

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 December 2001 (13.12.2001)

PCT

(10) International Publication Number  
**WO 01/93999 A2**

(51) International Patent Classification<sup>7</sup>: **B01J**

(21) International Application Number: PCT/US01/18565

(22) International Filing Date: 8 June 2001 (08.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/589,710 8 June 2000 (08.06.2000) US  
09/815,380 22 March 2001 (22.03.2001) US

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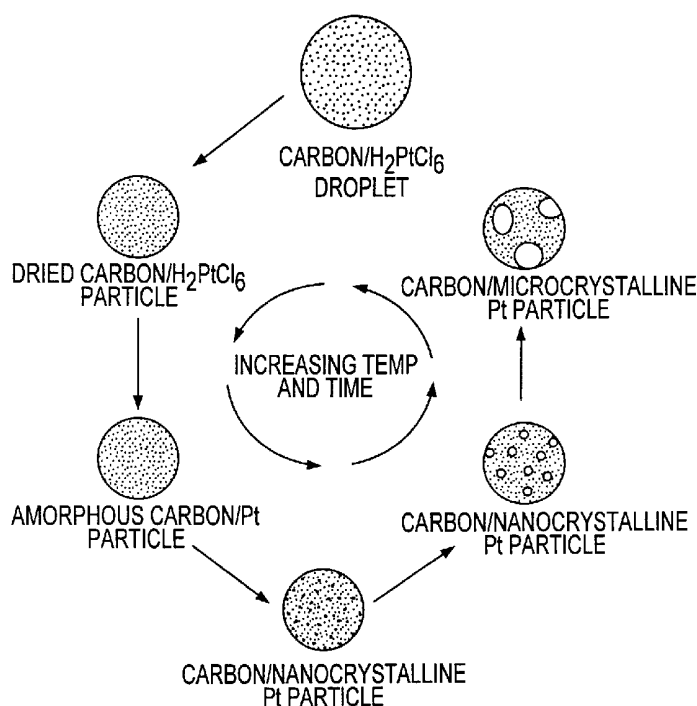
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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,

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(54) Title: ELECTROCATALYST POWDERS, METHODS FOR PRODUCING POWDERS AND DEVICES FABRICATED FROM SAME



(57) Abstract: Electrocatalyst powders and methods for producing electrocatalyst powders, such as carbon composite electrocatalyst powders. The powders have a well-controlled microstructure and morphology. The method includes forming the particles from an aerosol of precursors by heating the aerosol to a relatively low temperature, such as not greater than about 400°C.



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LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

**(84) Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# ELECTROCATALYST POWDERS, METHODS FOR PRODUCING POWDERS AND DEVICES FABRICATED FROM SAME

## BACKGROUND OF THE INVENTION

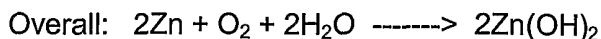
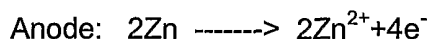
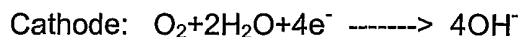
### 1. Field of the Invention

The present invention relates to particulate materials such as electrocatalyst powders for the fabrication of energy devices such as fuel cells and to methods for producing such powders, as well as products and devices incorporating the powders. The powders are preferably produced by spray processing of precursors to the particulate materials.

### 2. Description of Related Art

With the advent of portable and hand-held electronic devices and an increasing demand for electric automobiles due to the increased strain on non-renewable natural resources, there is a need for the rapid development of high performance, economical power systems. Such power systems require improved devices for energy storage using batteries and energy generation using fuel cells.

One type of battery which offers many competitive advantages is the zinc-air battery, which relies upon the redox couples of oxygen and zinc. Zinc-air batteries operate by adsorbing oxygen from the surrounding air and reducing the oxygen using an oxygen reduction catalyst at the cathode, referred to as the air electrode. As the oxygen is reduced, zinc metal is oxidized. The reactions of a zinc-air alkaline battery during discharge are:



Typically, the air electrodes are alternatively stacked with the zinc electrodes and are packaged in a container that is open to the air. When the battery cell discharges, oxygen is reduced to  $\text{O}^{2-}$  at the cathode while zinc metal is oxidized to  $\text{Zn}^{2+}$  at the anode. Since Zn can be electrodeposited from

aqueous electrolytes to replenish the anode, zinc-air batteries can be secondary batteries as well as primary batteries.

Among the advantages of secondary zinc-air batteries over other rechargeable battery systems are safety, long run time and light weight. The batteries contain no toxic materials and operate at one atmosphere of pressure. They can operate as long as 10 to 14 hours, compared to 2 to 4 hours for most rechargeable lithium-ion batteries and can be stored for long periods of time without losing their charge. The light weight of zinc-air batteries leads to good power density (power per unit of weight or volume), which is ideal for portable applications.

The two major problems associated with secondary zinc-air batteries, however, are limited total power and poor rechargeability/cycle lifetime. Increased power is becoming a major area of attention for battery manufacturers trying to meet the increased demands of modern electronics. Current zinc-air batteries can deliver from about 200 to 450 W/kg which may enable the batteries to be used in certain low-power laptops and other portable devices that have relatively low power requirements. Most laptops and other portable electronic devices, however, require batteries that are able to provide a level of power that is higher than the capabilities of current zinc-air batteries. The main reason for the low power of zinc-air batteries is believed to be related to the inefficiency of the catalytic reaction to reduce oxygen in the air electrodes. Poor accessibility of the catalyst and the local microstructural environment around the catalyst and adjoining carbon reduces the efficiency of the oxygen reduction. See, for example, P.N. Ross et al., Journal of the Electrochemical Society, Vol. 131, pg. 1742 (1984).

Rechargeability is also a problem with zinc-air batteries. The batteries have a short cycle life, degrading significantly in performance after about 200 recharging cycles or less. The short cycle life of zinc-air batteries is also believed to be related to the catalyst used in the air electrodes. Specifically, it is believed that corrosion of the carbon used for the electrocatalyst in these systems leads to a loss in capacity and hence, a decreased discharge time.

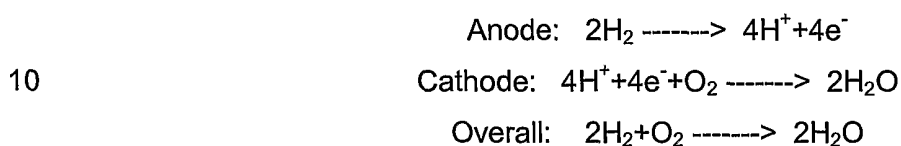
Primary (non-rechargeable) alkaline zinc-air batteries are currently used to power hearing aids and other devices that require low current densities over long periods of time. Zinc-air hearing aid batteries also include an air cathode and a zinc-based anode. The electrocatalyst powder is formed into a layer for the air  
5 cathode which catalytically converts oxygen in the air into hydroxide ion. The hydroxide ion is then transported in an alkaline electrolyte through a separator to the anode where it reacts with zinc to form zincate ( $\text{Zn}(\text{OH})_4^{2-}$ ) ion and zinc ion ( $\text{Zn}^{2+}$ ) and liberates electrons. Improved electrocatalyst powders at the air cathode would advantageously extend the life of such primary batteries.

10 In addition to improvements in energy storage, there is a need for improvements in environmentally friendly and economical energy production. Fuel cells are electrochemical devices which 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 because fuel cells convert  
15 chemical energy to electrical energy as the chemical reactants are continuously delivered to the fuel cell. When the fuel cell is off, it has zero electrical potential. As a result, fuel cells are typically used to produce a continuous source of electrical energy and compete with other forms of continuous electrical energy production such as the combustion engine, nuclear power and coal-fired power  
20 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) or solid polymer fuel cells.

One of the critical requirements for these energy devices is the efficient  
25 catalytic conversion of the reactants to electrical energy. A significant obstacle to the wide-scale commercialization of such devices is the need for highly efficient electrocatalyst materials for this conversion process.

One example of a fuel cell utilizing electrocatalysts for the chemical reactions is a Proton Exchange Membrane Fuel Cell (PEMFC). PEMFC stack  
30 includes hundreds of membrane electrode assemblies (MEA's) each including a cathode and anode constructed from, for example, carbon cloth. The anode and cathode sandwich a proton exchange membrane which has a catalyst layer on

each side of the membrane. Power is generated when hydrogen is fed into the anode and oxygen (air) is fed into the cathode. In a reaction typically catalyzed by a platinum-based catalyst in the catalyst layer of the anode, the hydrogen ionizes to form protons and electrons. The protons are transported through the proton exchange membrane to a catalyst layer on the opposite side of the membrane (the cathode) where another catalyst, typically platinum or a platinum alloy, catalyzes the reaction of the protons with oxygen to form water. The reactions can be written as follows:



The electrons formed at the anode are routed to the cathode through an electrical circuit which provides the electrical power.

The critical issues that must be addressed for the successful commercialization of fuel cells are cell cost, cell performance and operating lifetime. For automotive applications improved power density is critical whereas for stationary applications higher voltage efficiencies are necessary. In terms of fuel cell cost, current fuel cell stacks employ MEA's that include platinum electrocatalysts with a loading of about 4 milligrams of platinum per square centimeter of electrode on each of the anode and cathode. At a typical cell performance of 0.42 watts per square centimeter, then about 19 grams of platinum per kilowatt is required (8 mg Pt per cm<sup>2</sup> over 0.42 watts per cm<sup>2</sup>). Platinum metal is very expensive and a significant cost reduction in the electrocatalyst is necessary for these cells to become economically viable. However, reducing the amount of precious metal is not a suitable solution because there is also a strong demand for improved cell performance, which relies on the presence of the platinum electrocatalyst.

The major technical challenge is improving the performance of the cathode with air as the oxidant. Platinum metal electrocatalysts for oxygen reduction are used in both alkaline and acid electrolyte media and are used in PEM fuel cells, alkaline fuel cells, hybrid fuel cells and others.

The conventional synthesis of electrocatalyst powders that include active species on a support material involves several steps. First, an appropriate high surface area catalyst support (e.g., alumina, titania, silica or carbon) is impregnated with a solution containing the precursor of the active species.

5    Sufficient contact time is used for the adsorption of the active species precursor to occur and to achieve a uniform deposition of the precursor on the support surface. The catalyst is then dried to remove the solvent, for example at temperatures of 100°C to 120°C for about 2 to 12 hours. The catalyst is then heated to elevated temperatures, typically 400°C to 600°C in air, so that the

10   precursor is converted to the active species. Typically, the oxide catalysts do not require further treatment.

The foregoing method generally results in poor control over the composition and microstructure of the composite powders. The morphology and surface area of the electrocatalyst powders are characteristics that have a critical

15   impact on the performance of the catalyst. The morphology determines the packing density and the surface area determines the type and number of surface adsorption centers where the active species are formed during synthesis of the electrocatalyst. The inability to control the fundamental electrocatalyst powder characteristics is a major obstacle for the future development of energy storage

20   and production devices.

It would be advantageous to provide a flexible production method capable of producing electrocatalyst powders which would enable control over the powder characteristics such as particle size, surface area and pore structure as well as the versatility to accommodate compositions which are either difficult or

25   impossible to produce using existing production methods. It would be particularly advantageous if such powders could be produced in large quantities on a substantially continuous basis. It would also be advantageous to provide improved devices, such as batteries and fuel cells, having thin layers and improved properties.

30

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the steps of electrocatalyst particle formation according to an embodiment of the present invention.

Fig. 2 illustrates a spray dryer that is useful for the production of electrocatalyst powders according to an embodiment of the present invention.

Fig. 3 illustrates a hybrid vertical reactor system that is useful for spray conversion to form particles according to an embodiment of the present invention.

Figs. 4(a) and (b) illustrate direct-write deposition methods according to the present invention.

Fig. 5 illustrates the 3-phase boundary of an energy device such as a battery or fuel cell.

Fig. 6 illustrates an air cathode according to an embodiment of the present invention.

Fig. 7 illustrates an air cathode according to another embodiment of the present invention.

Fig. 8 illustrates an air cathode according to another embodiment of the present invention.

Fig. 9 illustrates an air cathode according to another embodiment of the present invention.

Fig. 10 illustrates an air cathode according to another embodiment of the present invention.

Fig. 11 illustrates an air cathode according to an embodiment of the present invention including a plurality of monolayers constituting the electrode.

Figs. 12(a) and (b) illustrate the incorporation of a carbon dioxide reduction layer into an air cathode according to the present invention.

Figs. 13(a) and (b) illustrate a zinc-air battery according to an embodiment of the present invention.

Fig. 14 schematically illustrates a membrane electrode assembly.

Fig. 15 illustrates a cross-section of a membrane electrode assembly.

Fig. 16 illustrates polarization curves for membrane electrode assemblies.



Fig. 17 illustrates a polarization curve for a membrane electrode assembly.

Fig. 18 illustrates a polarization curve and power curve for a membrane electrode assembly.

5 Fig. 19 illustrates active layers of having varying thickness.

Fig. 20 illustrates a polarization curve for a membrane electrode assembly.

Fig. 21 illustrates a polarization curve for a membrane electrode assembly.

10 Fig. 22 illustrates a difference plot between air and oxygen polarization curves for a membrane electrode assembly.

Fig. 23 illustrates a particle structure according to an embodiment of the present invention.

15 Fig. 24 illustrates a layered structure according to an embodiment of the present invention.

Fig. 25 illustrates layer thickness as a function of particle loading for layers deposited according to the present invention.

Fig. 26 illustrates particle layers deposited according to the present invention.

20 Fig. 27 illustrates a gas diffusion electrode deposited according to the present invention.

Fig. 28 illustrates a difference plot between air and oxygen polarization curves for a membrane electrode assembly.

25 Fig. 29 illustrates a particle structure including a polymer phase according to an embodiment of the present invention.

Fig. 30 illustrates a particle structure including a polymer phase according to an embodiment of the present invention.

Fig. 31 illustrates a particle structure including a polymer phase according to an embodiment of the present invention.

30 Fig. 32 illustrates a polarization curve for a membrane electrode assembly according to the present invention.

Fig. 33 illustrates a polarization curve for a membrane electrode assembly according to the present invention.

Fig. 34 illustrates a polarization curve for a membrane electrode assembly according to the present invention.

5        Fig. 35 illustrates surface area as a function of platinum loading for an electrocatalyst.

Fig. 36 illustrates the relationship between amount of precursor and support surface area.

10       Fig. 37 illustrates a polarization curve for a membrane electrode assembly in accordance with an embodiment of the present invention.

Fig. 38 illustrates a polarization curve for a membrane electrode assembly in accordance with an embodiment of the present invention.

Fig. 39 illustrates a polarization curve for a membrane electrode assembly in accordance with an embodiment of the present invention

15       Fig. 40 illustrates the performance of membrane electrode assembly over time in accordance with an embodiment of the present invention.

Fig. 41 illustrates the performance of membrane electrode assembly over time in accordance with an embodiment of the present invention.

20       Fig. 42 illustrates the affect of breaking secondary structure of electrocatalyst particles on the performance of membrane electrode assembly.

Fig. 43 illustrates a polarization curve for a membrane electrode assembly in accordance with an embodiment of the present invention.

Fig. 44 illustrate the performance of a membrane electrode assembly according to an embodiment of the present invention.

25       Fig. 45 illustrates the performance of a membrane electrode assembly according to an embodiment of the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

30       The present invention is generally directed to powders useful in the construction of energy devices, such as electrocatalyst powders useful in fuel cells and batteries, and to methods for producing the powders. One preferred embodiment of the present invention is directed to composite electrocatalyst

powders that are useful in batteries and fuel cells for catalyzing chemical reactions. The present invention is also directed to novel devices fabricated using the powders. One example is a fuel cell, such as a PEM fuel cell. Another example is a primary metal-air battery that utilizes an air cathode to reduce oxygen. The materials according to the present invention can advantageously be formed into thin layers using direct write deposition techniques to form unique structures.

According to one embodiment, the present invention is directed to composite electrocatalyst particles. As used herein, composite electrocatalyst powders or particles are those that include within the individual particles at least a first active species phase, such as a metal or a metal oxide that is dispersed on a support phase, such as carbon or a metal oxide. The composite powders of the present invention are not mere physical admixtures of different particles, but are comprised of particles that include both an active species phase and a support phase. The compositions and ratios of the particle components can be varied independently and various combinations of carbons, metals, metal alloys, metal oxides, mixed metal oxides, organometallic compounds and their partial pyrolysis products can be produced as may be required for a particular application. One embodiment of the present invention is directed to composite electrocatalyst particles with two or more different materials as the active species. As an example, combinations of Ag and  $\text{MnO}_x$  supported on carbon can be useful for some electrocatalytic applications. Other examples of multiple active species are mixtures of porphyrins, partially decomposed porphyrins, Co and CoO. Although carbon is a preferred material for the support phase, other materials such as metal oxides can also be useful for some electrocatalytic applications.

According to one embodiment of the present invention, the electrocatalyst powder includes composite metal-carbon electrocatalyst particles. The composite metal-carbon electrocatalyst particles include an active species of at least a first metal phase dispersed on a carbon support phase. The metal 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 includes intermetallic compounds between two or more metals. For example, the term platinum metal phase refers to a platinum alloy or intermetallic, as well as pure platinum metal. The metal-carbon electrocatalyst  
5 powders can also include two or more metals dispersed on the support as separate phases.

Preferred metals for the electrocatalytically 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 Ni,  
10 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 for use according to the present invention include alloys of Pt with other metals, such as Ru, Os, Cr, Ni, Mn and Co. Particularly preferred among these is Pt-Ru for use in hydrogen anodes and Pt-Cr-Co for use in oxygen  
15 cathodes.

Another preferred embodiment of the present invention is directed to metal oxide-carbon composite electrocatalyst particles which include an active metal oxide species dispersed on a carbon support. The metal oxide active species phase can be selected from the oxides of the transition metals,  
20 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 dispersed metal oxide can be an oxide of the metals 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 according to the present invention is  
25 manganese oxide ( $\text{MnO}_x$ , where x is 1 to 2). The dispersed active phase 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.

30 For some applications such as secondary metal-air batteries, examples of electrocatalyst materials that can be used to catalyze the reduction and oxidation reactions according to the present invention include oxygen deficient metal

oxides and metal oxides capable of undergoing reduction/oxidation reactions due to variations in the oxidation states of the metals contained in the metal oxide. Some compounds are multi-functional, providing numerous attributes in one compound. Such oxides do not necessarily have to be dispersed on a support phase.

For example, perovskite phase oxides can be used according to the present invention for electrocatalysts wherein the oxides provide electrocatalytic activity, a high surface area and electrical conductivity. Specific examples of such perovskite phase oxides include  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_3$  (where x is from 0 to 1) and  $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$  (where x is from 0 to 1). One particularly preferred metal oxide electrocatalyst according to the present invention is an oxygen-deficient cobalt-nickel oxide,  $\text{Co}_x\text{Ni}_y\text{O}_z$ , which is useful for electrodes in metal hydride batteries. Other metal oxides within this category include spinels of the general formula  $\text{AB}_2\text{O}_4$  where A is selected from divalent metals such as Mg, Ca, Sr, Ba, Fe, Ru, Co, Ni, Cu, Pd, Pt, Eu, Sm, Sn, Zn, Cd, Hg or combinations thereof and B is selected from trivalent metals such as Co, Mn, Re, Al, Ga, In, Fe, Ru, Os, Cr, Mo, W, Y, Sc, lanthanide metals or combinations thereof. Other useful metal oxides include manganese oxides, nickel oxides, cobalt oxides, iron oxides, titanium oxides, zirconium oxides, zinc oxides, indium oxide, indium tin oxide, gallium oxides and metal gallates, ruthenium oxides and metal ruthenates, chromium, molybdenum and tungsten oxides, copper oxides and copper containing perovskite phase metal oxides, vanadium, niobium and tantalum oxides.

A further class of catalysts that can be useful according to the present invention are those derived from molecular compounds that are either dispersed on a support phase or that have no support phase. Examples of such materials are metal porphyrin complexes which catalyze the reduction of  $\text{O}_2$  to  $\text{OH}^-$  but are oxidized during the oxidation of  $\text{OH}^-$ . These species are suitable for primary batteries and fuel cells such as alkaline fuel cells. Included in this group are metal porphyrin complexes of Co, Fe, Zn, Ni, Cu, Pd, Pt, Sn, Mo, Mn, Os, Ir and Ru. Other metal ligand complexes can be active in these catalytic oxidation and reduction reactions and can be formed by the methods described herein. Such

metal ligands can be selected from the class of N4-metal chelates, represented by porphyrins, tetraazaanulens, phtalocyanines and other chelating agents. In some cases the organic ligands are active in catalyzing reduction and oxidation reactions. In some cases the ligands are active when they remain intact, as  
5 might be the case for an intact porphyrin ring system, or they might be partially reacted during thermal processing to form a different species that could also be active in the catalytic reactions. An example is the reaction product derived from porphyrins or other organic compounds.

Carbon is required for the reduction of  $O_2$  to  $OH^-$  and is believed to be  
10 involved in the reduction of peroxide to hydroxide ion. Other carbon based active species include homo- and hetero- fullerene and carbon nanotube based materials.

Powders of metals and metal alloys (including intermetallic compounds) are also useful for electrodes, particularly anodes in certain battery cells.  
15 Examples of such metal compounds include  $LaNi_5$ , La-Ni-Co-Al, Nd-Ce-Ni-Co-Al and V-Ti-Cr-Ni.

In addition to the electrocatalytic powders, other fine powders are useful for fabricating energy device components according to the present invention. Among these are the supporting materials, hydrophobic materials,  
20 electroconductive materials and insulator materials such as dielectrics for separating membranes. For example, metals such as silver (Ag) and nickel (Ni) are useful for the current collectors in battery cells.

According to one embodiment of the present invention, the particles, such as carbon particles or electrocatalyst particles, are polymer-modified with a  
25 polymer, for example a tetrafluoroethylene (TFE) fluorocarbon polymer such as TEFLON (E.I. duPont de Nemours, Wilmington, DE) or a proton conducting polymer such as a sulfonated perfluorohydrocarbon polymer (e.g., NAFION, E.I. duPont de Nemours, Wilmington, DE). Polymer-modified carbon particles can be used, for example, to form hydrophobic layers in an energy device, as is  
30 discussed below. The hydrophobicity can be controlled by controlling the ratio of TEFLON to carbon. For some applications, TEFLON can also be incorporated in electrocatalyst particles to form polymer modified electrocatalyst particles.

The composite electrocatalyst powders discussed above include a secondary support phase, consisting of agglomerates of smaller primary particles such as carbon or metal oxide, which supports the active species. Two or more types of primary particles can be mixed to form the secondary support phase. As an example, two or more types of particulate carbon (e.g., amorphous and graphitic) can be combined to form the secondary support phase. The two types of particulate carbon can have different performance characteristics that combine to enhance the performance of the catalyst.

It is an advantage of the present invention that the composition of the electrocatalyst particles can be homogeneous. A degree of homogeneity in materials is often not obtainable by traditional forming methods such as liquid precipitation. However, it is also possible to intentionally provide compositional gradients within the electrocatalyst particles. For example, the active species concentration in a composite particle can be higher or lower at the surface of the support phase than near the center and gradients corresponding to compositional changes of 10 to 100 weight percent can be obtained. When the particles are deposited by direct-write deposition, discussed herein below, the particles retain their structural morphology and therefore the functionality of the compositional gradient can be exploited.

In addition, the electrocatalyst particles can have a high purity, thereby increasing the electrocatalytic activity. Many impurities in prior art electrocatalyst powders are derived from the precursors and from surfactants. The electrocatalyst particles of the present invention can advantageously have less than 1 atomic percent surface impurities, as measured by x-ray photoelectron spectroscopy (XPS).

The preferred form of carbon for crystalline supported active species are those which are amorphous. The preferred carbons for supported metals like Pt are carbons that are crystalline since Pt dispersion is favored by reduced carbon surfaces with substantially no surface hydroxyls. For supported  $\text{MnO}_x$ , it is also preferred to have a crystalline carbon support. Preferably, the crystallinity of the primary particles constituting the support phase is controlled through the selection of materials chosen for a specific application. Graphitic carbon is

preferred for long term operational stability of fuel cells and batteries. Amorphous carbon is preferred when a smaller crystallite size is desired for the supported active species.

5 The overall density of the secondary support phase (i.e., the agglomerated primary particles) in the composite particles is related to the porosity of the support phase. It is preferred that the accessible (e.g., open) porosity in the composite electrocatalyst particles is from about 5 to 98 percent and more preferably is at least about 40 percent and even more preferably is at least about 60 percent. The pore size distribution in the secondary support  
10 phase can also be controlled and the average pore size is preferably from about 10 to about 100 nanometers, such as from about 10 to 20 nanometers. In addition, it is preferred that the average internal pore size is not greater than about 20 nanometers and more preferably is not greater than about 15 nanometers. High porosity is advantageous for rapid transport of species into  
15 and out of the secondary structures. Lower particle densities also allow easier suspension of the particles for printing techniques such as ink-jet deposition where suspension of particles for long periods is required. As an example, an aerogel carbon or metal oxide can have a density much lower than  $1 \text{ g/cm}^3$ .

