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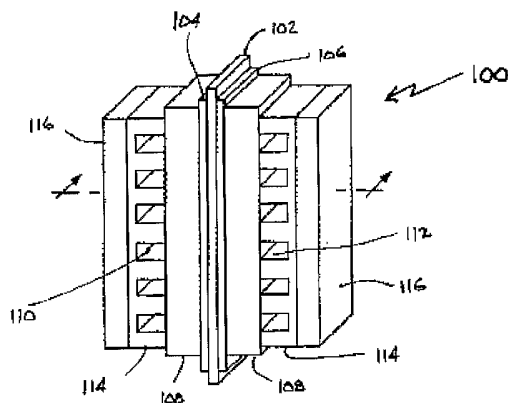
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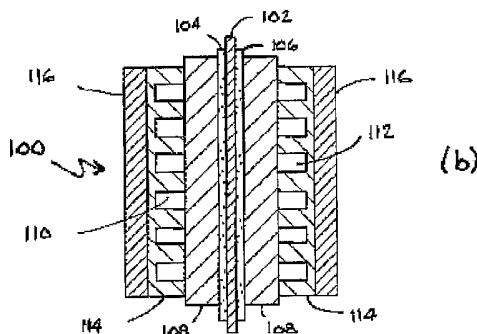
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(54) Title: MODIFIED CARBON PRODUCTS, THEIR USE IN FLUID/GAS DIFFUSION LAYERS AND SIMILAR DEVICES
AND METHODS RELATING TO THE SAME



(a)

(57) Abstract: Fuel cell compo-
nents incorporating modified carbon
products. The modified carbon
products advantageously enhance
the properties of the components
leading to more efficiency within
the fuel cell.



(b)



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MODIFIED CARBON PRODUCTS, THEIR USE IN FUEL CELLS AND SIMILAR DEVICES AND METHODS RELATING TO THE SAME

Background of the Invention

5 1. Field of the Invention

The present invention relates to the production and use of modified carbon products in fuel cell components and similar devices. Specifically, the present invention relates to proton exchange membranes, electrodes, gas and fluid diffusion layers and bipolar plates incorporating modified carbon products and methods for making such components. The modified carbon products can be used to enhance the properties of proton exchange membranes, electrode layers, gas and fluid diffusion layers or bipolar plates, particularly when such components are utilized in the membrane electrode assemblies (MEAs) of a fuel cell and/or a fuel cell stack.

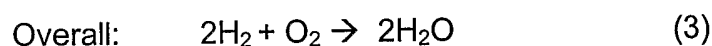
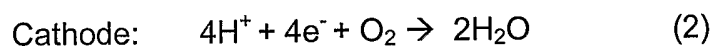
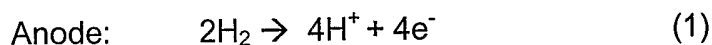
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2. Description of Related Art

Fuel cells are electrochemical devices that are capable of converting the energy of a chemical reaction into electrical energy without combustion and with virtually no pollution. Fuel cells are unlike batteries in that fuel cells convert chemical energy to electrical energy as the chemical reactants are continuously delivered to the fuel cell. As a result, fuel cells are used to produce a continuous source of electrical energy, and compete with other forms of continuous energy production such as the combustion engine, nuclear power and coal-fired power stations. Different types of fuel cells are categorized by the electrolyte used in the fuel cell. The five main types of fuel cells are alkaline, molten carbonate, phosphoric acid, solid oxide and proton exchange membrane (PEM), also known as polymer electrolyte fuel cells (PEFCs). One particularly useful fuel cell is the proton exchange membrane fuel cell (PEMFC).

A PEMFC typically includes tens to hundreds of MEAs each of which includes a cathode layer and an anode layer. One embodiment of a MEA is illustrated in Figs. 1(a) and 1(b). One embodiment of a cathode side of an MEA is also depicted in Figure 2. With references to Figures 1(a), 1(b) and 2, the anode electrocatalyst layer 104 and cathode electrocatalyst layer 106 sandwich a proton exchange membrane 102. In some instances, the combined membrane

and electrode layer is referred to as a catalyst coated membrane 103. Power is generated when a fuel (e.g., hydrogen gas) is fed into the anode 104 and oxygen (air) 106 is fed into the cathode. In a reaction typically catalyzed by a platinum-based catalyst in the catalyst layer of the anode 104, the hydrogen ionizes to form protons and electrons. The protons are transported through the proton exchange membrane 102 to a catalyst layer on the opposite side of the membrane (the cathode), where another catalyst, typically platinum or a platinum alloy, catalyzes an oxygen-reduction reaction to form water. The reactions can be written as follows:

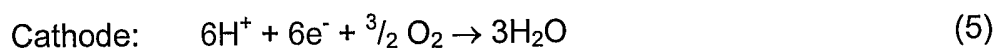
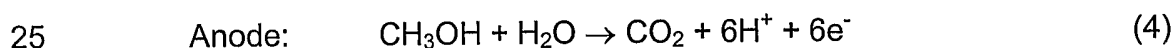


Electrons formed at the anode and cathode are routed through bipolar plates 114 connected to an electrical circuit. On either side of the anode 104 and cathode 106 are porous gas diffusion layers 108, which generally comprise a carbon support layer 107 and a microporous layer 109, that help enable the transport of reactants (H_2 and O_2 when hydrogen gas is the fuel) to the anode and the cathode. On the anode side, fuel flow channels 110 may be provided for the transport of fuel, while on the cathode side, oxidizer flow channels 112 may be provided for the transport of an oxidant. These channels may be located in the bipolar plates 114. Finally, cooling water passages 116 can be provided adjacent to or integral with the bipolar plates for cooling the MEA / fuel cell.

A particularly preferred fuel cell for portable applications, due to its compact construction, power density, efficiency and operating temperature, is a PEMFC that can utilize methanol (CH_3OH) directly without the use of a fuel reformer to convert the methanol to H_2 . This type of fuel cell is typically referred to as a direct methanol fuel cell (DMFC). DMFCs are attractive for applications that require relatively low power, because the anode reforms the methanol directly into hydrogen ions that can be delivered to the cathode through the PEM. Other liquid fuels that may also be used in a fuel cell include formic acid, formaldehyde, ethanol and ethylene glycol.

Like a PEMFC, a DMFC also is made of a plurality of membrane electrode assemblies (MEAs). A cross-sectional view of a typical MEA is illustrated in Figure 3 (not to scale). The MEA 300 comprises a PEM 302, an anode electrocatalyst layer 304, cathode electrocatalyst layer 306, fluid distribution layers 308, and bipolar plates 314. The electrocatalyst layers 304, 306 sandwich the PEM 302 and catalyze the reactions that generate the protons and electrons to power the fuel cell, as shown below. The fluid diffusion layer 308 distributes the reactants and products to and from the electrocatalyst layers 304, 306. The bipolar plates 314 are disposed between the anode and cathode of sequential MEA stacks, and comprise current collectors 317 and fuel and oxidizer flow channels, 310, 312, respectively, for directing the flow of incoming reactant fluid to the appropriate electrode. Two end plates (not shown), similar to the bipolar plates, are used to complete the fuel cell stack.

Operation of the DMFC is similar to a hydrogen-gas based PEMFC, except that methanol is supplied to the anode instead of hydrogen gas. Methanol flows through the fuel flow channels 310 of bipolar plate 314, through the fluid distribution layer 308 and to the anode electrocatalyst layer 304, where it decomposes into carbon dioxide gas, protons and electrons. Oxygen flows through the oxidizer flow channels 312 of the bipolar plate 314, through the fluid distribution layer 308, and to the cathode electrocatalyst layer, where ionized oxygen is produced. Protons from the anode pass through the PEM 302, and recombine with the electrons and ionized oxygen to form water. Carbon dioxide is produced at the anode 304 and is removed through the exhaust of the cell. The foregoing reactions can be written as follows:



There are a number of properties that are required for efficient fuel cell operation. For example, the PEM should have a high proton conductivity to enable efficient transport of protons from the anode to the cathode, be electrically insulative to prevent transport of electrons to the cathode, and act as a robust physical separator. The membrane should also be impermeable to gases. A common proton exchange material currently used is NAFION, a perfluorosulfonic

acid (PFSA) polymer available from E.I. duPont deNemours, Wilmington, DE, from which different membrane thicknesses can be formed.

One drawback to current PEMs is that they require a humid fuel to operate efficiently due to the intermittent spacing of the proton exchange materials within the membrane. Thus, water must be present to act as a bridge between such sites for proton transport. Water introduced into and/or produced at the electrodes must be removed from the fuel cell to prevent clogging of the electrode pores, a phenomenon known as "flooding".

Typical properties desired for electrode operation include high utilization of catalysts and effective mass transport. Typically, electrocatalyst materials, such as platinum (Pt) dispersed on a conductive support (e.g. carbon), are utilized in the electrode layers to catalyze the foregoing reactions. Current PEMFCs typically include platinum electrocatalysts with a total loading of about 1 milligram of platinum per square centimeter of electrode (1 mgPt/cm^2), including both the anode and cathode. At a typical cell performance of 0.42 Watts per square centimeter, about 2.4 grams of platinum per kilowatt is required (1 mgPt/cm^2 over 0.42 Watts/cm^2). In the case of liquid fuel, such as methanol, alloy catalyst such as PtRu can be used. Current DMFCs typically include PtRu electrocatalysts with a total loading of about 8 mg (Pt+Ru)/ cm^2 , which equates to about 200 grams of precious metal per kilowatt at a performance of 0.04 Watts per square centimeter.

Platinum metal is very expensive, which often equates to expensive fuel cell production costs. Reducing the amount of catalytically active material in the electrode, however, is not a suitable solution to reduce cost, because of the equivalently strong demand for improved cell performance. Moreover, excess platinum metal is often used to compensate for catalyst materials that go unutilized or are underutilized due to their remote location from gas/fluid distribution channels and/or proton conduction sites. Thus, there is a need to enhance catalyst use in the electrode to maintain performance, but at lower loading levels.

Other issues associated with increasing the performance of the electrodes include: a) prevention of active phase agglomeration and loss of catalyst active area during the operation of the fuel cell; b) locating the proton conductive sites proximal to the active catalytic sites; c) ensuring long term stability of the

electrode performance by minimizing the amount of impurities that poison the membrane and active sites; and d) enhancing porosity of the electrode for transport of reactants and products.

The gas/fluid diffusion layers, commonly referred to as gas diffusion layers (GDLs) in hydrogen gas based PEMFCs, and fluid diffusion layers in methanol fuel-based DMFCs, are used to control fluid distribution and water permeability in the fuel cell. Gas/fluid diffusion layers and similar structures are referred to in the literature by many different names. As used herein, the term gas/fluid diffusion layer includes all such structures including gas diffusion layers, gas diffusion media, gas diffusion electrodes and the like.

Ideally, gas/fluid distribution layers should be capable of transporting reactants to the electrodes, while removing by-products away from the electrodes. For example, in a PEMFC, the gas/fluid diffusion layer should enable efficient transport and distribution of hydrogen gas to the catalysts within the anode. In a DMFC, the gas/fluid diffusion layer should enable efficient transport and distribution of liquid methanol to the catalysts, while enabling removal of product carbon dioxide gas from the anode. In both PEMFCs and DMFCs, the gas/fluid distribution layer should enable efficient transport and distribution of oxygen-containing gas to the catalysts within the cathode and removal of water from the cathode.

Current techniques employed to control gas/fluid distribution include the incorporation of conventional hydrophilic and/or hydrophobic materials within the gas/fluid distribution layer. However, the use of such materials often results in decreased electrical performance and decreased porosity in the gas/fluid diffusion layer.

Bipolar plates are utilized to provide reactants, remove products and transport electrons to the circuit of the fuel cell. Bipolar plates are also utilized to prevent fluid communication between adjacent MEAs. There are several different types of bipolar plates utilized in fuel cells, differentiated by their material of construction and the manufacturing method. These include: 1) Graphite-filled Polymer – a molded graphite-loaded polymer/resin; 2) Machined Graphite – a machined single piece of graphite; 3) Expanded Foam – typically expanded porous metal foams; and 4) Stamped metal – a stamped metallic plate.

Bipolar plates are described in more detail in U.S. Patent No. 5,776,624 by Neutzler and U.S. Patent No. 6,255,012 by Wilson et al., each of which is incorporated herein by reference in its entirety.

5 Bipolar plates and similar structures are referred to in the literature by many different names, such as flow field plates, gas distribution manifolds, gas inlet manifolds, monopolar plates, collector plates, fuel manifolds and the like. As used herein, the term bipolar plate includes all such structures.

10 Some bipolar plates are manufactured from a resin compound, which is molded to form the bipolar plate. Most resin compounds are not very conductive and tend to decrease the electrical conductivity of the bipolar plates, thereby resulting in decreased performance of the fuel cell. Attempts have been made to add carbon materials and other additives to such resin compounds to increase electrical conductivity, but low solids loading levels are necessitated to maintain the viscosity of the resin compound within a useful range. Incorporation of such
15 carbon materials can also increase the brittleness of the bipolar plate.

Carbon is a material that has previously been used for some components of the fuel cell structure. For example, U.S. Patent No. 6,280,871 by Tosco et al. discloses gas diffusion electrodes containing carbon products. The carbon product can be used for at least one component of the electrodes, such as the
20 active layer and/or the blocking layer. Methods to extend the service life of the electrodes, as well as methods to reduce the amount of fluorine-containing compounds are also disclosed. Similar products and methods are described in U.S. Patent No. 6,399,202 by Yu et al. Each of the foregoing patents is incorporated herein by reference in its entirety.

25 U.S. Patent Application Publication No. 2003/0017379 by Menashi, which is incorporated herein by reference in its entirety, discloses fuel cells including a gas diffusion electrode, gas diffusion counter-electrode, and an electrolyte membrane located between the electrode and counter-electrode. The electrode, counter-electrode, or both, contain at least one carbon product. The electrolyte
30 membranes can also contain carbon products. Similar products and methods are described in U.S. Patent Application Publication No. 2003/0022055 by Menashi, which is also incorporated herein by reference in its entirety.

U.S. Patent Application Publication No. 2003/0124414 by Hertel et al., which is incorporated herein by reference in its entirety, discloses a porous

carbon body for a fuel cell having an electronically conductive hydrophilic agent and discloses a method for the manufacture of the carbon body. The porous carbon body comprises an electronically conductive graphite powder in an amount of between 60 and 80 weight percent of the body, carbon fiber in an amount of between 5 and 15 weight percent of the body, a thermoset binder in an amount between 6 and 18 weight percent of the body and an electronically created modified carbon black. Hertel et al. disclose that the carbon body provides increased wettability without any decrease in electrical conductivity, and can be manufactured without high temperature steps to add graphite to the body or to incorporate post molding hydrophilic agents into pores of the body.

Composite membranes with increased strength have been studied for use in industrial chloro-alkali electrolysis processes. Similar fibril reinforced membranes have been produced for use in PEMFCs. These membranes target the following properties: thin, flat, good mechanical strength, chemical robustness and high water permeability and proton conductivity. Such membranes were developed by companies such as W.L. Gore and Associates and Asahi Glass Co., Ltd., all utilizing polytetrafluoroethylene (PTFE) as the reinforcement agent, and an ion exchange material, such as a sulfonated polymer, to act as the proton conduction sites. Others have utilized inorganic fillers, such as silica, titania or tungstosilicic acid, with solids loadings that range from 5 to 70 weight percent. Fillers such as these have been incorporated into proton conducting and non-proton conducting polymers.

SUMMARY OF THE INVENTION

According to one aspect of the present invention, a proton conducting membrane including a modified carbon product and a polymer is provided. In one embodiment of the present aspect, the modified carbon product is a modified carbon black. In another embodiment of the present aspect, the modified carbon product is a modified carbon fiber. In yet another embodiment, the modified carbon product includes a proton conducting functional group. In one embodiment, the proton conducting functional group is selected from the group of SO_3H , CO_2H , PO_3H_2 and PO_3MH , where M is a monovalent cation. In another embodiment, the proton conducting functional group is selected from the group of

carboxylic acids, sulfonic acids, phosphonic acids and phosphonic acid salts. In one embodiment, the polymer is selected from the group of a sulfonated PTFE and a perfluorosulfonated PTFE. In another embodiment, the polymer is selected from the group of polyvinylidene fluoride (PVDF), acid-doped or derivatized hydrocarbon polymers, such as polybenzimidazole (PBI), polyarylenes, polyetherketones, polysulfones, phosphazenes and polyimides. In one embodiment, the modified carbon product is coated on a surface of the polymer. In another embodiment, the modified carbon product is dispersed within the polymer. In one embodiment, the modified carbon product is adapted to conduct protons in the absence of water. In another embodiment, the modified carbon product is adapted to selectively conduct protons in the presence of other hydrogen-comprising liquid fuels. In yet another embodiment, the modified carbon product is adapted to selectively conduct protons in the presence of methanol or ethanol. In one embodiment, the modified carbon product is adapted to yield an increased mechanical strength without a substantial decrease in proton conductivity. In another embodiment, the proton conducting membrane has a proton conducting group concentration of at least about 5.0 millimoles per milliliter, and, in some instances, a proton conducting group concentration of at least about 5.4 millimoles per milliliter. In yet another embodiment, the proton conducting membrane consists essentially of a modified carbon product.

According to another aspect of the present invention, a method for the fabrication of a proton conducting membrane is provided, the method including the steps of mixing a polymer with a modified carbon product to form a composite mixture and forming the composite mixture into a proton conducting membrane. In one embodiment of the present aspect, the forming step includes extruding the composite mixture. In another embodiment, the forming step comprises casting the composite mixture. In yet another embodiment, the proton conducting membrane has a volume density of proton conducting groups of at least about 5.0 millimoles per milliliter. In one embodiment, the composite mixture includes at least about 20 weight percent modified carbon product, and, in some instances, includes at least about 40 weight percent modified carbon product. In one embodiment, the modified carbon product includes carbon black. In another embodiment, the modified carbon product includes carbon fibers.

In yet another aspect of the present invention, a method for the fabrication of a proton conducting membrane is provided, the method including the steps of providing a modified carbon black product and forming the modified carbon black product into a thin membrane. In one embodiment of the present aspect, the forming step includes analog deposition. In another embodiment of the present aspect, the forming step includes digital deposition. In yet another embodiment, the forming step includes dispersing the modified carbon product in a liquid vehicle and ink-jet printing the modified carbon product. In one embodiment, the modified carbon product includes hydrophilic functional groups.

According to one aspect of the present invention, an electrocatalyst is provided, the electrocatalyst comprising an active species phase dispersed on a carbon support structure, wherein the carbon support structure is a modified carbon product. According to one embodiment of the present aspect, the modified carbon product includes a hydrophilic functional group. According to another embodiment, the modified carbon product includes a hydrophobic functional group. In one embodiment, the modified carbon product includes at least two different functional groups. In yet another embodiment, the modified carbon product includes at least a hydrophobic functional group and a hydrophilic functional group. In one embodiment, the modified carbon product includes a functional group that is proton conducting. In yet another embodiment, the modified carbon product includes a functional group that is polymeric. In another embodiment, the modified carbon product comprises a functional group that is adapted to reduce carbon oxidation. In yet another embodiment, the modified carbon product includes a functional group that is adapted to reduce agglomeration of the active species phase. In yet another embodiment, the modified carbon product includes at least two functional groups selected from the group of a proton conducting functional group or a polymeric functional group.

According to another aspect of the present invention, a fuel cell including an electrode is provided, where the electrode includes an electrocatalyst, the electrocatalyst comprising an active species phase dispersed on a carbon support structure, wherein the carbon support structure is a modified carbon product. In one embodiment of the present aspect, the modified carbon product may include a molecular or ionic metal species bonded to a surface functional

group. In one embodiment, the molecular or ionic metal species is within the electrode layer. In yet another embodiment, the modified carbon product includes a functional group that is polymeric. In another embodiment, the modified carbon product comprises a functional group that is adapted to reduce carbon oxidation. In yet another embodiment, the modified carbon product includes a functional group that is adapted to reduce agglomeration of the active species phase. In yet another embodiment, the modified carbon product includes at least two functional groups selected from the group of a proton conducting functional group or a polymeric functional group. In one embodiment, the modified carbon product is adapted to increase the adhesion of the electrode to at least one of an adjacent gas diffusion layer or a proton exchange membrane. In another embodiment, the electrode includes substantially no polymer proton conducting phase.

According to another aspect of the present invention, a method for making an electrocatalyst is provided, the method including the steps of providing a carbon support, covalently attaching a functional group to the carbon support to form a modified carbon support product, and depositing an active species phase on the modified carbon support product to form an electrocatalyst. In one embodiment of the present aspect, the attaching step includes the step of reacting a diazonium salt in the presence of the carbon support. In one embodiment, the carbon support is carbon black. In another embodiment, the carbon support is graphitic carbon. In yet another embodiment, the depositing step includes the step of reacting an active species phase precursor in the presence of the modified carbon support product. In one embodiment, the active species phase precursor preferentially attaches to the functional group. In another embodiment, the active species phase precursor preferentially attaches to the surface of the carbon support. In one embodiment, the functional group is a hydrophobic group. In another embodiment, the functional group is a hydrophilic group. In yet another embodiment, the functional group is a proton conducting group. In yet another embodiment, the functional group is a proton conducting group, where the proton conducting group is selected from the group of carboxylic acids, sulfonic acids, phosphonic acids and phosphonic acid salts. In one embodiment, the functional group is covalently attached to the carbon

support by a linking group, where the linking group is selected from the group of alkyls, aryls, halogenated alkyls, halogenated aryls, substituted alkyls, substituted aryls, polymers and substituted polymers. In yet another embodiment, the active species phase comprises platinum. In another embodiment, the active species phase comprises platinum and ruthenium. In another embodiment, the active species phase includes cobalt. In another embodiment, the active species phase includes nickel. In another embodiment, the active species phase includes platinum, nickel and cobalt. In yet another embodiment, the active species phase includes platinum, chromium and cobalt. In yet another embodiment, the active species phase includes iron. In one embodiment, the active species phase includes a metal oxide, where the metal oxide includes at least one of the elements selected from the group of Pt, Ag, Pd, Ru, Os, Ni, Rh, Ir, Co, Cr, Mo, W, V, Nb, Al, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, Ge, Sn, Y, La and lanthanide metals. In yet another embodiment, the active species phase includes an alloy of Pt with at least one other metal selected from the group of Ru, Os, Cr, Ni, Mn and Co. In yet another embodiment, the covalently attaching step includes spray processing a precursor solution including a carbon material and a diazonium salt. In another embodiment, the depositing step includes the step of spray processing the precursor solution, where the precursor solution further includes a precursor to the active species phase. In one embodiment, the precursor to the active species phase includes a platinum compound.

According to another aspect of the present invention, a method for making an electrocatalyst is provided, the method including the steps of providing an electrocatalyst particle including an active species phase dispersed on a carbon support phase and modifying the carbon support by covalently attaching a functional group to carbon support to form a modified carbon support phase. According to one embodiment of the present aspect, the modifying step includes the step of reacting a diazonium salt in the presence of the electrocatalyst particle. In another embodiment, the carbon support includes carbon black. In yet another embodiment, the active species phase includes platinum. In yet another embodiment, the active species phase includes platinum and ruthenium. In one embodiment, the functional group is a hydrophobic group. In another embodiment, the functional group is a hydrophilic group. In another embodiment,

the active species phase includes cobalt. In another embodiment, the active species phase includes nickel. In another embodiment, the active species phase includes platinum, nickel and cobalt. In yet another embodiment, the active species phase includes platinum, chromium and cobalt. In yet another embodiment, the active species phase includes iron. In one embodiment, the active species phase includes a metal oxide, where the metal oxide includes at least one of the elements selected from the group of Pt, Ag, Pd, Ru, Os, Ni, Rh, Ir, Co, Cr, Mo, W, V, Nb, Al, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, Ge, Sn, Y, La and lanthanide metals. In yet another embodiment, the active species phase includes an alloy of Pt with at least one other metal selected from the group of Ru, Os, Cr, Ni, Mn and Co. In yet another embodiment, the modifying step includes the step of spray processing the precursor solution, where the precursor solution includes electrocatalyst particles and a diazonium salt. In one embodiment, the spray processing step comprises spray processing in a spray dryer.

According to one aspect of the present invention, a fuel cell is provided comprising an anode, a cathode and a proton exchange membrane disposed between the anode and the cathode, where the fuel cell further includes a first gas/fluid diffusion layer adjacent to the anode and opposite the proton exchange membrane, and a second gas/fluid diffusion layer adjacent to the cathode and opposite the proton exchange membrane, where at least one of the first and second gas/fluid diffusion layers includes a modified carbon product. In one embodiment of the present aspect, the modified carbon products include carbon black. In another embodiment of the present aspect, the modified carbon product includes carbon fibers. In yet another embodiment, the modified carbon product comprises graphite fibers. In one embodiment, the modified carbon product includes graphite fibers modified with a hydrophilic functional group. In yet another embodiment, at least one of the gas/fluid diffusion layers includes a carbon support and a microporous layer disposed on the carbon support, where the microporous layer includes the modified carbon product. In one embodiment, at least one of the gas/fluid diffusion layers has an average pore size of from about 100 nm to about 500 nm. In another embodiment, the microporous layer has an average thickness of from about 2 microns to about 20 microns. In yet another embodiment, at least one of the gas/fluid diffusion layers includes a

carbon support, where the modified carbon product particles are dispersed within the carbon support. In one embodiment, the modified carbon product particles have an average particle size of from about 1 micron to about 30 microns. In yet another embodiment, at least one of the gas/fluid diffusion layers includes from
5 about 5 volume percent to about 70 volume percent of the modified carbon product particles. In another embodiment, at least one of the gas/fluid diffusion layers includes a carbon support that is a modified carbon product. In one embodiment, both the first and second gas/fluid diffusion layers comprise a modified carbon product. In one embodiment, the modified carbon product
10 includes a hydrophilic functional group. In another embodiment, the modified carbon product comprises a hydrophilic functional group selected from the group of carboxylic acids, carboxylic salts, sulfonic acids, sulfonic salts, phosphonic acids, phosphonic salts, amines, amine salts and alcohols. In another embodiment, the modified carbon product comprises a hydrophobic functional
15 group. In one embodiment, the modified carbon product includes a hydrophobic functional group selected from the group of saturated cyclics, unsaturated cyclics, saturated aliphatics, unsaturated aliphatics and polymeric. In yet another embodiment, the modified carbon product includes both a hydrophilic functional group and a hydrophobic functional group. In another embodiment, the modified
20 carbon product includes a steric inhibiting functional group. In one embodiment, at least one of the gas/fluid diffusion layers includes predominately hydrophilic modified carbon products on a first side and predominantly hydrophobic modified carbon products on a second side opposite the first side. In another embodiment, at least one of the gas/fluid diffusion layers includes a major planar
25 surface and comprises a chemical gradient lateral to the planar surface. In another embodiment, at least one of the gas/fluid diffusion layers includes a major planar surface and comprises a chemical gradient perpendicular to the planar surface.

According to another aspect of the present invention, a method for the
30 fabrication of the gas/fluid diffusion layer in a fuel cell provided, the method comprising providing a carbon support, depositing a first ink composition comprising a first modified carbon product on the carbon support to form a first sublayer and depositing a second ink composition comprising a second modified

carbon product over the first sublayer, where the first modified carbon product and the second modified carbon product have different hydrophilic properties. In one embodiment of the present aspect, the depositing step includes depositing with an ink-jet device. In another embodiment of the present aspect, the
5 depositing step includes depositing using a method selected from the group of the spraying, analog deposition, lithography, flexographic printing, slot-die, role-coating, xerography and electrostatic printing. In one embodiment, at least one of the first and second modified carbon products includes graphite. In another embodiment, at least one of the first and second modified carbon products
10 includes carbon black.

According to yet another aspect of the present invention, a method for the fabrication of gas/fluid diffusion layer is provided, the method comprising providing a carbon support, contacting the carbon support with the diazonium salt and treating the diazonium salt to covalently bond a functional group to the
15 carbon support and form a modified carbon support product. According to one embodiment of the present aspect, the carbon support includes carbon cloth. In another embodiment of the present aspect, the carbon support includes carbon paper. In one embodiment, the functional group is a hydrophilic group. In another embodiment, the functional group is a hydrophobic group.

20 According to one aspect of the present invention, a fuel stack including a plurality of membrane electrode assemblies and at least one bipolar plate separating the membrane electrode assemblies is provided, where the bipolar plate comprises at least a first modified carbon product. In one embodiment of the present aspect, the first modified carbon product comprises a hydrophilic
25 functional group. In another embodiment of the present aspect, the first modified carbon product comprises a hydrophobic functional group. In one embodiment, the bipolar plate includes a gradient hydrophilic structure. In another embodiment, the bipolar plate includes a gradient hydrophilic structure that is perpendicular to a major planar surface of the bipolar plate. In yet another
30 embodiment, the bipolar plate includes a gradient hydrophilic structure that is lateral to a major planar surface of the bipolar plate. In one embodiment, the modified carbon product has been surface modified by the direct reaction of a diazonium salt having a general formula of $YRN \equiv N^+X^-$, where X is an anion, R is

a linking group and Y is a functional group. In one embodiment, Y is a hydrophilic functional group. In another embodiment, Y is a hydrophobic functional group. In one embodiment, the bipolar plate includes a printed hydrophilic layer comprising the modified carbon product. In yet another
5 embodiment, the hydrophobic layer is printed with a direct write tool. In one embodiment, the hydrophobic layer is digitally printed. In another embodiment, the modified carbon product includes a surface-modifying group selected from the group of saturated and unsaturated cyclics and aliphatics.

According to another aspect of the present invention, a method for treating
10 a current collector having at least a first carbonaceous surface to increase the hydrophobicity of the first carbonaceous surface is provided, the method including the step of covalently bonding a surface-modifying group to the first carbonaceous surface.

According to another aspect of the present invention, a method for treating
15 a current collector having at least a first carbonaceous surface to decrease the hydrophobicity of the first carbonaceous surface is provided, the method including the step of covalently bonding a surface-modifying group to the first carbonaceous surface.

According to get another aspect of the present invention, a method for
20 treating a gas distribution system having at least a first carbonaceous surface to increase the hydrophobicity of the first carbonaceous surface is provided, the method including the step of covalently bonding a surface-modifying group to the first carbonaceous surface.

According to get another aspect of the present invention, a method for
25 treating a gas distribution system having at least a first carbonaceous surface to decrease the hydrophobicity of the first carbonaceous surface is provided, the method including the step of covalently bonding a surface-modifying group to the first carbonaceous surface.

BRIEF DESCRIPTION OF DRAWINGS

30 Figs. 1(a) and 1(b) illustrate a schematic cross-section of a PEMFC MEA and bipolar plate assembly according to the prior art.

Fig. 2 illustrates a cross-section of the cathode side of an MEA showing the membrane and bipolar plate and O_2 , H^+ and H_2O transport according to the prior art.

Fig. 3 illustrates a schematic cross-section of a direct methanol fuel cell (DMFC) according to the prior art.

Fig. 4 illustrates a method for modifying a carbon product to form modified carbon according to U.S. Patent No. 5,900,029 by Belmont et al.

Figs. 5(a) and 5(b) illustrate functional groups attached to a carbon surface according to one via a diazonium salt in accordance with the present invention.

Fig. 6 illustrates the increase in active species phase size as processing temperature increases.

Fig. 7 illustrates a method for formation of platinum/metal oxide active sites using a modified carbon product according to the present invention.

Fig. 8 illustrates the proton conduction mechanism in a PEM according to the prior art.

Fig. 9 illustrates the proton conduction mechanism in a PEM according an embodiment of the present invention.

Fig. 10 illustrates phosphonic groups incorporated into a PBI membrane according to an embodiment of the present invention.

Fig. 11 illustrates the use of sulphonic acid as a proton conducting functional group according to an embodiment of the present invention.

Fig. 12 illustrates the use of surface functional groups to decrease the agglomeration of active species on a carbon support according to an embodiment of the present invention.

Fig. 13 illustrates the decomposition of an active species precursor grouped to a linking group in accordance with an embodiment of the present invention.

Fig. 14 illustrates chelating or metal binding functional groups that are useful according to an embodiment of the present invention.

Fig. 15 illustrates a proton conducting functional group attached to a carbon surface where the functional group includes a large cone angled to permit rapid proton conduction according to an embodiment of the present invention.

Figs. 16(a) to 16(e) illustrate different methods for incorporating a modified carbon product in an electrode according to an embodiment of the present invention.

Fig. 17 illustrates the dispersion of electrocatalyst products into an ink in accordance with an embodiment of the present invention.

Fig. 18 illustrates modified carbon products used to form a microporous layer on a gas/fluid distribution layer in accordance with an embodiment of the present invention.

Fig. 19 illustrates impregnation of modified carbon products into a porous gas/fluid diffusion layer according to an embodiment of the present invention.

Fig. 20 illustrates a modified gas/fluid diffusion layer in accordance with an embodiment of the present invention.

Fig. 21 illustrates a method for forming a gas/fluid diffusion layer in accordance with an embodiment of the present invention.

Fig. 22 illustrates formation of through-plane gradient structures in accordance with an embodiment of the present invention.

Fig. 23 illustrates the use of modified carbon products to decrease cracking during drying as compared to the prior art and according to an embodiment of the present invention.

Fig. 24 illustrates mixing a modified carbon product with a resin compound to form a bipolar plate according to an embodiment of the present invention.

Fig. 25 illustrates modified carbon product fibers and a bipolar plate according to an embodiment of the present invention.

Fig. 26 illustrates the surface modification of a bipolar plate in accordance with an embodiment of the present invention.

Fig. 27 illustrates the surface modification of a bipolar plate in accordance with an embodiment of the present invention.

Fig. 28 illustrates the surface modification of a bipolar plate in accordance with an embodiment of the present invention.

Figs. 29(a) and 29(b) illustrate SEM photomicrographs of a printed ink formulation comprising a modified carbon product according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to fuel cell components that incorporate modified carbon products. Specifically, the present invention relates to proton exchange membranes, electrode layers, gas/fluid diffusion layers, and/or bipolar plates that incorporate modified carbon products. The use of such modified carbon products enables the production of fuel cell components having enhanced properties suited to the specific component.

For example, modified carbon products can be utilized in production of a proton exchange membrane (PEM) to enhance proton conductivity and electrical insulation properties, as well as physical robustness. Modified carbon products can also be utilized in the electrodes (e.g., the anode and cathode) and with electrocatalysts to enhance catalytic activity, proton and electrode conductivity and mass transport properties. Modified carbon products can also be utilized in gas/fluid diffusion layers to enhance mass transport properties, electrical conductivity and physical robustness. Modified carbon products can further be utilized in bipolar plates to enhance mass transport properties and electrical conductivity.

As used herein, a modified carbon product refers to a carbon-containing material having an organic group attached to the carbon surface. In a preferred embodiment, the modified carbon product is a carbon particle having an organic group covalently attached to the carbon surface.

A native (unmodified) carbon surface is relatively inert to most organic reactions, and the attachment of specific organic groups at high coverage levels has been difficult. However, U.S. Patent No. 5,900,029 by Belmont et al., which is incorporated herein by reference in its entirety, discloses a process (referred to herein as the Belmont process) that significantly improves the ability to modify carbon surfaces with organic groups. Utilizing the Belmont process, organic groups can be covalently bonded to the carbon surface such that the groups are highly stable and do not readily desorb from the carbon surface.

Generally, the Belmont process includes reacting at least one diazonium salt with a carbon material to reduce the diazonium salt, such as by reacting at least one diazonium salt with a carbon black in a protic reaction medium. The diazonium salt can include the organic group to be attached to the carbon. The organic group can be selected from an aliphatic group, a cyclic organic group or

an organic compound having an aliphatic portion and a cyclic portion. The organic group can be substituted or unsubstituted and can be branched or unbranched. Accordingly, carbon can be modified to alter its properties such as its surface energy, dispersability in a medium, aggregate size and size distribution, dispersion viscosity and/or chemical reactivity.

The modified carbon product can be formed using an electrically conductive crystalline form of carbon, such as graphite, or can be an amorphous carbon. The carbon, whether crystalline or amorphous, can be in the form of any solid carbon, including carbon black, activated carbon, carbon fiber, bulk carbon, carbon cloth, carbon nanotubes, carbon paper, carbon flakes and the like.

It will be appreciated that the carbon material utilized to form the modified carbon product can be selected to suit the specific application of the modified carbon product in which the carbon material will be utilized. For example, graphite has an anisotropic plate-like structure and a well-defined crystal structure, resulting in a high electrical conductivity. In one embodiment, a modified carbon product including graphite is utilized in a fuel cell component to increase or enhance its electrical conductivity.

Carbon fibers are long, thin, rod-shaped structures which are advantageous for physically reinforcing membranes and increasing in-plane electrical conductivity. In one embodiment, modified carbon fibers are utilized in a fuel cell component to increase or maintain its structural integrity.

Carbon blacks are homologous to graphite, but typically have a relatively low conductivity and form soft, loose agglomerates of primarily nano-sized particles that are isotropic in shape. Carbon black particles generally have an average size in the range of 9 to 150 nanometers and a surface area of from about 20 to 1500 m²/g. In one embodiment, a modified carbon product including carbon black is utilized in the fuel cell component to decrease its electrical conductivity. In another embodiment, modified carbon product including carbon black is dispersed in a liquid to form a modified carbon ink that can be utilized in the production of a fuel cell component due to its shape and small particle size.

Generally, a carbon material is modified utilizing the Belmont process via a functionalizing agent of the form: X-R-Y

where: X reacts with the carbon surface;

R is a linking group; and

Y is a functional group.

The functional group (Y) can vary widely, as can the linking group (R), by selection of the appropriate diazonium salt precursor. The diazonium precursor has the formula:



where: N is nitrogen;

X is an anion such as Cl^- , Br^- or F^- ; R is the linking group;

and

Y is the functional group.

10 Fig. 4 schematically illustrates one method of surface modifying a carbon material according to the Belmont process. The carbon material 420 is contacted with a diazonium salt 422 to produce a modified carbon product 424. The resulting modified carbon product 424 includes surface groups that include the linking group (R) and the functional group (Y), as discussed below in relation to
15 Figures 5(a) and 5(b).

Figs. 5(a) and 5(b) illustrate different embodiments of a modified carbon product 524a, 524b having a surface group, including a functional group (Y) and linking group (R) attached to the carbon material. In Fig. 5(a), sulfonic acid is attached to the carbon material 520 to produce a modified carbon product 524a.
20 In Fig. 5(b) polyamines are attached to the carbon material 520 to produce a modified carbon product 524b.

Examples of functional groups (Y) that can be used to modify the carbon material according to the present invention include those that are charged (electrostatic), such as sulfonate, carboxylate and tertiary amine salts. Preferred
25 functional groups for fuel cell components according to one aspect of the present invention include those that alter the hydrophobic/hydrophilic nature of the carbon material, such as polar organic groups and groups containing salts, such as tertiary amine salts. Particularly preferred hydrophilic functional groups are listed in Table I, and particularly preferred hydrophobic functional groups are listed in
30 Table II.

TABLE I

Hydrophilic Functional Groups (Y)	Examples
Carboxylic acids and salts	$(\text{C}_6\text{H}_4)\text{CO}_2^-\text{K}^+$, $(\text{C}_6\text{H}_4)\text{CO}_2\text{H}$
Sulfonic acids and salts	$(\text{C}_6\text{H}_4)\text{CH}_2\text{SO}_3\text{H}$
Phosphonic acids and salts	$(\text{C}_{10}\text{H}_6)\text{PO}_3\text{H}_2$
Amines and amine salts	$(\text{C}_6\text{H}_4)\text{NH}_3^+\text{Cl}^-$
Alcohols	$(\text{C}_6\text{H}_4)\text{OH}$

TABLE II

Hydrophobic Functional Groups (Y)	Examples
Saturated and unsaturated cyclics and aliphatics	$(\text{CH}_2)_3\text{CH}_3$, $(\text{C}_6\text{H}_4)\text{CH}_3$
Halogenated saturated and unsaturated cyclics and aliphatics	$(\text{C}_6\text{H}_4)\text{CF}_3$, $(\text{C}_6\text{H}_4)(\text{CF}_2)_7\text{CF}_3$
Polymeric	Polystyrene $[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_n$

5 According to another aspect, preferred functional groups for fuel cell components are those that increase proton conductivity, such as SO_3H , PO_3H_2 and others known to have good proton conductivity. Particularly preferred proton conductive functional groups according to the present invention are listed in Table III.

10

TABLE III

Proton Conducting Groups (Y)	Examples
Carboxylic acid and salt	$(\text{C}_6\text{H}_4)\text{COOH}$, $(\text{C}_6\text{H}_4)\text{COONa}$
Sulfonic acid and salt	$(\text{C}_6\text{H}_4)\text{SO}_3\text{H}$, $(\text{C}_6\text{H}_4)\text{SO}_3\text{Na}$
Phosphonic acid and salt	$(\text{C}_6\text{H}_4)\text{PO}_3\text{H}_2$, $(\text{C}_6\text{H}_4)\text{PO}_3\text{HNa}$

15

According to another aspect of the present invention, preferred functional groups for fuel cell components include those that increase steric hindrance and/or physical interaction with other material surfaces, such as branched and unbranched polymeric groups. Particularly preferred polymeric groups according to this aspect are listed in Table IV.

