PROTON CONDUCTIVE CARBON MATERIAL

The present invention provides methods for the incorporation of sulfonate functional groups onto the surface of particulate carbonaceous materials and provides several surface modified carbonaceous material compositions resulting therefrom. The composition can further comprise a conducting polymer. The composition can further comprise a metal. Devices comprising the composition can be constructed including supported electrocatalysts, membrane electrode assemblies, and fuel cells. A method for preparing the composition comprises sulfonating particulate carbonaceous material. The method can further comprise metallizing the sulfonated carbonaceous material.
PROTON CONDUCTIVE CARBON MATERIAL

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Serial No. 60/382,801 filed May 23, 2002, hereby incorporated by reference and is a continuation-in-part of U.S. Serial No. 10/229,933 filed August 28, 2002, hereby incorporated by reference.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates generally to particulate conductive carbons. The present invention relates to the surface modification of various carbonaceous materials and compounds. More specifically, the invention provides improved methods for the incorporation of sulfonate functional groups onto the surface of carbonaceous materials and compounds and similarly provides several surface modified carbonaceous materials resulting therefrom. The invention also relates to supported catalysts for fuel cells and proton exchange membranes.

BACKGROUND

A fuel cell (FC) is a device that converts energy of a chemical reaction into electrical energy (electrochemical device) without combustion. A fuel cell (see e.g., Figure 1) generally comprises an anode 20, cathode 50, electrolyte 10, backing layers 30, 60, and flow fields/current collectors 40, 70. There are five types of fuel cells, as defined by their electrolytes:

<table>
<thead>
<tr>
<th>Type</th>
<th>Electrolyte</th>
<th>Temperature</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>Liquid phosphoric acid soaked in a matrix</td>
<td>175-200 °C</td>
<td>Stationary power, commercially available</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>Liquid solution of lithium, sodium and/or potassium carbonates, soaked in a matrix</td>
<td>600-1200 °C</td>
<td>Molten carbonate salts, high efficiency</td>
</tr>
<tr>
<td>Type</td>
<td>Electrolyte</td>
<td>Temperature</td>
<td>Comments</td>
</tr>
<tr>
<td>---------------------</td>
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</tr>
<tr>
<td>Solid oxide</td>
<td>Solid zirconium oxide to which a small amount of ytrria is added</td>
<td>600-1800 °C</td>
<td>Ceramic, high power, industrial applications</td>
</tr>
<tr>
<td>Alkaline</td>
<td>Aqueous solution of potassium hydroxide soaked in a matrix</td>
<td>90-100 °C</td>
<td>Potassium hydroxide electrolyte, NASA, very expensive</td>
</tr>
<tr>
<td><strong>Proton exchange membrane</strong></td>
<td>Solid organic polymer polyperfluorosulfonic acid</td>
<td>60-100 °C</td>
<td>Ionomer membrane, high power density, can vary output quickly, portable/auto applications</td>
</tr>
<tr>
<td>Direct Methanol</td>
<td></td>
<td>60-100 °C</td>
<td>PEM that uses methanol for fuel</td>
</tr>
</tbody>
</table>

** = Currently of most interest

The current description deals with proton exchange membrane (a.k.a. polymer electrolyte membrane) (PEM) fuel cells (a.k.a. solid polymer electrolyte (SPE) fuel cell, polymer electrolyte fuel cell, and solid polymer membrane (SPM) fuel cell). A polymer electrolyte membrane fuel cell (PEMFC) comprises a proton conductive polymer membrane electrolyte 10 sandwiched between electrocatalysts (a cathode 50 and an anode 20) (see, e.g., Figure 1).

The oxidation and reduction reactions occurring within the fuel cell are:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \] oxidation half reaction

\[ + O_2 \rightarrow 2H_2O \] reduction half reaction

This electrochemical process is a non-combustion process which does not generate airborne pollutants. Therefore, fuel cells are a clean, low emission, highly efficient source of energy. Fuel cells can have 2-3 times greater efficiency than internal combustion engines and can use abundant and/or renewable fuels. Fuel cells produce electricity, water, and heat using fuel 90 and oxygen 80. Water (liquid and vapor) is the only emission when hydrogen is the fuel.

Since the voltage of a typical fuel cell is small, they are usually stacked in series.
The two half-reactions normally occur very slowly at the low operating
temperature of the fuel cell, thus catalysts 56 are used on one or both the anode 20 and
cathode 50 to increase the rates of each half reaction. Platinum (Pt) has been the most
effective noble metal catalyst 56 to date because it is able to generate high enough rates
of O₂ reduction at the relatively low temperatures of the PEM fuel cells. Kinetic
performance of PEM fuel cells is limited primarily by the slow rate of the O₂ reduction
half reaction (cathode reaction) which is more than 100 times slower than the H₂
oxidation half reaction (anode reaction). The O₂ reduction half reaction is also limited
by mass transfer issues.

As fuel 90, such as hydrogen, flows into a fuel cell on the anode side, a catalyst
56 facilitates the separation of the hydrogen gas fuel into electrons and protons
(hydrogen ions). The hydrogen ions pass through the membrane 10 (center of fuel cell)
and, again with the help of the catalyst 56, combine with an oxidant 80, such as oxygen,
and electrons on the cathode side, producing water. The electrons, which cannot pass
through the membrane 10, flow from the anode 20 to the cathode 50 through an
external circuit containing a motor or other electrical load, which consumes the power
generated by the cell.

A catalyst 56 is used to induce the desired electrochemical reactions at the
electrodes 20, 50. The catalyst 56 is often incorporated at the electrode/electrolyte
interface by coating a slurry of the electrocatalyst particles 56 to the electrolyte 10
surface. When hydrogen or methanol fuel feed 90 through the anode
catalyst/electrolyte interface, electrochemical reaction occurs, generating protons and
electrons. The electrically conductive anode 20 is connected to an external circuit,
which carries electrons by producing electric current. The polymer electrolyte 10 is
typically a proton conductor, and protons generated at the anode catalyst migrate
through the electrolyte 10 to the cathode 50. At the cathode catalyst interface, the
protons combine with electrons and oxygen to give water.

The catalyst 56 is typically a particulate metal, such as platinum, and is
dispersed on a high surface area electronically conductive support 52.
The electronically conductive support material 52 in the PEMFC typically consists of carbon particles. Carbon has an electrical conductivity \((10^{-1} - 10^2 \text{ S/cm})\) which helps facilitate the passage of electrons from the catalyst 56 to the external circuit. Proton conductive materials 54, such as Nafion®, are often added to facilitate transfer of the protons from the catalyst 56 to the membrane interface.

To promote the formation and transfer of the protons and the electrons and to prevent drying out of the membrane 10, the fuel cells are operated under humidified conditions. To generate these conditions, hydrogen fuel 90 and oxygen 80 gases are humidified prior to entry into the fuel cell. In a supported electrocatalyst \((52 + 56)\), carbon is relatively hydrophobic, and as such, the boundary contact between the reactive gases, water, and the surface of the solid electrodes made of carbon contributes to high electrical contact resistance and ohmic power loss in the fuel cell resulting in lower efficiency of the fuel cell.

In order to increase the mobility of protons in the electrocatalyst layer, the electrocatalyst is dispersed in proton conductive substrates. These substrates often reduce the efficiency of the electrocatalyst by blocking the active sites and also reduce the electronic conductivity.

In a Direct Methanol Fuel Cell (DMFC), the liquid methanol feed contains \(\text{H}_2\text{SO}_4\) to facilitate oxidation of methanol and to provide ionic conductivity in the carbon catalyst, which otherwise is limited to only the catalyst in direct contact with solid membrane. The \(\text{H}_2\text{SO}_4\) penetrates the anode structure providing ionic conductivity throughout the electrode, thus allowing most of the catalyst to be utilized resulting in improved performance. However, use of \(\text{H}_2\text{SO}_4\) is undesirable due to sulfate species adsorbing onto the electrode surface, and also the corrosive nature of the acid.

The above problems are addressed by the present invention, where the carbon support material in the electrocatalyst is sulfonated to increase proton conductivity and enhance the methanol oxidation. The sulfonic acid functional groups chemically bonded to the carbon support in an electrocatalyst aid the facile exchange of protons and thereby increase the fuel cell efficiency.
In the present invention, the sulfonated carbon material shows hydrophilic character and thereby enhances water management in fuel cell applications.

An ordinary electrolyte is a substance that dissociates into positively charged and negatively charged ions in the presence of water, thereby making the water solution electrically conducting. The electrolyte in a PEM fuel cell is a polymer membrane. Typically, the membrane material (e.g., Nafion®) varies in thickness from 50–175 μm. Polymer electrolyte membranes are somewhat unusual electrolytes in that, in the presence of water, which the membrane readily absorbs, the negative ions are readily held within their structure. Only the protons contained within the membrane are mobile and free to carry positive charge through the membrane. Without this movement within the cell, the circuit remains open and no current would flow.

Polymer electrolyte membranes can be relatively strong, stable substances. These membranes can also be effective gas separators. Although ionic conductors, PEM do not conduct electrons. The organic nature of the structure makes it an electronic insulator. Since the electrons cannot move through the membrane, the electrons produced at one side of the cell must travel through an external circuit to the other side of the cell to complete the circuit. It is during this external route that the electrons provide electrical power.