Agglomeration of the electrocatalyst particles can affect the properties of  
20 the powder batch such as the ability to disperse the powder into liquids used to deposit the particles. It is therefore preferred that minimal agglomeration of the particles exist in the powder batch.

It is also an advantage of the present invention that the electrocatalyst particles are substantially spherical in shape. That is, the particles are preferably  
25 not jagged or irregular in shape. Spherical particles can advantageously be deposited using a variety of techniques, including direct write deposition, and can form layers that are thin and have a high packing density.

In addition, the composite electrocatalyst powders according to the present invention preferably have a surface area of at least about  $10 \text{ m}^2/\text{g}$ , more  
30 preferably at least about  $25 \text{ m}^2/\text{g}$ , more preferably at least about  $90 \text{ m}^2/\text{g}$  and even more preferably at least about  $600 \text{ m}^2/\text{g}$ . Surface area is typically measured using the BET nitrogen adsorption method which is indicative of the



surface area of the powder, including the internal surface area of accessible pores within the catalyst particles. High surface area combined with high dispersion of the active species generally leads to increased catalytic activity.

According to one embodiment of the present invention, the composite  
5 electrocatalyst particles preferably include a carbon support with at least about 1 weight percent active species, more preferably at least about 5 weight percent active species and even more preferably at least about 10 weight percent of the catalytically active species dispersed on the support surface. In one  
10 embodiment, the particles include from about 20 to about 40 weight percent of the active species 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 dispersed on the carbon support will depend upon the total surface area of the carbon, the type of active species and the application of the powder. A carbon support having a low  
15 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.

It is preferred that the average size of the active species phase dispersed on the support phase is such that the particles include small single crystals or  
20 crystallite clusters, collectively referred to herein as clusters. According to one embodiment, the average active species cluster size is preferably not greater than about 10 nanometers, more preferably is not greater than about 4 nanometers and even more preferably is not greater than about 3 nanometers. In one embodiment, the average cluster size is from about 0.5 to 5 nanometers.  
25 According to another embodiment of the present invention, 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 clusters have a size of not greater than about 3 nanometers. Composite electrocatalyst powders having a dispersed active species with such small  
30 crystallite clusters advantageously have enhanced catalytic properties as compared to composite powders comprising an active species phase having larger clusters. The method of the present invention advantageously permits

control over the crystallinity by controlling the reaction temperature and/or residence time during particle formation.

When the active species includes a metal, the oxidation state of the metal in the metal phase is preferably close to zero, i.e., a pure metal. It is believed  
5 that higher oxidation states are detrimental to electrocatalyst powder activity. The method of the present invention advantageously enables good control over the oxidation state of the metal.

The electrocatalyst powders of the present invention preferably have a well-controlled particle size. According to one embodiment of the present  
10 invention, the volume average particle size is not greater than about 100  $\mu\text{m}$ , preferably is not greater than about 30  $\mu\text{m}$ , more preferably is not greater than about 20  $\mu\text{m}$  and even more preferably is not greater than about 10  $\mu\text{m}$ . Further, it is preferred that the volume average particle size is at least about 0.3  $\mu\text{m}$ , more preferably is at least about 0.5  $\mu\text{m}$  and even more preferably is at least  
15 about 1  $\mu\text{m}$ , such as from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ . 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 electrocatalytic layers which are advantageous for producing unique energy devices such as batteries and fuel cells according to the present  
20 invention.

The particle size distributions of the secondary support phase, the primary particles, and the active species are important in determining catalytic performance and can be well controlled according to the present invention. Narrower particle size distributions are preferred for the secondary support  
25 phase to allow deposition of the particles through a narrow orifice without clogging and to enable the formation of thin layers. 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  
30 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.

The powders produced by the processes described herein, namely spray processing, can include some agglomerates of spherical particles.

5 Micrometer-sized particles often form soft agglomerates as a result of their high surface energy. Such soft agglomerates may be dispersed by treatments such as exposure to ultrasound in a liquid medium or sieving. The particle size distributions described herein are measured by mixing samples of the powders in a medium such as water with a surfactant and a short exposure to ultrasound

10 through either an ultrasonic bath or horn. The ultrasonic horn supplies sufficient energy to disperse the soft agglomerates into the primary spherical particles. The primary particle size distribution is then measured by light scattering, such as in a MICROTAC particle size analyzer (Honeywell Industrial Automation and Control, Fort Washington, PA).

15 In one aspect, the present invention provides a method for preparing an electrocatalyst powder batch. A liquid precursor is converted to aerosol form and liquid from the droplets in the aerosol is then removed to permit formation of the desired particles in a dispersed state.

The method for the production of the composite electrocatalyst powders

20 according to the present invention, referred to herein as spray processing, spray conversion or spray pyrolysis, generally includes the steps of: providing a liquid precursor which, in the case of composite particles, includes a precursor to the support phase (e.g., carbon) and a precursor to the active species; atomizing the precursor to form a suspension of liquid precursor droplets; and removing liquid

25 from liquid precursor droplets to form the powder. For electrocatalysts that are not supported, the precursor to the support phase is not necessary. Typically, at least one component of the liquid precursor is chemically converted into a desired component of the powder. According to the present invention, the drying of the precursors and the conversion to a catalytically active species are

30 advantageously 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 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, the method of the present invention can produce catalyst morphologies and active species  
5 structures which yield improved catalytic performance.

More specifically, one important aspect of the method of the present invention is that the supported electrocatalyst particles are formed while the precursor to the active species phase is in intimate contact with the surface of the primary particles that constitute the support phase.

10 Another important aspect of the method in accordance with the present invention is that the active species precursor is rapidly reacted on the surface of the primary support particles. The reaction and formation of the active species occurs over a very short period of time such that the growth of large active species clusters is reduced and the migration of the active species clusters on  
15 the support surface is reduced. Preferably, the active species precursor is exposed to the elevated reaction temperature to form the active species for not more than about 600 seconds, more preferably not more than about 300 seconds, even more preferably not more than about 100 seconds and even more preferably not greater than about 10 seconds. The means by which the  
20 active species precursor is reacted is discussed in detail below.

Another unique aspect of spray processing according to the present invention is the simultaneous formation of a secondary support phase such as carbon. The secondary support phase forms as a result of the formation and drying of the droplets during spray processing and the characteristics of the  
25 primary support particles such as particle size, particle size distribution and surface area influence the properties of the support phase.

The spray processing methods for electrocatalyst production according to the present invention can be grouped by reference to several different attributes.

These attributes include: vertical or horizontal system (with respect to main gas  
30 flow direction); type of atomizer (e.g., submerged ultrasonic, ultrasonic nozzle, two-fluid nozzle, single pressurized fluid); type of 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); type of gas heating (e.g., hot system walls, hot gas introduction, combined hot gas and hot wall, plasma or flame); and type of powder collection system (e.g., cyclone, bag house, electrostatic or settling).

5            Spray processing according to one embodiment of the present invention starts with a precursor solution (e.g., colloidal carbon and  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  for the production Pt/C electrocatalyst powder) that is atomized to form droplets. The droplets are passed through a heated zone in which the solvent evaporates and the precursors react to form the desired material, which is collected from the gas  
10   stream on a filter or with a cyclone. When the droplets are in the heated zone the precursors decompose and crystallize into the particulate product. The active species phase crystallite size can be controlled through control of the temperature of the hot zone and the residence time that the particles are in the hot zone.

15            For example, metal/carbon and metal oxide/carbon electrocatalyst powders can be prepared by starting with an aqueous-based precursor liquid consisting of colloidal carbon and a dissolved metal salt. The processing temperature of the precursor droplets can be controlled so the metal salt precursor decomposes leaving the carbon intact. A schematic illustrating the  
20   formation of a Pt/carbon electrocatalyst particle is illustrated in Fig. 1.

            The first step in the process is the evaporation of the solvent (typically water) as the droplet is heated resulting in a particle of dried solids and metal 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  
25   be used. Plasma, flame, laser and other reactors can be viewed as variations of these. As the particles experience either higher temperature or longer time at a specific temperature, the metal precursor decomposes. Using the spray conversion method of the present invention, the temperature and time that the particles experience can be controlled and therefore the degree of crystallinity  
30   and dispersion of the metal particles supported on the carbon can also be controlled.

The manner in which the precursor droplets are generated has significant influence over the characteristics of the final electrocatalyst powder as well as the rate of aerosol generation. The characteristics determined by the generator include the size and spread of the particle (droplet) size distribution (PSD) and  
5 the rate of atomization of a specific fluid. In extreme cases, some generators cannot atomize fluids with even moderate particle loadings or high viscosities

Several atomization methods exist, each with advantages and disadvantages, for atomization of feed streams containing suspended particulates like carbon including: ultrasonic transducers (usually 1-3 MHz  
10 frequency); ultrasonic nozzles (10-150 KHz); two-fluid nozzles; and pressure atomizers, as well as others known in the art.

Two basic disc configurations, planar and point source, can be used to atomize fluids with submerged ultrasonic transducers. In one embodiment, scale-up of submerged ultrasonic transducers can be based on placing a large  
15 number of piezoelectrics in an array in a fluid. Scale-up of nozzle systems can be accomplished by either selecting a nozzle with a larger capacity or by increasing the number of units used in parallel. Typically, particles produced by nozzles are larger than those produced by ultrasonic atomizers. Particle size is also dependent on the gas flow rate. For a fixed liquid flow rate, an increased  
20 airflow decreases particle size and a decreased airflow increases particle size. It is difficult to change particle size without varying the liquid or airflow rates. However, two-fluid nozzles have the ability to process larger volumes of liquid per time than ultrasonic atomizers.

Ultrasonic spray nozzles have some advantages over single or two-fluid  
25 nozzles. Ultrasonic nozzles use high frequency energy to atomize a fluid. The primary advantage is the low velocity of the spray leaving the nozzle and lack of associated gas flow. The nozzles are available in various orifice sizes and orifice diameters that allow the system to be scaled for various production capacities. In general, higher frequency nozzles are physically smaller, produce smaller  
30 droplets, and have a lower flow capacity than nozzles that operate at lower frequencies. The drawback to this system of scaling is that increasing the nozzle size increases the particle size. If a particular particle size is required, then the

maximum production rate per nozzle is set. If desired production exceeds the nozzle's maximum production rate, additional nozzles or complete production units will be required to achieve desired production rates.

5 The shape of the atomizing surface determines the shape and spread of the spray pattern. Several types of atomizing nozzle surface shapes are available including conical, microspray and flat. 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  
10 flow rates where narrow spray patterns are needed. These nozzles are preferred for configurations where minimal gas flow is required in association with the droplets.

Particulate carbon suspensions that are often used for spray conversion production according to the present invention present several problems with  
15 atomization. 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 colloid. Other problems encountered when using submerged ultrasonic transducers is the coating of the transducer discs with the particles over time.  
20 Finally, the generation rate of carbon suspensions is very low on submerged ultrasonic transducer discs. This is at least in part due to energy being absorbed or reflected by the suspended particles.

Submerged ultrasonic transducers are preferred for precursor compositions having a low particulate carbon content, such as less than 40 wt.%,  
25 more preferably less than 20 wt.% and even more preferably less than 10 wt.% carbon in the final electrocatalyst. They are also preferred for any material product that is formed from dissolved precursors as opposed to particulate precursors.

Several configurations for introducing the aerosol produced from the  
30 nozzle into a carrier gas stream were tested on horizontal, tubular hot-wall furnaces. Process yields were improved from 40% to 60% of theoretical production rates by varying in inlet geometry, carrier gas flow rate, and precursor

flow rates. The majority of losses occur upon introducing the aerosol into the furnace. In contrast, the submerged ultrasonic systems with 9 transducers provided production rates of only about 1 to 0.4 grams per hour. The production rates described can be compared with those of a pure metal derived from a dissolved precursor for the same 9-transducer system, which is typically 10 grams per hour. The low production rates for the metal carbon precursor composition are due to the poor atomization of carbon suspensions with submerged ultrasonics.

Two-fluid nozzles are a common means of producing aerosol sprays and are used in many commercial applications typically in conjunction with spray drying processes. Large shearing forces that are generated when a low-velocity liquid stream encounters a high-velocity gas stream accomplish atomization. A direct result of this interaction is that the particle size characteristics of the aerosol are dependent on the flow rate of the gas. Thus, particle characteristics cannot be de-coupled from the carrier gas flow rate. The velocity of the particles as they leave the generation zone can be quite large which may lead to unwanted particle losses due to impaction. The aerosol also leaves the nozzle in a characteristic pattern, typically conical, and this may require that the dimension of the reactor be greater than some minimum value to prevent unwanted losses on the walls of the system.

The atomized precursor must then be heated to remove solvents and react precursor components. For example, a horizontal hot-wall tubular reactor allows the heating of 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 must occur through the bulk of the gas. 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 aid in increasing heat transfer.

Maximum temperatures and heating rates can be controlled independently of the inlet stream with small changes in residence time. The heating rate of the inlet stream can be controlled using a multi-zone furnace.



The preferred use of a horizontal hot-wall reactor according to the present invention is to produce product particles (secondary structures) with a size of less than about 5  $\mu\text{m}$  where settling of particles is not a cause of significant losses. The disadvantage is the poor ability of submerged ultrasonic atomization to atomize particulate carbons. For this reason this approach is preferred for products with high metal loadings corresponding to low carbon contents where atomization is sufficient to enable economical production.

In one embodiment, for very low carbon loadings, a horizontal hot-wall reactor can be used in conjunction with submerged ultrasonic transducers. In another embodiment, the horizontal hot-wall reactor can be used with a two fluid nozzle atomizer. This approach is preferred for products with sizes less than 5  $\mu\text{m}$ , because of the ability to atomize particulate carbons, and feed streams containing higher levels of carbon. The major disadvantage of this approach for particles less than 5  $\mu\text{m}$  is the low aerosol loading (low mass of product per volume of gas) making this an expensive method for powder production.

A horizontal hot-wall reactor can also be used with ultrasonic nozzle (horn) atomization techniques. This approach allows atomization of particulate carbons. The major disadvantage is the large droplet size, which leads to losses of materials on reactor walls and other surfaces making this an expensive method for powder production.

Spray conversion systems in the configuration of a spray drier are the preferred production method for large quantities of electrocatalyst according to the present invention. Spray drying is a process wherein powders are produced by atomizing a solids-containing liquid precursor to produce droplets and evaporating the liquid to produce a dry aerosol wherein thermal decomposition may take place to produce a final desired powder. 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 in the spray dryer is the maximum temperature of a particle, averaged throughout its diameter, while being processed/dried.

Three types of spray dryer systems are useful for the spray drying of electrocatalyst powders according to the present invention. An open system is useful for general spray drying of electrocatalyst powders using air as an aerosol carrier gas and an aqueous feed solution as a droplet precursor. A closed  
5 system is useful for spray drying of electrocatalyst powders using an aerosol carrier gas other than air and/or a non-aqueous or a semi-non-aqueous feed solution as a droplet precursor. A semi-closed system including a self-inertizing system is useful for spray drying of electrocatalyst powders that require an inert atmosphere and/or are potentially flammable.

10 Two basic spray drying design types are useful for the production of electrocatalyst powders. The co-current design type is useful for electrocatalyst powders that are sensitive to high temperature excursions (e.g., greater than 350°C) or require a rotary atomizing technique. Mixed flow type spray dryers are useful for producing powders that require relatively high temperature excursions  
15 (e.g., greater than 350°C) or require turbulent mixing forces.

In a co-current spray dryer the hot gas is introduced from the top of the unit, where the droplets are generated with a two-fluid nozzle. The temperature a particle is exposed to in co-current dryers is at best that of the outlet. Typically, the outlet temperature is limited to about 200° C, although some designs allow  
20 higher temperatures. In addition, since the particles experience the lowest temperature in the beginning of the time-temperature curve and the highest at the end, the possibility of precursor surface diffusion and agglomeration is high and therefore the decomposition of the precursor is more difficult compared to that of a highly dispersed precursor.

25 A more preferred spray conversion system is based on a mixed flow spray dryer arrangement. The mixed-flow system introduces the hot gas at the top of the unit and the precursor droplets are generated near the bottom in an upward-directed fountain. This gives the particles increased residence time compared to the co-current configuration, as the particles are forced towards the top of the unit, then fall and flow with the gas back down. The temperature the particles  
30 experience is higher as compared to a co-current spray dryer. This is important,

as most spray dryers are not capable of reaching the higher temperatures that are required for conversion of some of the precursor salts used.

These conditions are advantageous for electrocatalyst synthesis at lower platinum or platinum alloy loadings such as up to 50 wt.% Pt or Pt – based alloys on carbon. For mixed flow spray dryers the temperatures achieved can be high enough for the decomposition of Pt-based precursors (e.g., between 250°C and 300°C). The highest temperature in these spray dryers is the inlet temperature, and the outlet temperature is up to two times lower than the inlet temperature. Therefore, the electrocatalyst particles reach the highest temperature for relatively short time, which does not allow for significant precursor migration or surface diffusion. This spike of high temperature allows for fast conversion of the metal or metal oxide precursor followed by a “pseudo quench” since the spray dryer temperature quickly decreases after the temperature maximum is achieved. Thus the “spike” like temperature profile is advantageous for generation of highly dispersed metal or metal oxide clusters on the surface of electrocatalyst supports such as carbon. This is also preferred for other combinations of metal or metal oxide catalysts supported on various supports.

The range of useful residence times for producing electrocatalyst powders depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid, inlet temperature, and residual moisture content. In general, residence times for the production of electrocatalyst powders can range from 5 seconds up to 5 minutes. According to one embodiment, the residence time is from about 15 to 45 seconds using a mixed flow design type with air, a two-fluid nozzle (greater than 5:1 air:feed mass ratio), an aqueous feed solution at a 530°C inlet temperature with less than 2% residual moisture content.

The range of inlet temperatures for producing electrocatalyst powders depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid, and energy required to perform drying and/or decomposition functions. Useful inlet temperatures should be sufficiently high to accomplish the drying and/or decomposition functions without promoting significant surface diffusion of catalytic material to reduce its performance.

In general, the outlet temperature of the spray dryer determines the residual moisture content of the spray dried powder. For the production of electrocatalyst powder the range of useful outlet temperatures depends on the spray dryer design type, atmosphere used, nozzle configuration, feed liquid, inlet  
5 temperature, and residual moisture content. For example, a useful outlet temperature ranges from about 200°C to about 350°C.

Two types of nozzle configurations are useful for the production of electrocatalyst powders. Rotary atomizers are useful for co-current production of droplets less than about 120 µm in size. Multiple fluid nozzles such as a two  
10 fluid nozzle are useful for co-current or mixed flow production of droplets less than about 120 µm in size.

Other equipment that is desirable for producing electrocatalyst powders using a spray dryer include a gas heater and a collection system. Gas heating may be accomplished by two general configurations: direct heating or indirect  
15 heating. Heating can be achieved by burning fuel, heating electrically, liquid-phase heating, or steam heating. The most useful type of heating for the production of electrocatalyst processed with an inlet temperature greater than 350°C is a direct fuel burning method. Most collection methods are useful for collecting electrocatalyst powders produced on a spray dryer. These methods  
20 include, but are not limited to using: cyclone, bag/cartridge filter, electrostatic precipitator, and various wet collection techniques.

Most commercial spray dryers, however, are unable to achieve the high temperatures needed for the reduction of platinum since maximum inlet temperatures are usually limited to about 600° F (316° C). Thus, it has not been  
25 proposed prior to the present invention to use such a spray conversion system for the production of electrocatalyst.

A co-current spray dryer system that is useful according to the present invention is schematically illustrated in Fig. 3. The spray dryer 200 includes a precursor feed line 202 for delivering liquid precursor to the drying chamber 204  
30 and an atomizing gas line 203 for atomizing the liquid feed. The liquid precursor is dispersed into droplets through a spray nozzle 206, such as the two-fluid

nozzle illustrated in Fig. 3. Drying air is introduced at the top of the chamber 204 through a hot gas inlet 208. The liquid droplets are dried and collected in a cyclone 212.

In the foregoing description of the basic components of a spray dryer, it should be noted that during spray drying the precursor mixture actually undergoes a chemical conversion. For example, a manganese precursor, such as potassium permanganate, is converted to manganese oxide. The final phase and oxidation state of manganese oxide are critical to the electrocatalytic activity of the resulting powder. Minor variations in reaction temperature and precursor composition can result in powders with different electrocatalytic activities.

It has been advantageously found according to the present invention that relatively low conversion temperatures can be used to obtain quality electrocatalyst powder. In one embodiment, it is preferred that the reaction temperature is not greater than about 700°C, more preferably not greater than about 500°C, even more preferably not greater than about 400°C, even more preferably not greater than about 300°C and even more preferably not greater than about 250°C. Further, it is preferred that the reaction temperature is at least about 100°C, preferably at least about 150°C. Increasing the reaction temperature to over 400°C can remove excess surfactant which may remain on the powder and poison the oxide active sites. However, this is typically not necessary if the amount of surfactant in the precursor solution, if any, is low.

According to another embodiment of the present invention, a hybrid vertical hot-wall/hot-gas tubular reactor can be used. In the case of powders generated with a submerged ultrasonic transducer disk, particle settling is not a problem due to the low settling velocity of the micron-sized particles generated in this fashion. However, not all liquid precursors atomize well using an ultrasonic transducer disk, such as carbon colloidal carbon solutions. Therefore, a different atomization technique is preferred, such as an ultrasonic spray nozzle, or a two-fluid nozzle, which tend to produce larger droplets with sizes larger than about 5  $\mu\text{m}$  to 10  $\mu\text{m}$ . This requires such a vertical system to avoid settling losses.

The hybrid vertical system, illustrated in Fig. 3, takes advantage of both a high-temperature hot-wall system and a large capacity spray drying system that

uses hot air introduction along with a larger nozzle to produce larger droplets that increase overall output. The preferred system also has increased radial size over a standard horizontal system. A longer furnace, with adequate power (typically three times the thermodynamic requirement) is needed to insure a proper time-temperature history. The system is preferentially operated up to sufficiently high temperature (up to 700° C) to decompose most molecular precursors. A high-temperature resistant stainless steel is the preferred reaction tube. High-temperature gaskets with water-cooling are preferred. Once the high-temperature drying/reaction has taken place, a rapid cool-down or quench is preferred before powder collection occurs to minimize cluster growth. Another preferred aspect is the ability to use high-temperature gas (up to 700° C) as drying/reaction means, independent of a hot wall. This high-temperature gas can provide any type of desired atmosphere, from reducing to oxidizing.

Referring to Fig. 3, a nozzle 402 delivers precursor into the top of the system, similar to a co-current spray dryer. A carrier gas is pre-heated to a controlled temperature of up to about 700° C to 1000° C and is then introduced at the top of the system, through a cylindrical dispersion 404 just below the nozzle 402. The hot carrier gas and the droplets then flow down through a vertical hot-wall reactor tube 406 where the wall temperature can be controlled. After it is dried and converted, the powder is then cooled and collected in a cyclone or filter bag 408. This configuration increases the production rate relative to all other spray conversion systems by allowing larger droplets (with higher settling velocities) to be generated, along with decreasing losses when compared with a horizontal system. This system provides an order of magnitude increase in production rate over horizontal systems with other techniques. Another advantage of a vertical system is the ability to tailor the time-temperature history of the aerosol to virtually any useful profile.

This hybrid system allows for operation in three modes. The first is as a hot wall tubular reactor. The second is co-current flow hot gas drying similar to a spray dryer. The third mode uses hot wall and hot gas. Hot or cold gas flows can be introduced before or after the furnace to maintain the desired particle temperature.

Operation with three types of nozzles in the hybrid system were compared: a large capacity 25 kHz nozzle (12.5 Lph max) with a conical spray pattern; a medium capacity 48 kHz nozzle (4.5 Lph max) with a flat cylindrical spray pattern; and a low capacity 120 kHz nozzle (1.3 Lph max) with a conical spray pattern.

Conical tip nozzles have a spray pattern that is too wide for tubular systems, and low frequency ultrasonic nozzles produce droplets too large to dry in sufficient time. The medium and large capacity nozzles (lower frequencies) generated droplets that were too large for complete evaporation even at reduced liquid throughputs. Using the small 120 kHz nozzle, complete liquid evaporation was achievable at liquid flow rates less than 0.8 Lph at maximum gas and wall temperatures. Thus, in one preferred embodiment, a flat, high frequency ultrasonic nozzle is used. This type of nozzle gives a fairly narrow, monomodal size distribution and relatively small droplets, which evaporate and convert to electrocatalyst. In contrast to other systems of similar size, the hybrid reactor furnace is capable of drying and converting up to 700g/hr of 5 wt.% carbon suspended in water, depending on the nozzle and subsequent droplet size.

Regardless of the selected reactor system, the first step in the fabrication of the electrocatalyst particles according to the present invention is to form a liquid precursor to the particles. In the case of supported electrocatalyst powders, the liquid precursor includes a precursor to both the active species and the support phase. Proper selection of the precursors enables the production of particles having well-controlled chemical and physical properties.