TABLE IV

Polymeric Groups (Y)	Examples
Polyacrylate	Polymethyl methacrylate (C ₆ H ₄)[CH ₂ C(CH ₃)COOCH ₂] _n
Polystyrene	(C ₆ H ₄)[CH(C ₆ H ₅)CH ₂] _n
Polyethylene oxide (PEO)	(C ₆ H ₄)[OCH ₂ CH ₂ OCH ₂ CH ₂] _n
Polyethylene glycol (PEG)	(C ₆ H ₄)[CH ₂ CH ₂ O] _n
Polypropylene oxide (PPO)	(C ₆ H ₄)[OCH(CH ₃)CH ₂] _n

The linking group (R) of the modified carbon product can also vary. For example, the linking group can be selected to increase the "reach" of the functional group by adding flexibility and degrees of freedom to further enhance proton conduction, steric hindrance and/or physical interaction with other materials. The linking group can be branched or unbranched. Particularly preferred linking groups according to the present invention are listed in Table V.

TABLE V

Linking Group (R)	Examples
Alkyls	CH ₂ , C ₂ H ₄
Aryls	C ₆ H ₄ , C ₆ H ₄ CH ₂
Cyclics	C ₆ H ₁₀ , C ₅ H ₄
Unsaturated aliphatics	CH ₂ CH=CHCH ₂
Halogenated alkyl, aryl, cyclics and unsaturated aliphatics	C ₂ F ₄ , C ₆ H ₄ CF ₂ , C ₈ F ₁₀ CF ₂ CH=CHCF ₂

Generally, any functional group (Y) can be utilized in conjunction with any linking group (R) to create a modified carbon product for use according to the present invention. It will be also appreciated that any other organic groups listed in U.S. Patent No. 5,900,029 by Belmont et al. can be utilized in accordance with the present invention.

It will further be appreciated that the modified carbon product can include varying amounts of surface groups. The amount of surface groups in the modified carbon product is generally expressed either on a mass basis (e.g., mmol of surface groups / gram of carbon) or on a surface area basis (e.g., μ mol

of surface groups per square meter of carbon material surface area). In the latter case, the BET surface area of the carbon support material is used to normalize the surface concentration per specific type of carbon. In one embodiment, the modified carbon product has a surface group concentration of from about 0.1 $\mu\text{mol}/\text{m}^2$ to about 6.0 $\mu\text{mol}/\text{m}^2$. In a preferred embodiment, the modified carbon product has a surface group concentration of from about 1.0 $\mu\text{mol}/\text{m}^2$ to about 4.5 $\mu\text{mol}/\text{m}^2$, and more preferably of from about 1.5 $\mu\text{mol}/\text{m}^2$ to about 3.0 $\mu\text{mol}/\text{m}^2$.

The modified carbon product can also have more than one functional group and/or linking group attached to the carbon surface. In one such aspect of the present invention, the modified carbon product includes a second functional group (Y') attached to the carbon surface. In one embodiment, the second functional group (Y') is attached to the carbon surface via a first linking group (R), which also has a first functional group (Y) attached thereto. In another embodiment, the second functional group (Y') is attached to the carbon surface via a separate second linking group (R'). In this regard, any of the above referenced organic groups can be attached as the first and/or second organic surface groups, and in any combination.

In one embodiment of the present invention, the modified carbon products are modified carbon product particles having a well-controlled particle size. Preferably, the volume average particle size is not greater than about 100 μm , more preferably is not greater than about 20 μm and even more preferably is not greater than about 10 μm . Further, it is preferred that the volume average particle size is at least about 0.1 μm , more preferably 0.3 μm , even more preferably is at least about 0.5 μm and even more preferably is at least about 1 μm . As used herein, the average particle size is the median particle size (d_{50}). Powder batches having an average particle size within the preferred parameters disclosed herein enable the formation of thin layers which are advantageous for producing energy devices such as fuel cells according to the present invention.

In a particular embodiment, the modified carbon product particles have a narrow particle size distribution. For example, it is preferred that at least about 50 volume percent of the particles have a size of not greater than about two times the volume average particle size and it is more preferred that at least about 75 volume percent of the particles have a size of not greater than about two times

the volume average particle size. The particle size distribution can be bimodal or trimodal which can advantageously provide improved packing density.

In another embodiment, the modified carbon product particles are substantially spherical in shape. That is, the particles are preferably not jagged or irregular in shape. Spherical particles can advantageously be deposited using a variety of techniques, including direct-write deposition, as discussed in further detail below, and can form layers that are thin and have a high packing density.

Manufacture Of Modified Carbon Products Particles

Modified carbon products useful in accordance with the present invention can be manufactured using any known methodology, including, *inter alia*, the Belmont process, physical adsorption, surface oxidation, sulfonation, grafting, using an alkylating agent in the presence of a Friedel-Crafts type reaction catalyst, mixing benzene and carbon black with a Lewis Acid catalyst under anhydrous conditions followed by polymerization, coupling of a diazotized amine, coupling of one molecular proportion of a tetrazotized benzidine with two molecular proportions of an arylmethyl pyrazolone in the presence of carbon black, use of an electro-chemical reduction of a diazonium salt, and those disclosed in and by: Tsubakowa in Polym. Sci., Vol. 17, pp 417-470, 1992, U.S. Pat. No. 4,014,844 to Vidal et al., U.S. Pat. No. 3,479,300 to Riven et al., U.S. Pat. No. 3,043,708 to Watson et al., U.S. Pat. No. 3,025,259 Watson et al., U.S. Pat. No. 3,335,020 to Borger et al., U.S. Pat. No. Nos. 2,502,254 to Glassman, U.S. Pat. No. 2,514,236 to Glassman, U.S. Pat. No. 2,514,236 to Glassman, PCT Patent Application No. WO 92/13983 to Centre National De La Recherche Scientifique, and Delmar et al., J. Am. Chem. Soc. 1992, 114, 5883-5884, each of which is incorporated herein by reference in its entirety.

A particularly preferred process for manufacturing modified carbon product particles according to the present invention involves implementing the Belmont process by spray processing, spray conversion and/or spray pyrolysis, the methods being collectively referred to herein as spray processing. A spray process of this nature is disclosed in commonly-owned U.S. Patent No. 6,660,680 by Hampden-Smith et al., which is incorporated herein by reference in its entirety.

Spray processing according to the present invention generally includes the steps of: providing a liquid precursor suspension, which includes a carbon material and a diazonium salt or a precursor to a diazonium salt; atomizing the precursor to form dispersed liquid precursor droplets; and removing liquid from
5 the dispersed liquid precursor droplets to form the modified carbon product particles.

Preferably, the spray processing method combines the drying of the diazonium salt and carbon-containing droplets and the conversion of the diazonium precursor salt to a linking group and functional group covalently bound
10 to a carbon surface in one step, where both the removal of the solvent and the conversion of the precursor occur essentially simultaneously. Combined with a short reaction time, this method enables control over the properties of the linking group and functional group bound to the carbon surface. In another embodiment, the spray processing method achieves the drying of the droplets in a first step,
15 and the conversion of the diazonium salt to a linking group and functional group in a distinct second step. By varying reaction time, temperature, type of carbon material and type of precursors, spray processing can produce modified carbon product particles having tailored morphologies and structures that yield improved performance.

20 Spray processing advantageously enables the modified carbon product particles to be formed while the diazonium salt phase is in intimate contact with the carbon surface, where the diazonium salt is rapidly reacted on the carbon surface. Preferably, the diazonium salt is exposed to an elevated reaction temperature for not more than about 600 seconds, more preferably not more than
25 about 100 seconds and even more preferably not more than about 10 seconds.

Spray processing is also capable of forming an aggregate modified carbon product particle structure. The aggregate modified carbon product particles form as a result of the formation and drying of the droplets during spray processing, and the properties of the structure are influenced by the characteristics of the
30 carbon particles, such as the particle size, particle size distribution and surface area of the carbon particles.

Spray processing methods for modified carbon product particle manufacture according to the present invention can be grouped by reference to several different attributes of the apparatus used to carry out the method. These

attributes include: the main gas flow direction (vertical or horizontal); the type of atomizer (submerged ultrasonic, ultrasonic nozzle, two-fluid nozzle, single nozzle pressurized fluid); the type of gas flow (e.g., laminar with no mixing, turbulent with no mixing, co-current of droplets and hot gas, countercurrent of droplets and gas or mixed flow); the type of heating (e.g., hot wall system, hot gas introduction, combined hot gas and hot wall, plasma or flame); and the type of collection system (e.g., cyclone, bag house, electrostatic or settling).

For example, modified carbon product particles can be prepared by starting with a precursor liquid including a protic reaction medium (e.g., an aqueous-based liquid), colloidal carbon and a diazonium salt. The processing temperature of the precursor droplets can be controlled so the diazonium salt reacts, leaving the carbon intact but surface functionalized. The precursor liquid may also or alternatively include an aprotic reaction medium such as acetone, dimethyl formamide, dioxane and the like.

The atomization technique has a significant influence over the characteristics of the modified carbon product particles, such as the spread of the particle size distribution (PSD), as well as the production rate of the particles. In extreme cases, some techniques cannot atomize precursor compositions having only moderate carbon particle loading or high viscosities. Several methods exist for the atomization of precursor compositions containing suspended carbon particulates. These methods include, but are not limited to: ultrasonic transducers (usually at a frequency of 1-3 MHz); ultrasonic nozzles (usually at a frequency of 10-150 KHz); rotary atomizers; two-fluid nozzles; and pressure atomizers.

Ultrasonic transducers are generally submerged in a liquid, and the ultrasonic energy produces atomized droplets on the surface of the liquid. Two basic ultrasonic transducer disc configurations, planar and point source, can be used. Deeper fluid levels can be atomized using a point source configuration since the energy is focused at a point that is some distance above the surface of the transducer. The scale-up of submerged ultrasonic transducers can be accomplished by placing a large number of ultrasonic transducers in an array. Such a system is illustrated in U.S. Patent No. 6,103,393 by Kodas et al. and U.S. Patent No. 6,338,809 by Hampden-Smith et al., each of which is incorporated herein by reference in its entirety.

Spray nozzles can also be used, and the scale-up of nozzle systems can be accomplished by either selecting a nozzle with a larger capacity, or by increasing the number of nozzles used in parallel. Typically, the droplets produced by nozzles are larger than those produced by ultrasonic transducers.

5 Particle size is also dependent on the gas flow rate. For a fixed liquid flow rate, an increased airflow decreases the average droplet size and a decreased airflow increases the average droplet size. It is difficult to change droplet size without varying the liquid or airflow rates. However, two-fluid nozzles have the ability to process larger volumes of liquid per unit time than ultrasonic transducers.

10 Ultrasonic spray nozzles use high frequency energy to atomize a fluid and have some advantages over single or two-fluid nozzles, such as the low velocity of the spray leaving the nozzle and lack of associated gas flow. The nozzles are available with various orifice sizes and orifice diameters that allow the system to be scaled for the desired production capacity. In general, higher frequency
15 nozzles are physically smaller, produce smaller droplets, and have a lower flow capacity than nozzles that operate at lower frequencies. A drawback of ultrasonic nozzle systems is that scaling up the process by increasing the nozzle size increases the average particle size. If a particular modified carbon product particle size is required, then the maximum production rate per nozzle is set. If
20 the desired production rate exceeds the maximum production rate of the nozzle, additional nozzles or additional production units will be required to achieve the desired production rate.

The shape of the atomizing surface determines the shape and spread of the spray pattern. Conical, microspray and flat atomizing surface shapes are
25 available. The conical atomizing surface provides the greatest atomizing capability and has a large spray envelope. The flat atomizing surface provides almost as much flow as the conical, but limits the overall diameter of the spray. The microspray atomizing surface is for very low flow rates where narrow spray patterns are needed. These nozzles are preferred for configurations where
30 minimal gas flow is required in association with the droplets.

Particulate suspensions present several problems with respect to atomization. For example, submerged ultrasonic atomizers re-circulate the suspension through the generation chamber and the suspension concentrates over time. Further, some fraction of the liquid atomizes without carrying the

suspended carbon particulates. When using submerged ultrasonic transducers, the transducer discs can become coated with the particles over time. Further, the generation rate of particulate suspensions is very low using submerged ultrasonic transducer discs, due in part to energy being absorbed or reflected by the suspended particles.

For spray drying, an aerosol can be generated using three basic methods. These methods differ in the type of energy used to break the liquid masses into small droplets. Rotary atomizers (utilization of centrifugal energy) make use of spinning liquid droplets off of a rotating wheel or disc. Rotary atomizers are useful for co-current production of droplets in the range of 20 to 150 μm in diameter. Pressure nozzles (utilization of pressure energy) generate droplets by passing a fluid under high pressure through an orifice. These can be used for both co-current and mixed-flow reactor configurations, and typically produce droplets in the size range of 50 to 300 μm . Multiple fluid nozzles, such as a two fluid nozzle, produce droplets by passing a relatively slow moving fluid through an orifice while shearing the fluid stream with a relatively fast moving gas stream. As with pressure nozzles, multiple fluid nozzles can be used with both co-current and mixed-flow spray dryer configurations. This type of nozzle can typically produce droplets in the range of 5 to 200 μm .

For example, two-fluid nozzles are used to produce aerosol sprays in many commercial applications, typically in conjunction with spray drying processes. In a two-fluid nozzle, a low-velocity liquid stream encounters a high-velocity gas stream that generates high shear forces to accomplish atomization of the liquid. A direct result of this interaction is that the droplet size characteristics of the aerosol are dependent on the relative mass flow rates of the liquid precursor and nozzle gas stream. The velocity of the droplets as they leave the generation zone can be quite large which may lead to unacceptable losses due to impaction. The aerosol also leaves the nozzle in a characteristic pattern, typically a flat fan, and this may require that the dimensions of the reactor be sufficiently large to prevent unwanted losses on the walls of the system.

The next step in the process includes the evaporation of the solvent (typically water) as the droplet is heated, resulting in a carbon particle of dried solids and salts. A number of methods to deliver heat to the particle are possible: horizontal hot-wall tubular reactors, spray drier and vertical tubular reactors can

be used, as well as plasma, flame and laser reactors. As the carbon particles experience either higher temperature or longer time at a specific temperature, the diazonium salt reacts. Preferably, the temperature and amount of time that the droplets/particles experience can be controlled, and, therefore, the properties of the linking group and functional group formed on the carbon surface can also be controlled.

For example, a horizontal, tubular hot-wall reactor can be used to heat a gas stream to a desired temperature. Energy is delivered to the system by maintaining a fixed boundary temperature at the wall of the reactor and the maximum temperature of the gas is the wall temperature. Heat transfer within a hot wall reactor occurs through the bulk of the gas and buoyant forces that occur naturally in horizontal hot wall reactors aid this transfer. The mixing also helps to improve the radial homogeneity of the gas stream. Passive or active mixing of the gas can also increase the heat transfer rate. The maximum temperature and the heating rate can be controlled independent of the inlet stream with small changes in residence time. The heating rate of the inlet stream can also be controlled using a multi-zone furnace.

The use of a horizontal hot-wall reactor according to the present invention is preferred to produce modified carbon product particles with a size of not greater than about 5 μm . One disadvantage of such reactors is the poor ability to atomize carbon particles when using submerged ultrasonics for atomization.

Alternatively, a horizontal hot-wall reactor can be used with a two-fluid nozzle. This method is preferred for precursor feed streams containing relatively high levels of carbon. A horizontal hot-wall reactor can also be used with ultrasonic nozzles, which allows atomization of precursors containing particulate carbons. However, large droplet size can lead to material loss on reactor walls and other surfaces, making this an expensive method for production of modified carbon product particles.

While horizontal hot-wall reactors are useful according to the present invention, spray processing systems in the configuration of a spray dryer are the generally preferred production method for large quantities of modified carbon product particles. Spray drying is a process where particles are produced by atomizing a precursor to produce droplets and evaporating the liquid to produce a dry aerosol, where thermal decomposition of one or more precursors (e.g., a

carbon and/or diazonium salt) may take place to produce the particle. The residence time in the spray dryer is the average time the process gas spends in the drying vessel as calculated by the vessel volume divided by the process gas flow using the outlet gas conditions. The peak excursion temperature (i.e., the
5 reaction temperature) in the spray dryer is the maximum temperature of a particle, averaged throughout its diameter, while the particle is being processed and/or dried. The droplets are heated by supplying a pre-heated carrier gas.

Three types of spray dryer systems are useful for spray drying to form modified carbon product particles according to the present invention. An open
10 system is useful for general spray drying to form modified carbon product particles using air as an aerosol carrier gas and an aqueous feed solution as a precursor. A closed system is useful for spray drying to form modified carbon product particles using an aerosol carrier gas other than air. A closed system is also useful when using a non-aqueous or a semi-non-aqueous solution as a
15 precursor. A semi-closed system, including a self-inertizing system, is useful for spray drying to form modified carbon product particles that require an inert atmosphere and/or precursors that are potentially flammable.

Two spray dryer designs are particularly useful for the production of modified carbon product particles according to the present invention. A co-
20 current spray dryer is useful for production of modified carbon product particles that are sensitive to high temperature excursions (e.g., greater than about 350°C), or that require a rotary atomizer to generate the aerosol. Mixed-flow spray dryers are useful for producing modified carbon product particles that require relatively high temperature excursions (e.g., greater than about 350°C), or
25 require turbulent mixing forces. According one embodiment of the present invention, co-current spray-drying is preferred for the manufacture of modified carbon product particles, including modified carbon black.

In a co-current spray dryer, the hot gas is introduced at the top of the unit, where the droplets are generated with any of the above-described atomization
30 techniques. Generally, the maximum temperature that a droplet/particle is exposed to in a co-current spray dryer is the temperature at the outlet of the dryer. Typically, this outlet temperature is limited to about 200°C, although some designs allow for higher temperatures. In addition, since the particles experience the lowest temperature in the beginning of the time-temperature curve and the

highest temperature at the end, the possibility of precursor surface diffusion and agglomeration is high.

A mixed-flow spray dryer introduces the hot gas at the top of the unit while precursor droplets are generated near the bottom and directed upwardly. The droplets/particles are forced towards the top of the unit, and then fall and flow back down with the gas, increasing the residence time in the spray dryer. The temperature experienced by the droplets/particles is higher compared to a co-current spray dryer.

These conditions are advantageous for the production of modified carbon product particles having a wide range of surface group concentrations including surface concentrations up to $6 \mu\text{mol}/\text{m}^2$ organic groups on carbon. For co-current spray dryers the reaction temperatures can be high enough to enable reaction of the diazonium salt (e.g., between 25°C and 100°C). The highest temperature in co-current spray dryers is the inlet temperature (e.g., 180°C), and the outlet temperature can be as low as 50°C . Therefore, the carbon particles and surface groups reach the highest temperature for a relatively short time, which advantageously reduces migration or surface diffusion of the surface groups. This spike of high temperature can also quickly convert the diazonium salt to the bonded surface group, and is followed by a mild quench since the spray dryer temperature quickly decreases after the maximum temperature is achieved. Thus, the spike-like temperature profile can be advantageous for the generation of highly dispersed surface groups on the surface of the carbon.

The range of useful residence times for producing modified carbon product particles depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid inlet temperature and the residual moisture content. In general, residence times for the production of modified carbon product particles can range from less than 3 seconds up to 5 minutes.

For a co-current spray-drying configuration, the range of useful inlet temperatures for producing modified carbon product particles depends on a number of factors, including solids loading and droplet size, atmosphere used and energy required to perform drying and/or reaction of the diazonium salt. Useful inlet temperatures should be sufficiently high to accomplish the drying

and/or reaction of the diazonium salt without promoting significant surface diffusion of the surface groups.

In general, the outlet temperature of the spray dryer determines the residual moisture content of the modified carbon product particles. For example, a useful outlet temperature for co-current spray drying according to one embodiment of the present invention is from about 50°C to about 80°C. Useful inlet temperatures according to the present invention are from about 130°C to 180°C. The carbon solids (e.g., particulate) loading can be up to about 50 wt.%.

Other equipment that is desirable for producing modified carbon product particles using a spray dryer includes a heater for heating the gas, directly or indirectly, including by thermal, electrical conductive, convective and/or radiant heating. Collection apparatus, such as cyclones, bag/cartridge filters, electrostatic precipitators, and/or various wet collection apparatus, may also be utilized to collect the modified carbon product particles.

In one embodiment of the present invention, spray drying is used to form aggregate modified carbon product particles, wherein the aggregates include more than one modified carbon product particle. In this regard, the individual modified carbon product particles can all have essentially the same surface groups or varying types of modified carbon product particles can be utilized to provide an aggregate with a mixture of surface groups. For example, a first modified carbon product particle within the aggregate can have a hydrophilic surface group and a second modified carbon product particle can have a hydrophobic surface group.

In one aspect, first modified carbon product particles (e.g., modified carbon black particles having a hydrophilic surface group) and second modified carbon product particles (e.g., modified carbon black particles having a hydrophobic surface group) are dispersed in a aqueous precursor solution and spray dried to obtain an aggregate modified carbon product particle having both hydrophilic and hydrophobic properties. The aggregate may include various particle sizes, from nano-sized particles to large, sub-micron size particles.

Moreover, as described below with respect to electrocatalyst materials, the aggregate structure can include smaller primary carbon particles and two or more types of primary particles can be mixed. For example, two or more types of particulate carbon (e.g., amorphous and graphitic carbon) can be combined

within the aggregate to tailor the aggregate to the desired electrical and/or oxidation resistant properties.

In this regard, spray drying techniques can be used simply to form the aggregate modified carbon product particles, or to additionally effect a change in the structure of the individual modified carbon product particles. For example, spray processing techniques can be conducted at higher temperatures to effect at least a partial decomposition of the previously attached surface groups, such as those surface groups that are utilized to help the spray processing, but are subsequently not desired in the end-product. The specific temperature for the spray drying process may be chosen depending on the desired outcome, which is a function of the type and stability of the surface groups, the targeted final composition, and the treatment distribution.

Electrocatalyst Materials

Electrocatalysts are used in the fuel cell to facilitate the desired reactions. Particularly preferred electrocatalyst materials useful in accordance with the present invention include those having an active species phase, such as a metal, dispersed on a support phase, such as a carbon material. Such electrocatalyst materials are described in U.S. Patent 6,660,680 by Hampden-Smith et al. As used herein, the terms "electrocatalyst materials", "electrocatalyst particles" and/or "electrocatalyst powders" and the like refer to such electrocatalyst materials in a non-modified native state.

With respect to electrocatalyst materials, the larger structures formed from the association of discrete carbon particles supporting the dispersed active species phase are referred to as aggregates or aggregate particles, and typically have a size in the range from 0.3 to 100 μm . In addition, the aggregates can further associate into larger "agglomerates". The aggregate morphology, aggregate size, size distribution and surface area of the electrocatalyst powders are all characteristics that impact the catalyst performance. The aggregate morphology, aggregate size and size distribution determines the packing density, and the surface area determines the type and number of surface adsorption centers where the active species form during synthesis of the electrocatalyst.

The aggregate structure can include smaller primary carbon particles, constituting the support phase. Two or more types of primary particles can be

mixed to form the support phase. For example, two or more types of particulate carbon (e.g., amorphous and graphitic carbon) can be combined to form the support phase. The two types of particulate carbon can have different performance characteristics and the combination of the two types in the aggregate structure can enhance the performance of the catalyst.

The carbon support is a major component of the electrocatalysts. To achieve adequate dispersion of the active sites, the carbon support should have a high surface area, a large accessible porous surface area (pore sizes from about 2 nm to about 50 nm preferred), low levels of contaminants that are poisons for either the membrane or the active sites during long term operation of the fuel cell, and good stability with respect to oxidation during the operation of the fuel cell.

Among the forms of carbon available for the support phase, graphitic carbon is preferred for long-term operational stability of fuel cells due to its ability to resist oxidation. Amorphous carbon (e.g., carbon black) is preferred when a smaller crystallite size is desired for the supported active species phase. The carbon support particles typically have sizes in the range of from about 10 nanometers to 5 μm , depending on the nature of the carbon material. However, carbon particulates having sizes up to 25 μm can also be used.

The compositions and ratios of the aggregate particle components can be independently varied, and various combinations of carbons, metals, metal alloys, metal oxides, mixed metal oxides, organometallic compounds and their partial pyrolysis products can be used. The electrocatalyst particles can include two or more different materials as the dispersed active species. As an example, combinations of Ag and MnO_x dispersed on carbon can be useful for some electrocatalytic applications. Other examples of multiple active species are mixtures of metal porphyrins, partially decomposed metal porphyrins, Co and CoO.

The supported electrocatalyst particles preferably include a carbon support phase with at least about 1 weight percent active species phase, more preferably at least about 5 weight percent active species phase and even more preferably at least about 10 weight percent active species phase. In one embodiment, the particles include from about 20 to about 80 weight percent of the active species phase dispersed on the support phase. It has been found that such

compositional levels give rise to the most advantageous electrocatalyst properties for many applications. However, the preferred level of the active species supported on the carbon support will depend upon the total surface area of the carbon, the type of active species phase and the application of the electrocatalyst. A carbon support having a low surface area will require a lower percentage of active species on its surface to achieve a similar surface concentration of the active species compared to a support with higher surface area and higher active species loading.

Metal-carbon electrocatalyst particles include a catalytically active species of at least a first metal phase dispersed on a carbon support phase. The metal active species phase can include any metal and the particularly preferred metal will depend upon the application of the powder. The metal phase can be a metal alloy wherein a first metal is alloyed with one or more alloying elements. As used herein, the term metal alloy also includes intermetallic compounds between two or more metals. For example, the term platinum metal phase refers to a platinum alloy or platinum-containing intermetallic compound, as well as pure platinum metal. The metal-carbon electrocatalyst powders can also include two or more metals dispersed on the support phase as separate active species phases.

Preferred metals for the active species include the platinum group metals and noble metals, particularly Pt, Ag, Pd, Ru, Os and their alloys. The metal phase can also include a metal selected from the group consisting of Ni, Rh, Ir, Co, Cr, Mo, W, V, Nb, Al, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, Ge, Sn, Y, La, lanthanide metals and combinations or alloys of these metals. Preferred metal alloys include alloys of Pt with other metals, such as Ru, Os, Cr, Ni, Mn and Co. Particularly preferred among these is Pt or PtRu for use in the anode and Pt, PtCrCo or PtNiCo for use in the cathode.

Alternatively, metal oxide-carbon electrocatalyst particles that include a metal oxide active species dispersed on a carbon support phase can be used. The metal oxide can be selected from the oxides of the transition metals, preferably those existing in oxides of variable oxidation states, and most preferably from those having an oxygen deficiency in their crystalline structure. For example, the metal oxide active species can be an oxide of a metal selected from the group consisting of Au, Ag, Pt, Pd, Ni, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti or Al. A particularly preferred metal oxide active species

is manganese oxide (MnO_x , where x is 1 to 2). The active species can include a mixture of different oxides, solid solutions of two or more different metal oxides or double oxides. The metal oxides can be stoichiometric or non-stoichiometric and can be mixtures of oxides of one metal having different oxidation states. The metal oxides can also be amorphous.

It is preferred that the average size of the active species is such that the electrocatalyst particles include small single crystals or crystallite clusters, collectively referred to herein as clusters, of the active species dispersed on the support phase. Preferably, the average active species cluster size (diameter) is not greater than about 10 nanometers, more preferably is not greater than about 5 nanometers and even more preferably is not greater than about 3 nanometers. Preferably, the average cluster size of the active species is from about 0.5 to 5 nanometers. Preferably, at least about 50 percent by number, more preferably at least about 60 percent by number and even more preferably at least about 70 percent by number of the active species phase clusters have a size of not greater than about 3 nanometers. Electrocatalyst powders having a dispersed active species phase with such small crystallite clusters advantageously have enhanced catalytic properties as compared to powders including an active species phase having larger clusters.

It should be recognized that the preferred electrocatalyst powders are not mere physical admixtures of different particles, but are comprised of support phase particles that include a dispersed phase of an active species. Preferably, the composition of the aggregate electrocatalyst particles is homogeneous. That is, the different phases of the electrocatalyst are well dispersed within a single aggregate particle. It is also possible to intentionally provide compositional gradients within the individual electrocatalyst aggregate particles. For example, the concentration of the dispersed active species phase in a composite particle can be higher or lower at the surface of the secondary support phase than near the center and gradients corresponding to compositional changes of 10 to 100 weight percent can be obtained. When the aggregate particles are deposited using a direct-write tool, the aggregate particles preferably retain their structural morphology and therefore the functionality of the compositional gradient can be exploited in the device.

In addition, the electrocatalyst powders preferably have a surface area of at least about 25 m²/g, more preferably at least about 90 m²/g and even more preferably at least about 600 m²/g. Surface area is typically measured using the BET nitrogen adsorption method which is indicative of the surface area of the powder, including the surface area of accessible pores on the surface of the particles.

Moreover, many of the desired attributes of modified carbon products may be desired attributes of electrocatalyst, and any of the above-described attributes of the modified carbon products can be acknowledged as being useful in the production, use and application of electrocatalyst materials. For example, particle size, size distribution and spherical nature can be an important factor when utilizing such electrocatalyst materials in an electrocatalyst ink, as described in further detail below.

15 **Manufacture of Electrocatalyst Materials**

Electrocatalyst materials may be produced in a variety of ways including impregnation and co-precipitation. One preferred method for preparing particulate electrocatalyst materials is by spray processing, one approach of which is disclosed in U.S. Patent No. 6,660,680 to Hampden-Smith et al.

20 Production of electrocatalyst material by spray processing generally involves the steps of: providing a precursor composition which includes a support phase or a precursor to the support phase (e.g., a carbon-containing material) and a precursor to the active species; atomizing the precursor to form a suspension of liquid precursor droplets; and removing liquid from liquid precursor droplets to form the powder. At least one component of the liquid precursor is chemically converted into a desired component of the powder. The drying of the precursors and the conversion to a catalytically active species can be combined in one step, where both the removal of the solvent and the conversion of a precursor to the active species occur essentially simultaneously. Combined with
30 a short reaction time, this enables control over the distribution of the active species on the support, the oxidation state of the active species and the crystallinity of the active species. By varying reaction time, temperature, type of support material and type of precursors, electrocatalyst materials having well-

controlled catalyst morphologies and active species structures can be produced, which yield improved catalytic performance.

The precursor composition can include low temperature precursors, such as a molecular metal precursor that has a relatively low decomposition temperature. As used herein, the term molecular metal precursor refers to a molecular compound that includes a metal atom. Examples include organometallics (molecules with carbon-metal bonds), metal organics (molecules containing organic ligands with metal bonds to other types of elements such as oxygen, nitrogen or sulfur) and inorganic compounds such as metal nitrates, metal halides and other metal salts. The molecular metal precursors can be either soluble or insoluble in the precursor composition.

In general, molecular metal precursor compounds that eliminate ligands by a radical mechanism upon conversion to metal are preferred, especially if the species formed are stable radicals, and, therefore, lower the decomposition temperature of that precursor compound.

Furthermore, molecular metal precursors containing ligands that eliminate cleanly upon precursor conversion are preferred because they are not susceptible to carbon contamination or contamination by anionic species such as nitrates. Therefore, preferred precursors for metals include carboxylates, alkoxides or combinations thereof that convert to metals, metal oxides or mixed metal oxides by eliminating small molecules such as carboxylic acid anhydrides, ethers or esters.

Particularly preferred molecular metal precursor compounds are metal precursor compounds containing silver, nickel, platinum, gold, palladium, copper, ruthenium, cobalt and chromium. In one preferred embodiment of the present invention, the molecular metal precursor compound comprises platinum.

Various molecular metal precursors can be used for platinum metal. Preferred molecular precursors for platinum include nitrates, carboxylates, beta-diketonates, and compounds containing metal-carbon bonds. Divalent platinum (II) complexes are particularly preferred. Preferred molecular precursors also include ammonium salts of platinates such as ammonium hexachloro platinate $(\text{NH}_4)_2\text{PtCl}_6$, and ammonium tetrachloro platinate $(\text{NH}_4)_2\text{PtCl}_4$; sodium and potassium salts of halogeno, pseudohalogeno or nitrito platinates such as potassium hexachloro platinate K_2PtCl_6 , sodium tetrachloro platinate Na_2PtCl_4 ,

potassium hexabromo platinate K_2PtBr_6 , potassium tetranitrito platinate $K_2Pt(NO_2)_4$; dihydrogen salts of hydroxo or halogeno platينات such as hexachloro platinic acid H_2PtCl_6 , hexabromo platinic acid H_2PtBr_6 , dihydrogen hexahydroxo platinate $H_2Pt(OH)_6$; diammine and tetraammine platinum compounds such as diammine platinum chloride $Pt(NH_3)_2Cl_2$, tetraammine platinum chloride $[Pt(NH_3)_4]Cl_2$, tetraammine platinum hydroxide $[Pt(NH_3)_4](OH)_2$, tetraammine platinum nitrite $[Pt(NH_3)_4](NO_2)_2$, tetrammine platinum nitrate $Pt(NH_3)_4(NO_3)_2$, tetrammine platinum bicarbonate $[Pt(NH_3)_4](HCO_3)_2$, tetraammine platinum tetrachloroplatinate $[Pt(NH_3)_4]PtCl_4$; platinum diketonates such as platinum (II) 2,4-pentanedionate $Pt(C_5H_7O_2)_2$; platinum nitrates such as dihydrogen hexahydroxo platinate $H_2Pt(OH)_6$ acidified with nitric acid; other platinum salts such as Pt-sulfite and Pt-oxalate; and platinum salts comprising other N-donor ligands such as $[Pt(CN)_6]^{4+}$.

15 **Modified Electrocatalyst Products**

According to one embodiment of the present invention, the modified electrocatalyst products are a subclass of the above-described modified carbon products, and as used herein, modified electrocatalyst products generally refers to an electrocatalyst material having an organic group attached thereto.

20 In one embodiment of the present invention, a modified electrocatalyst product is provided having an active species phase, a carbon support phase, and an organic surface group covalently bonded to the carbon support phase.

In one preferred embodiment, the active species phase includes a first metal, such as platinum. The active species phase can also include a second metal, such as ruthenium, cobalt, chromium or nickel. The first and second metals can be in metallic, metal oxide or alloy form, as described in further detail below. In yet another embodiment, the active species phase includes at least three metals (e.g., Pt, Ni and Co). The active species phase may be any of the above-mentioned metals or metal oxides utilized in the above-described electrocatalyst materials.

30 The carbon support material can be any of the above-described materials utilized in a modified carbon product or electrocatalyst material. In one preferred embodiment, the carbon support material is carbon black.

The organic group may include aliphatic groups, cyclic organic groups and organic compounds having an aliphatic portion and a cyclic portion. The organic group can be substituted or unsubstituted and can be branched or unbranched. Generally, as described above, the organic groups include a linking group (R) and a functional group (Y), more generally known as surface groups.

Any of the above-described functional groups (Y) utilized to form a modified carbon product can also be used in the production of a modified electrocatalyst product, including those that are charged (electrostatic), such as sulfonate, carboxylate and tertiary amine salts. Preferred functional groups include those that alter the hydrophobic or hydrophilic nature of the carbon material, such as polar organic groups and groups containing salts, such as tertiary amine salts, including those listed in Tables I and II. Another particularly preferred class of functional groups include those that increase proton conductivity, such as SO_3H , PO_3H_2 and others known to be part of the backbone of a proton conducting membrane, including those listed in Table III. Yet another particularly preferred class of functional groups includes compounds that increase steric hindrance and/or physical interaction with other material surfaces, such as such as those listed in Table IV.

Any of the linking groups (R) utilized in the creation of a modified carbon product can also be used in the production of a modified electrocatalyst products, including those that increase the "reach" of the functional group by adding flexibility and degrees of freedom to further increase, for example, proton conduction, steric hindrance and/or physical and/or interaction with other materials, including branched and unbranched materials. Particularly preferred linking groups are listed in Table V, above.

It will be appreciated that, generally, any functional group (Y) can be utilized in conjunction with any linking group (R) to create a modified electrocatalyst product according to the present invention to produce the desired effect within the fuel cell component. It will be also appreciated that any other organic groups disclosed in U.S. Patent No. 5,900,029 by Belmont et al. can be utilized.

As noted above, modified electrocatalyst products are a subclass of modified carbon products. Thus, many of the desired attributes of modified carbon products are also desired attributes of modified electrocatalyst products,

and any of the above-described attributes of the modified carbon products can be acknowledged as being useful in the production, use and application of modified electrocatalyst products. For example, particle size, size distribution and spherical nature can be an important factor when utilizing such modified electrocatalyst products in a modified carbon ink, as described in further detail below. Moreover, many of the attributes of electrocatalyst materials are also desired attributes of modified electrocatalyst products and any of the above-described attributes of electrocatalyst materials can be acknowledged as being useful in the production, use and application of modified electrocatalyst products. For example, surface area, average active species cluster size and size distribution, mass ratio of active species phase to carbon support phase, and particle aggregation are important factors in catalytic activity. Other attributes are described below.

The modified electrocatalyst product may include varying concentrations of functional groups, such as from about $0.1 \mu\text{mol}/\text{m}^2$ to about $6.0 \mu\text{mol}/\text{m}^2$. In a preferred embodiment, the modified electrocatalyst product has a surface group concentration of from about $1.0 \mu\text{mol}/\text{m}^2$ to about $4.5 \mu\text{mol}/\text{m}^2$, and more preferably of from about $1.5 \mu\text{mol}/\text{m}^2$ to about $3.0 \mu\text{mol}/\text{m}^2$.

The modified electrocatalyst product may also have more than one functional group and/or linking group attached to the carbon material. In one aspect of the present invention, the modified electrocatalyst product includes a second organic surface group having a second functional group (Y') attached to the carbon support. In one embodiment, the second functional group (Y') can be attached to the carbon support via a first linking group (R), which also has the first functional group (Y) attached thereto. Alternatively, the second functional group (Y') can be attached to the carbon support phase via a separate second linking group (R'). In this regard, any of the above referenced organic groups can be attached as the first and/or second organic surface groups, and in any combination.

In a particular embodiment, the first organic surface group includes a first proton conductive functional group, such as a sulfuric and/or carboxylic group, and the second organic surface group includes a second proton conductive functional group, such as a phosphoric group. The use of two different proton conducting functional groups on the same carbon material is useful in

circumstances where a wide range of operating conditions may be utilized so one of the proton conducting groups is always functional. This enables a relatively flat rate of proton conduction over a wide range of operating conditions. For example, sulfuric groups are known to fail at temperatures of about 100°C. However, phosphoric groups are capable of conducting protons at temperatures above 100°C. Thus, utilizing a modified carbon product having two different proton conducting functional groups can enable proton conduction over a wide range of temperatures without requiring the incorporation of numerous conventional proton conducting materials in the fuel cell component. Such materials are especially useful in fuel cells utilized in automobiles and other transportation devices where temperatures can widely vary during start-up conditions.

Methods of producing modified electrocatalyst products are described in further detail below. It will be appreciated that many of such methods can be utilized to produce a modified electrocatalyst product having first and second organic surface groups attached thereto. Preferred methods for producing modified electrocatalyst products having two different types of organic surface group attached thereto (a multiply-modified electrocatalyst product) include spray processing and surface contacting techniques, such as immersion and spraying.

In one embodiment, a multiply-modified electrocatalyst product having first and second organic surface groups is produced by spray processing, where a diazonium salt and modified electrocatalyst product having a first organic surface group attached thereto are included in a precursor composition. The precursor composition is subsequently spray processed to attach a second organic group to the carbon support to produce the multiply-modified electrocatalyst product. The multiply-modified electrocatalyst product may then be utilized in the production of a fuel cell component.

In another embodiment, a multiply-modified electrocatalyst product having first and second organic surface groups is produced by placing a modified electrocatalyst product having a first organic surface group attached thereto in a solution comprising a diazonium salt having a second organic group. The second organic group from the diazonium salt will attach to the carbon support to create the multiply-modified electrocatalyst product. The multiply-modified

electrocatalyst product may then be utilized in the production of a fuel cell component.

It will be appreciated, that the multiply-modified electrocatalyst product can be formed by modifying with the second organic surface group before or after the multiply-modified electrocatalyst product is incorporated into a component of the fuel cell. For example, a modified electrocatalyst product can be utilized in the production of a fuel cell component. Subsequently, the modified electrocatalyst product can be contacted by a diazonium salt to attach the second organic surface group.

In a particular embodiment, a modified electrocatalyst product can be utilized in the production of an electrode. Subsequently, the electrode can be contacted with a second diazonium salt, such as by immersion and/or spraying, to attach the second organic surface group.

Manufacture of Modified Electrocatalyst Products

Modified electrocatalyst products according to the present invention can be manufactured by any appropriate method, including Impregnation, co-precipitation and other methods utilized by those skilled in the art to make supported electrocatalysts. One preferred method for manufacturing modified electrocatalyst products is spray processing, as described above in reference to modified carbon particles.

When a non-modified carbonaceous material is utilized in a spray processing precursor composition, a dispersant, such as a surfactant, is typically required to enable dispersion and increased loading of the carbonaceous material. Such dispersants typically require high temperature processing to facilitate their removal from the resultant products. Moreover, in the production of electrocatalyst materials, any unremoved dispersants typically poison the active sites.

However, according to the present invention, modified carbon products having surface groups that match the polar or non-polar nature of the precursor liquid composition can be used. Such modified carbon products decrease or eliminate the need for such dispersants as the modified carbon products may be more readily dispersed in the precursor composition. Utilizing modified carbon products may also lower spray processing manufacturing temperatures.

Processing at a lower temperature also enables reduction of the active species crystallite size in the electrocatalyst.