A polymer electrolyte membrane can be a solid, organic polymer, usually poly(perfluorosulfonic) acid. A typical membrane material, Nafion®, consists of three regions:

1. the Teflon-like, fluorocarbon backbone, hundreds of repeating -CF₂-CF₂-CF₂-units in length,
2. the side chains, -O-CF₂-CF₂-CF₂-O-, which connect the molecular backbone to the third region, and
3. the ion clusters consisting of sulfonic acid ions, SO₃⁻, H⁺.

The negative ions, SO₃⁻, are permanently attached to the side chain and cannot move. However, when the membrane becomes hydrated by absorbing water, the hydrogen ions become mobile. Ion movement occurs by protons, bonded to water molecules,
migrating from \( \text{SO}_3^- \) site to \( \text{SO}_4^2- \) site within the membrane. Because of this mechanism, the solid hydrated electrolyte is a good conductor of hydrogen ions.

The catalyst support 52 serves to conduct electrons and protons and to anchor the catalyst 56 (e.g., noble metal). Many efforts have been aimed at lowering the costs of fuel cells by lowering noble metal (e.g., platinum) catalyst 56 levels due to noble metal's cost. One way to lower this cost is to construct the catalyst support layer 52 with the highest possible surface area.

The electrodes 20, 50 of a fuel cell typically consist of carbon 52 onto which very small metal particles 56 are dispersed. The electrode is somewhat porous so that gases can diffuse through each electrode to reach the catalyst 56. Both metal 56 and carbon 52 conduct electrons well, so electrons are able to move freely through the electrode. The small size of the metal particles 56, about 2 nm in diameter for noble metal, results in a large total surface area of metal 56 that is accessible to gas molecules. The total surface area is very large even when the total mass of metal 56 is small. This high dispersion of the catalyst 56 is one factor to generating adequate electron flow (current) in a fuel cell.

Conducting polymers are a class of conjugated double bond polymers whose electrical conductivities are comparable to the conductivities of semiconductors to metals, in the range of 0.1 to 100 S/cm. Typical examples of conducting polymers include polyaniline, polypyrrole, polythiophene, polyfuran, and polyphenylene. Both polyaniline and polypyrrole catalyst support 52 materials have shown improved fuel cell efficiency (e.g., U.S. 5,334,292 and WO 01/15253). However, the long-term stability of these materials has not been demonstrated in electrode environments in cyclic operations.

Conducting polymers alone used as catalyst support 52 material have higher costs, lower surface area, and lower stability compared to those supports 52 based on carbon or the sulfonated carbon of the present invention.

An example of a current commercial carbon-supported catalyst for fuel cells is the HiSPEC \( ^\text{TM} \) series of products (Johnson Matthey, Reading, U.K.) which utilize Vulcan® XC72 (Cabot Corporation) carbon black loaded with various levels of
platinum (or other metal). These commercial carbon-supported catalysts are very expensive.

Factors such as surface area and electronic conductivity have historically been viewed as important for the carbon support material. However, relatively little research has been undertaken to understand the role of or to optimize the carbon support.

In the present invention, carbonaceous material is sulfonated, thereby increasing the protonic (and electronic) conductivity of the carbonaceous material. The sulfonation also provides anchoring sites for the metal, resulting in increased metal availability for electrode reaction.

The majority of the cost associated with electrodes is attributed to the high cost of the metal, which makes up the catalyst. Only those catalytic sites exposed on the surface of the catalytic particles contribute to the catalytic activity of the electrode and, thus, electrodes with the highest fraction of the metals accessible to the reaction should be the most effective. Carbon supports with high porosity result in "trapped" metal sites that are not accessible for electrode reaction. The extent of dispersion of the metal catalyst on the support material and the stability of such high dispersion in use, i.e., resistance of the catalyst against sintering and/or agglomeration, is directly related to the surface area and the availability of surface sites on which the dispersed metal can be anchored.

In the present invention, the sulfonated carbon material aids the uniform dispersion and stabilization of metal particles by anchoring the metal to the sulfonate groups present on the carbon material. Also, the anchoring groups resist the agglomeration and sintering of metal (e.g., platinum (Pt)) crystallite particles.

It is desirable to provide a catalyst support that has a higher surface area and also a higher surface density of anchoring surface sites than catalytic supports consisting exclusively of unsulfonated carbon. This would increase and stabilize the dispersion of the metal catalyst and, thus, limit the amount of catalyst needed. The present invention provides a PEMFC electrode which can be made more cost-effective than electrodes having exclusively carbon support or exclusively conducting polymer support.
The surface modification of carbonaceous compounds and materials has been widely explored as a means for achieving desired chemical and physical properties not normally exhibited by carbonaceous compounds and materials. Specifically, the introduction of sulfonate substituents, which are hydrophilic in nature, has been perceived as a potential means for increasing protonic and electronic conductivity and for facilitating water management in fuel cells.

To this end, several previous attempts have been made at sulfonating carbonaceous compounds and materials. However, these existing methods produce, at best, undesired and marginal results. Specifically, the processes of the prior art present a considerable problem in that it is extremely difficult to avoid oxidation of a carbonaceous compound or material and the subsequent formation of tarry byproducts during the sulfonation reaction. Therefore, the present invention provides an improved process for the formation of sulfonated carbonaceous materials that substantially minimizes the oxidation of the carbonaceous materials and formation of undesired and problematic tarry byproducts.

Additionally, the processes of the prior art only succeed in providing sulfonated carbonaceous materials having a minimal degree of surface substitution. The present invention provides sulfonated carbonaceous materials having a surprisingly substantially improved degree of surface modification thereby resulting in superior characteristics and properties in fuel cell applications.

For the above reasons, improvement of the supported catalyst is desired and has been achieved with the sulfonated carbonaceous material of the present invention.

SUMMARY OF THE INVENTION

In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention relates to conductive carbons, specifically proton conductive carbons.

The invention includes a composition comprising a sulfonated particulate carbonaceous material. The present invention provides a surface-modified carbonaceous material comprising a plurality of sulfonate substituents of the general
formula -SO₃M surface bonded thereto, wherein M is hydrogen or a cationic species. The surface-modified carbonaceous material can have a surface atomic concentration of sulfur present within the surface-bonded SO₃M moieties, measured by XPS, greater than about 0.25% relative to the total surface atomic concentration of the surface-treated carbonaceous material.

The present invention also provides several additional compositions comprising the surface-modified carbonaceous material of the present invention.

The present invention includes methods for the incorporation of sulfonate functional groups onto the surface of carbonaceous materials and provides surface-modified carbonaceous materials resulting therefrom.

The present invention provides a method for the preparation of a surface-modified carbonaceous material. The method comprises contacting an anhydride of the generic formula (R-CO)₂O with sulfuric acid under conditions effective to provide an organic sulfite intermediate of the generic formula R-(CO)O-SO₃H, wherein R is an aliphatic substituent. The method further comprises contacting a carbonaceous material with the organic sulfite intermediate provided in the first step under conditions effective to provide a surface-modified carbonaceous material comprising a plurality of surface-bonded sulfonate substituents of the general formula -SO₃H.

The invention provides a method for preparing a carbon with enhanced electronic and protonic conductivity comprising sulfonating a particulate carbonaceous material. Adding sulfonate functional groups onto particulate carbon material enhances the properties of the carbon material. Particularly, the functional groups are, for example, sulfonic acid groups. Sulfonic acid groups can be surface-bonded to the carbonaceous material via direct sulfonation.

A device is disclosed comprising a sulfonated particulate carbonaceous material.

This invention relates to the application of sulfonated carbons in fuel cell applications. This invention particularly relates to the application of sulfonated carbons as support material in fuel cell catalysts. A fuel cell comprising an anode, a cathode, and a PEM is further included.
Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several embodiments of the invention and together with the description, serve to explain the principles of the invention.

Figure 1 shows a "typical" PEMFC. Figure 1A shows a schematic drawing of PEMFC. Figure 1B shows a close up of an electrode and membrane of the PEMFC.

Figure 2 is a plot of the X-ray photoelectron spectroscopy (XPS) spectrum of the CDX-975 carbon black used to prepare the sulfonated products of the Examples.

Figure 3 is a plot of the XPS spectrum of the sulfonated carbon black produced in Example 4.

Figure 4 is a plot of the high resolution XPS spectrum of the sulfonated carbon black produced in Example 4, indicating the percentage of oxygen species that are present in the surface-bonded sulfonate substituents.

Figure 5 is a plot of the high resolution XPS spectrum of the sulfonated carbon black produced in Example 4, indicating the percentage of sulfur species that are present as the surface-bonded sulfonate substituents.

Figure 6 is an XPS survey spectrum of platinized sulfonated carbon black of Example 4.

Figure 7 is a high resolution XPS spectrum showing sulfonate on platinized carbon black of Example 4.

Figure 8 is a graph of MEA polarization curves comparing the commercial Johnson Matthey product and a platinized sulfonated carbon black of the present
invention demonstrating the performance of the two materials in membrane electrode assemblies. The potential was varied across the materials and the current was measured. Electrode was prepared via the "decal transfer" method developed by Los Alamos Laboratory. For each sample, both anode and cathode were prepared to an approx Pt loading of 0.3 mg/cm². Analysis conditions were
Cell temperature = 80°C
Anode humidification bottle temperature = 105°C, and
Cathode humidification bottle temperature = 90°C.
Reactant gases:
Anode hydrogen = 60 ml/min + 14 ml/min/A
Cathode oxygen = 60 ml/min + 8 ml/min/A
Backpressure of 30 psi was maintained on the cell during analysis. Potentials depicted were not corrected for iR drop.

