydrocarbon containing at least one low molecular weight alkyl group is used as the raw material in accordance with the present invention. Conjugated polycyclic hydrocarbons suitable for use in the present invention include: derivatives of conjugated polycyclic hydrocarbons such as naphthalene, anthracene, pyrene, coronene and the like, which contain at least one low molecular weight alkyl group; derivatives of heteropolycyclic hydrocarbons such as benzofuran, quinoline, thianaphthalene, and the like, containing at least one low molecular weight alkyl group; mixtures of the heteropolycyclic hydrocarbons with the aforementioned derivatives of polycyclic hydrocarbons; or coal tar distillates, petroleum distillates, residues from petroleum processing and the like. In the present invention, low molecular weight alkyl groups refers to alkyl groups attached to the aforementioned conjugated polycyclic hydrocarbons that have between 1 and 10 carbon atoms and particularly those having between 1 and 3 carbon atoms. In particular, the methyl group is preferred as the low molecular weight alkyl group and naphthalene derivatives including methyl naphthalene or dimethyl naphthalene as well as mixtures of such compounds with the methyl naphthalene fraction of coal tar and ethylene bottom oil and the like are particularly preferred.

Isotropic pitch is prepared by polymerizing the conjugated polycyclic hydrocarbon in the presence of a suitable polymerization catalyst. The preferred catalyst used in the polymerization reaction of the conjugated polycyclic hydrocarbons containing at least one low molecular weight alkyl group is hydrofluoric acid/boron trifluoride. The amount of hydrofluoric acid used with respect to one mole of the conjugated polycyclic hydrocarbon or its equivalent is on the order of between about 0.1 to about 10 moles per mole of conjugated polycyclic hydrocarbon or its equivalent and the amount of boron trifluoride is between about 0.05 to about 5 moles per mole of conjugated polycyclic hydrocarbon or its equivalent. The reaction temperature is between 20° C. and 250° C. and preferably between 40° C. and 220° C. If the reaction temperature is too low, the degree of polymerization is also too low, and a satisfactory optically isotropic pitch cannot be obtained. If the reaction temperature is too high, the pitch obtained has anisotropic properties and fundamentally has ceased to be an isotropic pitch. The amount of time required for the polymerization reaction is usually between 5 and 300 minutes and preferably between 30 and 240 minutes. The reaction pressure is not particularly limited and the reaction is normally conducted under self-generated pressure within the reaction vessel under the other conditions described herein.

After completing polymerization, the catalyst, the unreacted raw materials and other light fractions are removed by conventional methods, such as extraction or distillation. For example, after the reaction, the pressure in the reaction vessel may be reduced so that the catalyst can be recovered. A stripping gas and increased temperature may also be applied inside the reaction vessel to ensure the efficiency of catalyst recovery. Moreover, following catalyst recovery, unreacted raw materials or light fractions may be removed from the reaction product by passing through it a non-reactive stripping gas.

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The softening point of the pitch obtained by the polymerization reaction of the present invention is typically less than 200° C. and is preferably between about 40° C. and about 180° C. If the softening point is too low, the molecular weight of the pitch is generally small, and, later, the yield of optically isotropic pitch obtained by treatment with an oxidizing gas at elevated temperatures declines, which is an undesirable result. If the softening point exceeds 200° C., then depending upon the specific raw material used, but, within the isotropic optical structure of the pitch, the appearance of optical anisotropy becomes more common making the whole material, in fact, anisotropic so that the pitch, which is the object of this invention, is not obtained.

In the preferred isotropic pitch obtained from the polymerization reaction, a ratio of hydrogen atoms to carbon atoms in the pitch of 0.5 to 1.0, a pyridine insoluble fraction of less than 1.0% and a ratio of aliphatic hydrogen to total hydrogen of 30% to 80% are desired. The pitch obtained from the polymerization reaction is substantially 100% isotropic. The isotropic nature of the pitch can be measured by conventional methods. For example, pitch can be embedded in epoxy resin and then the epoxy is ground to expose the surface of the pitch.

In keeping with the invention, the synthetic pitch from the polymerization is further modified by blowing an oxidizing gas through the pitch while the polymerized pitch is in a molten condition. The oxidizing gas used in the modification is preferably oxygen, air, nitric oxide and the like. From the standpoint of economics, safety and controllability, the use of air is preferred. The temperature of the modification is not a fixed temperature, but instead depends upon the softening point of the pitch. The preferred range is from about 200° C. to about 400° C. and, preferably, from about 300° C. to about 360° C. If the temperature of the modification process is too low, the oxidation of the pitch proceeds too slowly and modification is difficult to attain. However, if the temperature is too high, the oxidation reaction accelerates, control becomes difficult and thermal autopolymerization of the pitch becomes more likely, making the obtaining of the modified pitch of the present invention more difficult. When the modification procedure is carried out, the flow of the oxidizing gas differs according to the type of gas, the softening point of the pitch, the reaction temperature and the like, but in the case where air, which is easy to control, is used as the oxidizing gas, then between about 1 and about 50 ml/gr of pitch and, preferably, about 3 to about 30 ml/gr of pitch are used. The method of modification is not particularly limited, but to increase the efficiency of the contact between the gas and the pitch, a mesh filter or stirrer is preferably attached over the opening through which the gas is introduced to the pitch. The point at which the modification by the oxidizing gas has been completed, because the softening point rises together with the advance of the improvement, can be judged by measuring the softening point.

The modified optically isotropic pitch, if desired, may be made into fibers by passing it through a nozzle of on the order of about 0.1 to about 0.3 mm diameter. The softening point of the modified optically isotropic pitch is preferably between about 180° C. and about 350° C. and preferably between about 200° C. and about 300° C. If the softening point is less than about 180° C., then either as pitch fibers or

as granules it is necessary to begin stabilization treatment from a low temperature, which necessitates longer procedures, and the degree of stabilization will be reduced. If the softening point is in excess of about 350° C., then it becomes difficult to draw the pitch through the necessary equipment, so from the standpoint of usability as a product, it becomes impractical. In spinning the molten pitch a softening point of less than about 300° C. is preferred. The modified pitch is substantially 100% isotropic. Moreover, when preparing carbon material for use in secondary batteries using a non-aqueous solvent, the modified optically isotropic pitch of the present invention preferably has a ratio of hydrogen atoms to carbon atoms of between 0.50 and 0.80 and the ratio between the intensity of the aliphatic stretch vibration peaks for C-H and that of the aromatic stretch vibration peaks for C-H is 0.5 or greater.

The pitch of the present invention, when viewed through a polarizing microscope, shows substantially 100% optical isotropy. The softening point can be measured by a fixed load weight extruder capillary rheometer. The conditions of stabilization of the pitch fiber can easily be determined by the lighter test. If when pitch fibers are placed within a lighter flame, the stabilization process is not complete, the fiber becomes limp or melts, whereas when stabilization is complete, the fiber's initial shape is maintained and the fibers begin to glow with a red color in the flame.

The modified optical isotropic pitch obtained by the method of the present invention, whether as pitch fibers or as pitch granules, can be stabilized very easily. The stabilization treatment may be carried out under an atmosphere of, for example, oxygen, oxygen rich air, air NO<sub>2</sub> gas or the like by raising the temperature at a rate of usually between about 2° C. to about 15° C./minute and preferably between about 3° C. to about 12° C./minute over a temperature range of between room temperature and about 400° C. and preferably up to about 360° C. When stabilizing most materials, after the temperature has risen, it should be maintained constant for several hours at the peak temperature. However, using the method of the present invention, it is not necessary to maintain the elevated temperature after the temperature rise has been completed so stabilization can be accomplished in a very short time.

The optically isotropic pitch modified by the methods of the present invention can be used ideally for the carbon materials of activated carbon fibers and the anode materials of secondary batteries as described below.

Following is an explanation of the preparation method for making activated carbon fibers using the modified optical isotropic pitch of the present invention. The optically isotropic pitch modified by the oxidizing gas in a molten condition is passed through a nozzle of about 0.1 to 0.3 mm or so in diameter to produce pitch fibers which are then stabilized. The pitch fibers which have been stabilized are then given the following activation treatment: With regard to the activation treatment there are no particular limits, and it should be possible to use the activation methods of the prior art. For example, activation can be carried out by steam, carbon dioxide, oxygen or a gas containing at least one of these passed over the fiber of a temperature preferably between 700° C. and 1000° C. for between about 10 to 150 minutes. It is also acceptable to carbonize the stabilized pitch fibers at low temperature prior to activation and they can be carbonized after activation as well. Either batch activation type and continuous activation type equipment, of which there are plentiful examples known to the prior art may be used.

Molten spinning fibers can be made from the modified optically isotropic pitch of the present invention readily and

accomplished in a very short period of time. Since activation can be carried out in a very short time, it is possible to manufacture activated carbon fibers industrially with high absorption capacity.

In addition, the activated carbon fibers obtained by the present invention can be used effectively in gas separation or water treatment.

Anode material for secondary batteries that use non-aqueous solvents using optically isotropic pitch obtained according to the present invention can be prepared as follows. After the modified optically isotropic pitch has been fashioned into granular, fiber or thin sheet form and stabilized, the stabilized pitch is calcined under a vacuum, or a non-oxidizing gas, to obtain the anode suitable carbon material of the present invention. The calcination temperature is between about 800° C. and about 1800° C. and preferably between about 1000° C. and about 1300° C. The calcination time is selected so as to provide optimum results depending upon the particular raw materials used at between about one and about 50 hours. Moreover, it is acceptable to carry out pre-calcination at about 800° C. or less. As the non-oxidizing gas, nitrogen or argon are preferred. The non-oxidizing gas is provided to the reaction in a continuous flow and methods that balance the rate of flow to complement off-gassing from the calcination reaction or methods that force the removal of gas generated during the reaction using a vacuum may be optically applied depending upon the materials and conditions used in a particular reaction.

The anode material for a secondary battery using a non-aqueous solvent of the present invention is characterized in that the ability of this material to discharge at a potential of between 0 and 1.5 V against a lithium metal potential represents a discharge capacity of 540 mAh/g or more. It also exhibits a flat discharge curve in the region between 0 and 0.2 V against a lithium metal potential representing a discharge capacity of 380 mAh/g and a first cycle capacity loss of 100 mAh/g or less. Therefore, the anode material for use in a secondary battery using a non-aqueous solvent of the present invention, in comparison with lithium secondary battery carbon anode materials used heretofore, is superior from the standpoints of produceability, it has a large discharge capacity and it has reduced the first cycle capacity loss. The anode material can be used for a large capacity, low cost secondary battery.

## EXAMPLES

The present invention will be explained in greater detail by the following examples which are illustrative of, but not in limitation of, the present invention. The analysis methods used in the examples are specified below.

### Elemental Analysis

Analyses for carbon, nitrogen and hydrogen are performed simultaneously using a 2400 CHN type elemental analyzer made by Perkin Elmer as the analysis equipment.

The measurement is carried out by precisely measuring a sample of pitch weighing 1.5±0.2 mg, heating the sample for 5 minutes at 975° C. and conducting a TCD using helium as the carrier gas. Additionally, in measuring the sample, a small amount of acetonitrile (2.0 mg±0.1 mg) was tested at first to serve as a standard.

### NMR Analysis

The <sup>1</sup>H-NMR method is used to determine the ratio of the amount of aliphatic hydrogen to the total hydrogen in the sample. Since almost the entire mass of pitch will dissolve in chloroform, a 1% solution of the pitch in chloroform is

placed in the sample tube and the measurement is carried out by a Japan Electric (Inc.) JNM-EX270 NWR measurement device. In addition, TMS (tetramethyl silane) is used as the standard and set at a value of 0 ppm.

#### FT-IR Analysis

One part by weight of modified optically isotropic pitch is added to 100 parts of KBr powder and mixed in an agate mortar. A Japan Spectrographic (Inc.) FT/IR-5300, wide band reflective type measuring device set to D-81 was used to obtain wide band spectra of the sample by comparing the intensity of the peak at 2930  $\text{cm}^{-1}$  (the intensity of the aliphatic stretch vibration) with the intensity of the 3050  $\text{cm}^{-1}$  peak (the aromatic stretching vibration in spectra obtained by the Kubelka Munk transformation).

#### Iodine Absorption Volume

About 50 mg of the activated carbon fiber is taken, measured precisely and placed it in a 100 ml Erlenmeyer flask, to which 50 ml of 0.05 mol/L iodine solution is added. After stirring for 15 minutes at room temperature using a mechanical stirrer, the sample is separated using a centrifugal separator. 10 ml of the supernatant liquid were titrated using a sodium thiosulfate solution and the amount of iodine absorbed was calculated as follows:

the amount of iodine absorbed (mg/g) =  $(10 \times f^2 - K \times f) \times 12.69 \times 5 / M$

where: f: the coefficient of the iodine solution consumed by an 0.1 mol/l sodium thiosulfate solution

K: the amount (ml) of 0.1 mol/l sodium thiosulfate solution needed for titration

f: the coefficient of the 0.1 mol/l sodium thiosulfate solution

12.69: the number of mg of 0.1 mol/l sodium thiosulfate solution consumed by 1 ml of iodine solution

M: the weight of the sample (g).

#### Example 1

Seven moles of a mixture of  $\alpha$  and  $\beta$  methyl naphthalene were mixed with 5.15 moles of hydrofluoric acid in a 3 L acid resistant autoclave equipped with a mechanical stirrer and 1.4 moles of boron trifluoride were added while stirring slowly. Next, after raising the temperature to 100° C. under the pressure self-generated by the reaction, the polymerization reaction was conducted with stirring at 100° C. over 4 hours. After the reaction was complete, the catalyst was recovered using reduced pressure. The removal by vaporization of any remaining catalyst or unreacted raw materials was accomplished by passing three liters per minute of nitrogen gas through the vessel at 200° C. for 16 hours. The synthetic pitch obtained had a softening point of 76° C. and the ratio of hydrogen atoms to carbon atoms (H/C) was found to be 0.87. Moreover, after grinding this pitch by conventional methods, when it was examined under a polarizing microscope, its makeup was found to be 100% optically isotropic.

The synthetic pitch prepared above was placed in a second reaction vessel and was stirred while raising the temperature to 340° C. and blowing nitrogen gas through the pitch. When the temperature inside the vessel was stabilized at 340° C., the gas being blown through the pitch was changed from nitrogen to air to begin modification of the pitch. The air volume blown through the pitch at that time was 20 L/kg. After conducting the modification reaction for one hour, the reaction was stopped by exchanging the gas blown through the pitch back to nitrogen and reducing the temperature in the reaction vessel. The softening point of the

modified optically isotropic pitch was 246° C., the H/C ratio was 0.63 and the optical makeup of the pitch was 100% isotropic.

Pitch fiber was obtained by spinning the modified optically isotropic pitch in a molten state through a nozzle having a diameter of 0.15 mm. The pitch fibers were heated from room temperature to 320° C. at a rate of 4° C./minute and after reaching 320° C. were taken from the apparatus. A degree of stabilization in which there was no melt adhesion of fibers was achieved completely following this stabilization treatment. The fibers were then calcined and following calcination, no melt adhesion was observed to have taken place.

In addition, the modified optically isotropic pitch was ground to a powder in a ball mill. Tests for melt adhesion of the modified pitch in powder form were conducted in the same way that the mill adhesion test had been conducted for the fibers. Stabilization of the modified pitch in powder form was again observed to have been successful.

#### Example 2

The modified optically isotropic pitch obtained in Example 1 was spun into fibers using the same methods as in Example 1. The pitch fibers thus obtained were stabilized using air and raising the temperature to 320° C. at a rate of 3° C./minute. The fibers thus obtained were observed to have been well stabilized such that they neither burned up nor fused together when heated.

These fibers were subjected to activation treatment at 1000° C. for 1 hour under in atmosphere of nitrogen containing 15% carbon dioxide to obtain activated carbon fibers. The activated carbon fibers thus obtained absorbed 1400 mg of iodine per gram of fiber.

#### Example 3

Two moles of the methyl naphthalene fraction of coal tar pitch, 1.46 moles of hydrofluoric acid and 0.4 moles of boron trifluoride in a 500 ml were mixed in an acid resistant autoclave and reacted at 135° C. under self-generated pressure. The reaction was continued for 4 hours at 135° C. After reaction, the catalyst was recovered by reducing the pressure, and low boiling components were removed by blowing through the pitch 1 L of nitrogen heated to 200° C. The resulting synthetic pitch had a softening point of 89° C. The synthetic pitch thus obtained had a hydrogen to carbon ratio (H/C) of 0.80. Moreover, after grinding the pitch to a powder by the usual means, when it was viewed under a polarizing microscope, it was observed to be 100% optically isotropic.

The synthetic pitch obtained above was placed in a second reaction vessel and was reacted for 40 minutes at 350° C. while air was were blown through the pitch at a rate of 20 L/kg. The modified pitch thus obtained had a softening point of 220° C. and an (H/C) ratio of 0.62. The optical makeup was 100% isotropic.

The modified optically isotropic pitch thus obtained above was spun into fibers by the same methods as in Example 1. The spun pitch fibers thus obtained were stabilized by heating them at a rate of temperature increase of 3° C./minute from room temperature until a temperature of 320° C. was attained under a flow of air. The stabilized fibers thus obtained were observed to be stabilized such that melt adhesion and burning did not occur. The stabilized fibers were activated according to the same methods as in Example 2, and activated carbon fibers were obtained. The iodine

absorption capacity of the activated carbon fibers thus obtained was 1940 mg of iodine per gram of fibers.

#### Example 4

Exactly 1420 grams of ethylene bottom oil, 5.25 moles of hydrofluoric acid, and 1.5 moles of boron trifluoride were mixed in a three liter acid resistant autoclave. After raising the temperature to 120° C. under self-generated pressure the reaction was conducted for 4 hours at 120° C. After reaction, catalyst was recovered by reducing the pressure. Low boiling components of the pitch were removed by passing 3 L/minute of nitrogen gas through the pitch at 120° C. to obtain a synthetic pitch having a softening point of 107° C. The synthetic pitch thus obtained had a hydrogen atom to carbon atom ratio of 0.95 and a pyridine insoluble fraction of 0.0%. The ratio of aliphatic hydrogen to all hydrogen present in the pitch was 66%, and the optical makeup was 100% isotropic.

The synthetic pitch obtained above was placed in a second vessel and heated to 340° C. and 20 L of air per kilogram of pitch were passed through the pitch to conduct the reaction over 2 hours. The modified optically isotropic pitch thus obtained had a softening point of 246° C., an (H/C) of 0.78 and the ratio of the intensity of the aliphatic C-H stretch vibration to the aromatic stretch vibration was 2.9 when measured by FT-IR. The optical makeup of the pitch was 100% isotropic.

After spinning the modified optically isotropic pitch thus obtained into fibers according to the same methods as in Example 1, the spun pitch fibers thus obtained were stabilized by heating from room temperature to 320° C. at a rate of temperature increase of 4° C./minute under a flow of air. The spun fibers thus obtained were stabilized well enough so that no melt adhesion or burning up were observed. The stabilized fibers were activated according to the methods described in Example 2 and activated fibers were obtained. The activated fibers thus obtained absorbed 1330 mg of iodine per gram of fiber.

#### Comparative Experiment 1

Exactly 10 moles of naphthalene, 2.07 moles of hydrofluoric acid and 1.16 moles of boron trifluoride were mixed in a 3 L acid resistant autoclave and, after raising the temperature to 210° C. under self-generated pressure, the reaction was maintained at 210° C. for four hours to complete the reaction. Next, the pressure was reduced to recover the catalyst and, after removing lighter boiling components of the pitch at 340° C. with 3 L/minute of nitrogen, a synthetic pitch with a softening point of 174° C. was obtained. The synthetic pitch thus obtained had a hydrogen atom ratio to carbon atom ratio (H/C) of 0.64. Moreover, when this pitch was ground by the usual methods, when viewed by polarizing microscope, the optical makeup was 100% isotropic. The synthetic pitch was placed in a second vessel, and reacted for 1 hour at 340° C. with 20 L per kilogram of air passed through the pitch. The softening point of the point thus obtained was 218° C., the (H/C) was 0.52 and the optical makeup was 100% isotropic.

The modified optically isotropic pitch thus obtained was spun into fibers under melted conditions according to the same methods as were used in Example 1. However, the pitch fibers so obtained could not be stabilized at a rate of 0.5° C./minute so as to avoid melt adhesion and burning up. At the slow rate of 0.25° C./minute temperature raise up to a maximum of 300° C. stabilization was conducted and it was then possible to obtain a stabilized pitch that did not

burn up or adhere to itself. The stabilized fiber was activated according to the same conditions as were employed in Example 2, and an activated fiber was obtained. However, the iodine absorption amount of the activated fiber was low at 210 mg/g pitch fiber.

#### Comparative Experiment 2

A commercially available coal tar pitch was placed in the reactor and the temperature inside the reaction vessel was raised to 320° C. while stirring and blowing nitrogen gas through it. When the temperature inside the vessel had been stabilized to 320° C., the gas being blown through the pitch was changed from nitrogen to air to modify the pitch. The volume of air in this instance was 20 L/kg. After the reaction had proceeded for one hour, the gas blown through the pitch was changed back to nitrogen from air and the reaction vessel was cooled to stop the reaction. The modified pitch thus obtained had a softening point of 227° C., and its optical makeup was 100% isotropic.

The modified optical isotropic pitch thus obtained was melt spun according to the method of Example 1 to obtain a pitch fiber. This pitch fiber was heated at a rate of temperature increase of 4° C./minute from room temperature to 320° C. and, after attaining 320° C., was removed from the apparatus. The fiber, following this stabilization procedure had adhered due to melting and the stabilization process was inadequate. Whenever the rate of temperature increase was 0.5° C./minute or more, it was not possible to stabilize the fibers. When heating was carried out at the very slow rate of 0.25° C./minute up to a temperature of 300° C., stabilization was achieved and a stabilized fiber that did not undergo melt adhesion could be obtained. When this stabilized fiber was activated according to the same methods as in Example 2, activated carbon fibers were obtained. The activated carbon fibers thus obtained exhibited the low iodine absorption value of 650 mg/g of activated carbon fibers.

#### Comparative Experiment 3

A pitch fiber was obtained by melt spinning the synthetic pitch of Comparative Experiment 1 without first modifying it. This pitch fiber was stabilized by heating at a rate of 4° C./minute from room temperature to 320° C. However, melted regions remained in the fiber and it was not possible to effect stabilization.

#### Example 5

This Example illustrates the preparation of pitch for use as the anode material for a lithium secondary battery.

Seven moles of methyl naphthalene, 3.68 moles of hydrofluoric acid and 1.16 moles of boron trifluoride were mixed in a 3 L acid resistant autoclave and after raising the temperature to 100° C. under self-generated pressure, the reaction was conducted at 100° C. for four hours. Next, the catalyst was recovered by reducing the pressure and after removing the low boiling components of the pitch by passing 3 L/minute of nitrogen gas through the pitch at 200° C., a synthetic pitch having a softening point of 76° C. was obtained. The synthetic pitch thus obtained had a hydrogen atom to carbon atom ratio of 0.95 and a pyridine insoluble fraction of 0.0%, the ratio of aliphatic hydrogen to all hydrogen present in the pitch was 58%.

The synthetic pitch obtained above was placed in a different vessel and heated to 320° C. and 20 L of air per kilogram of pitch were passed through the pitch to conduct

the reaction over 2 hours. The modified optically isotropic pitch thus obtained had a softening point of 200° C. The ratio of hydrogen atoms contained in the pitch to carbon atoms (H/C) was 0.66. The ratio of the intensity of the aliphatic C-H stretching vibration band to the intensity of the aromatic stretching vibration band measured by FT-IR was 1.1. This modified optical isotropic pitch was ground to particles having a diameter of 200  $\mu\text{m}$  or less. Ten grams of this material was placed on a flat ceramic dish and placed in a muffle furnace under a flow of 1 L per minute of air. The temperature in the muffle furnace was raised at a rate of 5° C./minute from 150° C. to 300° C. and maintained at 3000 for 10 minutes to obtain treated pitch. The treated pitch thus obtained was ground to an average particle diameter of 15  $\mu\text{m}$ . A small amount of this material was calcined at 1200° C. for two hours at 10 Torr under a slight flow of nitrogen gas.

#### Evaluation of Anode Material

Ten parts by weight of polyfluorovinylidene powder (binder) was added to 90 parts by weight of the calcined carbon material obtained above and dimethylformamide, and the mixture was thoroughly mixed to provide a substantially uniform paste.

The paste was coated onto a thin copper film and, after drying, the film was cut into 1 centimeter squares which served as test electrodes. Half cells were prepared with the test electrode, a 1.0 molar solution of  $\text{LiClO}_4$  dissolved in a three component solvent consisting of ethylene carbonate, dimethylcarbonate and diethylcarbonate mixed in a ratio of 1/0.5/0.5 respectively as the electrolyte and a 50  $\mu\text{m}$  thick microporous polypropylene film as the separator. Additionally, a lithium metal disk having a diameter of 16 mm and a thickness of 0.5 mm was employed as a counter electrode. A lithium metal disk meeting the same description served as the reference electrode.

Charging was carried out at a constant current at a current density of 2  $\text{mA}/\text{cm}^2$  up to a test electrode electrode potential versus the reference electrode of 1 mV. Constant potential charging was carried out at 1 mV for 40 hours. The stored capacity was observed to be 647 mAh/g. Constant current discharge was carried out at a current density of 1  $\text{mA}/\text{cm}^2$  up to a test electrode electrode potential versus the reference electrode of 1.5 V, and the discharge capacity was observed to be 562 mAh/g. There was a capacity loss of 85 mAh/g and the discharge capacity between 0 and 0.2 V was 417 mAh/g.

#### Example 6

This Example illustrates the preparation of pitch for use as the anode material for a lithium secondary battery.

Seven moles of dimethyl naphthalene, 4.90 moles of hydrofluoric acid and 1.40 moles of boron trifluoride were mixed in a 3 L acid resistant autoclave, and after raising the temperature to 120° C. under self generated pressure, the reaction was conducted at 120° C. for four hours. Catalyst was recovered by reducing the pressure, and after removing the low boiling components of the pitch by passing 3 L/minute of nitrogen gas through the pitch at 200° C., a synthetic pitch having a softening point of 40° C. was obtained. The synthetic pitch thus obtained had a hydrogen atom to carbon atom ratio of 0.91 and a pyridine impurity of 0.0%. The ratio of aliphatic hydrogen to all hydrogen present in the pitch was 66%.

The synthetic pitch prepared above was placed in a second vessel and heated to 320° C. Twenty liter of air per kilogram of pitch was passed through the pitch over a 2 hour

reaction time to obtain a 100% optically isotropic modified pitch with a softening point of 249° C. This modified optically isotropic pitch had a ratio of hydrogen atoms contained in the pitch to carbon atoms (H/C) of 0.65 and a ratio of the intensity of the aliphatic C-H stretching vibration band to the intensity of the aromatic stretching vibration band measured by FT-IR of 1.6. The modified optical isotropic pitch was round to particles having a diameter of 200  $\mu\text{m}$  or less. Ten grams of this material was placed on a flat ceramic dish and placed in a muffle furnace under a flow of 1 L per minute of air. After raising the temperature in the muffle furnace at a rate of 5° C./minute from 150° C. to 300° C. and maintaining this latter temperature for 10 minutes to obtain treated material. The treated material thus obtained was ground to particles having an average diameter of 15  $\mu\text{m}$ . A small amount of the treated material was calcined at 1200° C. for two hours at 10 Torr under a slight flow of nitrogen gas.

The treated material was converted to anode material, and the anode material was evaluated according to the methods of Example 5. A storage capacity of 635 mAh/g, and a discharge capacity of 547 mAh/g were observed. The capacity loss was 88 mAh/g and the discharge capacity between 0 and 0.2 V versus the lithium metal counterelectrode was 397 mAb/g.

#### Example 7

This Example illustrates the preparation of pitch for use as the anode material for a lithium secondary battery.

The modified optically isotropic pitch obtained in Example 4 was ground to a powder of less than 200  $\mu\text{m}$  in diameter. Ten grams of this powder were placed in a muffle furnace under a flow of 1 liter per minute of air and after raising the temperature from 150° C. at a rate of 5° C./minute from 150° C. to 280° C., the furnace was maintained at 280° C. for 10 minutes. The sample was then removed from the furnace. The material thus obtained was treated to give a powder having an average particle diameter of 15  $\mu\text{m}$ . The powder was then calcined for 2 hours at 1200° C. under a slight flow of nitrogen and a pressure of 12 Torr to obtain a carbon material in powdered form. The calcined powdered material was evaluated as an anode material according to the same methods as Example 5. The storage capacity was 658 mAh/g, and the discharge capacity was 600 mAh/g. The capacity loss was 58 mAh/g and the discharge capacity for the potential region of 0 to 0.2 volts versus the lithium metal potential was 429 mh/g.