As schematically depicted in Fig. 6, and with specific reference to platinum as the active species phase and carbon black as the carbon material, as processing temperature increases, as depicted left to right in the figure, crystallite size increases. Conversely, as temperature decreases, crystallite size also decreases. Reduced crystallite sizes at lower temperatures are also evidenced due to the decreased ability for the active species phase (e.g., platinum) to migrate during the production temperature.

An increased dispersability of the carbon material in the precursor composition also enables an expanded range of carbon products (e.g., graphite) and metal precursors that can be used. Other materials that may be added to the precursor composition include those that do not decompose during processing, such as ionomers (e.g., PTFE) and molecular species (e.g., metal porphyrins).

Thus, one approach of the present invention is directed to the production of modified electrocatalyst particles by spray processing utilizing a modified carbon product in the precursor composition. According to one particular aspect, modified electrocatalyst products are produced utilizing spray processing, where the precursor composition includes modified carbon product particles as the support phase and a precursor to the active species.

Preferred modified carbon products useful in accordance with this aspect include those that are miscible in an aqueous precursor composition, including those having polar surface groups, such as those terminating in hydrophilic and/or proton conducting functional groups as listed in Tables I and III, above.

Preferred modified carbon products useful in accordance with the present aspect also include those that are miscible in a non-aqueous precursor composition, including those having non-polar surface groups, such those terminating in hydrophobic functional groups as those listed in Table II above. Preferred modified carbon products useful in accordance with this aspect also include those that are readily atomizable to produce an aerosol comprising the modified carbon product.

In a particularly preferred embodiment, the modified carbon product used in the precursor composition is a low-conductivity carbon material (e.g., a carbon black) having a hydrophilic surface group (e.g., a sulfuric terminating functional

group). In a particular embodiment, the precursor solution includes from about 5 weight percent to about 15 weight percent of the modified carbon product.

Preferred active species precursors include those listed above for the production of non-modified electrocatalyst materials, including molecular metal precursor compounds, such as organometallics (molecules with carbon-metal bonds), metal organics (molecules containing organic ligands with metal bonds to other types of elements such as oxygen, nitrogen or sulfur) and inorganic compounds such as metal nitrates, metal halides and other metal salts. The molecular metal precursors can be either soluble or insoluble in the precursor composition.

Particularly preferred molecular metal precursor compounds are metal precursor compounds containing nickel, platinum, ruthenium, cobalt and chromium. In one preferred embodiment of the present invention, the molecular metal precursor compound comprises platinum.

Various molecular metal precursors can be used for platinum metal, such as those described above with reference to the molecular metal precursors utilized in the production of electrocatalyst materials. Any known molecular metal precursors can also be utilized for other metals, including molecular metal precursors of ruthenium, nickel, cobalt and chromium. Preferred precursors for ruthenium include ruthenium (III) nitrosyl nitrate $[\text{Ru}(\text{NO})\text{NO}_3]$ and ruthenium chloride hydrate. One preferred precursor for nickel is nickel nitrate $[(\text{Ni}(\text{NO}_3)_2)]$. One preferred precursor for cobalt is cobalt nitrate $[\text{Co}(\text{NO}_3)_2]$. One preferred precursor for chromium is chromium nitrate $[\text{Cr}(\text{NO}_3)_3]$.

In accordance with this aspect, low temperature spray processing conditions can be utilized to produce a modified electrocatalyst product. The processing temperature within the spray processor is preferably less than about 500°C , more preferably less than 400°C , and even more preferably less than 300°C . The residence time within the spray processor is preferably less than about 10 seconds, more preferably less than 5 seconds, and even more preferably less than 3 seconds.

In another embodiment, the precursor composition comprises previously manufactured electrocatalyst materials, such as any of those described above, and a diazonium salt or a diazonium salt precursor. The above-described spray

processing methods can be utilized to produce a modified electrocatalyst product based on this precursor composition.

In another aspect of the present invention, spray generation methods are utilized in conjunction with a precursor composition including a modified carbon product to generate an aerosol for use in the spray processing methods. As noted above, dispersants, such as surfactants, have previously been utilized to enable spray processing of non-modified carbon material. Surfactants increase the viscosity and change the surface tension, disallowing the use of certain generation methods like ultrasonic nebulization. In one embodiment, a precursor composition including modified carbon products and/or modified electrocatalyst products is utilized in a spray processing method to produce a modified carbon product, wherein the precursor composition is atomized utilizing ultrasonic generation, a vibrating orifice or spray nozzles.

Formation of Alloyed, Mixed Metal and/or Metal Oxide Modified Electrocatalyst Products

Another aspect of the present invention is directed to the use of modified carbon products to produce modified electrocatalyst particles including alloys or mixed metal/metal oxides as the active species. Traditionally, platinum is alloyed with various elements such as ruthenium, nickel, cobalt or chromium.

Typically, alloys are produced by the deposition of two or more metals or metal oxides on the surface of the carbon. Subsequently, the metals/metal oxides are subjected to a high temperature post-processing step in a reducing atmosphere to alloy the active species. This post-processing step reduces any metal oxides and allows the different species to migrate over the surface and coalesce to form an alloy.

According to one embodiment of the present invention, spray processing techniques are used to produce modified electrocatalyst products having a platinum alloy having a small metal and/or metal oxide crystallite size. Small crystallite sizes are possible because the metal can be bound to a surface group (e.g., such as an electron donating carboxylic and/or amine functional group) and steric hindrance of the surface group prevents large crystallite growth during consecutive steps of metal deposition and/or post-processing or reduction steps. Other electron donating surface groups useful in accordance with the present

embodiment include alcohols, ethers, polyalcohols, unsaturated alkyls or aryls, thiols and amines.

By way of illustration, a carbon material, such as carbon black, can be co-modified with carboxylic and amine groups (e.g., $(C_6H_4)CO_2H$ and $(C_6H_4)CH_2NH_2$). When this carbon material is treated with a metal salt (e.g., $RuCl_3$), the metal center will bind to the amine functionality on the carbon surface. When this material is subsequently exposed to a second metal salt (e.g. $Pt(NH_3)_4(OH)_2$ or $Pt(NH_3)_4(NO_3)_2$), it will weakly bind to the carboxylic group of the carbon surface. When this resulting multiply-modified carbon product is heated under mild reducing conditions, a finely dispersed alloy (e.g., a platinum plus ruthenium) electrocatalyst is produced.

Mixing of the alloy constituents (e.g., Pt and Ru) at the atomic level reduces the severity of, or eliminates, the post-processing conditions that are required for alloy formation, which in turn reduces crystallite sintering and improves alloy crystallite homogeneity. In one embodiment, the modified electrocatalyst products including a metal alloy are produced at temperatures not greater than $400^\circ C$. During processing, it is preferable to have chemically inert surface groups, such as C_5H_4N , $(C_6H_4)NH_2$, C_6H_5 , $C_{10}H_7$ or $(C_6H_4)CF_3$, due to pH effects with the precursor salts. Additionally, if both metals have the same affinity for the attached surface group(s), the addition of a homogeneous distribution of a different metal species leads to an even distribution over the carbon surface. Again, such an approach will result in an atomic distribution of the metal species, for example, Pt and Ru, anchored and distributed evenly over the carbon surface. This even distribution enables alloy formation at lower processing temperatures, and, hence, smaller alloy crystallite sizes and better catalytic performance.

According to another embodiment of the present invention, one or more metal or metal oxide precursors can be deposited on the modified carbon product where a post-processing step occurs between the two deposition steps. For example, a metal or metal oxide precursor can be added to a modified carbon support where a surface of the carbon that is not modified preferentially adsorbs the precursor, and after a post-processing decomposition step, first metal or metal oxide clusters are formed. This is followed by deposition of a second precursor, which preferentially adsorbs on the surface of previously formed first metal or metal oxide clusters. After the second decomposition step, a fine

composite cluster is formed (e.g., where the second element deposits either as a monolayer or as clusters onto the surface of the first metal clusters).

By way of example, and as depicted in Figure 7, a modified carbon product having surface groups relatively inert to an active species phase (e.g.,
5 SiMe_3) can be utilized to selectively produce an alloyed modified electrocatalyst product. A first metal/ metal oxide (e.g., RuO_2) can be deposited on the carbon material surface in locations where the surface groups are not located. After a post-processing step, a second metal/metal oxide (e.g., Pt) can then be selectively deposited, where the second metal/metal oxide preferentially is
10 adsorbed onto the surface of the first metal/metal oxide clusters to form a composite active species phase cluster and/or a thin surface active layer, which may be used as a support for other deposited materials.

It will be appreciated that one or more of the metal or metal oxide species described above can be deposited by any known method, including liquid phase
15 adsorption (as discussed above), spray-based processing, chemical vapor deposition, under potential deposition, electroless deposition or liquid-phase precipitation. In such cases, the carbon can be modified such that the metal/metal oxide precursors in the second deposition process cannot absorb onto anything other than the first metal/metal oxide initially deposited, resulting in
20 improved crystallite dispersion, uniformity of alloy formation and elimination of segregation phenomena.

As described above, alloy electrocatalysts typically require post-processing to ensure a proper degree of alloying to provide long-term stability of the active sites. During this post-processing step, the alloy crystallites have a
25 tendency to sinter, resulting in crystallite growth. Modified carbon products can be used to minimize this effect. With the integration of modified carbons as the support structure, the metal/metal oxide dispersion is significantly increased since the surface modification blocks part of the surface and inhibits migration. This prevents surface diffusion and agglomeration of the alloy clusters during the
30 reduction/alloying step.

For example, modifying the surface of the carbon material with thermally stable steric groups, such as phenyl (C_6H_5) or naphthyl (C_{10}H_7) groups acts to physically block migration of metal and metal oxide species across the surface of the carbon. When an electrocatalyst is produced with a greater metal/metal

oxide dispersion (i.e., smaller crystallite size), and the species to be alloyed (e.g. mixed metal/metal oxides) requires a lower temperature for alloy formation, a reduced grain growth and better dispersion of the alloy clusters results. Reduced grain growth leads to smaller alloy crystallite size, increased catalytic activity and increased precious metal utilization. Additionally, as described previously, where surface modification groups are intact after the post-processing procedure, they can sterically prevent the metal crystallites from growing by blocking diffusion paths.

10 **Manufacture of Fuel Cell Components**

As noted above, modified carbon products can be utilized in various fuel cell components, including a proton exchange membrane, an electrode, a gas/fluid diffusion layer and/or a bipolar plate. The production of each of these fuel cell components utilizing modified carbon products and/or diazonium salts will now be discussed in turn.

Various methods may be utilized to incorporate a modified carbon product in a fuel cell component. One method includes the steps of contacting a carbon material with a diazonium salt to form a modified carbon product and incorporating the modified carbon product into the fuel cell component. It will be appreciated that more than one type of carbon material and/or diazonium salt may be utilized in this approach to form a plurality of modified carbon products and/or multiply-modified carbon products.

One specific embodiment utilizes spray processing techniques, and includes the steps of providing a precursor composition including a carbon material and a diazonium salt, spray processing the precursor composition to form a modified carbon product, and incorporating the modified carbon product into a fuel cell component.

Another specific embodiment includes the steps of providing a precursor composition including an electrocatalyst material and a diazonium salt, spray processing the precursor composition to form a modified electrocatalyst product, and incorporating the modified electrocatalyst product into a fuel cell component.

Yet another specific embodiment includes the steps of providing a precursor composition including an existing modified carbon product and an active species precursor, spray processing the precursor composition to form a

modified electrocatalyst product, and incorporating the modified electrocatalyst product into a fuel cell component.

Another method for incorporating a modified carbon product in a fuel cell component, includes the steps of mixing a modified carbon product with another material (e.g., a second modified carbon product, a conventional polymer utilized in the production of a PEM, an electrocatalyst material, a conventional carbon material, a resin and/or other materials utilized in the production of a fuel cell component) to form a modified carbon-containing mixture and incorporating the mixture into the fuel cell component. It will be appreciated that more than one type of modified carbon product and other material may be utilized in this approach to form the mixture.

In one specific embodiment, modified carbon products are dispersed in an ink to create a modified carbon ink that may be utilized in the production of a fuel cell component, such as by analog or digital printing, as discussed in further detail below.

Yet another method includes the steps of incorporating a carbonaceous material, such as a modified carbon product and/or a conventional carbon material into a fuel cell component and contacting the carbonaceous material with a diazonium salt to form a modified carbon product in the fuel cell component. It will be appreciated that more than one type of carbonaceous material (e.g., modified carbon product) and/or diazonium salt may be utilized in this approach to form a plurality of modified carbon products and/or multiply-modified carbon products. In a specific embodiment, a diazonium salt is deposited using a direct-write tool, as discussed in further detail below, to form a modified carbon product in the fuel cell component.

Various aspects, approaches, and/or embodiments of the present invention are described below, primarily in reference to modified carbon products. However, it will be appreciated that electrocatalyst materials can be utilized in conjunction with modified carbon products in many of such aspects, approaches and/or embodiments, where appropriate, although not specifically mentioned, and the use of such electrocatalyst materials in such aspects, approaches and/or embodiments is expressly within the scope and spirit of the present invention.

Modified Carbon Products and Proton Exchange Membranes

Proton Conductivity

In a traditional PEM, protons conduct through a membrane, such as a sulfonated polytetrafluoroethylene (sulfonated PTFE) membrane, by means of protonated water (H_3O^+) that is hydrogen bonded to the sulfonic acid groups, which in turn are attached to the polymer backbone, as illustrated in Fig. 8. These PEMs generally require the presence of water for efficient proton conductivity.

According to one embodiment of the present invention, a modified carbon product is utilized to increase the amount of proton conducting sites within the PEM. Increasing the concentration of proton conducting sites is beneficial for several reasons, including increased transport of protons across the membrane and a decrease in the amount of water needed to be supplied with the anode reactant. In some situations, elimination of the water supplied with the anode reactant can be achieved, which greatly reduces the complexity and design of the fuel cell. An added benefit is that surface groups having proton conducting functional groups are also generally hydrophilic. Thus, increasing the amount of proton conducting material also increases the water retention capability of the fuel cell, thereby enabling rapid "dry" starts.

Similarly, the functional group can be tailored to increase K_a (proton donating strength, like K_a : $-\text{SO}_3\text{H} > -\text{CO}_2\text{H}$), to form a better proton conductor. In addition, a tailored functional group may also be utilized to introduce different chemical reactivity to the membrane, such as by increasing hydrogen bond strength, which may affect the bonding strength of a modified carbon product to the membrane surface.

The linking group can also vary. Particularly preferred branched and unbranched linking groups are listed in Table V. It will be appreciated that any proton conducting functional group (Y) can be utilized in conjunction with any linking group (R) to create a modified carbon product in accordance with the present invention. In a particular approach, the linking group is tailored to increase the "reach" of the proton-conducting functional group by adding flexibility and degrees of freedom and further increase proton conduction. According to one preferred embodiment, the linking group is selected such that the functional group extends to, but not substantially beyond, the adjacent functional group.

One example of increased proton conductivity utilizing tailored linking groups is the use of a modified carbon black having $(C_6H_4)(CH_2)_5SO_3H$ functional groups. This modified carbon product can be incorporated into a membrane to provide a longer effective "reach" and increased flexibility of the proton
5 conducting group. In the case of a $(C_6H_4)(CH_2)_5SO_3H$ modified carbon product, the saturated $(CH_2)_5$ chain attached to the phenyl ring adds significant length and an increased degree of rotational flexibility about several C-C single bonds, resulting in an increased cone angle. In this situation, the aliphatic chain allows for increased proton conductivity, especially in dry, reduced humidity or non-
10 humidified conditions.

Modified carbon products can be utilized in conjunction with any of a variety of types of PEMs. These include fluorinated PEMs such as sulfonated PTFE, perfluorosulfonated PTFE, polyvinylidene fluoride (PVDF), as well as acid-doped or derivatized hydrocarbon polymers, such as polybenzimidazole (PBI),
15 polyarylenes, polyetherketones, polysulfones, phosphazenes and polyimides and other similar membranes. A schematic illustration of a resulting structure is illustrated in Fig. 9. As illustrated in Fig. 9, a RSO_3H (R =linking group) modified carbon product is added to a sulfonated PTFE membrane, which results in an increased concentration of proton conductive groups.

20 PBI is a proton conducting membrane that is often used in high-temperature PEMFCs, and generally includes hydrogen-bonded H_3PO_4 species in high concentrations. H_3PO_4 is typically lost during fuel cell operation as it migrates toward the membrane surface due to electro-osmotic drag, where it subsequently evaporates. In one embodiment of the present invention, the
25 proton conducting modified carbon products, such as those having proton conducting surface groups (e.g., those containing sulfuric and/or phosphonic functional groups), can be incorporated into a PBI membrane to increase the concentration of the proton conducting sites, and hence proton conductivity of the PBI membrane.

30 In a particularly preferred embodiment, modified carbon products having phosphonic groups are incorporated into a PBI membrane, as is illustrated in Fig. 10. Adding modified carbon products having phosphonic functional groups to PBI-based membranes increases the number of proton conducting sites and

increases the hydrogen bonding to the H_3PO_4 acid bound within the pores of the membrane. This prevents the PBI membrane from losing H_3PO_4 acid over time.

One example of increased proton conductivity due to an increased proton conducting material density in a proton conducting membrane is the use of modified carbon black having $(\text{C}_6\text{H}_4)\text{SO}_3\text{H}$ surface groups. Preferably, the concentration of surface groups on the modified carbon black is at least about $3.0 \mu\text{mol}/\text{m}^2$, and more preferably at least about $5.0 \mu\text{mol}/\text{m}^2$. Preferably, the volume density of proton conducting groups on the modified carbon black is at least about $5.0 \text{ mmol}/\text{mL}$ and more preferably is at least about $5.4 \text{ mmol}/\text{mL}$. This modified carbon black, when mixed into a perfluorinated sulfonic acid (PFSA) (e.g., NAFION available from E.I. duPont de Nemours, Wilmington, DE) solution (e.g., at a 50:50 volume ratio), can be utilized to produce a modified proton exchange membrane. In one embodiment, the volume density of proton conducting groups on the resulting membrane is at least about $5 \text{ mmol}/\text{mL}$ (about $2.7 \text{ mmol}/\text{g}$).

Proton conducting modified carbon products can also be advantageously incorporated into non-proton conducting membranes, such as non acid-doped or derivatized PBI, polyimides, polysulfones, polyphosphazenes, polyetherketones (PEEKs) and polysiloxanes. Despite lacking proton conductivity, such membranes can provide chemical robustness, mechanical strength and good electrical insulation. By modification of such membranes with proton conducting modified carbon products, a modified membrane can be formed having proton conductivity. This is advantageous in cases where a certain set of physical and/or chemical properties are desired that can only be achieved through the use of a non-proton conducting "base" membrane. Furthermore, incorporating modified carbon products into a non-proton conducting membrane enables the disconnection of the proton conductivity of the final membrane from the membrane material utilized during fabrication.

Mechanical Strength Enhancement

Modified carbon products can also be utilized according to the present invention to increase the mechanical strength of the PEM. In one embodiment of the present invention, a modified carbon product having a polymeric functional group is utilized to create physical and/or chemical interactions with the membrane. For example, a modified carbon having a surface group with

aliphatic surface groups can physically interact (e.g., intertwine) with the polymer membrane backbone to increase the strength of the membrane. Surface groups useful in accordance with the present invention include acrylics, polypropyleneoxide (PPO), polyethyleneoxide (PEO) polyethylene glycol (PEG) and polystyrene. In a particularly preferred embodiment, the concentration of surface groups on the carbon material is from about 0.1 to about 5 $\mu\text{moles}/\text{m}^2$.

According to another embodiment of the present invention, the modified carbon product has at least one surface group that forms a chemical bond to the sulfonate proton exchange membrane. For example, a modified carbon product having an amine-containing (NH_2) surface group can be incorporated into a proton exchange membrane, such as a PTFE membrane. The NH_2 groups hydrogen bond to the oxygen-containing sulfonate groups, resulting in a membrane having increased strength. Other surface groups useful in accordance with the present embodiment include SO_3H , PO_3H_2 and CO_2H groups.

In another embodiment, modified carbon products having a surface functional group can be incorporated in the raw polymer material prior to forming the membrane to increase mechanical strength of the membrane. For example, a modified carbon product having an amine surface group can be added to a carboxylate-based PTFE membrane and processed to create a mechanically enhanced proton exchange membrane. In this regard, the NH_2 groups react with the carboxylate groups on the polymer during polymer formation, forming an amide of the form $\text{RC}(\text{O})\text{N}(\text{H})\text{R}$ and water.

In another embodiment, the surface groups on the carbon materials can be selected to covalently bond to the polymer backbone through a number of means, such as cross-polymerization or condensation. For example, an ethylene-terminated modified carbon product can be added to a batch of perfluorosulfonated PTFE comonomer prior to final membrane formation. Polymerization is initiated and the modified carbon product (through the ethylene surface functional group) co-polymerizes with the co-monomers resulting in a modified composite membrane including carbon covalently bound to the polymer.

It will be appreciated that the foregoing embodiments (e.g., increased proton conductivity and increased mechanical strength) are not mutually exclusive. The modified carbon product can advantageously increase the

mechanical strength while the resulting proton conductivity remains unchanged. Furthermore, the addition of proton conducting modified carbon products to the membrane can increase both the mechanical strength and the proton conductivity of the membrane. The modified carbon products can be co-modified with a long chain functional group and a proton-conducting group. That is, the carbon particles can include more than one type of surface modification. For example, carbon black (e.g., VULCAN XC-72, Cabot Corp., Boston MA) can be modified with $1 \mu\text{mol}/\text{m}^2$ of PEG and also with $3 \mu\text{mol}/\text{m}^2$ of $(\text{C}_6\text{H}_4)\text{SO}_3\text{H}$ to produce a multiply-modified carbon product. When this multiply-modified carbon product is introduced into a substantially non-proton conducting membrane, such as polyimide, the resultant membrane will evidence enhanced proton conductivity and increased mechanical strength. It will be appreciated that two different modified carbons can be utilized to derive the benefit of two different functional groups. For example, a first modified carbon product having a polymeric functional group (e.g., PEG) and a second modified carbon product having a proton conducting functional group (e.g., $(\text{C}_6\text{H}_4)\text{SO}_3\text{H}$) can be utilized in the production of a proton exchange membrane to produce a membrane with enhanced proton conductivity and mechanical strength.

The thermal stability of the membrane can also be enhanced according to the present invention. Carbon is very thermally stable compared to organic polymers, and increasing the loading of carbon within the PEM will increase the overall thermal stability of the membrane. A thermally stable PEM can be produced by the addition of a thermally stable modified carbon to a standard PEM. Moreover, the PEM can be reinforced with the addition of acicular, rod or whisker like modified carbon products. Alternatively, thermally stable PEM can be produced by the addition of a proton conducting modified carbon product to a non-proton conducting but thermally stable membrane such as, for example, polyimide. In either case, the blending of two or more constituents, such as a membrane and a modified carbon product or a membrane and two different modified carbon products or a carbon material modified with more than one surface group, can result in a unique combination of properties.

Water and Fuel Transport Control, Humidification and Porosity

Water transport is a key issue for PEMs. One feature that the modified PEMs according to the present invention can impart to the MEA structure is the ability to operate at decreased humidification levels due to an increased concentration of proton conducting groups per unit volume. In this regard, one aspect of the present invention relates to modified carbon products including proton conductive functional groups. This leads to a significant overall increase in the concentration of proton conducting sites per unit volume, and as well as increased mobility (reach), which allows protons to migrate through the membrane without water acting as a bridge. Moreover, the proton exchange membrane may also operate at a significantly lower humidification level. The ability to operate a proton exchange membrane in near humid and/or dry conditions greatly simplifies the fuel cell design, especially at high operating temperatures, where the difficulty associated with adding water to the membrane is heightened by the accelerated evaporation rate of the water.

The integration of modified carbon products can significantly affect the humidification requirements and water transport for fuel cell systems utilizing PEMs. In a particular embodiment, a composite modified carbon product/polymer membrane is utilized to increase proton conduction at reduced humidification levels. Moreover, even where the modified membranes do not have a high enough concentration of proton conduction groups to allow fully dry conduction, the addition of strongly hydrophilic groups, such as SO_3H , advantageously decreases the requisite water vapor pressure, allowing for water-based proton transfer at elevated temperatures and/or reduced humidification levels of the reactant gases.

According to another embodiment of the present invention, the average pore size within the polymer membranes is reduced through the use of modified carbon products having polymeric surface groups, as described above, to decrease permeability and, therefore, likelihood of water or fuel transport through the membrane. For example, the use of a modified carbon product having hydrophilic and long chained functional groups attached thereto increases proton conductivity while also forming a denser membrane with a smaller average internal pore size.

The porosity of the PEM can be tailored by selecting appropriate carbon materials, linking groups and functional groups. Porosity can be tailored to prevent and/or inhibit gas, water and/or fuel transport across the membrane. In one embodiment, porosity is tailored by utilizing a high surface area carbon black having a high density of proton conducting groups co-modified with large polymeric groups, such as PEG or PPO having a relatively low electrical conductivity. One such carbon black is KETJEN BLACK (available from Akzo Nobel), which has a surface area of about 1600 m²/g and an electrical resistivity of about 500 to 1500 milliOhm-cm. In a particular embodiment, the carbon black can be modified with a proton conducting group, such as a sulfonate, and long-chained polymeric group, such as PEG, and formulated into a membrane having a small pore size. In one preferred embodiment, the membrane has an average pore size of no greater than 3 angstroms.

As will be appreciated, the small pore size is achieved due to the polymeric groups (e.g., PEG) having significant steric bulk dangling from the carbon surfaces. To enhance/tailor porosity, it is important to utilize such large molecular groups, like PEG or PPO, to act as a binder and "filler" between the carbon materials. Without the addition of such steric inhibitors, it is difficult to achieve a dense membrane suitable for use in a fuel cell. The length of the linking group regarding the proton conducting functionality should be such that it extends to, but not substantially beyond, the next proton-conducting functional group. In one extreme, the resulting membrane is essentially based upon modified carbon products and is proton conducting.

One embodiment of such an approach utilizing sulfonic acid as the proton conducting functional group is depicted schematically illustrated in Fig. 11. Modified carbon products 1124 are protonically connected via the sulfonic acid functional groups 1150 extended by the linking groups (R), resulting in a membrane with increased proton conductivity and decreased porosity.

Direct methanol fuel cells (DMFCs), as well as fuel cells that utilize other hydrogen-containing liquid fuels, like ethanol, also utilize a proton conductive membrane. In a DMFC, methanol migration through the membrane (i.e., methanol cross-over) should be avoided to maintain fuel cell performance. Methanol cross-over results in both low fuel utilization and poisoning of active

catalyst sites at the cathode, which significantly decreases the efficiency and performance of the fuel cell.

According to the present invention, methanol cross-over through the membrane can be reduced by the addition of modified carbon products to the
5 membrane. As with PEMFCs, increasing the density of proton conduction sites will allow protons to be transported without the need for water. In addition, decreasing the porosity utilizing modified carbon products having a polymeric surface group, as described above, can also decrease methanol cross-over.

For purposes of illustration, a carbon material, such as carbon black, can
10 be modified with a proton conducting functional group and a functional and/or linking group having substantial steric bulk (e.g., PEG). This modified carbon product can be mixed with another modified carbon product having proton conducting functional groups (e.g., $(C_6H_4)SO_3H$). This mixture can be added to a perfluorosulfonated PTFE polymer co-monomer, and cast to form a modified
15 membrane having an increased proton conductivity and reduced porosity, resulting in lower methanol cross-over levels. Another embodiment of the present invention utilizes modified carbon products to tailor the hydrophilicity/hydrophobicity of the internal pores of the membrane to selectively transport water and inhibit the transport of other molecules, such as methanol.

20

Fabrication of PEMs Utilizing Modified Carbon Products

There are a variety of approaches to producing PEMs including modified carbon products, which are discussed in further detail below. It will be appreciated that any of the above-described modified carbon products, including
25 modified electrocatalyst products, and/or electrocatalyst materials may be utilized in any of the below-described approaches, aspects and/or embodiments to produce and/or modify a proton exchange membrane. It will also be appreciated that the thickness of the membrane should be suitable for the specific fuel cell application, irrespective of its manufacturing process. Preferably, the thickness
30 of the resultant proton exchange membrane is from about 25 to about 250 microns, more preferably from about 30 microns to about 150 microns, and even more preferably from about 35 microns to about 75 microns.

In one approach, a pre-existing PEM may be contacted with a diazonium salt to attach an organic group to carbon materials contained therein to create a

PEM including a modified carbon product. It will be appreciated that any of the below referenced deposition methods can be utilized to directly deposit a diazonium salt onto a carbonaceous surface for the purpose of directly modifying such carbonaceous surface. Additionally, such deposition techniques can be used to modify any carbonaceous materials contained in the PEM, including non-modified carbon materials, electrocatalyst materials, modified carbon products and/or modified electrocatalyst products. It will also be appreciated that such deposition techniques can be utilized to create a uniform modified carbon layer across the entire surface of the proton exchange membrane, or can be deposited in discrete patterns to produce patterned modified carbon layers.

In another approach, modified carbon products may be utilized in the extrusion and casting process to create a modified carbon PEM. In one aspect, a modified carbon product is mixed into a monomer prior to polymerization and casting/extrusion to form the modified carbon PEM. In another aspect, the modified carbon product is mixed into the polymer prior to casting/extrusion to form the PEM. In one embodiment, a modified carbon product is included in the fluid (e.g., monomer or polymer-containing fluid) utilized in the casting and extrusion process to create a modified carbon proton exchange membrane. In a particular embodiment, the modified carbon product is tailored to increase its solubility and/or dispersability in the fluid, such as by utilization of specific functional groups. Such increased solubility and/or dispersability within the fluid enables formation of a composite PEM with uniform distribution of the modified carbon product. In a particular embodiment, the surface group of the modified carbon product is both hydrophilic and proton conducting.

By way of illustration, a modified carbon product including a proton conducting functional group (e.g., $(C_6H_4)SO_3H$ attached to carbon black) can be added to a formulation including a PFSA. This formulation can be fabricated into a membrane by casting or extrusion. In one embodiment, the formulation includes various amounts of modified carbon products, such as at least about 20 wt.%, more preferably at least about 40 wt.% and up to about 70 wt.%. After fabrication, the PEM may include from 5 wt.% to 30 wt.% of a modified carbon product. The resulting membrane, after casting or extrusion, evidences an increased proton conductivity at, or even below, typical PTFE-type humidification levels. In addition, such membranes may also evidence an increased

mechanical stability, depending on the amount and type of modified carbon product utilized.

In another example, modified carbon products can be mixed with a non-proton conducting membrane material to form a composite mixture. Preferably, the modified carbon product constitutes at least about 10 vol.% of the dry mixture, up to about 70 vol.% of the dry mixture. The dry mixture can be added to a solvent and blended, if necessary, such as by using a ball mill. Solvent systems can include aqueous solvents, non-aqueous solvents and mixtures thereof. The resulting slurry can be cast and dried to form a membrane. The dried and cast membrane can be pressed (to further reduce thickness) and/or can be heated to an elevated temperature, such as near or slightly above the glass transition temperature (T_g) of the polymer.

In another approach, modified carbon products may be deposited onto or impregnated into a pre-existing PEM. In one aspect, the modified carbon products may be deposited or impregnated using a modified carbon ink, as discussed in further detail below. In one embodiment, the proton exchange membrane may be contacted by a modified carbon ink, such as by immersion or spraying, to impregnate and/or deposit the modified carbon product into/onto the membrane. In a particular embodiment, the modified carbon ink is deposited utilizing a direct-write tool. In another embodiment, the modified carbon ink is sprayed onto a membrane (e.g., a polybenzimidazole membrane) to form a coated membrane. In particular embodiment, the coated membrane can be further contacted with a solution containing additional materials, such as a proton conducting material or polymer backbone material. In a particular embodiment a coated polybenzimidazole membrane is immersed in a phosphoric acid (H_3PO_4) solution to increase the amount of proton conducting groups in the membrane.

In yet another approach, proton-conducting membranes may be fabricated directly from one or more modified carbon products. This approach alleviates the need for conventional polymers, membrane materials and/or binder systems, which eliminates the negative effects of such materials on the PEM. In this regard, it will be appreciated that large chain, polymeric insulating groups can be attached to the carbon materials, essentially coating them and making them electrically insulating, which aids in the production of PEMs without the above described conventional polymers, membrane materials and/or binder systems.

Moreover, by selecting the proper combination of proton conducting functional group, linking group and carbon, a PEM having the desired properties can be obtained. In one embodiment, the PEM is fabricated by deposition of a modified carbon ink, as is discussed in further detail below.

5

Modified Carbon Products and Electrodes

As discussed previously, the performance of the electrode layers within a fuel cell MEA is a function of many variables, including catalytic activity, electrical conductivity, proton conductivity and porosity. Typically, the electrode layers in a PEMFC include a catalytic material, such as platinum, platinum alloy or mixed metal/metal-oxide clusters, dispersed on a carbon support, a binder and a proton conductive additive. A typical proton conductive additive is a sulfonated polymer, such as PFSA, which can act both as a binder and a proton conductor. As described above, the dispersed metal or metal oxide clusters on the support serve the main function of catalysis, aiding the oxidation reaction of the fuel and the reduction reaction of the oxygen on the anode and cathode side of the MEA, respectively. The polymer additive is typically utilized to aid in binding the fabricated electrode together, aid in proton conductivity, and to aid in the reaction of protons and oxygen ions to form water. Some electrodes, such as those used in alkaline, phosphoric or high temperature acid fuel cells, contain a perfluorosulfonated PTFE type of polymer as a binder and a hydrophobicity modifier.

One embodiment of the present invention is directed to the use of modified carbon products in the electrode layer. Modified carbon products can be utilized to enhance the catalytic activity, proton conductivity, electron conductivity, mass transport, porosity, humidification requirements, adhesion to adjacent layers and reliability of the electrodes.

Catalytic Activity

According to one embodiment of the present invention, a modified carbon product having appropriate functional groups can be used to tailor the location of active sites within the electrode by tailoring the microporosity and mesoporosity of the carbon support material. Carbon support materials for electrocatalysts generally include microporous regions and mesoporous regions. It is generally

preferred to disperse the active species phase on the carbon support and within the mesoporous regions, where reactants may more easily access the active species phase. The functional groups can advantageously be selected to block the ability of the active species phase to reach the microporous regions of the carbon support, such as by decreasing the amount of available paths to the microporous regions and/or by attaching to the microporous regions. Subsequently, the active species phase can be dispersed on the modified carbon product, and will predominantly be located in the mesoporous regions due to the decreased availability of the microporous regions, thereby resulting in a modified electrocatalyst product having increased catalytic activity.

For example, a carbon material (e.g., carbon) black can be modified with a proton conducting functional group (e.g., a carboxylic or sulfonate group) to block the microporosity existing in the carbon black powder, which reduces the surface area of the powder. Preferably, the remaining surface area available to the active sites include pores having a size of at least about 1 nm. When this modified carbon product is used for the deposition of active sites, such as Pt clusters, the deposition of the sites will be reduced in microporous regions and will occur preferentially in mesoporous regions of the carbon support, thereby increasing accessibility of reactants to the active sites. In addition, the presence of hydrophilic functional groups, such as carboxylic and/or sulfonate groups, provide for better dispersability of the modified electrocatalyst product in liquids.

A major cause of supported catalyst deactivation is the agglomeration of the active sites, since the dispersion of the active species is directly related to catalyst performance. According to one embodiment of the present invention, modified carbon products are utilized for Me/carbon or MeOx/carbon electrocatalysts (e.g., where Me is the active species phase such as Pt or PtRu, Mn, PtNiCo, etc.), where the modification group improves the dispersion of the active species clusters and limits surface migration of the clusters, thus decreasing agglomeration of the active species, as depicted in Fig. 12. As depicted in Fig. 12, surface functional groups (Y) block migration/agglomeration of Pt crystallites 1240. The ability to retain the surface modification during catalyst processing and the ability to add a surface modification to a Pt/C or other Me/C catalyst provides multiple routes to introduce groups that will sterically

inhibit migration, and thus agglomeration, of the active species phase during processing and formation of the active sties.

Furthermore, similar modifications as described above can reduce active species agglomeration by limiting the extent of carbon oxidation. Carbon
5 oxidation is a process that occurs on the surface of the carbon under typical fuel cell operating conditions, and leads to changes in the surface properties and morphology of the carbon. For example, carbon oxidation can lead to the formation of more hydrophilic groups at the active species surface and/or to an erosion of the carbon surface, which may result in changes in the carbon surface
10 area and/or agglomeration of the active species phase clusters. The presence of surface functional groups can inhibit the carbon oxidation process and therefore limit, and in some cases even prevent, changes in the carbon surface properties and morphology. Such functional groups also prevent changes in the hydrophilic properties of the carbon surface and active phase dispersion, and, thus, increase
15 the long term stability of electrocatalysts made or post-treated with a surface functional group.

Another method for improving active species dispersion and limiting active species agglomeration is by using functional groups to direct the deposition of platinum on the carbon. By varying the type of surface group, the surface
20 concentration of the functional groups and/or the chain lengths of the linking groups, the surface properties such as adsorption characteristics, hydrophobic/hydrophilic characteristics and the surface modification adsorption mechanism for the active species phase or other precursor adsorption can be influenced to achieve better dispersion of active sites on the surface of the
25 carbon support, as described above.

According to another embodiment of the present invention, the catalytic activity is increased by using surface groups to anchor the catalyst precursor to the carbon support. According to another embodiment of the present invention, a modified carbon product is used to increase dispersion of the active species
30 phase (e.g., platinum) through the use of binding surface functional groups. Here, functional groups are used that can selectively bind to the active species phase, as described above.

For example, in the case of platinum, one metal atom will bind to one functional group, which leads to increased platinum dispersion and a smaller

platinum particle size. As the electrocatalyst is processed, the functional group decomposes leaving small platinum nanocrystallites.

Active species phase coverage can also be improved by blocking portions of the carbon surface, resulting in directed deposition with controlled platinum distribution and particle size. Functional groups, such as sulfonate groups, attached to the modified carbon product can be reduced utilizing a basic active species phase precursor solution, such as platinum nitrate. Reduction of the dried product will yield the catalyst. After reduction, the functional groups can be regenerated and the neutralization procedure can be repeated to form modified electrocatalyst products having higher dispersion of active species phase on the carbon support. In this regard, platinum loading can be from 0.5 wt % to about 60 wt % platinum supported on carbon.

In another embodiment of the present invention, the linking group (R) may be utilized to reduce or prevent migration and agglomeration of the active species phase. Generally, the linking group stays substantially intact (e.g., is substantially inert) during production of modified carbon products. For example, a modified carbon product may be dispersed in a solution comprising an active species phase precursor, such as a solution comprising a molecular metal precursor in water. The resulting solution including the modified carbon product and the active species phase may be processed, such as illustrated in Fig. 13, to decompose the active species precursor anchored to the linking group, (e.g., a pyridine group) thereby providing small active species clusters (e.g., crystallites) on the carbon surface that are protected from oxidation, poisoning and agglomeration by the remaining functional and/or linking groups (e.g., pyridine and toluene groups).

Another embodiment of the present invention is directed to the use of surface functional groups to act as a nucleation site for the active species phase. Here, a chelating surface functional group, such as RCO_2H , can chelate a metal, such as a Ru or Pt, which aids in the formation of small, well-dispersed active species crystallites. There are a variety of chelating or metal binding functional groups that can be used, some of which are depicted in Fig. 14. Examples of preferred chelating ligands according to the present invention include polyamines, polyphosphines, polycarboxylates, ligands with mixed functionality

such as amino acids, ethylenediaminetetraacetic acid (EDTA) and prochiral ligands.

The organic groups of the modified carbon products can also be used to interact with a metal active species to form what is referred to herein as metal-functionalized carbon products. There are two general classes of metal-functionalized carbon products. The first class is a carbon product that is functionalized with metal ions that are relatively weakly coordinated to the surface functional group. These metal ions are relatively easily exchanged and impart ion-exchange functionality to the material. The second class of metal-functionalized carbon products includes a metal species that is coordinated in a more covalent fashion to form a surface bound coordination complex. These metals are typically less easily exchangeable, are coordinated in a more rigid ligand environment, and impart a functionality that is based on having a metal species coordinated in a particular environment on the surface. In one embodiment, the coordinated metal complex acts as a precursor to a reduced metal species, typically metal nanoparticles that are subsequently dispersed over the surface of the support phase, leading to, in the case of Pt, finely dispersed Pt/C electrocatalysts.

In one embodiment of the present invention, where the metal species to be bound is required to exist in an ionic form, the surface functional group is typically easily ionizable. Examples of these terminating groups include sulfonic acids, e.g. $-\text{SO}_3^-$ and NH_3^+ . The metal species can be in the form of a discrete or hydrated metal ion, such as Li^+ , K^+ , Na^+ , Ca_2^+ or Mg_2^+ . In the case where the metal is bound in a covalent state to form a coordination compound, the surface functional terminating group is preferably an electron pair donor. In this case, the formed metal species is a coordination complex, where the surface function group can be neutral (e.g., NR_2 , SR) or can be charged, such as CO^{2-} . Other ligands may also be present in the coordination sphere of the metal ion to satisfy the coordination number of the species such as nitrogen donors (e.g., amines), phosphorus donors (e.g., phosphines), sulfur donors (e.g., thiols), oxygen donors such as alcohols, ketones aldehydes and carboxylic acids. Such approaches allow for the binding of Pt species like, for example, $\text{Pt}(\text{OH})_2(\text{NR}_3)_4$, where the surface functional groups can displace donor groups such as NR_3 anchoring the molecular Pt species to the individual surface sites on the carbon materials.