For the production of metal-carbon composite electrocatalyst particles according to the present invention, the precursor solution includes at least one metal precursor. The metal precursor may be a substance in either a liquid or solid phase. Preferably, the metal precursor will be a metal-containing compound, such as a salt, dissolved in a liquid solvent of the liquid feed. For example, the precursor solution can include nitrates, chlorides, sulfates, hydroxides, or carboxylates of a metal. However, chloride salts may lead to detrimental catalytic properties over time. The metal precursor will undergo one or more chemical reactions when heated to convert to a metallic state and form

the electrocatalyst particles of the present invention. It may be desirable to acidify the precursor solution to increase the solubility, such as by adding hydrochloric acid.

A preferred catalytically active metal according to one embodiment of the present invention is platinum (Pt). Preferred precursors for platinum metal according to the present invention include chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ), tetraamineplatinum (II) nitrate ( $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ) and hydroxoplatinic acid ( $\text{H}_2\text{Pt}(\text{OH})_6$ ). Other platinum precursors include Pt-nitrates, Pt-amine nitrates,  $\text{Na}_2\text{PtCl}_4$ , and the like. Chloroplatinic acid is soluble in water and the solutions advantageously maintain a low viscosity.  $\text{H}_2\text{Pt}(\text{OH})_6$  is advantageous since it converts to platinum metal at relatively low temperatures.

According to another embodiment of the present invention, palladium is preferred as the catalytically active metal. Palladium precursors include inorganic Pd salts such as palladium (II) chloride ( $\text{PdCl}_2$ ), palladium (II) nitrate ( $\text{Pd}(\text{NO}_3)_2$ ),  $\text{H}_2\text{PdCl}_4$ , or  $\text{Na}_2\text{PdCl}_4$ . Complex Pd salts such as  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  or  $\text{Pd}(\text{NH}_3)_2(\text{OH})_2$ , Pd-carboxylates, and the like are also useful.

Silver (Ag) is also useful as a catalytically active metal. For silver, inorganic salts can be used including Ag-nitrate ammine complexes, Ag-carboxylates and Ag-oxalate. Particularly preferred are silver carbonate ( $\text{Ag}_2\text{CO}_3$ ), silver nitrate ( $\text{AgNO}_3$ ) and silver acetate ( $\text{AgOOCCH}_3$ ).

Other useful catalytically active metals include osmium (Os) and copper (Cu). For osmium, inorganic salts such as  $\text{OsCl}_3$  can be used. For copper, copper (II) acetate ( $\text{Cu}(\text{OOCCH}_3)_2$ ), copper (II) chloride ( $\text{CuCl}_2$ ), copper (II) nitrate ( $\text{Cu}(\text{NO}_3)_2$ ), copper (II) perchlorate ( $\text{Cu}(\text{ClO}_4)_2$ ) and copper carboxylates can be used.

For the production of metal oxide-containing electrocatalyst powders, including supported and unsupported metal oxides, a precursor to the metal oxide must be included in the precursor solution. For metal oxides, including oxides of Au, Ag, Pt, Pd, Ni, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti or Al, inorganic salts including nitrates, chlorides, hydroxides, halides, sulfates, phosphates, carboxylates, oxylates and carbonates can be used as

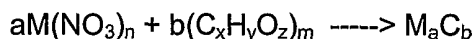


precursors. Oxides of the metals can also be used as a precursor to a metal oxide in the final powder.

Particularly preferred metal oxide precursors include:  $K_2Cr_2O_7$ , Cr carboxylates and chromium oxalate for chrome oxide;  $KMnO_4$ , Mn-nitrate, Mn-acetate, Mn-carboxylates, Mn-alkoxides and  $MnO_2$  for manganese oxide;  $Na_2WO_4$  and  $W_2O_3$ , for tungsten oxide;  $K_2MoO_4$  and  $MoO_2$  for molybdenum oxide; Co-amine complexes, Co-carboxylates and cobalt oxides for cobalt oxide; Ni-amine complexes, Ni-carboxylates and nickel oxides, for nickel oxide; and Cu-amine complexes, Cu-carboxylates and copper oxides for copper oxide.

According to one preferred embodiment of the present invention, the precursor to the metal or metal oxide is a cationic precursor. A cationic precursor is a precursor wherein the metal (e.g., Pt) is part of the cationic species of the precursor salt. For example, a preferred cationic precursor for platinum metal is tetraamineplatinum (II) nitrate.

For the production of composite powders having a carbon support phase, the precursor solution also includes at least one carbon precursor. The carbon precursor can be an organic precursor such as carboxylic acid, benzoic acid, polycarboxylic acids such as terephthalic, isophthalic, trimesic and trimellitic acids, or polynuclear carboxylic acids such as naphthoic acid, or polynuclear polycarboxylic acids. Organic precursors can react by a mechanism such as:



The use of a liquid organic carbon precursor typically results in amorphous carbon, which is not desirable for most electrocatalyst applications.

Preferably, the carbon support precursor is a dispersion of suspended carbon particles. The carbon particles can be suspended in water with additives, such as surfactants, to stabilize the suspension. The carbon particles used as the precursor are the primary particles which constitute the secondary support phase.

The primary carbon precursor particles preferably have a BET surface area of at least about  $20 \text{ m}^2/\text{g}$ , more preferably at least about  $80 \text{ m}^2/\text{g}$ , even more preferably at least about  $250 \text{ m}^2/\text{g}$  and most preferably at least about  $1400$

m<sup>2</sup>/g. The surface area of the particulate carbon precursor strongly influences the surface area of the composite electrocatalyst powder, and therefore strongly influences the electrocatalytic activity of the composite powder.

5 The particulate carbon is small enough to be dispersed and suspended in the droplets generated from the liquid precursor. According to one embodiment, the particulate carbon preferably has an average size of from about 10 to about 100 nanometers, more preferably from about 20 to about 60 nanometers. However, carbon particulates having a size of up to about 25 micrometers can also be used. The carbon can be crystalline (graphitic), amorphous or a  
10 combination of different carbon types. The particles can also have a graphitic core with an amorphous surface or an amorphous core with a graphitic surface.

The surface characteristics of the primary particles making up the secondary support structures can be varied. It is preferred that the surfaces before processing to form the final particles allow dispersion of the precursor  
15 particles into the precursor liquid. After processing to form the secondary structures, it is preferred that the surfaces have a controlled surface chemistry. Oxidized carbon surfaces can expose hydroxyl, carboxyl, aldehyde, and other functional groups which make the surface more hydrophilic. Reduced carbon surfaces terminate in hydrogen which promotes hydrophobicity. The ability to  
20 select the surface chemistry allows tailoring of the hydrophobicity of the surfaces, which in turn allows the formation of gradients in hydrophobicity within beds of deposited particles. Oxidized carbon surfaces also tend to be microetched, corresponding to higher surface areas while reduced carbon surfaces have lower surface areas. Oxidized carbon surfaces can be  
25 derivatized by reaction with various agents which allows coupling of various oxygen containing groups to the surface to further tailor the surface chemistry. This allows the addition of inorganic, organic, metal organic or organometallic compounds to the surface.

Among the convenient sources of dispersed carbon are commercially  
30 available carbon-based lubricants which are a suspension of fine carbon particles in an aqueous medium such as dispersed carbon black. Particularly preferred are acetylene carbon blacks having high chemical purity and good

electrical conductivity. Examples of such carbon suspensions that are available commercially are GRAFO 1322 (Fuchs Lubricant, Co., Harvey, IL) which is a suspension of VULCAN XC-72 carbon black (Cabot Corp., Alpharetta, GA) having an average size of about 30 nanometers and a surface area of about 254  
5  $\text{m}^2/\text{g}$ . Also preferred are BLACKPEARLS 2000 (Cabot Corp., Alpharetta, GA) and KETJENBLACK (Akzo Nobel, Ltd., Amersfoort, Netherlands), each of which includes carbon having a specific surface area of from about 1300 to 1500  $\text{m}^2/\text{g}$ .

Another preferred class of carbon materials are activated carbons which have a degree of catalytic activity. Examples include NORIT NK (Cabot Corp.,  
10 Alpharetta, GA) and PWA (Calgon Carbon Corp., Pittsburgh, PA) having an average particle size of about 20 micrometers and a surface area of about 820  $\text{m}^2/\text{g}$ .

A stable precursor suspension (carbon dispersion and metal salt) is necessary to ensure a homogeneous feedstock. A precursor that is unstable will  
15 settle in the feed reservoir during the course of the processing, resulting in droplets of varying composition, and ultimately affect the catalyst powder characteristics. In this case, a preferred mode of operation is one in which the suspension of carbon particles with molecular precursors to the metal, metal oxide or other catalytically active material is stirred to keep the particles from  
20 settling.

It is preferable to mechanically dissociate larger aggregates of the carbon powders by using, for example, a blade grinder or other type of high-speed blade mill. Thus, dispersing the carbon powder in water preferably includes: 1) if not  
25 already provided in suspension, wetting of the carbon black powder by mixing a limited amount of the dry powder with a wetting agent and a soft surfactant; 2) diluting the initial heavy suspension with the remaining water and a basic surfactant diluted in the water; and 3) breaking secondary agglomerates by sonification of the liquid suspension in an ultrasonic bath.

The precursor to the metal or metal oxide active species, for example  
30 potassium permanganate, is preferably dissolved separately in water and added in an appropriate amount to a carbon suspension, prior to breaking the secondary agglomerates. Adding the metal salt in this manner advantageously

facilitates breaking the larger agglomerates and the mixing results in a less viscous slurry. After sonification, the slurries are stable for several months without any apparent sedimentation or separation of the components.

It is also possible to control the temperature of the precursor, if desired.

- 5 For example, it may be desirable to heat the precursor composition prior to atomization thereby reducing the amount of heat needed from the system for solvent evaporation and/or initiating a reaction between compounds in the precursor. Alternatively, the precursor solution could be chilled if the precursor composition is unstable at room temperature.

- 10 The reactor systems described above are not commonly used for spray processing wherein precursors to a material component are dried and reacted in one step. Nanometer-sized particles are difficult to produce in the presence of other particles while maintaining control of their dispersion on a support surface. Converting the precursors in a spray dryer or similar apparatus is possible  
15 according to the present invention due to the use of precursors and additives that preferably decompose at a temperature of not greater than about 400°C, more preferably not greater than about 300°C and even more preferably not greater than about 250°C.

- 20 Low thermal decomposition temperature precursors that are useful at such low reaction temperatures according to the present invention to form metals include carboxylates, hydroxides, halides, nitrates, metal-organic complexes, amine adducts, isonitrile compounds, Schiff base complexes, beta-diketonates, alkyls, phosphine complexes, phosphite complexes and carbonyl complexes of metals such as Ni, Ag, Pd, Pt, Rh, Sn, Cu, Au, Co, Ir, Ru and Os.

- 25 For metal oxides, useful low temperature precursors include oxocomplexes, alkoxides, amides, carboxylates, hydroxides, halides, nitrates, metal-organic complexes, amine adducts, isonitrile compounds, Schiff base complexes, beta-diketonates, alkyls, phosphine complexes, phosphite complexes and carbonyl complexes of metals such as Sc, Y, La, lanthanides, Ti,  
30 Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir and Sn.

When a metal is the active species phase, additives to ensure reduction to the metal at a low temperature can advantageously be used and will generally

be soluble reducing agents and may either reduce the dissolved complex before spraying or during spraying. Preferably, the reducing agent will not substantially reduce the precursor at room temperature, but will cause reduction at an elevated temperature between about 100°C and 400°C. These reducing agents  
5 should also be water stable and any volatile species that form from the reduction should be capable of being removed from the system. Examples include boranes, borane adducts (e.g., trimethylamineborane,  $\text{BH}_3\text{NMe}_3$ ), silane derivatives, e.g.,  $\text{SiH}_{(4-x)}\text{R}_x$  (where R = an organic group, aryl, alkyl, or functionalized alkyl or aryl group, polyether, alkyl carboxylate) borohydrides, e.g.,  
10  $\text{NaBH}_4$ ,  $\text{NH}_4\text{BH}_4$ ,  $\text{MBH}_{(3-x)}\text{R}_x$  (where R = an organic group, aryl, alkyl, or functionalized alkyl or aryl group, polyether, alkyl carboxylate). Other reducing agents include alanes or tin hydrides.

According to a particularly preferred embodiment, a reducing agent for Pt metal is selected from the group consisting of primary alcohols (e.g., methanol  
15 and ethanol), secondary alcohols (e.g. isopropanol), tertiary alcohols (e.g., t-butanol), formic acid, formaldehyde, hydrazine and hydrazine salts. For example, an acidified solution of  $\text{H}_2\text{Pt}(\text{OH})_6$  in the presence of formic acid is stable at room temperature but is reduced to Pt metal at low reaction temperatures, such as about 100°C.

20 For a metal oxide as the active species phase, additives to ensure oxidation to the metal oxide at low temperature can also be used and will generally be soluble oxidizing agents and may either oxidize the dissolved complex before spraying or during spraying. Preferably, the oxidizing agent will not oxidize the precursor to the metal oxide at room temperature, but will cause  
25 reduction at elevated temperature between about 100°C and 400°C. These species should also be water stable and form volatile species that can be removed from the system. Examples include amine oxides, e.g., trimethylamine-N-oxide ( $\text{Me}_3\text{NO}$ ), oxidizing mineral acids such as nitric acid, sulfuric acid and aqua regia, oxidizing organic acids such as carboxylic acids, phosphine oxides  
30 hydrogen peroxide, ozone or sulfur oxides.

The precursor solution can include other additives such as surfactants, wetting agents, pH adjusters or the like. It is preferred to minimize the use of

such additives, however, while maintaining good dispersion of the precursors. Excess surfactants, particularly high molecular weight surfactants, can remain on the electrocatalyst particle surface and degrade the catalytic activity if not fully removed.

5           Spray processing or spray pyrolysis is a valuable processing method because the particles are raised to a high temperature for a short period of time. The relatively high temperature achieves conversion of the molecular precursor to the final desired phase, but the short time ensures little surface diffusion that can cause agglomeration of the nanometer-sized active phase. Hence, the  
10       support phase is formed with well dispersed nanometer-sized active phase particles.

          In many applications, the electrocatalyst powders and other powders are formed into a layer, often in combination with other materials as part of a device such as a fuel cell or battery. The method by which these materials are  
15       deposited has a strong influence on the characteristics of the deposited layer. In turn, the characteristics of the deposited layer also has a strong influence on the performance of the device. Layer characteristics that are important include average thickness, porosity, compositional homogeneity, nature of the interface with other layers, control over the gradient of composition within a layer and the  
20       hydrophobicity, hydrophilicity, wettability and accessible surface area.

          The electrocatalyst powders of the present invention can be deposited onto device surfaces or substrates by a number of different deposition methods which involve the direct deposition of the dry powder such as dusting, electrophotographic or electrostatic precipitation. Other deposition methods  
25       involve liquid vehicles such as ink jet printing, syringe dispense, toner deposition, slurry deposition, paste-based methods and electrophoresis. In all these deposition methods, the powders according to the present invention have a number of advantages over the powders produced by other methods. For example, small, spherical, narrow size distribution particles are more easily  
30       dispersed in liquid vehicles, they remain dispersed for a longer period of time and allow printing of smoother and finer features compared to powders made by alternative methods.

The electrocatalyst powders according to the present invention exhibit a high catalytic activity and also have a morphology and microstructure, which enables them to be formed into layers by methods that are not useful with electrocatalyst powders having different characteristics. The high catalytic activity enables thinner layers of these materials to be deposited since a reduced mass of the electrocatalyst is required to achieve the same level of performance. However, it is also important that in the process of printing the layer, the performance advantages of the powders is retained in the layers, for example access to the porosity of the individual particles.

One way of depositing the powders of the present invention is to apply the powders to a substrate through the use of a thick-film paste. In the thick film process, a viscous paste that includes a functional particulate phase (e.g., a carbon composite powder) is screen printed onto a substrate. More particularly, a porous screen fabricated from stainless steel, polyester, nylon or similar inert material is stretched and attached to a rigid frame. A predetermined pattern is formed on the screen corresponding to the pattern to be printed. For example, a UV sensitive emulsion can be applied to the screen and exposed through a positive or negative image of the design pattern. The screen is then developed to remove portions of the emulsion in the pattern regions.

The different components of the thick film paste are mixed in the desired proportions in order to produce a substantially homogenous blend wherein the functional phase is well dispersed throughout the paste. Typically, the thick film paste will include from about 5 to about 95 weight percent such as from about 60 to 85 weight percent, of the functional phase, including the carbon composite powders of the present invention.

Examples of thick film pastes are disclosed in U.S. Patent Nos: 4,172,733; 3,803,708; 4,140,817; and 3,816,097 all of which are incorporated herein by reference in their entirety.

Some applications of thick film pastes require higher tolerances than can be achieved using standard thick-film technology, as is described above. As a result, some thick film pastes have photo-imaging capability to enable the formation of lines and traces with decreased width and pitch (distance between

lines). In this type of process, a photoactive thick film paste is applied to a substrate substantially as is described above. The paste can include, for example, a liquid vehicle such as polyvinyl alcohol, that is not cross-linked. The paste is then dried and exposed to ultraviolet light through a patterned photomask to polymerize the exposed portions of paste. The paste is then developed to remove unwanted portions of the paste. This technology permits higher density lines and features to be formed. The combination of the foregoing technology with the composite powders of the present invention permits the fabrication of devices with higher resolution and tolerances as compared to conventional technologies using conventional powders.

According to one embodiment of the present invention, it is advantageous to print the layers containing the electrocatalyst powders of the present invention using a direct-write device (e.g., a printing method). There are a number of advantages of constructing an energy device such as a battery or fuel cell using printing methods. Printing methods enable the formation of layers that are thinner and with smaller feature sizes than those that can be produced by current manufacturing methods such as rolling and pressing. The thinner layers result in reduced mass and volume and therefore an increase in the volumetric and gravimetric energy density of the battery. The thin devices can be incorporated into unusual vehicles or be directly integrated with electronic devices to give compact self-contained operational systems.

Thinner layers can also facilitate faster transport of chemical species such as ions, electrons and gases due to the reduced diffusional distances. This can lead to improved battery or fuel cell performance where, for example, the diffusion of a chemical species is otherwise a rate-limiting factor. This is the case in metal-air batteries where the transport of O<sub>2</sub> or hydroxide ion in the air electrode can be rate limiting. Shorter diffusional distances and lower diffusional barriers will lead to a higher rate of drain for this type of device. The discharge rate can also be improved.

Printing methods can also facilitate better control over the construction of interfaces and layer compositions giving rise to tailored gradients in composition



and layer surface morphology that facilitate chemical transport and electrochemical reactions.

Certain printing methods facilitate the construction of features with combined functionalities such that multiple layers may be combined into a single layer with multiple functionality that provides benefits in both performance and energy density.

Thus, the electrocatalyst particles and other materials such as polymer-modified particles, according to the present invention can advantageously be deposited using a direct-write tool. To be deposited using a direct-write tool, the particles must be carried in a liquid vehicle. The particles should remain well-dispersed in the liquid vehicle for extended periods of time and therefore the cartridge or reservoir into which the suspension is placed will have a long shelf-life. In some instances, substantially fully dense particles can be adequately dispersed and suspended. Depending upon the density of the particle compound, however, particles with a high density relative to the liquid in which they are dispersed and with a size in excess of about 0.5  $\mu\text{m}$  cannot be suspended in a liquid that has a sufficiently low viscosity to be deposited using a direct-write tool, particularly an ink-jet device. In most cases, the apparent density of the particles must therefore be substantially lower than the theoretical density.

More specifically, it is desirable to maintain a substantially neutral buoyancy of the particles in the suspension while maintaining a relatively large physical size. The buoyancy is required for ink stability while the larger size maintains ink properties, such as viscosity, within useful ranges. Stated another way, it is desirable to provide particles having a low settling velocity but with a sufficiently large particle size. The settling velocity of the particles is proportional to the apparent density of the particle ( $\rho_s$ ) minus the density of the liquid ( $\rho_L$ ). Ideally, the fine particles will have an apparent density that is approximately equal to the density of the liquid, which is typically about 1  $\text{g/cm}^3$  (i.e., the density of water). Since a compound such as an oxide has a theoretical density ( $\rho_p$ ) in the range of from about 3 to about 7  $\text{g/cm}^3$ , it is preferable that the apparent density of such particles be a small percentage of the theoretical density.

According to one embodiment, the particles have an apparent density that is not greater than about 50 percent of the particles theoretical density, more preferably not greater than about 20 percent of the theoretical density. Such particles would have small apparent sizes when measured by settling techniques, but larger sizes when measured by optical techniques.

In the case of electrocatalyst powders, especially carbon-based electrocatalyst powders, they are designed to have a high degree of porosity and therefore relatively low density. This aids in the suspendability of these powders in low viscosity, high powder loading inks.

Some electrocatalyst formulations may be comprised of material with a relatively high density. One preferred method for obtaining a reduced apparent density of the fine particles according to the present invention is to produce particles having either a hollow or a porous microstructure (or a combination thereof). Hollow electrocatalyst particles might include carbon, metal or metal oxide based materials where the surface area of these materials is high with a desire to maintain a relatively low apparent density. That is, one preferred particle morphology is a particle comprised of a dense shell having an inner radius and an outer radius. Preferably, the shell has a high density and is substantially impermeable. Assuming that air fills the interior of such a hollow particle, the equation representing the conditions for neutral buoyancy can be written:

$$r_2 = \left[ \sqrt[3]{\frac{\rho_p}{\rho_p - 1}} \right] r_1$$

where:  $r_2$  = outer radius  
 $r_1$  = inner radius  
 $\rho_L = 1$  (water)  
 $\rho_p$  = theoretical density of the particle

For example, if a hollow particle has an outer radius of 2  $\mu\text{m}$  (4  $\mu\text{m}$  diameter) and a density of 5  $\text{g/cm}^3$ , then the optimum average wall thickness would be about 0.15  $\mu\text{m}$  for the particle to be neutrally buoyant in a liquid having

a density of 1 g/cm<sup>3</sup>. According to one preferred embodiment, the hollow particles have an average wall thickness that is not greater than about 10 percent of the particle diameter, and more preferably not greater than about 5 percent of the particle diameter.

5 It will be appreciated that other particle morphologies can be utilized while maintaining an apparent density within the desired range. For example, the electrocatalyst particles can have a sufficient amount of porosity to yield a particle having an apparent density that is lower than the theoretical density. Open (surface) porosity can also decrease the apparent density if the surface  
10 tension of the liquid medium does not permit penetration of the surface pores by the liquid.

Thus, the fine particles according to the present invention have a low settling velocity in the liquid medium. The settling velocity according to Stokes Law is defined as:

15

$$\text{where } V = \frac{D_{st}^2 (\rho_s - \rho_l) g}{18\eta}$$

20

$D_{st}$	=	Stokes diameter
$\eta$	=	fluid viscosity
$\rho_s$	=	apparent density of the particle
$\rho_l$	=	density of the liquid
$V$	=	settling velocity
$g$	=	acceleration due to gravity

25

Preferably, the average settling velocity of the particles is sufficiently low such that the suspensions have a useful shelf-life without the necessity of frequent mixing. Thus, it is preferred that a large mass fraction of the particles, such as at least about 50 weight percent remains suspended in the liquid. The particles  
30 preferably have an average settling velocity that is not greater than 50 percent, more preferably not greater than 20 percent, of a theoretically dense particle of the same composition. Further, the particles can be completely redispersed after settling, such as by mixing, to provide the same particle size distribution in suspension as measured before settling.

According to the present invention, more than one type of particle can be dispersed in a single liquid vehicle for deposition with a direct-write tool. The particles can be dispersed into the liquid vehicle by lightly mixing or, for example, by using ultrasound. For use in an ink-jet device, the viscosity of the suspension  
5 is preferably not greater than about 30 centipoise, more preferably not greater than about 20 centipoise. It is also important to control the surface tension of the liquid suspension and preferably the surface tension is from about 20 to 25 dynes/cm for an ink-jet device.

The solids loading of fine particles in the suspension is preferably as high  
10 as possible without adversely affecting the viscosity or other necessary properties of the direct-write composition. For example, the direct-write composition can have a particle loading of up to about 75 weight percent, such as from about 10 to about 50 weight percent.

The direct-write compositions are typically water-based, although other  
15 solvents or liquids may be used. Such compositions can include other chemicals including, but not limited to, surfactants, dispersion agents, defoamers, chelating agents, humectants and the like.

More specifically, ink-jet compositions generally include water and an alcohol. Organic solvent based systems can also be used and ink-jet print  
20 heads are often tailored for either organic or aqueous systems. Surfactants are also used to maintain the particles in suspension. Co-solvents, also known as humectants, are used to prevent the ink 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 ink-jet liquid vehicle compositions are disclosed in U.S.  
25 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 incorporated by reference herein in their entirety. The selection of such additives is based upon  
30 the desired properties of the composition, as is known to those skilled in the art. The fine particles are mixed with the liquid vehicle using a mill or, for example, an ultrasonic processor.

According to one embodiment of the present invention, the liquid vehicle into which the particles are dispersed includes soluble molecular precursors, such as metal precursors, that have a relatively low decomposition temperature.

The molecular precursor is preferably a soluble inorganic compound that can be  
5 co-deposited with the powders and then thermally treated to form an essentially continuous phase filling any void space between particles. Low temperature decomposition precursors such as those described herein with respect to spray drying can be used. A preferred type of precursor compound are the alpha hydroxycarboxylate (glycolate) derivatives. Metal carboxylates are often  
10 advantageous in this respect for the formation of metal compounds. It will be appreciated that the molecular precursors will have a composition that is specific to the material being deposited. Ligands on the molecular precursors can act as a surfactant or the actual liquid vehicle.