#### Comparative Experiment 4

A coal tar pitch having a softening point of 76° C., a ratio of hydrogen atoms to carbon atoms contained in the pitch (H/C) of 0.55, a pyridine insoluble fraction of 0.1% and a ratio of aliphatic carbon to total carbon in the pitch of 3% was placed within a reaction vessel and reacted for 1 hour in a flow of 20 liters of air per minute per kilogram of material to obtain a modified 100% optically isotropic pitch with a softening point of 243° C. The ratio of hydrogen atoms to carbon atoms contained in this modified optically isotropic pitch (H/C) was 0.48. The ratio of the intensity of the aliphatic C-H stretching band as opposed to the aromatic C-H stretching band as measured by FT-LR was 0.0. This modified optically isotropic pitch was ground to a powder having an average particle diameter of 200  $\mu\text{m}$  or less. Ten grams of this powder were placed on a ceramic dish and placed in a muffle furnace where, under a flow of 1 liter of air per minute, it was heated from 150° C. to 320° C. at a rate

of 5° C./minute and then maintained at 320° C. for 10 minutes following which it was removed from the furnace. The material thus obtained was melted by raising the temperature and then cooled to a mass. The mass was ground to a powder having a particle size of 15 μm, which was then calcined under a slight flow of nitrogen at 10 Torr and at 1200° C. for 2 hours to obtain a powdered carbon material. The calcined material was evaluated as an anode material according to the methods of Example 5. The storage capacity of the calcined anode material was observed to be 525 mAh/g and the discharge capacity was observed to be 398 mAh/g. The capacity loss was very large at 127 mAh/g and the overall discharge capacity of the battery was reduced. The discharge capacity for the potential region of 0 to 0.2 versus lithium metal was low at 230 mAh/g.

#### Comparative Experiment 5

Seven moles of naphthalene, 2.45 moles of hydrofluoric acid and 0.77 moles of boron trifluoride were added to a 3 liter acid resistant autoclave and reacted by raising the temperature at self-generated pressure to 100° C. and then maintaining it there for 4 hours. Catalyst was recovered by reducing the pressure after which the material was maintained at a temperature of 200° C. under a flow of 3 L of nitrogen per minute to remove lighter components to obtain a pitch having a softening point of 82° C. The ratio of hydrogen atoms to carbon atoms in this synthetic pitch was 0.76, the pyridine insoluble fraction was 0.0% and the ratio of the intensity of the aliphatic C-H stretching bands to total C-H stretching bands when measured by FT-IR was 35%. The synthetic pitch thus obtained was reacted by placing it in another reaction vessel and 20 L of air per kilogram of material were blown through it at 340° C. over 4 hours to obtain an modified 100% optically isotropic pitch having a softening point of 234° C. The ratio of hydrogen atoms to carbon atoms in this modified optically isotropic pitch (H/C) was 0.49, and the ratio of aliphatic C-H stretching band intensity to aromatic C-H stretching band intensity was 0.20. The modified pitch was ground to a powder having a particle diameter of 200 μm or less. Ten grams of the modified pitch

powder were placed on a ceramic dish and then placed in a muffle furnace where a flow of 1 L of air per minute was maintained while the temperature was raised at a rate of 5° C./minute from 150° C. to 320° C. after which it was maintained at 320° C. for 30 minutes. The material obtained was melted into a mass by heating it. This mass was ground to obtain a powder having a particle diameter of 15 μm. The treated powder was calcined at 1200° C., 10 Torr under a slight flow of nitrogen for 2 hours to obtain a powdered carbon material. The powdered carbon material thus obtained was evaluated as a battery anode material according to the methods of Example 5. The storage capacity was 535 mAh/g and the discharge capacity was 403 mAh/g. The capacity loss was very large at 132 mAh/g and the battery discharge capacity was also low. The discharge corresponding to the potential region of 0 to 0.2 volts versus lithium metal was very low at 240 mAh/g.

What is claimed is:

1. A method for preparing a modified optically isotropic pitch comprising:
  - preparing a synthetic pitch by reacting a member selected from the group consisting of a conjugated polycyclic hydrocarbon containing a low molecular weight alkyl group or a material containing such a substituted hydrocarbon in the presence of hydrofluoric acid/boron trifluoride, and
  - treating said synthetic pitch by passing an oxidizing gas through said synthetic pitch at elevated temperatures.
2. A method for preparing a modified optically isotropic pitch according to claim 1, wherein the low molecular weight alkyl group is the methyl group.
3. A method for preparing a modified optically isotropic pitch according to claim 1, wherein the softening point of the synthetic pitch is 200° C. or less.
4. A method for preparing a modified optically isotropic pitch according to claim 1, wherein the softening point of the modified optically isotropic pitch is between 180° C. and 350° C.

\* \* \* \* \*



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(12) **United States Patent**  
**Morita et al.**

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(45) **Date of Patent:** **Sep. 23, 2003**

(54) **NONAQUEOUS ELECTROLYTE SECONDARY BATTERY, CARBON MATERIAL FOR NEGATIVE ELECTRODE, AND METHOD FOR MANUFACTURING CARBON MATERIAL FOR NEGATIVE ELECTRODE**

6,337,159 B1 \* 1/2002 Peled et al. .... 429/231.4

**FOREIGN PATENT DOCUMENTS**

JP	5-28996	2/1993
JP	6-290781	10/1994
JP	9-55204	2/1997
JP	10-40914	2/1998
JP	10-214615	8/1998

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(73) Assignee: **Kabushiki Kaisha Toshiba**, Kawasaki (JP)

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(\* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 166 days.

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(21) Appl. No.: **09/739,778**

C. Menachem, et al., "Characterization of lithiated natural graphite before and after mild oxidation", *Journal of Power Sources* 76, 1998, pp. 180-185.

(22) Filed: **Dec. 20, 2000**

\* cited by examiner

(65) **Prior Publication Data**

US 2001/0018150 A1 Aug. 30, 2001

(30) **Foreign Application Priority Data**

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Sep. 29, 2000	(JP)	.....	2000-300991

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(51) **Int. Cl.**<sup>7</sup> ..... **H01M 10/24**

(57) **ABSTRACT**

(52) **U.S. Cl.** ..... **429/231.8; 252/502**

The present invention provides a nonaqueous electrolyte secondary battery, comprising a positive electrode, a negative electrode containing a carbon material having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1), and a nonaqueous electrolyte:

(58) **Field of Search** ..... 429/231.8; 252/502; 423/414

$$1.2 \leq \Delta H_i^n / \Delta H_i^h \leq 2 \tag{1}$$

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where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the carbon material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the carbon material.

**12 Claims, 2 Drawing Sheets**

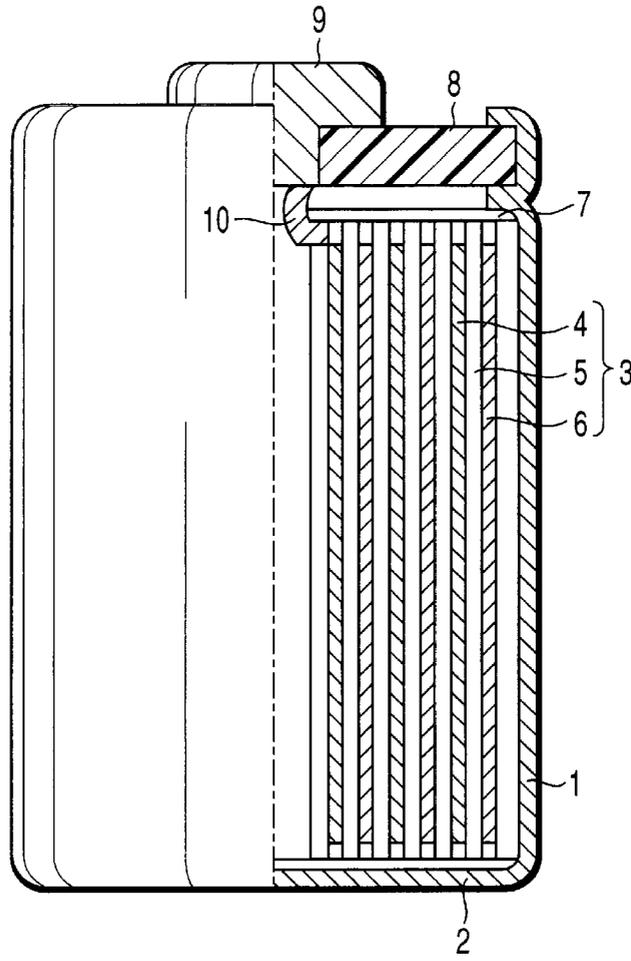


FIG. 1

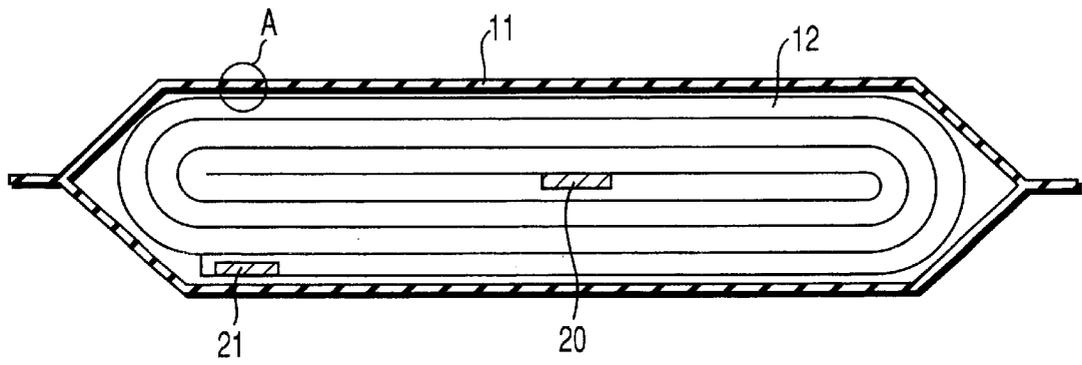


FIG. 2

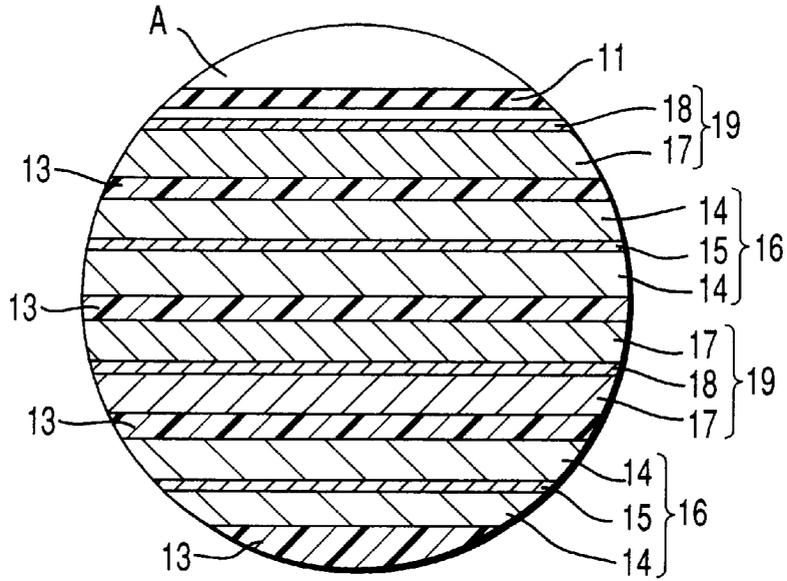


FIG. 3

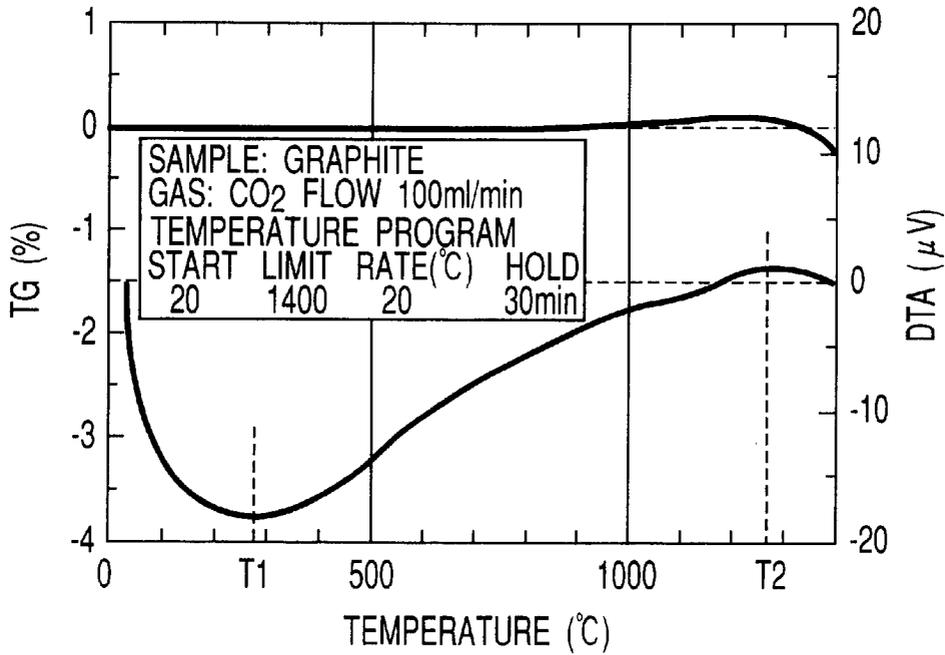


FIG. 4

**NONAQUEOUS ELECTROLYTE  
SECONDARY BATTERY, CARBON  
MATERIAL FOR NEGATIVE ELECTRODE,  
AND METHOD FOR MANUFACTURING  
CARBON MATERIAL FOR NEGATIVE  
ELECTRODE**

**CROSS-REFERENCE TO RELATED  
APPLICATIONS**

This application is based upon and claims the benefit of priority from the prior Japanese Patent Applications No. 11-361594, filed Dec. 20, 1999; and No. 2000-300991, filed Sep. 29, 2000, the entire contents of which are incorporated herein by reference.

**BACKGROUND OF THE INVENTION**

The present invention relates to a nonaqueous electrolyte secondary battery, a carbon material for a negative electrode used for preparing a negative electrode of a battery such as a nonaqueous electrolyte secondary battery, and a method of manufacturing a carbon material for the negative electrode.

In recent years, various portable electronic appliances are being propagated in accordance with a rapid progress in the miniaturization technology of an electronic equipment. Miniaturization is also required for a battery used as a power source of these portable electronic appliances, and a nonaqueous electrolyte secondary battery having a high energy density attracts attentions.

A nonaqueous electrolyte secondary battery using metal lithium as the negative electrode active material has a very high energy density. However, the secondary battery of this type is short in the battery life because a tree branch-like crystals called dendrite are precipitated on the negative electrode in the charging step. The secondary battery of this type also leaves room for further improvement in safety because the dendrite grows to reach the positive electrode so as to bring about a problem such as an internal short circuit.

Under the circumstances, it is attempted to use a lithium alloy, a carbon material, an amorphous chalcogen compound in place of the lithium metal as the negative electrode active material. However, when it comes to the negative electrode containing a lithium alloy, the lithium alloy tends to be finely pulverized in accordance with progress of the charge-discharge cycles, with the result that the secondary battery is rendered poor in the cycle life. Also, when it comes to the negative electrode containing an amorphous chalcogen compound, an irreversible reaction tends to take place in the initial charging step, leading to a problem that the initial charging efficiency is low. Such being the situation, a carbon material capable of ensuring a safety and a long cycle life of the secondary battery is put to a practical use substantially exclusively as the negative electrode active material of the nonaqueous electrolyte secondary battery.

It was customary in the past to use as a carbon material in a nonaqueous electrolyte secondary battery a carbonized material or a graphitized material obtained by subjecting a carbon precursor such as pitch, coke, and polymer to a heat treatment under an inert gas atmosphere as well as a natural graphite, synthetic graphite and a low temperature calcined carbon.

However, since the capacity of the carbon material used as a negative electrode material is small compared with, for example, lithium metal and a lithium alloy, the nonaqueous electrolyte secondary battery comprising a negative elec-

trode containing a carbon material gives rise to a problem that it is impossible to obtain a high discharge capacity.

Japanese Patent Disclosure (Kokai) No. 5-28996 recites a secondary battery comprising at least a positive electrode active material, a negative electrode active material, and an organic electrolyte, characterized in that a natural graphite subjected to a heat treatment at 400 to 800° C. in the presence of an atmosphere consisting of an inert gas or in the vacuum before use is used singly or in combination with another material as a negative electrode material.

On the other hand, Japanese Patent Disclosure No. 6-290781 discloses a lithium secondary battery in which a natural graphite is used as a negative electrode material capable of absorbing-desorbing lithium ions, characterized in that said natural graphite is subjected to a heat treatment under temperatures not lower than 1800° C. in the presence of an atmosphere consisting of an inert gas.

Further, Japanese Patent Disclosure No. 9-55204 discloses a method of manufacturing a lithium ion secondary battery comprising an anode containing carbon capable of reversibly inserting lithium, wherein the carbon is heated in a sufficiently long time and under a sufficient high temperature in the presence of an atmosphere containing O<sub>2</sub> before the battery is assembled so as to selectively oxidize and gasify the undesirable highly reactive carbon atoms, thereby removing the undesirable highly reactive carbon atoms.

Further, a method of removing the impurities by applying a heat treatment to a carbon material is described in "Journal of Power Sources, Vol. 76, pp 180-185, 1998".

On the other hand, claim 1 of Japanese Patent Disclosure No. 10-40914 recites a nonaqueous secondary battery, comprising a negative electrode containing as a negative electrode active material graphite particles having an amorphous carbon attached to the surface, a positive electrode containing a chalcogen compound containing lithium as a positive electrode active material, and a nonaqueous ionic conductor, characterized in that the negative electrode active material is prepared by subjecting graphite particles to an oxidizing treatment, followed by attaching an amorphous carbon to the surfaces of the graphite particles.

Also, claim 1 of Japanese Patent Disclosure No. 10-214615 discloses a nonaqueous secondary battery, comprising a negative electrode, a positive electrode containing a chalcogen compound, which contains lithium, as a positive electrode active material, and a nonaqueous ionic conductor, characterized in that the negative electrode contains as a negative electrode active material a carbon material prepared by attaching an amorphous carbon to the surfaces of graphite particles subjected to an oxidizing treatment with potassium permanganate.

However, any of the secondary batteries disclosed in the six publications referred to above failed to exhibit a sufficient discharge capacity.

**BRIEF SUMMARY OF THE INVENTION**

An object of the present invention is to provide a nonaqueous electrolyte secondary battery having a high capacity and excellent in the cycle life characteristics.

Another object of the present invention is to provide a carbon material for a negative electrode capable of increasing the capacity of a nonaqueous electrolyte secondary battery and a method of manufacturing the particular carbon material for a negative electrode.

According to a first aspect of the present invention, there is provided a nonaqueous electrolyte secondary battery,

comprising a positive electrode, a nonaqueous electrolyte, and a negative electrode containing a carbon material having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1):

$$1.2 \leq \Delta H_i^n/\Delta H_i^h \leq 2 \quad (1)$$

where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the carbon material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the carbon material.

According to a second aspect of the present invention, there is provided a carbon material for a negative electrode, having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1):

$$1.2 \leq \Delta H_i^n/\Delta H_i^h \leq 2 \quad (1)$$

where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the carbon material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the carbon material.

According to a third aspect of the present invention, there is provided a first method of manufacturing a carbon material for a negative electrode, comprising the step of applying a heat treatment to a carbonaceous material containing at least one material selected from the group comprising a carbonized material and a 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</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O.

According to a fourth aspect of the present invention, there is provided a second method of manufacturing a carbon material for a negative electrode, comprising the step of applying a heat treatment to a carbon precursor under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor.

According to a fifth aspect of the present invention, there is provided a third method of manufacturing a carbon material for a negative electrode, comprising the step of applying a heat treatment to a carbonaceous material containing at least one material selected from the group comprising a carbonized material and a graphitized material under an atmosphere containing at least one of a gas of an inorganic acid and a gas of an organic acid.

According to a sixth aspect of the present invention, there is provided a fourth method of manufacturing a carbon material for a negative electrode, comprising the step of:

applying a heat treatment to a carbonaceous material containing at least one material selected from the group comprising 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</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O; and

bringing the carbonaceous material into contact with a gaseous acid.

Further, according to a seventh aspect of the present invention, there is provided a fifth method of manufacturing a carbon material for a negative electrode, comprising the step of:

applying a heat treatment to a carbon precursor under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor; and bringing the carbon precursor into contact with a gaseous acid.

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a partial cross sectional view showing a cylindrical nonaqueous electrolyte secondary battery as an example of the nonaqueous electrolyte secondary battery of the present invention;

FIG. 2 is a cross sectional view showing a thin nonaqueous electrolyte secondary battery as another example of the nonaqueous electrolyte secondary battery of the present invention;

FIG. 3 is a cross sectional view showing in a magnified fashion a portion A shown in FIG. 2; and

FIG. 4 is a graph exemplifying a TG curve (Y axis) and a DTA curve (R axis) obtained by a differential thermal analysis of the graphite used in Examples of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

A method of manufacturing any of first to fifth carbon materials for a negative electrode according to the present invention will now be described.

##### 1. First Manufacturing Method of Carbon Material for Negative Electrode

The manufacturing method of a first carbon material for a negative electrode comprises the step of applying a heat treatment to a carbonaceous material containing at least one material selected from the group consisting essentially of a carbonized material and a 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</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O. The term "gaseous atmosphere" represents the gas introduced into the calcining furnace in the step of the heat treatment.

The carbonized material can be obtained by applying a heat treatment to a carbon precursor such as pitch, coke or polymer. The carbonized material used in the present invention includes, for example, an amorphous carbon and a soft

carbon. On the other hand, the graphitized material can be obtained by applying a heat treatment to a carbon precursor such as pitch, coke or polymer so as to carbonize the carbon precursor, followed by applying again a heat treatment to the carbonized material thus obtained. The carbonizing treatment and the graphitizing treatment can be performed by the methods that are to be described herein later in conjunction with a second manufacturing method. Also, it is possible to use, for example, carbon calcined at a low temperature as the carbonized material. On the other hand, it is possible to use, for example, a natural graphite or a synthetic graphite as the graphitized material.

In the present invention, it is possible to use a mixture of a carbonized material and a graphitized material as a carbonaceous material.

It is desirable for each of the carbonized material and the graphitized material to have 0.34 nm or less of an interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by an X-ray diffractometry. More desirably, the interplanar spacing  $d_{002}$  noted above should fall within a range of between 0.335 nm and 0.34 nm.

It is possible for each of the carbonized material and the graphitized material to contain another element such as boron, phosphorus and fluorine. In order to improve the reaction rate, it is desirable to add an alkaline metal or an alkaline earth metal to the carbonaceous material.

It is desirable for the heat treating temperature  $T$  ( $^{\circ}$  C.) to meet formula (2) given below:

$$(T_1+T_2)/2 \leq T \leq T_2 \quad (2)$$

where  $T$  denotes the temperature ( $^{\circ}$  C.) for the heat treatment,  $T_1$  denotes the peak temperature ( $^{\circ}$  C.) of the endothermic peak obtained when a differential thermal analysis is applied to the carbonaceous material under the gaseous atmosphere noted above, and  $T_2$  denotes the peak temperature ( $^{\circ}$  C.) of the exothermic peak obtained by the differential thermal analysis.

The differential thermal analysis is applied to a carbonaceous material before the heat treatment. The measuring atmosphere in the step of the differential thermal analysis is equal in composition to the gaseous atmosphere for the heat treatment. Also, since the peak temperature obtained by the differential thermal analysis is affected by the amount of the sample, the flow rate of the atmosphere gas, the temperature elevation rate, it is desirable to set the sample weight at about 50 mg, the flow rate of the atmosphere gas at about 100 mL (milliliter)/min, and the temperature elevation rate at about 20 $^{\circ}$  C./min in obtaining the values of  $T_1$  and  $T_2$ .

The peak temperature  $T_1$  of the endothermic peak is generated by the dehydrating reaction of the carbonaceous material or the gasifying reaction of the volatile component from the carbonaceous material. On the other hand, the peak temperature  $T_2$  ( $^{\circ}$  C.) of the exothermic peak is generated by the oxidizing reaction of the carbonaceous material. It is possible to improve markedly the capacity of the secondary battery by setting the heat treating temperature  $T$  to fall within the range defined by formula (2). If the heat treating temperature is set lower than  $(T_1+T_2)/2$ , the surface modifying reaction is unlikely to proceed, resulting in failure to obtain a high battery capacity. On the other hand, if the heat treating temperature is set higher than  $T_2$ , the entire carbonaceous material tends to be rapidly oxidized, making it difficult to improve sufficiently the capacity. Also, the weight reduction caused by the oxidation of the carbonaceous material tends to be increased.

It is desirable for the optimum heat treating time, which tends to differ depending on the manufacturing conditions

such as the heat treating temperature, to fall within a range of between 0.5 hour and 48 hours, more preferably between 1 hour and 12 hours.

The gas contained in the atmosphere for the heat treatment other than  $\text{CO}_2$  and  $\text{H}_2\text{O}$  includes at least one kind of gas selected from the group consisting of an oxygen gas, a nitrogen gas and an inert gas. The inert gas includes, for example, an argon gas, a helium gas, a xenon gas, and a krypton gas. Particularly, it is desirable to use the gas noted above in combination with a non-oxidizing gas represented by a nitrogen gas and the inert gas. Also, it is desirable for an oxygen gas not to be contained in the atmosphere for the heat treatment, i.e., the gas introduced into the calcining furnace. However, where an oxygen gas is contained in the atmosphere for the heat treatment, it is desirable for the oxygen gas content not to exceed 10% by volume. If an oxygen gas is contained in the atmosphere for the heat treatment in an amount exceeding 10% by volume, the combustion reaction between oxygen and carbon is tend to generate. As a result, it is possibly difficult to obtain a desirable surface state. At the same time, it is possible for the gasifying amount in the step of the surface treatment of the carbonaceous material to be increased so as to lower the yield.

The method of the present invention for manufacturing a first carbon material for a negative electrode described above comprises the step of applying a heat treatment to a carbonaceous material containing at least one material selected from the group consisting essentially of a carbonized material and a graphitized material under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$ , a second gaseous atmosphere containing at least 1% by volume of  $\text{H}_2\text{O}$ , and a third gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$  and at least 1% by volume of  $\text{H}_2\text{O}$ . The particular manufacturing method of the present invention makes it possible to provide a carbon material for a negative electrode capable of achieving a nonaqueous electrolyte secondary battery having a large capacity. The particular effect of the present invention is believed to be derived from the mechanism described below.

Specifically, the reaction for converting carbon into a carbon dioxide gas in the presence of  $\text{O}_2$  is a combustion reaction and, thus, an exothermic reaction. On the other hand, the reaction for converting carbon into a carbon dioxide gas in the presence of  $\text{H}_2\text{O}$  or  $\text{CO}_2$  is an endothermic reaction. It follows that carbon is unlikely to be gasified in the presence of  $\text{H}_2\text{O}$  or  $\text{CO}_2$ , compared with the case where carbon is gasified in the presence of  $\text{O}_2$ . If a heat treatment is applied to at least one of the carbonized material and the graphitized material under the first, second or third gaseous atmosphere, it is possible to selectively convert a portion having a low degree of graphitization, which is easier to be gasified, into a carbon dioxide gas while leaving unremoved a portion having a high degree of graphitization and a high electrical conductivity because the particular portion has a low gasifying rate. Also, since the gasifying reaction proceeds moderately, it is possible to have fine pores formed uniformly by the gasifying reaction on the surface of and inside the carbonaceous material. Further, it is possible to increase the crystallinity of the carbonaceous material by the heat treatment. As a result, it is possible to improve the electrical conductivity of the carbonaceous material and the utilization of the lithium absorbing site. Further, some of the pores can perform the function of the lithium absorbing site. As a result, it is possible to improve the capacity of the nonaqueous electrolyte secondary battery.

It should be noted that if the CO<sub>2</sub> content of the gaseous atmosphere is set lower than 10% by volume and, at the same time, if the H<sub>2</sub>O content of the gaseous atmosphere is set lower than 1% by volume, the gasifying reaction amount in a portion having a low degree of graphitization is rendered insufficient, with the result that it is difficult to obtain a high discharge capacity in a secondary battery. Also, if O<sub>2</sub> is used in place of H<sub>2</sub>O and CO<sub>2</sub>, the combustion reaction of carbon is generated rapidly, making it difficult to selectively gasify the portion having a low degree of graphitization.

Also, where the heat treating temperature T is not lower than 2,000° C., it is desirable to set the CO<sub>2</sub> concentration in the first gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 10% by volume and 60% by volume. If the CO<sub>2</sub> concentration exceeds 60% by volume in the case where the heat treating temperature T is not lower than 2,000° C., the gasifying reaction rate is increased, making it possible for even the portion having a high degree of graphitization to be gasified. On the other hand, where the heat treating temperature T is lower than 2,000° C., it is desirable to set the CO<sub>2</sub> concentration in the first gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 50% by volume and 100% by volume. If the CO<sub>2</sub> concentration in the first gaseous atmosphere is lower than 50% in the case where the heat treating temperature is lower than 2,000° C., the reaction is unlikely to proceed promptly so as to make it difficult to obtain a carbon material having a high capacity in a short heat treating time.

Where the heat treating temperature is not lower than 2,000° C., it is desirable to set the H<sub>2</sub>O content of the second gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 1.5% by volume and 30% by volume. If the H<sub>2</sub>O concentration in the second gaseous atmosphere exceeds 30% by volume in the case where the heat treating time is not lower than 2,000° C., the gasifying reaction rate is increased so as to make it possible for even the portion having a high degree of graphitization to be gasified. Also, where the heat treating temperature is lower than 2,000° C., it is desirable for the H<sub>2</sub>O concentration in the second gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 2% by volume and 100% by volume. If the H<sub>2</sub>O concentration in the second gaseous atmosphere is lower than 2% by volume in the case where the heat treating temperature T is lower than 2,000° C., the reaction is unlikely to proceed promptly so as to make it difficult to obtain a carbon material having a high capacity in a short heat treating time.