One embodiment of the present invention is directed to the use in spray-based processing to form modified carbon products to act as a nucleation site for metals like Pt and Ru. Another embodiment is the use of this process in solution-based precipitation processing, and yet another is the use of this approach is in
5 chemical vapor deposition (CVD), aerosol-assisted CVD (AACVD) or gas to particle conversion (GPC) processing.

Examples of these methods are disclosed in U.S. Patent No. 5,155,081, U.S. Patent No. 5,569,635, U.S. Patent No. 6,492,295, U.S. Patent No. 6,066,410, U.S. Patent No. 6,417,133, U.S. Patent No. 6,194,338, U.S. Patent
10 No. 6,339,038, U.S. Patent No. 5,110,779 and U.S. Patent No. 6,284,213, each of which is incorporated herein by reference in its entirety.

Proton Conductivity

As described above, the electrode can be formed by deposition of the
15 modified carbon product and/or modified electrocatalyst product on a PEM or a gas/fluid diffusion layer. In this regard, the electrode layers generally include proton conducting material to provide a proton conductive pathway from the active species phase site (e.g., location of the Pt clusters) to the proton conducting membrane, and vice versa.

20 Traditionally, proton conducting paths have been formed by mixing a conventional proton conducting material with an electrocatalyst material. Such proton conducting materials are generally only a few nanometers in size, and processing is difficult in a variety of respects, including non-uniform deposition within the electrode layer, covering and deactivation of some of the active sites
25 (e.g., Pt clusters), deposition of larger clusters within the layer pores, and segregation of the proton conducting material within the electrode leading to insufficient material in other areas. As a result, active species utilization in the electrodes is typically decreased since protons generated at the catalytic sites are not effectively transported from or to the proton exchange membrane.
30 Another disadvantage is that higher quantities of polymer are typically needed to increase catalyst utilization. However, this generally results in a decrease in the electrode porosity, which negatively affects the mass transport of gas and liquid reactants and products. An increased amount of active species is also often incorporated in the electrode to compensate for catalyst materials that go

unutilized or are underutilized due to their remote location from the proton conducting sites..

One embodiment of the present invention is directed to the use of a modified carbon product and/or modified electrocatalyst product having a proton
5 conducting functional group attached thereto, such as a sulfonate and/or
phosphonic group. In a particular embodiment, the proton conducting functional
group is attached to the carbon material and/or electrocatalyst material prior to
deposition and/or use. In another embodiment, the proton conducting functional
group is attached after the carbon material and/or electrocatalyst material has
10 been incorporated in the fuel cell component. Preferred proton conducting
functional groups according to the present invention are listed in Table III, above.

Active species phase utilization is significantly increased by creating an
efficient proton conducting pathway within the electrodes. Since the proton
conductive functional groups are covalently attached to the carbon surface, the
15 uniformity of the proton conductive pathways is significantly improved. As a
result of the dimensions and proton conductive properties of the functional
groups, an increase of from 40% up to 100% of the active species utilization in
the electrode layers can be achieved. Utilization percent is defined as the
percent of active species surface area (as measured *in-situ* in a single MEA)
20 normalized by the total active species surface area (as measured *ex-situ* by gas
absorption methods). By way of example, and as illustrated in Fig. 15, a proton
conducting functional group, such as a sulfonate group, having a large cone
angle can sweep over a wide area to ensure it is proximal to at least one active
site, which increases the efficiency of proton transport to active sites, and
25 therefore increase reaction activity..

Mixtures of conventional proton conducting materials and modified
electrocatalyst products can also be employed to provide a proton conductive
pathway. In one particular embodiment, a conventional proton conducting
material (e.g. NAFION) is mixed with a modified electrocatalyst product having a
30 proton conducting functional group (e.g., modified carbon black particles having a
sulfuric functional group), and this mixture is utilized (e.g., in an ink) to produce a
proton conducting pathway within the electrode. In this regard, the mass ratio of
conventional proton conducting materials to modified electrocatalyst product is

preferably at least 1:1, but no more than 5:1, and preferably in the range of 1.5:1 to about 3.5:1.

The sub-nanometer dimensions of the functional groups also enables the creation of proton conductive pathways that are proximal to the active species phase sites, which further ensures effective transport of protons without blocking the active sites and without decreasing the porosity of the electrodes. A further benefit of maintaining porosity is that fluids, such as hydrogen gas, water, methanol and carbon dioxide gas can be efficiently transported in and out of the fuel cell.

Electron Conductivity

Another embodiment of the present invention is directed to the use of modified carbon products to increase the electrical conductivity of the electrode layer. This can be achieved by: (1) minimizing the oxidation of the carbon surface during fuel cell operation; (2) using a higher conductivity carbon; (3) reducing the amount of proton conducting polymer in the electrode layer; (4) increasing the solids loading of carbon; and (5) using carbon with a higher structure (e.g., primary carbon particles are interconnected in aggregates).

A decrease in carbon oxidation during fuel cell operation will reduce the loss of conductivity, which is usually related to oxidation of the carbon surface. This is accomplished by the addition of non-hydrophilic/polar groups such as halogenated alkyls and aryls.

The ability to modify the surface of different carbons with, for example, hydrophilic functionality, allows the use of high conductivity carbons, such as graphitic carbon, in the electrodes, either as catalyst supports or as a conductivity enhancing additives. Since graphitic carbons are more conductive and more chemically inert, they are desirable for use in electrodes, but typically have a large particles size and are difficult to disperse for ink preparation. Therefore, the modification of the surface of graphitic carbons with hydrophilic functional groups (for aqueous-based inks) or hydrophobic functional groups (for organic-based inks) enable the use of graphitic carbons, and a corresponding increase in the electrical conductivity. In addition, graphitic carbons are less susceptible to oxidation than other carbon materials, such as carbons blacks, and, therefore, have long-term stability in the MEA.

One method for increasing the electrical conductivity of the electrode is by reducing the amount of conventional proton conducting polymer utilized in the electrode. Since proton conducting polymers are generally not electrically conductive, it is advantageous to replace all or a portion of conventionally utilized proton conducting polymer materials with a proton conducting modified carbon product, as described above.

By way of illustration, a modified carbon product having a proton conducting functional group attached thereto, such as a sulfonate group, can be utilized in an electrode to increase the density of proton conducting groups. Therefore, the amount of conventional proton conducting materials can be reduced and/or eliminated, resulting in an electrode having an increased electrical conductivity without affecting the proton conductivity of the layer.

Another method for increasing the electrical conductivity of the electrode is to increase the amount of carbon material utilized in the electrode. For example, modified carbon products having a hydrophilic functional group can be utilized in conjunction with a polar solvent, such as water, to create a modified carbon ink, as discussed in further detail below. The modified carbon ink can be subsequently deposited to create an electrode layer. In contrast to traditional solutions including such carbon products, the hydrophilic nature of the modified carbon product increases the amount of carbon that can be utilized in the solution, and correspondingly increases the amount of carbon in the electrode layer.

Carbons with a higher structure can form inter-penetrating/interconnected electrode structures. These higher structures, due to the increased carbon/carbon overlap, can increase electrical conductivity, which is even more pronounced at higher solids loadings. In addition, at the interface of the electrode at the gas/fluid diffusion layer, interconnected carbon supports (e.g., the carbon materials of the modified electrocatalyst products) ensure better contact with the conductive fibers of the gas/fluid diffusion layer, and, therefore, lower contact resistance can be achieved. Particularly, carbons with a higher structure, such as carbon black, can be formed into modified carbon products that can be added to the electrode (both as a catalyst support and/or conductivity enhancement additive) at low or high solids loadings. In one embodiment, the electrode

contains not more than about 70 wt. % carbon, inclusive of modified and non-modified carbon products.

Mass Transport, Porosity and Humidification

5 In another approach, modified carbon products having hydrophilic functional groups can be used in the anode of a PEMFC or a DMFC to improve the performance of the anode. The hydrophilic character of the modified carbon products enables water retention at the anode side, which translates into better water management and/or the ability to operate at reduced humidification levels.

10 In another example, the introduction of hydrophobic functional groups (e.g., fluorinated groups) can prevent water flooding at high currents, creating hydrophobic pores for the oxygen reduction reaction (ORR) and create paths for water to escape from the cathode. Hydrophobic treatment of the electrode is often necessary because, proton conducting polymers are hydrophilic, and their
15 use alone gives the electrode a hydrophilic character, which enables water retention and exacerbates flooding. Traditionally, a hydrophobic material is utilized with an electrocatalyst material as the electrode is created. The electrode is then heated at a relatively high temperature to flow the hydrophobic material and disperse it within the electrode. Proton conducting materials are
20 subsequently added to the electrode, instead of during manufacture due to the processing temperature. This results in uneven dispersment within the electrode. Moreover, flowing of the hydrophobic material often results in the hydrophobic material covering a portion of the active sites, which reduces active site utilization within the electrode.

25 Conversely, controlling distribution of the hydrophobic groups within the electrode, such as by utilizing modified carbon products and/or modified electrocatalyst products having a hydrophobic functional group, produces hydrophobic pores selectively proximal to active sites. These hydrophobic pores, in addition to their water rejection capability, facilitate the diffusion of gaseous
30 reactants to the catalytic sites by preventing water blockage of the active sites. As a result, active site utilization is increased. Moreover, in combination with selective placement of proton conducting functional groups, an organized three-phase interface (e.g., the interface of active species phase, the proton conducting phase and the hydrophobic phase) can be created, where reactants are

efficiently distributed to the active sites, and where products, such as protons and/or water, are efficiently transported away from the active sites.

According to another embodiment of the present invention, by using modified carbon products and/or modified electrocatalyst products, an electrode
5 layer with increased porosity and increased proton conductivity can be formed. As is discussed above, the presence of the proper degree of porosity is important for the performance of the electrode layers and/or the electrocatalysts. Electrodes having appropriate pore types, pore sizes and pore size distributions will ensure good gas permeability and adequate water ejection. According to the
10 present invention, utilizing modified carbon products and/or modified electrocatalyst products having hydrophilic and/or hydrophobic groups significantly affects the type, size and size distribution of the pores within the electrode.

According to one embodiment of the present invention, modified carbon
15 products, and/or modified electrocatalyst products, are utilized to achieve the desired electron and proton conductivity with increased porosity. The reduction in the amount of polymer additives by utilizing modified carbon products and/or modified electrocatalyst products to form the electrode results in electrodes with higher porosity, which is beneficial for electrode transport properties. The
20 addition of conventional polymer materials to the electrode layer lowers the porosity of the electrode layer, inhibiting the mass transport of reactants and products. The inclusion of appropriate modified carbon products, as described above, decreases the amount of conventional polymer additives that must be utilized, and correspondingly increases the porosity within the electrode layer.
25 Moreover, swelling, which is normally associated with conventional proton conducting material, will not be observed, which also contributes to an increased processed within electrode.

The use of modified carbon products and/or modified electrocatalysts products can also ensure better pore size distribution within the electrode. By
30 way of illustration, a high surface area carbon maybe modified with a proton conducting functional group. Since the carbon surface is occupied, the BET surface area of the carbon, which relates to microporosity, will significantly decrease. However, the T-area, which relates to mesoporosity, will only slightly decrease. Producing an electrode utilizing such modified carbon products will

result in an electrode having an increased proton conductivity and electrical conductivity as compared to an electrode formulated with polymeric materials. Thus, the use of modified carbon products can reduce the BET surface area of the electrode, preferably by about 10% to about 70%, but may not significantly
5 decrease the T-Area of the electrode as measured by DBP (Dibutyl-phthalate) oil adsorption (ASTM D-2414).

Water management within the fuel cell, especially the cathode, is an issue that can lead to significant transport and ohmic losses during operation. While operating at high current densities, cathodes can become flooded by water
10 generated at the catalytically active sites due to the hydrophilic nature of nearby carbon and proton conducting materials. Even in fuel cells operating at high pressure conditions, flooding is an issue, especially when the electrode comprises pores smaller than a few nanometers in size.

According to one embodiment the present invention, water management
15 within the electrodes can be significantly improved by incorporation of mixed hydrophilic/hydrophobic functionality in the electrodes by utilizing one or more modified carbon products, and/or modified carbon products that have different ratios of hydrophilic vs. hydrophobic functional groups. For example, a balance between hydrophilic and hydrophobic porosity can be achieved by using a
20 modified carbon product having a mixture of hydrophilic and hydrophobic functional groups, such as by using both a sulfonated group and a fluorinated group on the same carbon support material. In another embodiment, modified carbon products and/or modified electrocatalyst products having different functional groups can be mixed in pre-selected ratios. In a particular
25 embodiment, modified electrocatalyst products having both hydrophilic and hydrophobic functional groups attached thereto can be mixed with a modified carbon product having only hydrophobic functional groups attached thereto. These mixtures can be used to form electrodes, such as by deposition utilizing an ink. The electrode can also include consecutive layers, where the layer closest to
30 the gas/fluid diffusion layer includes only modified carbon products modified with a hydrophobic group, followed by layers including both modified carbon products and modified electrocatalyst products, where the ratio of the proton conducting groups and hydrophobic groups is varied to achieve differing degrees of hydrophobicity / hydrophilicity within the electrode.

One embodiment of the present invention is directed to the use of modified carbon products to form relatively thin electrodes. A thin electrode enables greater catalyst utilization by minimizing ohmic and transport losses, which result in lower costs and higher mass transport.

5 Traditionally, electrocatalyst products are not well dispersed, either in an ink incorporating such materials or the electrode itself, which results in gas cross-over and pinholes in the electrode layer. Moreover, the materials are often poorly interconnected and have a high degree of surface roughness, which makes the electrode layer more susceptible to degradation.

10 Modified carbon products and modified electrocatalyst products are advantageous in thin electrodes because they are able to enhance catalyst loading and interconnectivity. Moreover, modified carbon products and or modified electrode products can also be formed as small, spherical, unagglomerated particles, which are highly desirable properties for dispersing in
15 an ink. Moreover, dispersion within the ink can be increased when solvent matching functional groups are utilized (e.g., hydrophilic functional groups for polar aqueous-based inks and hydrophobic functional groups for organic based inks). Such inks can be utilized to create very thin electrode layers. Moreover, the small, spherical and unagglomerated particles produce a high packing density
20 in the electrodes, which aid in minimizing thickness of the electrode.

Interface with Adjacent Components / Adhesion

Another embodiment of the present invention is directed to the incorporation of modified carbon products and/or modified electrocatalysts
25 products to improve the interface contact between adjacent fuel cell components (e.g., PEM and the electrode layers, electrode layers and the PEM and/or the gas/fluid diffusion layers, the gas/fluid diffusion layers and the electrode layers and/or bipolar plates, and the bipolar plates and the gas/fluid diffusion layers). In this regard, the modifying group can form a physical or chemical bond to the PEM
30 or the gas/fluid diffusion layer, due to improved dispersability of the modified electrocatalyst product, forming a smoother surface and increasing contact area with the PEM or gas/fluid diffusion layer.

By way of illustration, modification of an electrocatalyst material with a hydrophilic functional group enables preparation of a uniform, low viscosity

aqueous ink, which can be formed into a smooth, crack-free electrode layer. Such a layer increases contact with the PEM because the hydrophilic functional groups of the modified electrocatalyst product hydrogen bond to the adjacent proton conducting polymer groups covalently bonded to the PEM polymer backbone. This improves bonding between the electrode and the proton exchange membrane, decreases contact resistance, and therefore, minimizes ohmic losses and enhances proton transport. Another benefit is reduced delamination and structural deterioration during long term operation of the fuel cell.

Another embodiment of the present invention is directed to the use of modified carbon products to increase the adhesion of the electrode layer to the gas/fluid diffusion layer and/or to the proton exchange membrane. An electrode made from modified carbon products and/or modified electrocatalyst products may form a physical interlocking bond or a chemical bond to the gas/fluid diffusion layer or the proton exchange membrane. In this regard, polymeric functional groups and/or linking groups can be utilized to increase adhesion of the electrode layer to the gas/fluid diffusion layer and/or the proton exchange membrane. Such polymeric functional groups can be physically intertwined with the surface of the gas/fluid diffusion layer and/or the proton exchange membrane, which increases adhesion. In another embodiment, hydrophilic functional groups can be utilized to increase hydrogen bonding between the electrode layer and the other surface. It will be appreciated that both hydrophilic functional groups and/or polymeric functional and/or linking groups can be utilized on a modified carbon product(s) to achieve such properties.

Long Term Reliability

Another embodiment of the present invention is directed to the use of modified carbon products to increase the long-term reliability of the fuel cell. Typically, performance of the electrode decreases over time due to several reasons, including carbon oxidation and active species agglomeration.

One object of the present invention is to increase the long-term stability of the electrode by using modified carbon products to reduce carbon oxidation. In one approach, hydrophobic and/or oxygen repellent functional groups such as fluorinated groups are utilized to reduce carbon oxidation. Groups that can be

used are hydrophobic surface functional groups, or a mixture of hydrophobic and proton conducting hydrophilic surface functional groups that include saturated and unsaturated alkyls, aryls, and halogenated species. In another approach, a mixture of carbons that have either hydrophobic surface groups or hydrophilic terminating groups or carbon materials that are co-modified with hydrophobic and hydrophilic groups can be used. Carbon oxidation can also be reduced by utilizing carbon materials that are resistant to oxidation, such as graphite.

Another embodiment of the present invention is directed to an increase in long-term reliability of an electrode by using modified carbon products to reduce active species agglomeration. Traditionally, as a fuel cell operates, the active species phase can migrate and agglomerate into large particles, thereby resulting in a drop in electrode performance (current density versus voltage). Utilizing large steric groups, such as polymeric functional groups, to modify the surface of the carbon materials blocks for migration and hence agglomeration of the active species phase.

Formation Of Electrode and Electrocatalyst Layer

Various methodologies may be utilized to incorporate a modified electrocatalyst product in an electrode, as described above. One approach, as depicted in Fig. 16(a), includes the steps of providing a precursor composition including a modified carbon product and active species precursor, spray processing the precursor composition to form a modified electrocatalyst product, and incorporating the modified electrocatalyst product into an electrode. It will be appreciated that more than one type of modified carbon product and/or active species precursor may be utilized in this approach to form a plurality of modified electrocatalyst products and/or multiply-modified electrocatalyst products .

Another approach, as depicted in Fig 16(b), includes the steps of contacting the electrocatalyst material with a diazonium salt to form a modified electrocatalyst product and incorporating the modified electrocatalyst product into an electrode. It will be appreciated that more than one type of electrocatalyst material and/or diazonium salt may be utilized in this approach to form a plurality of modified electrocatalyst products and/or multiply-modified electrocatalyst products .

A specific approach in this regard, as depicted in to Fig. 16(c), utilizes spray processing techniques, and includes the steps of providing a precursor composition including an electrocatalyst material and a diazonium salt, spray processing the precursor composition to form a modified electrocatalyst product, and incorporating the modified electrocatalyst product into an electrode. It will be appreciated that more than one type of electrocatalyst material and/or diazonium salt may be utilized in this approach to form a plurality of modified electrocatalyst products and/or multiply-modified electrocatalyst products.

Yet another approach, as depicted in Fig. 16(d), includes the steps of mixing a modified carbon product with an electrocatalyst material and/or a modified electrocatalyst product to form a mixture and incorporating the mixture into an electrode. It will be appreciated that more than one type of modified carbon product and/or electrocatalyst material and/or modified electrocatalyst product may be utilized in this approach to form the mixture.

Another approach, as depicted in Fig. 16(e), includes the steps of incorporating the modified carbon product into the electrode and then contacting the modified carbon product with a diazonium salt to form a modified electrocatalyst product in the electrode. It will be appreciated that more than one type of modified carbon product and/or diazonium salt may be utilized in this approach to form a plurality of modified electrocatalyst product types.

In one specific embodiment, modified electrocatalyst products are dispersed in an ink to for production of the electrocatalyst layer, such as by analog or digital printing, as discussed in further detail below. For example, and in reference to Fig. 17(a), the electrocatalyst material may be contacted by a diazonium salt, such as by the approaches of Figs. 16(b) or 16(c), above, to form a modified electrocatalyst product. Alternatively, a modified carbon product may be spray processed with an active species precursor, such as by the approach of Fig. 16(a), above, to form a modified electrocatalyst product. These modified electrocatalyst product may then be dispersed in an ink, as shown in Fig. 17(b), which may be utilized in the production of an electrocatalyst layer.

In another aspect, the modified carbon products can be intimately mixed with electrocatalyst material prior to forming the electrode. The mixture may then be deposited, for example in the form of a suspension or ink, to create the electrode. In one approach, the electrocatalyst material includes a precious

metal and the modified carbon product is a modified carbon black. In one embodiment, the precious metal is platinum.

In one aspect, a pre-existing electrode including carbonaceous material can be surfaced modified with a diazonium salt, as described above, to create a surfaced modified electrode layer. In one approach, the electrode may include
5 carbon black, and the functional group may include any of the previously listed organic groups, as appropriate depending on the properties desired to be imparted.

According to another embodiment of the present invention, modified
10 carbon products and/or modified electrocatalyst products are utilized in the process of preparing the electrode, where the modified carbon products and/or modified electrocatalyst products can be more easily dispersed in a solvent, such as a liquid used in an ink. For example, a modified carbon product including a hydrophilic functional group can be utilized to increase the dispersability of the
15 modified carbon product in a polar solvent such as water. In one preferred embodiment, the hydrophilic functional group is also a proton conductive group, such as a sulfonate group. For example, an electrocatalyst material including an active species phase, such as platinum, can be modified with a hydrophilic and/or proton conducting functional group, and subsequently placed in an aqueous
20 based solvent for use as an ink. The resulting ink can be deposited to produce an electrocatalyst layer.

A combination of a modified carbon products and proton conducting materials in solution are also useful when forming electrode layers in that they provide a mix of surface and bulk proton conductive pathways (bulk in this case is
25 defined as nano-sized aggregate that include more than one on a monolayer of polymer).

By way of illustration, a modified electrocatalyst product including a hydrophilic functional group can be mixed with varying amounts of a proton conducting polymer solution. Various concentrations of these constituents can
30 be utilized to create a wide variety of electrodes comprising proton conductive pathways, from electrodes including only of purely carbon surface-binded proton conductive groups, to electrodes including only connected nano-sized clusters of proton conducting polymer, and numerous variations there between. In one preferred embodiment, the solution contains not greater than 15 wt %, preferably

not greater than 10 wt %, and more preferably not greater than 5 wt % of conventional proton conducting polymer material (e.g., NAFION).

By way of illustration, an ink including a modified electrocatalyst product having both hydrophobic and proton conducting functional groups attached thereto can be deposited on the surface of a proton exchange membrane and/or a gas/fluid diffusion layer to generate an electrode layer with reduced pore size. The generated electrode layer will also have an intimate mixture of hydrophilic and hydrophobic domains, allowing for efficient transportation paths for electrons, protons, gases and water.

In another example, a modified electrocatalyst product including hydrophobic functional groups and a modified electrocatalyst product including proton conducting functional groups can be blended into an ink and deposited to generate electrode layer having desired hydrophilic and hydrophobic properties.

According to one embodiment of the present invention, the electrode includes sub-layers where each of the sub-layers has a different degree of modification, thereby creating a selectively manufactured gradient in the electrode. For example a layer closest to the proton exchange membrane can have a high concentration of proton conducting surface groups and a low concentration of hydrophobic surface groups. A layer closest to the gas/fluid diffusion layer can have a high concentration of hydrophobic surface groups and a low concentration of proton conducting surface groups. Gradients in the surface groups can be of an almost continuous nature (gradual increase or decrease of certain functionality) from one side of the electrode to the other (through-plane) or of a discrete nature, with abruptly and selectively tailored changes in properties between the layers.

Modified Carbon Products and Gas/Fluid Diffusion Layers

The present invention also relates to the use of modified carbon products in gas/fluid diffusion layers. Gas/fluid diffusion layers are utilized to distribute the gaseous and/or liquid reactants to the electrode layers, to enable removal of gaseous products and to conduct electrons from the electrode layer to the bipolar plate. Even distribution of the reactants is desirable to maximize the efficiency of the fuel cell by maximizing the utilization of the fuel (e.g., hydrogen gas or methanol) and the utilization of the electrocatalyst active sites in the electrode

layer. Efficient removal of reaction products, such as water, is important to prevent flooding of the fuel cell and prevent clogging. Efficient conduction of electrons is important to increase the electrical output efficiency of the fuel cell. Other important properties of the gas/fluid diffusion layer include heat conductivity and mechanical strength. Heat generated during operation of the fuel cell should be removed to manage the humidification levels and the system efficiency of the fuel cell.

A typical gas/fluid diffusion layer generally comprises a porous carbonaceous support material, such as carbon fibers woven into a paper or cloth, for conducting electrons to the bipolar plate. The carbon based fibers, typically graphite, are generally conductive, especially in the "in-plane" direction due to their anisotropic shape. A typical gas/fluid diffusion layer carbonaceous support material has a porosity of about 70% due to the spacing of the carbon fibers.

In some instances, the gas/fluid diffusion layer also includes a microporous layer for distributing reactants to the electrode. A traditional microporous layer typically includes of a mixture of binder, such as a PTFE polymer, and carbon-based particles. These materials change the degree of hydrophilicity and the pore size of the gas/fluid diffusion layer. When the mixture is added to a gas/fluid diffusion layer, the conventional polymer material may aid in water distribution and removal within the cell, but also detrimentally reduces porosity of the layer.

It is an object of the present invention to utilize modified carbon products to improve the efficiency of the gas/fluid diffusion layer. There are several approaches in which modified carbon products can be incorporated into a gas/fluid diffusion layer. In one approach, the modified carbon products can be layered onto and/or impregnated into an existing gas/fluid diffusion layer. In another approach, an existing gas/fluid diffusion layer can be chemically modified with a diazonium salt to add surface groups to the gas/fluid diffusion layer. In another approach, a combination of modified carbon products and conventional materials (e.g., polymeric) are used to modify and/or produce a gas/fluid diffusion layer. Any of these approaches can be utilized to tailor the properties of the gas/fluid diffusion layer, such as the porosity, electron conductivity and/or mass transport properties. It will be appreciated that any of these approaches can be

utilized to achieve the desired functionality, either alone, or in combination with the other approaches, and either in series or in parallel. It will be also appreciated that more than one type of modified carbon product can be utilized. In one embodiment, modified carbon products have two or more different functional groups on the same carbon particle, as described above. In another embodiment, modified carbon products having varying concentrations of surface groups are utilized to produce the desired functionality, such as gradients within the gas/fluid diffusion layer.

10 ***Layering of Modified Carbon Products***

According to one embodiment of the present invention, modified carbon products are applied to the surface of the gas/fluid diffusion layer to produce a microporous layer. While the below described aspects and embodiments are described as being applied to only a single side of the gas/fluid diffusion layer, it will be appreciated that modified carbon products can be added to both sides of the gas/fluid diffusion layer to achieve desired effects.

In a particular aspect, modified carbon products are added to the electrode side of the gas/fluid diffusion layer to produce a microporous layer having tailored hydrophobic and/or hydrophilic properties and porosity. In this aspect, modified carbon products utilizing hydrophobic and/or hydrophilic surface groups, such as those including hydrophilic and/or hydrophobic functional groups, can be utilized to manufacture a microporous layer by any of a variety of techniques, as described in a further detail below. In a preferred embodiment, the microporous layer comprises hydrophobic modified carbon products to increase the mass transport of water out of the fuel cell. In another embodiment, hydrophilic and/or a mixture of and/or a gradient of hydrophobic and hydrophilic modified carbon products are used to complete the microporous layer. Preferred hydrophobic functional groups according to this aspect are provided in Table I, and preferred hydrophilic functional groups according to this aspect are provided in Table II.

30 In one embodiment, the modified carbon products include a hydrophobic functional group. Such modified carbon products can be incorporated into a non-polar solution, such as a solution comprising PTFE. The resultant solution can be utilized to manufacture a microporous layer by any of a variety of techniques, as described in further detail below, having tailored hydrophobic and/or

hydrophilic properties. The manufactured microporous layer will generally comprise a significant less amounts of conventional hydrophobic ionomer, resulting in increased porosity of the gas/fluid diffusion layer.

In another embodiment, the modified carbon products include a hydrophilic functional group. Such modified carbon products can be incorporated into a polar solution, such as a solution comprising PFSA. The resultant solution can be utilized to manufacture a microporous layer by any of a variety of techniques, having tailored hydrophilic and/or hydrophobic properties. The manufactured microporous layer will comprise less conventional hydrophilic ionomer, resulting in an increased porosity of the gas/fluid diffusion layer.

In yet another embodiment, as illustrated in Fig. 18, modified carbon products 1824 are utilized to produce a microporous layer 1809 without the addition of any conventional polymeric materials. Such modified carbon products 1824 may include a surface group exhibiting hydrophilic and/or hydrophobic properties, such as one including a hydrophilic and/or hydrophobic functional group (Y), as applicable, to tailor the properties of the microporous layer for transport of reactants and/or products. The microporous layer 1809 is substantially more porous than traditional microporous layers using conventional polymeric additives.

The porosity of the gas/fluid diffusion layer may also be controlled by utilizing well-controlled modified carbon products having a small average particle size and/or a narrow particle size distribution. Small particle size enables the formation of dense and thin microporous layers with small pore sizes. In one embodiment of the present invention, microporous layers having a pore size in a range of 100 nm to 500 nm can be produced utilizing modified carbon products. In one embodiment, the microporous layers have a thickness of from about 2 μm to 20 μm , more preferably from about 4 μm to about 12 μm . In one embodiment, modified carbon products are utilized in conjunction with conventional polymeric materials to create a gas/fluid diffusion layer having tailor porosity and/or hydrophobic/hydrophilic properties. In a particular embodiment, modified carbon products are mixed in with hydrophobic ionomer solution to create a modified carbon ink, which may then be deposited to produce a microporous layer having tailored porosity and hydrophobic properties.

In any of the foregoing embodiments, the modified carbon products may include more than one surface group attached to the surface thereof to produce the modified microporous layer. For example, a modified carbon product including both hydrophilic and hydrophobic functional groups can be dispersed in an aqueous solution. The solution may then be deposited on the surface of the gas/fluid diffusion layer to produce a microporous layer having reduced pore size and an intimate mixture of hydrophilic and hydrophobic domains.

Impregnating The Gas/Fluid Diffusion Layer With Modified Carbon Products

As noted above, gas/fluid diffusion layers are often made of porous carbon papers or cloths. According to another aspect of the present invention, modified carbon products are utilized to change the hydrophilic, hydrophobic and/or permeability properties of the gas/fluid diffusion layer by impregnation of the modified carbon products into the internal pores of the gas/fluid diffusion layer. Modifying the properties of the gas/fluid diffusion layer by impregnation may eliminate the need for a microporous layer, which has many advantages, including reduced costs, fabrication time, and the elimination of handling and manufacture procedures associated with the microporous layer.

Gas/fluid diffusion layers generally have pore sizes of from 10 to 30 μm . In one embodiment of the present invention, modified carbon product particles having an average particle size of not greater than about 30 μm , such as from about 1 μm to 30 μm are utilized to impregnate a gas/fluid diffusion layer. In another embodiment, the solids loading of the modified carbon products in the gas/fluid diffusion layer is preferably from about 5 vol. % to 70 vol. %.

Fig. 19 illustrates an embodiment of the present invention where modified carbon products 1924 are impregnated into a porous gas/fluid diffusion layer 1908. The gas/fluid diffusion layer 1908 may be impregnated by a variety of techniques. In one embodiment, the gas/fluid diffusion layer is impregnated by depositing modified carbon products 1924 on the surface of the gas/fluid diffusion layer 1908, such as by ink-jet deposition, as described below, followed by filtering the deposited modified carbon products through the gas/fluid diffusion layer, such as by vacuum filtration.

In another embodiment, modified carbon products are impregnated into the gas/fluid diffusion layer during the manufacturing process of the gas/fluid

diffusion layer. With respect to the manufacture of carbon papers, typical manufacturing processes entail extruding and pressing the papers through a series of rollers, which expose the paper to various aqueous and/or non-aqueous solutions. In this embodiment, a modified carbon product can be dispersed in
5 any of the various aqueous and/or non-aqueous solutions. As the paper is manufactured, the modified carbon product is impregnated into the porous paper structure.

In yet another embodiment, the incorporated (e.g., layered or impregnated) modified carbon products comprise surface groups that undergo
10 further reactions, such as polymerization or thermal decomposition. For example, a gas/fluid diffusion layer may incorporate a modified carbon product having a carboxylate functional group. As the gas/fluid diffusion layer is heated, such as in a subsequent step, the hydrophilic CO_2H will decompose into a hydrophobic phenyl group.

15

Modification Of Carbonaceous Materials In The Gas/Fluid Diffusion Layer

Another aspect of the present invention is directed to the modification of the gas/fluid diffusion layer with surface groups, such as modification of the carbonaceous support structure (e.g., the carbon paper and/or carbon cloth), or
20 other carbonaceous materials contained therein, such as previously deposited and/or impregnated carbon materials and/or modified carbon products.

As described above, the gas/fluid diffusion layer generally comprises carbonaceous materials, such as carbon paper and/or carbon cloth. In one approach, these carbonaceous materials are modified by means of a diazonium
25 salt to covalently attach an organic group thereto, such as any of the above described organic surface groups. In another approach, non-modified carbon materials and/or modified carbon products may be layered and/or impregnated onto to a diffusion layer, as described above. Such non-modified materials and/or modified carbon products can be subsequently modified with a diazonium
30 salt to create modified carbon products and/or multiply-modified carbon products. A modified gas/fluid diffusion layer resulting from such a treatment is schematically illustrated in Fig. 20, where (Y) is a functional group attached to a carbon material 2020.

In one embodiment, the gas/fluid diffusion layer is immersed into a solution containing a diazonium salt. In another embodiment, the gas/fluid diffusion layer is contacted with a diazonium salt by means of an analog and/or digital printing technique. As will be appreciated, use of a digital printing enables the production of discrete patterns of surface groups on the gas/fluid diffusion layer, as described in further detail below.

By way of illustration, a solution including a carbon material, such as carbon black, can be deposited onto the surface of the gas/fluid diffusion layer, such as by screen printing. The gas/fluid diffusion layer can then be dried and treated with a diazonium salt, such as by spraying a diazonium salt-containing solution onto the gas/fluid diffusion layer. The resultant gas/fluid diffusion layer will comprise a microporous layer having surface groups attached thereto, and may evidence hydrophobic or hydrophilic properties.

As noted above, the modified carbon products can be used to control the hydrophilic/hydrophobic characteristics of the gas/fluid diffusion layer. Modified carbon products can also be used to tailor the pore size of the gas/fluid distribution layer to facilitate selective mass transport therein, such as by enabling a uniform gas/fluid distribution to the electrode. In one embodiment, the modified carbon products comprise steric inhibiting functional groups, such as polymeric groups. The characteristics of the steric inhibiting groups, such as length and branch quality can be selected to tailor the mass transport characteristics of the gas/fluid diffusion layer.

It will be appreciated, that both hydrophilic/hydrophobic functional groups and steric surface groups can be utilized to tailor the gas/fluid diffusion layer. In one embodiment, both the hydrophilic/hydrophobic and steric groups are added in a single step, such as by immersing the gas/fluid diffusion layer in a solution comprising diazonium salts corresponding to two or more functional groups. Thus, it is possible in one chemical treatment to tailor both the hydrophilic and/or hydrophilic nature and porosity of the gas/fluid diffusion layer.

In another embodiment, two different surface groups can be added to separate portions of the gas/fluid diffusion layer. For example, the gas/fluid diffusion layer can be placed in contact with a diazonium salt solution having a low concentration of a first surface group, such as one having a hydrophilic functional group. In a subsequent step, a solution comprising a modified carbon

product or a diazonium salt can be deposited onto one side or a portion of the gas/fluid diffusion layer. This embodiment enables a gradient to form within the gas/fluid diffusion layer, where hydrophilic pores exist in the interior and the surface is predominately hydrophobic. It will be appreciated that this order can
5 be reversed, where the interior is hydrophobic and the surface is hydrophilic.

In one embodiment, a solution comprising a modified carbon product or a diazonium salt is deposited in a discrete pattern on the gas/fluid diffusion layer to produce one or more discrete patterns of surface groups on the gas/fluid diffusion layer. In this regard, such patterns may be hydrophilic and/or hydrophobic to
10 influence the movement of reactants through the gas/fluid diffusion layer, as schematically shown in Fig. 21. As depicted, a first diazonium salt contacts the gas/fluid diffusion layer, 2108, and then a second diazonium salt contacts the gas/fluid diffusion layer. In one preferred embodiment, the deposited patterns definable a path for water removal through the gas/fluid diffusion layer.

15

Gradients

According to another aspect of the present invention, modified carbon products are patterned on the gas/fluid diffusion layer to produce lateral gradients or in-plane gradients to vary the hydrophilic/hydrophobic properties and/or fluid
20 permeability of the gas/fluid diffusion layer. In one approach, modified carbon products are deposited utilizing an analog and/or digital printing means, as discussed in further detail below, to produce the gradients. This aspect is useful, for example, to form defined water wicking and fluid distribution paths, which reduces the likelihood of water clogging in the gas/fluid diffusion layer and
25 enables reactants to quickly reach the electrode, thereby increasing fuel cell performance, especially at high currents.

In one embodiment, multiple layers of modified carbon products are deposited to produce through-plane gradients. These gradient structures can transition from very hydrophilic to hydrophobic, or vice versa, moving from one
30 side of the gas/fluid diffusion layer to the other.

According to another embodiment, through-plane gradient structures are fabricated by surface treatment of the native gas/fluid diffusion layers with a diazonium salt, or surface treatment of a deposited carbonaceous particulate layer by a diazonium salt, as illustrated in Fig. 22. By way of illustration, the

gas/fluid diffusion layer can be chemically modified with a sulfonic diazonium salt to attach hydrophilic surface groups (X). Subsequently, a modified carbon product including a slightly less hydrophilic functional group (Y), such as a carboxylic group, can be deposited on the hydrophilic gas/fluid diffusion layer to
5 form a less hydrophilic first layer. A final modified carbon product including a hydrophobic functional group (Z), can be deposited on the first layer to produce a hydrophobic layer. The resultant gas/fluid diffusion layer will have a through-plane gradient with respect to hydrophobic / hydrophilic properties.

According to another embodiment, the gradient structure, either in-plane or
10 through-plane, includes different layers of modified carbon products where the modified carbon products include the same surface group, but in varying concentrations.

In yet another embodiment, various layers are deposited on the gas/fluid diffusion layer, where the various layers each utilize modified carbon products
15 having one or more surface groups, where the ratios of the surface groups change from layer to layer to tailor the nature of gas/fluid diffusion layer.

By way of example, the first layer of the gas/fluid diffusion layer can be the carbonaceous support material, such as a carbon paper or a carbon cloth. A second layer can be deposited on the carbon support, where the second layer
20 includes a modified carbon product containing two surface groups, such as a hydrophobic surface group and a hydrophilic surface group, where the ratio of the hydrophobic surface group to the hydrophilic surface group is relatively high, such as about 4:1. A third layer can be produced on the second layer, where the third layer comprises modified carbon products having hydrophobic surface
25 groups and hydrophilic surface groups, where the ratio of hydrophobic surface groups to hydrophilic surface groups is less than that of the second layer, such as about 3:2. A fourth layer can be produced on the third layer, where the fourth layer comprises modified carbon products comprising hydrophobic surface
30 groups and hydrophilic surface groups, where the ratio of hydrophobic surface groups to hydrophilic surface groups is even less than that of the third layer, such as 2:3. A top layer can be produced on the fourth layer, where the top layer comprises modified carbon products comprising only hydrophilic surface groups or hydrophobic surface groups and hydrophilic surface groups, where the ratio of

hydrophobic surface groups to hydrophilic surface groups is even less than that of the third layer, such as 1:4, or even higher.

According to another embodiment of the present invention, through-plane gradient structures can be produced by utilizing different types of modified carbon products (e.g., one modified with a hydrophilic group and one modified with a hydrophobic group). The ratios of the different modified carbon products can be varied from layer to layer to achieve a gradient structure.

It will be appreciated, that the layers can be produced such that the most hydrophilic layer is on the electrode side and the most hydrophobic layer is near the bipolar plates of the gas/fluid diffusion layer, or vice versa. In one particular embodiment, a hydrophilic layer is produced on the electrode side of the gas/fluid diffusion layer in the cathode.

Pore Size

According to another aspect of the present invention, modified carbon products are utilized to tailor the porosity of the gas/fluid diffusion layer. In this regard, the steric bulk of the surface groups may be utilized to control (decrease) the average pore size and pore size distribution within the gas/fluid diffusion layer, resulting in more uniform fluid distribution during operation of the cell. Long chain polymeric surface groups clog internal pores, and optionally can provide hydrophilic or hydrophobic and binding functionality within the layer. In one embodiment, modified carbon products having polymeric surface groups are utilized to enhance the porosity of the gas/fluid diffusion layer. Particularly preferred long-chained groups, according to the present aspect include the polymeric functional groups listed in Table IV, above. It will be appreciated that the modified carbon products having polymeric surface groups can be incorporated into a gas/fluid diffusion layer by any useful means, including layering and/or impregnating.