DESCRIPTION OF THE INVENTION

Before the present compounds, compositions, articles, devices, and/or methods are disclosed and described, it is to be understood that this invention is not limited to specific synthetic methods; specific methods may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an oxidizing agent" includes mixtures of oxidizing agents, reference to "a reducing agent" includes mixtures of two or more such reducing agents, and the like.

Ranges may be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly,
when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

References in the specification and concluding claims to parts by weight, of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

“Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

By the term “effective amount” of a composition or property as provided herein is meant such amount as is capable of performing the function of the composition or property for which an effective amount is expressed. As will be pointed out below, the exact amount required will vary from process to process, depending on recognized variables such as the composition employed and the processing conditions observed. Thus, it is not possible to specify an exact “effective amount.” However, an appropriate effective amount may be determined by one of ordinary skill in the art using only routine experimentation.

“Fuel cell” (FC) as used herein is an electrochemical device that converts chemical energy into electrical energy without combustion. Various types of fuel cells include solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC), PEM, and direct methanol (DMFC) fuel cells.
A "proton exchange membrane" (PEM), is also known or referred to as polymer electrolyte membrane, solid polymer membrane (SPM), or solid polymer electrolyte (SPE) in the fuel cell art. A PEMFC is a type of fuel cell that utilizes a polymer electrolyte membrane to carry protons between two catalytic electrode layers, thus generating electrical current. A PEM typically operates at temperatures up to 100 °C.

"Membrane electrode assembly" (MEA) is a term used for an assembly which normally comprises a polymer membrane with affixed/adjacent electrode layers. In some cases the MEA may also include gas diffusion layer/materials.

"Metal" as used herein can be, e.g., a precious metal, noble metal, platinum group metals, platinum, alloys and oxides of same, and compositions that include transition metals and oxides of same. As used herein, it is a “metal” that acts as a catalyst for the reactions occurring in the fuel cell. The metal may be tolerant of CO contaminants and may also be used in direct methanol fuel cells.

"Ionomer," is an ionically conductive polymer (e.g., Nafion®). An ionomer is also frequently used in the electrode layer to improve ionic conductivity.

"Membrane," can be known as polymer electrolyte membrane, solid polymer electrolyte, proton exchange membrane, separator, or polymer membrane. The "membrane" is an ionically conductive, dielectric material against which catalytic electrodes are placed or affixed. Typically currently in the art, the membrane most frequently used is a perfluorosulfonated polymer (e.g., Nafion®), which can be obtained in varying thicknesses, equivalent weights, etc.

"Electrolyte" as used herein is a nonmetallic electric conductor in which current is carried by the movement of ions or a substance that when dissolved in a suitable solvent becomes an ionic conductor. The polymer membrane of a fuel cell is the electrolyte.

"Electrocatalyst," also referred to as a "catalyst," is a metal (as defined above) which is catalytic for fuel cell reactions, typically supported on a catalyst support (defined below).

"Supported catalyst" is a metal (as defined above) dispersed on a support.
“Catalyst support” is a material upon which metal (as defined above) is dispersed, typically conductive (e.g., carbon black, conducting polymer, or modified carbon black).

“Electrode,” as used herein, is the layer of supported electrocatalyst in contact with and/or affixed to a membrane. The electrode may include ionomer and other materials in addition to the electrocatalyst.

“Oxygen reduction reaction,” also known as ORR, cathode reaction, or cathodic process, is a reaction in which oxygen gas is reduced in the presence of protons, producing water.

“Hydrogen oxidation reaction” is also known as HOR, anode reaction, or anodic process. This is a reaction in which hydrogen gas is converted into protons and electrons.

“Protons,” sometimes referred to in a the fuel cell context as $H^+$, hydrogen ions, or positive ions, are a positively charged portion of hydrogen atom which results from reaction over catalyst material.

“Anode” is the electrode where fuel oxidation reaction occurs.

“Cathode” is the electrode where oxidant reduction reaction occurs.

“Gas diffusion layer,” or GDL or porous backing layer, is a layer adjacent to the electrodes which aides in diffusion of gaseous reactants across the electrode surface; it is typically a carbon cloth or carbon-based/carbon-containing paper (e.g., one manufactured by Toray). The GDL should be electrically conductive to carry electrons through an external circuit.

“Current collector” is the portion of a fuel cell adjacent to the GDL through which electrons pass to an external circuit; it may also contain channels or paths (flow field) to assist in gas distribution and is typically made of graphite or conductive composites.

“Flow field” is the scheme for distributing gaseous reactants across the electrode. A flow field may be part of a current collector and/or a GDL.

“Insulator,” or dielectric, is a material which is not electrically conductive.
“Electrical conductivity,” or electronic conductivity, is the ability of a material to conduct electrons.

“Protonic conductivity” or ionic conductivity (IC), is the ability of a material to conduct ions or protons.

“Platinization,” or more generically, “metallization,” is a process of depositing or precipitating metal (as defined above) onto the surface of a catalyst support. Specifically, platinization is a process of depositing or precipitating platinum (Pt) onto the surface of a catalyst support.

“Carbon black” is a conductive acinoform carbon utilized, for example, as a catalyst support (defined above).

“Porosity,” or permeability, can be used to refer to porosity of carbon black (i.e., difference in NSA and STSA surface area measurements), or to macroscopic porosity of an electrode structure (i.e., related to ability of diffusion of gaseous reactants through an electrode layer).

“Carbonaceous” refers to a solid material comprised substantially of elemental carbon. “Carbonaceous material” is intended to include, without limitation, i) carbonaceous compounds having a single definable structure; or ii) aggregates of carbonaceous particles, wherein the aggregate does not necessarily have a unitary, repeating, and/or definable structure or degree of aggregation.

“Particulate” means a material of separate particles.

“Polarization curve,” IV curve, or current-voltage curve, is the data/results from electrochemical analysis of MEAs or catalyst materials.

“X-ray diffraction” (XRD) is an analysis method for determining crystallographic properties of a material, specifically as used herein the size of dispersed metal particles.

“X-ray photoelectron spectroscopy” (XPS), or electron scanning chemical analysis (ESCA), is an analysis method for obtaining chemical state information on materials.

“CO chemisorption,” or more simply, CO, is an analysis method for determining the available surface area of a material, specifically metal particles.
As used herein, the term “alkyl” refers to a paraffinic hydrocarbon group which may be derived from an alkane by dropping one hydrogen from the formula. Non-limiting examples include C_1 - C_{12} alkane derivatives such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl. It should be understood that an alkyl substituent can be a branched or straight chain alkyl substituent.

“Sulfonate substituent” refers to a functional substituent comprising the generic formula -SO_3-. The sulfonate substituent in the present invention can further comprise M thereby creating a sulfonated substituent which has the general formula -SO_3M. M can be, e.g., hydrogen or a cationic species such as sodium, potassium, lithium, or ammonium.

As used herein, the term “flocculation” refers to the combination or aggregation of suspended or dispersed particles in such a way that they form small agglomerates.

“Surface-bonded” refers to a substituent that is substantially bonded, either covalently or ionically, primarily or only to the outer surface of the carbonaceous material. A substituent that is “surface bonded” is substantially absent from the inside, or core, of the carbonaceous material.

“Cationic species” refers to a positively charged molecular or elemental species capable of forming an ionic bond with a sulfonate substituent as defined above. Examples of cationic species include, without limitation, ammonium, the group I alkali metals, e.g., lithium, sodium, potassium, rubidium, cesium, and francium, as well as organic bases such as dimethylethanol amine (DMEA) and triethanolamine (TEA).

The present invention provides a method of sulfonating particulate carbonaceous material and the resulting composition. The sulfonated carbon serves as a unique catalyst support to increase the protonic and electronic conductivity and uniform distribution of metal particles in fuel cell supported catalysts. The sulfonated carbon also improves water management in a fuel cell environment. The present invention also provides devices comprising the composition.
COMPOSITION

The invention includes a composition comprising a sulfonated particulate carbonaceous material. The composition can further comprise a conducting polymer. The composition can further comprise a metal.

The carbonaceous material is described below. The sulfonated particulate carbonaceous material can be greater than about 0% to about 100% by weight of the composition of the present invention, for example, about 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, or 97%. The sulfonated particulate carbonaceous material can be about 1% to about 90% by weight of the composition, for example, about 2, 5, 10, 12, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 50, 52, 55, 57, 60, 62, 65, 67, 70, 72, 75, 77, 80, 82, 85, 87, or 88%. The sulfonated particulate carbonaceous material can be about 40% to about 90% by weight of the composition, for example, about 41, 44, 46, 50, 51, 54, 56, 60, 61, 64, 66, 70, 71, 74, 76, 80, 81, 84, 86, or 89%. The sulfonated particulate carbonaceous material can be about 80% by weight of the composition, for example, about 53, 54, 55, 57, 58, 60, 63, 65, 67, 68, 70, 73, 75, 77, 78, or 79%, of the present invention.

The composition can further comprise a conducting polymer. The conducting polymer is described below. The conducting polymer can be about 0% and less than about 100% by weight of the composition of the present invention, for example, about 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or 99%. The conducting polymer can be about 1% to about 50% by weight, for example, 2, 5, 7, 10, 12, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 48, or 49%. The conducting polymer can be about 20% to about 50% by weight, for example, about 22, 24, 25, 30, 35, 40, 45, 47, or 48%, of the composition of the present invention.