In one embodiment, the molecular precursor forms essentially the same  
15 compound as the particles. In this embodiment, the particles in the liquid vehicle can advantageously catalyze the molecular precursor to form the desired compound. The addition of precursors with decomposition temperatures below about 300°C allows the formation of functional features on a polymeric substrate, including polyamide, fluoro-polymers, epoxy laminates and other substrates.  
20 These molecular precursors are particularly useful when combined with hollow or porous particles because they contribute to higher densities when the deposited layer is sintered. That is, a portion of the final layer comes from the particles and a portion from the molecular precursor wherein the portion from the precursor fills in space between particles and thereby increases the solids fraction in the  
25 final structure.

The liquid vehicle can also include carriers to hold the particles together once the particles are deposited. Such a liquid vehicle would be advantageous when the particles are to be deposited and will not be sintered to adhere the particles to one another. The liquid vehicle could also include a polymer that,  
30 after deposition, would yield a polymer layer with particles dispersed throughout the polymer. Further, the liquid vehicle could also include a molecular species

which can react with the dispersed particles to modify the properties of the particles.

A direct-write deposition method according to the present invention is illustrated schematically in Fig. 4. In Fig. 4(a), a fine powder 1002 is dispersed in  
5 an organic vehicle 1004 including water and various organics to aid in the dispersion of the fine powder 1002. The direct-write tool 1006 ejects the suspension through an orifice and onto a substrate 1008. After deposition the substrate 1008 is thermally treated 1010 to remove the liquid vehicle 1004 including the organics and deposit a thin layer of fine particles 1002.

10 In the embodiment illustrated in Fig. 4(b), the particles 1012 are dispersed in a liquid vehicle 1014 which include water, organics and at least one molecular precursor to a compound or a metal. The liquid suspension including the particles 1012 and the precursor-containing liquid vehicle 1014 are deposited using a direct-write tool 1016 onto a substrate 1018. After deposition, the  
15 substrate 1018 is thermally treated 1020 to remove liquids and convert the precursors to their respective compound or metal. The resulting layer 1022 includes particles dispersed throughout a film of the compound or metal.

As used herein, a direct-write tool is a device that deposits a liquid or liquid suspension onto a surface by ejecting the liquid through an orifice toward  
20 the surface without the tool making substantial contact with the surface. The direct-write tool is preferably controllable over an x-y grid relative to the printed surface (i.e. either or both the substrate and device may move). One preferred direct-write tool according to the present invention is an ink-jet device. Other examples of direct-write tools include automated syringes, such as the  
25 MICROPEN tool, available from Ohmcraft, Inc., of Honeoye Falls, N.Y. and the DOTLINER dispense system (Manncorp, Huntingdon Valley, PA) which is capable of dispensing lines, dots and areas down to 200  $\mu\text{m}$  or smaller at speeds of up to 10,000 dots/hour.

According to the present invention, the orifice of the direct-write tool can  
30 have a reduced diameter. This is a direct result of the particle characteristics discussed hereinabove. A reduced diameter will enable the formation of finer features.

One preferred direct-write tool according to the present invention is an ink-jet device. Ink-jet devices operate by generating droplets of ink and directing the droplets toward a surface. Ink-jet printing, when applied to the particulate suspensions in accordance with the present invention is a means for delivering  
5 controlled quantities of the compound to a variety of substrates.

The position of the ink-jet head is carefully controlled and can be highly automated so that discrete patterns of the ink can be applied to the surface. Ink-jet printers are capable of printing at a rate of 1000 drops per second or higher and can print linear features with good resolution at a rate of 10 cm/sec or more,  
10 up to about 1000 cm/sec. Each drop generated by the ink-jet head includes approximately 2 to 200 picoliters of the liquid 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.

Typically, an ink-jet device includes an ink-jet head with one or more  
15 orifices having a diameter of less than about 100  $\mu\text{m}$ , such as from about 50  $\mu\text{m}$  to 75  $\mu\text{m}$ . Ink 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. Ink-jet devices are described in more detail in, for example, U.S. Patent No. 4,627,875  
20 by Kobayashi et al. and U.S. Patent No. 5,329,293 by Liker, each of which is incorporated herein by reference in their entirety. However, such devices have primarily been used to deposit inks of soluble dyes.

Ideally, the droplet generated by the printer head is identical in composition to the bulk fluid. However, some filtration of suspensions may occur  
25 if the particles are too large to pass through the channels or onboard filters. The small particle size and reduced number of particle agglomerates according to the present invention reduces the amount of particles collected by the filter and can enable removal of the filter.

According to the present invention, it is possible to deposit gradient layers  
30 of material wherein the composition of the layer changes through the thickness of the layer. In order to deposit such layers, it is preferred to form the layer using

multiple direct-write deposition steps wherein the composition of the suspension being deposited changes through the layer.

Utilizing the direct-write method of the present invention, it is also possible to form features and create device components on a non-planar surface, if  
5 required for a specific application or product geometry.

Other processes that can be utilized to fabricate the devices of the present invention include laser transfer and guided optical deposition. In a laser transfer method, a material that is to be deposited is placed onto a transfer substrate such as a glass disc or an organic polymer-based ribbon. The transfer  
10 substrate is then placed over the substrate upon which the material is to be deposited. A laser is then used to controllably transfer the material to the substrate from the transfer substrate.

Guided optical deposition is a technique wherein the materials or precursors to the materials are delivered through an optical fiber to the substrate  
15 in a controlled manner such that features on the substrate can be formed by controlling the position of the optical fiber relative to the substrate. Upon delivery of the material and or material precursor to the substrate, the material is heated if necessary to convert the material or otherwise modify the material properties. For example, the material can be heated in a localized manner by using a laser.

20 The particles can also be deposited electrophoretically or electrostatically. The particles are charged and are brought into contact with the substrate surface having localized portions of opposite charge. The layer is typically lacquered to adhere the particles to the substrate. Shadow masks can be used to produce the desired pattern on the substrate surface.

25 Patterns can also be formed by using an ink jet or small syringe to dispense sticky material onto a surface in a pattern. Powder is then transferred to the sticky regions. This transfer can be done in several ways. A sheet covered with powder can be applied to the surface with the sticky pattern. The powder sticks to the sticky pattern and does not stick to the rest of the surface.  
30 A nozzle can be used to transfer powder directly to the sticky regions.

Many methods for directly depositing materials onto surfaces require heating of the particles once deposited to sinter them together and densify the



layer. The densification can be assisted by including a molecular precursor to a material in the liquid containing the particles. The particle/molecular precursor mixture can be directly written onto the surface using ink jet, micro-pen, and other liquid dispensing methods. This can be followed by heating in a furnace or  
5 heating using a localized energy source such as a laser. The heating converts the molecular precursor into the functional material contained in the particles thereby filling in the space between the particles with functional material.

A number of other methods may be employed to construct layers containing the electrocatalyst powders according to the present invention. For  
10 example, the powders can be deposited by doctor blading, slot die or curtain coater methods. In these methods, an ink or paste containing the electrocatalyst powder is applied to the surface using blade which is held at a specified height from the substrate. The thickness of the layer can be controlled down to several micrometers in thickness. For slot die and curtain coater methods, the ink or  
15 paste is dispensed through a small gap onto a substrate that may be moving on a web drive.

Roll pressing methods can also be used. Roll pressing methods involve mixing components including the electrocatalyst powder, binders and other property modifiers and feeding them through a roll mill to form a pressed film.  
20 Roll pressing is often done directly on other active parts of the energy device such as a nickel mesh current collector.

Electrostatic printing methods can be used wherein the electrocatalyst particles are charged with an electric charge, transferred to the drum of a roller, then transferred to a substrate which has the opposite electric charge to that of  
25 the particles. This transfer can be carried out in a fashion that results in a blanket layer over the entire substrate or in a patterned manner with the pattern determined by the distribution of the electrical charge on the substrate surface. Typically this method enables the transfer of layers one particle thick and therefore enables very good control over layer thickness for thin layers.

30 Gravure, rotogravure and intaglio printing methods can be used wherein an ink or paste containing the electrocatalyst powder is transferred to a sunken surface feature, often on a cylinder, that defines the pattern to be transferred to

the substrate surface. The substrate is often a continuous feed from a web drive. Relief and flexographic printing methods can also be used which are the reverse of Gravure printing in that a material, often in the form of a paste or ink, is transferred from a raised pattern on a surface, often a roller, to a substrate.

5           Lithographic printing methods can also be used. In lithographic printing methods, a photosensitive ink or paste is placed on the substrate and exposed to a source of illumination or electromagnetic radiation, generally UV light, wherein the exposed areas interact with this radiation to undergo a change. The change may result in creation of a soluble or insoluble feature depending on the reactivity of the paste and the desire for positive or negative lithography. After  
10       removal of the unwanted matter the patterned layer containing the electrocatalyst powder remains for further processing.

          Laser transfer methods can be used in which the electrocatalyst containing material is dispersed on a tape or ribbon and a laser is used to  
15       transfer material from the underneath surface of the ribbon or tape to the surface of the desired substrate which is close proximity to the tape. Using this method, features can be built with controlled dimensions.

          Spray deposition methods can also be used. In spray deposition methods, an ink containing the electrocatalyst powder is fed through a spray  
20       nozzle and atomized to form droplets which are directed to a surface where the electrocatalyst layer is to be deposited.

          Thus, the electrocatalyst powders produced according to the present invention result in thinner and smoother powder layers when deposited by such liquid or dry powder based deposition methods. Smoother powder layers are the  
25       result of the smaller average particle size, spherical particle morphology and narrower particle size distribution compared to powders produced by other methods.

          The present invention is also directed to devices including thin film primary and secondary batteries and in one embodiment is directed to thin film  
30       air cathodes for use in such batteries. The thin film air cathodes are particularly useful in metal-air batteries such as Zn/Air primary batteries and Zn/Air secondary batteries and novel batteries referred to herein as metal hydride/air

(MH/Air) secondary batteries. The novel air cathode advantageously enables the reduction of oxygen ( $O_2$ ) to hydroxyl ion ( $OH^-$ ) and the transport of the  $OH^-$  ions to the anode during discharge and transport  $O_2$  to the liquid-solid interface during discharge. For this reason, the thin film air cathodes of the present invention are also referred to as bifunctional oxygen electrodes, since they combine both functions, namely oxygen reduction and oxygen evolution.

Metal-air batteries have the best potential for power density, peak power characteristics, voltaic efficiency and rate capability among all battery technologies. In addition, the components of a metal-air battery are very suitable for printing to produce a light-weight, thin battery. The high rate of discharge is also advantageous for portable devices that require frequent high current discharge with a background of low current continuous operation.

The metal-air batteries according to the present invention include multiple functional layers, two or more of which may be combined into a single multifunctional layer. The functional layers can include a membrane layer, current collector, hydrophobic layer, electrocatalyst layer, an electrolyte, separator and anode.

The main electrocatalytic processes in the air cathode of a metal/air battery, as well as in other devices such as a PEM fuel cell, take place in a 3-phase boundary (electrode/air/electrolyte), which is graphically illustrated in Fig. 5. The electrocatalyst for oxygen reduction must populate the zone of 3-phase contact 602 and be in electrical contact with the electrode (current collector) 604 and in diffusional contact with the electrolyte 606 and the air 608. To accomplish this, present metal air battery cathodes include a gas-diffusion layer, a catalytic layer and a current collection system. The gas-diffusion layer is characterized by high gas permeability and impermeability to aqueous solutions. The catalytic layer consists of a porous conductive matrix with a highly dispersed electrocatalyst to yield a distribution of hydrophobic pores for oxygen supply and hydrophilic pores for electrolyte exposure. The current collector is usually made from an inert metal mesh, such as nickel or nickel alloy mesh in intimate mechanical contact with the pressed matrix of highly dispersed carbon.

It is desirable to maximize the exposure of the active electrocatalytic sites to both air and the electrolyte. According to the present invention, a gradient of hydrophilic/hydrophobic properties across the catalytic layer in the zone of 3-phase contact can be utilized to enhance the properties of the device.

5 Hydrophobicity of a layer is a characteristic of a layer defined by its ability to have higher permeability to gases and lower permeability to liquids such as water, alcohols, acidic solutions or basic solutions. Graded hydrophobicity layers are structures consisting of at least one composite layer of carbon and a tetrafluoroethylene (TFE) fluorocarbon polymer or other material with  
10 hydrophobic properties, where the composite structure has a certain porosity, pore size distribution and permeability for particular gases or liquids. The goal of applying a graded hydrophobicity layer is to ensure preferential transport of one carrier, reactant or product of a reaction in the electrochemical device versus another carrier, reactant or product of the reaction.

15 A higher hydrophobicity layer is achieved by using a higher volume or weight ratio of hydrophobic material (e.g., TFE fluorocarbon polymer) versus carbon compared to a lower hydrophobicity layer for a given carbon support. At a constant ratio of hydrophobic material to carbon, when the type of carbon support is a variable the hydrophobicity of the layer depends on the intrinsic  
20 hydrophobicity of the carbon and the temperature and pressure conditions used for the preparation of the hydrophobic layer.

Various embodiments of an air cathode according to the present invention will now be described with particular reference to Figs. 6 to 12. It will be appreciated that the embodiments illustrated in Figs. 6 to 12 are also applicable  
25 to other energy devices, such as PEM fuel cells.

Fig. 6 illustrates an air cathode 3600 according to one embodiment of the present invention. The air cathode illustrated in Fig. 6 can advantageously utilize printing of the current collector 3602 and sequential printing of the electrocatalyst layer 3606 and carbon conductor layer 3604. The current collector 3602 is  
30 fabricated from a conductive metal such as nickel or silver and for many applications silver is preferred. The current collector 3602 can be deposited solely from metal precursors or from metal precursors combined with dispersed

metal powders. The dispersed metal powders can be nanometer-sized particulate powders or can be high aspect ratio powders (e.g., fibers), such as fibers having an average length of 2 to 10  $\mu\text{m}$ , which can provide good conductivity while being highly porous. The metal precursors should be capable  
5 of decomposing into the metal at relatively low temperatures, such as not greater than about 400°C, more preferably not greater than about 250°C. For example, silver metal precursors can be chosen from silver carboxylates and silver trifluoroacetate, which can also include silver nanoparticles. When silver nanoparticles are included in a silver trifluoroacetate precursor, the thermal  
10 decomposition temperature can be reduced from about 350°C to about 250°C. If the material is subjected to a rapid thermal anneal or is laser processed, then it may be possible to utilize higher temperature precursors due to the short exposure time. A thermally insulating layer, such as a porous aerogel layer, can also be used as a thermal insulator to reduce the thermal affects. Current  
15 collectors thinner than about 1  $\mu\text{m}$  can be formed solely from the metal precursors and will not require incorporation of metal powder, while those thicker than 1  $\mu\text{m}$  will typically require the use of a metal powder precursor.

The current collector 3602 must be deposited and processed at low temperatures onto a membrane gas diffusion layer 3603. The gas diffusion layer  
20 3603 is typically fabricated from TEFLON. TEFLON is a tetrafluoroethylene (TFE) fluorocarbon polymer available from E.I. duPont deNemours, Wilmington, Delaware. Although the term TEFLON is used throughout the present specification for convenience, it is understood that other similar fluorocarbon polymers can be substituted for TEFLON.

25 The current collector is preferably fabricated using a direct-write deposition process. Advantageously, the current collector comprises a plurality of elongated strips having an average width of preferably not greater than about 100  $\mu\text{m}$ , such as not greater than about 75  $\mu\text{m}$ . It will be appreciated that the metal current collector can be fabricated by other methods, including sputtering,  
30 evaporation, photolithography, electroless plating, electroplating, doctor blade, screen printed or electrochemical deposition.

A gas diffusion layer 3603 which allows maximum permeation of oxygen and no permeability to aqueous solutions using hydrophobic pores is necessary as the pores of the gas diffusion layer need to be protected from flooding by the electrolyte. This layer can be a continuous TEFLON membrane or a pressed  
5 TEFLON modified carbon layer. For example, one preferred TEFLON layer is about 90  $\mu\text{m}$  thick with a density of  $2.26 \text{ cm}^3/\text{g}$ . The average pore size is about 23 nm, with a distribution of pores ranging from about 0.2 nm to 70 nm, corresponding to a porosity of about 10 % and a surface area of  $7.3 \text{ m}^2/\text{g}$ .

In case of the TEFLON modified carbon (discussed below), the current  
10 collector is incorporated as a Ni mesh in the carbon with the metal mesh being closer to the gas-open side. However in the case of the current collector being deposited directly on the TEFLON, the TEFLON surface is preferably modified to promote adhesion between the current collector and the TEFLON surface. Several routes can be utilized to modify the surface of the TEFLON. A  
15 commonly used method to modify the TEFLON surface is to etch the surface. Tetra-etch is a commonly used industrial etchant for TEFLON. Tetra-etch is a mixture of sodium naphthalene in ethylene glycol dimethyl ether. The TEFLON molecule is a long chain of carbon atoms to which fluorine atoms are bonded. The etchant strips the fluorine atoms from the chain creating a deficiency of  
20 electrons, which are then replaced with water vapor, oxygen, and hydrogen when the TEFLON is exposed to air. The carboxyl, carbonyl and hydroxyl groups formed as a result of etching easily adhere the current collector on the TEFLON surface. Tetra-etch in the as received form is too strong to etch the thin TEFLON layer and should be diluted for etching the TEFLON surface.

25 Another approach to modify the TEFLON surface is to sputter a thin layer of metal film on the TEFLON surface. Examples of metals that can be sputtered are Au and Cu.

To deposit a conductive current collector 3602 it is often necessary to anneal the precursor to the conductive metal. Thus, it may be necessary to  
30 anneal the TEFLON membrane in the further processing steps to make a thin film battery. Preferably, such an anneal is carried out at less than  $300^\circ\text{C}$  to avoid a decrease in the surface area of the TEFLON.

An alternative to heating in a furnace is to use rapid thermal processing. Rapid thermal processing (RTP) is a versatile approach for several different processing functions, such as rapid thermal annealing (RTA), rapid thermal cleaning (RTC), and rapid thermal chemical vapor deposition (RTCVD). Rapid thermal systems are capable of increasing temperatures in excess of 200°C/s. A rapid thermal process heats the material to a processing temperature by radiative heating. Thus, it is possible to subject TEFLON to RTP at higher temperatures than heating in a furnace.

In one example, a silver current collector was deposited on an etched TEFLON membrane using a direct-write method. The silver precursor included silver trifluoroacetate and silver metal nanoparticles. After deposition, the assembly was heated at 250°C for 10 minutes to form the current collector. The average width of the current collector lines is about 75 µm.

Referring back to Fig. 6, the electrocatalyst 3608 is preferably an oxygen deficient Co-Ni-O metal oxide for secondary batteries and composite MnO<sub>x</sub>/C or Pt/C for primary batteries. To form the electrocatalyst layer 3606, the electrocatalyst particles 3608 are dispersed in a hydrophilic matrix 3610 having lower hydrophobicity than the hydrophobic matrix 3614. The carbon conductor layer 3604 is required to provide conductivity between the current collector and electrocatalyst layer 3606. In this layer, the carbon particles 3612 are dispersed in a hydrophobic matrix 3614. The separator 3616 preferably consists of a material that can be applied by a direct write method, however, screen print, doctor blade, or other approaches can also be used.

The hydrophobic matrix 3614 can include certain forms of carbon, fluorocarbon polymers such as TEFLON and other organic species. Hydrophilic layers can include metal oxide based materials such as a carbon electrocatalyst coated with metal oxide active phases. Some types of carbon and some organic polymers derivatized with hydrophilic functional groups (e.g., polyesters, polyethylene oxides, polyethers, polyalcohols and polycarboxylates) can also be used. A preferred hydrophilic polymer is a hydrophilic perfluorohydrocarbon polymer, such as NAFION.

To form the carbon conductor layer 3604 and the electrocatalyst layer 3606 the carbon particles 3612 and electrocatalyst particles 3608, respectively, can be dispersed into liquid vehicles and printed onto each other with controlled thickness. The carbon particles and/or electrocatalyst particles can be polymer  
5 modified by coating with TEFLON to form the hydrophobic matrix and the hydrophobicity can be controlled by adjusting the ratio of TEFLON to the particles or by incorporating a hydrophilic polymer.

One advantage of the embodiment illustrated in Fig. 7 is that the overall thickness is preferably not greater than about 100  $\mu\text{m}$  (excluding the separator  
10 3616). This results in several improvements including reduced diffusional resistance in these layers. The thickness of the current collector 3602 is reduced resulting in a smaller volume that corresponds to higher volumetric and gravimetric energy density, in addition to a higher drain rate. The drain rate is higher because once the kinetic limitation of the electrocatalyst is removed by  
15 using a more effective catalyst material, the next limitation on the catalytic conversion is the rate at which the species can diffuse between layers. Therefore, in this particular case (using a liquid electrolyte in contrast to a solid electrolyte) not only does the volumetric and gravimetric energy density increase due to a reduced mass and volume, but the diffusing species travel a shorter  
20 distance, resulting in a shorter transport time, hence a faster drain rate. This is an advantage over a Li-ion battery for example because even if a printed current collector is used, the diffusing species (Li ions) still diffuse relatively slowly through the metal oxide solid  $\text{LiMnO}_x$  spinel electrolyte.

Fig. 7 illustrates an air cathode 3700 according to another embodiment of  
25 the present invention including a printed current collector 3702 and a gradient in the electrocatalyst concentration through layer 3705. Layers 3604 and 3606 (Fig. 6) are combined into a single gradient layer 3705 (Fig. 7). The same current collector metals can be used as is discussed above with reference to Fig. 6. The carbon and electrocatalyst layers are combined into a single gradient  
30 layer 3705 wherein the portion contacting the current collector 3702 includes a hydrophobic matrix and the portion contacting the separator 3716 includes a hydrophilic matrix, resulting in a significant reduction in electrode thickness. The



ratio of hydrophobic matrix to hydrophilic matrix varies through the layer 3705 accordingly. The fabrication of a gradient in composition in the electrocatalyst/conductor layer 3705 requires printing sequential layers with varying compositions (e.g., ratio of TEFLON and/or NAFION to carbon particles) ranging in degree of hydrophobicity, concentration of electrocatalyst particles 3708 and concentration of carbon particles 3712, all of which lead to improvements in performance. Thus, thin layers of different compositions can be printed successively wherein the composition of each layer is systematically varied. This produces a tailored composition gradient and therefore the desired property can be achieved. Alternatively, the composition of the precursor may be continuously varied and the repeating layers leads to a composition gradient.

One advantage is that the overall thickness is further reduced leading to higher energy density. Preferably, the current collector and gradient layer have a total average thickness of not greater than about 50  $\mu\text{m}$ . In addition, the compositional gradient creates a larger 3-phase contact zone, also leading to better performance.

Fig. 8 illustrates another embodiment of an air cathode 3800 according to the present invention including an electrocatalyst particle layer 3808 printed directly over a current collector 3802. The combined functionality of several layers advantageously eliminates the carbon layer and provides an even thinner electrode. The carbon that was required for conductivity is eliminated due to the intimate contact between the current collector 3802 and the electrocatalyst particles 3808.

Several approaches can be used to deposit the electrocatalyst 3808 on the current collector 3802. The electrocatalyst 3808 can be deposited using a direct-write method or can be formed directly on the current collector 3802 by vapor phase deposition.

The thickness of the electrode (not including the separator 3816) is preferably not greater than about 30  $\mu\text{m}$ , compared to about 400  $\mu\text{m}$  for a conventional structure. Thus, diffusional resistances are reduced resulting in better performance.

Fig. 9 illustrates an air cathode 3900 including a composite current collector/ electrocatalyst 3903 according to another embodiment of the present invention. This structure combines the functions of the current collector and the electrocatalyst into a single porous conductive printed pattern 3903. No diffusion  
5 of oxygen is required through the layer 3903.

In this embodiment, the electrocatalyst and current collector are combined into a porous composite structure 3903 with controlled wetting to obtain the 3-phase interface. This is accomplished by combining the pre-formed electrocatalyst particles 3908 with precursors to the porous metal that can  
10 include metal particles and metal precursors. Thermal processing at low temperature converts the metal precursor to the metal, joining the metal particles to form a porous layer 3903 containing the electrocatalyst. Layer 3903 can be a metal ceramic composite such as a silver or nickel ink containing electrocatalyst particles such as a  $\text{NiCoO}_x$ . In this case, a lower temperature route compatible  
15 with the substrate (e.g., porous fluorocarbon polymer) can be used. Other additives that aid in the decomposition of the silver precursor to form silver such as reducing agents can be included. Silver pastes used in polymer thick film applications may also be useful.

Further, composite particles such as metal/metal oxide particles can be  
20 useful for this layer. For example, a metal or metal alloy such as Ag/Pd with embedded perovskite metal oxides (e.g.,  $\text{MgTiO}_3$ ) can be useful.

In this embodiment, the electrons generated at the surface of the electrocatalyst 3908 are captured directly by the current collector 3902. This leads to better current collection efficiency, as well as a faster drain rate.