By way of example, modified carbon products having a polymeric surface group attached thereto, such as PEG, can be suspended in a solvent. A second modified carbon product having a hydrophilic surface group, such as one including a sulfuric functional group, can also be suspended in the solvent. The resultant modified carbon solvent solution can be deposited on the gas/fluid

diffusion layer and dried to produce enhanced porosity and hydrophilicity within the gas/fluid diffusion layer.

Electrical Conductivity

5 The gas/fluid diffusion layer should also be relatively electrically conductive to conduct electrons to the bipolar plate. In one embodiment of the present invention, modified carbon products having an electrically conductive carbon are utilized in the production of the gas/fluid diffusion layer. In a particular embodiment, a microporous layer is manufactured utilizing a modified carbon
10 product based on graphite to increase its conductivity. Since graphite materials are typically hydrophobic, a graphite flake can be made hydrophilic by adding a hydrophilic group, such as a sulfuric group, to the surface of the graphite. The graphite-containing modified carbon product can then be deposited on to a gas/fluid diffusion layer to make an electrically conductive and/or hydrophilic
15 microporous layer.

Other Features of Modified Carbon Products in Gas/fluid diffusion Layers

Carbon oxidation is a significant issue in fuel cells. Carbon within the gas/fluid diffusion layer can oxidize, which decreases the conductivity of the
20 gas/fluid diffusion layer and its corresponding hydrophobic nature. Traditionally, control over oxidation has been difficult since many highly crystalline, oxidation resistant carbon materials, such as graphite, have been difficult to utilize in fuel cell components as there was no easy method for incorporating such products into the fuel cell. As noted, conventional graphite materials are very hydrophobic
25 and difficult to disperse in aqueous-based solutions. Thus, it was difficult to efficiently and effectively utilize such materials in spraying, immersion and other deposition techniques known in the production of fuel cells.

According to one embodiment of the present invention, carbon oxidation within the fuel cell is reduced/minimized by utilizing modified carbon products
30 having a high crystallinity carbon, such as graphite, and a hydrophilic surface group. Utilizing a modified carbon product based on graphite and hydrophilic surface groups enables the graphite to be more readily dispersed in an aqueous solution. Thus, aqueous solutions, such as a modified carbon ink, as discussed below, can be utilized to produce fuel cell components, such as gas/fluid diffusion

layers, that include graphite. Such a modified carbon product can be utilized in the production of a gas/fluid diffusion layer to increase the oxidation resistance of the gas/fluid diffusion layer. In another aspect, carbon oxidation is controlled by increasing the amount of surface groups attached to the surface of the carbon material.

Another issue associated with the gas/fluid diffusion layer, and more specifically gas/fluid diffusion layers including a microporous layer, is cracking. Cracking is an issue because it inhibits even fluid distribution through the gas/fluid diffusion layer. If cracks are present in the gas/fluid diffusion layer, the incoming fluids may flow through the cracks (following the path of least resistance), which may prohibit/eliminate their transport to the active catalytic sites in the electrode layer. Typically, cracks occur when drying rates are too fast and/or are not uniform.

Thus, according to one aspect of the present invention, modified carbon products are utilized in the gas/fluid diffusion layer to reduce or substantially eliminate cracking. In one approach, cracking is controlled / eliminated by adjusting the hydrophilic or hydrophobic nature of the modified carbon product to slow the drying process during layer formation, such as by selecting a modified carbon product having miscibility characteristics that coincide with the solvent utilized to form the microporous layer. Such an approach is depicted in Fig. 23, as compared to a normal drying process. A normal drying process, such as depicted in Fig. 23(a), using standard products may result in cracks and/or a disconnected surface. Conversely, utilizing modified carbon products to create a layer, as shown in Fig., 23(b), for example, such as those including a long chain polymeric groups and or surface groups that have miscibility characteristics that coincide with the solvent used to produce the layer, results in a greater retention period of the liquid solvent, and, thus, a more uniform surface with minimal surface cracks. Another way to increase solvent retention time is by increasing the solids loading of the modified carbon products in the modified carbon ink. In one preferred embodiment, the modified carbon ink has a solids loading of up to about 70 wt.%. Increased solids loading of modified carbon produced results in more uniform drying and less volume fraction of solvents being removed during drying process.

For example, a modified carbon product including a hydrophilic surface group, such one having a sulfuric functional group, can be used in an aqueous-based solvent system. Use of a hydrophilic surface group in an aqueous-based solvent system slows water evaporation due to the hydrogen bonding between the water molecules and the hydrophilic group. Similarly, using a modified carbon product having a non-polar surface group in an organic solvent will also slow evaporation of the organic solvent.

In another approach, modified carbon products including a long chain polymeric surface groups (e.g., a PEG functional group) are utilized to decrease cracking. Such polymeric surface groups will entangle during concentration/drying. Cracking is thus prevented by the cross-linking between the surface groups and/or the gas/fluid diffusion layer materials. Other surface groups useful in accordance with this embodiment include long chain branched and unbranched alkyls, aryl and polymeric such as PPO, polystyrene, and polyalcohols.

In another embodiment, multipass printing (e.g., printing the microporous layer more than once but over the same area and in series) is used to minimize crack formation. With multipass printing, subsequent prints fill cracks formed from previous drying steps, resulting in a substantially crack-free layer. In one particular embodiment, the last deposited layer of the multiple deposited layers is dried more slowly than the other layers to eliminate non-uniform drying.

In yet another embodiment, relatively thin layers of modified carbon products are deposited to eliminate cracking. Thinner layers generally are more likely to dry without cracks because of the small volume change involved as compared to thicker layers. In a particular embodiment, the deposited layers have a thickness of between 8 and 12 microns, and preferably between 2 and 8 microns.

Another embodiment of the present invention is directed to the use of dry coating techniques, such as dry electrostatic printing, to add modified carbon products to the gas/fluid diffusion layer. This embodiment advantageously eliminates a drying step, which in turn eliminates any mechanism of crack formation. In this embodiment, the surface groups are selected to act as the charge carrier and binder system typically utilized in electrostatic (or xerographic) printing processes. In a particular embodiment, a modified carbon product

including two surface groups is used, such as one having a hydrophilic functional group and another having a polymeric functional group, where the hydrophilic group is utilized for dispersability purposes and the polymeric groups act as both the binder and the charge carrier. It will be appreciated that these specific surface groups can be added to the same or different carbons materials.

Another embodiment of the present invention is directed to the use of modified carbon products as a sorbent/trap for impurities in the reactant steam or corrosion byproducts, such as sulfur, chloride ions or sodium ions. Surface groups, such as those including sulfuric functional groups and carboxylic functional groups, can be utilized to bind chemical species such as sodium ions. In this embodiment, the removal for such chemical species helps minimize poisoning and degradation of the catalyst and proton exchange membrane, which leads to increased MEA lifetime and fuel cell reliability.

Modified Carbon Products and Bipolar Plates

As noted above, the bipolar plates are generally utilized to provide reactants (e.g., fuel and oxidant), remove products (e.g., water) and conduct electrons. In addition, bipolar plates also provide mechanical support for the MEAs, and conduct heat out of the cell. According to the present invention, modified carbon products can be used to tailor the channel structure, hydrophilic/hydrophobic properties, thermal conductivity, electrical conductivity, physical and chemical integrity, structural rigidity and manufacturability of the bipolar plate.

The channel structure of the bipolar plates is typically serpentine in shape and enables the introduction of reactants into the fuel cell stack, directing them to the gas/fluid diffusion layer. In one aspect, modified carbon products are utilized to tailor the properties of the channel structure for efficient transport of the reactants to the gas/fluid diffusion layer, as described in further detail below.

The hydrophilic/hydrophobic properties of the bipolar plate impact water removal, both on the anode and cathode side of the MEA. Water is typically introduced into the fuel cell by humidification of the fuel gas. On the cathode side, the generated water must be removed via the bipolar plate. In one aspect of the present invention, modified carbon products are utilized to tailor the properties of the bipolar plate to efficiently permit introduction of humid and/or

polar fuels at the anode side, while enabling efficient removal of water from the cathode side.

High thermal conductivity is important for removing excess heat generated by the fuel cell stack, which affects fuel cell performance. Accordingly, in one aspect of the present invention, modified carbon products are utilized to enhance the thermal conductivity of the bipolar plate.

Good electrical conductivity is desirable and impacts the ability to supply generated electrons to the external load. In one aspect of the present invention, modified carbon products are utilized to increase and/or maintain the electrical conductivity of the bipolar plate.

Physical and chemical integrity of the bipolar plate is important to control and/or maintain the properties of the bipolar plate over time, such as the hydrophobicity/hydrophilicity, electrical conductivity and structural rigidity of the bipolar plate. In one aspect of the present invention, modified carbon products are utilized to maintain the physical and chemical integrity of the bipolar plate over time.

Structural integrity is important to support adjacent MEAs and the fuel cell stack. In one aspect of the present invention, modified carbon products are used to increase the structural integrity of the bipolar plate. A bipolar plate must be also be reproducible, reliable and relatively low cost to manufacture. Use of modified carbon products in the manufacture of bipolar plates can enable reproducible results and reliability while reducing manufacturing cost.

In accordance with the foregoing, modified carbon products can be utilized in a bipolar plate by: (a) incorporating modified carbon products in compounds used to manufacture the bipolar plate, like a polymer/resin compound; or (b) direct surface modification of a carbonaceous bipolar plate. Such modified carbon products can enhance the properties of the bipolar plates as necessary to achieve the desired effect.

It is common to manufacture bipolar plates by molding or extruding a carbon-filled polymer/resin composite. In one embodiment of the present invention, modified carbon products are used as fillers in the polymer / resin based compound utilized to produce the bipolar plates, as is schematically illustrated in Fig. 24, where a modified carbon product is mixed with a resin compound and then molded into bipolar plate. This approach enables the

impartation of a number of unique attributes to the bipolar plate. It will be appreciated that the term "resin compound" is used for illustrative purposes only, and that any compound utilized in the production of bipolar plates can be utilized in accordance with the present invention

5 According to the present approach, any carbon material that is capable of having a surface group attached to it can be used. In one embodiment, electrically conductive crystalline carbon materials are utilized. In another embodiment, amorphous carbon materials are utilized.

10 In one aspect of the present invention, surface groups that increase the dispersability of the modified carbon product in the resin compound are utilized. Polymers that can be utilized in the fabrication of carbon polymer/resin filled bipolar plates according to the present invention are given in Table VI.

TABLE VI

Examples of Resins Compounds
Polyvinylidenefluoride (PVDF)
Polyphenylene
Polypropylene
Polyphenylene Sulfide
Phenolic Resins
Vinyl Esters

15 Surface groups useful in accordance with this embodiment include those having polymeric groups miscible in the above resin compounds, such as a polymeric functional group and/or a polymeric linking group as listed in Tables III and IV, above. Particularly, preferred surface groups include those having PEG (polyethylene glycol), PEO (polyethylene oxide), PPO (polypropylene oxide) and
20 polystyrene groups.

 Generally, a resin compound becomes very viscous when the solids loading is too high. This complicates downstream processing (e.g., molding or extrusion) of the bipolar plates, as the viscous composite will have difficulty flowing to completely fill the interior of the mold, resulting in a poor "fill-factor".
25 Typically, carbon materials are immiscible in such resin compounds, and, therefore, are unable to be effectively utilized in the production of bipolar plates.

Incorporating modified carbon products in a resin compound according to the present invention can reduce viscosity changes in the resin compound, even at high solids loading. Maintaining viscosity at high solids loading increases the fill-factor in the molding process and simplifies the manufacture of the bipolar plate. Increasing the fill-factor also permits better control over the dimensional tolerances of the bipolar plate, which can enable production of narrower, more closely spaced channels and grooves. According to one aspect of the present invention, solids loading of modified carbon products in a resin compound can be as high as 70 wt.% carbon.

By way of illustration, native carbon blacks have a non-polar surface. A modified carbon product including carbon black and a hydrophilic surface group (e.g., one having a sulfuric functional group) can be dispersed at high loading levels in a polar phenolic resin. The resulting resin containing the modified carbon products will have a low viscosity as compared to a similar resin incorporating non-modified carbon black.

In another aspect of the present invention, the viscosity of the resin compound can be controlled by utilizing well-controlled modified carbon product particles and size distributions, such as controlled modified carbon product particle shapes (e.g., spherical) and size distributions. It is often important to tailor the particle size of a filler to maximize solids loading and reduce viscosity. In one embodiment, spray-processing methods are utilized to produce spherical, non-agglomerated carbon-based particulates, which may be subsequently utilized in native (non-modified) form or as modified carbon product particles in a resin compound to produce a bipolar plate. One particular embodiment in this regard is illustrated in Fig. 24, where a modified carbon product is mixed with a resin compound, which is subsequently molded to create a surface modified bipolar plate.

By way of illustration, a modified carbon product (e.g., a carbon black including a hydrophilic surface group) can be processed by spray processing to make spherical aggregate modified carbon product particles having a narrow and monomodal particle size distribution (e.g., 2 μm). This modified carbon black product particles can be added to a phenolic resin, and the resulting resin can be molded and cured to form a bipolar plate.

Native carbon fibers are also generally hydrophobic. In another example, a modified carbon product including a hydrophilic surface group attached to the carbon fiber can be dispersed at high loading levels into a phenolic resin. In this regard, because the fibers are anisotropic, they will tend to overlap one another in the bipolar plate, leading to a well-defined electron conduction path as illustrated in Fig. 25.

It will be appreciated that modified carbon products can be utilized in a resin compound to increase solids loading, by themselves or in the presence of other, non-modified carbon material, to produce resin compound filler blends having controlled particle size distribution, and mono-, bi- and/or tri-modal particle size distributions.

By way of illustration, a modified carbon product (e.g., a carbon black including a hydrophilic surface group) can be processed through a spray-pyrolysis reactor to make spherical aggregate modified carbon product particles having a narrow and monomodal particle size distribution ($2\ \mu\text{m}$). This modified carbon black product can be added to a graphite powder in a phenolic resin, and the resulting mixture can be molded and cured to form a bipolar plate.

In another embodiment, modified carbon products are utilized in a resin compound to maintain and/or increase the structural integrity of the bipolar plates. Traditionally, high solids loading in a resin compound not only increases viscosity, as described above, but the resultant bipolar plate is generally more brittle and fragile. The use of modified carbon products in conjunction with a resin compound according to the present invention can advantageously enhance the physical and chemical properties of the bipolar plates to decrease their brittleness and fragileness.

According to a preferred embodiment of the present invention, modified carbon products having surface groups that can chemically or physically bond to the resin itself, such as hydrophilic and/or long-chained polymeric functional and/or linking groups, are utilized to increase the mechanical strength of the bipolar plates.

By way of illustration, a modified carbon product, such as modified carbon black including a polymeric surface group, such as PEG, can be mixed into a polar resin compound, such as a phenolic resin. A bipolar plate manufactured using the modified carbon product-containing resin compound will evidence an

increased mechanical strength due to chemical effects (e.g., hydrogen bonding) and/or physical interactions of the surface group with the resin (e.g., physically intertwinement of the surface group with the resin material).

In yet another approach, modified carbon products including hydrophilic and/or hydrophobic surface groups are utilized to tailor mass transport properties of the bipolar plate. Generally, the bipolar plate is a porous carbonaceous product exhibiting hydrophobic properties. Utilizing modified carbon products according to the present invention, bipolar plates can be manufactured having selectively tailored properties to facilitate transport of reactants and products to and from the electrodes of the fuel cell.

In one embodiment, modified carbon products including a hydrophilic group are utilized in a bipolar plate to increase its hydrophilic properties. Water can be attracted into the pores of the bipolar plate through use of a hydrophilic modified carbon product as a means of extracting the water from the MEAs and the fuel cell stack on the cathode side. Advantageously, the retention of water in the porous bipolar plate also forms a wet seal, thereby substantially preventing reactant and/or product gases from traveling through the bipolar plate.

According to another embodiment, modified carbon products are utilized to change the surface properties of the bipolar plate. When a bipolar plate is manufactured with a resin compound including relatively low amounts of solids, the nature of the bipolar plate surface will be dominated by the properties of the polymer/resin. Generally, as the amount of solids in the resin compound increases a larger percentage of solids will reside at the surface of the bipolar plate. Hence, the hydrophilic and/or hydrophobic properties of the bipolar plate surface can be controlled by increasing or decreasing the amount of modified carbon product in the resin compound.

In one particular embodiment, the modified carbon product includes a hydrophilic surface group and this modified carbon product is incorporated into a resin compound. In a particularly preferred embodiment, the solids loading of the modified carbon product in the resin compound is from about 50 weight percent to about 85 weight percent. In such a case, the hydrophilic properties of the surface of the bipolar plate will be increased. In a particularly preferred embodiment, the modified carbon product includes a graphite material having a hydrophilic surface group.

In yet another embodiment, the modified carbon products include surface groups that facilitate deposition and adhesion to the bipolar plate. For example, a modified carbon product may include both hydrophilic surface groups and a surface group having a polymeric functional and/or linking group. Utilizing the hydrophilic surface group enables the modified carbon product to be more easily dispersed in an aqueous solvent, and, in some instances, tailors the properties of the bipolar plate after deposition. Utilizing the polymeric groups promotes adhesion of the modified carbon product to the bipolar plate by promoting physical and/or chemical interaction with other materials of the bipolar plate. Adhesion to the bipolar plate surface can be further promoted by heating the deposited modified carbon products to intertwine the polymeric groups with the resin utilized in the production of the bipolar plate. Methods for depositing modified carbon products on bipolar plates include analog and digital printing methods, as discussed in further detail below.

In yet another embodiment, a modified carbon product including both a hydrophilic surface group (e.g., one including a sulfuric, carboxylic, or amine functional group) and a long-chained surface group (e.g., one including a polymeric group such as PEG, PPO, and/or PEO group) is utilized in the production of a bipolar plate. In this regard, the hydrophilic properties of the plate can be tailored utilizing the hydrophilic surface groups, as described above, while also increasing the mechanical strength of the bipolar plate.

In another embodiment of the present invention, modified carbon products utilized in a resin compound can be post-processed (e.g., subjected to heat and/or pressure treatment) to make a composite modified carbon-resin composite product. This composite can subsequently be used to produce a bipolar plate, such as by casting and molding.

Gradients

In another approach, modified carbon products are utilized to form gradient structures in the bipolar plates, such as through-plane and/or in-plane gradients. These gradient structures can be produced by layering or molding the parts in a distinct order using varying concentrations of the modified carbon products and/or by utilizing different modified carbon products in the resin compound.

In one embodiment, modified carbon products are utilized to form a hydrophilic and/or hydrophobic gradient in the bipolar plate structure, either in the through-plane or the in-plane. For example, a modified carbon product having a first surface group can be utilized in a first resin compound to create a first portion of the bipolar plate. A modified carbon product having a second surface group can be utilized in the first resin compound and/or a separate second resin compound to create a second portion of the bipolar plate. In a particularly preferred embodiment, the first surface group is a hydrophobic surface group, and the second surface group is a hydrophilic surface group. In another particularly preferred embodiment, the modified carbon product includes graphite. Graphite is preferred due to its conductive nature and its ability to fuse to adjacent layers.

In another embodiment, modified carbon products are deposited on pre-existing bipolar plates to form gradient structures. In this regard, modified carbon products varying in concentration and/or attached surface groups can be utilized in the deposition to create gradient structures in the through-plane. For example, a modified carbon product having a first surface group can be deposited on a first portion of a bipolar plate. A modified carbon product having a second surface group can be deposited on a second portion of the bipolar plate and/or the first deposited portion. In a particularly preferred embodiment, the first surface group is a hydrophobic surface group, and the second surface group is a hydrophilic surface group. In another particularly preferred embodiment, the modified carbon product includes graphite.

In another embodiment, in-plane gradients can be produced utilizing modified carbon products. For example, modified carbon products can be deposited on the channels and/or ribs of the bipolar plate to create gradients thereon. In a particular embodiment, modified carbon products including hydrophilic surface groups are deposited into channels of the bipolar plate. Modified carbon products including hydrophobic surface groups may also be deposited into other channels of the bipolar plate. Thus, the channels of the bipolar plate can be selectively tailored to enhance the transport of reactants/product by deposition of modified carbon products having properties suited for the transport of the desired reactants/product. Advantageously, a selective wet seal can be formed, where the hydrophilic areas are substantially

impermeable to gases due to the presence of water, and the hydrophobic areas are more permeable to gases due to the absence of water.

Direct Surface Modification of the Bipolar Plate

5 Aside from utilizing modified carbon products to tailor the properties of bipolar plates, a diazonium salt can also be used to directly surface modify a carbonaceous material within the bipolar plate. As noted, bipolar plates generally include a non-trivial amount of carbonaceous material to increase the electron conductivity of its structure. In many instances, the bipolar plate includes
10 graphite.

 According to one aspect of the present invention, the carbonaceous materials within the bipolar plate are directly surface modified utilizing a diazonium salt. Direct surface modification of the bipolar plate is beneficial as it is an inexpensive and simple means of modifying the properties of the bipolar
15 plate, such as its hydrophilic properties and permeability.

 One embodiment of this aspect is illustrated in Fig. 26, where the surface of the bipolar plate is contacted by a diazonium salt, such as by immersion. Another embodiment of this aspect is illustrated in Figs. 27 and 28, where only a portion of the bipolar plate surface is modified with a surface group, such as by
20 utilizing a mask (Fig. 27), discussed in further detail below, or a direct-write tool (Fig. 28), discussed in further detail below.

 In one embodiment, a mask/barrier is utilized on the surface of the bipolar plate to prevent attachment of surface groups. The mask/barrier can be applied by, for example, deposition of a film (e.g., a UV curable polymer) that is inert to
25 chemical attachment. Subsequently, a diazonium salt can be contacted with a surface of the bipolar plate, such that surface groups attach to the exposed carbon surfaces. Subsequently, the mask/barrier can be physically and/or chemically removed (e.g., stripped by acids) resulting in a patterned bipolar plate. This method is useful when analog printing methods, such as dip coating, doctor
30 blading or brushing/painting are used.

 In another embodiment, a solution comprising a diazonium salt can be selectively deposited onto discrete portions of the bipolar plate to produce a patterned bipolar plate surface and/or to tailor specific components of the bipolar plate. For example, a digital printing method, such as direct-write

deposition, can be utilized to deposit an ink solution comprising a diazonium salt onto select portions of the bipolar plate surface, such as the channels and/or ribs of the bipolar plate.

In a particularly preferred embodiment, one portion of the bipolar plate is contacted by a first diazonium salt, and a second portion of the bipolar plate is contacted by a second diazonium salt, thereby resulting in different surface groups attached to discrete surfaces of the bipolar plate. For example, a hydrophilic diazonium salt can be deposited into the channels of the bipolar plate to make them hydrophilic. A hydrophobic diazonium salt can be deposited onto the ribs of the bipolar plate to make them hydrophobic. The resultant bipolar plate thus includes a gradient water pathway to enable rapid water removal.

As noted above, analog methods for depositing diazonium salts generally require the use of the mask to produce a discrete pattern on the surface of the bipolar plate. Digital printing methods generally do not require such a mask, and, therefore, are preferred in many applications requiring the creation of discrete patterns on the bipolar plate surface.

In another embodiment, the bipolar plate surface is modified to enable water retention over long periods of time, in some instances even in relatively dry conditions. Long-term retention of water, such as on the anode side of the fuel cell, enables the fuel cell to begin operating from a "dry" start, thereby obviating and/or minimizing the need for external water at the anode. In this regard, the surface of the bipolar plate can be modified with very hydrophilic surface groups. Additionally, the concentration of hydrophilic surface groups on the surface of the bipolar plate can be increased. Deposition of a diazonium salt onto the surface of the bipolar plate by any of the above-mentioned methods can be utilized in this regard.

It will be appreciated, with respect to the above approaches, aspects and embodiments, that the diazonium salt can be any salt that will enable the formation of appropriate surface group(s) to tailor the properties of bipolar plate. Surface groups including hydrophobic and/or hydrophilic functional groups and/or including a polymeric functional and/or linking group are often preferred. Particularly preferred hydrophilic, hydrophobic and polymeric functional and linking groups are provided above in Tables II, III, IV and V. For example, the bipolar plate can be contacted by a hydrophobic diazonium salt, such as a fluoric

salt, to produce hydrophobic surface groups on the bipolar plate surface. The bipolar plate may also or alternatively be contacted by a hydrophilic diazonium salt, such as a sulfuric salt, to produce hydrophilic surface groups on the bipolar plate surface.

5 The bipolar plate may also or alternatively be contacted by an ionic diazonium salt, such as a sodic and/or potassic salt to produce ionic surface groups on the bipolar plate surface. The bipolar plate also can be contacted by a diazonium salt that will produce an inert surface on the bipolar plate. Inert surface groups useful in this regard include C_5H_4N , $(C_6H_4)NH_2$, C_6H_5 , $C_{10}H_7$ and
10 $(C_6H_4)CF_3$. It will be appreciated, that the bipolar plate can be contacted with one or more diazonium salts, and for various times to partially or fully modify the bipolar plate surface with one or more surface groups.

Other Features

15 Metal foams are often utilized in bipolar plates and generally have a hydrophobic nature. According to one embodiment of the present invention, modified carbon products are impregnated into the pores of the metal foams to increase the hydrophilic properties of the bipolar plates. For example, a modified carbon product including a hydrophilic surface group can be mixed into a resin
20 compound, such as an acrylic polymer, and the modified carbon-containing resin compound can be contacted with a metallic foam. Upon extraction and curing, the resin compound will adhere to the metallic structure, and the modified carbon products contained therein will modify the hydrophilic properties of the metal foam. In this regard, it should be noted that the above described dispersability
25 properties of the modified carbon products are useful in this embodiment, as higher solids loading results in a higher degree of hydrophilic properties being imparted to the metal foam.

 In yet another embodiment of the present invention, the surface groups of a modified carbon product and/or the surface groups attached to the bipolar plate
30 undergo subsequent reactions, such as during a curing step. For example, a surface group can be selected that will decompose or partially decompose at selected temperatures, such as temperatures used to cure the resin compound. By way of illustration, a carboxylic functional group is slightly hydrophilic.

However, at sufficient temperatures the carboxyl group will decompose to a phenyl group, which is slightly hydrophobic.

Deposition of Modified Carbon Products and/or Diazonium Salts

5 Use of modified carbon products and/or diazonium salts to produce and/or modify the properties of the various fuel cell components has been described above. Specific techniques for manufacturing such fuel cell components utilizing inks including such modified carbon products and/or diazonium salts are now discussed.

10 The cost of fuel cells is one of the most significant issues facing their successful widespread commercialization and membranes constitute a significant cost of the MEA. For these reasons, alternative processing and manufacturing scenarios to reduce the cost of the membrane in the MEA are desirable.

15 In one aspect of the present invention, deposition of a modified carbon ink and/or an electrocatalyst ink can be utilized to produce and/or modify the various components of the fuel cell. As used herein a "modified carbon ink" refers to any liquid phase solution, such as an ink, resin or paste, that contains one or more of the above-described modified carbon products and includes the subclass of modified electrocatalyst products. As used herein "electrocatalyst inks" refers to
20 a liquid phase solution, such as an ink, resin or paste, that contains one or more of the above-described electrocatalyst materials.

 Various aspects, approaches, and/or embodiments of the present invention are described below, primarily in reference to modified carbon inks. However, it will be appreciated that electrocatalyst inks can be utilized in
25 conjunction with a modified carbon ink in some of such aspects, approaches and/or embodiments, where appropriate, although not specifically mentioned, and the use of such electrocatalyst inks in such aspects, approaches and/or embodiments is expressly within the scope and spirit of the present invention.

 In a particular embodiment, deposition of a modified carbon ink and/or an
30 electrocatalyst ink can be utilized to produce and/or modify a proton exchange membrane. In another particular embodiment, deposition of a modified carbon ink and/or an electrocatalyst ink can be utilized to produce and/or modify a gas/fluid diffusion layer, such as a gas/fluid diffusion layer. In yet another particular embodiment, deposition of a modified carbon ink and/or electrocatalyst

ink can be utilized to produce and/or modify the electrodes and/or the electrocatalyst layers. In another particular embodiment, deposition of a modified carbon ink can be utilized to modify the bipolar plates.

5 The incorporation of modified carbon products in a modified carbon ink significantly improves ink uniformity, homogeneity, ease of manufacture and ease of use. Various methods and mixing techniques are currently utilized to improve the properties of inks that include electrocatalysts, carbons and polymer solutions (e.g., PFSA or PTFE) and combinations thereof, such as ball milling and sonication. The incorporation of modified carbon products having surface groups
10 that coincide with the solubility requirements of the ink they are dispersed in significantly simplifies ink preparation. As a result, the homogeneity and uniformity of the inks, and hence the homogeneity of the deposited layer/feature may be increased. Homogenous deposition enables control over the concentration and drying rate of the materials being deposited. For example, a
15 modified carbon product having hydrophilic surface groups simplifies dispersion of carbon-based materials in aqueous-based inks due to increased wetting and dispersability of the modified carbon product. Other surface modifications can be chosen to improve the wettability and dispersability of modified carbon products when organic solutions are used.

20 In one embodiment of the present invention, modified carbon products are utilized in a PFSA solution and/or a PTFE suspension to create a modified carbon ink, where the aggregate size of the modified carbon product particles is not larger than the size of the largest particle within the ink.

In a particular embodiment, a modified carbon product having two different
25 surface groups (e.g. a hydrophilic and a hydrophobic group) is utilized in a PFSA solution and/or PTFE suspension to create a modified carbon ink, where the aggregate size of the modified carbon products is not larger than the size of the largest particle within the ink.

Deposition of modified carbon inks and/or electrocatalyst inks preferably
30 produce and/or modify the fuel cell components to enhance one or more attributes. For example, modified carbon inks and/or an electrocatalyst ink utilized in the production of and/or modification of a PEM may enhance proton conductivity, physical separation, and/or electrical insulation, after deposition and/or post-processing. Modified carbon inks and/or electrocatalyst inks utilized

in the production of and/or modification of the electrodes / electrocatalyst layers may enhance catalytic activity, proton electrical conductivity and/or adequate porosity after deposition and/or post-processing. Modified carbon inks utilized in the production of and/or modification of gas/fluid diffusion layers may enhance
5 electrical conductivity, proton conductivity and physical separation after deposition and/or post-processing. Modified carbon inks utilized in the modification of bipolar plates may enhance liquid and/or gas transport, such as by tailoring the hydrophilic / hydrophobic properties of the bipolar plate. In this regard, it should be noted that any combination of surface groups described in
10 U.S. Patent No. 5,900,029 by Belmont et al. can be utilized in conjunction with any modified carbon product used in any modified carbon ink to create and/or modify any of the proton exchange membrane, the electrode or electrocatalyst layer, the gas/fluid diffusion layer and/or the bipolar plate. Preferably, the modified carbon ink is formulated for deposition (e.g., via analog or digital
15 printing) to maintain a low manufacturing cost while retaining the above noted properties, as suitable for the respective component of the fuel cell.

The modified carbon inks and/or electrocatalyst inks according to the present invention can be deposited to form patterned or unpatterned layers using a variety of tools and methods. In one embodiment, a modified carbon ink is
20 deposited using a direct-write deposition tool. As used herein, a direct-write deposition tool is a device that can deposit a modified carbon ink / electrocatalyst ink onto a surface by ejecting the composition through an orifice toward the surface without the tool being in direct contact with the surface. The direct-write deposition tool is preferably controllable over an x-y grid. One preferred direct-
25 write deposition tool according to the present invention is an ink-jet device. Other examples of direct-write deposition tools include aerosol jets and automated syringes, such as the MICROPEN tool, available from Ohmcraft, Inc., of Honeoye Falls, N.Y.

An ink-jet device operates by generating droplets of a liquid suspension
30 and directing the droplets toward a surface. The position of the ink-jet head is carefully controlled and can be highly automated so that discrete patterns of the modified carbon ink / electrocatalyst ink can be applied to the surface. Ink-jet printers are capable of printing at a rate of 1000 drops per second per jet, or higher, and can print linear features with good resolution at a rate of 10 cm/sec or

more, such as up to about 1000 cm/sec. Each drop generated by the ink-jet head includes approximately 25 to 100 picoliters of the suspension / ink that is delivered to the surface. For these and other reasons, ink-jet devices are a highly desirable means for depositing materials onto a surface.

5 Typically, an ink-jet device includes an ink-jet head with one or more orifices having a diameter of not greater than about 100 μm , such as from about 50 μm to 75 μm . Droplets are generated and are directed through the orifice toward the surface being printed. Ink-jet printers typically utilize a piezoelectric driven system to generate the droplets, although other variations are also used.

10 Ink-jet devices are described in more detail in, for example, U.S. Patent No. 4,627,875 by Kobayashi et al. and U.S. Patent No. 5,329,293 by Liker, each of which is incorporated herein by reference in its entirety. Functionalized carbon particles have been demonstrated to be stable in inks at relatively high carbon loadings by Belmont et al. in U.S. Patent No. 5,554,739, which is incorporated

15 herein by reference in its entirety. Ink-jet printing for the manufacture of DMFCs is disclosed by Hampden-Smith et al. in commonly-owned U.S. Patent Application Serial No. 10/417,417 (Publication No. 20040038808) which is also incorporated herein by reference in its entirety.

It is important to simultaneously control the surface tension and the

20 viscosity of the modified carbon inks and/or electrocatalyst inks to enable the use of industrial ink-jet devices. Preferably, the surface tension of the ink is from about 10 to 50 dynes/cm, such as from about 20 to 40 dynes/cm. For use in an ink-jet, the viscosity of the modified carbon inks and/or electrocatalyst inks is preferably not greater than about 50 centipoise (cp), such as in the range of from

25 about 10 cp to about 40 cp. Automated syringes can use compositions having a higher viscosity, such as up to about 5000 cp.

According to one embodiment, the solids loading of modified carbon products in the modified carbon inks and/or the solids loading of electrocatalyst materials in the electrocatalyst ink is preferably as high as possible without

30 adversely affecting the viscosity or other necessary properties of the composition. For example, a modified carbon ink and/or electrocatalyst ink can have a solids loading of up to about 20 wt.%. In one embodiment the solids loading is from about 2 wt.% to about 10 wt.%. In another particular embodiment, the solids loading is from about 2 wt. % to about 8 wt %. As is discussed above, the

surface modification of a carbon product can advantageously enhance the dispersion of the carbon product, and lead to higher obtainable solids loadings.

The modified carbon inks and/or electrocatalyst inks for use in an ink-jet device can also include water and/or an alcohol. Surfactants can also be used to maintain the modified carbon products in the ink. Co-solvents, also known as humectants, can be used to prevent the modified carbon inks from crusting and clogging the orifice of the ink-jet head. Biocides can also be added to prevent bacterial growth over time. Examples of such liquid vehicle compositions for use in an ink-jet are disclosed in U.S. Patent No. 5,853,470 by Martin et al.; U.S. Patent No. 5,679,724 by Sacripante et al.; U.S. Patent No. 5,725,647 by Carlson et al.; U.S. Patent No. 4,877,451 by Winnik et al.; U.S. Patent No. 5,837,045 by Johnson et al.; and U.S. Patent No. 5,837,041 by Bean et al. Each of the foregoing U.S. patents is hereby incorporated herein by reference in its entirety. The selection of such additives is based upon the desired properties of the composition. If necessary, modified carbon products can be mixed with the liquid vehicle using a mill or, for example, an ultrasonic processor. In this regard, it should be noted that modified carbon products that are dispersible in their corresponding solvent (e.g. a modified carbon product having a hydrophilic surface groups in an aqueous solution) may require minimal or no mixing due to their improved dispersability in their corresponding solvents.

The modified carbon inks and/or electrocatalyst inks according to the present invention can also be deposited by aerosol jet deposition. Aerosol jet deposition can enable the formation of features having a feature width of not greater than about 200 μm , such as not greater than 100 μm , not greater than 75 μm and even not greater than 50 μm . In aerosol jet deposition, the modified carbon ink and/or electrocatalyst ink is aerosolized into droplets and the droplets are transported to a substrate in a flow gas through a flow channel. Typically, the flow channel is straight and relatively short. For use in an aerosol jet deposition, the viscosity of the ink is preferably not greater than about 20 cp.

The aerosol in the aerosol jet can be created using a number of atomization techniques, such as by ultrasonic atomization, two-fluid spray head, pressure atomizing nozzles and the like. Ultrasonic atomization is preferred for compositions with low viscosities and low surface tension. Two-fluid and pressure atomizers are preferred for higher viscosity inks.

The size of the aerosol droplets can vary depending on the atomization technique. In one embodiment, the average droplet size is not greater than about 10 μm , and more preferably is not greater than about 5 μm . Large droplets can be optionally removed from the aerosol, such as by the use of an impactor.

5 Low aerosol concentrations require large volumes of flow gas and can be detrimental to the deposition of fine features. The concentration of the aerosol can optionally be increased, such as by using a virtual impactor. The concentration of the aerosol can be greater than about 10^6 droplets/ cm^3 , such as greater than about 10^7 droplets/ cm^3 . The concentration of the aerosol can be
10 monitored and the information can be used to maintain the mist concentration within, for example, 10% of the desired mist concentration over a period of time.

Examples of tools and methods for the deposition of fluids using aerosol jet deposition include U.S. Patent No. 6,251,488 by Miller et al., U.S. Patent No. 5,725,672 by Schmitt et al. and U.S. Patent No. 4,019,188 by Hochberg et al.
15 Each of these patents is hereby incorporated herein by reference in its entirety.

The modified carbon inks and/or electrocatalyst inks of the present invention can also be deposited by a variety of other techniques including intaglio, roll printer, spraying, dip coating, spin coating and other techniques that direct discrete units, continuous jets or continuous sheets of fluid to a surface.
20 Other printing methods include lithographic and gravure printing.

For example, gravure printing can be used with modified carbon inks and/or electrocatalyst inks having a viscosity of up to about 5000 centipoise. The gravure method can deposit features having an average thickness of from about 1 μm to about 25 μm and can deposit such features at a high rate of speed, such
25 as up to about 700 meters per minute. The gravure process also enables the direct formation of patterns onto the surface.

Lithographic printing methods can also be utilized. In the lithographic process, the inked printing plate contacts and transfers a pattern to a rubber blanket and the rubber blanket contacts and transfers the pattern to the surface
30 being printed. A plate cylinder first comes into contact with dampening rollers that transfer an aqueous solution to the hydrophilic non-image areas of the plate. A dampened plate then contacts an inking roller and accepts the ink only in the oleophilic image areas.

The aforementioned deposition / printing techniques may require one or more subsequent drying and/or curing (e.g., heating) steps, such as by thermal, ultraviolet and/or infrared radiation, to induce a chemical or physical bond formation. For example, if a long chain fluorine substituted aryl is used, the
5 resulting deposited layer can be dried (e.g., at 100°C) and heated (e.g., 350°C) to induce mobility and physical bond formation between adjacent modified carbon products through a surface substituted aryl group.

By way of illustration, and with reference to the modification of a gas/fluid diffusion layer, a low viscosity modified carbon ink including a modified carbon
10 product having a hydrophobic surface group can be deposited using a direct-write tool (e.g., an ink jet printer) onto the gas/fluid diffusion layer to form a hydrophobic layer on the electrode side of the gas/fluid diffusion layer. After the deposited layer is dried (e.g., at about 100°C), it can be heated (at about 350°C) for a certain period of time (e.g., 30 minutes) to enable the hydrophobic groups to
15 become mobile and intertwine with adjacent surface groups on the same and different carbon particles, thereby resulting in a hydrophobic layer with a greater level of structural integrity.

Using one or more of the foregoing deposition techniques, it is possible to deposit the modified carbon inks and/or electrocatalyst ink on one side or both
20 sides of a surface (e.g., a membrane surface) to form and/or modify a component of the fuel cell (e.g., a proton exchange membrane, an electrocatalyst layer, an electrode, a gas/fluid diffusion layer and/or, a bipolar plate). According to one embodiment, such deposition techniques are utilized to form a modified proton exchange membrane (e.g., a catalyst modified proton exchange membrane)
25 and/or a modified gas/fluid diffusion layer (e.g., a catalyst modified gas/fluid diffusion layer) and/or a bipolar plate. In another embodiment, such deposition techniques are used to directly create the component, such as the gas/fluid diffusion layer(s), the electrode layer(s) and/or the proton exchange membrane, such as by depositing a modified carbon ink and/or an electrocatalyst ink onto
30 another component of the MEA, such as a bipolar plate, a proton exchange membrane and/or a gas/fluid diffusion layer.

It will be appreciated that any of the above-noted processes can be utilized in parallel or serial to deposit multiple layers of the same or different modified carbon inks and/or electrocatalyst inks onto a surface, and can be printed in one

or more dimensions and in single or multiple deposition steps. In this regard, one embodiment of the present invention is directed to printing multiple layers of modified carbon inks and/or electrocatalyst inks to generate gradients in one or more components of the fuel cell.

5 In one particular embodiment, gradient structures can be prepared that have material properties that transition from very hydrophilic to very hydrophobic, such as by utilizing a plurality of layers including modified carbon products or modified carbon products having varying concentrations of surface groups. In this regard, a first layer may include a modified carbon product that is very
10 hydrophilic, such as a modified carbon product having a hydrophilic terminated surface group attached to the surface (e.g., a sulfuric group). On this first layer, a second, slightly less hydrophilic layer can be formed, such as by using a modified carbon product / modified electrocatalyst product that has slightly hydrophilic surface groups (e.g., a carboxylic group). A third, hydrophobic layer can be
15 formed on the second layer utilizing a hydrophobic modified carbon product having a hydrophobic surface group. It will be appreciated that in any of these layers, more than one type of surface group can be utilized with the various modified carbon products.