In the method of the present invention for manufacturing the first carbon material for a negative electrode, the heat treating temperature T is set to meet formula (2) described previously. The nonaqueous electrolyte secondary battery comprising a negative electrode containing the carbon material manufactured by the method of the present invention exhibits a further improved capacity and also exhibits an improved initial charge-discharge efficiency and improved large current characteristics.

## 2. Second Manufacturing Method of Carbon Material for Negative Electrode

The manufacturing method of a second carbon material comprises the step of applying a heat treatment to a carbon precursor under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous material containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor.

It is possible to use as the carbon precursor any of a material containing carbon as a main component, a material capable of carbonization, and a material capable of graphitization. To be more specific, the carbon precursor used in the present invention includes, for example, pitch, coke and polymer. It is possible for the carbon precursor to contain another element such as boron, phosphorus or fluorine. Also, in order to increase the reaction rate, it is effective to add an alkaline metal or an alkaline earth metal to the carbon precursor.

It is desirable to set the heat treating temperature at 800° C. to 3,000° C. If the heat treating temperature is lower than 800° C., a carbon material having the graphite structure not developed therein sufficiently and having a volatile component, which was originally contained in the carbon precursor, left contained therein in a large amount is likely to be obtained. Since the carbon material thus obtained has a low electrical conductivity, the large current discharge characteristics and the cycle characteristics of the secondary battery are lowered. On the other hand, if the heat treatment is carried out under temperatures exceeding 3,000° C., it is possible for the manufacturing cost to be increased. Alternatively, the manufacturing process tends to be made complex. Particularly, it is possible to improve the discharge capacity and the cycle life characteristics of the secondary battery by setting the heat treating temperature to fall within a range of between 2,000° C. and 3,000° C. Naturally, it is more desirable for the heat treating temperature to fall within a range of between 2,000° C. and 3,000° C., and most desirably to fall within a range of between 2,500° C. and 3,000° C.

Where the heat treating temperature is not lower than 2,000° C., it is desirable for the CO<sub>2</sub> concentration in the first gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 10% by volume and 60% by volume for the reasons described previously in conjunction with the manufacturing method of the first carbon material. Also, it is desirable for the H<sub>2</sub>O concentration in the second gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 1.5% by volume and 30% by volume for the reasons described previously in conjunction with the manufacturing method of the first carbon material.

On the other hand, where the heat treating temperature T is lower than 2,000° C., it is desirable to set the CO<sub>2</sub> concentration in the first gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 50% by volume and 100% by volume for the reasons described previously in conjunction with the manufacturing method of the first carbon material. Further, it is desirable to set the H<sub>2</sub>O concentration in the second gaseous atmosphere and the third gaseous atmosphere to fall within a range of between 2% by volume and 100% by volume for the reasons described previously in conjunction with the manufacturing method of the first carbon material.

It is desirable for the optimum heat treating time, which tends to differ depending on the manufacturing conditions such as the heat treating temperature, to fall within a range of between 0.5 hour and 48 hours, more preferably between 1 hour and 12 hours.

The gas contained in the atmosphere for the heat treatment other than CO<sub>2</sub> and H<sub>2</sub>O includes at least one kind of gas selected from the group consisting of an oxygen gas, a nitrogen gas and an inert gas. The inert gas includes, for example, an argon gas, a helium gas, a xenon gas, and a krypton gas. Particularly, it is desirable to use the gas noted above in combination with a non-oxidizing gas represented

by a nitrogen gas and the inert gas. Also, it is desirable for an oxygen gas not to be contained in the atmosphere for the heat treatment, i.e., the gas introduced into the calcining furnace. However, where an oxygen gas is contained in the atmosphere for the heat treatment, it is desirable for the oxygen gas content not to exceed 10% by volume for the reasons described previously in conjunction with the first manufacturing method of the carbon material.

The method of the present invention described above for manufacturing the second carbon material comprises the step of applying a heat treatment to a carbon precursor under an gaseous atmosphere selected from the group consisting of the first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, the second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and the third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor. The particular method of the present invention makes it possible to provide a carbon material for a negative electrode that permits realizing a nonaqueous electrolyte secondary battery of a high capacity. The particular effect of the present invention is believed to be derived from the mechanism described below.

Specifically, in the present invention, a region having a low degree of graphitization can be selectively gasified while carbonizing or graphitizing the carbon precursor so as to improve the electrical conductivity and to improve the utilization of the lithium absorbing site. In addition, it is possible to manufacture a carbon material in which some of pores perform the function of the lithium absorbing site. As a result, a nonaqueous electrolyte secondary battery comprising a negative electrode containing the particular carbon material exhibits an improved capacity.

### 3. Third Manufacturing Method of Carbon Material for Negative Electrode

The third manufacturing method of the carbon material comprises the step of applying a heat treatment to a carbonaceous material containing at least one material selected from the group consisting essentially of a carbonized material and a graphitized material under an atmosphere containing at least one of a gas of an inorganic acid and a gas of an organic acid.

The carbonized material can be obtained by applying a heat treatment to a carbon precursor such as pitch, coke or polymer. The carbonized material used in the present invention includes, for example, an amorphous carbon and a soft carbon. On the other hand, the graphitized material can be obtained by applying a heat treatment to a carbon precursor such as pitch, coke or polymer so as to carbonize the carbon precursor, followed by applying again a heat treatment to the carbonized material thus obtained. It is desirable to carry out the carbonizing treatment and the graphitizing treatment by the method described previously in conjunction with the second manufacturing method of a carbon material. Also, it is possible to use, for example, carbon calcined under a low temperature as the carbonized material. On the other hand, it is possible to use, for example, a natural graphite or a synthetic graphite as the graphitized material.

In the present invention, it is possible to use a mixture of a carbonized material and a graphitized material as a carbonaceous material.

It is desirable for each of the carbonized material and the graphitized material to have not larger than 0.34 nm of an interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by X-ray diffractometry. More desirably, the interplanar spacing  $d_{002}$  noted above should fall within a range of between 0.335 nm and 0.34 nm.

It is possible for each of the carbonized material and the graphitized material to contain another element such as boron, phosphorus or fluorine. Also, in order to promote the reaction rate, it is effect to add an alkaline metal or an alkaline earth metal to at least one of the carbonaceous materials noted above.

The inorganic acid used in the present invention includes, for example, nitric acid, hydrochloric acid, sulfuric acid, hydrofluoric acid, boric acid and phosphoric acid. On the other hand, the organic acid used in the present invention includes, for example, formic acid, acetic acid, propionic acid, phenol and oxalic acid.

Among the organic acids and inorganic acids exemplified above, it is particularly desirable to use a Lewis acid having a high oxidizing power and capable of imparting an oxygen atom in order to improve the electrode capacity. Particularly, it is desirable to use an acid having a high oxidizing power such as nitric acid and organic acid such as acetic acid in order to improve the electrode characteristics. The most desirable acid is nitric acid. In the case of using nitric acid, it is desirable for the reaction temperature to be not lower than 130° C. that is the boiling point of a nitric acid aqueous solution.

The inorganic acid and the organic acid exemplified above make it possible to introduce into the carbonaceous material a functional group having a polar group such as a functional group having a boron atom, a functional group having a nitrogen atom, a functional group having an oxygen atom, and a functional group having a phosphorus atom. Particularly, a functional group having an oxygen atom such as a carboxyl group, a carbonyl group, a hydroxyl group, a lactone group, or a ketone group can be introduced easily into the carbonaceous material. These functional groups are considered to be introduced into the carbonaceous material in the heat treating step. Also, these functional groups, which perform the function of a lithium absorbing site, serve to improve the wettability between a polar solvent of liquid nonaqueous electrolyte and the carbon material in the negative electrode so as to improve the electrode characteristics.

As a gas of an inorganic acid, it is possible to use a water vapor containing a vapor of an inorganic acid, which is prepared by boiling an aqueous solution of an inorganic, in addition to a vapor of an inorganic acid. On the other hand, as a gas of an organic acid, it is possible to use a water vapor containing a vapor of an organic acid, which is prepared by boiling an aqueous solution of an organic acid, in addition to a vapor of an organic acid.

The gas contained in the atmosphere other than the gas of an inorganic acid and the gas of an organic acid includes at least one kind of a gas selected from the group consisting of an oxygen gas, a nitrogen gas and an inert gas. The inert gas used in the present invention includes, for example, an argon gas, a helium gas, xenon gas, and krypton gas. Particularly, it is desirable to use a non-oxidizing gas represented by a nitrogen gas and the inert gas together with the gas of the inorganic acid or the gas of the organic acid.

It is desirable for the heat treating temperature to be not higher than 800° C. If the heat treating temperature exceeds 800° 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. More desirably, the heat treating temperature should not be higher than 500° C. Also, the lower limit of the heat treating temperature should be set to permit the inorganic acid or the organic acid to be present in a gaseous state in the atmosphere under which the heat treatment is performed. It follows that it is desirable to set the heat treating temperature to fall within a range

between the vaporizing temperature of the inorganic acid or the organic acid and 800° C.

The heat treating method includes methods (a) to (c) given below, though the heating treating method is not limited to these methods (a) to (c):

- (a) At least one of the gaseous inorganic acid and the gaseous organic acid is circulated onto a carbonaceous material consisting of at least one of the carbonized material and the graphitized material, and the heating is applied under the particular condition.
- (b) An acid is added to the carbonaceous material so as to prepare a dispersion or a slurry, followed by applying a heat treatment to the dispersion or the slurry at a temperature not lower than the boiling point of the acid.
- (c) An acid acting as a granulating agent is added to the carbonaceous material so as to granulate the carbonaceous material, and the reaction is performed when the resultant grains are dried at high temperatures.

The third method of the present invention for manufacturing a carbon material for a negative electrode comprises the step of applying a heat treatment to a carbonaceous material containing at least material selected from the group consisting essentially of the carbonized material and the graphitized material under an atmosphere containing at least one of an inorganic gas and an organic gas. The nonaqueous electrolyte secondary battery comprising a negative electrode containing the carbon material manufactured by the particular method exhibits an improved initial charge-discharge efficiency, an improved discharge capacity and an improved charge-discharge cycle life. The particular effect is believed to be produced by the mechanism described below.

Specifically, if a heat treatment is applied to the carbonaceous material under an atmosphere containing at least one of a vapor of an organic acid and a vapor of an inorganic acid as in the third manufacturing method of the present invention, it is possible to form fine pores on the surface of the carbonaceous material. It is also possible to introduce a functional group, particularly, a functional group having a polar group such as a carboxyl group, a carbonyl group, a hydroxyl group, a lactone group or a ketone group, into the surface region of the carbonaceous material. These functional groups perform the function of lithium absorbing site and, at the same time, serve to improve the wettability between the liquid nonaqueous electrolyte, which is a polar solvent, and the carbon material in the negative electrode. As a result, the nonaqueous electrolyte secondary battery comprising the negative electrode containing the carbon material manufactured by the method of the present invention is enabled to exhibit an improved initial charge-discharge efficiency, an improve discharge capacity and an improved charge-discharge cycle life.

It is possible to apply both the third manufacturing method and the first manufacturing method described previously to the carbonaceous material as a surface modifying treatment. It is also possible to apply the first manufacturing method and/or the third manufacturing method as a surface modifying treatment to the carbon material prepared by the second manufacturing method of the carbon material described previously.

Particularly preferred combinations are that (I) a surface modifying treatment is applied by the third manufacturing method to the carbon material for a negative electrode manufactured by the second manufacturing method, and that (II) a surface modifying treatment is applied by the first manufacturing method to the carbonaceous material consisting of at least one of the graphitized material and the carbonized material, followed by applying a finish surface

modifying treatment by the third manufacturing method. According to methods (I) and (II) described above, it is possible to obtain a carbon material for a negative electrode having better characteristics produced by the synergetic effect of each treatment.

#### 4. Fourth Manufacturing Method of Carbon Material for Negative Electrode

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</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O, and bringing the carbonaceous material into contact with a gaseous acid.

It is desirable to use a vapor of an acid as the gaseous acid.

The heat treating step can be performed by the method similar to that described previously in conjunction with the first manufacturing method of the carbon material for a negative electrode.

It is possible to use as the gaseous acid at least one kind of a gas selected from the group consisting of a gas of an inorganic acid and a gas of an organic acid. The inorganic acid used in the present invention includes, for example, nitric acid, hydrochloric acid, sulfuric acid, hydrofluoric acid, boric acid and phosphoric acid. On the other hand, the organic acid used in the present invention includes, for example, formic acid, acetic acid, propionic acid, phenol and oxalic acid.

In addition to an inorganic acid vapor, it is possible to use as a gaseous inorganic acid, for example, a water vapor containing a vapor of an inorganic acid that is prepared by boiling an aqueous solution of an inorganic acid. On the other hand, in addition to an organic acid vapor, it is possible to use as a gaseous organic acid, for example, a water vapor containing a vapor of an organic acid that is prepared by boiling an aqueous solution of an organic 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° C. If the heat treating temperature exceeds 800° 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° 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° C. and 500° C.

The gaseous acid can be brought into contact with the carbonaceous material having a heat treatment applied thereto by methods (A) to (C) given below, though the contact method is not limited to these methods (A) to (C):

- (A) A gas containing at least one of a gaseous inorganic acid and a gaseous organic acid is circulated onto the carbonaceous material consisting of at least one of the carbonized material and the graphitized material, and the carbonaceous material is heated under circulation of the gaseous material.

(B) An acid is added to the carbonaceous material so as to prepare a dispersion or a slurry, followed by subjecting the dispersion or the slurry to a heat treatment under temperatures higher than the boiling point of the acid.

(C) An acid acting as a granulating agent is added to the carbonaceous material so as to granulate the carbonaceous material and, then, the resultant grains are subjected to reaction when these grains are dried under high temperatures.

As described above, the fourth method of the present invention for manufacturing a carbon material for a negative electrode comprises the step 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</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O. Since that portion of the carbonaceous material which has a relatively high degree of graphitization has a low gasifying rate, compared with the portion having a low degree of graphitization, it is possible to selectively gasify the that portion of the carbonaceous material which has a low degree of graphitization. As a result, it is possible to form fine pores uniformly in the surface region and the inner region of the carbonaceous material.

In the next step, the carbonaceous material is brought into contact with the gaseous acid, making it possible to introduce uniformly a functional group, particularly, a functional group having a polarity such as a carboxyl group, a carbonyl group, a hydroxyl group, a lactone group or a ketone group into the surface region and the fine pores in the inner region of the carbonaceous material.

The carbon material thus prepared has a high crystallinity and an excellent electrical conductivity. Also, the fine pores formed in the surface region and the inner region of the carbonaceous material and the functional group introduced into the surface region and the fine pores perform the function of a lithium absorbing site. Further, since the polar functional group is present on the surface and in the inner region of the carbonaceous material, it is possible to improve the wettability between the liquid nonaqueous electrolyte, which is a polar solvent, and the carbon material contained in the negative electrode. As a result, it is possible for the nonaqueous electrolyte secondary battery comprising the negative electrode containing the carbon material manufactured by the method of the present invention to exhibit a markedly improved initial charge-discharge efficiency, a markedly improved discharge capacity, and a markedly improved charge-discharge cycle life.

#### 5. Fifth Manufacturing Method of Carbon Material for Negative Electrode

The fifth manufacturing method of a carbon material for a negative electrode comprises the steps of applying a heat treatment to a carbon precursor under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor and, thus, to obtain a carbonaceous material, and bringing the carbonaceous material into contact with a gaseous acid.

It is desirable to use a vapor of an acid as the gaseous acid.

The carbonizing treating step and the graphitizing treating step can be performed by the methods similar to those

described previously in conjunction with the second manufacturing method of a carbon material for a negative electrode.

On the other hand, the acid treating step can be performed by the method similar to that described previously in conjunction with the fourth method of manufacturing a carbon material for a negative electrode.

According to the fifth method of the present invention for manufacturing a carbon material for a negative electrode, a heat treatment is applied to a carbon precursor under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O so as to carbonize or graphitize the carbon precursor and, thus, to obtain a carbonaceous material. As a result, fine pores are formed uniformly in the surface region and inner region of the carbonaceous material, making it possible to obtain a carbonaceous material having a high electrical conductivity.

In the next step, the carbonaceous material is brought into contact with a gaseous acid so as to make it possible to introduce uniformly a functional group, particularly, a functional group having a polarity such as a carboxyl group, a carbonyl group, a hydroxyl group, a lactone group or a ketone group, into the surface region and the fine pores present in the inner region of the carbonaceous material.

The carbon material thus prepared exhibits a high electrical conductivity. Also, the fine pores formed in the surface region and inner region of the carbon material and the polar functional group present within the pore and on the surface region perform the function of a lithium absorbing site. Further, since the polar functional group is present in the surface region and inner region of the carbon material, it is possible to improve the wettability between the liquid nonaqueous electrolyte, which is a polar solvent, and the carbon material contained in the negative electrode. As a result, it is possible for the nonaqueous electrolyte secondary battery comprising the negative electrode containing the carbon material manufactured by the method of the present invention to exhibit a markedly improved initial charge-discharge efficiency, a markedly improved discharge capacity, and a markedly improved charge-discharge cycle life.

A nonaqueous electrolyte secondary battery of the present invention will now be described.

A nonaqueous electrolyte secondary battery of the present invention comprises a container, a positive electrode housed in said container, a negative electrode housed in said container, said negative electrode containing a carbon material having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1), and a nonaqueous electrolyte housed in the container:

$$1.2 \leq \Delta H_i^n / \Delta H_i^h \leq 2 \quad (1)$$

where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the carbon material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the carbon material.

The negative electrode, the positive electrode, the nonaqueous electrolyte and the container will now be described in detail.

#### 1) Negative Electrode

The negative electrode comprises a current collector and an active material-containing layer containing a carbon material, said layer being formed on one surface or both surfaces of the current collector.

The carbon material will now be described in detail.

As apparent from formula (I) given below, the immersion heat  $\Delta H_i$  denotes the sum of the dispersion force  $h_i^d$ , the polarizing force  $h_i^a$ , and the mutual function  $h_i^m$  between the permanent dipole of the liquid and the static electric field on the surface of the solid:

$$\Delta H_i = h_i^d + h_i^a + h_i^m \quad (I)$$

If  $h_i^d + h_i^a$  in formula (I) is considered to be constant,  $\Delta H_i$  corresponds to the change in  $h_i^m$ . If  $F$  represents the intensity of the static electric field on the solid surface, the relationship denoted by formula (II) given below is established:

$$h_i^m = -n\mu F \quad (II)$$

It follows that formula (III) given below is established:

$$\Delta H_i = n\mu F + \text{const.} \quad (III)$$

In formulas (II) and (III) given above,  $\mu$  represents the dipole efficiency of the immersion liquid, and  $n$  represents the number of adsorbed molecules per unit surface area.

If the immersion heat is obtained by using a series of adsorbates differing from each other in the dipole efficiency and being equal to each other in the absorption area of a single molecule, it is possible to obtain the intensity of the static electric field on the surface, i.e., the surface polarity, from the relationships specified in formulas (I) to (III) given above.

N-heptane and 1-nitropropane are equal to each other in the adsorption area of a single molecule. It should be noted that n-heptane has a dipole efficiency  $\mu$  of 0D. On the other hand, 1-nitropropane has a dipole efficiency  $\mu$  of 3.75D. It follows that the difference in the immersion heat between these two solvents reflects the surface polarity. A ratio of the immersion heat  $\Delta H_i^n$  of the carbon material for 1-nitropropane to the immersion heat  $\Delta H_i^h$  of the carbon material for n-heptane, i.e., the ratio  $\Delta H_i^n/\Delta H_i^h$ , reflects mainly the surface polarity of the carbon material and the magnitude of the dispersion force of the carbon material relative to the solvent. To be more specific, the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  tends to be increased with increase in the surface polarity of the carbon material and also tends to be decreased with decrease in the particle diameter of the carbon material to increase the contribution of the carbon material to the dispersion force relative to the solvent.

The polarity on the surface of the carbon material is generated by a heterogeneous atom other than carbon present on the surface of the carbon material and by the functional group owned by the heterogeneous atom. The heterogeneous atom includes, for example, a boron atom, a nitrogen atom, an oxygen atom, and a phosphorus atom. Since the heterogeneous atom present on the surface of the carbon material and the functional group owned by the heterogeneous atom perform the function of an absorption-desorption site of lithium, it is possible to increase the lithium adsorption-desorption site of the carbon material. Also, it is possible to improve the affinity between the carbon material and the liquid nonaqueous electrolyte, which is a polar solvent, by increasing the polarity on the surface of the carbon material.

It should be noted that the immersion heat of n-heptane contained in the carbon material is substantially constant regardless of the magnitude of the polarity on the surface of the carbon material. On the other hand, the immersion heat of 1-nitropropane included with the carbon material is increased with increase in the polarity of the surface of the carbon material. Where the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$

is less than 1.2, the immersion heat for 1-nitropropane included with the carbon material is small, and the polarity on the surface of the carbon material is low. It follows that the lithium absorption-desorption capacity of the carbon material is lowered so as to lower the discharge capacity of the secondary battery. On the other hand, where the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  exceeds 2, the immersion heat for 1-nitropropane included in the carbon material is large, and the polarity on the surface of the carbon material is high. However, an excessively large amount of the heterogeneous atoms present on the surface of the carbon material tends to lower the electrical conductivity of the carbon material and to invite a side reaction such as decomposition of the nonaqueous electrolyte. More desirably, the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  should fall with a range of between 1.25 and 1.75.

It is desirable for the average particle diameter of the carbon material to fall within a range of between 5  $\mu\text{m}$  and 100  $\mu\text{m}$ . If the average particle diameter is smaller than 5  $\mu\text{m}$ , the end faces of the carbon layers constituting the graphite crystallite are exposed in large amounts to the surface of the carbon material. As a result, the cycle life characteristics and initial charge-discharge efficiency tend to be lowered. On the other hand, if the average particle diameter exceeds 100  $\mu\text{m}$ , the reaction area of the carbon material is rendered insufficient, giving rise to the difficulty that the reaction rate of the lithium absorption-desorption reaction tends to be lowered so as to lower the discharge capacity of the secondary battery. More desirably, the average particle diameter of the carbon material should fall within a range of between 10  $\mu\text{m}$  and 80  $\mu\text{m}$ .

In the conventional carbon material, the polarity on the surface is small. Therefore, the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  is substantially 1 when the average particle diameter of the carbon material falls within a range of between 5  $\mu\text{m}$  and 100  $\mu\text{m}$ . It should be noted that the negative electrode containing a carbon material having the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  falling within a range of between 1.2 and 2 and having an average particle diameter falling within a range of between 5  $\mu\text{m}$  and 100  $\mu\text{m}$  permits improving the lithium absorption-desorption site of the negative electrode and also permits improving the affinity between the carbon material and the nonaqueous electrolyte. It follows that it is possible to markedly improve the discharge capacity and the cycle characteristics of the secondary battery.

It is possible for the carbon material to be spherical, fibrous, or a granular. In other words, it is possible for the negative electrode included in the secondary battery of the present invention to contain at least one kind of a carbon material selected from the group consisting of a fibrous carbon material, a spherical carbon material and a granular carbon material.

It is desirable for the average fiber length of the fibrous carbon material to fall within a range of between 5  $\mu\text{m}$  and 100  $\mu\text{m}$ , more desirably between 10  $\mu\text{m}$  and 60  $\mu\text{m}$ .

It is desirable for the average fiber diameter of the fibrous carbon material to fall within a range of between 0.1  $\mu\text{m}$  and 30  $\mu\text{m}$ , more desirably between 1  $\mu\text{m}$  and 15  $\mu\text{m}$ .

Further, it is desirable for the average aspect ratio of the fibrous carbon material to fall within a range of between 1 and 50, more desirably between 1.5 and 20. Incidentally, the term "aspect ratio" represents a ratio of the fiber length to the fiber diameter (a ratio of fiber length/fiber diameter).

It is desirable for a ratio of the minor radius to the major radius of the spherical carbonaceous material (a ratio of minor radius/major radius) to be at least 1/10, more preferably at least 1/2.

The term "granular carbonaceous material" noted above represents a carbonaceous material powder having a shape that a ratio of the minor radius to the major radius, i.e., a ratio of minor radius/major radius, falls within a range of between 1/100 and 1. More desirably, the ratio noted above should fall within a range of between 1/10 and 1.

It is desirable for the carbon material of the present invention to have an interplanar spacing  $d_{002}$  derived from (002) reflection of the graphite structure obtained by the X-ray diffractometry, which falls within a range of between the theoretical value of 0.335 nm (3.35 Å) and 0.34 nm (3.4 Å). Since the particular carbon material permits suppressing the potential for the lithium absorption-desorption, it is possible to improve the energy density of the nonaqueous electrolyte secondary battery.

It is desirable for the specific surface area of the carbon material determined by the BET method to fall within a range of between 1 and 50 m<sup>2</sup>/g. If the specific surface area is smaller than 1 m<sup>2</sup>/g, it is possibly difficult to increase sufficiently the lithium absorption-desorption site on the surface of the carbon material. On the other hand, if the specific surface area exceeds 50 m<sup>2</sup>/g, the decomposition reaction (reducing reaction) of the nonaqueous electrolyte is promoted, with the result that it is possibly difficult to obtain an excellent cycle characteristics of the secondary battery. More desirably, the specific surface area of the carbon material should fall within a range of between 2 and 20 m<sup>2</sup>/g.

The carbon material having the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  defined in formula (1) can be obtained by any of the first to fifth methods of manufacturing the carbon material for a negative electrode. To be more specific, according to the first and second manufacturing methods of the carbon material for a negative electrode, it is possible to form uniformly fine pores in the surface region and the inner region of the carbon material and to introduce uniformly heterogeneous atoms such as oxygen atoms into the fine pores including those inside the carbon material. As a result, it is possible to increase the polarity on the surface of the carbon material, making it possible to obtain a carbon material having the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  defined in formula (1). Particularly, according to the fourth and fifth manufacturing methods of the carbon material for a negative electrode, it is possible to form uniformly fine pores in the surface region and the inner region of the carbon material. It is also possible to apply an acid treatment to not only the surface but also the inner region of the carbon material. As a result, it is possible to introduce uniformly at least one kind of a functional group having a high polarity selected from the group consisting of a functional group having a boron atom, a functional group having a nitrogen atom, a functional group having an oxygen atom, and a functional group having a phosphorus atom into the surface of the carbon material including the surfaces of the fine pores present inside the carbon material. It follows that it is possible to increase the polarity on the surface of the carbon material, compared with the first and second manufacturing methods of the carbon material for a negative electrode. In other words, the fourth and fifth methods of manufacturing the carbon material for a negative electrode described above make it possible to obtain a carbon material having the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  defined in formula (1) and having an average particle diameter of 5 to 100 μm.

The negative electrode can be prepared by, for example, adding a binder to the carbon material, followed by suspending the carbon material in a suitable solvent and subsequently coating a current collector with the suspension and drying and pressing the current collector coated with the

suspension. It is possible to add a conducting agent to the suspension noted above.

The binder used in the present invention includes, for example, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), ethylene-propylenediene copolymer (EPDM), and styrene-butadiene rubber (SBR).

It is possible to use as a current collector a conductive substrate having a porous structure or a non-porous conductive substrate. Each of these conductive substrates can be formed of, for example, copper, stainless steel, or nickel. It is desirable for the thickness of the current collector to fall within a range of between 5 μm and 20 μm. Where the thickness of the current collector falls within the range noted above, it is possible to obtain a sufficient strength of the electrode and a sufficient lightweight of the electrode in a good balance.

It is desirable for the thickness of the active material-containing layer to fall within a range of between 10 μm and 150 μm. It follows that, where the active material-containing layer is formed on each surface of the current collector, the sum of the thicknesses of the active material-containing layers formed on both surfaces of the current collector falls within a range of between 20 μm and 300 μm. It is more desirable for the thickness of a single active material-containing layer to fall within a range of between 30 μm and 100 μm. Where the thickness falls within the range noted above, it is possible to markedly improve the large current discharge characteristics and the cycle life of the secondary battery.

## 2) Positive Electrode

The positive electrode comprises a positive electrode current collector and an active material-containing layer formed on one surface or each surface of the current collector.

The positive electrode can be prepared by, for example, suspending a positive electrode active material, a conducting agent and a binder in a suitable solvent, followed by coating the current collector with the resultant suspension and subsequently drying and pressing the current collector to form a band-like electrode.

It is desirable for the positive electrode active material to be formed of various oxides including, for example, manganese dioxide, lithium manganese complex oxide, lithium-containing nickel cobalt oxide (e.g., LiCoO<sub>2</sub>), lithium-containing nickel cobalt oxide (e.g., LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>), and a lithium manganese complex oxide (e.g., LiMn<sub>2</sub>O<sub>4</sub> or LiMnO<sub>2</sub>). In the case of using the particular positive electrode active material, it is possible to obtain a high voltage in the secondary battery.

The conducting agent used in the present invention includes, for example, acetylene black, carbon black and graphite.

The binder used in the present invention includes, for example, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), ethylene-propylenediene copolymer (EPDM), and styrene-butadiene rubber (SBR).

Concerning the mixing ratio of the positive electrode active material, the conducting agent and the binder, it is desirable to set the amount of the positive electrode active material to fall within a range of between 80 and 95% by weight, to set the amount of the conducting agent to fall within a range of between 3 and 20% by weight, and to set the amount of the binder to fall within a range of between 2 and 7% by weight.