The composition can further comprise a metal. The metal is described below. The metal can be about 2% to about 80% of the composition, for example, about 3, 5, 7, 8, 10, 12, 13, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 50, 52, 55, 57, 60, 62, 65, 67, 70, 72, 75, or 78%. The metal can be about 2% to about 60% of the composition, for example, about 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 57%.
The metal can be about 20% to about 40% of the composition for example, about 22, 25, 30, 35, or 38%. The metal can be distributed on the surface of the composition.

**SULFONATED CARBONACEOUS MATERIAL**

The carbonaceous material can be any particulate, substantially carbonaceous material that is an electronically conductive carbon and has a "reasonably high" surface area. For example, carbon black, graphite, nanocarbons, fullerenes, fullerenic material, finely divided carbon, or mixtures thereof can be used.

**Carbon Black**

The carbonaceous material can be carbon black. The choice of carbon black in the invention is not critical. Any carbon black can be used in the invention. Carbon blacks with surface areas (nitrogen surface area, NSA) of about 200 to about 1000 m²/g, for example, about 200, 220, 240, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, or 950 m²/g can be used. Specifically, a carbon black with a surface area of 240 m²/g (NSA, ASTM D6556) can be used. It is preferred that the carbon black have fineness effective for metal dispersion. It is preferred that the carbon black have structure effective for gas diffusion.

The sulfonated carbon black can be greater than about 0% to about 100% by weight of the composition of the present invention, for example, about 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, or 97%. The sulfonated carbon black can be about 1% to about 90% by weight of the composition, for example, about 2, 5, 10, 12, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 50, 52, 55, 57, 60, 62, 65, 67, 70, 72, 75, 77, 80, 82, 85, 87, or 88%. The sulfonated carbon black can be about 40% to about 90% by weight of the composition, for example, about 41, 44, 46, 50, 51, 54, 56, 60, 61, 64, 66, 70, 71, 74, 76, 80, 81, 84, 86, or 89%. The sulfonated carbon black can be about 50% to about 80% by weight of the composition, for example, about 53, 54, 55, 57, 58, 60, 63, 65, 67, 68, 70, 73, 75, 77, 78, or 79%, of the present invention.

Those skilled in the art will appreciate that carbon black particles have physical and electrical conductivity properties which are primarily determined by the particle
and aggregate size, aggregate shape, degree of graphitic order, and surface chemistry of
the particle.

Also, the conductivity of highly crystalline or highly graphitic particles is higher
than the conductivity of more amorphous particles. Generally, any of the forms of
carbon black particles is suitable in the practice of the present invention and the
particular choice of size, structure, and degree of graphitic order depends upon the
physical and conductivity requirements desired for the carbon black.

One of skill in the art could readily choose an appropriate carbon black for a
particular application.

Carbon blacks are commercially available (e.g., Columbian Chemical Company,
Atlanta, GA).

**Other Carbonaceous Material**

The particulate carbonaceous material can be a material other than carbon black.
The choice of other carbonaceous material in the invention is not critical. Any
substantially carbonaceous material that is an electronically conductive carbon and has
a “reasonably high” surface area can be used in the invention. For example, graphite,
nanocarbons, fullerenes, fullerenic material, finely divided carbon, or mixtures thereof
can be used.

It is preferred that the carbonaceous material have fineness effective for metal
dispersion. It is preferred that the carbonaceous material have structure effective for
gas diffusion.

One of skill in the art could readily choose a carbonaceous material for a
particular application.

These carbonaceous materials are commercially available.

The sulfonated carbonaceous material can be greater than about 0% to about
100% by weight of the composition of the present invention, for example, about 2, 5,
10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, or 97%. The
sulfonated carbonaceous material can be about 1% to about 90% by weight of the
composition, for example, about 2, 5, 10, 12, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40,
42, 45, 47, 50, 52, 55, 57, 60, 62, 65, 67, 70, 72, 75, 77, 80, 82, 85, 87, or 88%. The sulfonated carbonaceous material can be about 40% to about 90% by weight of the composition, for example, about 41, 44, 46, 50, 51, 54, 56, 60, 61, 64, 66, 70, 71, 74, 76, 80, 81, 84, 86, or 89%. The sulfonated carbonaceous material can be about 50% to about 80% by weight of the composition, for example, about 53, 54, 55, 57, 58, 60, 63, 65, 67, 68, 70, 73, 75, 77, 78, or 79%, of the present invention.

The sulfonated carbonaceous material can be made by a method described below in METHOD.

The present invention provides the surface-modified carbonaceous materials that result from the methods described below. The surface-modified carbonaceous materials exhibit several improved characteristics over those previously obtained in the art.

In one embodiment, the invention provides a surface-modified carbonaceous material comprising a plurality of sulfonate substituents of the general formula $-\text{SO}_3\text{H}$ surface bonded thereto.

In an alternative embodiment, the invention provides a surface-modified carbonaceous material comprising a plurality of sulfonate substituents of the general formula $-\text{SO}_3\text{M}$, wherein M represents a cationic species as defined herein, e.g., ammonium and the group I alkali metals, such as lithium, sodium, or potassium.

In an alternative embodiment, the degree of sulfonation or presence of sulfonate substituents surface-bonded to the carbonaceous material can be measured by XPS. Accordingly, several embodiments of the sulfonated carbonaceous material of the present invention provide surface-modified carbonaceous materials that exhibit a surface atomic concentration of sulfur within the sulfonate substituents, as measured by XPS (using the Physical Electronics 5802 Multitechnique with Al Kα X-ray source), of at least about 0.25%, 0.30%, 0.35%, 0.5%, 0.8%, 1.0%, 1.3%, 1.5%, 1.7%, 1.8%, 2.0%, 3.0%, 4.0%, 4.5%, or 5.0%. In a preferred embodiment, the surface atomic concentration of sulfur is in the range of from at least about 0.25% to about 5.0%, or in the range of from about 0.30% to about 5.0%, or in the range of from about 0.35% to about 5.0% relative to the total surface atomic concentration of the surface-modified.
carbonaceous material. When practiced with an appropriate carbonaceous material and reaction conditions, the present invention will further provide a surface-modified carbonaceous material, wherein the surface atomic concentration of sulfur exceeds the above-referenced ranges and values. Therefore, the degree of surface modification and measured surface atomic concentration of sulfur will be dependent, at least in part, on the surface area of the initial carbonaceous material that is used.

For example, Figure 3 which indicates the XPS surface atomic concentration spectrum of the sulfonated carbon black composition of Example 4, the sulfur species contained within the sulfonate substituent is present in an amount of about 1.5% relative to the total surface atomic concentration of the sulfonated carbon black compound. When compared to Figure 2, which indicates the XPS surface atomic concentration spectrum of the carbon black compound prior to sulfonation, i.e., 0.2%, it is revealed that, in accordance with one embodiment, the surface atomic concentration of surface-bonded sulfur species has been enhanced by about 750%, from about 0.2% to about 1.5%.

Furthermore, specific reference to Figure 5 reveals that about 89% of the surface-bonded sulfur species measured in Figure 3 is present as a component of the surface-bonded sulfonate substituent. Therefore, the surface-modified carbon black of Example 4 has a surface atomic concentration of sulfur present within the surface-bonded sulfonate substituents of about 1.34%, i.e., 89% of the 1.5% surface atomic concentration of sulfur species measured in Figure 3.

XPS measurement can be used to indicate the degree of surface modification by measuring the surface atomic concentration of oxygen species surface-bonded to the carbonaceous material before and after the sulfonation reaction.

For example, with specific reference again to Figure 3, the surface atomic concentration of oxygen present within the sulfonated carbon composition of Example 4 is about 8.3%. This compares to an initial oxygen concentration of 1.9% prior to sulfonation, as indicated by Figure 2. Reference to Figure 4 indicates that about 61.8% of the surface-bonded oxygen species are present as a component of the surface-bonded sulfonate substituents. Therefore, the surface-modified carbon black of Example 4 has
a surface atomic concentration of oxygen present within the surface-bonded sulfonate substituents of about 5.13%, i.e., 61.8% of the 8.3% surface atomic concentration of oxygen species measured in Figure 3.

An XPS measurement can also be utilized to indicate the degree of surface modification by measuring the surface atomic concentration of the entire sulfonate substituent, e.g., -SO₂M, wherein M is hydrogen or a cationic species as defined herein. The surface-modified carbonaceous materials of the present invention preferably exhibit a surface atomic concentration of the sulfonate substituent, when measured by XPS, in the range of from about 0.25% to about 5.0%, including values of at least about 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, and 4.5%.

As previously described, the carbonaceous materials can be any carbonaceous material, especially provided it contains sufficient C-H edge sites capable of interacting with the organic sulfite intermediate under conditions effective to provide a desired surface-modified carbonaceous material.

Specific examples of suitable carbonaceous materials are disclosed above.

Among the advantages of the present invention, the surface-modified carbonaceous materials of the present invention exhibit improved protonic and electronic conductivity and water management when used in fuel cells.

CONDUCTING POLYMER

The composition may further comprise a conductive material. The conductive material is any conductive material which is effective for the discussed purposes of the invention. Specifically, the conductive material can be a conducting polymer. The conducting polymer can be any organic polymer capable of electronic conductivity, for example, attributable to extended conjugated/delocalized multiple bonds and containing unshared electron pairs as provided by the presence of hetero atoms.