25 Fig. 10 illustrates an air cathode 4000 according to a further embodiment of the present invention wherein the cathode 4000 includes a porous composite current collector/electrocatalyst 4003. The composite layer 4003 combines the current collector and electrocatalyst in a continuous porous layer 4003 which also includes a hydrophobicity modifier, such as a fluorocarbon polymer. An  
30 example is liquid TEFLON, an emulsion containing small TEFLON particles, or various modified fluorocarbon polymers. A TEFLON emulsion can be

incorporated by one of the methods such as those described above. Oxygen is able to diffuse through the porous layer, which is about 30  $\mu\text{m}$  thick.

This composite layer approach relies on the mixing of several components including particles of a metal, TEFLON and electrocatalyst with other  
5 components. The metal particles have a controlled particle size distribution. This leads to a well-controlled pore size distribution wherein the pore size is defined by the size of the spaces between particles.

Various types of compositional gradients can be fabricated for the composite layer 4003. For example, a porosity gradient can be formed through  
10 control of the particle size distribution as a function of location in the layer. A hydrophobicity gradient can be formed by varying the concentration of the TEFLON-type material. The electrocatalyst concentration can also be varied. Further, conductivity can be varied by control of the metal particles and molecular metal precursors.

15 Vapor infiltration can also be used to form various useful structures such as those discussed above. In this process, a bed of particles is first deposited using a direct write process. The bed is heated and exposed to a reactive vapor that carries out CVD or ALE to deposit metals or metal oxides. This vapor-infiltration method has several potential benefits including enhanced catalytic  
20 activity, the ability to fuse particles to each other, the ability to oxidize or reduce certain species, the ability to control site specific reactions, the ability to deposit  $\text{MnO}_2$ , silver, and other metals and metal oxides at low temperatures and the ability to modify the hydrophobicity of materials with suitable silanating or similar agents.

25 For the construction of 3-dimensional layered devices, alternating "monolayers" of particles can be deposited that will form three-dimensional architectures with considerable performance improvements. This approach will be most beneficial when alternating monolayers of metal particles as the current collector with monolayers of electrocatalyst particles. This 3-dimensional  
30 structure leads to performance improvements as a result of the high surface area and intimate contact between conductor and electrocatalyst particles. This design is schematically illustrated in Fig. 11.

In the embodiment illustrated in Fig. 11, the device 4100 can be fabricated as follows. The base 4102 (gas diffusion layer) is coated with a composite layer 4103, preferably using a direct-write method. This can be done with multiple jets/heads in series with different compositions in each to form a quasi-gradient.

5 The layer 4103 includes alternating thin layers of current collector particles (4105, 4106, 4107, 4108) and electrocatalyst particles (4109, 4110 and 4111). The particle layers are dispersed in a hydrophobic matrix near the base 4102 and a hydrophilic matrix near the separator 4116. The hydrophobic/hydrophilic ratio changes accordingly through the thickness of the layer 4103. Then an

10 overcoat of electrolyte composition is applied using similar methods or other technologies. For example, the electrolyte can be an aqueous solution of potassium hydroxide, KOH. It can be deposited as part of the ink formulation throughout the printed layer in which case an additional overcoat may not be necessary. The layers can also be deposited without the electrolyte, which can

15 then be applied as an overcoat afterwards to infiltrate the underlying layers when it can be deposited using a method that can withstand the corrosion of the KOH. A separator layer 4116 is then applied using a direct-write method.

It is expected that when decreasing feature size and layer thickness in the air cathode there will be a point at which further reduction in size will be

20 detrimental to battery performance. It is possible to print layers that are about one particle thick which corresponds to dimensions of about 1 to 2  $\mu\text{m}$ . At these sizes it is possible that certain parameters such as pH, concentration, and electric field gradients may dominate the performance of the device and possibly be detrimental. The layer in which this is likely to have the most significant effect

25 is in the current collector. The line width and pitch can be varied from the extreme of a largely "transparent" grid to a microporous layer that could limit battery performance due to a large IR drop. Calculations indicate that down to a layer thickness and feature size of 20  $\mu\text{m}$ , there is no significant problem of IR drop.

30 One of the problems associated with batteries that use electrolytes is carbonate formation from  $\text{CO}_2$ . A  $\text{CO}_2$  reduction layer can be used to alleviate this problem. For example, selective adsorption of  $\text{CO}_2$  by a high surface area

metal oxide such as Group II metal oxide can be used. The molar volume increase on formation of  $\text{MCO}_3$  from MO on reaction with  $\text{CO}_2$  is considerable which may result in restricted mass transport of  $\text{O}_2$  in the cell depending on the porosity and other factors. Therefore, heavy metal oxides are preferred since

5 the expansion in volume decreases with increasing atomic weight of the metal ion. As an alternative, the layer can be used to initiate a catalytic reaction to convert the  $\text{CO}_2$  to an inert or even useful species. This can have the additional advantage that oxygen is formed which can benefit cell performance. This layer must be placed between the air and the electrocatalyst layer. Figs. 12(a) and

10 12(b) illustrate two placements for this layer. In Fig. 12(a) the  $\text{CO}_2$  reduction layer 4218a is placed between the electrocatalyst layer 4206a and the carbon conductor layer 4204a. In the embodiment illustrated in Fig. 12(b), the  $\text{CO}_2$  reduction layer 4218b is placed between the base 4201b and the current collector 4202b.

15 The thin film air cathodes of the present invention and described above are also particularly advantageous for use in the electrodes of rechargeable batteries such as rechargeable zinc-air batteries. A zinc-air battery is schematically illustrated in Figs. 13(a) and 13(b).

Specifically, Fig. 13(a) illustrates a zinc-air battery 500 in charging mode.

20 The battery 500 includes air electrodes (cathodes) 502 and 508 and a zinc electrode (anode) 504 which includes a layer of zinc 506. The electrodes are typically packaged in a flat container that is open to the air. When the battery cell discharges, the zinc metal 506 is oxidized to  $\text{Zn}^{2+}$ . When all the zinc has been oxidized, the battery 500 is recharged and  $\text{Zn}^{2+}$  is reduced back to zinc

25 metal 506. The direct-write deposition methods of the present invention can advantageously be used to produce such electrocatalytic devices by depositing the metal-carbon composite powders in discrete patterns, having a thin, dense structure.

Typically, the active components of a battery such as a zinc-air battery are

30 encased in a metal can. According to the present invention, a thin battery construction that does not utilize a traditional metal can is provided. In this embodiment, a thin current collector is printed on a thin gas diffusion layer, such

as porous TEFLON. A thin composite layer of hydrophobic/catalyst material can be deposited on the current collector, as is described above. An electrolyte, preferably a gel electrolyte, is deposited over the catalyst layer and an anode is deposited on the electrolyte. Thereafter, a water impermeable and gas impermeable layer such as an epoxy or silicone can be coated over the entire upper structure to seal the active components. The end result is a thin battery package with a significantly reduced volume as compared to traditional battery packages.

The present invention is also directed to a novel battery system that is a hybrid of existing metal hydride and zinc/air technologies, referred to as a metal hydride/air (MH/Air) battery. The properties of different battery systems are illustrated in Table 1.

**Table 1** Characteristics of Battery Systems

Battery System	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Specific Power (W/kg)	Cycle Life
Li-ion	250	200	100-200	1000
Metal Hydride	70	250	70-280	500
Zinc/Air	250	200	200-450	200
Metal Hydride/Air	320	250	100-350	1000

The metal hydride/air battery according to the present invention advantageously combines the advantages of the anode from a metal hydride battery with the air cathode of the present invention. As is illustrated in Table 1, the metal hydride/air battery provides many of the advantages of a zinc/air battery such as high specific energy and specific power, but also has an increased cycle life.

The metal hydride/air battery according to the present invention includes a metal hydride anode and an air cathode, with an alkaline electrolyte disposed between the two electrodes. During discharge, oxygen and water are converted to hydroxyl ions which are transported to the anode where they react with the metal hydride to form electrons which can be routed to produce energy. During recharge, the water is reacted at the metal hydride electrode to create hydroxyl ions which are then reacted at the oxygen electrode to liberate oxygen.

The metal hydride/air batteries of the present invention are particularly useful in miniaturized devices such as GPS (Global Positioning System) transceivers. Each metal hydride/air battery cell can provide approximately 0.9 volts of power and at least four such cells would be utilized in a GPS battery to provide a total voltage of 3.6 volts, which is sufficient for GPS requirements. The battery is thin, light-weight and can be recharged many times. It is estimated that each cell would have a mass of about 4 grams. Although the battery has a slightly lower power density than a zinc air battery, the battery has a much longer useful life. The air cathode which permits recharge can be combined with different anodes to tailor the performance for different applications. Such applications can include, but are not limited to unmanned vehicles, smart cards, GPS transceivers, RF tags, various sensors, immunoassays, telemetry and other portable communications.

Metal-air rechargeable batteries were previously limited by problems with the air electrode. The problems included rechargeability, cycle life and environmental stability. The direct-write deposition process of the present invention enables high performance battery such as the foregoing to be fabricated. The method is adaptable to different performance requirements, produces thin and lightweight layers, is cost effective and efficiently uses the materials. The ability to digitally control the deposition allows simple design changes to be made.

The batteries advantageously provide improved volumetric and gravimetric energy density, increased capacity, increased cycle life, higher discharge rate and a wide temperature range of operation.

The present invention is also applicable to a number of other battery technologies. For example, the methodology can advantageously be applied to the production of prismatic batteries. The methodology of the present invention advantageously enables an increase in the number of recharge cycles, increase in power density, increase in specific power, reduction of layer thickness and reduction of cell thickness thereby resulting in a smaller device.

The electrocatalyst powders and other materials that can be fabricated according to the present invention are also useful in fuel cells. Examples of fuel

cells include proton exchange membrane fuel cells (PEMFC) and phosphoric acid fuel cells. A class of fuel cell reactions that is required to be catalyzed is the reaction of a fuel such as hydrogen gas ( $H_2$ ) to form  $H^+$  where, in the case of a PEMFC, the  $H^+$  is transported through a  $H^+$  ion transport membrane to the  
5 cathode. In this case, the fuel cell generally operates in acidic media and the cathode reduces  $O_2$  to ultimately form water as the final product. Other fuels may also be employed such as methanol, natural gas or other hydrocarbons such as methane. In some of these cases other gases which may poison the reaction or catalytically active sites such as CO are also present. These gases  
10 must be removed by the presence of an alternative active composition to that which oxidizes the fuel. As a result, the electrocatalysts aid in the removal or conversion of such species to benign products. In some cases, catalysts are also required to convert the feedstock fuel such as natural gas to a reactant having a higher  $H_2$  content. This improves the efficiency of the fuel cell and  
15 reduces formation of catalyst poisons. The catalytic compositions of the present invention are also useful to catalyze this reaction.

A PEMFC comprises the following sections: The Fuel Processor or Reformer; the Power Section of Fuel Cell Stack; and the Power Conditioner and Balance of Plant. These components are discussed below.

20 The fuel processor, or reformer, converts natural gas or other fuels into a hydrogen-rich, low-carbon monoxide gas stream. The composition and performance of the electrocatalyst powders in the PEMFC has a strong influence on the design of this component due to the presence of low concentrations of species in the reformed natural gas that can poison the electrocatalysts, such as  
25 CO. The ideal case is to supply pure hydrogen to the PEMFC in which case there is no need for a reformer, but this is unlikely to be the case for the foreseeable future due to a lack of an existing hydrogen distribution infrastructure.

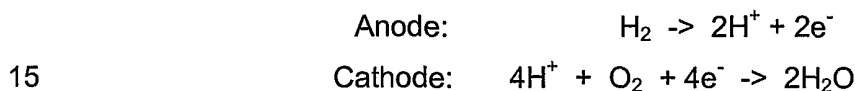
Each fuel cell stack comprises a number of membrane electrode  
30 assemblies (MEAs). The MEAs are the regions to which the gases (fuel and air) are delivered and the conversion of chemical to electrical energy takes place, as catalyzed by the electrocatalysts. Each MEA will generate a useful voltage of



around 0.6 V and the number of MEAs connected in series used in the stack dictates the overall voltage of the system.

A MEA is schematically illustrated in Fig. 14. Each MEA is comprised of a number of components. The proton exchange membrane (PEM) 1702 is a  
5 proton conductive electronically insulating membrane that selectively transports protons formed at the anode to the cathode where they react with oxygen ions to form water and electricity. The PEM is typically a sulfonated perfluorohydrocarbon, referred to herein by the trade name NAFION.

The electrodes are comprised mainly of electrocatalyst in which the active  
10 catalyst is platinum or platinum group metals, supported on a conductive support such as carbon, generally written Pt/C. The requirements for the composition of the electrode catalyst are different because a different reaction occurs at each electrode.



The cathode electrocatalyst 1704 is generally Pt dispersed on carbon. For the case of pure hydrogen, the anode catalyst 1706 is also Pt/C, which simplifies and lowers the cost of the fuel cell. However, due to the unreliability of reformers, which could produce a temporary increase in CO concentration and  
20 completely destroy the Pt/C catalysts, an alloy catalyst is typically used containing ruthenium/platinum alloy on carbon (PtRu/C). As mentioned above, the performance of these materials and their design to accommodate the reformer performance is critical to cost reliability and performance of the fuel cell. The cost and performance of these precious metal-based electrocatalysts is the  
25 major contributor to the cost and performance of the fuel cell.

The gas diffusion layer is a layer of porous hydrophobic material, generally carbon-based, which is provided between the gas delivery channels contained within the bipolar plates and the electrodes to evenly distribute the gas over the surface of the electrodes.

30 In each MEA there is typically a pair of current collectors integrated into the bipolar plates to capture the electrons (i.e., electricity) produced during the conversion of the chemical fuel to electrical power. The bipolar plates are used

to mechanically support the MEA and to distribute the gas uniformly over the surface of the gas diffusion and electrode layers.

The Balance of Plant entails the remainder of the fuel cell. Operational modules, electrical and fuel interfaces are all part of this group of standard  
5 equipment.

The operation of a PEMFC will be explained in further detail with the focus on the operation of MEA, where the electrical power is generated from the fuel. An understanding of the operational requirements of the materials systems involved is critical for the successful performance and reliability of the fuel cell  
10 and provides the rationale for the significant contribution of the materials of the present invention as well as the associated direct-write technologies that are enabled. There is a critical interplay between the need for advanced materials systems and the method by which these materials are deposited to achieve the optimum structure and function in these layers. In many cases there are multiple  
15 functions that, in principle, require competing structures. This is the basis of the present invention which enables deposition of high-performance, multi-functional layers through direct-write processes.

The operation of a PEMFC MEA is described by the four stages illustrated in Fig. 15. It should be noted that a fuel cell operates continuously and these  
20 stages are identified here for purposes of understanding the process. The cell operates at a steady state at a given load, thus the processes are connected and balanced.

In this case hydrogen is used as the fuel assuming it has either been supplied as the pure fuel or is derived from the reformer uncontaminated. The  
25 hydrogen is delivered from its source via the bipolar plates and is distributed over the face of the gas diffusion layer (GDL). The hydrogen diffuses through the gas diffusion layer until it reaches the anode layer. The GDL is a gas permeable layer with the pore structure that facilitates a uniform distribution of gas by passage through its pores, but it does not result in a large pressure drop over the  
30 system. The hydrogen gas is generally humidified in order to prevent drying of the anode layer, which would result in a loss of ionic conductivity. Thus, the GDL must be capable of handling water without significantly affecting the gas diffusion

capability. Therefore, the GDL is designed to have the necessary materials combination to achieve a balance of hydrophobic and hydrophilic nature with a distribution of pores that are not blocked by varying levels of water.

The anode (and cathode) layer contains a mixture of electrocatalyst (e.g., Pt/C), water and proton conduction polymer and must have a structure that allows for the following attributes: gas diffusion; selective ionic diffusion and conductivity; and selective electronic conductivity. The role of the anode layer is to catalytically oxidize the hydrogen to form hydrogen ions and electrons at the lowest possible temperature. The layer must be designed to be porous to hydrogen gas so that all the catalytically active Pt surfaces are accessible to the hydrogen molecules for maximum efficiency. Once the protons and electrons have been formed, the electrons are selectively removed (i.e., they must not travel through the proton exchange membrane to the cathode) through a conducting network of the carbon electrocatalyst support to the current collectors. Therefore the layer must not be so porous that the carbon particles are not connected. The protons formed at the Pt catalyst must be transported through the remainder of the anode layer to the membrane. This ionic diffusion requires a medium that facilitates this kind of diffusion, the requirements for which are almost completely opposed to optimization of the gaseous diffusion. The ionic proton diffusion requires that the catalytically active sites are also in intimate contact with a liquid or solid network, such as aqueous proton conducting polymer, that transports the protons to the proton exchange membrane. This situation described in the anode (which also applies to the cathode) is well known in electrochemical systems and is commonly referred to as the 3-phase interface. (See Fig. 5) The construction of the 3-phase interface has been a problem for a long time in electrochemical systems in general. The materials systems and deposition methods of the present invention provide the enabling solution to this problem of tailoring the structure and function of the 3-phase interface.

The protons are selectively transported through the proton exchange membrane to the cathode. This is achieved by using a membrane that is electrically insulating (to avoid electron conduction) but which selectively enables

proton transport and prevents significant leakage of water. Issues associated with the performance of the PEM include the temperature of its operation and its mechanical strength. Operating the fuel cell at a higher temperature allows for higher current density, but the operating temperature of the fuel cell is limited by  
5 the thermal stability of the NAFION PEM. In order to manufacture MEAs in large volume, it will be necessary to use a high speed manufacturing process which is likely to be based on reel-to-reel web drives which will require a PEM of higher mechanical strength than is currently achievable using pure NAFION.

After being selectively transported by the PEM, the protons must now find  
10 their way to the catalyst of the cathode where they can react with oxygen ions to form water. This ionic transport requires a facilitating medium analogous to the case of the ionic transport requirements in the anode. Meanwhile, oxygen has been supplied to the cathode with similar requirements to diffuse through the gas diffusion layer to reach the cathode in a uniformly distributed manner. However,  
15 in this case, since water is formed at the cathode, the oxygen source (usually air) is supplied dry to facilitate removal of the water that is produced. This is achieved through humidification of the remaining air constituents as they pass through and out of the cathode. The electrons produced at the anode are transported via their workload in the outside environment, back to the cathode  
20 where they are distributed by the current collector back to the cathode layer. The conductive carbon particles in the cathode distribute the electrons to the active sites in the electrocatalyst, where the oxygen atoms arrive and are reduced to form oxygen ions ( $O^{2-}$ ). Two protons react with each oxygen ion to form one molecule of water. The design requirements for the cathode are  
25 therefore similar to those of the anode in that gas and ion diffusion are required together with electronic conductivity. The cathode must also be able to accommodate the formation and removal of water without adverse effect.

The GDL covering the cathode must now be capable of removing the water produced in the cathode in addition to the delivery of the dry air from which  
30 the oxygen selectively reacts in the cathode. This must also be achieved with the appropriate choice of materials, layer structure and layer deposition method as described above for the anode GDL.

The performance of an MEA is primarily judged by reference to the relationship between MEA potential and current density, often referred to as a polarization curve. An example of a polarization curve is shown in Fig. 16 and a brief explanation of the influence of the MEA design on the nature of the polarization curve follows.

The polarization curve shows the typical shape of the relationship between cell potential and current density. For a given MEA performance (e.g., a specific polarization curve) if better fuel and operating efficiency is required, then it is desirable to move to higher voltage. Operating a PEMFC at higher voltage generally leads to higher efficiency of that cell, but it also requires a larger cell because the power density is lower. This increases capital cost in the construction of the cell but results in a lower operating cost. For a given polarization curve, operating at lower voltage generally leads to lower efficiency, but requires a smaller cell (because the power density is higher) and therefore smaller capital costs, but higher operating costs. It is advantageous to move the vertical position of the curve higher (i.e., achieve higher current density at lower voltage). The vertical position of the curve is strongly influenced by a number of materials and operating factors including platinum loading. More platinum is better, but increasing the amount of platinum significantly contributes to the cost. Other operating parameters include temperature, gas composition and gas utilization, all of which influence the cost and reliability of the PEMFC. The goal in designing an MEA is to maximize the vertical position of the polarization curve (i.e. performance) while minimizing the cost of the materials components, the capital cost and operating costs.

The connection between the shape of the polarization curve and the structure of an MEA is well understood and can be divided into different regions as indicated in Fig. 17. These regions comprise the kinetic-, ohmic-, and transport-limited regions of operation of the PEMFC MEA.

In the kinetic region, the performance is primarily dictated by the kinetic performance, or reactivity of the catalyst. A more active catalyst will give a higher cell potential at a given current density. The activity of the catalyst is dictated by its structure and number of active sites.

In the ohmic region, the performance is primarily dictated by the transport of ions and electrons. Better performance is therefore dictated by good connection between highly conductive carbons particles for electrical conductivity and a good network of proton conducting polymer connecting the catalytically active sites in the electrocatalyst to the PEM.

In the transport region, the performance is primarily dictated by the diffusion of gaseous species to and from the active site of the electrocatalysis. Better performance is manifest by rapid diffusion through the appropriate pore of the gas from the gas distribution manifold in the bipolar plates through the gas diffusion layer and the electrode.

From this description it is clear that there is a very strong influence of the materials and the structure of the layer comprising these materials on the performance and cost of the PEMFC system.

One of the major goals in this area is to increase the utilization of Pt to have the best performance at the lowest possible Pt loading. This can be achieved in a number of different ways based on both the loading of the Pt on the carbon support and the loading of the carbon supported electrocatalyst in the electrode layer of the MEA. As is described above, there is a subtle trade-off in terms of performance and Pt utilization (hence cost) depending on the conditions of operation of the fuel cell.

A purely kinetic improvement derived from the improved utilization of Pt would result in a change, for example, of up to  $0.35\text{A}/\text{cm}^2$ . Therefore, if the goal is to run the fuel cell under conditions of either current densities lower than  $0.35\text{A}/\text{cm}^2$  or voltages higher than  $0.75\text{V}$ , the kinetic improvement is sufficient. However for operation under different conditions, i.e., at voltages lower than  $0.75\text{V}$  and current densities above  $0.35\text{A}/\text{cm}^2$ , the kinetic improvement has a less significant impact that an improvement in the layer structure and materials because this is the region dominated by ohmic and transport characteristics. So an improvement in the layer structure could lead to a polarization curve shown in Fig. 18 under these conditions. The importance of this improvement is magnified by the power curve also shown in Fig. 18.

This background is important for an understanding of the method of optimization of the platinum utilization by varying both the Pt content in the electrocatalyst and the thickness and structure of the electrode layer. This point can be exemplified as follows. Fig. 19 illustrates three layers of active material, A, B and C, which could be an electrocatalyst layer deposited onto a support such as a gas diffusion layer or an ion conducting membrane. If the same loading of Pt on carbon is used, for example 20 wt.% Pt on C then the total weight loading of Pt measured in  $\text{mgPt}/\text{cm}^2$  of B would be twice A and C would be equal to 3x the loading of A. The polarization curve measured for each of these three layers may appear quite similar in the kinetic region (i.e., at low current or power density) but are likely to be considerably different in the ohmic and transport limited region even assuming the same structure as a result of the different layer thicknesses. As an alternative approach, the same Pt loading in  $\text{mgPt}/\text{cm}^2$  as described in the last example for layer B could be achieved using 40% Pt on C and a layer half the thickness (i.e., A). Assuming the same Pt utilization for the 40% Pt on C as the 20% Pt on C (i.e., the same kinetic performance of the electrocatalyst), then the performance at higher current and power densities would be expected to be superior for the 40% Pt on C layer (other things being equal). Therefore, it is clearly important to optimize the Pt utilization at the higher Pt mass loading while simultaneously optimizing layer thickness.

Typical electrocatalyst layers can include compositions that range from pure Pt black (e.g., DMFC and electrochemical sensor applications) to very low Pt loadings on carbon such as 1 wt.% Pt on C (e.g., for electrochemical sensors). Typical layer thickness can vary between 1 and 100 micrometers.

An example of this trade off is illustrated by comparing Figs. 20 and 21. In Fig. 20, the polarization curve is given for a cathode layer comprised of 20 wt.% Pt on carbon with a Pt laydown of  $0.2 \text{ mgPt}/\text{cm}^2$  in the cathode. In Fig. 21, 5 wt.% Pt on carbon was employed with a laydown of  $0.1 \text{ mgPt}/\text{cm}^2$ . The latter loading is an extremely low loading to achieve the performance indicated by the polarization curve compared to conventionally manufactured electrocatalysts.

These measurements were made at atmospheric pressure gases using H<sub>2</sub> and air at 50°C using a NAFION 112 membrane.

A related influence on the performance at higher current densities is the pore structure of the carbon that is used to support the Pt. This can have a dramatic affect on the ohmic and transport properties. This aspect of the present invention is illustrated in Fig. 22 which shows the difference between the oxygen and air polarization curves for two catalyst powders with the same Pt loading, same layer thickness and same measurement conditions but with different carbon support material. The improvement in performance is measured by the smaller difference in potential between oxygen and air gas (i.e., a lower number is better). Therefore, as can be seen from the plot, the alternative carbon support, which is SHAWINIGAN BLACK, is better than VULCAN XC-72.