It is possible to use as a current collector a conductive substrate having a porous structure or a non-porous conductive substrate. Each of these conductive substrates can be

formed of, for example, aluminum, stainless steel, or nickel. It is desirable for the thickness of the current collector to fall within a range of between 5  $\mu\text{m}$  and 20  $\mu\text{m}$ . Where the thickness of the current collector falls within the range noted above, it is possible to obtain a sufficient strength of the electrode and a sufficient lightweight of the electrode in a good balance.

It is desirable for the thickness of the active material-containing layer to fall within a range of between 10  $\mu\text{m}$  and 150  $\mu\text{m}$ . It follows that, where the active material-containing layer is formed on each surface of the current collector, the sum of the thicknesses of the active material-containing layers formed on both surfaces of the current collector falls within a range of between 20  $\mu\text{m}$  and 300  $\mu\text{m}$ . It is more desirable for the thickness of a single active material-containing layer to fall within a range of between 30  $\mu\text{m}$  and 100  $\mu\text{m}$ . Where the thickness falls within the range noted above, it is possible to markedly improve the large current discharge characteristics and the cycle life of the secondary battery.

### 3) Nonaqueous Electrolyte

The nonaqueous electrolyte used in the present invention includes a liquid nonaqueous electrolyte, a gel nonaqueous electrolyte, a polymer solid electrolyte, and an inorganic solid electrolyte having a lithium ion conductivity. Particularly, it is desirable to use a liquid nonaqueous electrolyte in the present invention.

The liquid nonaqueous electrolyte can be prepared by dissolving a solute in a nonaqueous solvent.

It is also possible to use a gel nonaqueous electrolyte, which comprises a polymer material and a liquid nonaqueous electrolyte forming a complex with the polymer material. The gel nonaqueous electrolyte can be prepared by, for example, mixing the nonaqueous solvent, the solute and the polymer material, followed by applying a heat treatment to the resultant mixture so as to permit the mixture to gel. The polymer material used in the present invention includes, for example, polyacrylonitrile, polyacrylate, polyvinylidene fluoride (PVdF), polyethylene oxide (PEO) and a copolymer containing acrylonitrile, acrylate, vinylidene fluoride or ethylene oxide as a monomer. Particularly, it is desirable to use a gel electrolyte prepared by the method described in the following. Specifically, in the first step, a solution prepared by dissolving a polymer material such as a copolymer between polyvinylidene fluoride and hexafluoropropylene in a solvent such as tetrahydroxy furan (THF) is mixed with a liquid nonaqueous electrolyte so as to obtain a paste. Then, a substrate is coated with the resultant paste, followed by drying the coating so as to obtain a thin film. An electrode group is prepared by arranging a positive electrode and a negative electrode with thin film thus obtained interposed therebetween. After the electrode group is impregnated with the liquid nonaqueous electrolyte, the thin film noted above is plasticized by a gelling treatment such as a heat treatment so as to obtain an electrode group having a gel electrolyte layer interposed between the positive electrode and the negative electrode.

The solid electrolyte can be obtained by dissolving a lithium salt in a polymer material, followed by solidifying the polymer material. The polymer material used in the present invention includes, for example, polyacrylonitrile, polyvinylidene fluoride (PVdF), polyethylene oxide (PEO), and a copolymer containing acrylonitrile, vinylidene fluoride or ethylene oxide as a monomer.

The inorganic solid electrolyte used in the present invention includes a ceramic material containing lithium. Particularly, it is desirable to use as the inorganic solid electrolyte  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{PO}_4\text{—Li}_2\text{S—SiS}_2$  glass.

The nonaqueous solvent and the solute contained in the nonaqueous electrolyte will now be described.

It is desirable for the nonaqueous solvent to be formed of a mixed solvent consisting of at least one kind of solvent (hereinafter referred to as a first solvent) selected from propylene carbonate (PC) and ethylene carbonate (EC) and a solvent (hereinafter referred to as a second solvent) having a viscosity lower than that of PC and EC.

The second solvent includes, for example, a chain-like carbonate such as dimethyl carbonate (DMC), methyl ethyl carbonate (MEC) or a diethyl carbonate (DEC), as well as methyl propionate, ethyl propionate,  $\gamma$ -butyrolactone (BL), acetonitrile (AN), ethyl acetate (EA), toluene, xylene and methyl acetate (MA). It is possible to use as the second solvent one kind of the compound selected from the group of the compounds exemplified above or a mixture of at least two kinds of these compounds. Also, it is desirable for the donor number of the second solvent not to exceed 16.5.

It is desirable for the viscosity of the second solvent to be not larger than 2.8 cmp at 25° C.

It is desirable for the first solvent to be used in the mixed solvent in an amount of 10 to 80% by volume, more preferably, in an amount of 20 to 75% by volume.

The solute used in the present invention includes, for example, lithium salts such as lithium perchlorate ( $\text{LiClO}_4$ ), lithium hexafluoro phosphate ( $\text{LiPF}_6$ ), lithium borofluoride ( $\text{LiBF}_4$ ), lithium hexafluoro arsenate ( $\text{LiASF}_6$ ), lithium trifluoro meta-sulfonate ( $\text{LiCF}_3\text{SO}_3$ ), and bistrifluoromethyl sulfonyl imide lithium [ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ]. Particularly, it is desirable to use  $\text{LiPF}_6$  and  $\text{LiBF}_4$  as the solute.

It is desirable for the solute to be dissolved in the nonaqueous solvent at a rate of 0.5 to 2 mol/L.

### 4) Separator

The separator performs the function of an insulating layer between the positive electrode and the negative electrode and is constructed such that the nonaqueous electrolyte is movable through the separator.

It is possible to use a porous body made of an insulating material for forming the separator. The insulating material used for forming the separator in the present invention includes, for example, a porous film such as a polyethylene film, a polypropylene film or a polyvinylidene fluoride film, and an unwoven fabric of a synthetic resin such as polyethylene, polypropylene or polyvinylidene fluoride. Particularly, it is desirable to use a porous film made of polyethylene, polypropylene or both polyethylene and polypropylene because the separator made of the particular porous film permits improving the safety of the secondary battery.

It is desirable for the separator to have a thickness not larger than 30  $\mu\text{m}$ . If the thickness of the separator exceeds 30  $\mu\text{m}$ , the distance between positive electrode and the negative electrode is rendered large so as to increase the internal resistance of the secondary battery. Also, it is desirable to set the lower limit in the thickness of the separator at 5  $\mu\text{m}$ . If the thickness is smaller than 5  $\mu\text{m}$ , the mechanical strength of the separator is markedly lowered. As a result, an internal short circuit tends to take place in the secondary battery. More desirably, the upper limit in the thickness of the separator should be set at 25  $\mu\text{m}$  and the lower limit should be set at 10  $\mu\text{m}$ .

It is desirable for the thermal shrinkage of the separator, when the separator is left to stand at 120° C. for one hour, to be not higher than 20%. If the thermal shrinkage exceeds 20%, it is highly possible for the short-circuiting to be generated by heating. More desirably, the thermal shrinkage of the separator should be not higher than 15%.

It is desirable for the separator to have a porosity falling within a range of between 30% and 70%. If the porosity is lower than 30%, it is difficult for the separator to exhibit a high capability of retaining the electrolyte. On the other hand, if the porosity exceeds 70%, it is possible for the separator to fail to exhibit a sufficiently high mechanical strength. It is more desirable for the porosity of the separator to fall within a range of between 35% and 70%.

It is desirable for the air permeability of the separator not to exceed 500 seconds/100 cm<sup>3</sup>. If the air permeability exceeds 500 seconds/100 cm<sup>3</sup>, it is difficult to obtain a high lithium ion mobility in the separator. On the other hand, the lower limit of the air permeability should be 30 seconds/100 cm<sup>3</sup>. If the air permeability is lower than 30 seconds/100 cm<sup>3</sup>, it is possibly difficult to obtain a sufficient mechanical strength of the separator. More desirably, the upper limit of the air permeability of the separator should be set at 300 seconds/100 cm<sup>3</sup>, and the lower limit should be set at 50 seconds/100 cm<sup>3</sup>.

#### 6) Housing Container

The electrode group including the positive electrode and the negative electrode and the nonaqueous electrolyte are housed in the housing container.

It is possible for the housing container to be in the form of a cylinder having a bottom and circular in cross section, in the form of a cylinder having a bottom and rectangular in cross section, or in the form of a bag.

The housing container can be formed of, for example, a film material or a metal plate.

The film material used in the present invention for forming the housing container includes, for example, a metal film, a resin film made of, for example, a thermoplastic film, and a sheet including a flexible metal layer and a resin layer such as a thermoplastic resin layer formed on one surface or each surface of the metal layer. It is possible for the resin sheet and the resin layer noted above to be formed of a single kind of resin and a plurality of different kinds of resins, respectively. On the other hand, the metal layer noted above can be formed of single kind of metal or a plurality of different kinds of metals. Also, the metal film can be made of, for example, aluminum, iron, stainless steel, or nickel.

It is desirable for the film material constituting the wall of the housing container to have a thickness not larger than 0.25 mm. It is particularly desirable for the thickness of the film material to fall within a range of between 0.05 mm and 0.2 mm. In this case, it is possible to achieve a secondary battery small in thickness and light in weight.

Particularly, it is desirable to use the sheet including a flexible metal layer and a resin layer formed on one surface or each surface of the metal layer because the sheet of this type is light in weight, has a high mechanical strength, and is capable of preventing a substance such as water from entering the secondary battery from the outside. The housing container formed of the particular sheet is sealed by, for example, a heat seal. Therefore, it is desirable to arrange a thermoplastic resin layer on the inner surface of the housing container. It is desirable for the thermoplastic resin to have a melting point not lower than 120° C., more preferably a melting point falling within a range of between 140° C. and 250° C. The thermoplastic resin used in the present invention includes, for example, a polyolefin such as polyethylene or polypropylene. Particularly, it is desirable to use polypropylene having a melting point not lower than 150° C. because the sealing strength of the heat seal portion is increased. On the other hand, it is desirable for the metal layer to be made of aluminum because it is possible to prevent water from entering the secondary battery.

FIGS. 1 to 3 collectively show as an example the construction of a nonaqueous electrolyte secondary battery of the present invention.

Specifically, FIG. 1 is a partial cross sectional view showing a cylindrical nonaqueous electrolyte secondary battery as an example of the nonaqueous electrolyte secondary battery of the present invention. FIG. 2 is a cross sectional view showing a thin nonaqueous electrolyte secondary battery as an example of the nonaqueous electrolyte secondary battery of the present invention. Further, FIG. 3 is a cross sectional view showing in a magnified fashion portion A shown in FIG. 2.

As shown in FIG. 1, an insulator 2 is arranged in the bottom portion of a cylindrical container 1 having a bottom, circular in cross section, and made of stainless steel. An electrode group 3 is arranged within the container 1. The electrode group 3 consists of a band-like laminate structure including a positive electrode 4, a separator 5, a negative electrode 6, and a separator 5, said laminate structure being spirally wound such that the separator 5 constitutes the outermost layer of the spirally wound laminate structure.

A nonaqueous electrolyte is housed in the container 1. An insulating paper sheet 7 having a hole made in the central portion is arranged above the electrode group 3 within the container 1. An insulating sealing plate 8 is arranged in an upper open portion of the container 1, and the sealing plate 8 is fixed to the container 1 by caulking inward the region in the vicinity of the upper open portion of the container 1. A positive electrode terminal 9 is fitted into the center of the insulating sealing plate 8. One end of a positive electrode lead 10 is connected to the positive electrode 4, with the other end being connected to the positive electrode terminal 9. Further, the negative electrode 6 is connected via a negative electrode lead (not shown) to the container 1 acting as a negative electrode terminal.

As shown in FIG. 2, an electrode group 12 is housed in a housing container 11 formed of, for example, a sheet containing a resin layer. The electrode group 12 consists of a laminate structure including a positive electrode, a separator, and a negative electrode, said laminate structure wound in a flattened shape. The construction of the laminate structure is shown in detail in FIG. 3. As shown in FIG. 3, the laminate structure comprises a separator 13, a positive electrode 16 including an active material-containing layer 14, a positive electrode current collector 15, and another active material-containing layer 14, the separator 13, a negative electrode 19 including a negative electrode layer 17, a negative electrode current collector 18 and another negative electrode layer 17, the separator 13, the positive electrode 16 including the active material-containing layer 14, the positive electrode current collector 15, and the active material-containing layer 14, the separator 13, and the negative electrode 19 including the negative electrode layer 17 and the negative electrode current collector 18, which are laminated one upon the other in the order mentioned as viewed from the lowermost layer shown in the drawing. It should be noted that the negative electrode current collector 18 constitutes the outermost circumferential layer of the electrode group 12. One end of a band-like positive electrode lead 20 is connected to the positive electrode current collector 15, with the other end extending outward from the housing container 11. On the other hand, one end of a band-like negative electrode lead 21 is connected to the negative electrode current collector 18 of the electrode group 2, with the other end extending outward from the housing container 11.

As described above, the nonaqueous electrolyte secondary battery of the present invention comprises a positive

electrode, a negative electrode containing a carbon material having an immersion heat ratio ( $\Delta H_i^s/\Delta H_i^h$ ) defined by formula (1) described previously, and a nonaqueous electrolyte. The carbon material used in the present invention has fine pores distributed uniformly and a suitably high polarity on the surface. As a result, it is possible to increase the lithium absorption-desorption sites and to increase the affinity with the liquid nonaqueous electrolyte. It follows that it is possible to provide a nonaqueous electrolyte secondary battery that permits exhibiting an improved initial charge-discharge efficiency, an improved discharge capacity, and an improved charge-discharge cycle life characteristics.

It should also be noted that at least one kind of a functional group selected from the group consisting of a functional group having a boron atom, a functional group having a nitrogen atom, a functional group having an oxygen atom, and a functional group having a phosphorus atom is present on the surface region and on the surface of the pores formed inner region of the carbon material. As a result, it is possible to increase the lithium absorption-desorption sites of the carbon material. It is also possible to improve the affinity between the carbon material and the liquid nonaqueous electrolyte. It follows that it is possible to further increase the discharge capacity and the charge-discharge cycle life of the nonaqueous electrolyte secondary battery. It should be noted in particular that at least one kind of a functional group is selected from the group consisting of a carboxyl group, a carbonyl group, a hydroxyl group, a lactone group and a ketone group so as to markedly improve the charge-discharge capacity and the charge-discharge cycle life.

Examples of the present invention will now be described so as to set forth clearly the prominent effects produced by the present invention. Needless to say, the technical scope of the present invention is not limited by the Examples which follow.

#### EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLES 1 TO 3

##### Preparation of Carbon Material for Negative Electrode

A sample was prepared by spinning a petroleum pitch, followed by applying a heat treatment to the spun sample at 350° C. under the air atmosphere so as to make the spun sample infusible. Then, a treatment to graphitize the sample was performed under the heat treating temperature and the atmosphere shown in Table 1 so as to obtain a carbon material. The heat treating time was set at 8 hours. Before the heat treatment, a 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.

##### Preparation of Negative Electrode

Polytetrafluoroethylene was added to the carbon material thus obtained so as to prepare a sheet. The sheet thus prepared was pressed against a stainless steel mesh, followed by drying the sheet at 150° C. under vacuum so as to obtain a test electrode.

##### Assembling of Test Cell

A liquid nonaqueous electrolyte was prepared by dissolving 1M of  $\text{LiPF}_6$  in a nonaqueous solvent prepared by mixing ethylene carbonate (EC) and methyl ethyl carbonate (MEC) at a mixing ratio by volume of 1:2. A cell including

a counter electrode and a reference electrode each formed of metal lithium was assembled under an argon gas atmosphere by using the test electrode and the liquid nonaqueous electrolyte described above. Then, a charge-discharge test was applied to the cell thus prepared.

For the charge-discharge test, the cell was charged with a current density of 1 mA/cm<sup>2</sup> until the potential difference between the reference electrode and the test electrode was increased to reach 0.01V. Then, charging was continued for 5 hours with a constant voltage of 0.01V, followed by discharging the cell under a current density of 1 mA/cm<sup>2</sup> until the voltage was lowered to 2V. Table 1 also shows the conditions of the heat treatment and the capacity per unit weight of the negative electrode material obtained by the charge-discharge test.

TABLE 1

	Heating temperature (° C.)	Composition of atmosphere gas	Capacity per unit weight (%)
Comparative example 1	3000	Ar (100 vol. %)	100
Example 1	3000	CO <sub>2</sub> (30 vol. %)/Ar (balance)	136
Example 2	3000	CO <sub>2</sub> (15 vol. %)/Ar (balance)	121
Example 3	3000	H <sub>2</sub> O (10 vol. %)/Ar (balance)	129
Example 4	3000	H <sub>2</sub> O (5 vol. %)/Ar (balance)	117
Comparative example 2	3000	CO <sub>2</sub> (5 vol. %)/Ar (balance)	101
Comparative example 3	3000	H <sub>2</sub> O (0.5 vol. %)/Ar (balance)	100

As apparent from Table 1, the secondary battery for each of Examples 1 to 4 comprising the negative electrode containing the carbon material obtained by the second manufacturing method was found to be superior to the secondary battery for each of Comparative Examples 1 to 3 in the negative electrode capacity per unit weight.

On the other hand, where the carbon dioxide gas concentration in the heat treating atmosphere is lower than 10% by volume as in Comparative Example 2, or where the water vapor concentration in the heat treating atmosphere is less than 1% by volume as in Comparative Example 3, it is impossible improve the capacity.

#### EXAMPLES 5 TO 10

##### Differential Thermal Analysis of Carbonaceous Material

FIG. 4 is a graph showing as an example a TG (Y axis) curve and a DTA curve (R axis) obtained by a differential thermal analysis of a highly crystalline synthetic graphite available on the market. The differential thermal analysis was performed under the conditions that 50 mg of a highly crystalline synthetic graphite available on the market was used as a sample, a carbon dioxide gas was used as an atmosphere gas within the furnace, the gas flow rate was set at 100 mL/min, the temperature at which the measurement was started was set at 20° C., the measurement was finished at 1,400° C., the temperature elevation rate was set at 20° C./min, and  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference substance. Peak temperature  $T_1$  of the endothermic peak in the DTA curve shown in FIG. 4 is 280° C. On the other hand, peak temperature  $T_2$  of the exothermic peak is 1,270° C.

Then, prepared was a highly crystalline synthetic graphite having 0.3354 nm of the interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the X-ray diffractometry, and a differential thermal analysis was

applied to the highly crystalline synthetic graphite by using 4 kinds of atmospheres, i.e., gas atmospheres No. 1 to No. 4 shown in Table 2, as the atmosphere gas. Concerning the other conditions of the differential thermal analysis, the sample weight was 50 mg, the gas flow rate was 100 mL/min, the temperature elevation rate was 20° C./min, and the reference substance used was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The peak temperature T<sub>1</sub> of the endothermic peak and the peak temperature T<sub>2</sub> of the exothermic peak were obtained from the DTA curve thus obtained, and the value of (T<sub>1</sub>+T<sub>2</sub>)/2 was calculated from the values of T<sub>1</sub> and T<sub>2</sub> thus obtained. Table 2 shows the results.

TABLE 2

Gas atmosphere	T <sub>1</sub> (Endo-thermic peak temperature)	T <sub>2</sub> (Exo-thermic peak temperature)	(T <sub>1</sub> + T <sub>2</sub> )/2
No. 1 CO <sub>2</sub>	160° C.	1235° C.	698° C.
No. 2 CO <sub>2</sub> (50 vol. %)/Ar (balance)	177° C.	1310° C.	744° C.
No. 3 H <sub>2</sub> O (20 vol. %)/Ar (balance)	205° C.	1280° C.	743° C.
No. 4 Dry air	180° C.	879° C.	530° C.

Incidentally, the term "dry air" shown in Table 2 denotes a mixed gas consisting of 80% by volume of N<sub>2</sub> gas and 20% by volume of O<sub>2</sub> gas.

Preparation of Carbon Material for Negative Electrode

Five grams of the highly crystalline synthetic graphite having 0.3354 nm of the interplanar spacing d<sub>002</sub> derived from (002) reflection, which was determined by the X-ray diffractometry, was put in an alumina crucible and subjected to a heat treatment for 3 hours in the presence of the atmosphere gas No. 1 shown in Table 2 and under temperatures shown in Table 3. In performing the heat treatment, the inner space of the heating furnace was evacuated to set up a vacuum state so as to prevent the air from remaining within the heating furnace and, then, a gas was introduced into the heating furnace. During the temperature elevation, during the heating and during the cooling, the gas was continued to flow at a flow rate of 0.8 L (liter)/min. Also, the temperature elevation time was set at 3 hours. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a carbon material.

By using the carbon material thus obtained, preparation of the negative electrode, the assembling of a test cell, and the charge-discharge test were conducted as in Example 1. Table 3 also shows the results of the charge-discharge test.

COMPARATIVE EXAMPLE 4

Preparation of the negative electrode, the assembling of a test cell, and the charge-discharge test were conducted as in Example 5, except that a heat treatment was not applied to the highly crystalline synthetic graphite. Table 3 also shows the results of the charge-discharge test.

TABLE 3

	Heat treating temperature (° C.)	Composition of atmosphere gas	Capacity per unit weight (%)
Comparative example 4	No heat treatment	—	100
Example 5	1400	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	109
Example 6	1200	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	121
Example 7	1000	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	127
Example 8	800	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	119
Example 9	600	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	107
Example 10	400	Composition of No. 1 · CO <sub>2</sub> (100 vol %)	101

As apparent from Table 3, the secondary battery for each of Examples 5 to 10 comprising the negative electrode containing the carbon material prepared by the first manufacturing method was found to be superior in the negative electrode capacity per unit weight to the secondary battery for Comparative Example 4.

EXAMPLES 11 TO 16 AND COMPARATIVE EXAMPLES 7 TO 12

Preparation of the negative electrode, the assembling of a test cell, and the charge-discharge test were conducted as in Example 5, except that the composition of the atmosphere gas within the heating furnace and the heat treating temperature were changed as shown in Table 4 in applying a heat treatment to the highly crystalline synthetic graphite. Table 4 also shows the results of the charge-discharge test.

Incidentally, the term "dry air" shown in Table 4 denotes a mixed gas consisting of 80% by volume of N<sub>2</sub> gas and 20% by volume of O<sub>2</sub> gas.

TABLE 4

	Heat treating temperature (° C.)	Composition of atmosphere gas	Capacity per unit weight (%)
Example 11	1200	Composition of No. 2 · CO <sub>2</sub> (50 vol. %)/Ar (balance)	130
Example 12	1000	Composition of No. 2 · CO <sub>2</sub> (50 vol. %)/Ar (balance)	125
Example 13	1200	Composition of No. 3 · H <sub>2</sub> O (20 vol. %)/Ar (balance)	121
Example 14	1000	Composition of No. 3 · H <sub>2</sub> O (20 vol. %)/Ar (balance)	119
Example 15	800	Composition of No. 3 · H <sub>2</sub> O (20 vol. %)/Ar (balance)	116
Example 16	600	Composition of No. 3 · H <sub>2</sub> O (20 vol. %)/Ar (balance)	114
Comparative example 4	No heat treatment	—	100
Comparative example 7	800	Composition of No. 4 · Dry air	108
Comparative example 8	600	Composition of No. 4 · Dry air	111
Comparative example 9	500	Composition of No. 4 · Dry air	109
Comparative example 10	800	CO <sub>2</sub> (5 vol. %)/Ar (balance)	102
Comparative example 11	1000	CO <sub>2</sub> (5 vol. %)/Ar (balance)	104
Comparative example 12	1000	H <sub>2</sub> O (0.5 vol. %)/Ar (balance)	100

As apparent from Table 4, the secondary battery for each of Examples 11 to 16 comprising the negative electrode

containing the carbon material prepared by the first manufacturing method was found to be superior in the negative electrode capacity per unit weight to the secondary battery for each of Comparative Examples 4 and 7 to 12.

As apparent from Tables 1 to 4, the carbon material processed by the manufacturing method of the present invention permits markedly improving the electrode capacity. It should be noted that the highly crystalline synthetic graphite to which the heat treatment was applied under a gas flow containing CO<sub>2</sub> or H<sub>2</sub>O exhibited an increase in the capacity superior to the effect produced by the heat treatment performed under the air atmosphere. Also, in the case of performing the graphitizing treatment under an atmosphere containing CO<sub>2</sub> or H<sub>2</sub>O, it is possible to obtain a capacity larger than that obtained in the case of applying a graphitizing treatment under an argon gas atmosphere. It should be noted that the effect of increasing the capacity was scarcely recognized in each of the Comparative Examples in which the CO<sub>2</sub> concentration in the heating atmosphere was set at 5% by volume or the H<sub>2</sub>O concentration in the heating atmosphere was set at 0.5% by volume.

#### EXAMPLES 17 TO 20 AND COMPARATIVE EXAMPLES 13 TO 14

Five grams of the highly crystalline synthetic graphite having 0.3354 nm of the interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the X-ray diffractometry, was put in an alumina crucible and subjected to a heat treatment. In performing the heat treatment, the inner space of the heating furnace was evacuated to set up a vacuum state so as to prevent the air from remaining within the heating furnace and, then, an atmosphere gas was introduced into the heating furnace. The atmosphere gas introduced into the heating furnace was prepared by passing an argon gas through a boiling aqueous solution of an acid so as to permit the argon gas to contain the vapor of the acid. Table 5 shows the kinds of the acids used and the concentrations (% by weight) of the aqueous solutions of the acids. The gas was allowed to flow through the heating furnace at a flow rate of 0.4 L/min during the temperature elevation and during the heating. Also, the heat treating temperature was set as shown in Table 5. The temperature elevation time was set at one hour, and the holding time was set at 30 minutes. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a carbon material.

By using the carbon material thus obtained, preparation of the negative electrode, the assembling of a test cell, and the charge-discharge test were conducted as in Example 1. Table 5 also shows the results of the charge-discharge test.

TABLE 5

	Kind of acid used	Concentration of acid aqueous solution (wt %)	Heat treating temperature (° C.)	Capacity per unit weight (%)
Example 17	Nitric acid	68	450	124
Example 18	Hydrochloric acid	37	450	112
Example 19	Sulfuric acid	96	450	115
Example 20	Acetic acid	98	450	118
Comparative example 13	None	—	None	100
Comparative example 14	None	—	450	101

As apparent from Table 5, the capacity can be markedly improved by applying a heat treatment to the carbon mate-

rial in the presence of an acid vapor. The effect is particularly large in the case of using a 68% aqueous solution of nitric acid as the acid.

#### EXAMPLES 21 TO 23

A heat treatment was applied to a highly crystalline synthetic graphite having 0.3354 nm of an interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the X-ray diffractometry, under the conditions similar to those employed in Example 11. To reiterate, the heat treatment was performed under a heat treating temperature of 1,200° C. by using as the atmosphere gas a mixed gas consisting of 50% by volume of a carbon dioxide gas and 50% by volume of an argon gas. Then, an after-heat treatment was applied to the highly crystalline synthetic graphite under the conditions similar to those employed in Example 17. Specifically, the after-heat treatment was performed at a heating temperature of 450° C. by using a 68% aqueous solution of nitric acid so as to obtain a carbon material for Example 21.

Similarly, a heat treatment was applied to a highly crystalline synthetic graphite having 0.3354 nm of an interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the x-ray diffractometry, under the conditions similar to those employed in Example 17. To reiterate, the heat treatment was performed by using a 68% aqueous solution of nitric acid under a heat treating temperature of 450° C. Then, an after-heat treatment was applied to the highly crystalline synthetic graphite under the conditions similar to those employed in Example 11. Specifically, the after-heat treatment was performed at a heating temperature of 1,200° C. by using a mixed gas consisting of 50% by volume of a carbon dioxide gas and 50% by volume of an argon gas, so as to obtain a carbon material for Example 22.

Further, a heat treatment was applied to a highly crystalline synthetic graphite having 0.3354 nm of an interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the X-ray diffractometry, under the conditions similar to those employed in Example 17. To reiterate, the heat treatment was performed by using a 68% aqueous solution of nitric acid under a heat treating temperature of 450° C. Then, an after-heat treatment was applied to the highly crystalline synthetic graphite under the conditions similar to those employed in Example 13. Specifically, the after-heat treatment was performed at a heating temperature of 1,200° C. by using a mixed gas consisting of 20% by volume of water vapor and 80% by volume of an argon gas, so as to obtain a carbon material for Example 23.

By using the three kinds of the carbon materials thus obtained, preparation of the negative electrode, the assembling of a test cell, and the charge-discharge test were conducted as in Example 1. Table 6 also shows the results of the charge-discharge test. It should be noted that the capacity per unit weight shown in Table 6 is a relative value, with the capacity per unit weight for the test cell of Comparative Example 4 set at 100(%). In Table 6, the heat treatment performed first is indicated as "First Stage Heat Treatment (I)", and the heat treatment performed later is indicated as "Second Stage Heat Treatment (II)".