For example, polyaniline, polypyrrole, polythiophene, polyfuran, poly(p-phenylene-oxide), poly(p-phenylene-sulfide), substituted conducting polymers, or mixtures thereof can be used. Specifically, the conducting polymer can include polyaniline, polypyrrole, polyfuran, polythiophene, or mixtures thereof. Mixtures of
these polymers can include physical mixtures as well as copolymers of the monomers of the respective polymers. As used herein, reference to a polymer also covers a copolymer. More specifically, the conducting polymer can comprise polyaniline or polypyrrole.

The conducting polymer can be, for example, coated on, mixed with, or grafted to the sulfonated particulate carbonaceous material surface. If grafted, the polymer can be grafted to the sulfonated carbonaceous material in a process such as oxidative polymerization. A method for oxidative polymerization is described below and in co-pending applications “Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications” and “Sulfonated Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications,” filed May 23, 2003.

The presence of polymers in a final composition can be supported by XPS results and by the observed physical properties (e.g., ability to press films from the composition).

One of skill in the art could readily choose a conductive material (e.g., conducting polymer) for a particular application. Conducting polymers are commercially available and are readily prepared by a person of ordinary skill in the art.

The conducting polymer can contain hetero atoms. The hetero atoms can be N, S, and O, for example. The amount of hetero atoms in weight % of the resulting polymer is the same weight % as the hetero atoms in the monomer(s) used for the polymer (e.g., 15% N for aniline/polyaniline and 21% N for pyrrole/polypyrrole). The location of the hetero atoms in the conducting polymer also depends on the corresponding monomer(s).

One of skill in the art could readily choose which hetero atoms to have in a particular conducting polymer for a particular application. Conducting polymers with hetero atoms are commercially available and are readily prepared by a person of ordinary skill in the art.

A conducting polymer can be coated onto the sulfonated carbonaceous material surface, for example, by sufficiently mixing the sulfonated carbonaceous material and a conducting polymer warmed to the point it will coat the carbonaceous material.
The conducting polymer, e.g., with hetero atoms, can be grafted onto the carbon surface, for example, thereby increasing the electrical conductivity of the sulfonated carbonaceous material and the stability of the hybrid (i.e., polymer + sulfonated carbon) material is expected to be enhanced. The polymer grafting process also reduces the porosity of the sulfonated carbon. The grafting process is described below and in co-pending applications “Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications” and “Sulfonated Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications,” filed May 23, 2003.

Hetero atom containing conductive polymer-grafted sulfonated carbon material also shows hydrophilic character and thereby enhances the humidification process when used in a fuel cell application, for example. Also, the higher conductivity of these polymers facilitates the electron transfer process.

The conducting polymer can be about 0% and less than about 100% by weight of the composition of the present invention, for example, about 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or 99%. The conducting polymer can be about 1% to about 50% by weight, for example, 2, 5, 7, 10, 12, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 48, or 49%. The conducting polymer can be about 20% to about 50% by weight, for example, about 22, 24, 25, 30, 35, 40, 45, 47, or 48%, of the composition of the present invention.

A grafted conducting polymer (e.g., with hetero atoms) grafted on sulfonated carbonaceous material behaves differently, when used as a catalyst support, than the carbonaceous material alone or the conducting polymer alone.

**CATALYST SUPPORT**

A composition of the present invention can be utilized as a catalyst support. A catalyst support of the present invention comprises a sulfonated particulate carbonaceous material. The sulfonated carbonaceous material is described above.

A catalyst support can further comprise a conductive material (e.g., a conducting polymer containing hetero atoms). The conductive material can be coated on the...
sulfonated particulate carbonaceous material or grafted to the sulfonated particulate carbonaceous material, thus forming a single material.

A method for making the catalyst support is described below.

Example 6 below demonstrates the increase in protonic and electronic conductivity for a catalyst support of the present invention over non-sulfonated carbon.

METAL/CATALYST

A composition of the present invention can further comprise a metal. The metal can be, for example, platinum, iridium, osmium, rhenium, ruthenium, rhodium, palladium, vanadium, chromium, or a mixture thereof, or an alloy thereof. Specifically, the metal can be platinum.

As defined above, the metal can also be alloys or oxides of metals effective as catalysts.

It is desired that the form and/or size of the metal provide the highest surface area of the metal possible per unit mass. It is desired that the size of the metal particles be kept as small as possible to achieve this end. Generally, in the art, metal particles end up as approximately 2 to about 6 nm during use in fuel cells due to sintering. A size less than about 2 nm can provide better performance. Atomic platinum, for example, would be ideal and found in groups of about 3 atoms.

The amount of metal can be any amount. The amount of metal can be an effective catalytic amount. One of skill in the art can determine an amount effective for the desired performance.

The metal can be about 2% to about 80% of the composition, for example, about 3, 5, 7, 8, 10, 12, 13, 15, 17, 20, 22, 25, 27, 30, 32, 35, 37, 40, 42, 45, 47, 50, 52, 55, 57, 60, 62, 65, 67, 70, 72, 75, or 78%. The metal can be about 2% to about 60% of the composition, for example, about 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 57%. The metal can be about 20% to about 40% of the composition for example, about 22, 25, 30, 35, or 38%. The metal can be uniformly distributed on the composition, e.g., on the surface of the composition or in/on the conducting polymer of the composition.
One of skill in the art could readily choose a metal to use in the composition for a particular application. Metals are commercially available.

**SUPPORTED CATALYST/ELECTRODE**

The catalyst support above can further comprise a metal. This resulting composition can be a supported catalyst (or electrode), such as in a fuel cell.

The catalyst support and metal are described above. The metal can be uniformly distributed on and/or in the catalyst support.

The supported catalyst can be made by methods described below. For example, the supported catalyst can be made by sulfonating a particulate carbonaceous material and then metallizing the sulfonated particulate carbonaceous material. Alternatively, a particulate carbonaceous material can be metallized and then sulfonated. Further, a conducting polymer can be formed and grafted to a sulfonated carbonaceous material (e.g., carbon black) by oxidative polymerization of the monomer of the conducting polymer in the presence of the sulfonated carbonaceous material and then subsequently metallized (e.g., platinized). Still further, a conducting polymer can be coated on a carbonaceous material and the composition subsequently metallized.

The supported catalyst can be used in various applications requiring such a supported catalyst. One example of such an application is in a fuel cell, specifically as an electrode in a fuel cell.

Factors such as surface area and conductivity of the supported catalyst have historically been viewed as important. Relatively little research has been undertaken until the present invention to understand the role of and optimize the carbon support portion.

In the present invention, the sulfonated particulate carbonaceous material (e.g., carbon black) aids the uniform dispersion of metal such as by anchoring the metal to the sulfur atoms present on the black. Also, the anchoring groups facilitate prevention of agglomeration and sintering of platinum (Pt) (or other metal) particles.
The current standard in the industry for carbon-supported catalysts in fuel cells is the Johnson Matthey HiSPEC™ series typically loaded with about 10-40% or 10-60% platinum.

5 DEVICE

The invention includes various devices.

ELECTRODE

An electrode of the present invention is described above. An electrode of the invention can serve as either an anode, a cathode, or both.

MEMBRANE ELECTRODE ASSEMBLY (MEA)

The combination of anode/membrane/cathode (electrode/electrolyte/electrode) in a fuel cell is referred to as the membrane/electrode assembly (MEA). The evolution of MEA in PEM fuel cells has passed through several generations. The original membrane/electrode assemblies were constructed in the 1960s for the Gemini space program and used 4 mg Pt/cm² of membrane area, which generated about 0.5 amperes per mg Pt. Current technology varies with the manufacturer, but total Pt loading has decreased from the original 4 mg/cm² to about 0.5 mg/cm². Laboratory research now uses Pt loadings of 0.15 mg/cm² which are able to generate about 15 amperes per mg Pt.

Membrane/electrode assembly construction varies greatly, but the following is one of the typical procedures. The supported catalyst/electrode material is first prepared in liquid “ink” form by thoroughly mixing together appropriate amounts of supported catalyst (powder of metal, e.g., Pt, dispersed on carbon) and a solution of the membrane material (ionomer) dissolved in a solvent, e.g., alcohols. Once the “ink” is prepared, it is applied to the surface of the solid membrane, e.g., Nafion®, in a number of different ways. The simplest method involves painting the catalyst “ink” directly onto a dry, solid piece of membrane. The wet supported catalyst layer and the membrane are heated until the catalyst layer is dry. The membrane is then turned over...
and the procedure is repeated on the other side. Supported catalyst layers are then on both sides of the membrane. The dry membrane/electrode assembly is next rehydrated by immersing in dilute acid solution to also ensure that the membrane is in the H⁺ form needed for fuel cell operation. The final step is the thorough rinsing in distilled water. The membrane/electrode assembly is then ready for insertion into the fuel cell hardware.

The membrane/electrode assembly can have a total thickness of about 200 μm, for example, and conventionally generate more than 0.5 an ampere of current for every square cm of membrane/electrode assembly at a voltage between the cathode and anode of 0.7 V, when encased within well-engineered components.

**Supported Catalyst/Electrode**

The supported catalyst/electrode of the present invention is described above in SUPPORTED CATALYST/ELECTRODE. The supported catalyst/electrode can be applied to the membrane of the MEA which is described below. For example, the supported catalyst of the present invention can be added to a solvent and “painted” onto the membrane. One of skill in the art could easily determine methods for applying the supported catalyst to the membrane.