The use of spray methods according to the present invention to produce complex multicomponent, composite particles containing electrocatalyst, carbon, hydrophobic polymer, proton conducting polymer and other components has not been disclosed in the prior art. The present invention relates to the use of spray conversion to produce particles with complex compositions useful for fabrication of MEAs in fuel cell applications.

As is discussed above, MEAs are most often constructed from particulates (electrocatalyst consisting of metal supported on carbon and electrically conducting carbon powders) and suspensions of colloidal (NAFION-containing liquids) and polymeric (PTFE suspensions in various liquids) materials. This current palette of materials that an MEA designer has to choose from is very limited. It would be highly advantageous to have other starting materials that combine these materials in different manners to allow fabrication of MEAs with characteristics that address the problems outlined above.

Fig. 23 graphically illustrates a particulate composite structure that can be fabricated according to the present invention. The structure includes electrocatalyst particles dispersed in a polymer matrix. The secondary structure of the electrocatalyst particles is micron-sized while the primary carbon support particles are 10s to 100s of nanometers in size and are decorated with clusters of the precious metal. The polymer is dispersed throughout the particle.



A conceptually ideal electrode layer (cathode) is illustrated in Fig. 24. It is widely accepted that the ideal solution must provide several features including: a connected pathway of conducting carbon particles (the support for the precious metal) from the gas diffusion layer to allow electron transport; a connected  
5 pathway of proton conducting polymer (e.g., NAFION) to allow transport of hydrogen ions to electrocatalyst sites; hydrophobic passages to allow water to escape thereby avoiding flooding from water generated at the catalyst sites; electrocatalyst metal exposed to the proton conducting polymer to allow the protons to be readily transported to the reaction sites; sufficiently large pores to  
10 allow oxygen gas transport from the gas diffuser to all locations in the electrode; and finer scale porosity in agglomerates of electrocatalyst to allow transport of oxygen over shorter distances to reaction sites. Existing attempts at achieving this ideal situation are hindered by the lack of engineered particles, the limited printing processes dictated by the types of materials available and the types of  
15 structures derived from conventional materials.

Various deposition techniques for layer structures are discussed hereinabove. The preferred deposition technique for the active layer of an MEA structure depends on the structure and morphology of the catalyst particles and the hydrophobic component. For particle sizes smaller than about 25  $\mu\text{m}$ ,  
20 syringe dispensing is more appropriate while for particles greater than about 25  $\mu\text{m}$ , techniques such as screen-printing or coating with wire-cators may be more appropriate.

The deposition method that is selected dictates the components of the flowable medium that can be used. For example, isoproponal is not suitable for  
25 syringe dispensing due to its low viscosity and high vapor pressure. An example of a formulation that is suitable for syringe dispensing is a metal oxide catalyst mixed with TEFLON powder in a 5:1 weight ratio and dispersed in alpha-terpineol. The resulting active layer is composed of 20 wt.% to 40 wt. % solids. Similarly, a formulation made for screen-printing can include a metal oxide  
30 supported on carbon and mixed with polymer-modified carbon, which are then

dispersed in iso-propanol. The solids loading of this formulation can be varied from 10 wt.% to 40 wt. %.

The thickness of a layer can be controlled by controlling the solids loading of the active material in the flowable medium and the writing speed during deposition. Layers having a wide range of thickness can be deposited. Fig. 25 illustrates a average layer thickness as a function of solids loading as well as several SEM photomicrographs of layers deposited using a syringe dispense technique. As the layer thickness increases, there is a linear increase in the total loading of solids in the layer. A gradient in the layer composition can also be formed by controlling the composition of the ink, the writing speed and the number of sub-layers that are deposited.

While the kinetics of the electrode are controlled by the dispersion and composition of the electrocatalyst, the ohmic and transport limitations of the electrode in a power device arise mainly due to the thickness, composition and porosity of the layers. The thickness of the layers can be controlled by changing weight loadings of the powders in the layer and by changing the deposition method. The deposition method and the composition of the layer will in turn determine the porosity of the layer and the accessibility of the catalytic layers. For example, Fig. 26(a) illustrates a 60  $\mu\text{m}$  thick layer deposited by syringe dispense and Fig 26(b) illustrates a 60  $\mu\text{m}$  thick layer fabricated by screen printing. Active layer loadings from as small as 2  $\text{mg}/\text{cm}^2$  of active layer to 20  $\text{mg}/\text{cm}^2$  and higher are enabled by this approach.

The energy densities that are obtained by the power device depend on the volume of the different layers in the power device and hence the thickness of the various layers. Higher volumetric densities are obtained from the power device when thinner layers are utilized.

The formulation of an ink containing electrocatalyst powders and other hydrophobic powders to control transport processes was produced and deposited with the goal of producing a thin layer of this material on the surface of a printed silver current collector. The thickness of the layer can be as low as one particle layer thick.

As a result of the ability to rapidly determine the optimum structure-performance relationship, a complete gas diffusion electrode can be constructed using the foregoing approaches. An illustration of a printed gas diffusion electrode in cross-section is shown in Fig. 27. This gas diffusion electrode is comprised of a porous gas diffusion layer on which a silver current collector has been printed. The current collector (lighter areas in Fig. 27) has dimensions of 40  $\mu\text{m}$  lines, 15  $\mu\text{m}$  in height with 300  $\mu\text{m}$  spacing. The active layer deposited onto the current collector/gas diffusion layer is comprised of materials that catalyze the chemical conversion of the gas and materials that control the hydrophobicity of the layer. The layer is about 30  $\mu\text{m}$  thick.

The other active layers were deposited using direct write syringe dispense with a series of different mass loadings. Different direct write mass loadings of 5 and 12  $\text{mg}/\text{cm}^2$  in air have similar performance and have lower performance as compared to the 20  $\text{mg}/\text{cm}^2$  layer deposited conventionally. This might be expected based on the lower mass of active material present. However, in air, the 5 $\text{mg}/\text{cm}^2$  direct-write layer has only slightly lower performance in air compared to a conventionally deposited layer with 4 times more material because the layer structure has improved transport and catalyst utilization characteristics. Thus, in air, the performance of these two layers is comparable.

The difference between the electrochemical performance in oxygen vs. air (effectively an oxygen concentration dependence measurement) reveals information on the diffusion characteristics of the layer. The difference plots in Fig. 28 reveal this difference and show the improved layer characteristics of the layers formed by direct-write deposition.

MEAs are currently fabricated from particulates of conducting carbon supporting precious metal compositions such as Pt and Pt alloys. This material must be combined with a variety of other materials through complex MEA fabrication recipes to attempt to form the idealized structure outlined above. However, the characteristics of these particles simply do not allow for straightforward fabrication of the optimum structures.

It would be highly advantageous to be able to use more complex particle structures containing:

- Agglomerated Pt/C
- PCP-Pt/C (PCP = proton conducting polymer)
- 5     • PTFE-Pt/C (PTFE = polytetrafluoroethylene polymer)
- PCP-PTFE-Pt/C
- Pt/C (proton conducting and electrically conducting polymer)

Examples of the foregoing particulate structures are illustrated in Figs. 29 to 31. The PTFE-Pt/C (hydrophobic polymer) polymer modified particle offers the following advantages. The hydrophobic material is already incorporated into the powders and does not have to be mixed in later allowing for better control over the uniformity of the hydrophobization. The same advantages described above for the structures with this polymer are also found. The PCP-Pt/C (proton conducting polymer) polymer modified particles offer the following advantages in addition to those described above. The PCP is incorporated into the secondary structure providing intimate contact of reaction sites with the polymer that transports the protons to the reaction sites. The PTFE-PCP-Pt/C polymer modified particles combine the advantages of all the materials described above and offer the possibility of fabrication of an electrode through a single material. Finally the functions of the PCP and PTFE can be combined into one through the use of a polymer that is both a conductor of electrons and protons.

The polymer-modified particles are produced by spray conversion starting with the ingredients for the particles that are dissolved and suspended into a liquid. The liquid is atomized to form droplets that are then thermally processed to form the final particle structures. It is possible to pre-fabricate high-quality Pt/C particles, suspend them in a liquid along with the other desired components and then to spray process to form the final material.

For example, polymer-modified particles that include carbon can be fabricated in accordance with the present invention. The starting carbon material can have different degrees of initial hydrophobicity. For example, acetylene blacks such as SHAWINIGAN BLACK (Chevron Chemical Co., Houston, TX) are

more hydrophobic than furnace blacks such as VULCAN XC-72 (Cabot Corp., Alpharetta, GA). The volumetric weight ratio of the hydrophobic material (e.g., TFE fluorocarbon polymer) can be varied from 5:95 to 95:5.

As is discussed above, graded hydrophobicity layers can include  
5 unmodified carbon material, such as activated carbon, or an electrocatalyst such as one including an active species dispersed on a carbon support. Graded hydrophobicity layers having an average layer thickness of from 5  $\mu\text{m}$  up to 200  $\mu\text{m}$  for each individual layer can be formed in accordance with the present invention for a total layer thickness of 5  $\mu\text{m}$  up to 1 mm or higher.

10 If the graded hydrophobicity layer consists of a single sublayer and this layer is placed between the electrocatalyst layer and a gas diffusion layer, the hydrophobicity of this layer is substantially different than the hydrophobicity of the gas diffusion layer or the electrocatalyst layer. For example, if the electrocatalyst layer contains 5 wt.% TFE fluorocarbon polymer and the gas  
15 diffusion layer is pure TFE fluorocarbon polymer, the graded hydrophobicity layer would contain at least 25 wt.% and less than 95 wt.% of the TFE fluorocarbon polymer. In another example, if the electrocatalyst layer contains 20 wt.% TFE fluorocarbon polymer and the gas diffusion layer contains 35 wt.% of the TFE fluorocarbon polymer, the graded hydrophobicity layer would have a TFE  
20 fluorocarbon polymer content anywhere between 25 wt.% and 95 wt.%.

For applications using liquid electrolytes, such as for batteries and sensors, the graded hydrophobicity layer may consist of more than one sublayer. The sublayer with the highest hydrophobicity would interface the gas diffusion layer and the lowest hydrophobicity layer would interface the electrocatalyst  
25 layer. For example, if the electrocatalyst layer includes 10 wt.% TFE fluorocarbon polymer and the graded hydrophobicity layer consists of 3 sublayers, the sublayer interfacing the electrocatalyst layer would have at least 25 wt. % TFE fluorocarbon polymer or more, the intermediate sublayer would have 30 wt. % TFE fluorocarbon polymer or more and the sublayer interfacing  
30 the gas diffusion electrode would have at least 35 wt.% TFE fluorocarbon polymer or more.

The graded hydrophobicity layer may serve as a microscopic gas diffusion layer in combination with macroscopic gas distribution layers such as carbon cloth or carbon paper. In one embodiment, if the electrocatalyst layer does not contain TFE fluorocarbon polymer but a proton conductive material, and the gas  
5 distribution layer is a carbon cloth or carbon paper with hydrophilic properties, the graded hydrophobicity layer can consist of several sublayers with increasing or decreasing TFE fluorocarbon polymer content towards the gas distribution layer.

For example, in PEM membrane electrode assembly in which the  
10 electrocatalyst layer contains a proton conductive material and a carbon cloth or carbon paper is used for a gas distribution layer, the graded hydrophobicity layer can consist of a single sublayer with 35 wt.% TFE fluorocarbon polymer and 65 wt.% carbon black, or can include several sub layers wherein the one with the lowest TFE fluorocarbon polymer content interfaces the electrocatalyst  
15 layer, and the one with the highest TFE fluorocarbon polymer content interfaces the gas distribution layer.

In another embodiment, for direct methanol fuel cells (DMFC), the graded hydrophobicity layer may consist of several sublayers, where the lowest hydrophobicity sublayer interfaces the gas distribution layer at the anode side  
20 and the highest hydrophobicity layer interfaces the electrocatalyst, or of a single layer with TFE fluorocarbon polymer concentration between 5 and 95 wt.% TFE fluorocarbon polymer.

In one embodiment the graded hydrophobicity layer can be combined with the current collector of the electrochemical device and serve as a gas distribution  
25 layer with hydrophilic/hydrophobic properties tailored to the particular application.

The ultimate goal of the graded hydrophobic layers is to provide an electrode design solution for humidity control. Hydrophobicity gradients developed within an intermediate layer between the catalytic and the gas-diffusion layers enables conditions that permit capillary condensation of water to  
30 take place within its length. Such conditions create difference in the rate of transport of water through the gas-diffusion electrode and the transport of oxygen or other gas species not subject to capillary condensation.

The present invention is also applicable to the fabrication of supercapacitors. A major constraint on the life of a battery is the peak power requirement where the energy storage in the battery is compromised for a burst of high power. One approach to solve this problem is to provide separate  
5 energy storage and power supply units where the battery would handle low power requirements and a supercapacitor could provide short duration peak power pulses.

Supercapacitors are a type of capacitor that store energy within the electrochemical double-layer at the electrode/electrolyte interface.  
10 Supercapacitors have much higher power density than conventional batteries and can store much more energy on a weight and volume basis that can also deliver that energy at high discharge rate or for longer time periods than a normal capacitor. If used in combination with a battery they can become a highly efficient energy source where high currents are involved. Some of the  
15 advantages that supercapacitors have over the traditional batteries are: they can be charged and discharged almost indefinitely; their recharge rate is high; and they can provide high discharge currents.

Supercapacitors are essentially Electric Double Layer Capacitors (EDLC) and utilize the separation of a charge that occurs when an electrolyte is in  
20 contact with a conductor material. Electron accumulation or depletion at the electrode caused by an external power source is counter balanced by the ionic species in the electrolyte. Since the charge separation in these systems is in the order of molecular dimensions, the resultant capacitance per unit area is large. No mass or charge transfer takes place across the interface and hence  
25 the benefit of supercapacitors over batteries, that they can deliver millions of cycles and maintain high current drains and cycling efficiency. However a limitation of the double layer capacitors is the low cell voltage, limited to 1 V for aqueous electrolytes and 2.5 V for organic electrolytes. High surface area electrodes result in higher capacitance. Further highly porous electrodes provide  
30 larger internal effective surface area. Thus, carbon is a typical material used as the electrode due to its high surface area, low cost and ready availability.

Metal oxides such as  $\text{RuO}_2$  and  $\text{IrO}_2$  have been researched as a potential candidate for the electrodes. The cyclic voltamogram of  $\text{RuO}_2$  is almost rectangular as for a typical capacitor due to a series of redox reactions occurring in this metallic oxide. Specific capacitance as high as 750 F/g has been reported  
5 for  $\text{RuO}_2$  electrodes made at low temperatures. The cost of these electrodes has however been a limiting factor in the rapid development of these electrodes commercially. The electrolyte in the supercapacitors can be an aqueous acid or an organic electrolyte. The advantage of the organic electrolyte is the higher achievable voltage. Although the aqueous electrolyte provides less voltage, it is  
10 cheaper and has higher conductance.

The supercapacitor electrodes in accordance with the present invention consist of  $\text{RuO}_x \cdot n\text{H}_2\text{O}$  (hydrous ruthenium hydroxide) dispersed on high surface area carbon. The hydrous ruthenium oxide phase in the 50:50 Pt-Ru /Carbon black catalysts is responsible for the methanol electro-oxidation in direct  
15 methanol fuel cells and hydrogen oxidation in proton exchange membrane fuel cells using reformat gas as fuel.

The supercapacitor materials can be manufactured as printed layers on a proton conductive polymer membrane (such as NAFION 117) that will act as the electrolyte, the separator and the adhesive layer between the electrodes.  
20 Characteristics of the supercapacitor will be tailored to match those of required for the high peak power of the battery. As a result, the supercapacitor will be made suitable for integrating into a hybrid power source device with low volume and high effective power density.

25



### EXAMPLES

The foregoing description and the following examples make reference to a number of materials by use of a trade name for an example of that material. However, the embodiments of the present invention are not limited to the use of  
 5 such specific materials.

For example, TEFLON (E.I. duPont de Nemours, Wilmington, DE) refers to a hydrophobic polymer, more specifically a tetrafluoroethylene (TFE) fluorocarbon polymer. NAFION (E.I. duPont de Nemours, Wilmington, DE) refers to a hydrophobic and proton-conducting polymer, specifically a sulfonated  
 10 perfluorohydrocarbon polymer.

The description and examples also make reference to various forms of carbon by reference to trade names. The general properties of these carbon supports are listed in Table 2. SHAWINIGAN BLACK is an acetylene black available from Chevron Chemical Co., Houston, TX. VULCAN XC-72 is a  
 15 furnace black available from Cabot Corp., Alpharetta, GA, and is also available in graphitized form. NORIT SA-3 is an activated carbon also available from Cabot Corp., Alpharetta, GA. PWA is an activated carbon available from Calgon Carbon Corp., Pittsburgh, PA. BLACKPEARLS is available from the Cabot Corp., Alpharetta, GA and KETJENBLACK is available from Akzo Nobel, Amersfoort,  
 20 Netherlands.

**Table 2** Carbon Blacks used as Catalyst Supports

Carbon Source	Particle Size (micrometers)	BET Surface Area (m <sup>2</sup> /g)
SHAWINIGAN BLACK	0.055	80
VULCAN XC-72	0.039	240
Graphitized VULCAN XC-72	0.5*	100*
NORIT SA-3	22	700
PWA	22	820
BLACKPEARLS	0.4*	1400*
KETJENBLACK	0.4*	1400*

\*These values are approximate.

GRAFO 1300 and GRAFO 1322 are aqueous dispersions containing 20  
 25 and 22 wt. % carbon respectively and are available from Fuchs Lubricant,

Harvey, IL. The GRAFO suspensions used the same cellulose-based binder system to aid in the long-term stability of these carbon dispersions. This binder decomposes by about 300°C, and has a long shelf life. GRAFO 1300 is a dispersion of SHAWINIGAN BLACK and GRAFO 1322 is a dispersion of VULCAN XC-72.

These GRAFO dispersions are slightly alkaline, with a pH of about 9. Due to the nature of the binder, it is only stable at pH above 6. This was not a problem when making Pt/C electrocatalysts using  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  as a platinum precursor, as the dissolved salt has a neutral pH.

10

#### 1. $\text{MnO}_x/\text{C}$ Supported Electrocatalyst Particles

Two groups of  $\text{MnO}_x/\text{C}$  composite electrocatalyst examples were prepared according to the present invention. A first group was prepared by ultrasonic aerosol generation of  $\text{KMnO}_4$ , Mn-nitrate or both with GRAFO 1300 at a precursor concentration of 5 weight percent. The aerosol was heated in a hot-wall reactor (tubular furnace) at a reaction temperature ranging from 200°C to 400°C. A second group was prepared using a spray nozzle to generate an aerosol from  $\text{KMnO}_4$  and GRAFO 1300 which was heated in a spray dryer at temperatures ranging from 149°C to 315°C. Air was used for the carrier gas for all examples.

The aqueous dispersions also included an anionic surfactant. Additional amounts of a nonionic surfactant (TRITON X-405, Sigma-Aldrich, St. Louis, MO) were added in some of the examples. Triton X-405 is a 70 wt. % solution of polyoxyethylene(40)-isooctylphenylether in water. The GRAFO 1300 was suspended in water and the Mn precursor, previously dissolved in water, was slowly added to the carbon suspension while stirring. The surfactant, added to the carbon suspension prior to the Mn precursor, reduces precipitation when the Mn precursor is added. The reaction temperature for all examples was maintained below about 400°C since excessive temperatures (e.g., above 600°C) can burn-off carbon when air is used as the carrier gas.

More specifically, for the spray nozzle generation, a batch of  $\text{MnO}_x/\text{C}$  powder was prepared in a spray drying apparatus in the following manner.

kg (78.3 lbs) of carbon paste was added to a batching vessel. 65 kg (143 lbs) of de-ionized water was then added to the carbon paste and mixed thoroughly. 0.13 kg (0.286 lbs) of the nonionic surfactant was added to the mixture and the mixture was stirred for approximately 10 minutes. In a separate vessel, 2.27 kg  
5 (5 lbs) of potassium permanganate was dissolved in 65 kg (143 lbs) of de-ionized water. The solution was mixed for 20 minutes to allow the  $\text{KMnO}_4$  to dissolve. The  $\text{KMnO}_4$  solution was then slowly added to the carbon paste.

The ultrasonically-generated particles had a spherical shape with the particle size varying between about 0.3  $\mu\text{m}$  and 10  $\mu\text{m}$ . The support phase  
10 consists of primary carbon particles. Transmission electron microscopy (TEM) indicated that the support phase has a porous structure.

For the spray-dried powder, the secondary particles are larger, with diameters up to 20  $\mu\text{m}$ , but the powder has an average particle size of about 5  $\mu\text{m}$ . The differences in the secondary particles are related to the droplet size  
15 typical for the two aerosol generation approaches.

BET nitrogen absorption was used to measure the surface area and porosity of the electrocatalyst powders generated ultrasonically and by a spray nozzle. The results indicate that the conversion temperature has an effect on the surface area. A sample converted at 400°C had a surface area of 93  $\text{m}^2/\text{g}$ ,  
20 while a sample converted at 350°C had a surface area of 37  $\text{m}^2/\text{g}$ . However, further reduction in the temperature to 300°C and 250°C did not produce a significant decrease in the catalyst surface area.

The presence of surfactant has an impact on the surface area. At identical conversion temperatures, the sample, which had additional amounts of  
25 surfactant in the precursor solution had a lower surface area than the same powder with no additional surfactant.

Therefore, the selected aerosol generation method primarily impacts the particle size distribution, while the conversion temperature primarily impacts the surface area of the  $\text{MnO}_x/\text{C}$  particles. However, the effect of conversion  
30 temperature on the surface area at temperatures below 300°C is minimal. No significant changes were observed in the pore size distribution for the catalysts

as a function of the preparation conditions. For all spray nozzle generated samples the average pore size was on the order of 20 nanometers, which indicates a secondary carbon support phase with no significant micro-porosity.

XPS analysis (X-ray Photoelectron Spectroscopy) was also performed on these  $\text{MnO}_x/\text{C}$  powders. XPS analysis provides information about the surface composition and Mn oxidation state for the electrocatalysts. XPS data indicated that different precursor formulations result in different  $\text{MnO}_x$  surface species in the electrocatalysts, and therefore different catalytic activity. An average oxidation state close to Mn (IV) was obtained using  $\text{KMnO}_4$  as a precursor and is likely most beneficial for the electrocatalytic activity of the samples.

XPS data also indicated that the spray conversion temperature influences the presence of surfactant in the catalyst powders. Since the remaining surfactant is deposited either on top of the active  $\text{MnO}_x$  species or on the carbon surface, it could potentially influence the catalytic activity of the samples. Therefore, in order to minimize eventual negative effect of the surfactant, either higher conversion temperatures (e.g.,  $300^\circ\text{C}$  to  $400^\circ\text{C}$ ) should be used or the presence of surfactant in the spray solution should be minimized. An average  $\text{MnO}_x$  particle (cluster) size was estimated for each sample. The estimated average particle size varied from 2 nanometers to 40 nanometers. The XPS modeling data indicated uniform deposition of the  $\text{MnO}_x$  throughout the carbon support surface area.

## 2. **$\text{NiCoO}_x$ Bifunctional Electrocatalysts**

Bifunctional catalysts for oxygen reduction/evolution are complex electrochemical catalyst systems. These electrocatalysts must possess at least two different types of catalytic active centers, based on the fact that oxygen evolution and oxygen electro-reduction are both irreversible reactions. Among several possible chemistries, the mixed oxide system  $\text{NiO}:\text{CoO}$  (1:2) was selected for evaluation. This is one of the least sophisticated bifunctional electrocatalyst, yet demonstrates exceptional activity and sufficient cycle life.

Example catalysts were prepared by using an ultrasonic aerosol generator. The precursor solutions used to produce the catalysts were

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (nickel nitrate) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (cobalt nitrate) such that the NiO:CoO ratio is 1:2.

The catalysts on a carbon support were prepared using the nickel and cobalt precursors with a GRAFO 1300 dispersion. To prepare 10 to 20 wt.% NiO-CoO on carbon, solutions of GRAFO 1300 were diluted with water and mixed with nickel and cobalt oxide precursors such that the solutions were 5 wt.% in solids. These precursor solutions were processed at 300° C or 400° C to form supported catalyst particles.

The self-supported catalysts used the same nickel and cobalt precursors diluted with deionized water. These solutions were then ultrasonically generated using transducers and processed at temperatures ranging from 400° C to 600° C.

A silver phase (Ag) was introduced into some of the catalyst particles to improve the conductivity of the catalyst. Silver is also known to act as a promoter in catalyst formulations. The silver content in the catalyst formulations varied from 1 to 80% by weight.

Electrodes were prepared with the self-supported bifunctional catalyst, electrocatalysts supported on carbon black and a standard catalyst made by a traditional precipitation procedure. The polarization curves of the electrodes tested demonstrated that the self-supported electrocatalyst prepared according to the present invention has the most advantageous performance in oxygen reduction. The superiority of the same electrocatalyst was even more pronounced in the reaction of oxygen evolution. In this case, the NiO:CoO electrocatalyst of the present invention allows evolution of the molecular oxygen at the lowest anodic potential.