TABLE 6

	First stage heat treatment (I)	Second stage heat treatment (II)	Capacity (%) per unit weight
Example 21	CO <sub>2</sub> (Example 11)	Nitric acid (Example 17)	146
Example 22	Nitric acid (Example 17)	CO <sub>2</sub> (Example 11)	132
Example 23	Nitric acid (Example 17)	H <sub>2</sub> O (Example 13)	133

As apparent from Table 6, it was possible to obtain a secondary battery having a high capacity in each of Examples 21, 22 in which both the heat treatment under an atmosphere containing at least 10% by volume of a carbon dioxide gas and the heat treatment under an atmosphere containing an acid vapor were applied to the highly crystalline synthetic graphite and Example 23 in which both the heat treatment under an atmosphere containing at least 1% by volume of a water vapor and the heat treatment under an atmosphere containing an acid vapor were applied to the highly crystalline synthetic graphite. Particularly, the capacity was markedly improved in the secondary battery for Example 21, in which the heat treatment under an atmosphere containing an acid vapor was applied after the heat treatment performed under an atmosphere containing at least 10% by volume of a carbon dioxide gas.

## EXAMPLES 24 TO 27

5 grams of a graphitized carbon fiber available on the market, which had an average fiber length of 40  $\mu\text{m}$  and an average particle diameter shown in Table 8, was put in an alumina crucible and subjected to a heat treatment for 3 hours under the temperatures shown in Table 7 in the presence of the atmosphere gas having the composition shown in Table 7. In performing the heat treatment, the inner space of the heating furnace was evacuated to set up a vacuum state so as to prevent the air from remaining within the heating furnace and, then, an atmosphere gas was introduced into the heating furnace. During the temperature elevation, during the heating and during the cooling, a gas was allowed to flow at a flow rate of 0.8 L/min. Also, the temperature elevation time was set at 3 hours. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a fibrous carbon material.

The average particle diameter, the interplanar spacing  $d_{002}$  derived from (002) reflection, which was determined by the X-ray diffractometry, and the specific surface area, which was determined by the BET method, was measured in respect of the carbon material thus obtained. Table 8 shows the results. Incidentally, for measuring the specific surface area of the carbon material determined by the BET method, used was a mixed gas of He—N<sub>2</sub> (70:30), and the specific surface area was measured by a one-point type BET method. Also, the average particle diameter was measured by a microtrac particle analyzer manufactured by Leeds & Northrup Corp., the granulometer having a type number of 9320-X100. To be more specific, the carbon material particles are suspended in a dispersion medium of ethyl alcohol. The suspended carbon material particles are irradiated with a laser light, and the intensity distribution of the scattering light is measured. The intensity distribution thus measured is converted into the particle size distribution by a computer analysis. The accumulated average diameter (accumulated

50% diameter) in the particle size distribution thus obtained is indicated in Table 8 as the average particle diameter.

Further, the immersion heat  $\Delta H_i^h$  for n-heptane and the immersion heat  $\Delta H_i^n$  for 1-nitropropane were measured in respect of the carbon material thus obtained by using a Calvet type heat conduction calorimeter manufactured by Tokyo Riko Inc., the calorimeter having a type number MMC-5111.

To be more specific, a solvent is poured into a sample vessel. Also, a sample is put in a glass ampoule and, then, the glass ampoule is subjected to a vacuum deaeration, followed by heat-sealing the glass ampoule. After the ampoule is immersed in the solvent within the sample vessel, the sample vessel is set in the twin type heat transmission calorimeter. After an equilibrium temperature is reached, the ampoule is broken and the solvent is stirred so as to mix the sample with the solvent. Further, the amount of heat generated is measured.

Within the twin type heat transmission calorimeter, the sample vessel is connected to a homeothermal body via a heat conductive electric conductor that also acts as a heat sensitive body. It is possible to determine the heat generation amount and a rate of change by measuring the change with time in the temperature difference between both edges of the heat sensitive body.

The measuring conditions were as follows:

Amount of sample (carbon material): 1.2 g;

Pretreatment of sample: 150° C., 10 mm Hg to 5 mm Hg, 6 hours;

Measuring temperature: 25° C.;

Immersion medium: n-hexane or 1-nitropropane;

Amount of immersion medium: 22 mL;

Heat amount calculation: data processing by computer;

The immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  was calculated from the values of  $\Delta H_i^n$  and  $\Delta H_i^h$  thus obtained. Table 8 also shows the results.

## EXAMPLE 28

5 grams of a graphitized carbon fiber available on the market, which had an average fiber length of 40  $\mu\text{m}$  and an average particle diameter of 25  $\mu\text{m}$ , was put in an alumina crucible and subjected to a heat treatment for 3 hours at 1,000° C. in the presence of an atmosphere gas consisting of 100% by volume of a carbon dioxide gas. In performing the heat treatment, the inner space of the heating furnace was evacuated to set up a vacuum state so as to prevent the air from remaining within the heating furnace and, then, an atmosphere gas was introduced into the heating furnace. During the temperature elevation, during the heating and during the cooling, a gas was allowed to flow at a flow rate of 0.8 L/min. Also, the temperature elevation time was set at 3 hours. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a fibrous carbon material.

Then, a heat treatment was applied again to the fibrous carbon material thus prepared. The atmosphere gas introduced into the heating furnace was prepared by passing an argon gas through a boiling aqueous solution containing 68% by weight of nitric acid so as to allow the argon gas to contain a nitric acid vapor. During the temperature elevation and during the heating, the gas was circulated at a flow rate of 0.4 L/min. Also, the heat treating temperature was set at 450° C. and the heat treating time was set at 3 hours. Further, the temperature elevation time was set at one hour and the

holding time was set at 30 minutes. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a carbon material.

The average particle diameter, the interplanar spacing  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

#### EXAMPLE 29

A carbon material was obtained as in Example 28, except that an aqueous solution containing 98% by weight of acetic acid was used as the acid aqueous solution forming a gaseous acid.

The average particle diameter, the interplanar spacing  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

#### EXAMPLE 30

A carbon material was obtained as in Example 28, except that an aqueous solution containing 85% by weight of phosphoric acid was used as the acid aqueous solution forming a gaseous acid.

The average particle diameter, the interplanar spacing  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

#### EXAMPLE 31

A sample was prepared by spinning a petroleum pitch used as a carbon precursor, followed by applying a heat treatment to the spun sample at 300° C. for one hour so as to make the spun sample infusible. Then, a heat treatment was applied to the carbon precursor at 900° 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° 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  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

#### EXAMPLE 32

A sample was prepared by spinning a petroleum pitch used as a carbon precursor, followed by applying a heat treatment to the spun sample at 300° C. for one hour so as to make the spun sample infusible. Then, a heat treatment was applied to the carbon precursor at 900° C. for 3 hours in the presence of an atmosphere gas consisting of 20% by volume of H<sub>2</sub>O gas and 80% by volume of CO<sub>2</sub> 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° C. for 3 hours in the presence of an atmosphere gas consisting of 20% by volume of H<sub>2</sub>O gas and 80% by volume of CO<sub>2</sub> 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.

Then, a heat treatment was applied to the fibrous carbon material. The atmosphere gas introduced into the heating furnace was prepared by introducing an argon gas into a boiling aqueous solution containing 68% by weight of nitric acid so as to allow the argon gas to contain a vapor of nitric acid. During the temperature elevation and during the heating, the gas was circulated at a flow rate of 0.4 L/min. The heat treating temperature was set at 450° C., and the heat treating time was set at 3 hours. Also, the temperature elevation time was set at one hour, and the holding time was set at 30 minutes. After the heat treatment, the heating chamber was cooled until the sample temperature was lowered to room temperature. Then, the sample was taken out of the heating furnace so as to obtain a carbon material.

The average particle diameter, the interplanar spacing  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

#### COMPARATIVE EXAMPLES 15 TO 23

Carbon materials for Comparative Examples 16 to 23 were obtained by applying a heat treatment at the temperatures shown in Table 7 for 3 hours to the graphitized carbon fiber available on the market, the carbon fiber having an average fiber length of 40  $\mu$ m and an average particle diameter shown in Table 8, in the presence of the atmosphere gas whose compositions are also shown in Table 7. Also, a graphitized carbon fiber to which a heat treatment was not applied at all was also prepared as a carbon material for Comparative Example 15. Incidentally, a mixed gas consisting of 80% by volume of a N<sub>2</sub> gas and 20% by volume of an O<sub>2</sub> gas was used as the heat treating atmosphere for each of Comparative Examples 16 and 17.

The average particle diameter, the interplanar spacing  $d_{002}$  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  $\Delta H_i^n/\Delta H_i^h$  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.

A test cell was assembled by using the carbon material obtained in each of Examples 24 to 32 and Comparative Examples 15 to 23 by the method described below.

In the first step, polytetrafluoroethylene was added to each of the carbon materials thus obtained so as to prepare a sheet. The sheet thus prepared was pressed against a stainless steel mesh, followed by drying the sheet at 150° C. under vacuum so as to obtain a test electrode. Also, a liquid nonaqueous electrolyte was prepared by dissolving 1M of LiPF<sub>6</sub> in a nonaqueous solvent prepared by mixing ethylene carbonate (EC) and methyl ethyl carbonate (MEC) at a mixing ratio by volume of 1:2. A test cell including a counter electrode and a reference electrode each formed of metal lithium was assembled under an argon gas atmosphere by using the test electrode and the liquid nonaqueous electrolyte described above.

A charge-discharge test was conducted under conditions (1) and (2) given below in respect of the test cell for each of the Examples 24 to 32 and Comparative Examples 15 to 23. Table 8 also shows the results.

(1) The test cell was charged with a current density of 1 mA/cm<sup>2</sup> until the potential difference between the reference

electrode and the test electrode was increased to reach 0.01V. Then, charging was continued for 5 hours with a constant voltage of 0.01V, followed by discharging the test cell under a current density of 1 mA/cm<sup>2</sup> until the voltage was lowered to 2V so as to measure the discharge capacity. Table 8 also shows the discharge capacity per gram of the carbon material for the negative electrode.

(2) The charge-discharge was repeated under the conditions given below so as to measure the number of charge-discharge cycles required for the discharge capacity to be lowered to 80% of the capacity for the first charge-discharge cycle. Table 8 also shows the results.

Charge: The test cell was charged with a current density of 1 mA/cm<sup>2</sup> until the potential difference between the reference electrode and the test electrode was increased to reach 0.01V. Then, charging was continued for 5 hours with a constant voltage of 0.01V.

Discharge: The test cell was discharged under a current density of 1 mA/cm<sup>2</sup> until the voltage was lowered to 2V.

TABLE 7

	Heat treating conditions			Acid treating conditions		
	Atmosphere	Temperature (° C.)	Time	Acid	Temperature (° C.)	Time
Example 24	CO <sub>2</sub>	700	3h	—	—	—
Example 25	CO <sub>2</sub>	900	3h	—	—	—
Example 26	CO <sub>2</sub>	1000	3h	—	—	—
Example 27	H <sub>2</sub> O(20 vol. %)/ Ar (balance)	1000 1000	3h	—	—	—
Example 28	CO <sub>2</sub>	1000	3h	Nitric acid	450	3h
Example 29	CO <sub>2</sub>	1000	3h	Acetic acid	450	3h
Example 30	CO <sub>2</sub>	1000	3h	Phosphoric acid	450	3h
Example 31	CO <sub>2</sub>	2800	3h	—	—	—
Example 32	H <sub>2</sub> O(20 vol. %)/ CO <sub>2</sub> (balance)	2800	3h	Nitric acid	450	3h
Comparative example 15	—	—	—	—	—	—
Comparative example 16	Air	700	3h	—	—	—
Comparative example 17	Air	600	3h	—	—	—
Comparative example 18	Ar	1000	3h	—	—	—
Comparative example 19	N <sub>2</sub>	1000	3h	—	—	—
Comparative example 20	CO <sub>2</sub>	500	3h	—	—	—
Comparative example 21	Ozone	200	3h	—	—	—
Comparative example 22	NO <sub>2</sub>	450	3h	—	—	—
Comparative example 23	SO <sub>3</sub>	500	3h	—	—	—

TABLE 8

	Carbon material					
	Average particle diameter (μm)	Immersion heat ratio (ΔH <sub>i</sub> <sup>n</sup> /ΔH <sub>i</sub> <sup>p</sup> )	Interplanar spacing d <sub>002</sub> (nm)	Specific surface area (m <sup>2</sup> /g)	Battery capacity (mAh/g)	Cycle life
Example 24	25	1.2	0.3357	1.56	338	72
Example 25	24	1.28	0.3357	2.85	343	68
Example 26	23	1.25	0.3357	4.36	347	66
Example 27	24	1.48	0.3356	5.22	346	62
Example 28	25	1.61	0.3354	4.40	381	68
Example 29	26	2	0.3359	4.74	376	56
Example 30	26	1.58	0.3357	4.43	370	60

TABLE 8-continued

	Carbon material					Cycle life
	Average particle diameter ( $\mu\text{m}$ )	Immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ )	Interplanar spacing $d_{002}$ (nm)	Specific surface area ( $\text{m}^2/\text{g}$ )	Battery capacity (mAh/g)	
Example 31	22	1.52	0.3354	10.6	365	58
Example 32	23	1.65	0.3357	10.3	358	55
Comparative example 15	23	1.05	0.3354	0.48	310	62
Comparative example 16	24	1.01	0.3355	3.43	315	56
Comparative example 17	25	1	0.3357	1.23	314	70
Comparative example 18	24	1.02	0.3358	0.86	318	64
Comparative example 19	25	1.1	0.3355	0.65	322	63
Comparative example 20	25	2.5	0.3354	0.49	328	60
Comparative example 21	26	2.6	0.3357	3.86	336	34
Comparative example 22	24	2.5	0.3355	4.21	333	48
Comparative example 23	23	2.8	0.3358	4.02	329	21

As apparent from Tables 7 and 8, the secondary battery for each of Examples 24 to 32 comprising a negative electrode containing a carbon material having the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  defined in formula (1) described previously has a high discharge capacity and exhibits a long cycle life.

On the other hand, the secondary battery for each of Comparative Examples 16 to 18 comprising a negative electrode containing a carbon material to which a heat treatment was applied under the air atmosphere or an argon gas atmosphere is substantially equal in the immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  to the secondary battery for Comparative Example 15 comprising a negative electrode containing a carbon material to which a heat treatment was not applied and is inferior in the discharge capacity and the cycle life to the secondary battery for each of Examples 24 to 32. It is also seen that the secondary battery for each of Comparative Examples 19 to 23 is inferior in the cycle life to the secondary battery for each of Examples 24 to 32.

As described above in detail, the present invention provides a carbon material for a negative electrode capable of improving the initial charge-discharge efficiency, the discharge capacity, the large current discharge characteristics and the cycle life of a nonaqueous electrolyte secondary battery. The present invention also provides a nonaqueous electrolyte secondary battery capable of improving the initial charge-discharge efficiency, the discharge capacity, the large current discharge characteristics and the cycle life of the nonaqueous electrolyte secondary battery.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

What is claimed is:

1. A nonaqueous electrolyte secondary battery, comprising:

- a positive electrode;
- a negative electrode containing a graphitized material having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1); and
- a nonaqueous electrolyte;

$$1.2 \Delta H_i^n/\Delta H_i^h \geq 23 \quad (1)$$

where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the graphitized material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the graphitized material.

2. The nonaqueous electrolyte secondary battery according to claim 1, wherein said graphitized material is prepared by subjecting a carbonaceous material containing at least one material selected from the group consisting of a carbonized material and a second graphitized material to a heat treatment under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$ , a second gaseous atmosphere containing at least 1% by volume of  $\text{H}_2\text{O}$ , and a third gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$  and at least 1% by volume of  $\text{H}_2\text{O}$ .

3. The nonaqueous electrolyte secondary battery according to claim 1, wherein said graphitized material is prepared by subjecting a carbonaceous material containing at least one material selected from the group consisting of a carbonized material and a second graphitized material to a heat treatment under a gaseous atmosphere selected from the group consisting of a first gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$ , a second gaseous atmosphere containing at least 1% by volume of  $\text{H}_2\text{O}$ , and a third gaseous atmosphere containing at least 10% by volume of  $\text{CO}_2$  and at least 1% by volume of  $\text{H}_2\text{O}$ , followed by applying an additional heat treatment to said carbonaceous material under an atmosphere containing at least one vapor selected from the group consisting of an inorganic acid vapor and an organic acid vapor.

4. The nonaqueous electrolyte secondary battery according to claim 1, wherein said immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) falls within a range of between 1.25 and 1.75.

5. The nonaqueous electrolyte secondary battery according to claim 1, wherein said graphitized material has an average particle diameter falling within a range of between 5  $\mu\text{m}$  and 100  $\mu\text{m}$ .

6. The nonaqueous electrolyte secondary battery according to claim 5, wherein said graphitized material has a specific surface area determined by BET method, which falls within a range of between 1  $\text{m}^2/\text{g}$  and 50  $\text{m}^2/\text{g}$ .

7. The nonaqueous electrolyte secondary battery according to claim 1, wherein said graphitized material has an interplanar spacing  $d_{002}$  derived from (002) reflection, which is determined by an X-ray diffractometry, falling within a range of between 0.335 nm and 0.34 nm.

8. The nonaqueous electrolyte secondary battery according to claim 1, wherein said nonaqueous electrolyte is any

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one of nonaqueous electrolytes selected from the group consisting of a liquid nonaqueous electrolyte, a gel nonaqueous electrolyte and a solid nonaqueous electrolyte.

9. A graphitized material for a negative electrode, having an immersion heat ratio ( $\Delta H_i^n/\Delta H_i^h$ ) defined by formula (1):

$$1.2 \leq \Delta H_i^n / \Delta H_i^h \leq 2.3 \quad (1)$$

where  $\Delta H_i^h$  denotes the immersion heat for n-heptane of the graphitized material, and  $\Delta H_i^n$  denotes the immersion heat for 1-nitropropane of the carbon graphitized material.

10. The graphitized material for a negative electrode according to claim 9, wherein said graphitized material is prepared by subjecting a carbonaceous material containing at least one material selected from the group consisting of a carbonized material and a second graphitized material to a heat treatment under a gaseous atmosphere selected from the

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group consisting of a first gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub>, a second gaseous atmosphere containing at least 1% by volume of H<sub>2</sub>O, and a third gaseous atmosphere containing at least 10% by volume of CO<sub>2</sub> and at least 1% by volume of H<sub>2</sub>O, followed by applying an additional heat treatment to said carbonaceous material under an atmosphere containing at least one vapor selected from the group consisting of an inorganic acid vapor and an organic acid vapor.

11. The graphitized material for a negative electrode according to claim 9, wherein said immersion heat ratio  $\Delta H_i^n/\Delta H_i^h$  falls within a range of between 1.25 and 1.75.

12. The nonaqueous electrolyte secondary battery according to claim 1, wherein the graphitized material has a specific surface area determined by BET method, which falls within a range of 2 m<sup>2</sup>/g to 20 m<sup>2</sup>/g.

\* \* \* \* \*



US006656637B2

(12) **United States Patent**  
Yoon et al.

(10) **Patent No.:** **US 6,656,637 B2**  
(45) **Date of Patent:** **\*Dec. 2, 2003**

(54) **CARBON-BASED ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY AND METHOD OF PREPARING CARBON-BASED ACTIVE MATERIAL**

(51) **Int. Cl.<sup>7</sup>** ..... **H01M 4/58**  
(52) **U.S. Cl.** ..... **429/231.4; 429/209; 429/213; 429/231.9; 429/231.95**  
(58) **Field of Search** ..... **429/209, 213, 429/231.4, 231.9, 231.95**

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(\*) **Notice:** This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

\* cited by examiner

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(57) **ABSTRACT**

(21) **Appl. No.:** **09/478,857**

Disclosed is a carbon-based active material for a rechargeable lithium battery that is capable of increasing charge and discharge efficiency of the battery.

(22) **Filed:** **Jan. 7, 2000**

(65) **Prior Publication Data**

The carbon-based active material has no hydroxyl groups on a surface by heat-treating under a fluorine atmosphere.