**Transfer Membrane/Electrolyte**

The PEM carries the necessary protons from the anode to the cathode while keeping the gases safely separate.

The thickness of the membrane in a membrane/electrode assembly can vary with the type of membrane. The thickness of the supported catalyst layers depends on how much metal is used in each electrode. For example, for supported catalyst layers containing about 0.15 mg Pt/cm², the thickness of the supported catalyst layer can be close to 10 μm. The thickness of the supported catalyst layer can be, for example, about 0.1 to about 50 μm, more specifically on the order of about 20 to about 30 μm. Thicknesses above 50 μm appear to increase the mass transfer problems too much to be
effective. An appropriate thickness of supported catalyst can be determined by one of skill in the art.

The membrane of the MEA can be a dielectric, ionically-conductive material. It is desired that the membrane be sufficiently durable to withstand conditions within a fuel cell. An appropriate membrane can be determined by one of skill in the art.

The membrane of the MEA can be an ionomer, specifically a perfluorosulfonate ionomer. More specifically, the membrane can be a poly(tetrafluoroethylene)-based cation exchange ionomer such as Nafion® (DuPont, Wilmington, DE; Fayetteville, NC). Nafion® is a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups. Its general chemical structure can be seen below, where X is either a sulfonic or carboxylic functional group and M is either a metal cation in the neutralized form or an H⁺ in the acid form.

\[
\begin{align*}
(CF_2CF_2)_{x} & \quad (CF_2CF_2)_y \\
\text{C} & \\
\text{CF}_3 & \\
F-C & \text{CF}_2-CF_2-X \text{M}^+ \\
\text{CF}_3 & 
\end{align*}
\]

The MEA comprises an anode, a cathode, and a membrane.

The anode can be an electrode of the present invention. The electrode should be electrically conducting, porous enough to let reactants diffuse to the metal, and able to carry protons to the membrane. The cathode can also be an electrode of the present invention.

Figure 8 demonstrates the functionality of MEA of the present invention.

**FUEL CELL**

A fuel cell comprises an MEA, fuel feed, and oxidant feed. A fuel cell typically comprises an MEA, backing layers, and flow fields/current collectors, fuel feed, and oxidant feed.
An MEA is described above.

The hardware of the fuel cell can include backing layers. The layers are generally one next to the anode and another next to the cathode and made of a porous carbon paper or carbon cloth. They layers are made of a material that can conduct the electrons exiting the anode and entering the cathode.

Backing layers are commercially available or can be prepared by one of skill in the art. Appropriate backing layers can be chosen by one of skill in the art.

The hardware of the fuel cell can include flow fields and current collectors. Pressed against the outer surface of each backing layer can be a piece of hardware, called a bipolar plate, which often serves the dual role of flow field and current collector. The plates are generally made of a lightweight, strong, gas impermeable, electron-conducting material; graphite, metals, or composite plates are commonly used.

The bipolar plates can provide a gas flow field such as channels machined into the plate. The channels carry the reactant gas from the point at which it enters the fuel cell to the point at which the gas exits. The pattern, width, and depth have a large impact on the effectiveness of the distribution of the gases evenly across the active area of the membrane/electrode assembly. The flow field also affects water supply to the membrane and water removal from the cathode.

The bipolar plates can also serve as current collectors. Electrons produced by the oxidation of hydrogen can be conducted through the anode, through the backing layer and through the plate before they can exit the cell, travel through an external circuit, and re-enter the cell at the cathode plate.

Flow fields and current collectors are commercially available or can be prepared by one of skill in the art. Appropriate flow fields and current collectors can be chosen by one of skill in the art.
The devices and methods of the present invention are useful in preparing and using fuel cells. Other applications can include electrodes and bipolar plates (or current collector plates) in energy conversion devices (such as fuel cells, batteries, or capacitors) when the current modified carbon products are used in combination with other materials.

**METHOD**

**SULFONATED CARBONACEOUS MATERIAL**

The particulate carbonaceous material is described above in detail under the COMPOSITION section. The sulfonated particulate carbonaceous material is described above in the COMPOSITION section.

The particulate carbonaceous material is sulfonated by a method comprising sulfonating a particulate carbonaceous material. See, for example, co-pending application, Ser. No. 10/229,933, filed August 28, 2002, hereby incorporated by reference for its teachings regarding sulfonated carbonaceous compositions and methods of making them. The particulate carbonaceous material can be sulfonated by reacting the particulate carbonaceous material with an organic sulfite intermediate of the generic formula:

\[
\text{R} \quad \begin{array}{c}
\text{O} \\ \text{O} \\ \text{SO}_3\text{H}
\end{array}
\]

The method can comprise reacting an anhydride of the generic formula:

\[
\text{R} \quad \begin{array}{c}
\text{O} \\ \text{O} \\ \text{O} \\ \text{O}
\end{array}
\]

with a sulfuric acid under conditions effective to produce the organic sulfite intermediate which is then reacted with the particulate carbonaceous material.

If desired, the method of the present invention can be performed by simultaneously reacting the particulate carbonaceous material to be surface modified...
with: (1) the anhydride; and (2) sulfuric acid, in a single reaction under conditions effective to provide the organic sulfite intermediate in the presence of the particulate carbonaceous material.

Examples of sulfonation and diazotization schemes are shown below.

Sulfonation

\[(R-CO)\textsubscript{2}O + H\textsubscript{2}SO\textsubscript{4} \rightarrow R-COO\textsubscript{3}H + R-COOH\]

\[\text{CB} + R-COO-SO\textsubscript{3}H \rightarrow \text{CB} + R-COOH\]

\[R = H, \text{C}_1 - \text{C}_{12} \text{ alkyl}\]

Scheme I
Diazotization

As indicated above, the present invention relates to the incorporation of sulfonate derivatives, which are hydrophilic functional groups, onto the surface of various particulate carbonaceous materials. The invention provides a method for the preparation of surface-modified carbonaceous materials.

The method can comprise reacting an anhydride of the generic formula:

\[
\text{RCO}_2\text{O}_2\text{RCO}_2
\]

with a sulfuric acid under conditions effective to provide an organic sulfite intermediate of the generic formula:

\[
\text{RCSO}_2\text{H}
\]
A plurality of C-H surface sites present on a carbonaceous material to be surface modified can then be reacted with the resulting organic sulfite intermediate produced above, under conditions effective to produce a surface-modified carbonaceous material having a plurality of sulfonate substituents, -SO$_3$H, surface-bonded thereto.

R is aliphatic, preferably selected from the C1- C12 alkyl substituents. Additionally, it should be understood that these alkyl substituents can be straight chain or branched. Suitable examples include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, and the like. In a preferred embodiment, R represents a methyl substituent such that the anhydride employed in the process is an acetic anhydride. It will be appreciated by one of ordinary skill in the art that such anhydrides, e.g., acetic anhydride, are well-known and commercially available and, therefore, need not be described in detail.

The anhydride serves not only as a reactant for the formation of the sulfite intermediate, but can also serve as the solvent medium in which the reaction takes place. Therefore, the anhydride is preferably present in excess relative to the weight amount of both the carbonaceous material and the acid. It will be appreciated by one of ordinary skill that any excess amount will be suitable for carrying out the desired reaction, however, in a preferred embodiment, the weight ratio of anhydride relative to the carbonaceous material is greater than about 2:1. Likewise, the weight ratio of anhydride relative to the acid is preferably greater than about 5:1.

As indicated above, the preferred acid for use in the present invention is a sulfuric acid capable of reacting with a suitable anhydride in order to form an organic sulfite intermediate. Sulfuric acid having a wide variety of concentration strengths can be employed in the process. It will be appreciated by one of ordinary skill in the art that the particular concentration desired will ultimately be dependent upon the particular anhydride and/or carbonaceous material utilized. In a preferred embodiment, the sulfuric acid is a commercially available sulfuric acid having a concentration in the range of from about 90% to about 99%, for example, about 91, 92, 93, 94, 95, 96, or 97%. In a more preferred embodiment, the sulfuric acid concentration is in the range of
from approximately 93% to about 97%, for example, about 94, 94.5, 95, 95.5, 96, or 96.5%. In a most preferred embodiment, the sulfuric acid is about 95% concentrated sulfuric acid.

A varying amount of acid relative to the anhydride and/or carbonaceous material can be used in the method of the present invention. In a preferred embodiment, the weight ratio of acid relative to the anhydride is preferably not greater than about 1:5. Likewise, the weight ratio of acid relative to the carbonaceous material is preferably in the range of from about 1:2 to about 1:3, including such ratios as about 1:2.5.

As indicated above, the method of the present invention can be used with a variety of carbonaceous materials. Any carbonaceous material can be used provided there are sufficient C-H edge sites capable of interacting with the organic sulfite intermediate under conditions effective to provide a desired surface-modified carbonaceous material.

Specific examples of suitable carbonaceous materials are described above. If desired, the surface-modified carbonaceous material containing a plurality of surface-bonded sulfonate substituents, e.g., -SO_3M and/or -SO_3H moieties, wherein M is defined as above, can be washed with distilled water, filtered, and/or dried in order to obtain substantially purified and/or isolated surface-modified product.

In an alternative embodiment, the organic sulfite intermediate that reacts with the carbonaceous material can be formed in situ the method as described above can be performed in a single reaction. Accordingly, if desired, the method of the present invention can be performed by simultaneously reacting a carbonaceous material to be surface modified with: (1) an anhydride as defined above; and (2) sulfuric acid as defined above, in a single reaction under conditions effective to provide an organic sulfite intermediate of the generic formula:
in situ and to subsequently provide a surface-modified carbonaceous material comprising a plurality of sulfonate substituents, e.g., -SO$_3$H moieties, surface-bonded thereto.