Due to the superior performance of the NiO:CoO electrocatalyst of the present invention in both reactions, oxygen reduction and oxygen evolution, voltaic efficiency of the electrode made with this catalyst is the highest: between 65% and 62% within the expected range of operating current densities of 10 to 20 mA/cm<sup>2</sup>. This is very promising, as voltaic efficiencies above 55% are considered practical, and in commercial battery systems they usually do not exceed 60%.

As discussed above, Ag was incorporated in some of the catalysts. The Ag content was varied from 1 wt.% to 80 wt.% and the precursor solutions were spray dried at 800° C. The BET surface area of the catalyst particles dropped drastically from 29 m<sup>2</sup>/g for no Ag to about 2 m<sup>2</sup>/g for 80 wt.% Ag.

5 It was also observed that with increasing reaction temperature, the surface area of the particles as measured by the nitrogen adsorption method decreases. The electrochemical performance also decreases in the direction of decreasing surface area. Higher surface area implies a higher exposure of catalytic sites and hence better performance of the catalyst.

10 The foregoing examples demonstrate that self-supported nickel cobalt oxide catalyst can be produced using the spray processing technology of the present invention. The catalysts demonstrate good catalytic activity. High surface areas and the presence of the nickel cobalt mixed oxide phase results in superior catalytic performance. Short cycling lifetime of the bifunctional air  
15 electrode is caused by the corrosion of the electrode during oxygen evolution. In view of the fact that the gas-diffusion layer is under oxidative erosion, it is possible to replace the carbon material with a carbon that is more resistant to oxidation. TEFLON treated acetylene black (35 wt.%) used for the gas-diffusion layer may be replaced with a TEFLON treated graphite powder since high  
20 crystallinity graphite is more resistant to oxidation than carbon blacks. Another modification may be to completely eliminate carbon from the electrode by using a different gas diffusion layer such as a pure TEFLON sheet.

### 3. Metal-Carbon Supported Electrocatalyst Particles

25 Further examples in accordance with the present invention utilizing metal dispersed on a carbon support were prepared. A first set of powder batch examples were prepared by ultrasonic generation of a precursor composition including carbon dispersed in a solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> or H<sub>2</sub>Pt(OH)<sub>6</sub>. The resulting aerosol was carried in either air or nitrogen and was heated in a tubular  
30 furnace reactor at temperatures ranging from 200°C to 700°C. All of these examples were prepared using GRAFO 1300 as a carbon source.

The resulting secondary carbon particles were substantially spherical with the particle size varying between 1  $\mu\text{m}$  and 2  $\mu\text{m}$ . The secondary particles (support phase) consist of primary carbon particles of about 30 nanometers in diameter with various sizes of Pt particles and particle clusters dispersed thereon. The secondary electrocatalyst particles have a highly porous structure.

The BET nitrogen absorption method was used to analyze the surface area of the ultrasonically generated Pt/C catalyst powders. Both the conversion temperature and the carrier gas composition had an effect on the catalyst surface area. When air is used as a carrier gas, the surface area is higher at a conversion temperature of 300°C (89  $\text{m}^2/\text{g}$ ) compared to 200°C (22  $\text{m}^2/\text{g}$ ). However, a further increase of the conversion temperature to 400°C did not lead to significant change in the surface area. In contrast, when nitrogen is used as carrier gas, the catalyst surface area increases to 125  $\text{m}^2/\text{g}$  at 500°C and a further increase of the conversion temperature to 700°C also decreases the surface area.

Analysis of the changes in the surface area as a function of the spray conversion temperature and carrier gas composition led to the following conclusions:

- when air is used as a carrier gas, spray conversion temperatures above 300°C are not significantly beneficial for increasing the surface area;
- when nitrogen is used as a carrier gas, the powder surface area is generally higher compared to powders generated with air as a carrier gas;
- if nitrogen is used as a carrier gas, a conversion temperature of 500°C is advantageous for producing a high surface area powder; and
- the surface area after spray conversion is at least three times lower than the surface area of the original carbon support.

XPS analysis was performed on the samples to provide information about the Pt oxidation state and dispersion in the catalysts.

It should be noted that for Pt-based fuel cell catalysts supported on carbon highly dispersed Pt metal clusters are required for achieving high catalytic activity. Therefore, achieving high dispersion of Pt in the Pt (0) state can be used as criteria for the prediction of catalytic performance of the fuel cell catalysts.

In order to find optimal spray conversion conditions for achieving complete Pt reduction and high dispersion, the changes in these characteristics as a function of the spray conversion temperature and the carrier gas composition were analyzed. It was determined that a conversion temperature of at least 500°C is necessary with air as a carrier gas to achieve a reasonably high degree of conversion to the Pt (0) oxidation state. There are no significant differences observed when nitrogen is used as a carrier gas. An increase of the conversion temperature to 700°C did not lead to improved results. Therefore, when  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  precursor is used in the formulations, a temperature of at least about 500°C seems adequate for achieving complete conversion of the precursor and formation of Pt metal species.

As mentioned above, the dispersion of the Pt clusters is of significant importance for achieving high catalytic activity. In general, at identical spray processing temperatures, the catalysts made with nitrogen as a carrier gas show better dispersion of Pt on the support surface as measured by XPS. An increase of the spray processing temperature up to 500°C leads to improved Pt dispersion for both air and nitrogen as the carrier gases. Increasing the spray processing temperature to 700°C was not beneficial for the Pt dispersion. The highest dispersion was observed for an example which was prepared at 500°C processing temperature in nitrogen. Further, no nitrogen impurities were detected for this sample, whereas about 1.5 atomic percent impurities were detected for a prior art Pt/C catalyst powder.

Two examples were synthesized with a different Pt precursor ( $\text{H}_2\text{Pt}(\text{OH})_6$ ), with only 10 weight percent Pt. The XPS data for these samples showed that a reaction temperature of at least 400°C in air is necessary for achieving the Pt (0) oxidation state from this precursor. The Pt has higher dispersion for the sample



prepared at 300°C compared to the sample prepared at 400°C. This result is in contrast with the XPS data for samples based on  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  precursor, for which higher conversion temperatures led to better Pt dispersion. This result suggests that  $\text{H}_2\text{Pt}(\text{OH})_6$  precursor converts at lower temperatures compared to  
5  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ , and undesirable diffusion and agglomeration of Pt clusters occurs at higher conversion temperatures.

TEM data indicated that the overall cluster size distribution for a sample that was spray converted at 500°C in nitrogen was significantly better compared to a sample that was spray converted at 500°C in air. This observation is in  
10 agreement with the XPS data for Pt dispersion and confirms that carrier gas has influence on the catalyst formation and Pt dispersion in particular.

Samples of the foregoing Pt/C electrocatalysts were evaluated in PEM fuel cells and the results of the electrochemical characterization were compared to two commercially available electrocatalysts.

15 Gas diffusion cathodes were fabricated by the catalyst ink method. The Pt/C catalyst was dispersed in a NAFION/alcohol/water solution to give a stable ink suspension. Specifically, 1 g of the electrocatalyst was mixed in 2 ml *i*-propanol (after being wetted with a small amount of water to avoid pyrogenic effects), and suspended in 10 ml of stock NAFION solution (5 wt. % of polymer  
20 in water/*i*-propanol mix). This ink yields a Catalyst/NAFION ratio of 2:1, which is to remain during the electrode preparation in order to incorporate the electrocatalyst particles into the NAFION polymer electrolyte membrane.

The gas diffusion electrode is prepared by brush application of a suspension of SHAWINIGAN BLACK and TEFLON emulsion to give a 35 to 40  
25 weight percent TEFLON/carbon ratio onto a carbon cloth. The gas-diffusion electrode, soaked with the TEFLON/carbon suspension, is heat treated at 300°C to 350°C for 1 hour. This temperature range is near the glass-transition point of the TEFLON material.

The Pt/Carbon electrocatalyst ink is applied on the impregnated cloth by a  
30 brush when the electrode is mounted on a hot plate at 90 to 100°C. The electrode is then treated at 155°C in air for 20 to 30 minutes, which is close to

the melting point of NAFION material. The catalyst loading is determined from the electrode weight.

The platinum loading of the cathodes was  $0.20 \pm 0.01 \text{ mg/cm}^2$  which is considered low by industrial standards for oxygen electrocatalysts. All hydrogen electrodes (anodes) were loaded with  $0.05 \text{ mg/cm}^2$  of platinum using a 10 % Pt/C commercial catalyst.

Membrane electrodes assemblies (MEAs) were fabricated by hot pressing electrodes symmetrically (catalyst side facing the membrane) onto both sides of a NAFION 112 PEM at  $200^\circ\text{C}$ , to allow melting of the membrane and the NAFION material from the catalytic layers. The performance evaluation of MEAs was carried out in test cell with a working area of  $50 \text{ cm}^2$  between ribbed graphite plates and copper end plates at  $50^\circ\text{C}$  and an atmospheric pressure of humidified reactant gases.

Fig. 32 illustrates a comparison of voltamograms (cell potential vs. current density plots) for MEAs comprising different commercial catalysts (Samples 4A and 5A) and a catalyst according to the present invention, prepared and measured under identical conditions. The results were obtained with electrocatalysts containing 20 weight percent platinum on an identical carbon black support. It is evident from these curves that the electrocatalyst of the present invention demonstrates superior performance in the MEA. Numerical expression of this superiority can be derived from the current density corresponding to a cell potential of 0.6 V. Both prior art electrocatalysts provide about  $400 \text{ mA/cm}^2$  while the electrocatalyst of the present invention provides  $600 \text{ mA/cm}^2$ , a 50% improvement of MEA performance at a cell potential of 0.6 V.

Fig. 32 illustrates that the electrode fabricated with the electrocatalyst of the present invention demonstrates overall higher current densities within the entire investigated range of potentials. At the same time, the polarization curve is characterized by lower dependence of the current on the potential (lower negative slope of the curve in its "linear" portion), which indicates lower ohmic resistance of the catalytic layer. The dependence of the potential on current density remains practically linear even at high current densities, indicating that

there is no expression of any diffusion limitations in the investigated current density range. TAFEL plots of this data indicated that the improvement was due to higher catalytic activity of the electrocatalyst.

The improvement in catalytic activity of the electrocatalyst of the present invention when compared to the prior art samples can be explained by the platinum cluster size and its distribution on the carbon surface. SEM microphotographs of the electrocatalysts of the present invention compared to the prior art electrocatalyst show that the catalyst of the present invention possesses a significant amount of smaller size platinum clusters (1 - 2 nm) compared to the prior art samples. This results in an increased platinum utilization and a larger reaction interface in the active layer of the oxygen electrode.

Fig. 33 illustrates the performance of two examples of the present invention with different Pt content when ambient air is used to feed the oxygen gas diffusion electrode in the cell. As expected, the electrocatalyst with the lower Pt content (10% Pt/Carbon) provides lower current densities compared to the one with higher metal content (20% Pt/Carbon). It should be noted, however, that the curves are obtained with electrodes that have been prepared with identical total amount of Pt. Thus, the lower Pt content sample has been applied in an amount doubling the use of the catalyst. Reduction of the electrochemical performances however, is still to the level of those obtained with the prior art electrocatalysts (compare Fig. 33 and Fig. 32). The 10% Pt/Carbon sample curve of the present invention overlaps with the 20% Pt/Carbon prior art samples.

Fig. 34 is obtained with the same MEA as Fig. 33 and illustrates the performance of the electrocatalysts of the present invention with different Pt content when pure oxygen is used to feed the oxygen gas diffusion electrode in the cell. Flowing pure oxygen through the electrode largely eliminates the mass transport limitations, especially those associated with macro-diffusion processes. The curve obtained from the electrocatalysts with lower Pt content (10% Pt/Carbon) is shifted to approximate the one obtained from the catalyst with higher metal content (20% Pt/Carbon). Thus, Fig. 34 demonstrates that lower

performance of the 10% sample (as illustrated in Fig. 33) is associated with the thickness of the catalytic layer formed when double the amount of material is used.

5 An additional set of examples were prepared to identify the optimum set of structural parameters that give the most active electrocatalyst for the oxygen reduction reaction at the air cathode of a Proton Exchange Membrane Fuel Cell (PEMFC). The activity of the electrocatalyst is dependant on the oxidation state and dispersion of the platinum, which will be influenced by the spray conversion process conditions, carrier gas, precursor salt, and type of the carbon support.

10 The evaluation of these Pt/C electrocatalysts was accomplished by a variety of techniques such as nitrogen adsorption (BET), XRD, TEM, XPS, CO chemisorption, as well as electrochemical evaluation.

A number of examples were prepared as follows: one sample comprised of 10 wt% Pt on SHAWINIGAN BLACK with Pt crystallites of 6.3nm and a Pt

15 loading of 1.43 mgPt/cm<sup>2</sup>; a second sample comprised 20 wt% Pt on SHAWINIGAN BLACK with Pt crystallites of 5.2 nm and a Pt loading of 2.66mgPt/cm<sup>2</sup>; a third sample comprised 10 wt% Pt on VULCAN XC-72 with Pt crystallites of 4.6 nm and a Pt loading of 1.23mgPt/cm<sup>2</sup>; and a fourth sample comprised 20 wt% Pt on VULCAN XC-72 with Pt crystallites of 11.4 nm and a Pt

20 loading of 2.95mgPt/cm<sup>2</sup>.

The examples were tested in an alkaline electrolyte and a Tafel plot was obtained. Some general conclusions can be drawn. SHAWINIGAN BLACK appears to have better performance than VULCAN XC-72. A smaller crystallite size performs better than a larger crystallite size (as determined by x-ray

25 diffraction). A lower Pt content powder at a lower loading is as good or better than a higher Pt content powder at a higher loading.

The purity of the dispersed phase on the carbon surface is also important in determining the electrocatalytic performance of powder. Typical solution precipitation processes that are used to produce precious metal-based carbon

30 supported electrocatalysts use sulfur containing reagents or surfactants. Since sulfur is a poison to the catalytic activity of Pt, any trace amounts of residual sulfur can lead to a significant reduction in performance. The materials

produced by the process described herein do not require the use of ligands, complexing agents or surfactants that contain elements that poison the activity of the final catalyst. As a result, the process described herein results in materials with a high purity level.

5        In yet another set of examples, 10 weight percent and 20 weight percent platinum on carbon commercial catalysts were analyzed for comparison with catalysts of the present invention. The fuel cell catalysts of the present invention were prepared by one of four routes: ultrasonic transducer (single and multiple); spray dryer; ultrasonic spray nozzle; and post-processing.

10       All samples were prepared in similar fashion regardless of the processing system used. The carbon dispersion was first diluted with water while shear mixing, and then the dissolved metal salt was slowly added. The precursor dispersion was sheared for 10 minutes following the addition of the metal salt to insure a homogeneous suspension.

15       Samples generated using ultrasonic transducers utilized a precursor composition including 20, 50 or 60 wt.% Pt (as either  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  or  $\text{H}_2\text{Pt}(\text{OH})_6$ ) and GRAFO 1300 as a carbon support. Reaction temperatures varied from 250°C to 600°C. Samples produced using an ultrasonic spray nozzle utilized a precursor including 5 wt.% to 60 wt.% Pt (as either  
20        $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  or  $\text{H}_2\text{PtCl}_6$ ) and either GRAFO 1300 or GRAFO 1322 as a carbon support. Reaction temperatures varied from 350°C to 700°C. Samples generated using a spray dryer utilized a precursor composition including 5 wt.% to 40 wt.% Pt (as either  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  or  $\text{H}_2\text{PtCl}_6$ ) and GRAFO 1300 or GRAFO 1322 as a carbon support. The inlet temperatures varied up to 526°C and the  
25       outlet temperature varied up to 287°C.

Fig. 35 illustrates the inverse relationship between the platinum loading and surface area. Since the surface area is normalized per gram of catalyst and the loading of the Pt increases (the density of Pt is significantly higher compared to that of the carbon support) this result is expected. It is important to note,  
30       however, that the changes in the surface area of the catalysts generated by ultrasonic spray nozzle and on the spray dryer are almost identical if the same carbon support is used (GRAFO 1300, which is a dispersion of SHAWINIGAN

BLACK). For a higher surface area support such as VULCAN XC-72 (GRAFO 1322), the effect is even more strongly expressed due to the lower density of the carbon support.

5 The spray conversion temperature must be high enough to convert the platinum, but not so high that the carbon burns. Also, it is observed that the surface area of the powder increases as the reaction temperature is increased. Although this may suggest using the highest temperature possible, the loss due to the burning of carbon at elevated temperatures must also be considered.

10 It is generally accepted that increased dispersion of the Pt metal clusters on the carbon support will result in increased catalytic activity. The degree of metal dispersion on the surface is influenced by the metal salt used, the metal loading (weight percent of metal), and the surface area of the carbon support. It stands to reason that increasing the amount of metal on the carbon surface will result in larger metal crystallites, thus a lower dispersion and reduced metal  
15 surface area that is exposed. The carbon used will also influence the process temperature. It is believed that a higher surface area results in a lower decomposition temperature. An example is illustrated by comparing the processing of SHAWINIGAN BLACK vs. VULCAN XC-72. When 20 wt. % platinum was run on both SHAWINIGAN BLACK and VULCAN XC-72 at 210° C,  
20 increased conversion was seen for the higher-surface area VULCAN XC-72 than for the lower-surface area SHAWINIGAN BLACK. This may suggest the ability to further lower the conversion temperature by using a carbon with an even higher surface area, such as about 800 m<sup>2</sup>/g. It may also be advantageous to use a mixture of carbon supports having different surface areas. This may be  
25 catalytically advantageous, for if the higher surface area carbon converts at a lower temperature, it may act as a catalyst for the conversion of the lower-surface area carbon.

X-ray diffraction (XRD) patterns of GRAFO 1300, platinum precursor Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, and a mixture of GRAFO 1300 and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> dried at room  
30 temperature were also obtained. This series shows that when mixed, the diffraction patterns of the starting materials (GRAFO 1300 and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) are not merely additive. The interaction between the two compounds gives rise

to a completely new diffraction pattern for the dried precursor dispersion. The diffraction pattern that is seen for the precursor dispersion dried at room temperature is identical to that of catalyst powder that has been processed at elevated temperature, but not high enough to convert the platinum precursor.

5        Generally, the size of the crystallites is inversely proportional to the dispersion of the platinum on the carbon support – highly dispersed platinum will have a small crystallite size. For example, for Pt dispersed on SHAWINIGAN BLACK, XRD analysis also showed a maximum peak broadening at 10 to 20 weight percent platinum, indicating optimal small crystallite size, and therefore  
10    high dispersion.

          The processing of the catalysts under nitrogen to reduce the possibility of burning carbon at these high processing temperatures was also investigated. However, air proved to have superior structural results. The superior performance of catalysts generated in air is most likely due to the  
15    presence of oxygen, which aids in the decomposition of the platinum precursor ligands, carbon dispersion binders, and surfactants. When nitrogen was used, the catalyst surface was most likely poisoned with these organics that were unable to decompose.

          The x-ray diffraction peak of Pt <111> FWHM was plotted against furnace  
20    temperature for catalysts made under both air and nitrogen. The FWHM parameter was used to estimate the dispersion of the Pt crystallites - the higher the FWHM the higher the dispersion of Pt species on the carbon support surface. For temperatures in the region of 500° C to 600° C, the use of air as both carrier and quench gases resulted in larger FWHM values than those for  
25    nitrogen, therefore a better Pt dispersion was achieved using air as a carrier and quench gas.

          An illustration of the relationship between the amount of precursor and support surface area is shown in Fig. 36. For this model, the area of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  was compared to the surface area of a given carbon support.  
30    The calculation was carried out based on the weight percent of platinum against three carbon supports of increasing surface area. The surface areas of the carbon supports used were 80, 240, and 800 m<sup>2</sup>/g, and the area of one

Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> molecule was estimated to be 2.25 nm<sup>2</sup>. If the total area covered by the Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> is equal to that of the carbon, it should result in a monolayer of precursor molecules on the carbon surface. This will not result in a platinum monolayer, as the Pt precursor ligands are responsible for a significant portion of the precursor molecule's area. Therefore, individual Pt atoms or small clusters of platinum atoms that are well spaced should form. Additional Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> molecules result in multiple layers, which increases the probability of larger agglomerates of metal. Following this thought, if the metal loading is high enough, the entire carbon surface could become coated, resulting in a catalyst with lower activity than that of one with small metal crystallites, as the metal surface area will be lower.

The inset in Fig. 36 shows that for 20 wt.% platinum, the number of layers increases from 0.64 to 2.12 to 6.36 as the carbon surface area decreases from 800 to 240 to 80 m<sup>2</sup>/g. This suggests that not all platinum loadings are optimal for a given carbon surface area. Further, each carbon may have an ideal window of metal loadings, allowing tailoring of the Pt/C catalyst to loading requirements. This point becomes more pronounced as the metal loading is increased. Although it is impossible to predict at what point the metal loading becomes so large that the entire particle is covered, to avoid this possibility the carbon should be chosen so the number of layers is minimized, combined with experimental results.

Prior art methods of platinum catalyst preparation employ a platinum chloride precursor due to its low cost. The majority of platinum catalysts fabricated in accordance with the present invention have used Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (platinum amine) to avoid possible system corrosion common to chloride use. The chlorides are also acidic when in solution, coagulating the binders in the carbon dispersions. Coagulation of the binders results in an unstable dispersion, and settling occurs within an hour. For this reason, the amine has been the precursor salt most commonly used.

However, using the chloride precursor, the conversion temperature is lowered from about 400° C to under 350° C. This became a key point once a spray dryer was enlisted to attempt platinum catalyst production.



An alternative to post-processing is the use of reduction agents. If conventional spray dryers are unable to reach the temperatures required for the reduction of platinum, then additives can be used to allow for the reduction to occur at lower temperatures. This method keeps the drying/calcinations to one  
5 step, eliminating some of the problems associated with post-processing.

Experiments with various reducing agents suggested that an alcohol, such as ethanol or methanol, reduces the conversion temperature of platinum by about 150° C, while retaining well-dispersed crystallites.

Transmission electron microscopy (TEM) was used to measure the size of  
10 the platinum crystallites and visually inspect their dispersion. Crystallites were measured and counted to produce a rough estimate of crystallite size, as the assumption is that the crystallites at the edges of the secondary particles that can be seen are representative. Further, it is difficult to include very large particles, as the difference between what is a large particle and overlap is not  
15 always apparent.

It was observed that the crystallites dispersed on SHAWINIGAN BLACK (average size of 3.0 nm) were almost 66 percent larger as compared to those dispersed on VULCAN XC-72 (average size of 1.8 nm). The surface area of VULCAN XC-72 (240 m<sup>2</sup>/g) is a factor of 3 greater than that of SHAWINIGAN  
20 BLACK (80 m<sup>2</sup>/g). These results illustrate the dependence of the dispersion of the platinum on the surface area of the carbon support. Additionally, the Pt size distribution for the VULCAN XC-72 sample was significantly narrower than that of the SHAWINIGAN BLACK sample. The 60% difference in crystallite size also supports the claim that no identical metal loadings will be optimal for every  
25 carbon support.

As a further illustration of the present invention, hydrogen-air cells were made of a NAFION 112 membrane with a working area of 50 cm<sup>2</sup> and 0.2 mg/cm<sup>2</sup> platinum loading on the cathode side of the membrane with atmospheric pressure gases. Platinum electrocatalysts were prepared from Pt-amine and Pt-  
30 chloride using either GRAFO 1300 or GRAFO 1322 as the support.

The overall performance of the MEA is given as the PRF, which is the current density at a potential of 0.7 V. The electrochemical performance of

catalysts formulated with platinum chloride was considerably lower than that of those with platinum amine. The difference in the crystallite size estimated via XRD is about four times lower for the amine-based catalyst than for that of the chloride. These results suggest a better dispersion is required if platinum  
5 chloride is to be used as a precursor. Since MEA preparation is labor-intensive, some of the catalysts were tested as alkaline cathodes as an approach to rapid screening. The results are not directly comparable to those obtained from MEAs, however it is believed that the relative activity is useful in ranking catalytic activity.

10        Comparison of a sample supported on SHAWINIGAN BLACK and an otherwise identical sample supported on VULCAN XC-72, made using the same spray dryer conditions again illustrates the contribution of the support to the conversion temperature. A higher surface area carbon support should be used in combination with spray dryer processing conditions.

15        It was concluded that the particles are exposed to a lower temperature in the spray dryer than in hot wall reactors. This finding suggests higher temperatures are needed for SHAWINIGAN BLACK than VULCAN XC-72, but whether the mechanism is surface area-dependent or due to the structural differences between the carbons is not readily evident.

20        The comparison of the Pt cluster size distribution between the Pt/C electrocatalysts of the present invention and prior art 10 wt.% and 20 wt.% Pt/VULCAN XC-72 was derived from TEM data. The data show that for an identical carbon support, VULCAN XC-72, and 10 wt.% Pt concentration, an average Pt crystallite size of 2.5 nm is observed for the prior art sample and an  
25 average size of 1.8 nm was observed for the electrocatalyst of the present invention. This result shows that at identical Pt concentration and when the same support is used, the spray generation method of the present invention produces electrocatalysts with higher Pt dispersion.