US 2003/0143463 A1 Jul. 31, 2003

(30) **Foreign Application Priority Data**

Jan. 7, 1999 (JP) ..... 11-002364

**2 Claims, 8 Drawing Sheets**

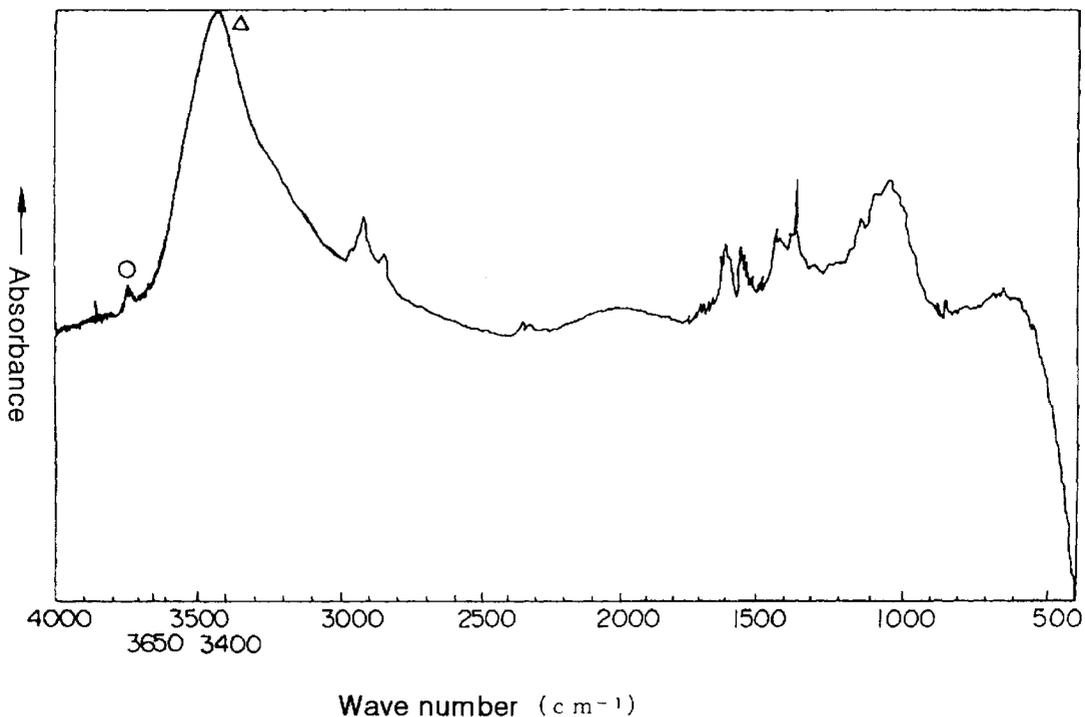


FIG. 1

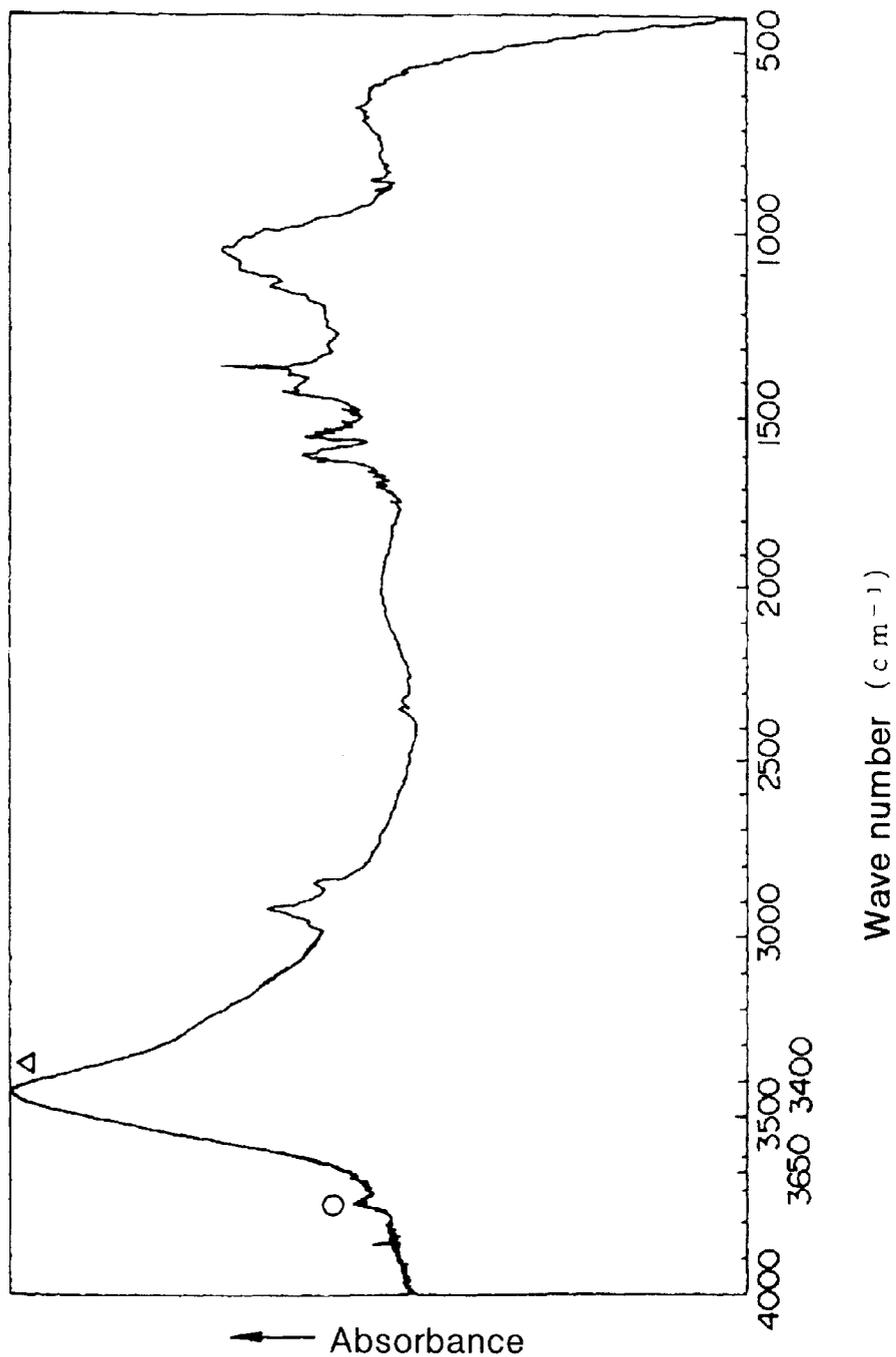


FIG. 2

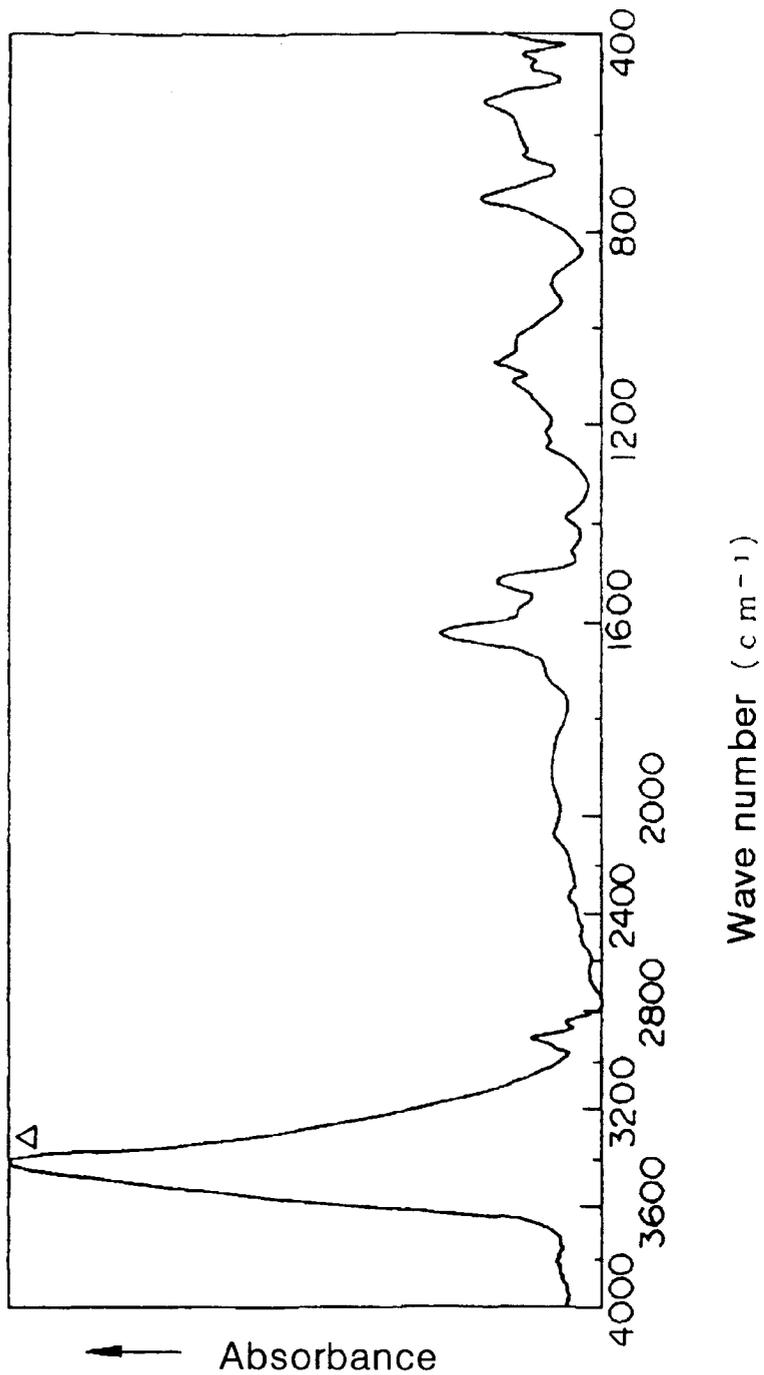


FIG. 3

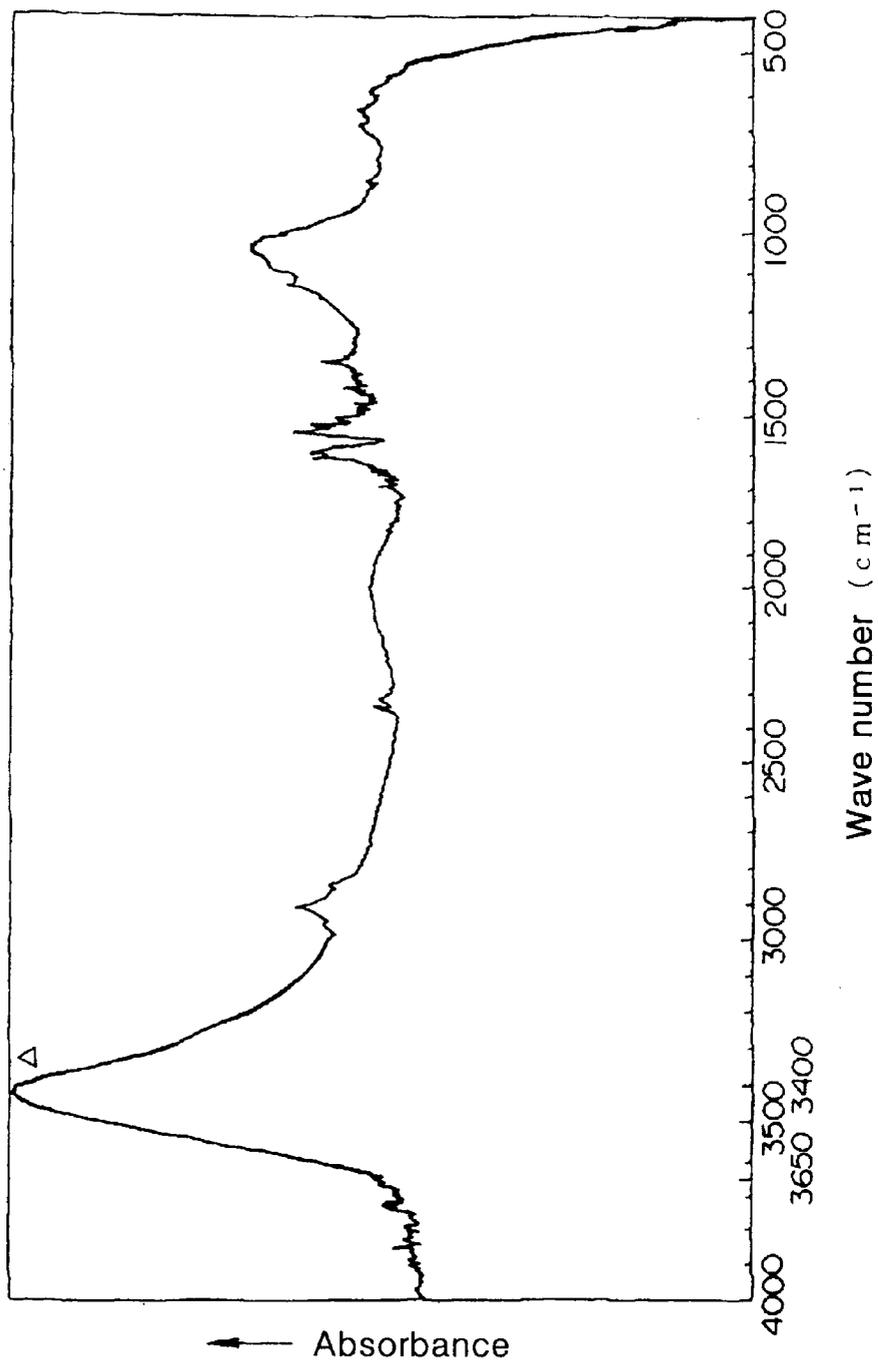


FIG. 4

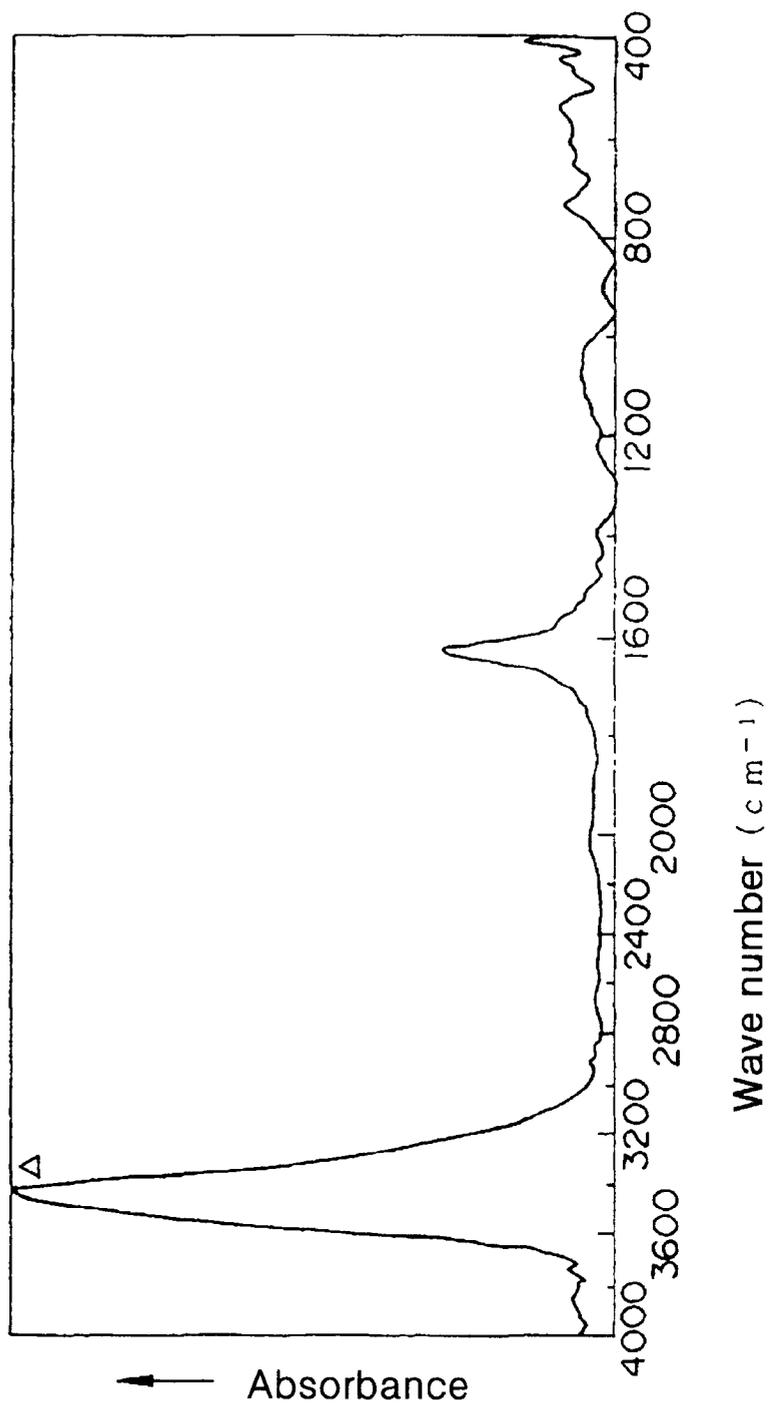


FIG. 5

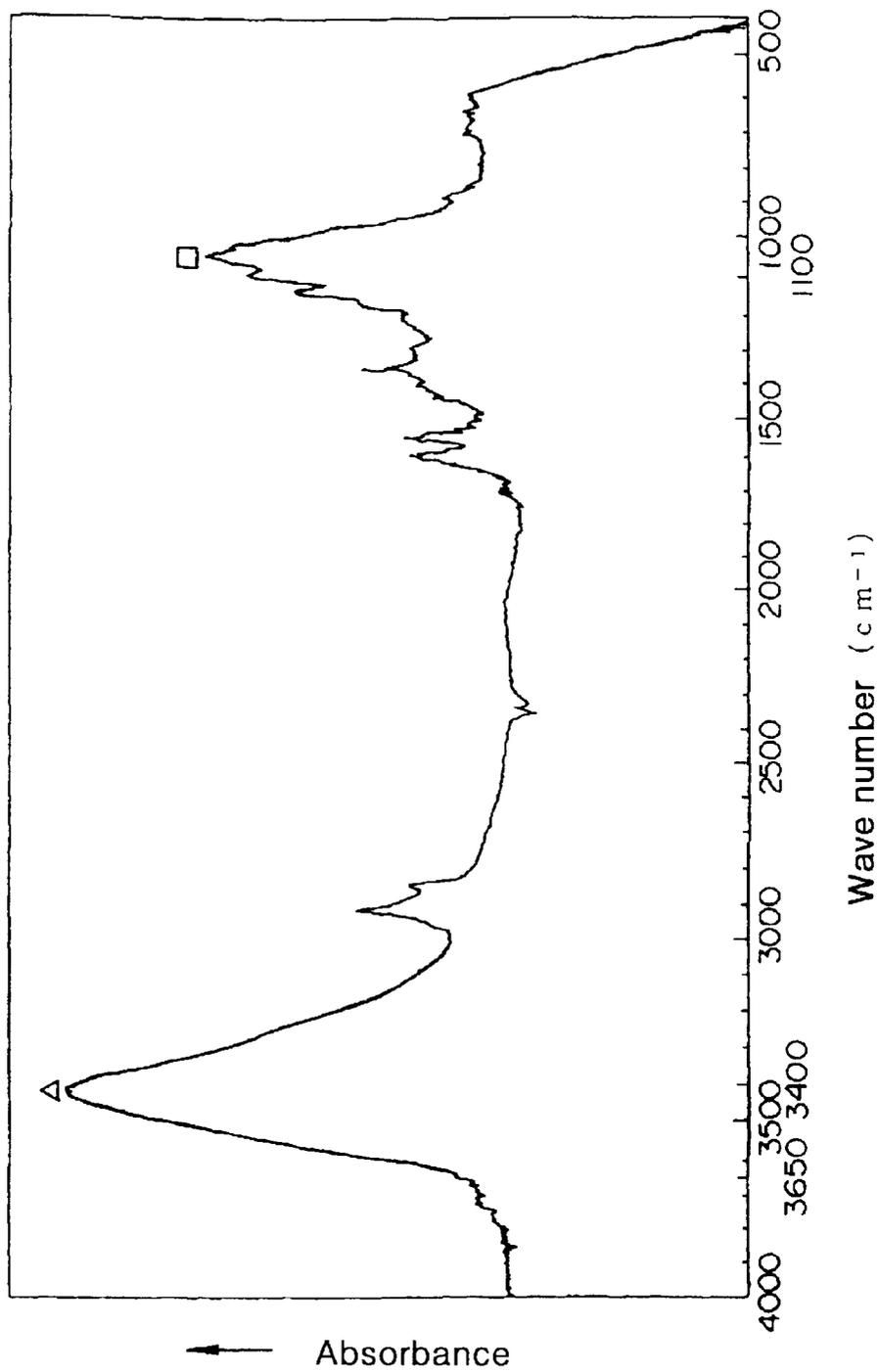


FIG. 6

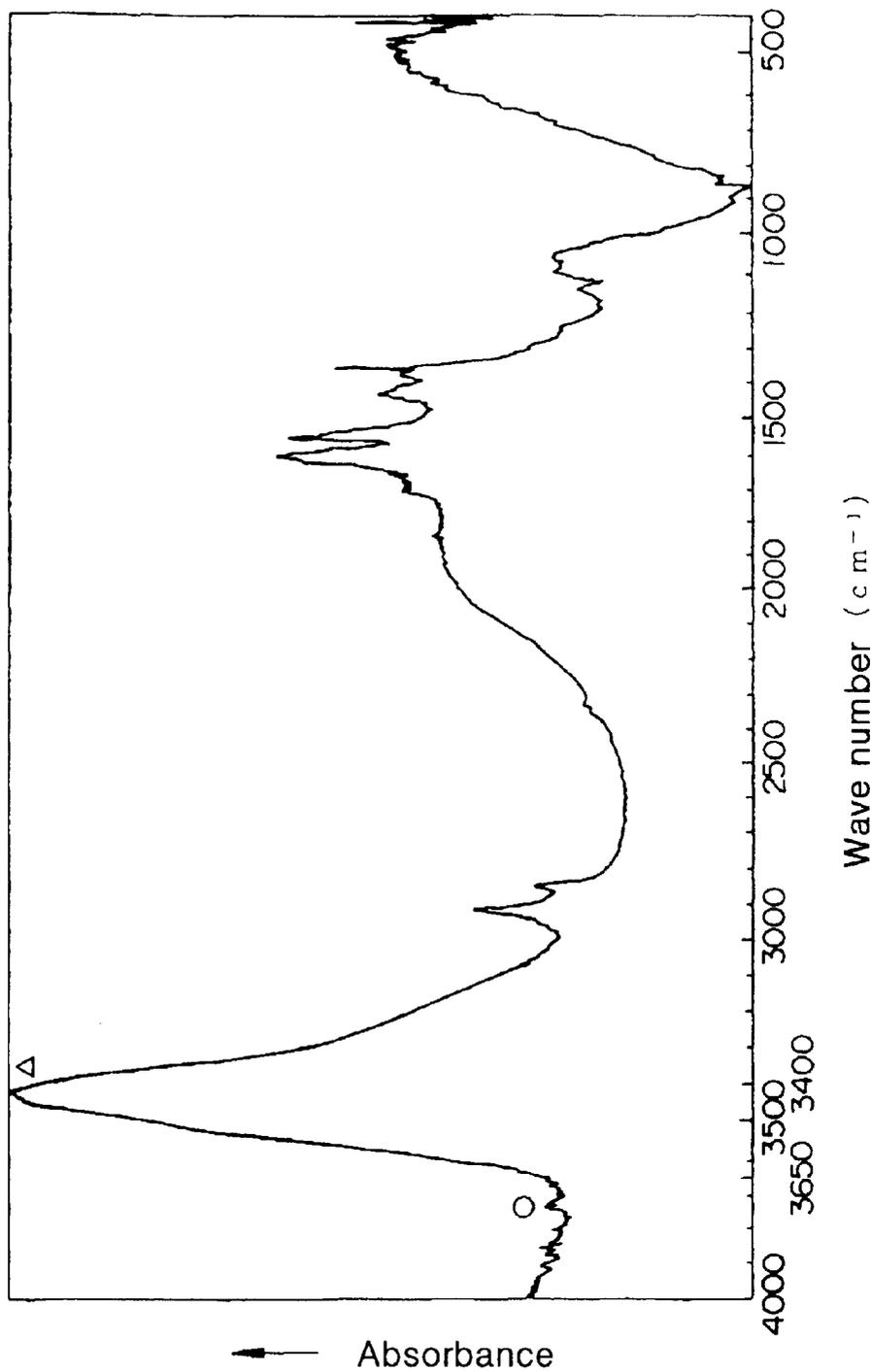


FIG. 7

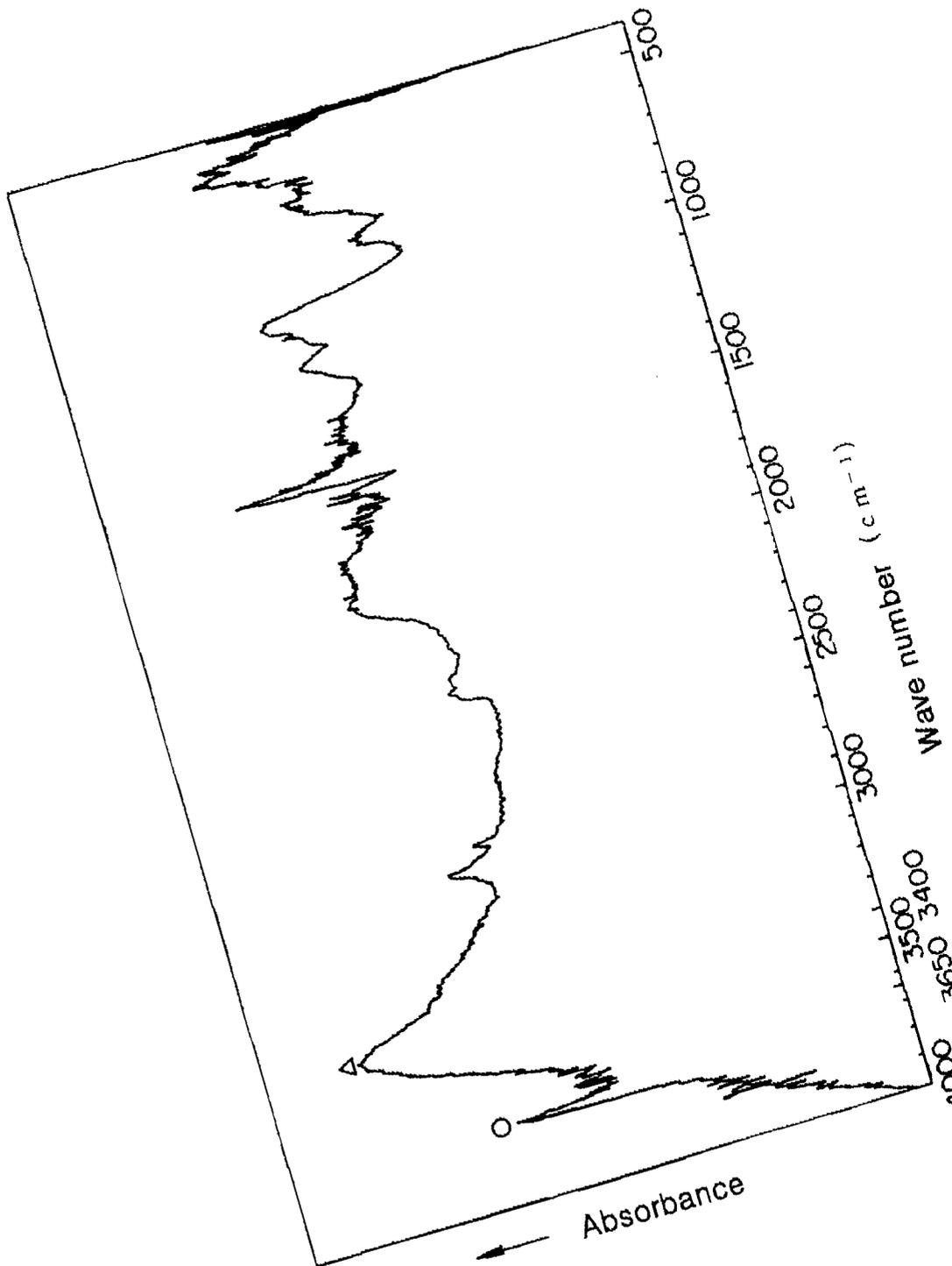
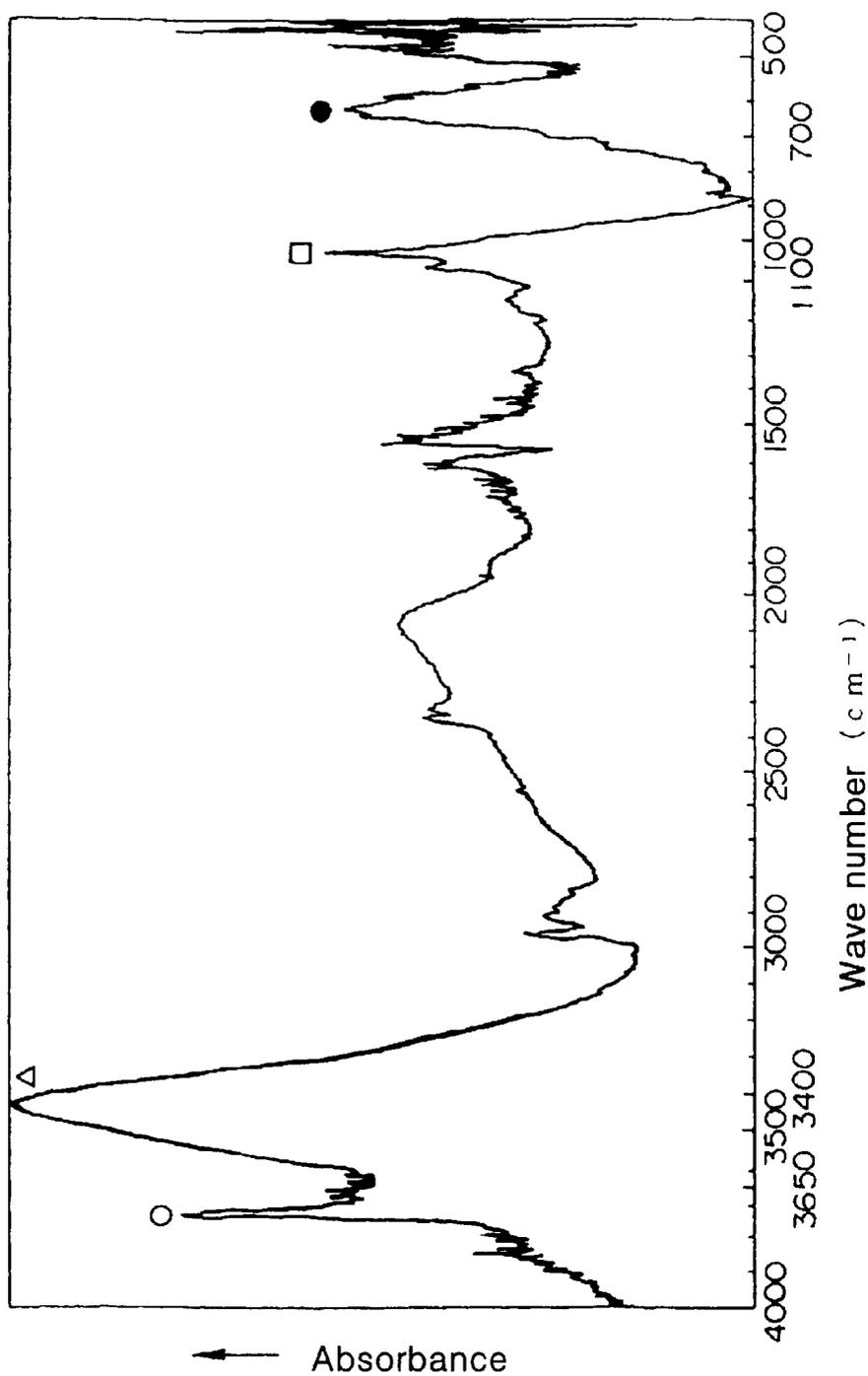


FIG. 8



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**CARBON-BASED ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY AND METHOD OF PREPARING CARBON-BASED ACTIVE MATERIAL**

**CROSS REFERENCE TO RELATED APPLICATION**

This application is based on application No. Hei. 11-2364 filed in the Japanese Patent Office on Jan. 7, 1999, the content of which is incorporated hereinto by reference.

**BACKGROUND OF THE INVENTION**

(a) Field of the Invention

The present invention relates to a carbon-based active material for a rechargeable lithium battery, the rechargeable lithium battery and a method of preparing the carbon-based active material.

(b) Description of the Related Art

In recent years, the development of miniaturized portable electronics provokes needs for a rechargeable battery having a high capacity as well as a light weight. From the viewpoint of the capacity improvement per unit weight, the rechargeable lithium battery is preferably adopted because lithium has a high standard potential as well as a low electrochemical equivalent weight.

Metallic lithium has been used for the negative active material in a rechargeable lithium battery. However, during charging, lithium is electroplated onto the metallic lithium electrode, it deposits to form a dendritic layer that increases the reactivity of lithium.

The problem of lithium has been addressed by replacing the lithium metal with carbon-based materials. Owing to the use of the carbon-based materials, the potential safety problem present in metallic lithium-based batteries can be prevented while achieving a relatively higher energy density as well as the reasonable shelf life.

Among carbon-based material, graphite-based material has a high charge and discharge efficiency and voltage flatness. Graphite-based material is produced by heat-treating petroleum pitch or polymer resin at 2,000 to 3,000° C. The resulting graphite-based material has hydroxyl groups on its surface, which react with an electrolyte during charge and cause decreases in a charge and discharge efficiency.

**SUMMARY OF THE INVENTION**

It is an object of the present invention to provide a carbon-based active material for a rechargeable lithium battery, which can increase charge and discharge efficiency.

It is another object to provide a rechargeable lithium battery having high charge and discharge efficiency.

It is still another object to provide a method of preparing the carbon-based active material.

These and other objects may be achieved by a carbon-based active material for a rechargeable lithium battery produced by heat-treating a carbon-based material under a fluorine atmosphere. The fluorine atmosphere serves to remove hydroxyl groups on the surface without the generation of C—F covalent bonds. Accordingly, the carbon-based active material of the present invention has no hydroxyl groups or C—F covalent bonds on the surface.

In order to achieve these and other objects and others, the present invention provides a rechargeable lithium battery

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including a positive active material and a negative carbon-based active material. The carbon-based active material has no hydroxyl groups and C—F covalent bonds and produced by heat-treating a carbon-based material under a fluorine atmosphere. The positive active material is a material into or from which lithium ions are reversibly intercalated or deintercalated. The carbon-based active material is a material into or from which lithium ions are intercalated or deintercalated.

The present invention further includes a method of preparing a carbon-based active material for a rechargeable lithium battery. In the method, a carbon-based material is heat-treated under a fluorine atmosphere to remove hydroxyl group from a surface thereof without the generation of C—F bond. The heat-treating step preferably includes the steps of injecting the carbon-based material into a reactor, and heating the reactor by the suitable temperature under vacuum. Next, gaseous fluorine is charged into the reactor and the carbon-based material is heat-treated for a suitable time. The gaseous fluorine preferably includes fluorine gas of at least 99.7% purity. The pressure of the gaseous fluorine is preferably 10 to 100 kPa. The second heat-treating step is preferably performed at 80 to 150° C. for 15 to 30 minutes.

**BRIEF DESCRIPTION OF THE DRAWINGS**

A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

FIG. 1 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 1;

FIG. 2 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 2;

FIG. 3 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 3;

FIG. 4 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 4;

FIG. 5 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 5;

FIG. 6 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 6;

FIG. 7 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 7; and

FIG. 8 is a graph showing an infrared spectrum of a surface of carbon-based material Sample No. 8.

**DETAILED DESCRIPTION OF THE INVENTION**

The carbon-based active material of the present invention has no hydroxyl groups on its surface. The carbon-based active material is prepared by heat-treating a carbon-based material under a fluorine atmosphere. The fluorine atmosphere serves to remove hydroxyl groups on the surface without the generation of C—F covalent bonds. In addition, the carbon-based active material has no C—F covalent bond on its surface. It is preferred that no absorption peaks due to hydroxyl groups and C—F covalent bonds occur in infrared spectrum.

The carbon-based material may include graphite or amorphous carbon. The graphite may include natural graphite or artificial graphite. The amorphous carbon may include cokes. Natural graphite, artificial graphite or cokes have a layered structure into or from which lithium ion can be

intercalated or deintercalated. As the carbon-based material, graphite or amorphous carbon as well as materials prepared by sintering fibrous carbon, amorphous carbon, plant matter, or synthetic polymer such as phenol resin, are used.

The carbon-based active material of the present invention has no hydroxyl groups which react with an electrolyte and decompose during charge, particularly during the first charge cycle such that the carbon-based active material can prevent the decreases in the efficiency of a battery due to the decomposition of the electrolyte. In addition, the carbon-based active material has no C—F covalent bonds that decrease the discharge capacity per unit weight of the carbon-based material.

The fluorine atmosphere also results in the scatter of the surface of the carbon-based material and increases sites into which lithium ion is intercalated. Accordingly, the carbon-based active material of the present invention can increase discharge capacity.

The rechargeable lithium battery of the present invention includes the negative carbon-based active material and a positive active material into or from which lithium ions are intercalated or deintercalated. The battery further includes a separator and an organic electrolyte.

The positive active material may include  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMnO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiFeO}_2$ ,  $\text{TiS}_2$ ,  $\text{FeS}_2$ ,  $\text{Nb}_3\text{S}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}_3\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_3\text{O}_8$ ,  $\text{FeOCl}$  or  $\text{FeVO}_4$ . Preferably, the positive active material has an oxidation-reduction potential of at least 2.5V compared to lithium so as to increase the voltage of the rechargeable lithium battery.

An solvent for the organic electrolyte may include propylene carbonate, ethylene carbonate, butylene carbonate, benzonitrile, acetonitrile, tetrahydrofuran, 2-methyltetrahydrofuran,  $\gamma$ -butyrolactone, dioxolane, dimethylformamide, dimethylacetamide, dimethylsulfoxide, dioxane, dimethoxyethane, sulfonane, dichloroethane, chlorobenzene, nitrobenzene, dimethylcarbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methylisopropyl carbonate, ethylbutyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate or a mixture thereof.

An solute for the organic electrolyte may include  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)\text{N}$  or  $\text{LiC}_4\text{F}_9\text{SO}_3$ .

Alternatively, instead of the organic electrolyte solution, a solid polymer electrolyte may be used. It is preferable to use a polymer having high Li ion-conductivity. Polyethylene oxide, polypropylene oxide or polyethylene imide may be used. In addition, a gel phase electrolyte may be used. The gel phase electrolyte is produced by adding the organic electrolyte solution to the polymer.