It will be appreciated by one of ordinary skill in the art that the optimum reaction conditions for the in situ formation of the organic sulfite and subsequent reaction with the carbonaceous material will, of course, vary depending on the particular anhydride, strength of the sulfuric acid, and/or the particular carbonaceous material selected to be surface modified. Determining such optimum conditions would be readily achievable by one of ordinary skill in the art or otherwise can be obtained through no more than routine experimentation.

In a preferred embodiment, wherein the anhydride is acetic anhydride and the carbonaceous material is a carbon black, preferred reaction conditions comprise heating the reactants to a temperature in the range of from about 60°C to about 80°C for at least about 2 hours. In still a more preferred embodiment, the reaction components are heated to a temperature of about 70°C for at least about 2 hours. The reaction can be done at ambient pressure and a minimum temperature commensurate with a reasonable reaction rate and a maximum temperature where undesirable levels of undesirable by-products are made.

Additionally, the method comprising the in situ formation of the organic sulfite intermediate and subsequent reaction with a carbonaceous material to provide a surface-modified carbonaceous material can further comprise washing with distilled water, filtering, and/or drying the desired surface-modified carbonaceous material in order to obtain substantially purified and/or isolated product.

The methods set forth above advantageously arrive at the desired surface-modified carbonaceous materials in relatively high yields while substantially minimizing the production of undesired oxidative and tarry byproducts typically encountered in the art, such as those discussed in U.S. Patent No. 3,442,679 to Rivin, et al.
CONDUCTING POLYMER

A conducting polymer can be coated on the sulfonated carbonaceous material, mixed with the sulfonated carbonaceous material, or grafted on the sulfonated carbonaceous material.

The conducting polymer, corresponding monomer, and any hetero atoms are described above in detail under the COMPOSITION section.

The conducting polymer can be coated on the sulfonated carbonaceous material by various methods known to one of skill in the art.

The conducting polymer can be mixed with the sulfonated carbonaceous material by various methods known to one of skill in the art.

The conducting polymer can be grafted on the sulfonated carbonaceous material by oxidative polymerization of a corresponding monomer of the conducting polymer in the presence of the sulfonated carbonaceous material. See, for example, co-pending applications entitled “Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications” and “Sulfonated Conducting Polymer-Grafted Carbon Material For Fuel Cell Applications,” filed May 23, 2003.

ADDITION OF METAL/METALLIZING

Metal can be added to the sulfonated carbonaceous material, or a composition comprising the sulfonated carbonaceous material, subsequent to its preparation. The metal can be added by metallizing. For example, if the metal is platinum, one method of platinization is described below.

Alternatively, the metal can be added to the carbonaceous material prior to sulfonation of the particulate carbonaceous material.

One of skill in the art would be able to determine choice of metallizing method for a particular application. Various metallizing agents are known in the art. These metallizing agents are readily commercially available or readily synthesized by methods known to one of skill in the art.

The amount of metallizing agent is readily determined by one of skill in the art for a desired application.
**Platinizing**

A platinizing agent can be used to add platinum to the sulfonated carbonaceous material (or non-sulfonated carbonaceous material or conducting polymer- sulfonated carbonaceous material). Various platinizing agents are known in the art. These platinizing agents are readily commercially available or readily synthesized by methods known to one of skill in the art.

Choice of appropriate platinizing agent is readily determined by one of skill in the art for the desired application. Generally, anything containing the desired metal can be used, for example, any salt or organo-compound containing the metal.

Examples of platinizing agents that can be used include platinum salts: chloroplatinic acid, platinum nitrate, platinum halides, platinum cyanide, platinum sulfide, organoplatinum salts, or a combination thereof.

The amount of platinizing agent is readily determined by one of skill in the art for a desired application.

**Reducing Agent**

A reducing agent can be used to reduce the metal to metallic form. Various reducing agents are known in the art. These reducing agents are readily commercially available or readily synthesized by methods known to one of skill in the art.

The amount of reducing agent for the current method is always in excess of stoichiometric.

Choice of appropriate reducing agent is readily determined by one of skill in the art for the desired application.

Examples of reducing agents that can be used include formaldehyde, formic acid, sodium borohydride, hydrogen, hydrazine, hydroxyl amine, or a combination of reducing agents.
EXAMPLES

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices, and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

Example 1

Direct sulfonation of carbon black

This example illustrates direct sulfonation of carbon black using concentrated sulfuric acid with aliphatic anhydride.

Sulfuric acid reacts with anhydride to form organic sulfite, an intermediate, and thereby sulfonates carbon black surface as shown in Scheme I.

The method was the following

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle size (nm)</td>
<td>21</td>
</tr>
<tr>
<td>NSA surface area (m²/g)</td>
<td>242</td>
</tr>
</tbody>
</table>

CDX-975 “typical” properties
The reaction mixture was heated to ~70°C for 4 hours. It was then cooled and filtered by washing with deionized (DI) water.

The carbon cake was dried at 110°C for 4 hrs. and pulverized. The resultant carbon powder contains sulfonic acid groups (SO₃H) attached to the carbon black surface.

### Example 2

**Substitution of sulfonic groups on carbon black**

This example illustrates substitution of benzene sulfonic acid groups to carbon black by using sulfanilic acid and sodium nitrite in the presence of mineral acid.

The diazotization reaction is shown in Scheme II.

The method was the following:

- 10 g p-sulfanilic acid (Aldrich) was dissolved in 200 ml hot water (~80°C).
- 20 g CDX-975 carbon black powder (NSA surface area 240 m²/g and oil absorption of 170 ml/100 g) (Columbian Chemical Company, Atlanta, GA) was added to the above solution with constant stirring, followed by 5 ml concentrated nitric acid.
A solution containing 5 g of NaNO₂ in 25 ml of deionized water was added to the carbon black slurry. The carbon black slurry was stirred, maintaining the temperature at ~70°C until the bubbling stopped and cooled to room temperature.

The carbon black slurry was filtered, washed with DI water, dried at 110°C for 4 hrs., and pulverized. The resultant carbon powder contains benzene sulfanic acid (-C₆H₅-SO₃H) groups attached to the carbon black surface.

**Example 3**

**Platinization of sulfonated carbon black**

This example illustrates the platinization of sulfonated carbon black using chloroplatinic acid and formaldehyde.

4 g of sulfonated carbon black (made in Example 1) was dispersed in 300 ml DI water.

200 ml of 1% solution of chloroplatinic acid was added dropwise for a period of 1 hr. with continuous stirring. The pH of the slurry was adjusted to 8-11 by using 1 M sodium bicarbonate solution.

200 ml of 3% solution of formaldehyde was added for a period of 1 hr., and the temperature was kept at 70°C for 1 hr.

The slurry was cooled to room temperature and was filtered by washing with DI water. The carbon cake was dried at 110°C for 4 hrs. and pulverized. The resultant catalyst contained ~20% platinum with sulfonic acid (SO₃H) groups attached to the carbon surface.

**Example 4**

**Direct sulfonation of catalyst**

This method illustrates direct sulfonation of catalyst using concentrated sulfuric acid with aliphatic anhydride.
5g of catalyst powder (20% platinum supported on carbon black with surface area of 240 m²/g and oil absorption of 170 ml/100g) was added to a flask containing a 50 ml of acetic anhydride with continuous stirring.

5 ml of concentrated sulfuric acid (95.7%) was added to the slurry. The reaction mixture was heated ~70°C for 4hr, cooled and filtered by washing with deionized water. The cake was dried at 110°C for 4 h. and pulverized.

The resultant catalyst powder has sulfanic acid (SO₃H) groups attached to the carbon black surface.

Example 5
Substitution of benzene sulfonic acid groups to catalyst

This example describes substitution of benzene sulfonic acid groups to catalyst by using sulfanilic acid and sodium nitrite in the presence of sulfuric acid.

1g of p-sulfanilic acid was dissolved in 50 ml hot water (~70°C). 5 g of catalyst powder (20% platinum supported on carbon black with surface area of 240 m²/g and oil absorption of 170 ml/100g) was added to the above solution with constant stirring followed by 1 ml of concentrated sulfuric acid.

A solution containing 0.7 g of NaNO₂ in 15 ml of deionized water was added to the slurry. The slurry was stirred maintaining the temperature at ~70°C until the bubbling stopped and cooled to room temperature.

The carbon black slurry was filtered, washed with deionized water, dried at 110°C for 4 h. and pulverized.

The resultant catalyst powder has benzene sulfanic acid (CB-C₆H₅-SO₃H) groups attached to the carbon black surface.
Example 6

Comparative Electronic Conductivity Measurements

Electronic conductivity was measured on pressed pellets of carbon black material using a four probe resistivity meter (Loresta AP Resistivity, MCP400, Mitsubishi Petrochemical Company, Tokyo, Japan). ASTM D257 was used.

The pellets of carbon black material included non-sulfonated CDX-975 carbon black and sulfonated CDX-975 carbon black from Example 4 above. Each carbon black was bound together with Nafion® in order to form the pellets.