With particular respect to the electrode layers, such a gradient structure
20 may enable a novel water removal path for removing water from the electrode in a controlled fashion, thereby preventing gas blockage and subsequent fuel cell flooding. An intimate mixture of hydrophobic modified carbon products within the electrode enables provides for effective water ejection at lower pressure, which is especially advantageous for operating fuel cells at lower pressures (e.g.,
25 atmospheric or slightly above atmospheric). In addition to utilizing hydrophilic modified carbon products, water removal properties may also be improved by reducing microporosity, as described above.

It will be appreciated that any of the above referenced deposition methods can be utilized to directly deposit a diazonium salt onto carbonaceous surface for
30 the purpose of directly modifying such carbonaceous surface, such as any of the surfaces of the bipolar plates, the gas/fluid diffusion layer, the electrode layer and/or the proton exchange membrane. Additionally, such depositions can be used to modify any previously deposited carbonaceous materials, including non-modified carbon materials, electrocatalyst materials, modified carbon products

and/or modified electrocatalyst products, such as any of those contained in any of the proton exchange membrane, the electrode, the gas/fluid diffusion layers and/or the bipolar plates. It will also be appreciated that such deposition techniques can be utilized to create a uniform modified carbon layer across the entire surface of the fuel cell component, or can be deposited in discrete patterns to produce patterned modified carbon layers. It will further appreciated, with respect to the above approaches, aspects and embodiments, that the diazonium salt can be any salt that will enable the formation of appropriate surface group(s) to tailor the properties of the fuel cell component. Surface groups including hydrophobic and/or hydrophilic functional groups and/or including a polymeric functional and/or linking group are often preferred. Particularly preferred hydrophilic, hydrophobic and polymeric functional and linking groups are provided above in Tables II, III, IV and V.

Examples

15 A. Production of PEG-VULCAN XC-72-reinforced PFSA PEM

90 mL of deionized water, 26.5 g of a treating agent (aminophenylated polyethylene glycol ether, MW~2119 and having the formula $(\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CO}-[\text{O}-(\text{C}_2\text{H}_4\text{O})_n-\text{CH}_3])$) and 2.25 g of a 70% aqueous solution of nitric acid are added to a beaker and slowly mixed. The temperature is slowly raised to 40°C using a hot plate. When the temperature reaches 40°C, 10 g of VULCAN XC-72 carbon black is added and the mixture is stirred and heated to 50°C. When the temperature reaches 50°C, 4.3 g of a 20 wt.% aqueous sodium nitrite solution is added slowly drop wise. The mixture is then allowed to react at 50°C for 2 hours. When the reaction is substantially complete, the sample is diafiltered using 10 volumes of fresh deionized water to remove any reaction by-products. The resulting PEG-modified VULCAN XC-72 carbon is added to a PFSA water/isopropanol solution to give a modified carbon solids loading of 55 wt.%. The slurry is cast and dried at 80°C overnight to form a membrane.

30 B. Increased proton conductivity composite modified membrane

Example B-1: Cast a 70 wt. % SO_3H modified carbon black/PFSA membrane

To 70g of (C₆H₄)SO₃H modified VULCAN XC-72 (3 μmols/m²) is added 2000g of a 5 wt.% PFSA isopropanol/water solution to give a 70 wt.% modified carbon black/PFSA suspension. The resulting viscous suspension is mixed for several minutes and poured onto a Teflonized glass plate. The resulting film is doctor bladed to a thickness (wet) of 5 mils. The resulting film is dried in air at room temperature for 24 hours.

Example B-2: To cast a 15 wt. % SO₃H modified carbon black/PFSA membrane

To 15g of (C₆H₄)SO₃H modified VULCAN XC-72 (3 μmols/m²) is added 2000g of a 5 wt. % PFSA isopropanol/water solution to give a 15 wt % modified carbon black/PFSA suspension. The resulting suspension is mixed for several minutes and poured onto a Teflonized glass plate. The resulting film is doctor bladed to a thickness (wet) of 20 mils. The resulting film is dried in air at room temperature for 24 hours. The resulting membrane has increased mechanical stability and higher proton conductivity at lower humidification levels.

C. Direct printed modified carbon product/PFSA PEM

A modified carbon suspension containing modified carbon black includes from about 2 to 10 wt.% solids loading of the carbon black, a humectant, viscosity, surface tension modifier and/or a biocide. CAB-O-JET 200 (Cabot Corporation, Boston, MA) is a dispersion of 20 wt.% BLACKPEARLS 700, modified with (C₆H₄)SO₃H, in water. The dispersion has a viscosity of 3.8 cP with a surface tension of 75.5 dynes/cm. The acceptable viscosity for ink-jetting with the Spectra ink-jet heads is about 12 cP with a surface tension of about 30 dynes/cm.

Table VII illustrates an example of a low viscosity, ink-jettable modified carbon black/PFSA ink composition.

Table VII

Component	Wt. %
Modified carbon black	5.9
PFSA	52.4

Isopropyl alcohol	12.6
Water	29.1
Total	100.0

The formulation is ink jet printed on the electrode side of a gas diffusion electrode with a Spectra ink-jet head. The ink-jet head temperature was set at 30°C, fire pulse width of 8 μ s, pulse rise and fall time of 3 μ s, and firing voltage of 120 V. An ink-jet print is obtained at a speed of 10 inches/sec. The printed film is dried at 80°C for 3 hours and the printing and drying process is repeated two additional times.

D. Modified Polyimide-based PEM

A mixture of C₆H₄SO₃H surface functionalized VULCAN XC-72 is mixed with finely divided polyimide to give a final composition 70 wt.% modified carbon black. The mixture is blended in a ball mill for 2 hours and is then suspended in a water/ethanol solvent to form a slurry. The slurry is cast and dried overnight at 80°C. The resulting film is pressed to a thickness of 0.12 mm and heated to a temperature of 250°C for 2 hours. The resulting modified carbon black polyimide composite membrane has structural integrity and strength and is proton conducting with and without humidification.

E. Printed modified carbon product-based PEM

A powder batch of VULCAN XC-72 modified with (C₆H₄)SO₃H is suspended in water at a concentration of 5 wt.%. To this suspension is added VULCAN XC-72 that has been modified with polyethylene glycol (PEG), where the ratio of PEG modified carbon to (C₆H₄)SO₃H modified carbon is 5:1 and the total ink solids loading is 5 wt.%. The resulting ink is ink jet printed directly onto an electrode layer, which is supported by a gas/fluid diffusion layer (e.g., a gas diffusion electrode). The printed layer is then dried and heated at 130°C for 2 hours to remove the solvent and bind the carbon black particles together via the PEG surface molecules. The printing, drying and heating process is repeated two more times.

F. Ink jet printed modified carbon product-based PEM

VULCAN XC-72 that has been co-modified with PEG and $(C_6H_4)SO_3H$ in a 5:1 wt. ratio is dispersed into an isopropanol/water solvent with a total solids content of 5 wt.%. The resulting ink is printed by means of a piezoelectric, drop-on-demand GALAXY ink-jet head (Spectra Corporation) in three passes. The resulting layer is heated at 120°C for 30 minutes to allow the PEG surface groups to intertwine and to remove the solvent.

G. Ink jet printed modified carbon product/TEFLON PEM

To VULCAN XC-72 modified with $(C_6H_4)SO_3H$ groups ($3 \mu\text{mol}/\text{m}^2$) is added a NAFION/isopropanol-water solution to give an ink that consists of 5 wt.% carbon where the carbon:NAFION weight ratio is 1:5. The resulting carbon black/NAFION ink is ink jet printed utilizing a piezoelectric drop on demand Galaxy ink jet head (Spectra Corporation) onto the electrode side of a catalyst coated gas/fluid diffusion layer and is subsequently dried at 25 °C for 12 hours. The printing and drying process is repeated two more times.

H. Preparation of Pt electrocatalysts by spray-based processing utilizing modified carbon products**Example H-1: 50% Pt/C, 1g batch**

3.7g of a 13.6 wt. % $Pt(NO_3)_2$ solution is added to 0.77g of SO_3H -modified KETJEN BLACK 600 dispersed in 15.5g distilled water. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

Example H-2: 60% Pt/C, 1g batch

4.4g of a 13.6 wt. % $Pt(NO_3)_2$ solution is added to 0.61g of SO_3H -modified KETJEN BLACK 600 dispersed in 15g distilled water. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

Example H-3: 60% Pt/C, 1g batch

4.4g of a 13.6 wt. % $\text{Pt}(\text{NO}_3)_2$ solution is added to 0.61g of SO_3H -modified KETJEN BLACK 600 dispersed in 5g distilled water. The resulting 10 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The
5 spray pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

Example H-4: 50% Pt/C, 1g batch

3.7g of a 13.6 wt. % $\text{Pt}(\text{NO}_3)_2$ solution is added to 0.76g of SO_3H -modified KETJEN BLACK 600 dispersed in 35.6g distilled water. The resulting 2.5 wt. %
10 solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The spray-pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

Example H-5: 60% Pt/C, 1g batch

4.4g of a 13.6 wt. % $\text{Pt}(\text{NO}_3)_2$ solution is added to 0.5g of CO_2H -modified
15 KETJEN BLACK 600 dispersed in 15g distilled water. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The spray-pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

Example H-6: 60% Pt/C, 1g batch

20 4.4g of a 13.6 wt. % $\text{Pt}(\text{NO}_3)_2$ solution is added to 0.5g of CF_3 -modified KETJEN BLACK 600 dispersed in 15g distilled water. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The spray-pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

25 Example H-7: 60% Pt/C, 1g batch

4.4g of a 13.6 wt. % $\text{Pt}(\text{NO}_3)_2$ solution is added to 0.5g of SO_3H and CF_3 -
modified KETJEN BLACK 600 dispersed in 15g distilled water. The ratio of $\text{SO}_3\text{H}:\text{CF}_3$ groups in the starting carbon is 2:1. The resulting 5 wt. % solids dispersion is sheared for 5 minutes, then fed into a spray-pyrolysis system. The
30 spray-pyrolysis is conducted on an ultrasonic transducer system at a furnace temperature of 500°C, with air as the carrier gas at 5 SLPM.

I. Preparation of Pt/C and PtRu/C electrocatalysts utilizing modified carbon products through a secondary, surface modification procedure.

Example I-1

5 Supported 60% Pt/C and 60% PtRu/C are modified by addition of SO₃H groups on the carbon surface. The level of treatment on the electrocatalyst is dependent on a number of factors such as surface area of the sample and metal content of the sample. 0.75 mmole/g of SO₃H groups are attached to the Pt/C electrocatalyst and 0.8 mmole/g of SO₃H group are attached to the PtRu/C electrocatalyst, determined experimentally. Surface area of the 60% Pt and 60% PtRu modified electrocatalysts is determined to be 260 m²/g and 205 m²/g respectively. A smaller particle size distribution is obtained upon surface modification with SO₃H groups. There is a decrease in d₅₀ from 5 μm to 3 μm for the modified Pt/C electrocatalyst and a decrease in d₅₀ from 9 micron to 4.5 micron for the modified PtRu/C electrocatalyst. Smaller PSD for the modified electrocatalysts is promising and desirable for ink-jetting as particle sizes greater than 2 μm result in clogging of ink-jet heads. Further, dispersability of the modified electrocatalysts increased compared to the as prepared electrocatalysts.

20

TABLE VIII

	60% Pt/C	modified 60% Pt/C	60% PtRu/C	modified 60% PtRu/C
BET Surface Area	320 m ² /g	260 m ² /g	315 m ² /g	205 m ² /g
PSD	2.4, 5.3, 15.9	0.3, 3.4, 12.5	3.3, 9, 21	0.5, 4.5, 18.1
XRD Area	80	50	120	115
EDS (S wt%)	0	1.35	0	1.9
TGA, %metal	61	55	73	59

J. Preparation of Pt/C electrocatalyst for high temperature applications utilizing modified carbon products through a secondary, surface modification procedure.

Example J-1

A 20% Pt/VULCAN XC-72 catalyst is dispersed in an aqueous solution of ArNH_2 , NaNO_2 and HX , where $\text{Ar} = \text{HO}_3\text{P}-(\text{C}_6\text{H}_4)-$ and $\text{X} = \text{Cl}$, resulting in the formation of the diazonium salt $\text{ArN}\equiv\text{N}^+\text{X}^-$ which reacts with the carbon surface of the above mentioned catalyst to form a Pt/modified carbon product) catalyst whose carbon surface is modified with $-(\text{C}_6\text{H}_4)-\text{PO}_3\text{H}$ groups.

The Pt/modified carbon product catalyst is rinsed thoroughly to remove by-products of the reaction and the isolated Pt/Carbon catalyst is then re-dispersed in a 4:1 isopropanol/water solution as to give approximately 2 wt % catalyst solution. The solution further contains approximately 0.2 wt % Teflon, 10% based on Pt/modified carbon product.

The resulting solution is sprayed onto a high temperature PBI (polybenzimidazole) membrane or gas/fluid diffusion layer to form a catalyst coated membrane. The catalyst layer is then doped with phosphoric acid, H_3PO_4 , by placing the catalyst layer in contact with a solution, approximately 1 molar, of H_3PO_4 /ethanol.

The $-\text{PO}_3\text{H}$ modified carbon product results in increasing proton conductivity in the catalyst layer as well as decreasing the leaching of phosphoric acid from the catalyst layer during fuel cell operation through increased hydrogen bonding.

K. Examples of modified carbon products in hydrogen-air fuel cell electrodes relating to increased proton conductivity.

Example K-1

An electrocatalyst, made by spray processing or any other method, where SO_3H or mixed $\text{SO}_3\text{H}/\text{CF}_3$ and $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ groups (in a molar ratio of 3:1) are preformed on the carbon support and present at the electrocatalyst surface after conversion of Pt precursor either at the same amount as before the electrocatalyst formation or at a reduced amount, is incorporated in an electrocatalyst ink, where the ratio of electrocatalyst to NAFION (introduced as standard NAFION suspension) is varied from 4:1 to 2:1.

Example K-2

A 50 wt.% PtRu/KETJEN BLACK 600 or 50 wt.% Pt/KETJEN BLACK 600 electrocatalyst, is modified with SO_3H post-treatment with concentrations of 0.15, 0.3 and 0.6 mmol/g level treatments, is incorporated into an electrode layer, preferably in an anode layer for DMFC or anode layer for hydrogen-air fuel cell, respectively.

Example K-3

A 50 wt.% Pt/KETJEN BLACK with SO_3H post treatment with 0.15, 0.3 and 0.6 mmol/g level treatments is incorporated into an electrode layer, where the ratio of electrocatalyst to NAFION is from 8:1 to 2:1.

Example K-4

A modified carbon black or modified electrocatalyst with different levels of $(\text{C}_6\text{H}_4)\text{SO}_3\text{H}$ groups (0.4 and 10.7 wt.%) was used to form electrocatalyst ink suspension that was then hot-pressed onto polycarbonate films (polycarbonate is used instead of NAFION because it is a nonconductor and prevents current losses outside the catalyst layer). The total DC resistance of this assembly was determined from the impedance response by reading the low frequency intercept with the real axis. (Reference: A.P. Saab, F.H. Garzon and T.A. Zawodzinski, *Journal of The Electrochemical Society*, 150, (2) A214-A218, 2003). A DC polarization is used to obtain the iV response and from there the electronic resistance. Assuming that the overall resistance is the parallel combination of the ionic and electronic resistances, the ionic resistance can be calculated from the following equation:

$$\frac{1}{R_{DC_overall}} = \frac{1}{R_{ionic}} + \frac{1}{R_{electronic}}$$

$R_{DC_overall}$ is the overall DC resistance obtained from the impedance spectrum

$R_{electronic}$ is the electronic resistance obtained from the DC polarization experiment

R_{ionic} is the ionic resistance of the assembly

The ionic resistivity of the modified carbons, electrocatalysts or electrodes decreases drastically as the degree of the treatment is increased. The ionic resistivity decreases from 245 ohm-cm for the untreated carbon to 110 ohm-cm for the 4 wt. % treated carbon to 20 ohm-cm for the 10.7 wt % treated carbon.

The electronic resistivity increases from 0.16 ohm-cm for the untreated carbon to 0.32 ohm-cm for the 4 wt % treated carbon to 9.9 ohm-cm for the 10.7 wt % treated carbon. These measurements confirm that the attached $(C_6H_4)SO_3H$ groups are proton conducting.

Example K-5

A supported Pt catalyst, e.g., 20% Pt on VULCAN XC-72, was used to prepare the following fuel cell cathodes:

(1) 20% Pt/VXC-72 is mixed with a PTFE suspension and then deposited on a commercially available hydrophobic gas/fluid diffusion layer (ELAT, available from ETEK). The resulting coated GDL is then heat treated at ca. 360°C for about an hour to make the PTFE flow and disperse throughout the catalytic layer. No NAFION ionomer is added to the catalytic layer so there are no $-SO_3H$ groups within the electrode;

(2) Same as (1), but NAFION is sprayed onto the resulting catalytic layer introducing in this way a certain (calculable) loading of $-SO_3H$ groups.

(3) Same as (1), but either the carbon support, the electrocatalyst or the resulting electrode is subjected to a diazonium salt reaction to attach $(C_6H_4)SO_3H$ groups to the carbon support. This introduces a loading of $-SO_3H$ groups.

The 3 cathodes are pressed on NAFION membranes with common anodes. Testing the 3 MEAs provides in-situ proof that the introduction of the –SO₃H groups gives the catalytic layer of cathode (3) proton conductivity when compared with cathode (1). The performance of MEA made with cathode (3) is significantly better than the performance of MEA made with cathode (1). The performance of MEA made with cathode (2) serves as a baseline for tailoring the content of –SO₃H groups that need to be added via the diazonium salt reaction.

It is, perhaps, beneficial to test MEAs with cathodes at various treatment levels in an attempt to determine the optimum –SO₃H loadings. If the loading of –SO₃H groups in the case of cathode (3) is smaller than the loading of –SO₃H groups in the case of cathode (2) but the performances are similar, it means that some of the –SO₃H groups in the case of cathode (2) do not exercise their functionality.

L. Examples of modified carbon products in hydrogen-air fuel cell electrodes relating to improved water management

Example L-1

As discussed previously, the introduction of –SO₃H groups in the catalyst layer confer the electrode is hydrophilic in character. The introduction of these groups at the cathode side of the H₂-air fuel cell have to be balanced with the introduction of hydrophobic groups to prevent water flooding. However, some water retention at the anode of a fuel cell is beneficial in order to run the electrode at reduced levels of relative humidity. In order to probe the potential advantage of the above-mentioned anodes, the following experiment is performed.

One MEA with a classic cathode (see the MEA with cathode 2 described above in the previous section) and an anode prepared in the same way as cathode 3 above in the previous experiment) are prepared and run at anode humidification levels between 0 and 100% relative humidity. The modification is proven successful (due to the increase in performance of the carbon helps with the water management) from the increase in performance of the fuel cell at decreasing humidification levels at higher currents.

Example L-2

A CF_3 and/or C_8F_{18} pretreated BLACK PEARLS 700 (carbon black) at 0.15, 0.3 and 0.6 mmol total/g level was applied in an electrode layer in combination with 50 wt.% Pt/KETJEN BLACK 600 standard catalyst with addition
5 of NAFION to the ink formulation.

Example L-3

A 40 wt.% Pt/ Vulcan XC -72 post treated with SO_3H and/or C_8F_{18} modification at 0.15, 0.3 and 0.6 mmol total/g level of treatment (molar ratio of SO_3H to C_8F_{18} was 1:1) was mixed with SHAWINAGAN BLACK or BLACK
10 PEARLS 700 carbon blacks in an electrocatalyst ink including NAFION suspension. The electrocatalyst to carbon blacks volume ratio was varied from 10 :1 to 5 :1 and the NAFION to total carbon ration was varied from 5 :1 to 1:1.

Example L-4

A spray processed or made by any other method 20 wt.%
15 Pt/SHAWINIGAN BLACK carbon that contained in its final form a $\text{SO}_3\text{H}/\text{CF}_3$ or $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is mixed in an electrocatalyst ink with or without Teflon and NAFION additives.

Example L-5

20 A post-treated 50 wt.% Pt/KETJEN BLACK 600 with $\text{SO}_3\text{H}/\text{CF}_3$ and/or $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is mixed in an electrocatalyst ink and printed onto a membrane or a gas/fluid diffusion layer and the MEA constructed of these was able to operate at lower humidification levels of reactant gases.

Example L-6

25 A treated 50 wt.% Pt/KETJEN BLACK 600 with $\text{SO}_3\text{H}/\text{CF}_3$ or $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is mixed with various amounts of NAFION and printed onto a membrane or to a gas/fluid diffusion layer to create an MEA capable of operation
30 at low pressure and at a range of humidity conditions.

Example L-7

A treated 50 wt.% Pt/KETJEN BLACK 600 with $\text{SO}_3\text{H}/\text{CF}_3$ and $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is used to print a vertical hydrophobicity gradient electrode.

Example L-8.

- 5 A treated 50 wt.% Pt/KETJEN BLACK 600 with $\text{SO}_3\text{H}/\text{CF}_3$ and $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is used to print a patterned hydrophobicity electrode where certain parts of the pattern are more hydrophobic than other parts of the pattern.

Example L-9.

- 10 A mix of treated 50 wt.% Pt/KETJEN BLACK 600 with $\text{SO}_3\text{H}/\text{CF}_3$ or $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 3:1 and 2:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments and 20 wt.% Pt/SHAWINIGAN BLACK with $\text{SO}_3\text{H}/\text{CF}_3$ or $\text{SO}_3\text{H}/\text{C}_8\text{F}_{18}$ treatments at 5:1 and 3:1 molar ratio and 0.15, 0.3 and 0.6 mmol total/g level treatments is mixed with various amounts of NAFION and printed
15 onto a membrane or to a gas/fluid diffusion layer to create an MEA capable of operation at low pressure and at a range of humidity conditions.

M. Examples of modified carbon products in hydrogen-air fuel cell electrodes relating to increased proton catalyst utilization.

20 **Example M-1**

Supported catalysts on modified carbon blacks can be achieved in two ways.

- 1) modification of the carbon and then addition of the catalyst;
- 2) addition of the modifying groups on commercially available (or
25 experimental) catalysts. C Either way, Pt utilization is determined by performing the following experiment:

The resulting powder is characterized by XRD and TEM to determine the particle size of the catalyst. This is compared to the particle size of the unmodified catalyst.

The powder is subjected to an ex-situ carbon monoxide adsorption experiment, which provides the surface area (A_1 m²/g) of the Pt before the powder is converted in an MEA.

The powder is then converted in an MEA and the surface area is
5 determined by means of CO adsorption and anodic stripping of the adsorbed CO (A_2 m²/g).

The utilization of the catalyst is calculated with the following formula:

$$\eta = \frac{A_2}{A_1} \cdot 100$$

10 The value of utilization (η) is compared with the value of utilization obtained for the traditional unmodified catalysts, prepared by the classic methods (with NAFION and PTFE).

N. Preparation of Alloy Electrocatalysts

15 Example N-1: 60% PtRu/Modified Carbon Black KB SO₃H , 1g batch

2.4g of a 13.7 wt.% Pt(NO₃)₂ solution is added to 0.76g of SO₃H-modified KB dispersed in 15g distilled water, followed by 1.6g of a 10.7 wt % Ru(NO)(NO₃)₃ solution. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray pyrolysis system. The spray pyrolysis is conducted
20 on an ultrasonic transducer system at a furnace temperature of 500 °C, with air carrier gas at 5 SLPM. The collected powder is then post-processed under forming gas for 2 hours at 250 °C.

Example N-2: 20% PtNiCo/Modified Carbon Black Vulcan XC-72 SO₃H , 1g batch

25 2.8g of a 13.7 wt.% Pt(NO₃)₂ solution is added to 0.55g of SO₃H-modified Vulcan XC-72 dispersed in 8g distilled water. 0.3g Ni(NO₃)₂·6H₂O and 0.3g Co(NO₃)₂·6H₂O were each dissolved in 4g distilled water. The resulting 5 wt.% solids dispersion is sheared for 5 minutes, then fed into a spray pyrolysis system. The spray pyrolysis is conducted on an ultrasonic transducer system at a furnace

temperature of 500 °C, with air carrier gas at 5 SLPM. The collected powder is then post-processed under forming gas for 2 hours at 250 °C.

O-1. Printed SO₃H and CF₃ terminated VULCAN XC-72 Microporous Layer

5 A solution containing ArNH₂, NaNO₂ and HCl (where Ar is –C₆H₆–SO₃H), is added to a solution containing unmodified VULCAN XC-72 to form the diazonium salt, ArN≡N:⁺Cl[–] which in turn reacts with the surface of the VULCAN XC-72 to form the modified carbon black (MCB) product. The quantity of diazonium salt formed is sufficient to only give a partial surface coverage, 0.4 μmol/m². The
10 resulting MCB is isolated and redispersed in deionized water. To this solution additional ArNH₂, NaNO₂ and HCl are added. However, in this case Ar is –C₆H₆–CF₃. The resulting reactions yield a MCB product containing 0.4 μmol/m² SO₃ groups and 0.2 μmol/m² CF₃ groups, approximate total loading of MCBs is 0.6 μmol/m². The resulting MCB is then dispersed in a low viscosity ink, i.e.,
15 dispersed in deionized water and is sprayed onto the surface of a carbon cloth GDL to form the microporous layer. The resulting mix of hydrophobic/hydrophilic surface groups provides a percolation path for both O₂ to the catalyst and H₂O away from the catalyst.

O-2. Printed PEG-VULCAN XC-72 Microporous Layer

20 90 ml of deionized water, 26.5 g of a treating agent (aminophenylated polyethylene glycol ether having a MW ~ 2119 and a formula of H₂N–C₆H₄–CO–[O–(C₂H₄O)_n–CH₃]) and 2.25 g of a 70% aqueous solution of nitric acid are added to a beaker and slowly mixed. The temperature is slowly raised to 40°C using a hot plate. When the temperature reaches 40°C, 10 g of VULCAN XC-72 carbon
25 black is added and the mixture is stirred and heated to 50°C. When the temperature reaches 50°C, 4.3 g of a 20 wt. % aqueous sodium nitrite solution is added slowly dropwise. The mixture is then allowed to react at 50°C for 2 hours. When the reaction is complete, the sample is diafiltered using 10 volumes of fresh deionized water to remove any reaction byproducts. The PEG-modified
30 VULCAN XC-72 is formulated into an ink by the addition of ethylene glycol with a final solids loading of 40 vol.%. The ink is printed onto a carbon paper gas/fluid

diffusion layer to a wet thickness of about 5 mil (125 μm) by roll coating on a web drive and is subsequently heated at 130°C for 30 minutes.

P-1. Ink-jetable microporous layers including carbon black

- 5 A typical formulation for ink-jetted Modified Carbon Black (MCB) contains 2 - 10 wt % solids loading. The rest of the ink contains a humectant, viscosity, surface tension modifier and/or a biocide. CAB-O-JET 200 (Cabot Corporation, Boston, MA) is a dispersion of 20 wt. % (C₆H₄)SO₃H terminated Black Pearls 700 in water. The dispersion has a viscosity of 3.8 cP with a surface tension of 75.5
10 dynes/cm. The acceptable viscosity for ink-jetting with the Spectra ink-jet heads is ~ 12 cP with a surface tension of ~ 30 dynes/cm.

Below in Table IX to XI are examples of low viscosity ink-jetable modified carbon black inks.

Table IX

Formulation 1	Weight %	Properties at 21.4°C	
MCB	5.9		
DI H ₂ O	52.4		
IPA	12.6		
Ethylene Glycol	29.1		
Total	100.0		
		Viscosity	14.8 cP
		Shear Stress	19.6 dynes/cm ²
		Shear Rate	132 s ⁻¹
		Torque	19.6 %
		Surface Tension	35.1 dynes/cm

15

Table X

Formulation 2	Weight %	Properties at 20.6°C	
MCB	5.5		
DI H ₂ O	40.0		

IPA	15.0		
Ethylene Glycol	40.0		
Total	100.0		
		Viscosity	14.4 cP
		Shear Stress	15.5 dynes/cm ²
		Shear Rate	132 s ⁻¹
		Torque	22.0 %
		Surface Tension	30.8 dynes/cm

Table XI

Formulation 3	Weight %	Properties at 19.6°C	
MCB	5.5		
DI H ₂ O	57.8		
IPA	12.7		
Ethylene Glycol	19.0		
CARBITOL	5.0		
Total	100.0		
		Viscosity	12.5 cP
		Shear Stress	16.7 dynes/cm ²
		Shear Rate	132 s ⁻¹
		Torque	42.1 %
		Surface Tension	34.3 dynes/cm

- 5 Formulation 3 is prepared with 5.5 wt.% loading of modified carbon black. Jetting is achieved with a Spectra ink-jet head. The ink-jet head temperature was set at 30°C, fire pulse width of 8 μ s, pulse rise and fall time of 3 μ s, and firing voltage of 120 V. An ink-jet print was obtained at a speed of 10 inches/sec. Figs 29(a) and 29(b) show the dried ink-jet printed formulation (Formulation 3).
- 10 Thickness of the coating in a single pass is approximately 2 μ m.

Q-1. Surface modification of a machined graphite bipolar plate with a hydrophilic modifying group

270 ml of deionized water, 6.48 g of a functionalizing (treating) agent ($\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$) and 6.75 g of a 70% aqueous solution of nitric acid are added to a beaker and slowly mixed. The temperature is slowly raised to 40°C using a hot plate. When the temperature reaches 40°C, a machined graphite bipolar plate is
5 immersed into the solution and the solution is continually stirred and heated to 50°C. When the temperature reaches 50°C, 12.9 g of a 20 wt.% aqueous sodium nitrite solution is added slowly dropwise. The mixture is then allowed to react at 50°C for 24 hours. The graphite plate is removed and washed with deionized water three times and dried at 50°C overnight.

10

Q-2. A polymer/resin type bipolar plate incorporating a PEG modified carbon

90 ml of deionized water, 26.5 g treating agent (aminophenylated polyethylene glycol ether (MW 2119) ($\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CO}-[\text{O}-(\text{C}_2\text{H}_4\text{O})_n-\text{CH}_3]$)) and 2.25
15 g of a 70% aqueous solution of nitric acid are added to a beaker and slowly mixed. The temperature is slowly raised to 40°C using a hot plate. When the temperature reaches 40°C, 10 g of VULCAN XC-72 carbon black is added and the mixture is stirred and heated to 50°C. When the temperature reaches 50°C, 4.3 g of a 20 wt. % aqueous sodium nitrite solution is added slowly dropwise.
20 The mixture is then allowed to react at 50°C for 2 hours. When the reaction is complete, the sample is diafiltered using 10 volumes of fresh deionized water to remove any reaction byproducts. The PEG-modified VULCAN XC-72 is formulated into a mixture of graphite powder (75% from TIMCAL COMPANY, KS75), 22% phenolic thermoset resin (VARCUM 29302 from DUREZ Company)
25 and 3% of the above- described PEG-modified VULCAN XC-72. The mixture is place in a mold and pressed at 500 psi for 30 minutes at a temperature of 400°C.

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations to those embodiments will occur to those skilled in the art. It is to be expressly understood, however,
30 that such modifications and adaptations are within the scope and spirit of the present invention, as set forth in the claims below. Further, it should be

recognized that any feature of any embodiment disclosed herein can be combined with any other feature of any other embodiment in any combination.

What is Claimed is:

1. A proton conducting membrane, said membrane comprising a modified carbon product and a polymer.
- 5 2. A proton conducting membrane as recited in Claim 1, wherein said modified carbon product comprises modified carbon black.
3. A proton conducting membrane as recited in any of the preceding claims, wherein said modified carbon product comprises a proton conducting functional group.
- 10 4. A proton conducting membrane as recited in any of the preceding claims, wherein said polymer is selected from the group consisting of sulfonated PTFE and perfluorosulfonated PTFE.
5. A proton conducting membrane as recited in any of Claims 1 to 3, wherein said polymer is selected from the group consisting of polyvinylidene fluoride (PVDF), acid-doped or derivatized hydrocarbon polymers, such as
15 polybenzimidazole (PBI), polyarylenes, polyetherketones, polysulfones, phosphazenes and polyimides.
6. A proton conducting membrane as recited in any of the preceding claims, wherein said modified carbon product is coated on a surface of said
20 polymer.
7. A proton conducting membrane as recited in any of Claims 1 to 6, wherein said modified carbon product is dispersed within said polymer.
8. A proton conducting membrane as recited in Claim 1, wherein said modified carbon product is adapted to conduct protons in the absence of water.
- 25 9. A proton conducting membrane as recited in Claim 1, wherein said modified carbon product is adapted to selectively conduct protons in the presence of other hydrogen-comprising liquid fuels.
10. A proton conducting membrane as recited in Claim 1, wherein said modified carbon product is adapted to selectively conduct protons in the
30 presence of methanol or ethanol.

11. A proton conducting membrane as recited in Claim 1, wherein said modified carbon product is adapted to yield an increased mechanical strength without a substantial decrease in proton conductivity.
12. A proton conducting membrane as recited in Claim 1, wherein said
5 modified carbon product comprises at least one proton conducting functional group selected from the group consisting of SO_3H , CO_2H , PO_3H_2 and PO_3MH , where M is a monovalent cation.
13. A proton conducting membrane as recited in any of the preceding claims, wherein said proton-conducting membrane has a proton conducting
10 group concentration of at least about 5.0 mmol/mL.
14. A proton conducting membrane as recited in any of the preceding claims, wherein said proton-conducting membrane has a proton conducting group concentration of at least about 5.4 mmol/mL.
15. A proton conducting membrane, wherein said proton conducting
15 membrane consists essentially of a modified carbon product.
16. A proton conducting membrane as recited in Claim 15, wherein said modified carbon product comprises proton-conducting functional groups.
17. A proton conducting membrane as recited in Claim 15, wherein said
20 modified carbon product comprises proton-conducting functional groups selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids and phosphonic acid salts.
18. A proton conducting membrane as recited in any of Claims 15 to 17, wherein said modified carbon product comprises modified carbon black.
19. A proton conducting membrane as recited in any of Claims 15 to
25 17, wherein said modified carbon product comprises modified carbon fibers.
20. A method for the fabrication of a proton conducting membrane, comprising the steps of:
- a) mixing a polymer with a modified carbon product to form a composite mixture; and

b) forming said composite mixture into a proton conducting membrane.

21. A method as recited in Claim 20, wherein said forming step comprises extruding said composite mixture.

5 22. A method as recited in Claim 20, wherein said forming step comprises casting said composite mixture.

23. A method as recited in any of Claims 20 to 22, wherein said proton conducting membrane has a volume density of proton conducting groups of at least about 4.8 mmol/mL.

10 24. A method as recited in any of Claims 20 to 23, wherein said composite mixture comprises at least about 20 wt.% modified carbon product.

25. A method as recited in any of Claims 20 to 23, wherein said proton conducting membrane comprises at least about 40 wt.% modified carbon product.

15 26. A method as recited in any of Claims 20 to 25, wherein said carbon product comprises carbon black.

27. A method as recited in any of Claims 20 to 25, wherein said carbon product comprises carbon fibers.

20 28. A method for the fabrication of a proton conducting membrane, comprising the steps of:

a) providing a modified carbon black product; and

b) forming said modified carbon black product into a thin membrane.

25 29. A method as recited in Claim 28, wherein said forming step comprises analog deposition.

30. A method as recited in Claim 28, wherein said forming step comprises digital deposition.

30 31. A method as recited in Claim 28, wherein said forming step comprises dispersing said modified carbon product in a liquid vehicle and ink-jet printing said modified carbon product.

32. A method as recited in Claim 31, wherein said modified carbon product comprises hydrophilic functional groups.

33. An electrocatalyst, said electrocatalyst comprising an active species phase dispersed on a carbon support structure, wherein said carbon support
5 structure is a modified carbon product.

34. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a hydrophilic functional group.

35. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a hydrophobic functional group.

10 36. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises at least two different functional groups.

37. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises at least a hydrophobic functional group and a hydrophilic functional group.

15 38. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a functional group that is proton conducting.

39. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a functional group that is polymeric.

20 40. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a functional group that is adapted to reduce carbon oxidation.

41. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises a functional group that is adapted to reduce agglomeration of said active species phase.

25 42. An electrocatalyst as recited in Claim 33, wherein said modified carbon product comprises at least two functional groups selected from the group consisting of proton conducting functional groups and polymeric functional groups.

30 43. A fuel cell comprising an electrode, said electrode comprising an electrocatalyst as recited in Claim 33.

44. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises a molecular or ionic metal species bonded to a surface functional group.

5 45. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises a molecular or ionic metal species bonded to a surface functional group where the metal species is within the electrode layer.

46. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises a polymeric functional group.

10 47. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises a functional group that is adapted to reduce carbon oxidation.

48. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises a functional group that is adapted to reduce agglomeration of said active species phase.

15 49. A fuel cell as recited in Claim 43, wherein said modified carbon product comprises at least two functional groups selected from the groups consisting of proton conducting functional groups and polymeric functional groups.

20 50. A fuel cell as recited in Claim 43, wherein said modified carbon product is adapted to increase the adhesion of the electrode to at least one of an adjacent gas diffusion layer or a proton exchange membrane.

51. A fuel cell as recited in Claim 43, wherein said electrode comprises substantially no polymer proton conducting phase.

52. A method for making an electrocatalyst, comprising the steps of:

- 25 a) providing a carbon support;
- b) covalently attaching a functional group to said carbon support to form a modified carbon support product; and
- c) depositing an active species phase on said modified carbon support product to form an electrocatalyst.

53. A method as recited in Claim 52, wherein said attaching step comprises the step of reacting a diazonium salt in the presence of said carbon support.

54. A method as recited in Claim 52, wherein said carbon support
5 comprises carbon black.

55. A method as recited in Claim 52, wherein said carbon support comprises graphitic carbon.

56. A method as recited in Claim 52, wherein said step of depositing an active species phase comprises the step of reacting an active species phase
10 precursor in the presence of said modified carbon support product.

57. A method as recited in Claim 52, wherein said active species phase precursor preferentially attaches to said functional group.

58. A method as recited in Claim 52, wherein said active species phase precursor preferentially attaches to the surface of said carbon support.

59. A method as recited in Claim 52, wherein said functional group is a
15 hydrophobic group.

60. A method as recited in Claim 52, wherein said functional group is a hydrophilic group.

61. A method as recited in Claim 52, wherein said functional group is a
20 proton conducting group.

62. A method as recited in Claim 52, wherein said functional group is a proton conducting group selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids and phosphonic acid salts.

63. A method as recited in Claim 52, wherein said functional group is
25 covalently attached to said carbon by a linking group selected from the group consisting of alkyls, aryls, halogenated alkyls, halogenated aryls, substituted alkyls, substituted aryls, polymers and substituted polymers.

64. A method as recited in Claim 52, wherein said active species phase comprises Pt.

65. A method as recited in Claim 52, wherein said active species phase comprises PtRu.

66. A method as recited in Claim 52, wherein said active species phase comprises Co.

5 67. A method as recited in Claim 52, wherein said active species phase comprises Ni.

68. A method as recited in Claim 52, wherein said active species phase comprises PtNiCo.

10 69. A method as recited in Claim 52, wherein said active species phase comprises PtCrCo

70. A method as recited in Claim 52, wherein said active species phase comprises Fe.

15 71. A method as recited in Claim 52, wherein said active species phase comprises a metal oxide of at least one of the elements selected from the group consisting of Au, Ag, Pt, Pd, Ni, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti or Al.

20 72. A method as recited in Claim 52, wherein said active species phase comprises at least one metal selected from the group consisting of Pt, Ag, Pd, Ru, Os, Ni, Rh, Ir, Co, Cr, Mo, W, V, Nb, Al, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, Ge, Sn, Y, La and lanthanide metals.

73. A method as recited in Claim 52, wherein said active species phase comprises an alloy of Pt with at least one other metal selected from the group consisting of Ru, Os, Cr, Ni, Mn and Co.

25 74. A method as recited in Claim 52, wherein said step of covalently attaching a functional group comprises spray processing a precursor solution comprising a carbon material and a diazonium salt.

75. A method as recited in Claim 52, wherein said depositing step comprises the step of spray processing said precursor solution, wherein said precursor solution further comprises a precursor to an active species phase.

76. A method as recited in Claim 75, wherein said spray processing step comprises spray processing in a spray dryer.

77. A method as recited in Claim 75, wherein said precursor to an active species phase comprises a platinum compound.

5 78. A method for making an electrocatalyst, comprising the steps of:

a) providing an electrocatalyst particle comprising an active species phase dispersed on a carbon support phase; and

b) modifying said carbon support by covalently attaching a functional group to said carbon support to form a modified carbon support phase.
10

79. A method as recited in Claim 78, wherein said modifying step comprises the step of reacting a diazonium salt in the presence of said electrocatalyst particle.

80. A method as recited in Claim 78, wherein said carbon support comprises carbon black.
15

81. A method as recited in Claim 78, wherein said active species phase comprises Pt.

82. A method as recited in Claim 78, wherein said active species phase comprises PtRu.

83. A method as recited in Claim 78, wherein said functional group is a hydrophobic group.
20

84. A method as recited in Claim 78, wherein said functional group is a hydrophilic group.

85. A method as recited in Claim 78, wherein said active species phase comprises Co.
25

86. A method as recited in Claim 78, wherein said active species phase comprises Ni.

87. A method as recited in Claim 78, wherein said active species phase comprises PtNiCo.

88. A method as recited in Claim 78, wherein said active species phase comprises PtCrCo

89. A method as recited in Claim 78, wherein said active species phase comprises Fe.

5 90. A method as recited in Claim 78, wherein said active species phase comprises a metal oxide of at least one element selected from the group consisting of Au, Ag, Pt, Pd, Ni, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti and Al.