The rechargeable lithium battery of the present invention includes positive and negative electrodes. The positive or negative electrode is prepared by adding a polyvinylidene-fluoride binder to the positive or negative active material to make a slurry and applying the slurry on a collector, such as metal foil or net. Between the positive and negative electrodes, a separator is interposed and the positive and negative electrodes and the separator are wound. The wound positive and negative electrodes and the separator refer to an electrode assembly. The electrode assembly is inserted into a battery case and an electrolyte is then added to the case. The case may have cylindrical or square shape.

Alternatively, the positive and negative slurry is pressed to make pellets with a separator interposed between the pellets. The pellets and separator are referred to as the electrode assembly. The electrode assembly is inserted into

a coin-type case and an electrolyte is then added to the case. Furthermore, a sheet-type battery may also be produced.

The carbon-based active material is prepared by heat-treating a carbon-based material under a fluorine atmosphere. The fluorine atmosphere has good effect on the removal of hydroxyl groups from the surface of the carbon-based active material, but has bad effect on the generation of surface C—F covalent bonds. Accordingly, it is important to control the heat-treating time sufficient to completely remove the hydroxyl group and to generate no C—F covalent bonds on the surface.

In the present invention, the heat-treating step is preferably performed by injecting the carbon-based material into a reactor, reducing the pressure of the reactor to a vacuum and heating the reactor at a suitable temperature. Thereafter, gaseous fluorine is charged into the reactor and the carbon-based material is again heat-treated in the reactor for a suitable time. The heat-treating step is performed until functional groups on the surface are removed and no fluorination (i.e., the generation of C—F covalent bonds) occurs on the surface.

The carbon-based material may include graphite or amorphous carbon. The graphite may include natural graphite or artificial graphite. The amorphous carbon may include cokes. As the carbon-based material, natural graphite, artificial graphite, cokes, fibrous carbon, amorphous carbon, materials prepared by sintering plant matter or synthetic polymer such as phenol resin, are used. Preferably, artificial graphite is used. The artificial graphite is preferably prepared by sintering coal tar pitch at 2,000 to 3,000° C.

The shape of the carbon-based material may include powder, fiber or another type. The carbon-based material powder with an extremely large average diameter is not desirable for a negative active material. Preferably, the average diameter of the carbon-based material powder is 10 to 30  $\mu\text{m}$ .

The heat-treatment is performed under a fluorine atmosphere. The fluorine atmosphere is preferably obtained by charging gaseous fluorine of a high purity into a heating bath. The fluorine gas of at least 99.7% purity is more preferably used, and most preferably, the fluorine gas of at least 99.9% purity is used. When the fluorine gas having a purity of less than 99.7% is used in the heat-treating step, impurities may react with the surface of the carbon-based active material, which decrease charge and discharge efficiency of the rechargeable lithium battery.

The pressure of the fluorine atmosphere is preferably 10 to 100 kPa, more preferably, 20 to 50 kPa. If the pressure is less than 10 kPa, it is difficult to remove OH groups. Whereas the pressure is more than 100 kPa, C—F bonds easily occur.

The heat-treating is preferably performed at 80 to 150° C., more preferably, about 100° C. for 15 to 30 minutes. If the heat-treating temperature is less than 80° C., various functional groups are not completely removed from the surface of the carbon-based material. Whereas, the heat-treating temperature is more than 150° C., C—F covalent bonds occur on the surface of the carbon-based material. When the heat-treating step is performed at the more preferred temperature of about 100° C., discharge capacity and, charge and discharge efficiency increase.

If the heat-treating time is less than 15 minutes, various functional groups are not completely removed from the surface of the carbon-based material. Whereas, the time is more than 30 minutes, C—F covalent bond occur on the surface of the carbon-based material.

Various analysis that gives to structural information about materials can be used to check the presence of functional groups on the surface of the carbon-based active material. For example, X-ray photoelectron spectroscopy, secondary ion mass analysis or auger electron spectroscopy can be used. Preferably, infrared spectroscopic analysis can be used to easily and quickly check the presence of functional groups on the surface of the carbon-based active material.

The hydroxyl group generally has absorption wavenumbers (wavelength) of  $3650$  to  $3584\text{ cm}^{-1}$  ( $2.74$  to  $2.79\text{ }\mu\text{m}$ ). Accordingly, the infrared spectrum in the region can be used to check the presence of hydroxyl group on the carbon-based active material. The hydroxyl group in the region is a "free" hydroxyl group which is not bonded with another hydroxyl group and different from a hydroxyl group which is bonded with another hydroxyl group by hydrogen bond ( $3550$  to  $3200\text{ cm}^{-1}$  ( $2.82$  to  $3.13\text{ }\mu\text{m}$ )).

The C—F covalent bond generally has absorption wavenumber of  $1100$  to  $1000\text{ cm}^{-1}$ . Accordingly, an infrared spectrum can be used for confirming the presence of C—F covalent bond on the carbon-based active material.

Because the carbon-based active material of the present invention has no surface hydroxyl group, the reaction of the carbon-based active material with an electrolyte can be prevented. Accordingly, the carbon-based active material of the present invention can increase charge and discharge efficiency during initial charging. Furthermore, as the carbon-based active material of the present invention also has no C—F covalent bond on the surface thereof, the carbon-based active material has a high discharge capacity per unit weight of the carbon-based active material.

Accordingly, the rechargeable lithium battery with the carbon-based active material of the present invention has high charge and discharge efficiency and discharge capacity.

The carbon-based active material without hydroxyl group does not react with an electrolyte. Accordingly, the carbon-based active material can prevent the generation of gas due to the reaction of the carbon-based active material with the electrolyte, and the increases in the internal pressure of the battery. Because the decomposed electrolyte does not adhered to the surface of the negative active material, cycle life characteristics of the rechargeable lithium battery can be greatly improved.

The following examples further illustrate the present invention.

#### EXAMPLE 1

Coal tar pitch was dissolved in a tetrahydrofuran solvent, and the insoluble components were removed and the residual component was sintered. Thereafter, the sintered residual component was carbonized and graphitized. As a result, synthetic graphite was obtained. The obtained synthetic graphite and natural graphite (with an average diameter of  $15\text{ }\mu\text{m}$ ) were used for a carbonaceous material.

The carbonaceous material was injected into a reactor made of nickel. The pressure of the reactor was reduced to  $10^{-4}$  torr and the reactor was heated to  $50$ – $300^\circ\text{C}$ . Next, fluorine gas of 99.7% purity was flowed into the reactor for 15 minutes to obtain a reactor pressure of 230 torr. The condition was maintained for 30 minutes in order to produce carbonaceous materials (Sample Nos. 1 to 8).

Each of the carbonaceous materials was mixed with a polyvinylidene fluoride binder and N-methylpyrrolidone to form a slurry. The slurry was coated on a copper foil and N-methylpyrrolidone was evaporated from the slurry on the

copper foil. As a result, a disk-shaped carbonaceous electrode having the maximum diameter of 13 millimeters (mm) and thickness of 0.1 mm was obtained. At this time, the ratio of carbonaceous material to the binder was 90:10.

The carbonaceous electrode, a lithium electrode made of metallic lithium, and a separator made of a porous polypropylene film were used. The separator was interposed between the carbonaceous and the lithium electrodes. The positive and negative electrodes and separator were put into a coin-type case with an electrolyte to produce a half cell. The electrolyte included 1M LiPF<sub>6</sub> in a mixture (EC:DMC=1:1) of ethylene carbonate (EC) and dimethyl carbonate (DEC).

A charge and discharge test was performed under the condition of a charge current density of  $0.4\text{ mA/cm}^2$ , a discharge terminal voltage of 0V, a discharge current density of  $0.4\text{ mA/cm}^2$  and a discharge terminal voltage 2V with respect to the half cells. The charge and discharge capacity of the first cycle was measured. In addition, the discharge capacity to charge capacity at the initial cycle (charge and discharge efficiency) was measured. The results and the associated heat-treating condition are presented in Table 1. Further, the carbonaceous material was dried under reduced pressure and an infrared spectroscopic analysis was performed with the respect to the surface of the carbonaceous material. The results are represented in FIGS. 1 to 8.

TABLE 1

Sample No.	Raw material	Reaction temperature [° C.]	Charge capacity at a first cycle [mAh/g]	Discharge capacity at a first cycle [mAh/g]	Charge and discharge efficiency
1	Artificial graphite	No heat-treatment	352.21	303.27	86.1
2		$50^\circ\text{C}$ .	388.33	304.16	78.3
3		$100^\circ\text{C}$ .	343.03	314.16	91.5
4		$200^\circ\text{C}$ .	357.36	310.91	87.0
5		$300^\circ\text{C}$ .	349.75	305.08	87.2
6	Natural graphite	No heat-treatment	414.31	372.23	89.8
7		$100^\circ\text{C}$ .	434.00	381.00	87.8
8		$300^\circ\text{C}$ .	474.67	353.61	74.5

The carbonaceous material of Sample No. 1 was artificial graphite without heat-treatment. As shown in FIG. 1, the absorption peak expressed by "0" occurs at about  $3600\text{ cm}^{-1}$ . The peak indicates a "free" hydroxyl group on the surface of the carbonaceous material. Further, a broad peak expressed by "Δ" is shown between  $3400$  to  $3500\text{ cm}^{-1}$  and it is considered that the peak is caused by hydroxyl group of water which can not be removed by drying.

The charge and discharge test result of the carbonaceous material is shown in Table 1.

The carbonaceous materials of Sample Nos. 2 to 5 were made by heat-treating Sample No. 1 at temperature ranging from  $50$  to  $300^\circ\text{C}$ . As shown in FIG. 2, no absorption peak due to a "free" hydroxyl group occur at about  $3600\text{ cm}^{-1}$  and the peak due to hydroxyl group of water, which are attached to the carbonaceous material, occurs at  $3400$  to  $3500\text{ cm}^{-1}$  and is expressed by Δ. The Sample No.5 has a peak due to C—F covalent bond expressed by □ at about  $1100\text{ cm}^{-1}$ . It was found that the heat-treatment under a fluorine atmosphere serves to remove hydroxyl group on the surface of artificial graphite.

As shown in Table 1, Samples Nos. 2 to 5 have higher discharge capacities than Sample No.1. Additionally,

Samples Nos. 3 to 5 have higher charge and discharge efficiency than Sample No.1. Sample No.3 (heat-treated at 100° C.) has a high discharge capacity of at least 314 mA/g as well as a high charge and discharge efficiency of at least 90%.

The carbonaceous material of Sample No. 6 was natural graphite prepared without the heat-treatment. As shown in FIG. 6, the peak expressed by  $\Delta$  occurs at 3600  $\text{cm}^{-1}$ , which means that "free" hydroxyl group is remained on the surface of the carbon-based material. The peak due to hydroxyl group of water attached to the carbon-based material occurs at 3400 to 3500  $\text{cm}^{-1}$  and is expressed by  $\Delta$ .

The charge and discharge test result of the electrode using the carbon-based active material is shown in Table 1.

Next, the carbon-based active materials of Sample Nos. 7 and 8 were made by heat-treating Sample No. 6 to 100 and 300° C., respectively. As shown in FIGS. 7 and 8 which are infrared spectrums of Sample Nos. 7 and 8, the broad peak of "free" hydroxyl groups occur at about 3600  $\text{cm}^{-1}$ . In FIG. 8, a peak due to a C—F covalent bond occurs and expressed by  $\square$  at 1100  $\text{cm}^{-1}$  and a peak due to a  $\text{CF}_2$  group or a  $\text{CF}_3$  group also occurs and is expressed by  $\bullet$  at 700  $\text{cm}^{-1}$ .

As shown in Table 1, the carbon-based active material of Sample No. 7 has larger discharge capacity than that of Sample No. 6, but has lower charge and discharge efficiency than that of Sample No. 6. The carbonaceous material of Sample No. 8 has lower discharge capacity and charge and discharge efficiency than that of Sample No. 6.

The results shown in Table 1 and in FIGS. 1 and 8 indicate that an increases in a charge and discharge efficiency by heat-treatment with fluorine is higher in artificial graphite rather than in natural graphite. Whereas the increases in a discharge capacity is higher in natural graphite rather than in artificial graphite.

As described above, the carbonaceous material of the present invention has no hydroxyl groups on the surface, preventing the reaction of the carbonaceous material with an electrolyte and increasing charge and discharge efficiency. The effective surface of the carbonaceous material is scattered by treating a surface thereof with a fluorine such that the number of sites into which lithium ions are intercalated and the charge and discharge capacity can be increased.

The rechargeable lithium battery of the present invention employs the carbonaceous material without hydroxyl groups on the surface and thus has good charge and discharge efficiency and discharge capacity.

The carbonaceous material has no hydroxyl group and does not react with an electrolyte, preventing gas generation caused by decomposing the electrolyte, and the increases in the internal pressure of the battery. As the decomposed electrolyte does not adhered to the surface of the carbonaceous material, the cycle life of the rechargeable lithium battery can be remarkably increased.

The method of preparing the carbonaceous material of the present invention is characterized in that the raw carbonaceous material is heat-treated under a fluorine atmosphere. The heat-treating is performed until functional groups on the surface of the carbonaceous material are removed by fluorine without fluorination (the generation of C—F covalent bond) occur on the surface. Accordingly, the method of the present invention can easily manufacture carbonaceous materials having good charge and discharge efficiency and discharge capacity.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

What is claimed is:

1. A method of preparing a carbon-based active material for a rechargeable lithium battery comprising the step of:

heat-treating a carbon-based material under a fluorine atmosphere at a temperature of more than about 100° C. and less than or equal to 150° C. such that free hydroxyl groups, whose presence would be indicated by a peak at an absorption wave n of about 3600  $\text{cm}^{-1}$ , are removed from a surface thereof without the generation of C—F bonds whose presence would be indicated by a peak at an absorption wave number of about 1100  $\text{cm}^{-1}$ .

2. The method of claim 1, wherein the heat-treating step comprises the sub-steps of injecting the carbon-based material into a reactor;

heat-treating the carbon-based material under vacuum;

charging gaseous fluorine into the reactor; and

heat-treating the carbon-based material to remain in the reactor for 15 to 30 minutes.

\* \* \* \* \*



US006780388B2

(12) **United States Patent**  
**Masuko et al.**

(10) **Patent No.:** **US 6,780,388 B2**  
(45) **Date of Patent:** **Aug. 24, 2004**

(54) **ELECTRICALLY CONDUCTING FINE CARBON COMPOSITE POWDER, CATALYST FOR POLYMER ELECTROLYTE FUEL BATTERY AND FUEL BATTERY**

(75) Inventors: **Tsutomu Masuko**, Nagano (JP); **Yoichi Nanba**, Nagano (JP)

(73) Assignee: **Showa Denko K.K.**, Tokyo (JP)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 169 days.

(21) Appl. No.: **09/867,596**

(22) Filed: **May 31, 2001**

(65) **Prior Publication Data**

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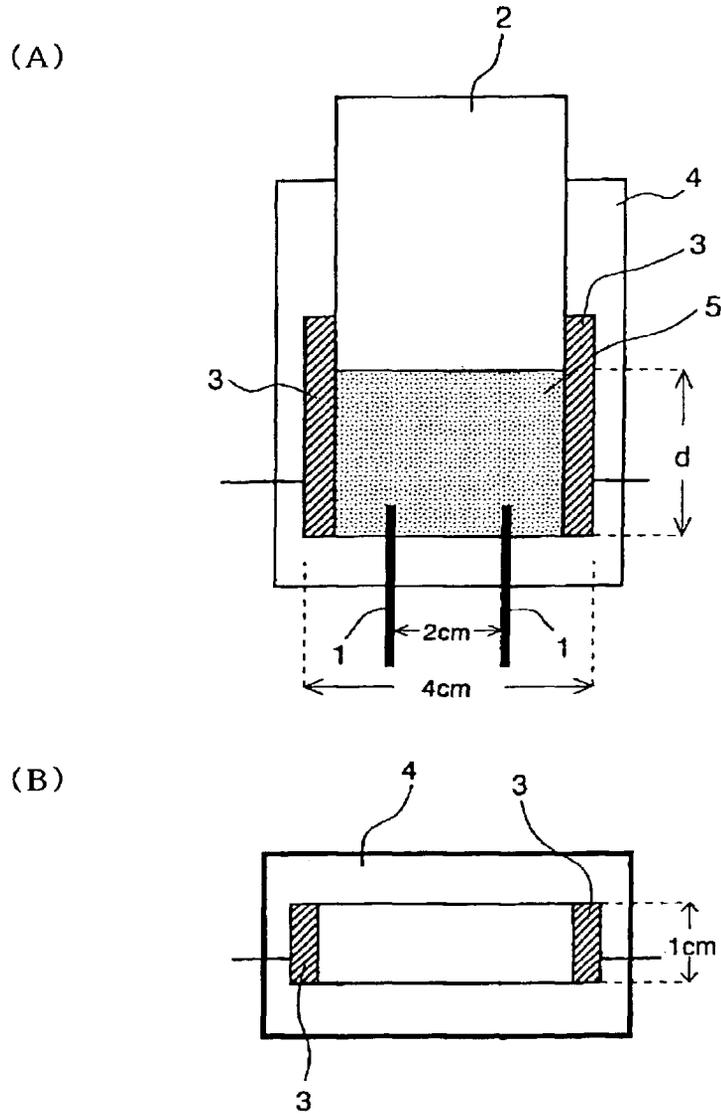
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(57) **ABSTRACT**

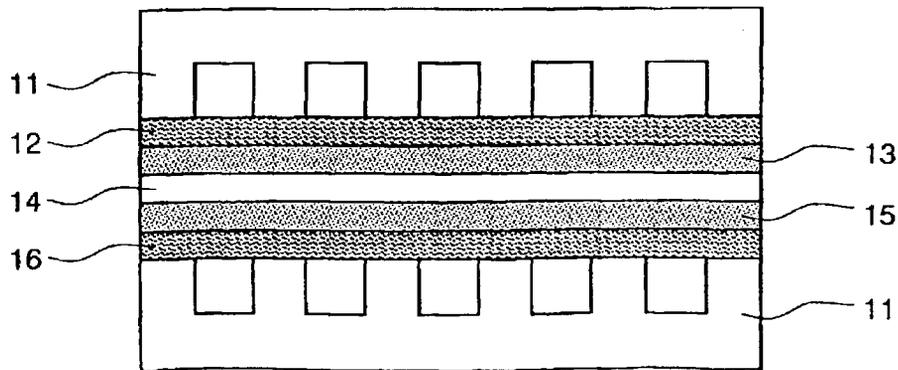
The present invention relates to (1) carbon powder having a primary particle size of 100 nm or less and an X-ray crystallite plane spacing C<sub>0</sub> of less than 0.680 nm, preferably of 0.6730 nm or less, which shows a volume resistivity of 0.1 Ω·cm or less in the pressurized state under a pressure of 2 MPa, and containing boron in a range of 0.1 to 5% by mass, (2) a method for producing the carbon powder, (3) an electrically conducting carbon composite powder wherein above-described carbon powder is mixed with fibrous carbon, particularly vapor grown carbon fiber, (4) a catalyst for solid polymer electrode fuel battery using above-described carbon powder or electrically conducting carbon composite powder, (5) a polymer electrolyte fuel battery cell using the catalyst, and (6) a polymer electrolyte fuel battery using the catalyst.

By using the carbon powder containing boron or an electrically conducting carbon composite powder, a high-performance polymer electrolyte fuel battery wherein power generation efficiency and durability are improved, can be obtained.

**FIG 1**



**FIG 2**



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**ELECTRICALLY CONDUCTING FINE  
CARBON COMPOSITE POWDER,  
CATALYST FOR POLYMER ELECTROLYTE  
FUEL BATTERY AND FUEL BATTERY**

**CROSS-REFERENCE TO RELATED  
APPLICATIONS**

This application is based on the provisions of 35 U.S.C. Article 111(a) with claiming the benefit of filing dates of U.S. provisional applications Ser. Nos. 60/245,712 and 60/245,716 filed on Nov. 6, 2000 under the provisions of 35 U.S.C. 111(b), pursuant to 35 U.S.C. Article 119(e) (1).

**TECHNICAL FIELD**

The present invention relates to an electrically conducting fine carbon composite powder. More specifically, the present invention relates to fine carbon composite powder useful as an electrically conducting material for an electrode material used particularly in a Lithium(Li) battery, electrical double-layer capacitor and the like, and fine carbon composite powder useful for supporting a catalyst for use in a fuel battery, and also relates to the method for producing the powder, a catalyst for polymer electrolyte fuel battery using the carbon composite powder, a polymer electrolyte fuel battery cell and battery using the catalyst.

**BACKGROUND ART**

In recent years, use of carbon powder materials for Li battery, electrical double-layer capacitor, fuel battery and the like is increasing. Particularly, fine carbon powder represented by carbon black has heretofore been used as an electrical conductivity-imparting material (for example, added to a resin) or a sliding member and in addition thereto, is being widely used in a battery as an electrode material, an additive or a support for supporting a catalyst.

For example, in a Li battery, the fine carbon powder is used as an additive for maintaining the electrical conductivity between graphite powder particles which are the main material of the negative electrode. In a fuel cell, the fine carbon powder in the state of supporting platinum is coated on a carbon substrate and used as an electrode catalyst for the anode electrode, cathode electrode or the like. In an electrical double-layer capacitor, the fine carbon powder is used as an additive for maintaining the electrical conductivity between fine activated carbon particles which are the main material of the electrode. The carbon powder used in these applications is so-called submicron order sized carbon powder smaller than normal carbon powder having a size of  $\mu\text{m}$  order obtained by the pulverization of coke or the like. By virtue of its small size, the carbon powder is useful as an electrical conducting material for improving the electrical conductivity between larger particles having a size of several  $\mu\text{m}$  to tens of  $\mu\text{m}$ .

This fine carbon powder 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.

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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° C. to reduce the  $d_{002}$  of carbon crystal, which is an index of showing the graphitization, even to 3.41 Å (0.341 nm), thereby attaining the graphitization. However, according to the study by the present inventors,  $d_{002}$  of carbon black cannot be lowered to less than 3.40 Å which is by far larger than the theoretical value for complete graphite (i.e. 3.354 Å). 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.

In order to cope with recent environmental pollution issue due to exhaust gas from the internal combustion engine of an automobile or the like, an electric vehicle (EV) is being developed as an alternative in recent years. To keep up with this tendency, a fuel cell is increasingly expected to undertake the power source for EV and therefor a compact and high-performance fuel cell is demanded.

The fuel cell includes various types of fuel cells such as, according to the kind of electrolytic solution used, alkali type, phosphoric acid type, fused carbonate type and polymer electrolyte type. Among these, a polymer electrolyte fuel cell is attracting an attention as a power source for electric vehicle (EV) because of its operability at a lower temperature, easy handling and high output density.

For example, FIG. 2 shows a cross-sectional structure of one example of a unit cell used in a polymer electrolyte fuel battery. The fundamental structure of a unit cell is such that an ion exchange membrane **14** having appropriate water content is disposed in the center and sandwiched by the electrode comprising an anode catalyst layer **13** and a cathode catalyst layer **15**. The anode catalyst layer **13** and the cathode catalyst layer **15** each is usually a sheet coated with a paste of carbon powder having supported thereon platinum or platinum alloy powder. The carbon powder is not particularly limited on the kind thereof as long as it has electrical conductivity, but those having a specific surface area large enough to support a catalyst are preferred and in general, carbon black is used.

In the outer side of the anode catalyst layer **13** and the cathode catalyst layer **15**, electrically conducting anode gas-diffusing porous sheet **12** and cathode gas-diffusing porous sheet **16** for passing water and gas generated at the reaction are disposed respectively and in the outermost side, a carbon-based separator plate with grooves **11** is disposed to provide reaction gas passages, thereby constructing a unit cell. By stacking the many unit cells (several hundreds of cells) to form a multilayer structure, a high-output fuel battery is constructed.

Since the reaction of a fuel battery takes place on the catalyst layers, the greatest factor determining the energy amount of a fuel cell is how effectively to use the catalyst. In order to use the platinum catalyst with highest efficiency, the characteristics of carbon as the support such as electrical conductivity, adhesion of platinum (supporting property), corrosion resistance against electrolytic solution (ion) and heat conductivity need to be improved.

Furthermore, adhesion as a constituent element of a cell, for example, plane pressure to the ion exchange membrane and the gas diffusion sheet must be maintained over a long period of time.

The fuel battery having a structure such that hundreds of unit cells are stacked and the whole is cramped up under a predetermined cramping pressure is operated over a long period of time, the separator plate, the gas diffusion sheet and the like undergo creeping (a phenomenon that the thickness decreases) and although this creeping amount is small per unit cell, the sum total in the creeping amount of hundreds of cells as a whole is fairly large.

In this meaning, simple carbon black currently used as a support is not only deficient in the electrical conductivity necessary for a high-performance battery but also, when the battery is operated for a long period of time and the plane pressure between respective parts decreases to cause increase in the contact resistance between respective parts, the internal resistance of the battery increases and the battery performance disadvantageously deteriorates. Specifically, in the durability test over a time period in excess of ten hundreds of hours, the output often lowers to the level of 70 to 80%.

Therefore the second object of the present invention is to develop a catalyst support capable of compensating for the deterioration in the long-term durability of elemental carbon conventionally used as a catalyst support, to provide a catalyst support ensuring a higher maximum output, and a catalyst and a battery using the support.

#### DISCLOSURE OF THE INVENTION

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  $C_0$  value (double of  $d_{002}$ ) of less than 0.680 nm (namely,  $d_{002}$  is less than 3.40 Å) can be obtained. Furthermore the present inventors succeeded to obtain a high-performance fuel battery by using the powder as a catalyst support for fuel battery.

In addition, the present inventors have found that by using an electrically conducting carbon composite powder for supporting catalyst, wherein carbon powder for supporting catalyst (carbon black) currently used is mixed with fibrous carbon, particularly with vapor grown carbon fiber, as a material for supporting a catalyst, a catalyst electrode having high output and high durability can be obtained.

Namely, the present invention relates to a carbon powder, the production method thereof, an electrically conducting carbon composite powder for supporting a catalyst having mixed therewith fibrous carbon, a catalyst for polymer electrolyte fuel battery, polymer electrolyte fuel battery cell, and polymer electrolyte fuel battery as described below.

1. Carbon powder having a primary particle size of 100 nm or less and an X-ray crystallite plane spacing  $C_0$  of less than 0.680 nm.
2. The carbon powder as described in 1 above, which has a primary particle size of 100 nm or less and an X-ray crystallite plane spacing  $C_0$  of 0.6730 nm or less.
3. The carbon powder as described in 1 or 2 above, which is carbon black.
4. The carbon powder as described in any one of 1 to 3 above, which shows a volume resistivity of 0.1 Ω·cm or less in the pressurized state under a pressure of 2 MPa.
5. The carbon powder as described in any one of 1 to 4 above, wherein boron content is in a range of 0.001 to 5% by mass.

6. The carbon powder as described in 5 above, wherein boron content is in a range of 0.1 to 5% by mass.
7. A method for producing the carbon powder as described in any one of 1 to 6 above, comprising adding boron carbide ( $B_4C$ ) to carbon black in an amount of 0.01 to 7% by mass in terms of boron and heat-treating the mixture at 2,500° C. or more in a non-oxidative atmosphere.
8. The method for producing the carbon powder as described in 7 above, comprising adding boron carbide ( $B_4C$ ) to carbon black in an amount of 0.5 to 7% by mass in terms of boron.
9. The method for producing the carbon powder as described in 7 or 8 above, wherein the carbon black is at least one kind selected from the group consisting of oil furnace black, acetylene black, thermal black, and channel black.
10. An electrically conducting carbon composite powder for supporting a catalyst, comprising carbon powder as described in any one of 1 to 6 above, having mixed therewith fibrous carbon.
11. The electrically conducting carbon composite powder for supporting a catalyst as described in 10 above, wherein the fibrous carbon is vapor grown carbon fiber.
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° 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° C. or more and boron content in the fiber is in a range of 0.001 to 5% by mass.
15. The electrically conducting carbon composite powder for supporting a catalyst as described in 14 above, wherein the boron content in the vapor grown carbon fiber is in a range of 0.1 to 5% by mass.
16. A catalyst for polymer electrolyte fuel battery, primarily comprising platinum or a platinum alloy and the carbon powder as described in any one of 1 to 6 above for supporting the catalyst.
17. A catalyst for polymer electrolyte fuel battery, primarily comprising platinum or a platinum alloy and the carbon composite powder as described in any one of 10 to 15 above for supporting the catalyst.
18. A polymer electrolyte fuel battery cell using the catalyst as described in 16 or 17 above for anode catalyst layer and/or cathode catalyst layer.
19. A solid polymer electrode fuel battery comprising at least more than two of the stacked polymer electrolyte fuel battery cell as described in 18 above.
20. A polymer electrolyte fuel battery using the catalyst as described in 16 or 17 above for anode and/or cathode electrode.

#### BRIEF DESCRIPTION OF DRAWINGS

FIG. 1(A) is a schematic longitudinal cross-sectional view of a cell for measuring the volume resistivity of the carbon powder of the present invention.

FIG. 1(B) is a schematic plan view of a cell for measuring the volume resistivity of the carbon powder of the present invention.

FIG. 2 is a cross-sectional view showing a basic constitution of a unit cell of a polymer electrolyte fuel battery, in which the complex powder according to the present invention is used in the catalyst layer.

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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 invention can preferably contain boron. This carbon powder containing boron can be produced, for example, carbon black and boron compound such as boron carbide ( $B_4C$ ), boron oxide and boron nitride are mixed, and the mixture is heat-treated at 2,500° C. or more in a non-oxidative atmosphere.