Protonic conductivity measurements were obtained based on the technique developed by Saab et al. (Saab et al., J. Electrochem. Soc. 150, A214 (2003) and Saab et al., J. Electrochem. Soc. 149, A1514 (2002)). Thin films of each material were coated onto a polycarbonate substrate. A thin film of Nafion® (1100 equiv. weight) was then affixed to the substrate adjacent to the material, contacting the edge of the material. Electrical contact was made using silver paint. Impedance measurements were obtained using a Solartron 1255B Frequency Response Analyzer, connected to a Solartron 1287 Electrochemical Interface. The samples were mixed with Nafion® in order to obtain conductivity values, as the carbon species alone does not provide sufficient protonic conductivity for the measurement technique.

The following table (Table 1) demonstrates comparative electronic and protonic conductivity of the materials listed above.

Table 1. Electronic and protonic conductivity.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Electronic Conductivity S/cm</th>
<th>Protonic Conductivity S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CDX-975</td>
<td>2.9x10^{-1}</td>
<td>2.5x10^{-3}</td>
</tr>
<tr>
<td>2 CDX-975-SO_3H</td>
<td>1.7</td>
<td>1.6x10^{-1}</td>
</tr>
</tbody>
</table>

* 10% (weight) Nafion® added as binder

Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference.
into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.
What is claimed is:

1. A device comprising
   a sulfonated particulate carbonaceous material.
2. The device of claim 1 wherein the carbonaceous material is carbon black.
3. The device of claim 1 wherein the carbonaceous material is carbon black,
   graphite, nanocarbons, fullerenes, fullerene material, finely divided carbon, or
   mixtures thereof.
4. The device of claim 1 wherein the sulfonated carbonaceous material comprises a
   plurality of sulfonate substituents of the general formula −SO₃M surface-bonded
   thereto, wherein M is hydrogen or a cationic species, and wherein the surface
   atomic concentration of sulfur present within the surface bonded SO₃M
   moieties, measured by XPS, is greater than or equal to approximately 0.25%
   relative to the total surface atomic concentration of the carbonaceous material.
5. The device of claim 4 wherein the surface atomic concentration of the sulfur is
   in the range of from about 0.25% to about 5.0%.
6. The device of claim 4 wherein the surface atomic concentration of the sulfur is
   in the range of from about 0.35% to about 5.0%.
7. The device of claim 4 wherein M is a cationic species of sodium, potassium,
   lithium, or ammonium.
8. The device of claim 1 wherein the carbonaceous material is less than about 98%
   of the composition.
9. The device of claim 1 wherein the carbonaceous material is about 50% to about
   80% of the composition.
10. The device of claim 1 further comprising a conducting polymer.
11. The device of claim 10 wherein the conducting polymer contains hetero atoms.
12. The device of claim 10 wherein the conducting polymer is polyaniline,
    polypyrrole, polyfuran, polythiophene, or mixtures thereof.
13. The device of claim 10 wherein the conducting polymer is polyaniline,
    polypyrrole, polyfuran, polythiophene, poly(p-phenylene-oxide), poly(p-
phenylene-sulfide), substituted conducting polymers, or mixtures thereof.

14. The device of claim 11 wherein the hetero atoms are N, O, and S.

15. The device of claim 11 wherein the hetero atoms are about 0.2 to about 15% of the composition according to XPS data.

16. The device of claim 10 wherein the conducting polymer is greater than about 0% and less than about 100% of the composition.

17. The device of claim 10 wherein the conducting polymer is about 2% to about 50% of the composition.

18. The device of claim 10 wherein the conducting polymer is about 20% to about 50% of the composition.

19. The device of claim 10 wherein the polymer is grafted to the particulate sulfonated carbonaceous material.

20. The device of claim 10 wherein the polymer coats the sulfonated carbonaceous material.

21. The device of claim 1 further comprising a metal.

22. The device of claim 21 wherein the metal is platinum.

23. The device of claim 21 wherein about 2% to about 80% of the composition is the metal.

24. The device of claim 21 wherein about 2% to about 60% of the composition is the metal.

25. The device of claim 21 wherein about 20% to about 40% of the composition is the metal.

26. The device of claim 21 wherein the metal is uniformly distributed on the surface of the material.

27. A method for preparing a particulate carbonaceous material with enhanced electronic and protonic conductivity comprising sulfonating a particulate carbonaceous material.

28. The method of claim 27 wherein the carbonaceous material is carbon black, graphite, nanocarbons, fullerenes, fullerenic material, finely divided carbon, or mixtures thereof.
29. The method of claim 27 wherein the carbonaceous material is carbon black.
30. The device of claim 1 further comprising an electrolyte membrane.
31. The device of claim 30 wherein the electrolyte membrane is Nafton®.
32. A fuel cell comprising an anode, a cathode, and a proton exchange membrane (PEM).
33. The fuel cell of claim 32 wherein the PEM comprises a sulfonated particulate carbonaceous material.
34. The device of claim 1 wherein the device is a fuel cell, battery, or a capacitor.
35. A method of making a fuel cell comprising
   a) producing a sulfonated particulate carbonaceous material by a method comprising
      i) contacting an anhydride of the generic formula \((R-CO)\_2O\) with sulfuric acid under conditions effective to produce an organic sulfite intermediate of the generic formula \(R-(CO)O-SO_3H\), wherein \(R\) is an aliphatic substituent;
      ii) contacting a carbonaceous material with the organic sulfite intermediate produced in a) under conditions effective to produce a surface-modified carbonaceous material comprising a plurality of sulfonate substituents of the general formula \(-SO_3H\) surface-bonded thereto;
      iii) treating the surface-modified carbonaceous material produced in b) with a neutralizing agent under conditions effective to produce a surface-modified carbonaceous material comprising a plurality of sulfonate substituents of the general formula \(-SO_3M\) surface-bonded thereto, wherein \(M\) is sodium, potassium, lithium, or ammonium;
   b) platinizing the sulfonated particulate carbonaceous material;
   c) making at least one electrode comprising the platinized sulfonated particulate carbonaceous material; and
   d) making a fuel cell comprising the at least one electrode.
36. A surface modified carbonaceous material, comprising a plurality of sulfonate substituents of the general formula \(-SO_3M\) surface bonded thereto, wherein \(M\) is
hydrogen or a cationic species, and wherein the surface atomic concentration of sulfur present within the surface-bonded SO₃M moieties, measured by XPS, is greater than or equal to about 0.25% relative to the total surface atomic concentration of the surface-treated carbonaceous material.

37. The material of claim 36 wherein the surface atomic concentration of the sulfur is in the range of from about 0.25% to about 5.0%.

38. The material of claim 36 wherein the surface atomic concentration of the sulfur is in the range of from about 0.35% to about 5.0%.

39. The material of claim 36 wherein the carbonaceous material is carbon black, graphite, finely divided carbon, activated charcoal, fullerenic carbon, or nanocarbon.

40. The material of claim 36 wherein the carbonaceous material is carbon black.

41. A process for the manufacture of a surface-modified carbonaceous material, wherein the process comprises the steps of:
   a) contacting an anhydride of the generic formula (R-CO)₂O with sulfuric acid under conditions effective to provide an organic sulfite intermediate of the generic formula R-(CO)O-SO₃H, wherein R is an aliphatic substituent; and
   b) contacting a carbonaceous material with the organic sulfite intermediate provided in step a) under conditions effective to provide a surface modified carbonaceous material comprising a plurality of surface bonded sulfonate substituents of the general formula –SO₃H.

42. The process of claim 41 wherein the carbonaceous material is carbon black, graphite, finely divided carbon, activated charcoal, fullerenic carbon or nanocarbon.

43. The process of claim 41 wherein the carbonaceous material is carbon black.

44. The process of claim 41 wherein the anhydride is acetic anhydride.

45. The process of claim 41 wherein the sulfuric acid is at least about a 95% concentrated sulfuric acid.
46. The process of claim 41 wherein steps a) and b) are performed in a single reaction by simultaneously contacting the carbonaceous material with:
   i) the anhydride of the generic formula (R-CO)₂O; and
   ii) the sulfuric acid,
under conditions effective to provide the organic sulfite intermediate of the generic formula R-(CO)O-SO₃H \textit{in situ} and to provide the surface-modified carbonaceous material comprising a plurality of surface bonded sulfonate substituents of the general formula \(-\text{SO}_3\text{H}\).

47. The process of Claim 46, wherein the conditions effective to provide the organic sulfite intermediate of the generic formula R-(CO)O-SO₃H \textit{in situ} and to provide the surface-modified carbonaceous material comprising a plurality of surface-bonded sulfonic substituents of the general formula \(-\text{SO}_3\text{H}\) comprise heating the components i) and ii) to at least approximately 70°C for at least approximately 2 hours.

48. The surface modified carbonaceous material of Claim 36, produced by a process comprising the steps of:
   a) contacting an anhydride of the generic formula (R-CO)₂O with sulfuric acid under conditions effective to provide an organic sulfite intermediate of the generic formula R-(CO)O-SO₃H, wherein R is an aliphatic substituent;
   b) contacting a carbonaceous material with the organic sulfite intermediate produced in step a) under conditions effective to provide a surface modified carbonaceous material comprising a plurality of sulfonate substituents of the general formula \(-\text{SO}_3\text{H}\) surface bonded thereto.
Figure 1B
FIGURE 2
FIGURE 3
FIGURE 5

SO$_3$ (89%)

$S^2$ (11%)

Intensity, c/s

Binding Energy, eV
FIGURE 7

Binding Energy (eV)

SO₃⁻
sulfide

c/s