10 91. A method as recited in Claim 78, wherein said active species phase comprises at least one metal from the group consisting of Pt, Ag, Pd, Ru, Os, Ni, Rh, Ir, Co, Cr, Mo, W, V, Nb, Al, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, Ge, Sn, Y, La and lanthanide metals.

15 92. A method as recited in Claim 78, wherein said active species phase comprises an alloy of Pt at least one metal selected from the group consisting of Ru, Os, Cr, Ni, Mn and Co.

93. A method as recited in Claim 78, wherein said modifying step comprises the step of spray processing a precursor solution comprising said electrocatalyst particles and a diazonium salt.

20 94. A method as recited in Claim 93, wherein said spray processing step comprises spray processing in a spray dryer.

25 95. A fuel cell, comprising an anode, a cathode and a proton exchange membrane disposed between said anode and said cathode, and further comprising a first gas/fluid diffusion layer adjacent to said anode and opposite said proton exchange membrane and a second gas/fluid diffusion layer adjacent to said cathode and opposite said proton exchange membrane, wherein at least one of said first and second gas diffusion layers comprises a modified carbon product.

96. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises carbon black.

30 97. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises carbon fibers.

98. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises graphite fibers.

99. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises graphite fibers modified with a hydrophilic functional group.

5 100. A fuel cell as recited in Claim 95, wherein said at least one gas diffusion layer comprises a carbon support and a microporous layer disposed on said carbon support, wherein said microporous layer comprises said modified carbon product.

10 101. A fuel cell as recited in Claim 100, wherein said at least one gas diffusion layer has an average pore size of from about 100 nanometers to about 500 nanometers.

102. A fuel cell as recited in Claim 100, wherein said microporous layer has an average thickness of from about 2 μm to about 20 μm .

15 103. A fuel cell as recited in Claim 95, wherein said at least one gas diffusion layer comprises a carbon support and wherein modified carbon product particles are disposed within said carbon support.

104. A fuel cell as recited in Claim 103, wherein said modified carbon product particles have an average particle size of from about 1 μm to about 30 μm .

20 105. A fuel cell as recited in Claim 103, wherein said at least one gas diffusion layer comprises from about 5 vol.% to about 70 vol.% of said modified carbon product particles.

106. A fuel cell as recited in Claim 95, wherein said at least one gas diffusion layer comprises a carbon support that is a modified carbon product.

25 107. A fuel cell as recited in Claim 95, wherein both of said first and said second gas diffusion layers comprises a modified carbon product.

108. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises a hydrophilic functional group.

30 109. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises a hydrophilic functional group selected from the group

consisting of carboxylic acids, carboxylic salts, sulfonic acids, sulfonic salts, phosphonic acids, phosphonic salts, amines, amine salts and alcohols.

110. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises a hydrophobic functional group.

5 111. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises a hydrophobic functional group selected from the group consisting of saturated cyclics, unsaturated cyclics, saturated aliphatics, unsaturated aliphatics and polymeric.

10 112. A fuel cell as recited in Claim 95, wherein said modified carbon product comprises a hydrophilic functional group and a hydrophobic functional group.

113. A fuel cell as recited in Claim 95, wherein said modified carbon products comprise a steric inhibiting functional group.

15 114. A fuel cell as recited in Claim 95, wherein said at least one gas diffusion layer comprises predominately hydrophilic modified carbon products on a first side and predominately hydrophobic modified carbon products on a second side opposite said first side.

20 115. A fuel cell as recited in Claim 95, wherein said gas diffusion layer comprises a major planar surface and comprises a chemical gradient lateral to said planar surface.

116. A fuel cell as recited in Claim 95, wherein said gas diffusion layer comprises a major planar surface and comprises a chemical gradient perpendicular to said planar surface.

25 117. A method for the fabrication of a gas diffusion layer in fuel cell, comprising the steps of:

- a) providing a carbon support;
- b) depositing a first ink composition comprising a first modified carbon product on said carbon support to form a first sublayer; and
- c) depositing a second ink composition comprising a second
30 modified carbon product over said first sublayer, wherein said first

modified carbon product and said second modified carbon product have different hydrophilic properties.

118. A method as recited in Claim 117, wherein at least one of said depositing steps comprise depositing with an ink-jet device.

5 119. A method as recited in Claim 117, wherein said depositing steps comprise depositing using a method selected from the group consisting of spraying, analog deposition, lithography, flexographic printing, slot die, roll-coating, xerography and electrostatic printing.

10 120. A method as recited in Claim 117, wherein at least one of said first and second modified carbon products comprises graphite.

121. A method as recited in Claim 117, wherein at least one of said first and second modified carbon products comprises carbon black.

122. A method for the fabrication of a gas diffusion layer, comprising the steps of:

- 15 a) providing a carbon support; and
- b) contacting said carbon support with a diazonium salt; and
- c) treating said diazonium salt to covalently bond a functional group to said carbon support and form a modified carbon support product.

20 123. A method as recited in Claim 122, wherein said carbon support comprises carbon cloth.

124. A method as recited in Claim 122, wherein said carbon support comprises carbon paper.

125. A method as recited in Claim 122, wherein said functional group is a hydrophilic group.

25 126. A method are recited in Claim 122, wherein said functional group is a hydrophobic group.

30 127. A fuel cell stack comprising a plurality of membrane electrode assemblies and at least one bipolar plate separating said membrane electrode assemblies, wherein said bipolar plate comprises at least a first modified carbon product.

128. A fuel cell stack as recited in Claim 127, wherein said modified carbon product comprises a hydrophilic functional group.

129. A fuel cell stack as recited in Claim 127, wherein said modified carbon product comprises a hydrophobic functional group.

5 130. A fuel cell stack as recited in Claim 127, wherein said bipolar plate comprises a gradient hydrophilic structure.

131. A fuel cell stack as recited in Claim 127, wherein said bipolar plate comprises a gradient hydrophilic structure that is perpendicular to a major planar surface of said bipolar plate.

10 132. A fuel cell stack as recited in Claim 127, wherein said bipolar plate comprises a gradient hydrophilic structure that is lateral to a major planar surface of said bipolar plate.

133. A fuel cell stack as recited in Claim 127, wherein said modified carbon product has been surface modified by the direct reaction of a diazonium salt of the general formula $YRN=N^+X^-$, where X is an anion, R is a linking group and Y is a functional group.

15

134. A fuel cell stack as recited in Claim 133, wherein Y is a hydrophilic functional group.

135. A fuel cell stack as recited in Claim 133, wherein Y is a hydrophobic functional group.

20

136. A fuel cell stack as recited in Claim 127, wherein said bipolar plate comprises a printed hydrophilic layer comprising said modified carbon product.

137. A fuel cell stack as recited in Claim 127, wherein said bipolar plate comprises a printed hydrophobic layer comprising said modified carbon product.

25 138. A fuel cell stack as recited in Claim 127, wherein said hydrophobic layer is printed with a direct-write tool.

139. A fuel cell stack as recited in Claim 127, wherein said hydrophobic layer is digitally printed.

140. A fuel cell stack as recited in Claim 127, wherein said modified carbon product comprises a surface-modifying group selected from the group consisting of saturated and unsaturated cyclics and aliphatics.

5 141. A fuel cell stack as recited in Claim 127, wherein said modified carbon product comprises a surface-modifying group selected from the group consisting of halogenated saturated and unsaturated cyclics and aliphatics.

142. A fuel cell stack as recited in Claim 127, wherein said modified carbon product comprises a surface-modifying group selected from the group consisting of sulfonic, carboxylic and phosphonic acids and salts.

10 143. A method for treating a current collector having at least a first carbonaceous surface to increase the hydrophobicity of said first carbonaceous surface, comprising the step of covalently bonding a surface-modifying group to said first carbonaceous surface.

15 144. A method for treating a current collector having at least a first carbonaceous surface to decrease the hydrophobicity of said first carbonaceous surface, comprising the step of covalently bonding a surface-modifying group to said first carbonaceous surface.

20 145. A method for treating a gas distribution system comprising at least a first carbonaceous surface to increase the hydrophobicity of said first carbonaceous surface, comprising the step of covalently bonding a surface-modifying group to said first carbonaceous surface.

25 146. A method for treating a gas distribution system comprising at least a first carbonaceous surface to decrease the hydrophobicity of said first carbonaceous surface, comprising the step of covalently bonding a surface-modifying group to said first carbonaceous surface.

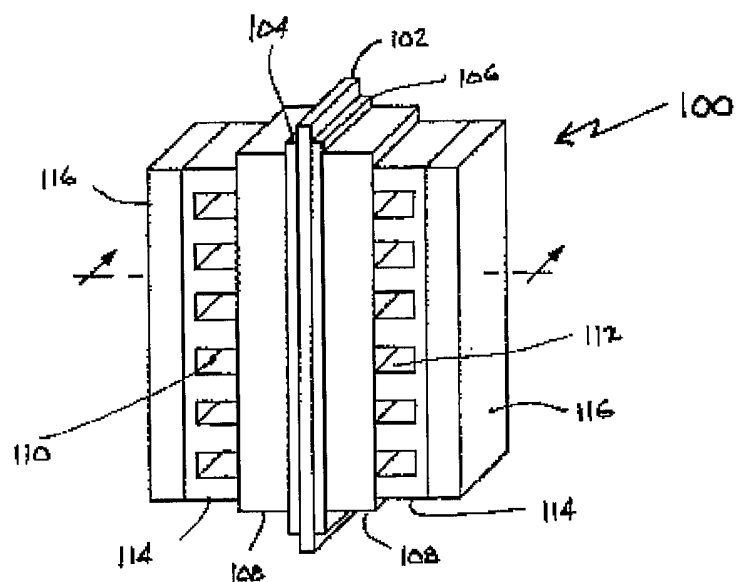


FIG. 1 (a)

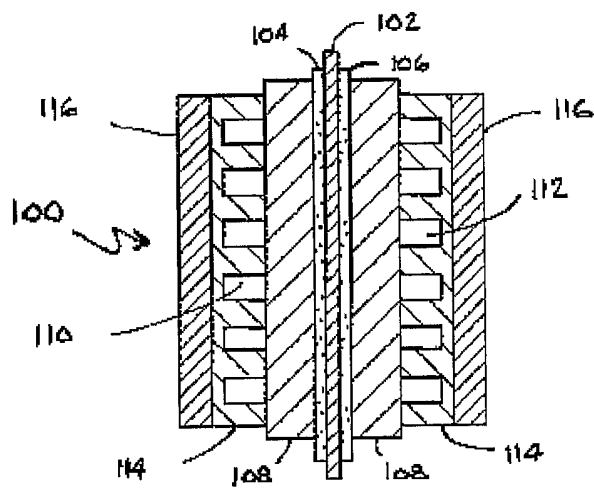


FIG. 1 (b)