Among these methods, one preferable method where the carbon black is mixed with boron carbide ( $B_4C$ ) 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

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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° 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 ( $C_0$  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  $C_0$  value cannot be attained by the graphitization, and it is difficult to make the  $C_0$  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  $C_0$  crystallite plane spacing (double of  $d_{002}$ ) generally used as an index for showing the graphitization degree is less than 0.680 nm, furthermore 0.6730 nm or less.  $C_0$  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.  $N_2$  absorption specific surface area (BET), which is decreased by graphitization, is preferably in a range of 50 to 400  $m^2/g$  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  $\mu\text{m}$ .

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.

The electrical conductivity (volume resistivity) can be measured by the following method.

A fine powder sample is filled in a resinous container shown in FIG. 1 and compressed from upper and lower sides using a compression rod. Under a constant pressure, a current is passed, the voltage between voltage measuring terminals provided in the powder is read, and the resistivity is calculated from the observed value, the cross-sectional area of the container and the distance between voltage terminals. The resistivity varies depending on the pressurization conditions and as the pressure applied is lower, the resistivity is higher. When the pressure applied is increased and exceeds a certain pressurization value, the resistivity is settled to almost a fixed value regardless of the pressurizing condition. In the present invention, a volume resistivity at the time when the pressure applied to the electrode of a normal battery is 2 MPa, is used as the object of comparison.

The volume resistivity-measuring cell used in the present invention is, as shown in FIG. 1, a resinous cell **4** equipped with copper plate-made current terminals **3** for passing a current through the powder material to be measured and having a plane area of  $1 \times 4 \text{ cm}^2$  in the depth of 10 cm. The cell has voltage measuring terminals **1** in the way and is combined with a compression rod **2** for pressing the powder material. A fixed amount of powder **5** (the sample to be measured) is filled in the cell and the powder is compressed by loading a pressure on the compression rod **2** from the above.

While measuring the pressure, a current of 0.1 A is sequentially passed and at the point of 2 MPa, the voltage (E) V between two voltage measuring terminals **1** at a distance of 2.0 cm inserted through the container bottom is read and the resistivity (R)  $\Omega \cdot \text{cm}$  is calculated according to the following formula:

$$R(\Omega \cdot \text{cm}) = (E/0.1) \times D(\text{cm}^2) / 2(\text{cm})$$

wherein D is a cross-sectional area (depth  $\times$  width) = 10 d of the powder material in the current direction.

When this measuring method is applied, the fine carbon powder of the present invention exhibits a volume resistivity of 0.1  $\Omega \cdot \text{cm}$  or less under the pressurizing condition of 2 MPa. Particularly, for improving the electrical conductivity, the heat-treatment is preferably performed together with boron carbide so that the carbon powder can contain from 0.001 to 5% by mass, particularly 0.1 to 5% by mass of boron.

In order to use this fine carbon powder as a catalyst for electrode of a polymer electrolyte fuel battery, A mixture of powdery platinum or platinum alloy and this fine carbon powder can be used as main raw materials to construct an electrode.

FIG. 2 shows a cross-sectional structure of a unit cell of a polymer electrolyte fuel battery. The electrode is constructed such that an ion exchange membrane **14** having appropriate water content is disposed in the center and

sandwiched by an anode catalyst layer **13** and a cathode catalyst layer **15**. The anode catalyst layer **13** and the cathode catalyst layer **15** each is a sheet coated with a paste of carbon powder having supported thereon platinum or a platinum alloy. For this carbon powder, the carbon powder of the present invention can be used.

The unit cell is constructed such that in the outer side of each of the anode catalyst layer **13** and the cathode catalyst layer **15**, an electrically conducting anode gas-diffusing porous sheet **12** and a cathode gas-diffusing porous sheet **16** are respectively disposed for passing water and gas generated at the reaction and in the outermost side, a carbon-based separator plate with grooves **11** is disposed to provide reaction gas passages. By stacking the unit cells to form a multilayer structure, a fuel battery is completed.

By using the carbon powder of the present invention as a raw material of the above-described catalyst, improvement can be attained in the electrical conductivity, chemical stability, power generation efficiency (power generated per unit volume), and also in durability owing to the decreased functional group on the surface of carbon black, and improvement of thermal decomposition initial temperature, as compared with the case where a conventional carbon black available on the market is similarly used as a raw material.

Next, the second group of the present invention: an electrically conducting carbon composite powder for supporting a catalyst comprising carbon powder mixed therewith fibrous carbon, a catalyst for polymer electrolyte fuel battery using the carbon composite powder, solid polymer fuel battery cell and solid polymer fuel battery using the catalyst, will be described below.

As a composite powder of the carbon powder and a fibrous carbon is used as a collector of catalyst support for fuel battery or the like, particularly as a support for catalyst layer of solid polymer fuel battery, a durability for a long time use is improved, and higher output can be attained.

The carbon powder used in the composite powder of the present invention is the same powder as described in the first group of the invention of the graphitized fine carbon powder, commercially available carbon powder usually having an average primary particle size of 1  $\mu\text{m}$  or less, particularly carbon black. According to the production process, carbon black is classified into oil furnace black obtained by incompletely combusting aromatic hydrocarbon oil, acetylene black 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.

In particular, oil furnace black and acetylene black are preferred, because the high structure state can be easily formed in these.

Among these, graphitized fine carbon powder having good crystallinity as described in the first group of the present invention is preferred.

The fibrous carbon for use in the present invention may be any of those called PAN-type or called pitch-type, those obtained by the vapor phase process, and those called nanotube having a size of the order of nanometer. Among these, vapor grown carbon fiber that is heat-treated and enhanced in the electric conductivity is preferred because of its appropriate elasticity.

The vapor grown carbon fiber (hereinafter simply referred to as "VGCF") is produced by thermally vapor-phase decomposing a gas such as hydrocarbon, in the presence of a metal-based catalyst.

Examples of the production method include a method where an organic compound such as benzene is used as a starting material, an organic transition metal compound such as ferrocene is used as a metal-based catalyst, and these are introduced together with a carrier gas into a high temperature reaction furnace to produce VGCF on a substrate (see, JP-A-60-27700), a method where VGCF is produced in the suspension state (see, JP-A-60-54998 (U.S. Pat. No. 4,572, 813)), and a method where VGCF is grown on a reaction furnace wall (see, Japanese Patent 2,778,434).

In JP-B-3-64606 (the term "JP-B" as used herein means an "examined Japanese patent publication") (WO86/03455), a metal-containing particle previously supported on a refractory support such as alumina or carbon, is contacted with a carbon-containing compound at a high temperature to obtain VGCF of 70 nm or less.

VGCF produced by any of these methods can be used in the present invention.

VGCF constituting carbon composite powder of the present invention suitably has a fiber diameter of 20 to 300 nm and a fiber length of less than 100  $\mu\text{m}$ . This VGCF is mixed with carbon black in a ratio from 1 to 7% by mass, preferably from 2 to 6% by mass, of the carbon powder (carbon black).

The diameter of VGCF is preferably 20 nm or more because if the diameter is less than 20 nm, the VGCF can be hardly mass-produced in industry, which is not practical, and due to the fineness, the handling is cumbersome but the effect is not so high. On the other hand, if the diameter exceeds 300 nm, the fibers are poorly entangled for the particle size or shape of carbon black and the effect on the electrical conductivity cannot be obtained by the addition thereof.

If the fiber length exceeds 100  $\mu\text{m}$ , the fibers cannot be uniformly blended with carbon black and the effect as a composite powder can be hardly obtained.

The vapor grown carbon fiber takes a branched structure in many cases. In this case, the fiber length means a length from a branch point of a branch to the distal end or to the next branch point.

If the amount of VGCF added is less than 1% by mass, the addition effect can be hardly obtained, whereas if it exceeds 7% by mass, the ratio of carbon black as a support on which a platinum catalyst is supported, decreases and the cell characteristics are reduced.

The pitch-type carbon fiber and PAN-type carbon fiber have a fiber length in excess of 100  $\mu\text{m}$  and each fiber as it is cannot be uniformly blended with carbon black, and taking account that the electrical conductivity imparting effect is low, VGCF is preferred.

In the present invention, the carbon black is preferably heat-treated at a temperature of 2,500° C. or more, more preferably heat-treated in the state of the carbon black being mixed with a boron compound such as boron carbide, boron oxide or boron nitride particularly boron carbide, at 2,500° C. or more in a non-oxidative atmosphere such that the carbon black comprises from 0.001 to 5% by mass, preferably from 0.1 to 5% by mass, more preferably from 0.5 to 5% by mass of boron.

By heat-treating the carbon black at 2,500° C. or more, not only high electrical conductivity is attained but also the characteristics such as chemical stability and heat conductivity are improved and when this carbon black is used as a catalyst support of a fuel battery, the power generation efficiency (power generated per unit volume) is improved and the durability (the ratio of maximum output after the continuous use for 1,000 hours or more, to the initial maximum output) is also improved.

Particularly, in the case of carbon black elevated in the crystallinity by the heat-treatment at 2,500° C. or more, these improvements on the characteristics of a battery are remarkable. For this purpose, the crystallinity is elevated in the present invention by the addition of boron as means for elevating graphitization crystallinity.

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

The heat-treatment furnace may be any furnace as long as the heat-treatment can be performed at a desired temperature and, for example, an Acheson furnace, a high frequency furnace and a furnace using a graphite heating element may be used.

The non-oxidative atmosphere can be obtained, in the case of Acheson furnace, by burying the material to be heated in the carbon powder and in the case of other furnaces, by purging the atmosphere with an inert gas such as nitrogen or argon, according to the necessity.

The heat-treatment time is not particularly limited as long as the time period is long enough for the heated material as a whole to reach a predetermined temperature.

VGCF is usually used after burning it at a temperature around 1,000° C. after the production. However, when VGCF used is heat-treated in the same manner as in the carbon black, particularly, by mixing with a boron compound and then heat-treated, the VGCF can have improved electrical conductivity, and VGCF can contribute to the improvement of the battery characteristics (power generation efficiency, durability) as a catalyst in a cell manufactured.

The boron compound used here may be any compound as long as a desired boron content can be obtained after the heat-treatment, but in view of easy availability and workability, it is preferably an inorganic boron compound, more preferably boron carbide.

The amount of the boron compound added before the heat-treatment must be in excess of the target content because boron may be volatilized out depending on the heat-treatment conditions. The appropriate amount of the boron compound added is in a range of 0.01 to 10% by mass as calculated in terms of boron.

By mixing from 1 to 7% by mass of VGCF with carbon black and using the uniform mixture as the powder for supporting a catalyst in the catalyst layer, the cell characteristics can be greatly improved. In the mixing, the powder is uniformly mixed using a continuous system mixer such as screw feeder and cycle feeder, or a batch-system mixer such as mixing roll and banbury mixer.

The carbon black and VGCF may also be previously mixed before the heat-treatment and then heat-treated. At this time, the above-described boron compound may also be previously added and heat-treated. In these heat-treatments, the same effect can be obtained.

Platinum or a platinum alloy may be supported on the composite powder by the method described below or the like. The composite powder is added to an ethanol solution having dissolved therein, for example, chloroplatinic acid hexahydrate and mixed, the resulting solution is evaporated to dryness on a hot plate while stirring to obtain platinum compound-supported powder, this platinum compound-supported powder is added to a hydrazine monohydrate solution, and the mixture is stirred, washed with ion exchanged water and dried to obtain metal platinum-supported powder.

To a mixture of this platinum-supported powder and ion exchange resin or a mixture of this platinum-supported

powder, ion exchange resin, water-repellent resin, and added distilled water or a solvent and thoroughly stirred in a ball mill or the like to form a paste. This paste is coated on a carbon paper and dried at a temperature sufficiently high to thoroughly volatilize the solvent and the formed layer can be used as a catalyst layer.

Examples of the ion exchange resin include perfluorocarbon resin having, as the ion exchange group, a sulfonic acid group or a carboxylic acid group. Examples of the water-repellent resin include polytetrafluoroethylene.

THE BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be explained in more detail with reference to the following examples and comparative examples, but the present invention is not particularly limited by these examples.

EXAMPLES 1 TO 7 AND COMPARATIVE EXAMPLES 1 TO 9

The raw material carbon black used was furnace black (N330 and N110 (trade names), produced by Showa Cabot K.K.; Valcan XC-72, black pearl 2000(trade name), produced by Cabot; and Ketjen Black EC-600JD (trade name), produced by Lion Corp.) or acetylene black (Denka Black (trade name), produced by Denki Kagaku Kogyo K.K.). Any of these carbon black used are particulate type (aggregated type).

Above-described carbon black and previously ground boron carbide powder having an average particle size of about 20 μm were mixed in a dry system in an amount described in Table 1 using a LABOMIXER manufactured by Hosokawa Micron K.K. and the obtained powder was used as the sample for Examples 1 to 7 of the present invention.

For the purpose of comparison, boron carbide was not added (Comparative Examples 2, 5 and 8), boric acid and carbon black were mixed in warm water at 70° C. to prepare a slurry and this slurry was dried at 130° C., measured on the weight to determine the amount of boric acid added (Comparative Examples 3, 4, 6 and 7), and used as the Comparative Sample.

In the heat-treatment, each sample was placed in a graphite box and the box was buried in an Acheson furnace and kept at a predetermined temperature for 5 minutes. In the comparative example 1, the predetermined temperature (heat-treatment temperature) is set under 2500° C. (2180° C.). The experimental conditions of Examples 1 to 7 and Comparative Examples 1 to 8 are shown in Table 1.

TABLE 1

	Raw Material Carbon Black	Heat-Treatment Temperature ° C.	Amount of Boron Carbide Added (% by mass, as boron)	Amount of Boric Acid Added (% by mass, as boron)
Example 1	N330	2830	0.5	0
Example 2	Valcan XC-72	2780	3.0	0
Example 3	N110	2910	7.0	0
Example 4	N330	3020	4.0	0
Example 5	EC-600JD	2990	4.0	0
Example 6	Denka Black	2650	4.0	0
Example 7	Black Pearl 2000	2720	4.0	0
Comparative Example 1	N330	2180	7.0	0

TABLE 1-continued

	Raw Material Carbon Black	Heat-Treatment Temperature ° C.	Amount of Boron Carbide Added (% by mass, as boron)	Amount of Boric Acid Added (% by mass, as boron)
Comparative Example 2	Valcan XC-72	2970	0	0
Comparative Example 3	N110	2690	0	6.3
Comparative Example 4	N330	3010	0	5.7
Comparative Example 5	EC-600JD	3010	0	0
Comparative Example 6	EC-600JD	3000	0	4.3
Comparative Example 7	Denka Black	2890	0	4.8
Comparative Example 8	Black Pearl 2000	2880	0	0

After the heat-treatment, each sample was cooled to normal temperature in a non-oxidative atmosphere and ground by the LABOMIXER described above.

Thereafter, the C<sub>0</sub> value was measured by X-ray diffraction and the volume resistivity was calculated from the voltage decrease at 2 MPa using the measuring cell described above. Boron (B) in the carbon powder at this time was pre-treated and analyzed by Inductively Coupled Plasma (ICP) Emission Spectroscopy.

The results obtained are shown in Table 2. For Reference, the measured data of 6 kinds of commercially available carbon black products are shown together.

TABLE 2

	B Content, mass %	Co Value (nm)	Consolidation Resistivity (mΩ · cm)
Example 1	0.3	0.6719	72
Example 2	1.9	0.6719	60
Example 3	4.3	0.6715	74
Example 4	2.0	0.6710	52
Example 5	2.1	0.6711	37
Example 6	3.0	0.6719	50
Example 7	2.2	0.6771	82
Comparative Example 1	6.9	0.6890	176
Comparative Example 2	—	0.6875	120
Comparative Example 3	1.5	0.6823	138
Comparative Example 4	1.4	0.6805	117
Comparative Example 5	—	0.6861	87
Comparative Example 6	0.9	0.6807	72
Comparative Example 7	1.2	0.6819	122
Comparative Example 8	—	0.6850	121
N110	—	immeasurable (no peak)	221
N330	—	immeasurable (no peak)	238
Valcan XC-72	—	immeasurable (no peak)	158
EC600JD	—	immeasurable (no peak)	119
Denka Black	—	0.6980	144
Black Pearl 2000	—	immeasurable (no peak)	122

Then, using Denka Black, a boron(B)-containing heat-treated sample (Example 6) or a boron(B)-free heat-untreated normal commercially available sample (granular product) (Comparative Example 9) was used after pulverizing for supporting the catalyst, evaluation of the unit cell of a polymer electrolyte fuel battery was performed.

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Using each of the above-described two samples, a catalyst layer was formed as follows and a unit cell comprised as shown in FIG. 2 for a polymer electrolyte fuel battery was manufactured and evaluated on the battery characteristics.

In a ball mill, 1.5 g of carbon black sample powder having supported thereon 30% by mass of platinum, 10 g of a 5% by mass solution of fluorine-type ion exchange resin (Nafion, trade name, produced by Du Pont) and 5 g of distilled water were mixed for 30 minutes to obtain a paste. This paste was coated on a gas diffusion layer comprising carbon sheet (SCT sheet, trade name, produced by Showa Denko K.K.) treated with 30% by mass of water-repellent polytetra fluoroethylene resin. Subsequently, the paste was dried at 60° C. for 10 minutes and heated at 130° C. and 200 N/cm<sup>2</sup> for 1 minute to manufacture a gas diffusion electrode in which a catalyst layer supporting 1 mg/cm<sup>2</sup> of platinum was formed.

As shown in FIG. 2, the thus-manufactured electrode (one is anode catalyst layer 13/anode gas diffusion porous sheet 12 and another is cathode catalyst layer 15/cathode gas diffusion porous sheet 16) and a separator plate with grooves 11 (250 mm×250 mm×8 mm) were disposed to oppose each other with intervention of an ion exchange membrane (Nafion, trade name, produced by Du Pont) 14 and thereby constitute a unit cell of a polymer electrolyte fuel battery.

This unit cell was operated using hydrogen as the fuel gas and air as the oxidizing gas under an applied pressure of 10 N/cm<sup>2</sup>. From the maximum output in this operation, the battery characteristics of a polymer electrolyte fuel battery were evaluated.

For the evaluation of durability, a continuous operation was performed at an output of 0.3 W/cm<sup>2</sup> for 4,000 hours and the output retention (a ratio of the output after the operation for 4,000 hours to the output at the initiation of operation) was determined.

Carbon black, boron(B) content, and cell characteristics (maximum output, retention) of a unit cell employing a catalyst using the carbon black are shown in Table 3.

TABLE 3

Sample Powder Used	Conditions in the Production of Carbon Black Used		Characteristics of Single Cell	
	Amount of B Added, mass %	Heat-Treatment Condition, ° C.	Maximum Output, W/cm <sup>2</sup>	Durability, %
Example 6	4.0	2650	0.31	84
Comparative Example 9	0	none	0.13	75

From the results of Tables 1 to 3, according to the present invention, submicron carbon powder succeeded in the progress of graphitization which has been heretofore impossible, can be obtained. Due to the graphite crystallization, this carbon powder is improved in the chemical stability and the electrical conductivity and therefore, is useful as a material for battery. The polymer electrolyte fuel battery using this carbon powder as a catalyst is obviously improved in the power generating property and the durability as compared with conventional batteries.

#### EXAMPLES 8 TO 19 AND COMPARATIVE EXAMPLES 10 TO 12

As the carbon black, the following powder samples were prepared.

##### (1) Heat-Untreated Product

Acetylene black (Denka Black, trade name, granular type) (hereinafter simply referred to as KCB) produced by Denki Kagaku Kogyo K.K. was used as a sample as it is.

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##### (2) Graphitization Heat-Treated Product

Furnace black (Shoblack, trade name, granular type) produced by Showa Cabot K.K. was filled in a graphite-made crucible and burned at respective temperatures of 2,500° C. and 2,700° C. in an Acheson furnace over 10 days to prepared samples different in the treatment temperature. This heat-treated carbon black is hereinafter simply referred to as GrCB.

##### (3) Graphitization Heat-Treated Product Comprising Boron

Furnace black produced by Showa Cabot K.K. and previously pulverized boron carbide powder produced by Denki Kagaku Kogyo K.K. were mixed, filled in a graphite-based crucible and burned at respective temperatures of 2,500° C. and 2,700° C. in an Acheson furnace to prepare samples different in the treatment temperature. After the heat-treatment, the boron content of each sample was confirmed by the chemical analysis. This heat-treated carbon black comprising boron is hereinafter simply referred to as B-GrCB.

As the vapor grown carbon fiber, 5 samples of vapor grown carbon fibers (VGCF, trade name) produced by Showa Denko K.K. having an approximate diameter size of 30 nm, 50 nm, 100 nm, 200 nm and 300 nm were prepared.

As a result of observation through scanning electron microscope (SEM), these all had a fiber length of less than 100 μm and all showed a branched structure form.

These fibers were treated in a condition described in Table 4 to prepare various samples of vapor grown carbon fiber samples that were individually burned in a non-oxidative atmosphere (VGCF1 to VGCF6), samples that were subjected to the same graphitization heat-treatment as the (3) graphitization heat-treated product comprising boron described above, and samples that were heat-treated boron carbide produced by Denki Kagaku Kogyo K.K. which had been pulverized and mixed in a screw feeder (B-VGCF1 to B-VGCF6).

TABLE 4

Sample No.	Heat-Treatment Temperature (° C.)	Fiber Diameter Size (nm)	Boron Content (mass %)
VGCF 1	1200	300	0
VGCF 2	1200	200	0
VGCF 3	1200	30	0
VGCF 4	2800	300	0
VGCF 5	2800	200	0
VGCF 6	2800	50	0
B-VGCF 1	2500	200	0.5
B-VGCF 2	2500	200	3
B-VGCF 3	2500	200	7
B-VGCF 4	2700	300	5
B-VGCF 5	2700	200	0.5
B-VGCF 6	2700	100	3

Using each of these samples, a catalyst layer was formed as follows and then, as shown in FIG. 2, a unit cell of a polymer electrolyte fuel battery was manufactured and evaluated on the battery characteristics.

1.5 g of carbon black having supported thereon 30% by mass of platinum or 1.5 g of composite powder of the carbon black and VGCF or B-VGCF (see, Table 5 (5-1,2-2)) having supported thereon 30% by mass of platinum, 10 g of a 5% by mass concentrated solution of fluorine type ion exchange resin (Nafion, trade name, produced by Du Pont) and 5 g of distilled water were mixed for 30 minutes in a ball mill to obtain a paste. This paste was coated on a gas diffusion layer comprising carbon sheet (SCT sheet, trade name, produced by Showa Denko K.K.) treated with 30% by mass of water-repellent polytetrafluoroethylene resin. Subsequently,

the paste was dried at 60° C. for 10 minutes and heated at 130° C. under a pressure of 200 N/cm<sup>2</sup> for 1 minute to

retention) of a unit cell employing a catalyst using the carbon black and VGCF are shown in Table 5 (5-1, 5-2)

TABLE 5-1

Production Conditions and Blending Ratio of Composite Powder								
Carbon Black				Blending Ratio		Characteristics of		
Type	Heat-Treatment Temperature, ° C.	Boron Content, mass %	Kind	VGCF Boron Content, mass %	Amount of VGCF Added, mass %	Unit Cell		
						Maximum Output, W/cm <sup>2</sup>	Durability, %	
Example 8	KCB	—	—	VGCF 1	—	5	0.43	93
Example 9	KCB	—	—	VGCF 4	—	5	0.45	95
Example 10	KCB	—	—	B-VGCF 1	0.5	3	0.42	98
Example 11	KCB	—	—	B-VGCF 4	5	3	0.46	97
Example 12	GrCB	2500	—	VGCF 3	—	7	0.45	93
Example 13	GrCB	2700	—	VGCF 4	—	7	0.49	96
Example 14	GrCB	2500	—	B-VGCF 2	3	4	0.50	97
Example 15	GrCB	2700	—	B-VGCF 5	0.5	4	0.49	98
Example 16	B-GrCB	2500	3	VGCF 1	—	2	0.51	93
Example 17	B-GrCB	2700	0.5	VGCF 5	—	2	0.47	98
Example 18	B-GrCB	2500	5	B-VGCF 3	7	1	0.49	97
Example 19	B-GrCB	2700	7	B-VGCF 6	3	1	0.48	98

TABLE 5-2

Production Conditions and Blending Ratio of Composite Powder								
Carbon Black				Blending Ratio		Characteristics of		
Type	Heat-Treatment Temperature, ° C.	Boron Content, mass %	Kind	VGCF Boron Content, mass %	Amount of VGCF Added, mass %	Unit Cell		
						Maximum Output, W/cm <sup>2</sup>	Durability, %	
Comparative Example 10	KCB	—	—	—	—	—	0.11	73
Comparative Example 11	GrCB	2700	—	—	—	—	0.28	81
Comparative Example 12	B-GrCB	2700	7	—	—	—	0.32	85

manufacture a gas diffusion electrode in which a catalyst layer supporting platinum corresponding to 1 mg/cm<sup>2</sup> was formed.

As shown in FIG. 2, the thus-manufactured electrode (one is anode catalyst layer 13/anode gas diffusion porous sheet 12 and another is cathode catalyst layer 15/cathode gas diffusion porous sheet 16) and a separator plate 11 with grooves (250 mm length×250 mm width×8 mm thickness) were disposed to oppose each other with intervention of an ion exchange membrane (Nafion, trade name, produced by Du Pont) 14 and thereby constitute a unit cell of a polymer electrolyte fuel battery.

This unit cell was operated using hydrogen as the fuel gas while passing an oxidizing gas (air) under an applied pressure of 10 N/cm<sup>2</sup>, and the battery characteristics of a polymer electrolyte fuel battery were evaluated.

For the evaluation of durability, a continuous operation was performed at an output of 0.3 W/cm<sup>2</sup> for 4,000 hours and the output retention (a ratio of the output after the operation for 4,000 hours to the output at the initiation of operation) was determined.

The blending conditions of carbon black and VGCF, and the evaluated battery characteristics (maximum output,

From the results of Table 4 to 5 (5-1,2-2), instead of using conventional simple carbon black as a catalyst support in a polymer electrolyte fuel battery, by using the composite powder of the present invention as the support and a catalyst layer mainly comprising a mixture of this composite powder and platinum or a platinum alloy for the electrode, the power generation efficiency is greatly elevated and also the long-term durability over ten hundreds of hours is enhanced.

What is claimed is:

1. Carbon black having a primary particle size of 100 nm or less and an X-ray crystallite plane spacing C<sub>0</sub> of 0.6730 nm or less, and having a boron content in a range of 0.001 to 5% by mass, which shows a volume resistivity of 0.1 Ω·cm or less in the pressurized state under a pressure of 2 MPa.

2. The carbon black as claimed in claim 1, wherein the boron content is in a range of 0.1 to 5% by mass.

3. The carbon black as claimed in claim 1, wherein N<sub>2</sub> absorption specific surface area (BET) is in a range of 50 to 400 m<sup>2</sup>/g.

4. A method for producing the carbon black as claimed in claim 1, comprising adding boron carbide (B<sub>4</sub>C) to carbon black in an amount of 0.01 to 7% by mass in terms of boron and heat-treating the mixtures at 2,500° C. or more in a non-oxidative atmosphere.

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5. The method for producing the carbon black as claimed in claim 4, comprising adding boron carbide (B<sub>4</sub>C) to carbon black in an amount of 0.5 to 7% by mass in terms of boron.

6. The method for producing the carbon black as claimed in claim 4 or 5, wherein the carbon black is at least one kind selected from the group consisting of oil furnace black, acetylene black, thermal black, and channel black.

7. An electrically conducting carbon composite powder for supporting a catalyst, comprising carbon black as claimed in any one of claims 1, 2 or 3 having mixed therewith fibrous carbon.

8. The electrically conducting carbon composite powder for supporting a catalyst as claimed in claim 7, wherein the fibrous carbon is vapor grown carbon fiber.

9. The electrically conducting carbon composite powder for supporting a catalyst as claimed in claim 8, wherein from 1 to 7% by mass of vapor grown carbon fiber is mixed with carbon black.

10. The electrically conducting carbon composite powder for supporting a catalyst as claimed in claim 7, wherein the carbon black is heat-treated at a temperature of 2,500° C. or more.

11. The electrically conducting carbon composite powder for supporting a catalyst as claimed in claim 8, wherein the vapor grown carbon fiber is graphitized at a temperature of

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2,500° C. or more and boron content in the fiber is in a range of 0.001 to 5% by mass.

12. The electrically conducting carbon composite powder for supporting a catalyst as claimed in claim 11, wherein the boron content in the vapor grown carbon fiber is in a range of 0.1 to 5% by mass.

13. A catalyst for polymer electrolyte fuel battery, primarily comprising platinum or a platinum alloy and the carbon black as claimed in any one of claims 1, 2 or 3 for supporting the catalyst.

14. A catalyst for polymer electrolyte fuel battery, primarily comprising platinum or a platinum alloy and the carbon composite powder as claimed in claim 7 for supporting the catalyst.

15. A polymer electrolyte fuel battery cell using the catalyst as claimed in claim 13 for anode catalyst layer and/or cathode catalyst layer.

16. A solid polymer electrode fuel battery comprising at least more than two of the stacked polymer electrolyte fuel battery cell as claimed in claim 15.

17. A polymer electrolyte fuel battery using the catalyst as claimed in claim 13 for anode and/or cathode electrode.

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