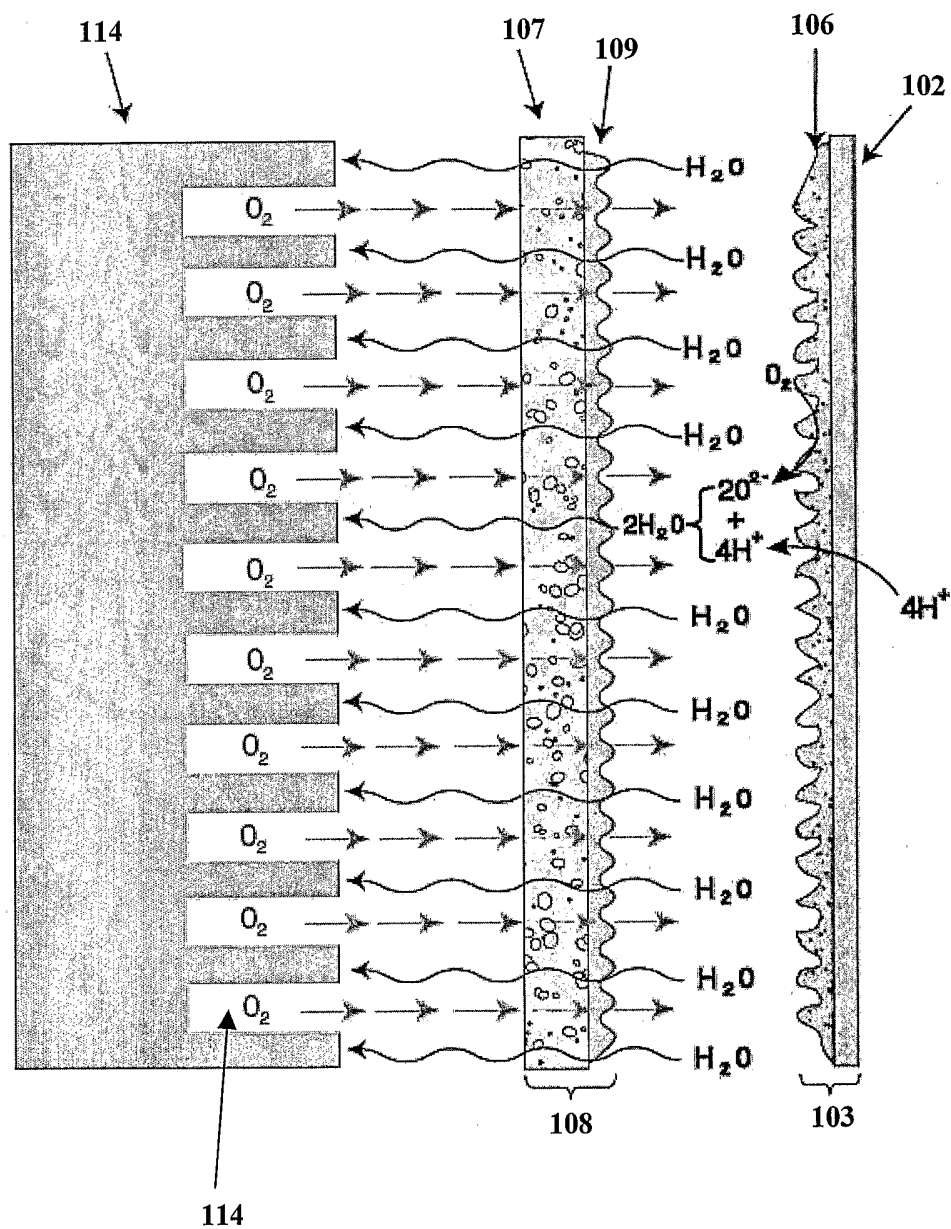


Fig. 2

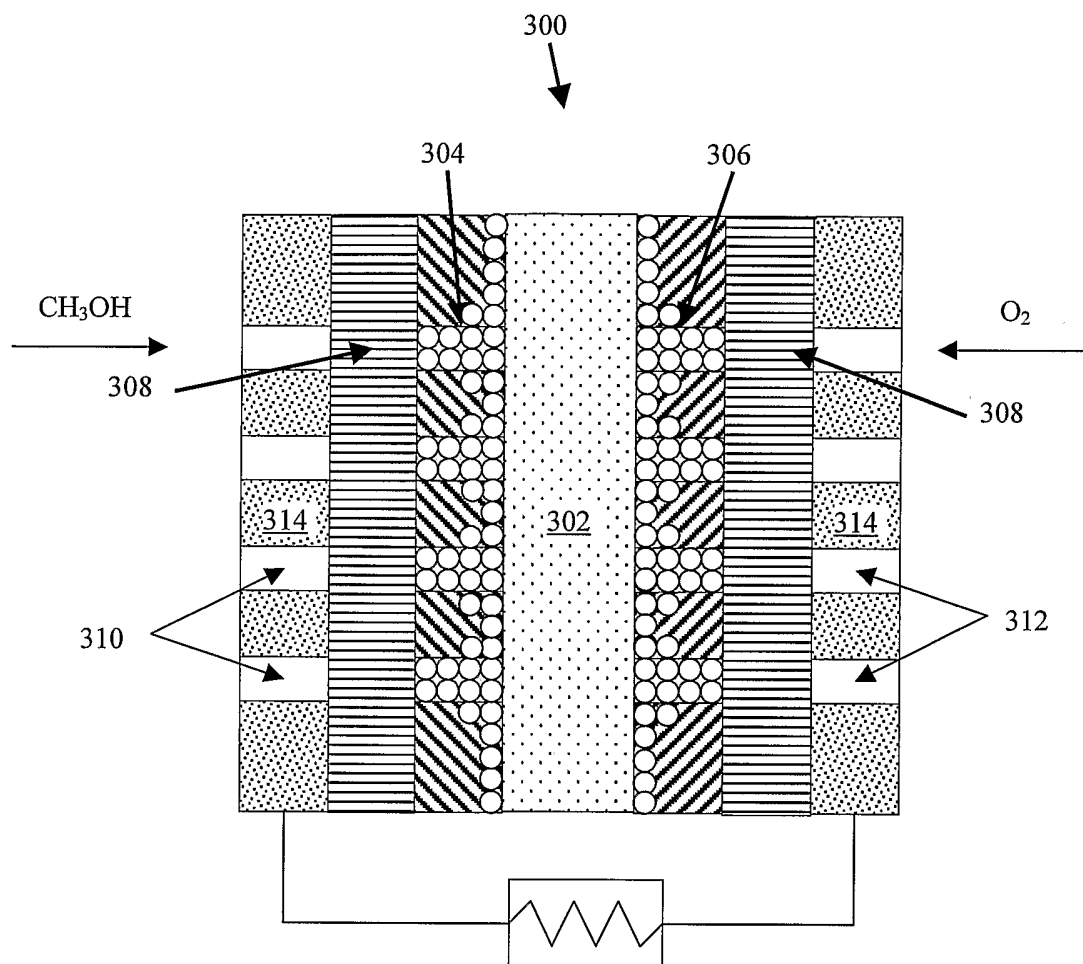


Fig. 3

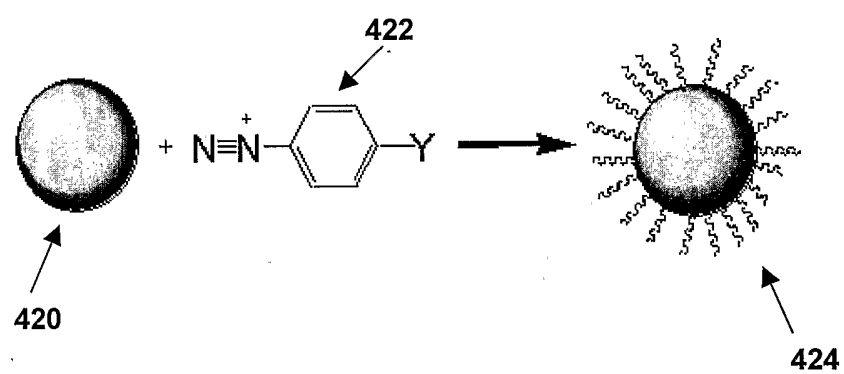


Fig. 4

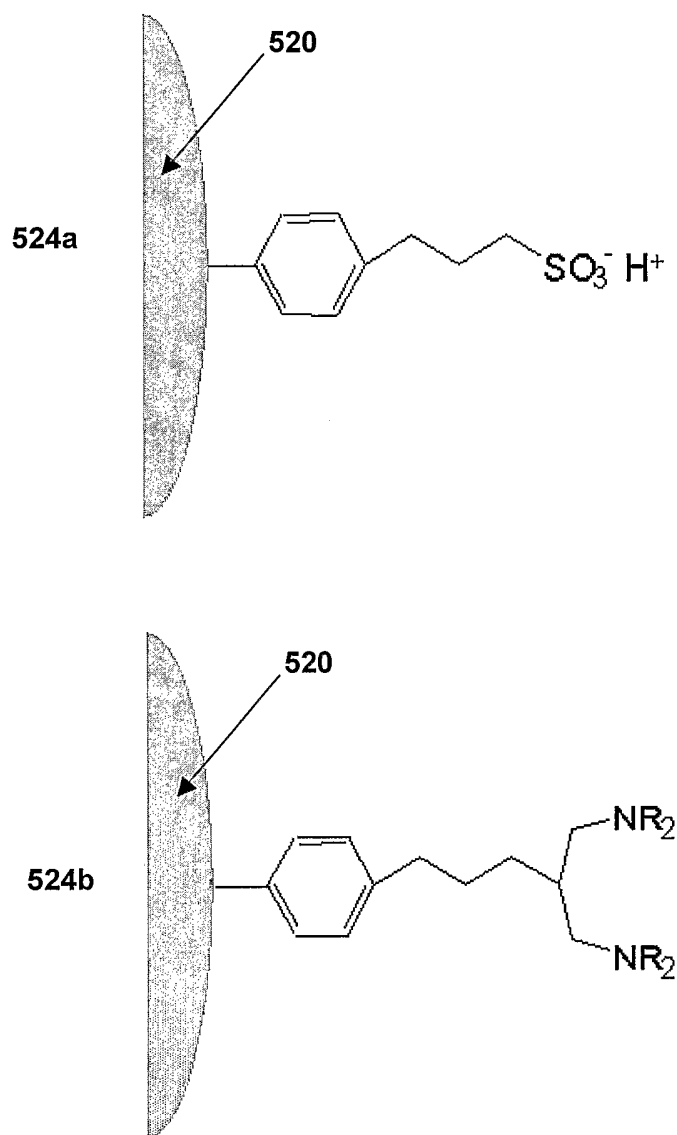


Fig. 5

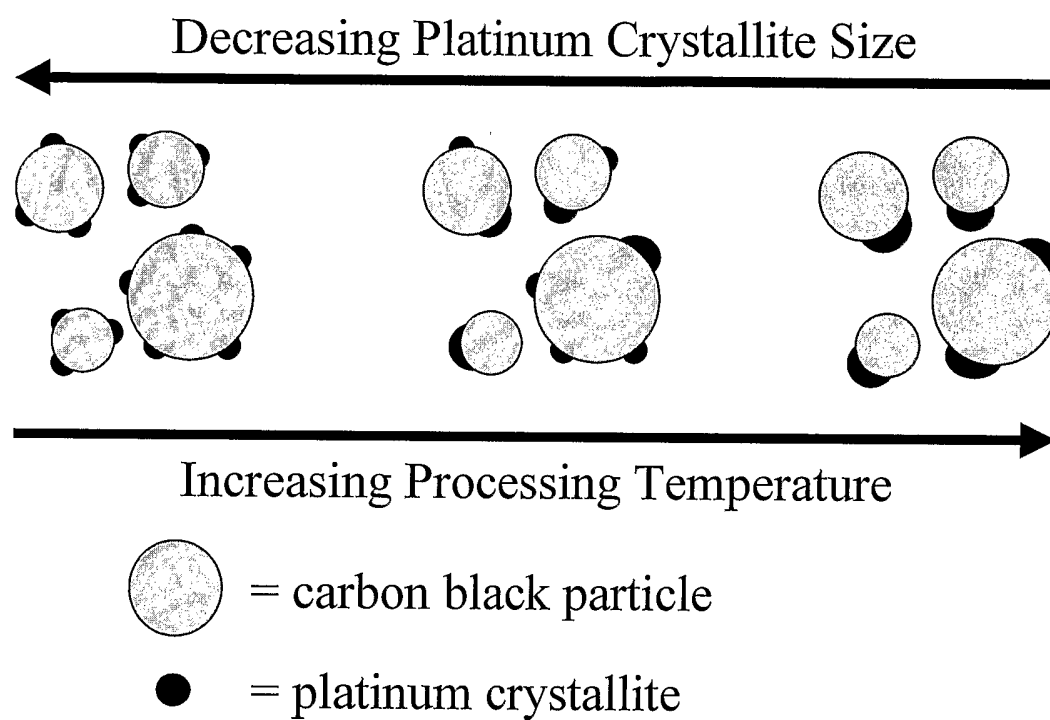


Fig. 6

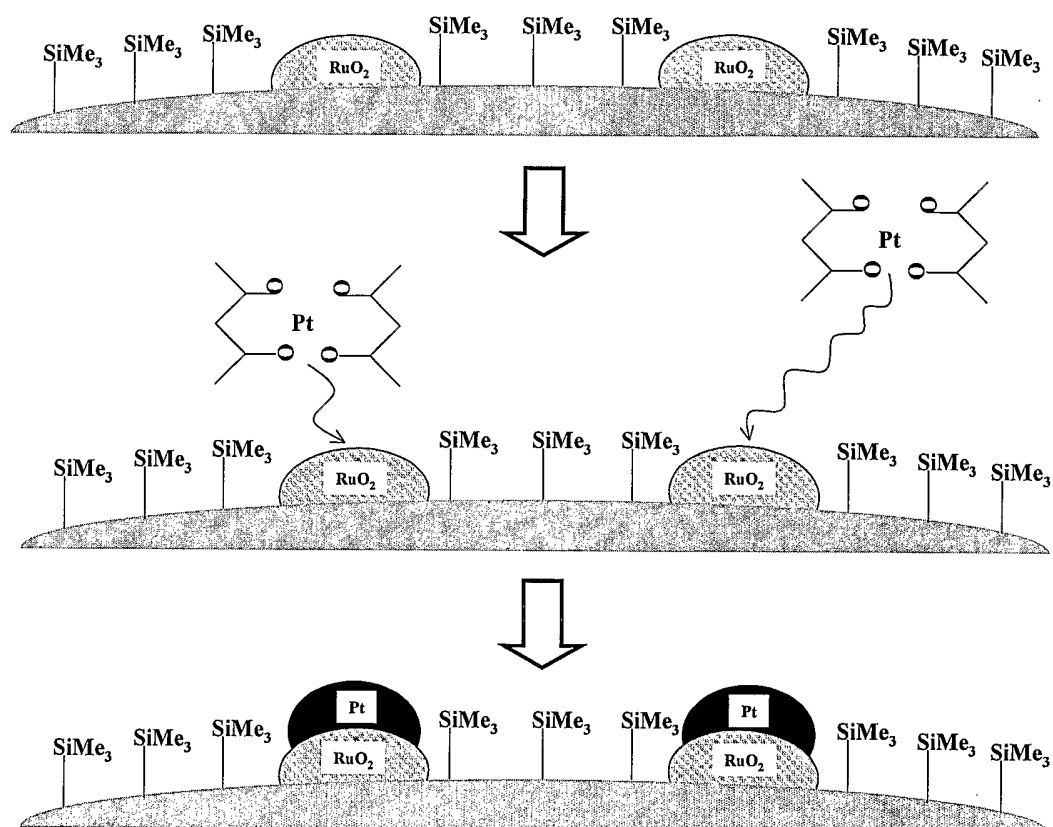


Fig. 7

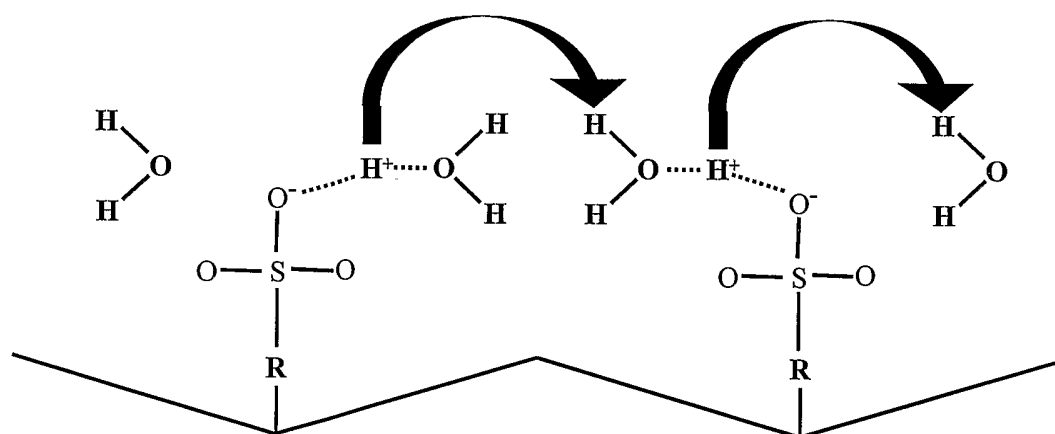


Fig. 8

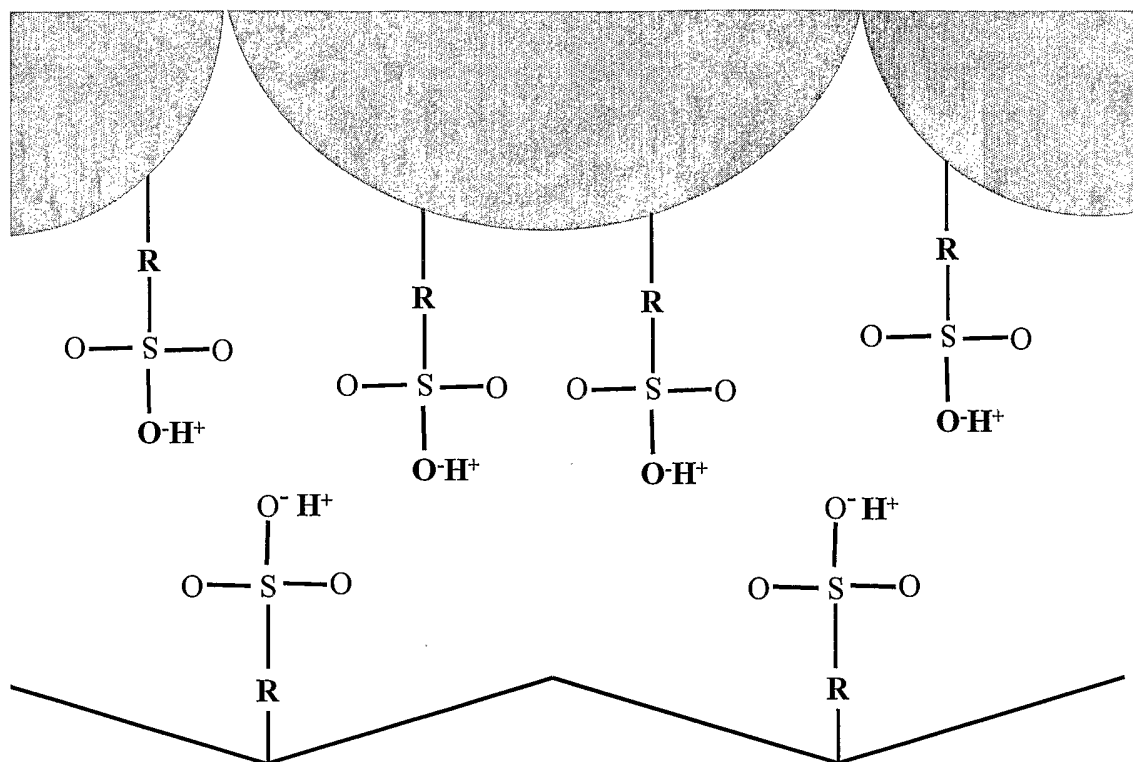


Fig. 9

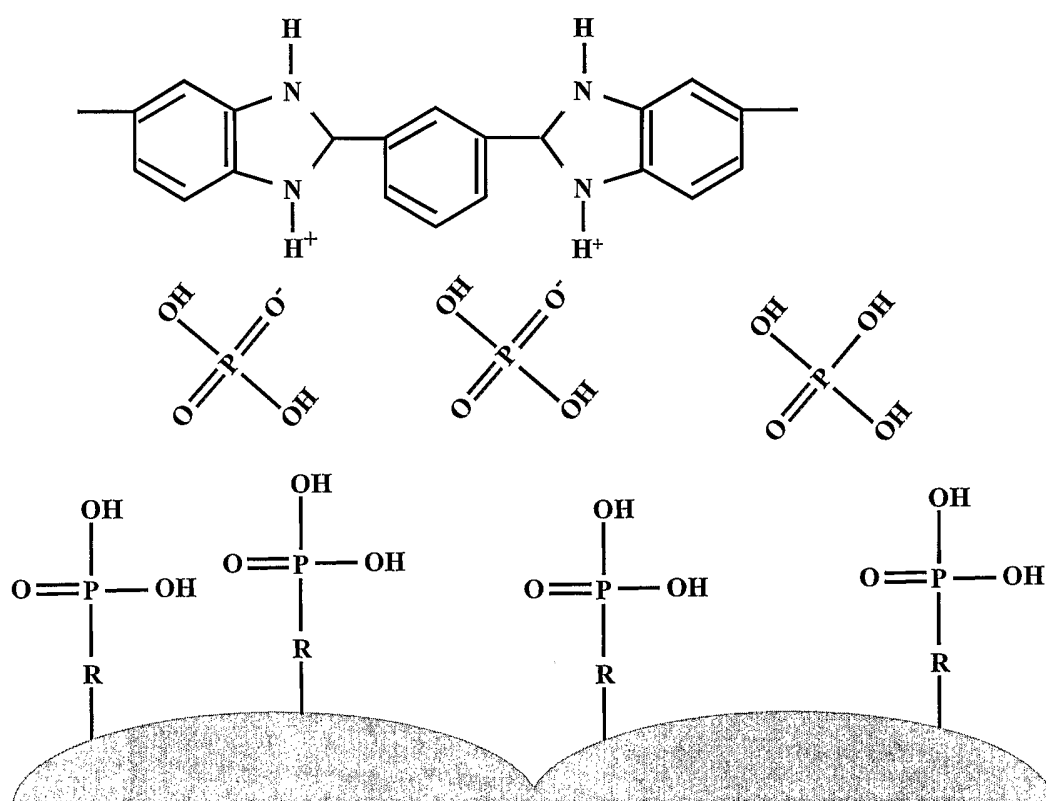


Fig. 10

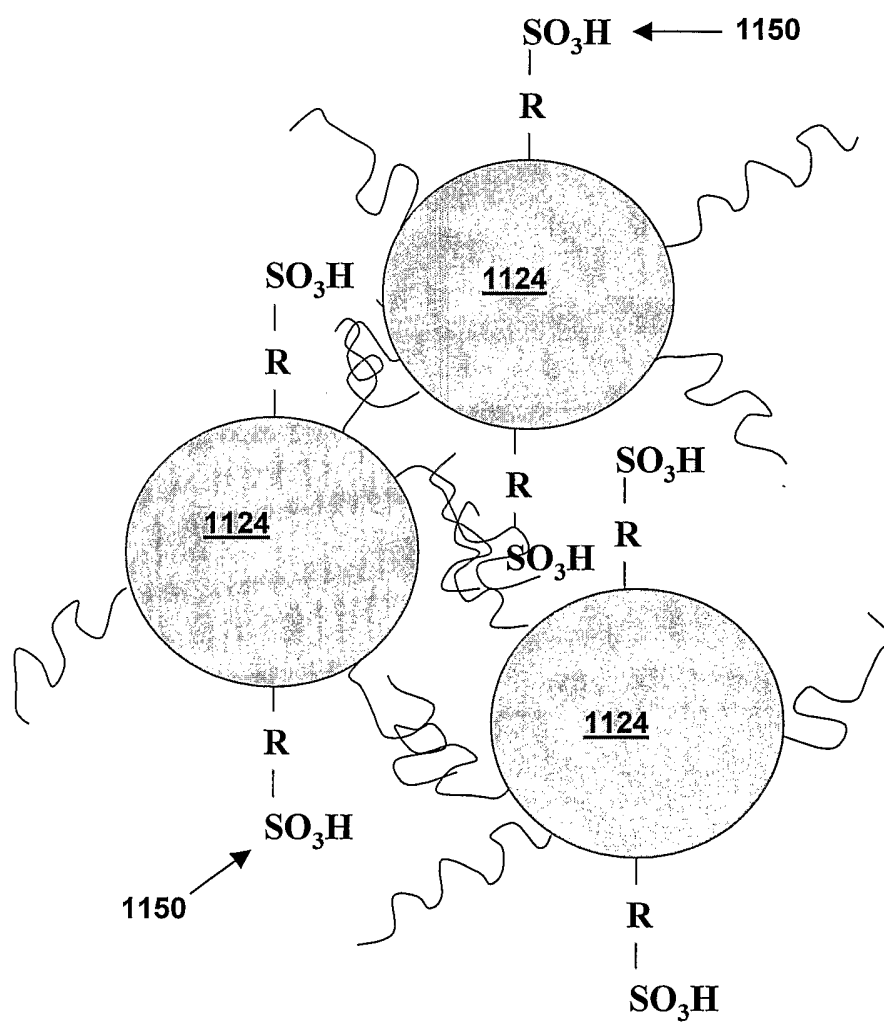


Fig. 11

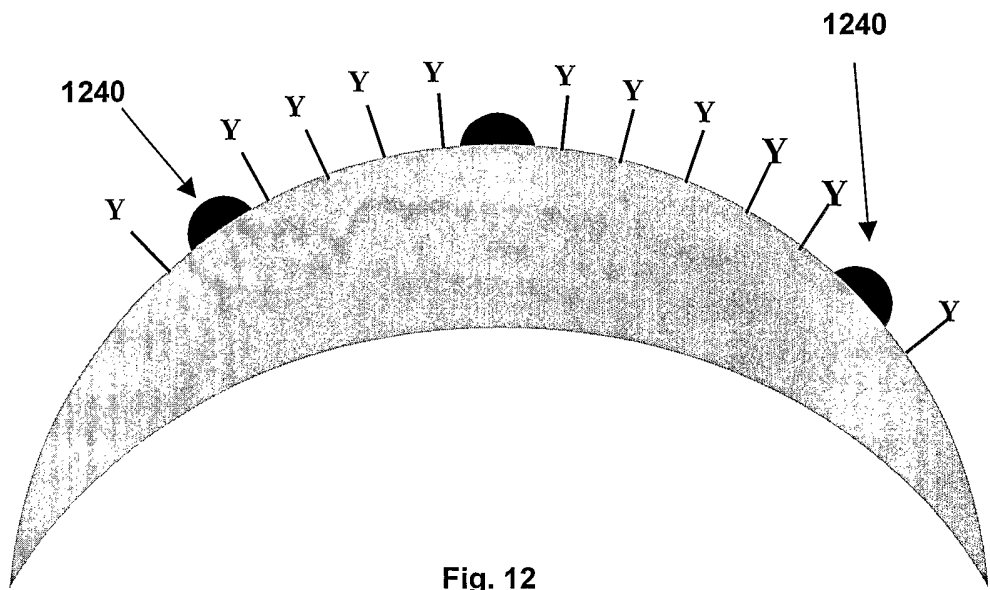


Fig. 12

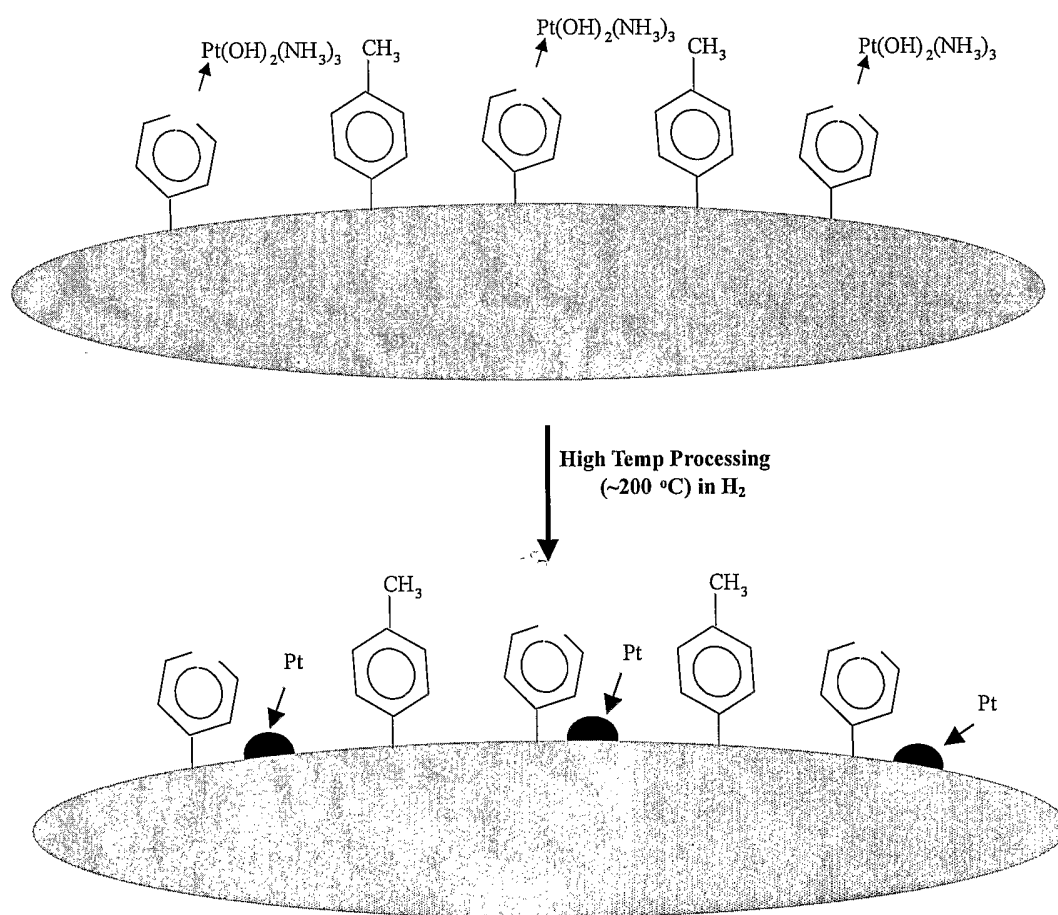


Fig. 13

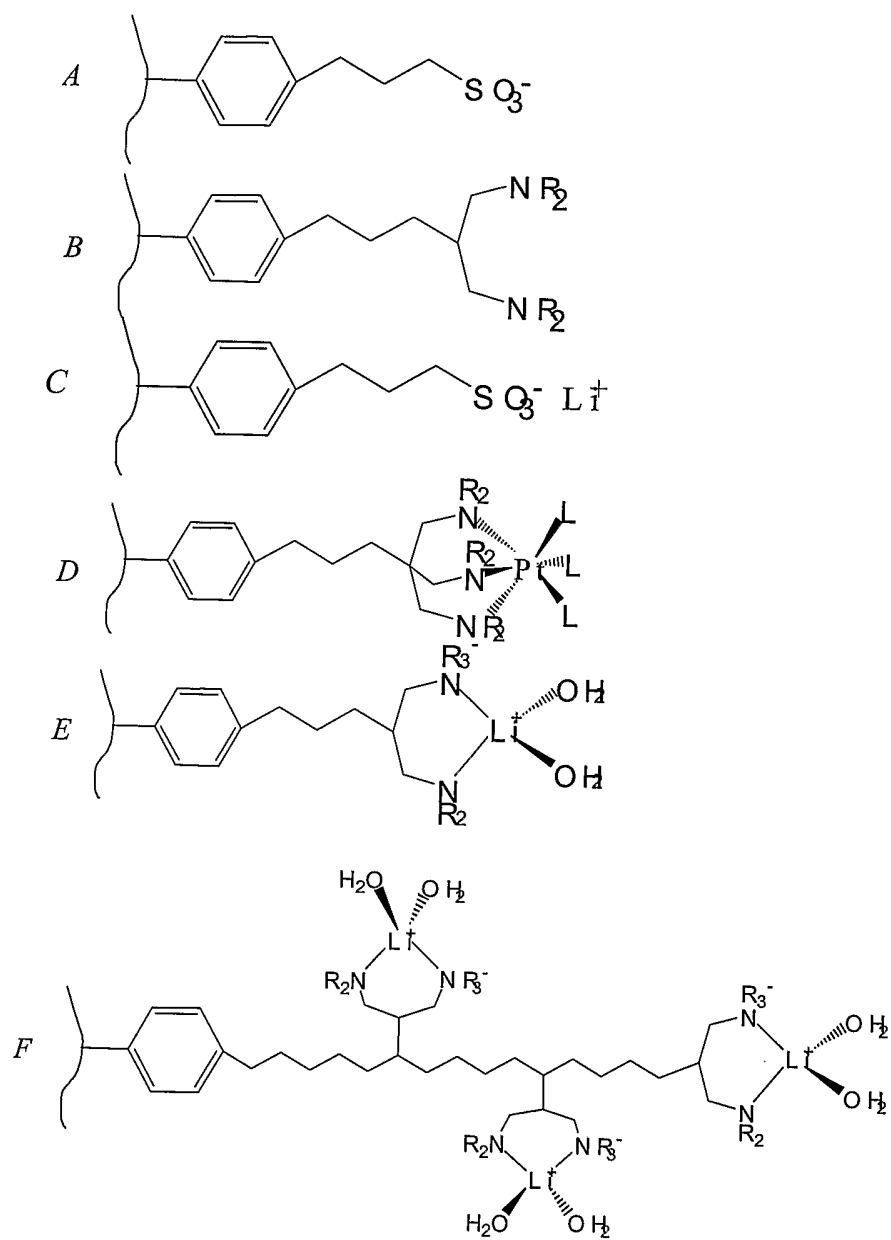


Fig. 14

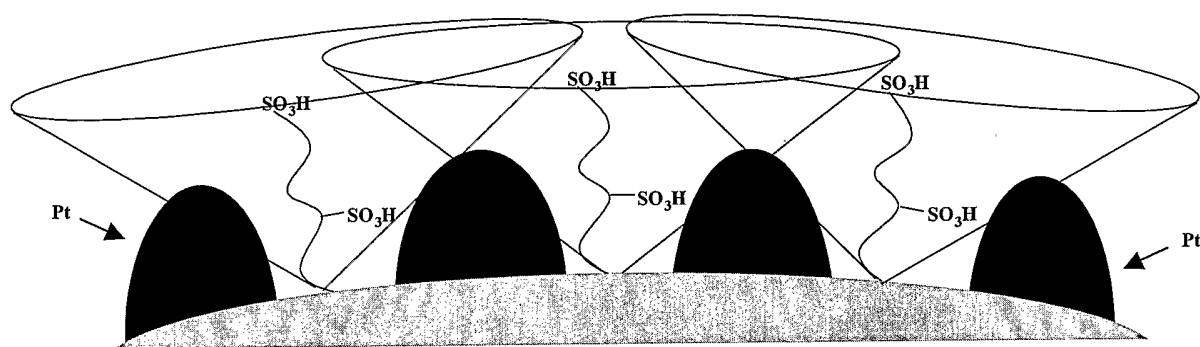
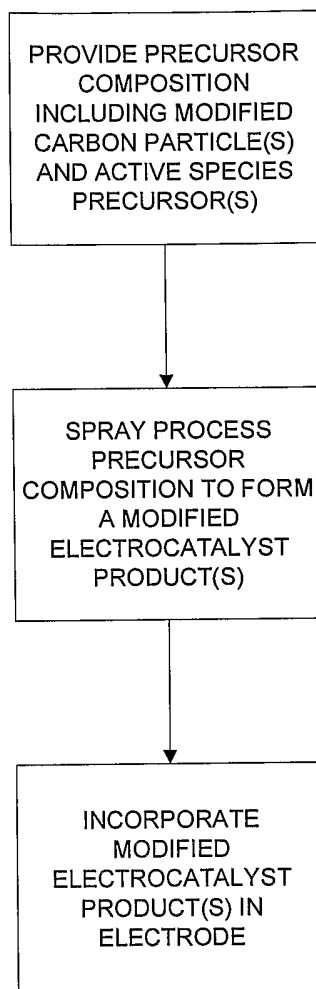
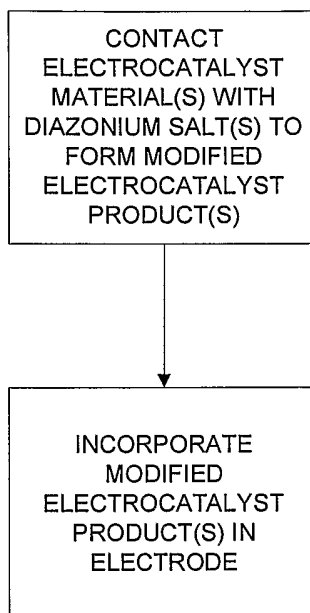


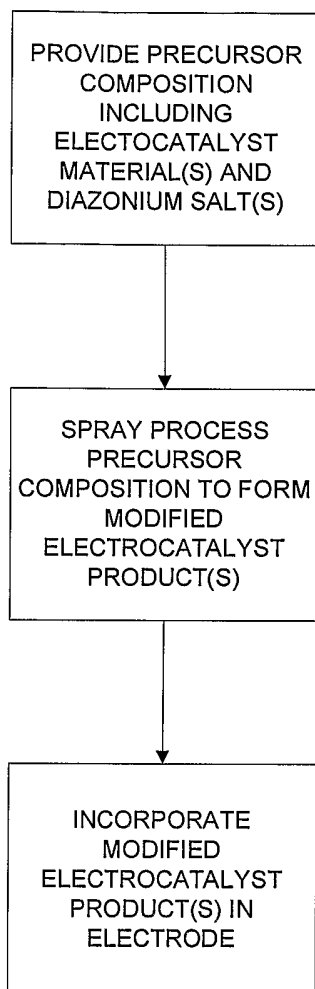
Fig. 15



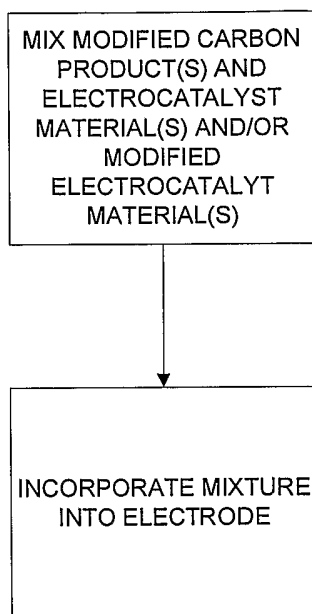
16(a)



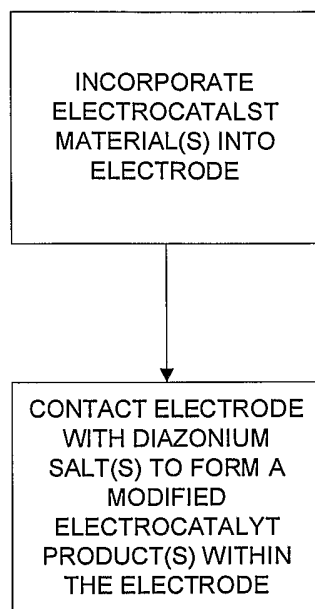
16(b)



16(c)



16(d)



16(e)

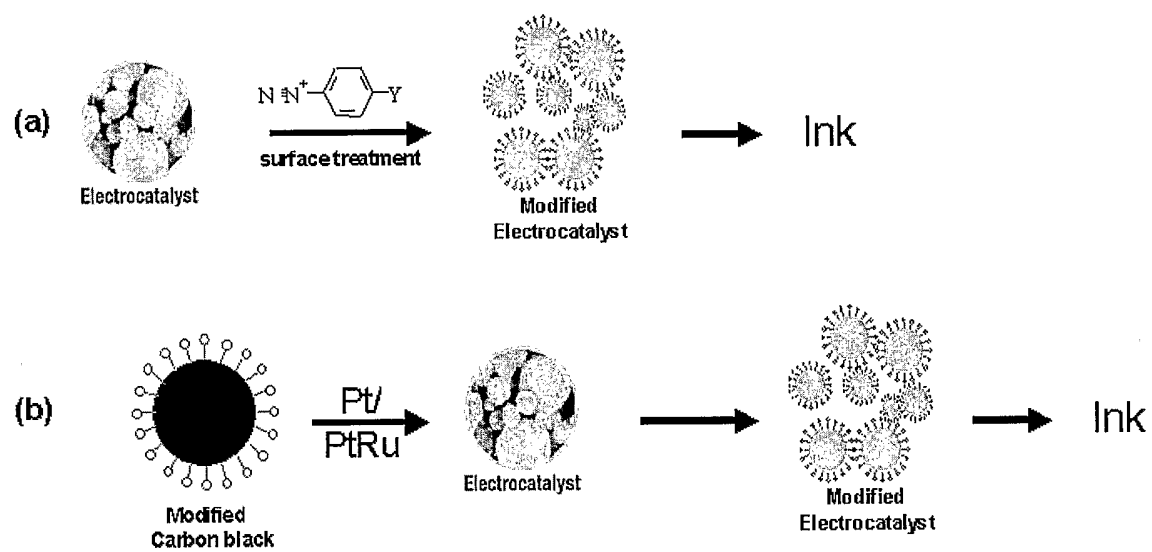


Fig. 17

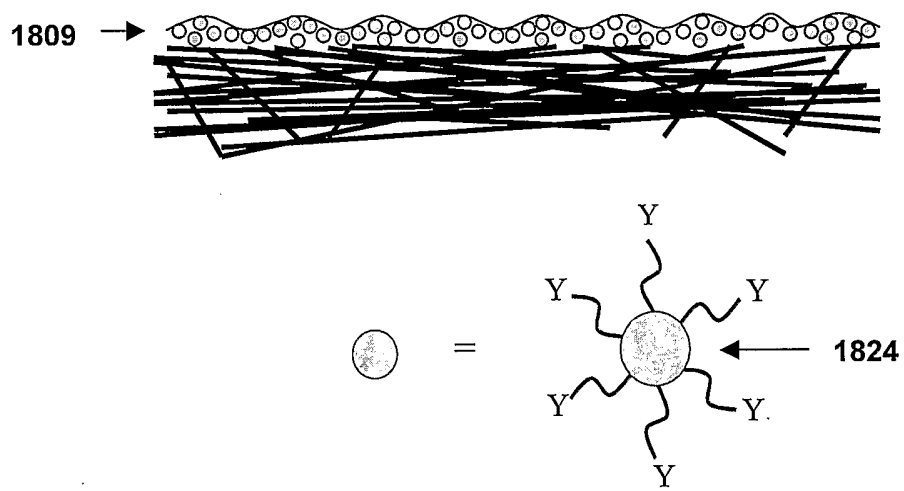


Fig. 18

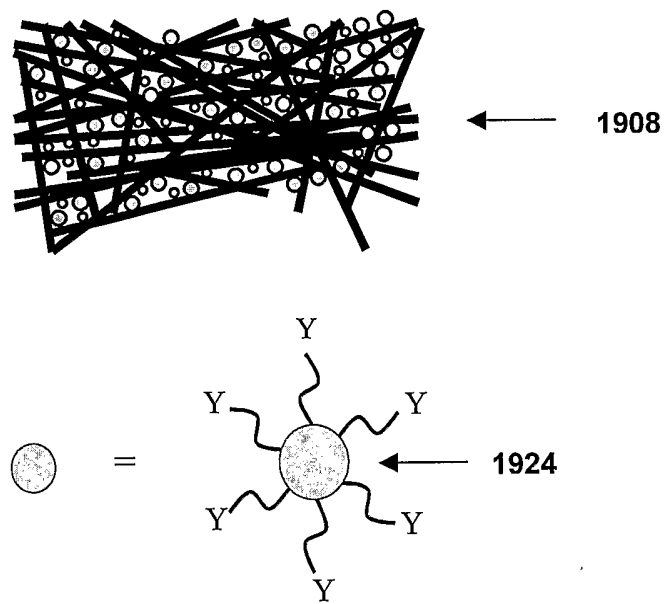


Fig. 19

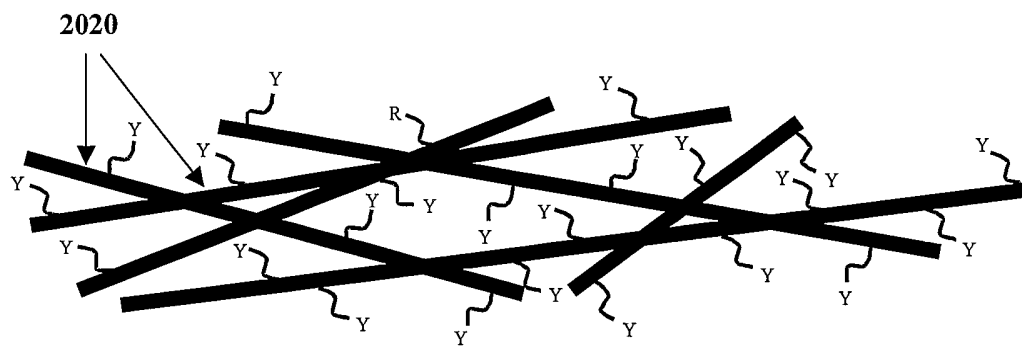


Fig. 20

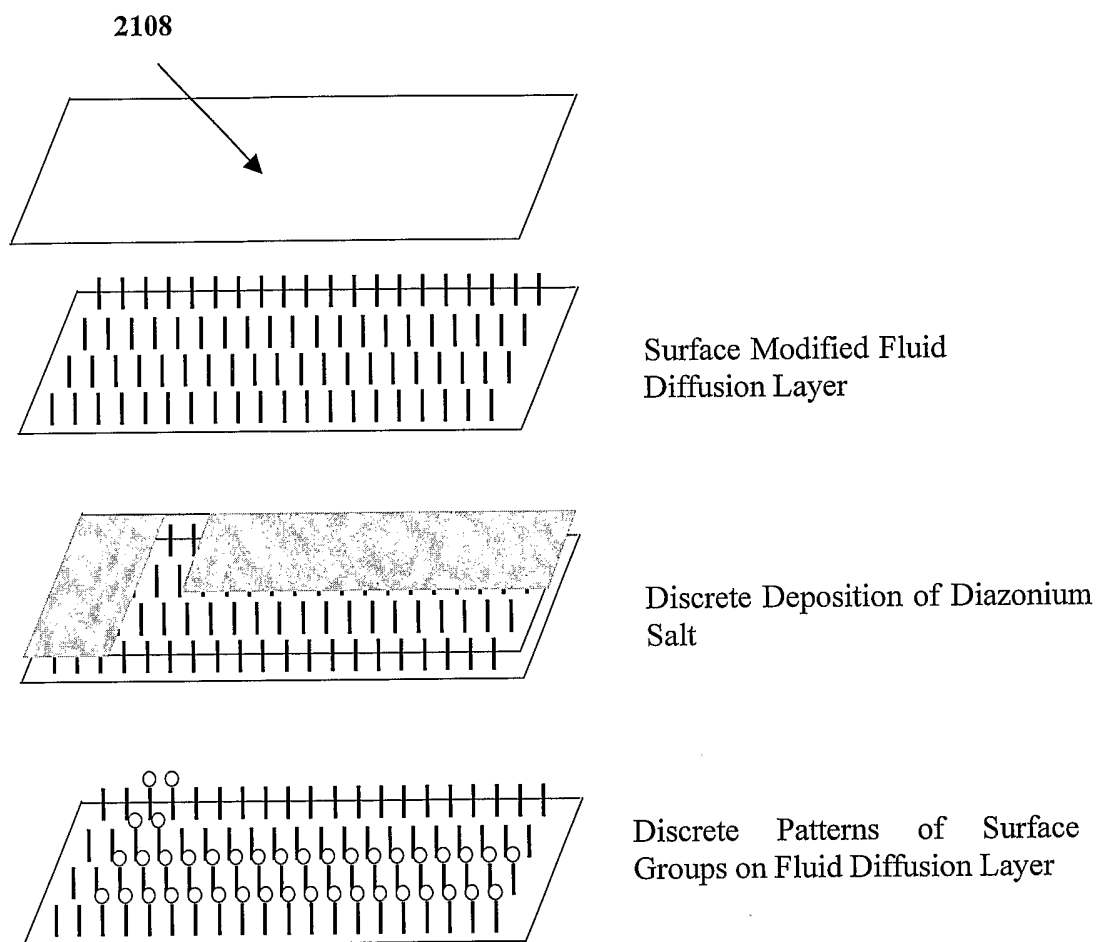


Fig. 21

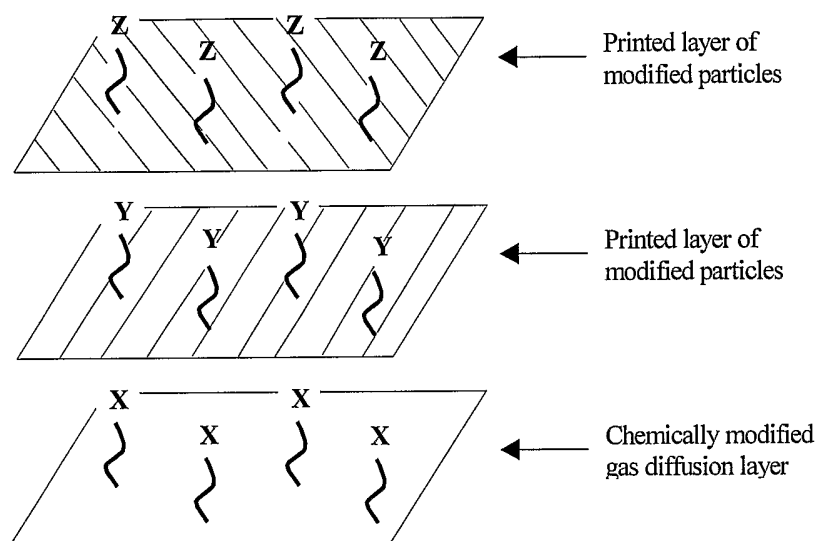


Fig. 22

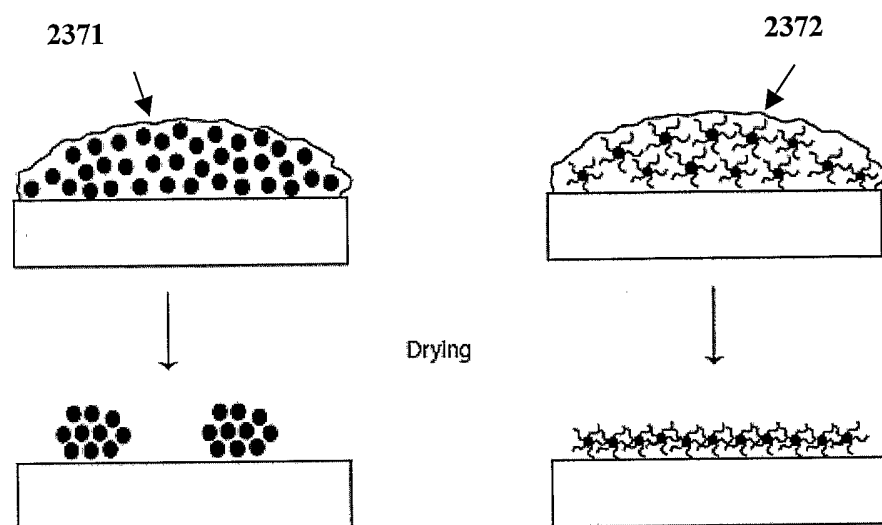


Fig. 23

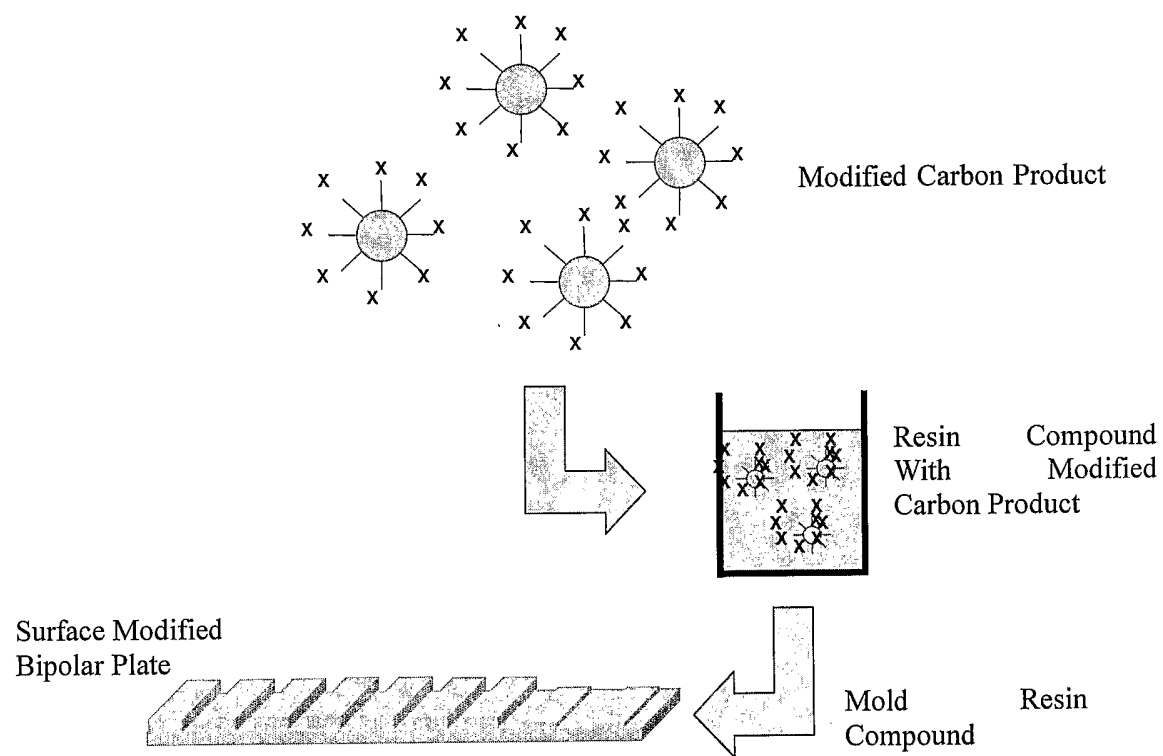


Fig. 24

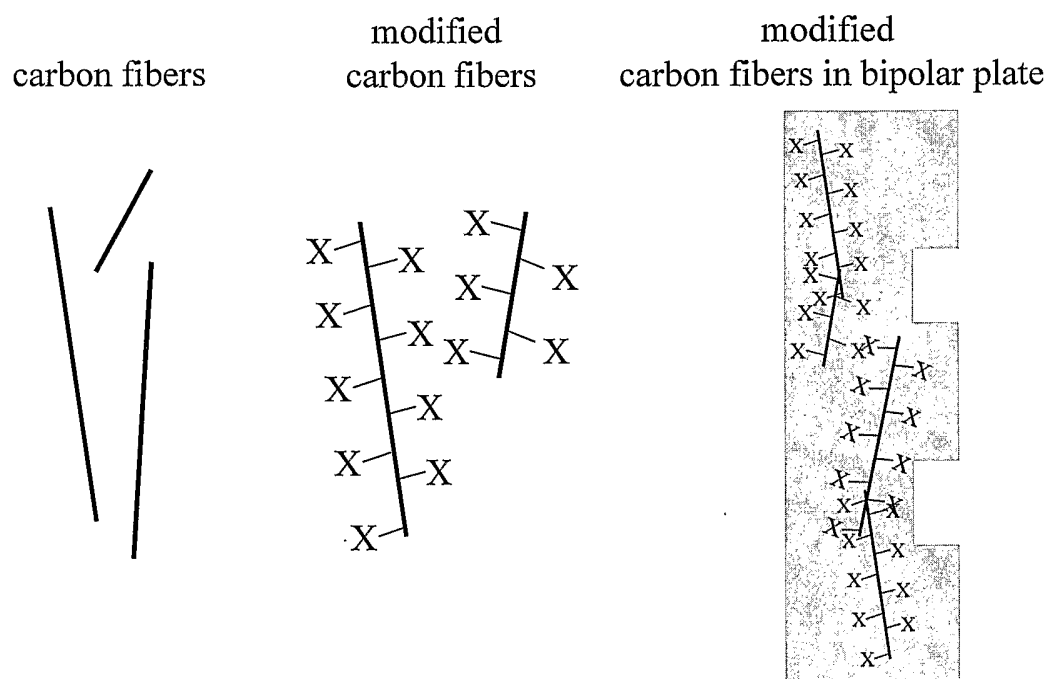
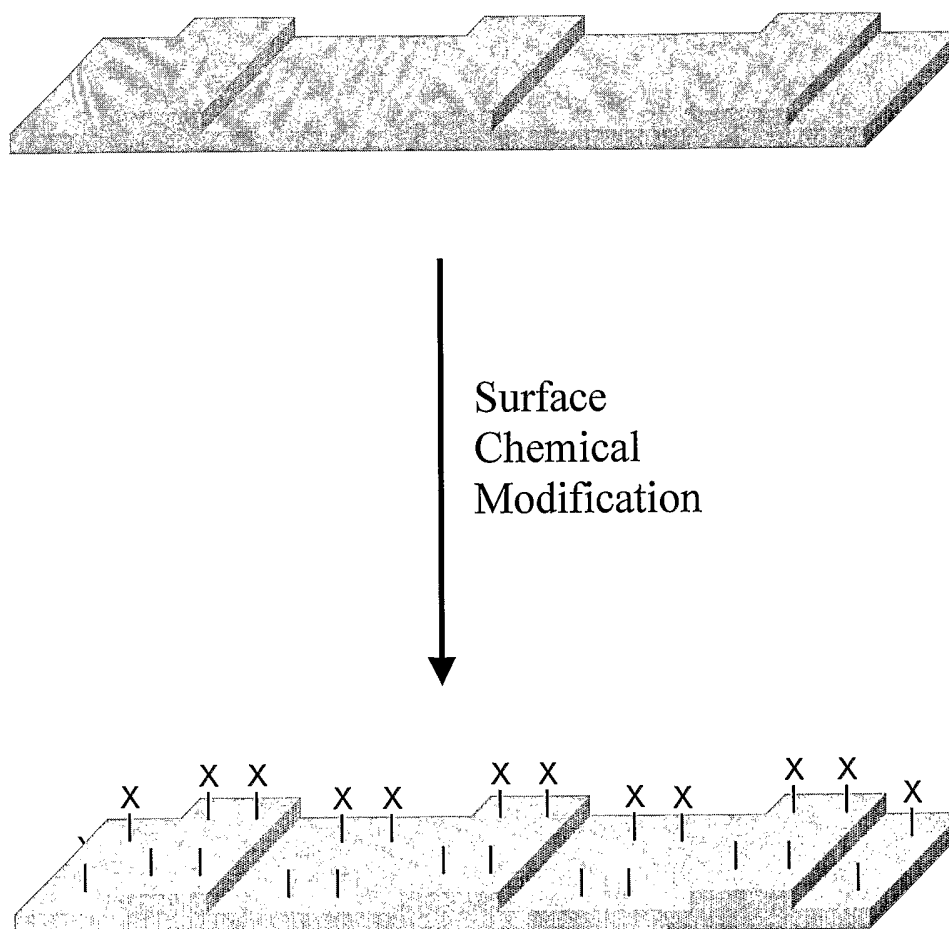
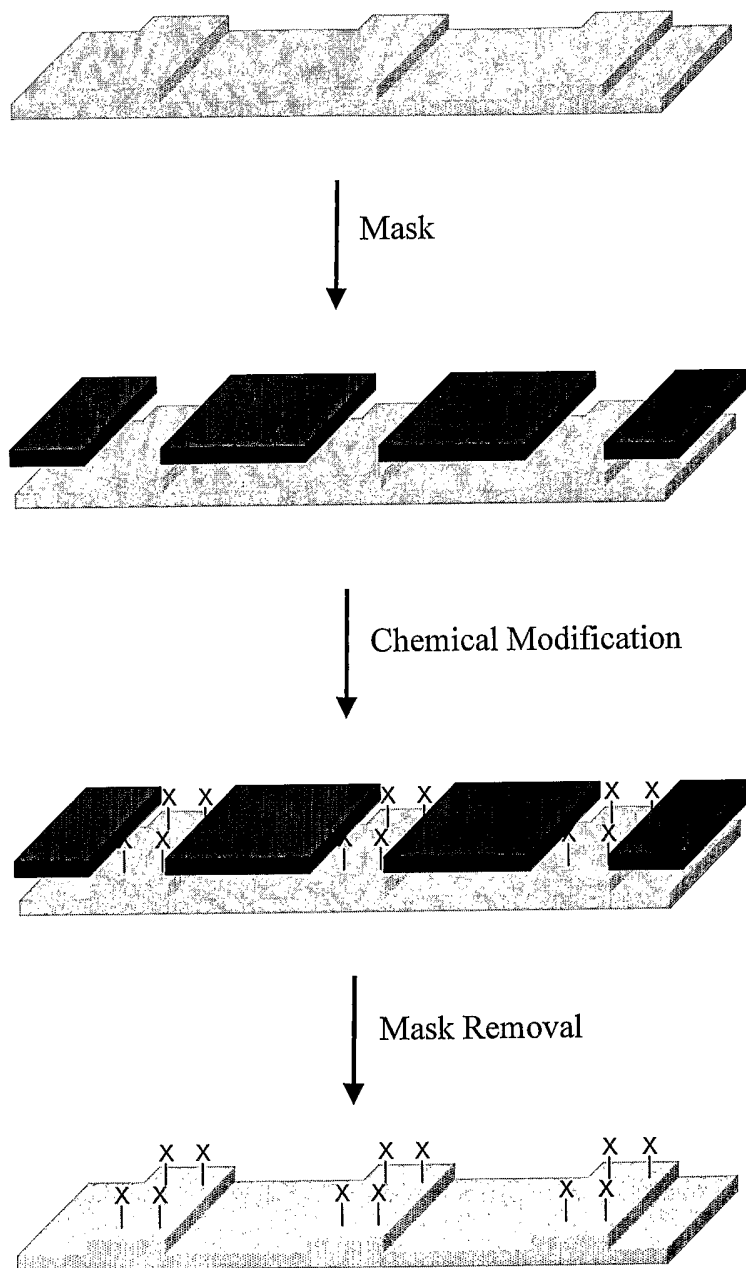


Fig. 25

**Fig. 26**

**Fig. 27**

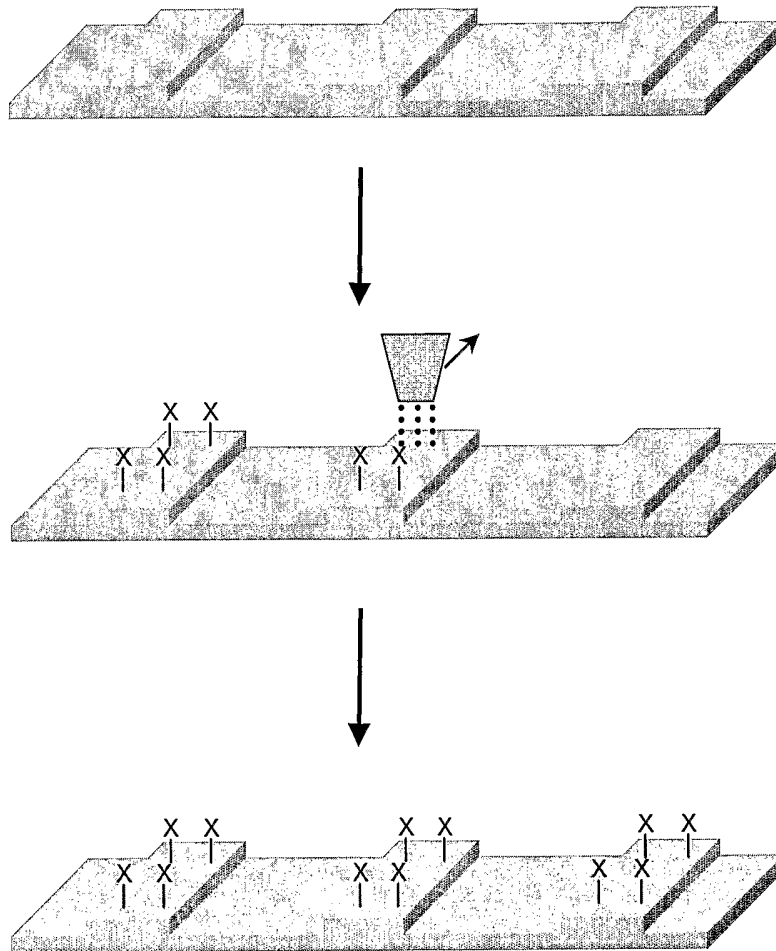


Fig. 28

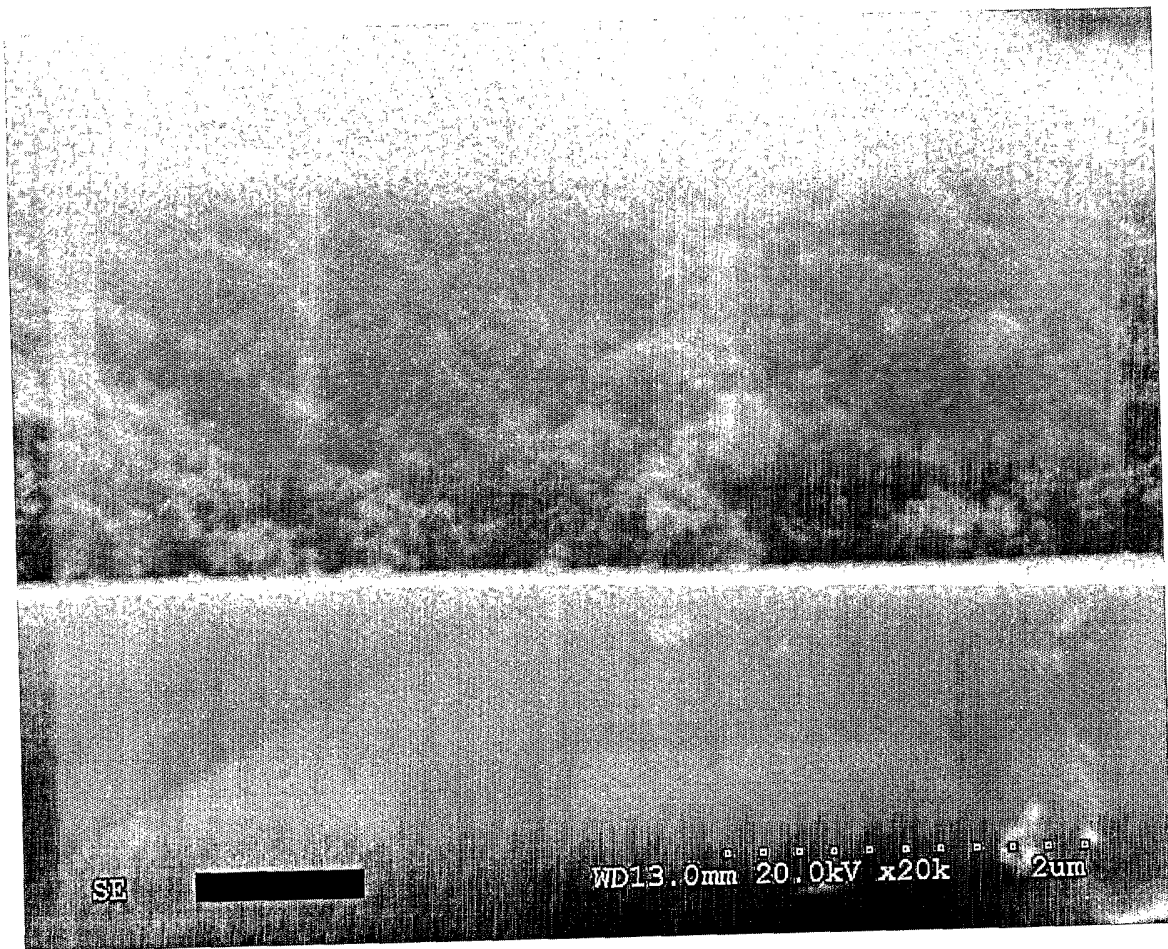


Fig. 29(a)

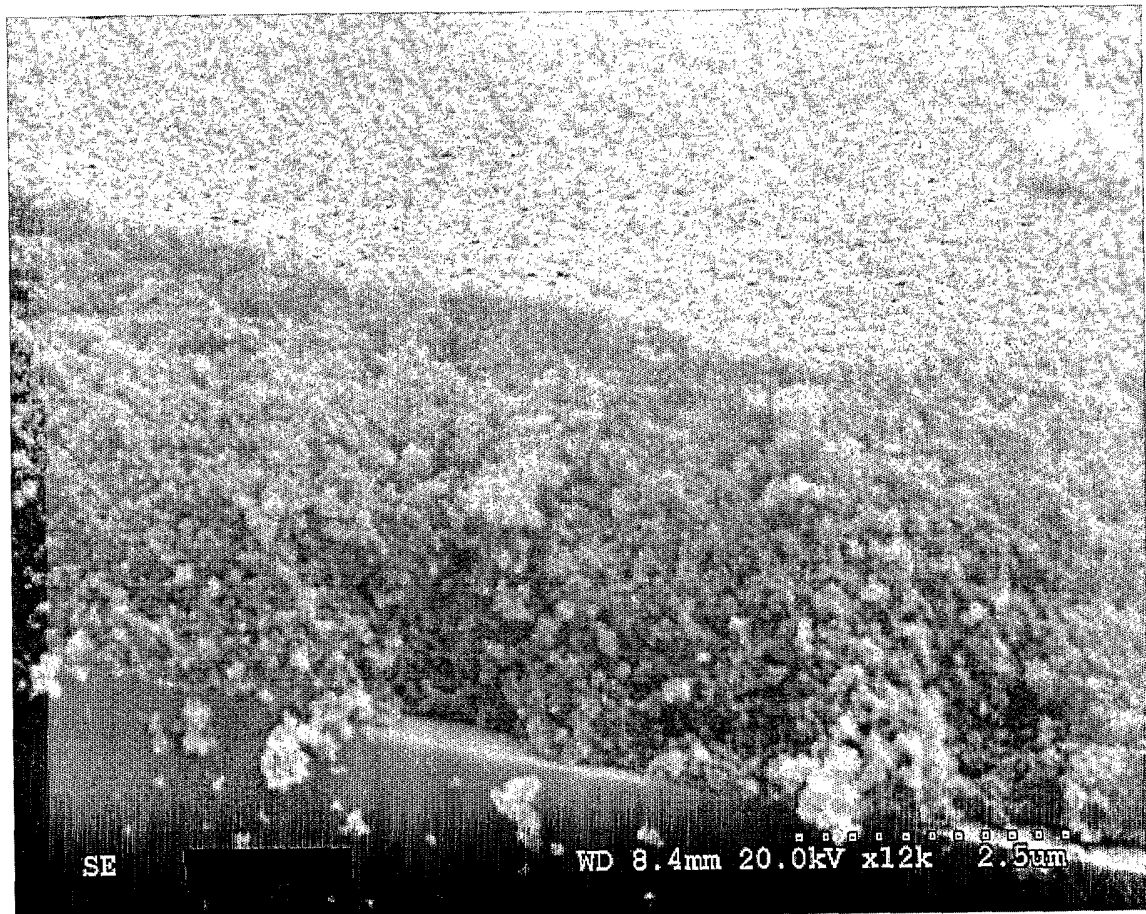


Fig. 29(b)