30        The results of electrochemical testing are shown in Fig. 37 for 10 wt.% Pt samples fabricated in a spray dryer, on VULCAN XC-72 and SHAWINIGAN BLACK supports. These electrocatalysts closely match the superior performance of the ultrasonically generated laboratory scale samples. The

results of electrochemical testing are shown in Fig. 38 for 20 wt.% Pt samples fabricated in a spray dryer on VULCAN XC-72 and SHAWINAGAN BLACK. The sample prepared on VULCAN XC-72 demonstrates superior performance (about a 40% improvement) compared to the 20 wt.% prior art commercial sample.

5        These Pt/C electrocatalysts were then used to produce laboratory prototype MEAs for comparison to the existing commercial MEAs. The MEAs were tested by an independent laboratory overseen by a fuel cell manufacturer. The goal was to construct MEAs with performance that meets the performance of about 600 mA/cm<sup>2</sup> at 0.6V with the lowest Pt loading possible. The low Pt  
10       loading provides the longer-term avenue to commercialization since the Pt loadings of the current commercial MEAs are too high for long-term commercialization.

         A comparison of the performance of a MEA comprising 20 wt.% Pt/C catalyst at a total loading of 0.25 mgPt/cm<sup>2</sup> compared to the prior art MEA with a  
15       total Pt loading of 0.8 mgPt/cm<sup>2</sup> is shown in Fig. 39. This plot illustrates the similar performance of the 2 MEAs, under conditions where the MEA containing the electrocatalyst of the present invention contains over 3 times less Pt.

         To illustrate that this result is not confined to a particular sample or Pt dispersion, another polarization curve was generated in which the application  
20       has a different set of performance specifications. In this case a 60 wt.% Pt/C sample was prepared which was tested in an MEA against pure Pt black (i.e. 100% Pt). The lower Pt content electrocatalyst of the present invention had comparable performance at low current densities and higher performance at higher current densities.

25       An additional aspect important in the commercial applications of these materials is the timescale over which the performance is maintained. This can be measured by recording either the voltage at constant current or the current at constant voltage. Figs. 40 and 41 provide some information on the variation of the current density at constant voltage under the conditions indicated.

30       Thus, MEAs constructed using the electrocatalyst of present invention have demonstrated equal performance with 0.25 mgPt/cm<sup>2</sup> as compared to prior art MEAs with 0.8 mgPt/cm<sup>2</sup>.

A further set of Pt/C electrocatalysts with 5, 10, 20, 40 and 60 weight percent Pt loadings were tested under identical conditions of atmospheric pressure at 50°C, with a NAFION 112 membrane, 0.05 mg Pt/cm<sup>2</sup> loading at the cathode and using a 10 wt.% Pt/C catalyst for the anode. The polarization curves reflect the performance, which is a function of the cathode electrocatalyst loading, thickness and Pt utilization.

The polarization curve illustrated in Fig. 21 above demonstrates that at 0.6 V, a current density of 400 mA/cm<sup>2</sup> is achieved with 0.1 mg Pt/cm<sup>2</sup> loading, which is identical performance as compared to a prior art electrocatalyst having a loading of 0.2 mg Pt/cm<sup>2</sup> and to that of a prior art MEA having 0.4 mg Pt/cm<sup>2</sup> cathode electrocatalyst loading. Therefore, identical performance is achieved with the electrocatalyst according to the present invention at a Pt loading that is 4 times lower.

As is discussed above, Fig. 37 illustrates that two electrocatalysts prepared in a mixed flow spray dryer show either identical performance or out-perform the catalyst formed in a horizontal, hot-wall reactor. The spray dryer system, however, is capable of a production rate that is 1500 times higher than the horizontal hot-wall system.

The secondary structure of the electrocatalyst particles is critical to the performance of devices such as MEA's fabricated from the particles. To demonstrate this importance, two identical MEA's were fabricated wherein one MEA utilized the electrocatalyst particles of the present invention that were substantially intact and the other MEA utilized identical particles that had been broken down ultrasonically prior to being made into the MEA.

Specifically, 1 gram of a Pt/C electrocatalyst prepared according to the present invention (20 wt.% Pt dispersed on a VULCAN XC-72 support) was dispersed in 2 ml of deionized water and 10 ml of NAFION (66.67wt% catalyst, 33.33 wt% NAFION). This ink was sonicated in a water bath for one hour. The particle size distribution for this ink had a d<sub>10</sub> of 1.9 μm, a d<sub>50</sub> of 4.7 μm and a d<sub>95</sub> of 16.0 μm. This ink was used to print MEA 68B (Fig. 42).

In addition, 1 gram of the same electrocatalyst was dispersed in 50 ml of deionized water and sonicated using a sonicator for 30 minutes. The catalyst particles were broken down to a particle size distribution wherein  $d_{10}$  was 0.5  $\mu\text{m}$ ,  $d_{50}$  was 1.53  $\mu\text{m}$  and  $d_{95}$  was 4.9  $\mu\text{m}$ . This solution was then dried to obtain the dry catalyst. The catalyst was then re-dispersed in Nafion as above to print the MEA 68C (Fig. 42). The particle size distribution of the ink showed a  $d_{10}$  of 0.2  $\mu\text{m}$ , a  $d_{50}$  of 0.4  $\mu\text{m}$  and a  $d_{95}$  of 6.8  $\mu\text{m}$ .

The MEA cathodes were both loaded with 0.2 mg Pt/cm<sup>2</sup>. The results in oxygen and in air are illustrated in Fig. 42. The polarization curves in Fig. 42 illustrate the following:

1. The performance of the MEA with the electrocatalysts secondary structure intact has a higher performance both in air and oxygen compared to the broken secondary structure particles measured under identical conditions with identical loadings.
2. The performance in the range up to 200 mA/cm<sup>2</sup> is identical in air for 68B and 68C indicating that breaking the particles did not affect the kinetic performance of the catalyst in the kinetically limited performance regime.
3. The particles with intact secondary structure showed a marked improvement in performance, which increases with increasing current density.
4. The performance difference in air versus oxygen is smaller for the particles with the secondary structure intact compared to the broken particles.

The foregoing gives a strong indication that the secondary structure is critical to the performance in the ohmic and transport limited regimes.

#### **4. Pt-Ru/C and Pt-Pd-Ru/C Electrocatalysts for PEMFC Anodes**

Platinum metal alloys of Pt-Ru and Pt-Pd-Ru as an active species dispersed on a carbons support were also fabricated according to the present

invention. The goal of the following structural and compositional characterization of binary and ternary catalysts is to identify the processing conditions that yield catalysts with the best electrochemical activity. A PEMFC anode catalyst must possess CO tolerance in addition to electrocatalytic activity for the hydrogen oxidation reaction. An important aspect of this characterization is to determine the degree of alloying between the metals. The most important analysis information is obtained from XRD, TEM, and electrochemical evaluation.

XRD spectra showed a peak corresponding to Pt-Ru and indicating alloying of the metals. TEM analysis showed that the Pt-Ru crystallites were well-dispersed.

The relative electrochemical activity of the Pt-Ru/C and Pt-Ru-Pd/C catalysts of the present invention was tested. The catalysts were pressed into electrodes and evaluated as 20 mg/cm<sup>2</sup> active layers with a gas diffusion layer of 50 mg/cm<sup>2</sup> XC-35 in 7 N KOH.

The addition of palladium significantly increased the electrochemical activity of the catalyst. A Pt-Pd-Ru/C was made into an MEA and tested with reformat. The result of the reformat test is illustrated by the polarization curve in Fig. 43.

Fig. 43 compares the electrochemical activity of a sample including 20 wt.% of a Pt-Pd-Ru alloy in a 2:2:1 ratio in both pure hydrogen and reformat. The excellent CO tolerance of this catalyst can be seen from the nearly overlapping polarization curves. This Pt-Pd-Ru/C catalyst performs almost as well on reformat as it does on pure hydrogen.

Excellent performance in the presence of small concentrations of CO and low concentrations of hydrogen is therefore possible using Pt-Ru/C and Pt-Ru-Pd/C electrocatalysts.

## 5. Polymer-Modified Particles

The gas diffusion layer (GDL) in any power device should allow maximum gas permeability combined with impermeability to aqueous solutions. There are various methods to obtain a gas diffusion layer. Depending on the application this layer can be a continuous fluorocarbon polymer membrane, a composite

material such as hydrophobized carbon black or a hydrophobized metal oxide. The hydrophobic layer needs to be deposited with the right structure to form a layer that has the optimum size channels and hydrophobic pores to allow transport of the active species while preventing the electrolyte from weeping out.

- 5 Further, the hydrophobic pores need to prevent the ambient water vapor from entering the power device. The control on the hydrophobicity of the hydrophobic layer can be achieved by varying the ratio of the support and the hydrophobic component and/or by depositing a gradient of hydrophobic layers.

- Table 3 summarizes the hydrophobized powder composites (polymer-  
10 modified carbon) manufactured in accordance with the present invention. Dispersions of various carbons such as SHAWINIGAN BLACK and PWA were shear mixed in different ratios varying from 5 to 60% by weight of the fluorocarbon polymer. The dispersions were then spray dried at different temperatures as shown in Table 3. Dispersions of metal oxides such as SiO<sub>2</sub>,  
15 Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were prepared using surfactants. The fluorocarbon polymer dispersions were shear mixed at lower power with the metal oxide dispersions to prevent foaming in the presence of the surfactants. The dispersions were then spray dried.

- The surface area and pore volume of the final powders was determined  
20 by a nitrogen adsorption-desorption technique. The surface area of the final composite is determined by the surface area of the hydrophobized carbon or metal oxide.

**Table 3** Polymer-modified Powder Composites

Substrate	Temp. (°F)	TEFLON (wt. %)	S.A. (m <sup>2</sup> /g)	Pore vol (cm <sup>3</sup> /g)	Avg Pore D (nm)
SHAWINIGAN BLACK	400	5	33	0.1384	16.8
SHAWINIGAN BLACK	600	5	30.3	0.1361	18
SHAWINIGAN BLACK	400	35	28.5	0.11	15.4
SHAWINIGAN BLACK	600	35	27	0.1294	19.2
Silica	600	60	81	0.614	30.3
SHAWINIGAN BLACK	640	50	31.6	0.0843	10.6
SHAWINIGAN BLACK	610	50	23	0.11	18.9
SHAWINIGAN BLACK	640	35	101	0.13	5
SHAWINIGAN BLACK	600	35			
PWA	615	50	226	0.17	3
PWA	600	50			
PWA	630	35	352	0.22	2.5
PWA	600	35			
Al <sub>2</sub> O <sub>3</sub>	600	50			
Al <sub>2</sub> O <sub>3</sub>	600	35			
TiO <sub>2</sub>	600	50			
TiO <sub>2</sub>	600	35			
TiO <sub>2</sub> (Hydrophobic)	600	50	19.9	0.0747	14.9
TiO <sub>2</sub> (Hydrophobic)	600	35			

The polymer-modified carbon composites were then post-treated at 300°C for 15 minutes to burn any surfactants or binders that were present, as these surfactants can affect the performance of the gas diffusion layer.

The polymer-modified carbon was pressed into a gas diffusion layer with MnO<sub>x</sub>/C catalyst and measured electrochemically. Similarly, polymer-modified carbon blacks from other sources were pressed with the same catalyst to compare electrochemical performance of polymer-modified carbon blacks in accordance with the present invention.

Fig. 44 is a polarization curve plotted for polymer-modified carbon blacks prepared from different sources. As can be seen from the polarization curve, polymer-modified carbons according to the present invention perform better in oxygen and in air, especially at a current density of 100 mA/cm<sup>2</sup>, where transport and diffusion limitations become predominant. This is further obvious from Fig. 45, which is a Delta E plot of the performance difference in air vs. in oxygen. The difference in oxygen vs. air is very small for the polymer-modified carbon of the present invention, which proves that the gas diffusion layer prepared with the polymer-modified carbon of the present invention is better in performance.



Printing these materials thinner with methods such as syringe dispensing and screen printing can further decrease the thickness of the gas diffusion layers. Formulations of polymer-modified carbons were prepared in alpha-terpeniol and in isoproponal for depositing thin layers, which should further increase performance in the transport and diffusion regimes of a polarization curve.

The polymer-modified blacks are hydrophobized using a TFE fluorocarbon polymer (TEFLON) sprayed with carbon. Similar composites can be made for different applications such as to facilitate transport of species to the catalytic sites. The polymer dispersed on the support can be selected for a particular application. For example, polymer-modified NAFION carbons were prepared to facilitate the transport of protons to the NAFION membrane. NAFION solution was mixed with different carbon dispersions of SHAWINIGAN BLACK and VULCAN XC-72 and spray dried at 400°F. Table 30 is a summary of these polymer-modified materials.

**Table 30** Polymer-Modified Composite Powders

Product # PNF	Composition (wt.%) NAFION	Carbon Support	SA (M <sup>2</sup> /g)	Pore Vol (cm <sup>3</sup> /g)	Avg pore (D nm)	PSD d90 microns
056129B	15	VULCAN XC-32	71.36	0.262	14.7	19
056129C	10	VULCAN XC-32	76.8	0.284	14.8	0.7
056130A	5	VULCAN XC-32	86.43	0.334	15.46	0.8
056130C	15	SHAW. BLACK	36.97	0.171	18.51	1.2
056131A	10	SHAW. BLACK	36.96	0.167	18.06	1.2
056131B	5	SHAW. BLACK	37.8	0.174	18.4	1.5

## 6. Graded Hydrophobicity Layers

A number of graded hydrophobicity layers were produced in accordance with the present invention. In a first example, a single layer of TEFLON-modified carbon was printed on top of an electrocatalyst layer, the other side of the electrocatalyst layer interfacing the electrolyte. The TEFLON-modified carbon layer consisted of 35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK. The average thickness of the layer was 90  $\mu$ m and the loading of the TEFLON-modified carbon was about 2.5 mg/cm<sup>2</sup>. The printing suspension consisted of SHAWINIGAN BLACK, TEFLON particles, surfactants and water. The printed

layer was then subjected to roll pressing and the sample was heated at 300°C for 5 minutes to drive out surfactants used in the printing suspension

In a second example, two 50  $\mu\text{m}$  thick sublayers of TEFLON-modified carbon were printed on top of an electrocatalyst layer, the other side of the electrocatalyst layer interfacing the electrolyte. The first sublayer of TEFLON-modified carbon interfacing the electrocatalyst layer consists of 35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK. The second sublayer of TEFLON-modified carbon consists of 50 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK. The average thickness of the layer was 90  $\mu\text{m}$  and the loading of the TEFLON-modified carbon was about 2.5  $\text{mg}/\text{cm}^2$ . The printing suspension consists of SHAWINIGAN BLACK, TEFLON particles, surfactants and water. The printed layer was subjected to roll pressing and the samples were heated at 300°C for 5 minutes to drive out surfactants used in the printing suspension.

In a third example, the various layers were consecutively added to a nickel mesh. First, a 100  $\mu\text{m}$  electrocatalyst layer then a 100  $\mu\text{m}$  TEFLON-modified carbon layer. The TEFLON-modified carbon layer consisted of 35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK. The electrocatalyst layer consisted of 65 wt.% electrocatalyst (with a ratio of 15 wt.%  $\text{MnO}_2$  with respect to the PWA activated carbon support) and 35 wt.% TEFLON-modified carbon (35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK). The electrocatalyst layer and the TEFLON-modified carbon layers were deposited at 10  $\text{mg}/\text{cm}^2$  loadings. All layers were simultaneously pressed at pressure (600  $\text{kg}/\text{cm}^2$  or 160  $\text{kg}/\text{cm}^2$ ) and no heating was employed.

In another example, a nickel mesh was again used and layers were deposited on the nickel mesh. First, a 100  $\mu\text{m}$  electrocatalyst layer was deposited and then a 100  $\mu\text{m}$  TEFLON-modified carbon layer was deposited. The TEFLON-modified carbon layer consists of 50 wt.% TEFLON and 50 wt.% SHAWINIGAN BLACK. The electrocatalyst layer consists of 65 wt.% electrocatalyst (with a ratio of 15 wt.%  $\text{MnO}_2$  with respect to the PWA activated carbon support) and 35 wt.% TEFLON-modified carbon (35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK). The electrocatalyst layer and the TEFLON-modified carbon layer were deposited at 10  $\text{mg}/\text{cm}^2$  loadings. All layers were

simultaneously pressed under pressure ( $600 \text{ kg/cm}^2$  or  $150 \text{ kg/cm}^2$ ) and no heating was employed.

In yet another example, layers were again deposited on nickel mesh. First, a  $100 \mu\text{m}$  electrocatalyst layer was deposited. Then a first  $100 \mu\text{m}$  thick  
5 TEFLON-modified carbon layer was deposited over which a second  $100 \mu\text{m}$  thick TEFLON-modified carbon layer was deposited. The first TEFLON-modified carbon layer consisted of 35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK. The second TEFLON-modified carbon layer consisted of 50 wt.% TEFLON and 50 wt.% SHAWINIGAN BLACK. The electrocatalyst layer consisted of 65 wt.%  
10 electrocatalyst (with a ratio of 15 wt.%  $\text{MnO}_2$  with respect to the PWA activated carbon support) and 35 wt.% TEFLON-modified carbon (35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK). The electrocatalyst layer and the TEFLON-modified carbon layers were deposited at  $10 \text{ mg/cm}^2$  loadings. All layers were simultaneously pressed under pressure ( $600 \text{ kg/cm}^2$  or  $150 \text{ kg/cm}^2$ ) and no  
15 heating was employed.

In a further example, two layers were deposited on a nickel mesh. First, a  $100 \mu\text{m}$  thick electrocatalyst layer was deposited and then a  $100 \mu\text{m}$  TEFLON-modified carbon layer was deposited. The TEFLON-modified carbon layer consisted of 35 wt.% TEFLON and 65 wt.% VULCAN XC-72. The electrocatalyst  
20 layer consisted of 65 wt.% electrocatalyst (15 wt.%  $\text{MnO}_2$  dispersed on PWA) and 35 wt.% TEFLON-modified carbon (35 wt.% TEFLON and 65 wt.% SHAWINIGAN BLACK). The electrocatalyst layer and the TEFLON-modified carbon layers were deposited at  $10 \text{ mg/cm}^2$  loadings. The layers were simultaneously pressed under pressure ( $600 \text{ kg/cm}^2$  or  $160 \text{ kg/cm}^2$ ) and no  
25 heating was employed.

**What is Claimed is:**

1. A method for making an electrocatalyst powder batch, comprising the steps of:
  - a) providing a liquid-containing precursor composition to said electrocatalyst powder;
  - b) atomizing said liquid-containing precursor into precursor droplets;
  - c) heating said precursor droplets to a reaction temperature of not greater than about 700°C to form electrocatalyst particles; and
  - d) collecting said electrocatalyst particles.
2. A method as recited in Claim 1, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and an active species phase dispersed on said support phase.
3. A method as recited in Claim 1, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and an active species phase selected from the group consisting of platinum metal phases and ruthenium metal phases dispersed on said support phase.
4. A method as recited in Claim 1, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and a manganese-containing phase dispersed on said support phase.
5. A method as recited in Claim 1, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and a cobalt-containing phase dispersed on said support phase.
6. A method as recited in Claim 1, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and a nickel-containing phase dispersed on said support phase.
7. A method as recited in Claim 1, wherein said electrocatalyst particles are unsupported electrocatalyst particles.
8. A method as recited in Claim 1, wherein said electrocatalyst particles are unsupported metal electrocatalyst particles.
9. A method as recited in Claim 1, wherein said electrocatalyst particles are unsupported metal oxide electrocatalyst particles.

10. A method as recited in Claim 1, wherein said electrocatalyst particles have a unimodal size distribution with a volume average particle size in the range of from about 1  $\mu\text{m}$  to about 20  $\mu\text{m}$ .
- 5 11. A method as recited in Claim 1, wherein said electrocatalyst particles have a bimodal size distribution with a volume average particle size in the range of from about 1  $\mu\text{m}$  to about 20  $\mu\text{m}$ .
12. A method as recited in Claim 1, wherein said electrocatalyst particles have a trimodal size distribution with a volume average particle size in the range of from about 1  $\mu\text{m}$  to about 20  $\mu\text{m}$ .
- 10 13. A method as recited in Claim 1, wherein said heating step comprises heating said suspended droplets in a spray-dryer.
14. A method as recited in Claim 1, wherein said heating step comprises heating said suspended droplets in a mixed-flow spray-dryer.
- 15 15. A method as recited in Claim 1, wherein said heating step comprises heating to a temperature of not greater than about 500°C.
16. A method as recited in Claim 1, wherein said heating step comprises heating to a temperature of not greater than about 400°C.
17. A method as recited in Claim 1, wherein said heating step comprises heating to a temperature of not greater than about 300°C.
- 20 18. A method as recited in Claim 1, wherein said heating step comprises heating for not greater than about 100 seconds.
19. A method as recited in Claim 1, wherein said electrocatalyst particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .
- 25 20. An energy device assembly batch as recited in Claim 1, wherein said electrocatalyst particles comprise an active species phase dispersed on a support phase and wherein said support phase comprises primary carbon particles having an average primary particle size of from about 10 to about 100 nanometers.
- 30 21. A method as recited in Claim 1, wherein said electrocatalyst particles have an internal porosity of at least about 60 percent.

22. A method as recited in Claim 1, wherein said electrocatalyst particles comprise a supported active species phase having an average particle size of not greater than about 4 nanometers.

23. A method as recited in Claim 1, wherein said electrocatalyst  
5 particles comprise a proton conducting phase.

24. A method as recited in Claim 1, wherein said electrocatalyst particles comprise a proton conducting organic polymer.

25. A method as recited in Claim 1, wherein said electrocatalyst particles comprise a proton conducting fluorinated organic polymer.

10 26. A method as recited in Claim 1, wherein said electrocatalyst particles comprise a fluorinated organic polymer comprising functional groups selected from the group consisting of sulfate functional groups and phosphate functional groups.

27. A method as recited in Claim 1, wherein said electrocatalyst  
15 particles comprise a polymer phase.

28. A method as recited in Claim 1, wherein said electrocatalyst particles comprise a polymer phase having fluorinated groups.

29. A method for making a powder batch of polymer-modified particles, comprising the steps of:
- a) providing a precursor composition comprising a first precursor phase to an inorganic material and a second precursor phase to a polymer;
  - b) atomizing said precursor composition to form precursor droplets;
  - c) heating said precursor droplets to remove liquid therefrom and form polymer-modified particles; and
  - d) collecting said polymer-modified particles.
30. A method for making a powder batch as recited in Claim 29, wherein said polymer is a proton conducting polymer.
31. A method for making a powder batch as recited in Claim 29, wherein said polymer is a fluorinated organic polymer.
32. A method for making a powder batch as recited in Claim 29, wherein said polymer comprises functional groups selected from the group consisting of sulfate functional groups and phosphate functional groups.
33. A method for making a powder batch as recited in Claim 29, wherein said polymer is a hydrophobic polymer.
34. A method for making a powder batch as recited in Claim 29, wherein said polymer comprises fluorinated groups.
35. A method for making a powder batch as recited in Claim 29, wherein said inorganic material is carbon.
36. A method for making a powder batch as recited in Claim 29, wherein said inorganic material is carbon black.
37. A method for making a powder batch as recited in Claim 29, wherein said inorganic material is furnace black.
38. A method for making a powder batch as recited in Claim 29, wherein said inorganic material is acetylene black.
39. A method for making a powder batch as recited in Claim 29, wherein said inorganic material is carbon having a surface area greater than about 400 m<sup>2</sup>/g.

40. A method for making a powder batch as recited in Claim 29, wherein said inorganic material comprises highly crystalline carbon.

41. A method for making a powder batch as recited in Claim 29, wherein said inorganic material comprises carbon and said polymer is a proton  
5 conducting polymer.

42. A method for making a powder batch as recited in Claim 29, wherein said inorganic material comprises carbon and said polymer is a hydrophobic polymer.

43. A method for making a powder batch as recited in Claim 29,  
10 wherein said polymer-modified particles have a volume average particle size in the range of from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ .

44. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating said precursor droplets in a spray-dryer.

15 45. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating said precursor droplets in a mixed-flow spray-dryer.

46. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating to a temperature of not greater than  
20 about 500°C.

47. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating to a temperature of not greater than about 400°C.

48. A method for making a powder batch as recited in Claim 29,  
25 wherein said heating step comprises heating to a temperature of not greater than about 300°C.

49. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating for not greater than about 600 seconds.



50. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating for not greater than about 300 seconds.

51. A method for making a powder batch as recited in Claim 29,  
5 wherein said heating step comprises heating for not greater than about 100 seconds.

52. A method for making a powder batch as recited in Claim 29, wherein said heating step comprises heating for not greater than about 10 seconds.

10 53. A method for making a powder batch as recited in Claim 29, wherein said polymer-modified particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .

54. A method for making a powder batch as recited in Claim 29, wherein said polymer-modified particles have an internal porosity at least about  
15 40 percent.

55. A method for making a powder batch as recited in Claim 29, wherein said composite particles have a substantially spherical morphology.

56. A method for making an electrocatalyst powder batch comprising electrocatalyst particles, said particles comprising an active species phase dispersed on a support phase, said method comprising the steps of:

- 5       a) providing a precursor composition including a support phase precursor and an active species precursor;
- b) atomizing said precursor composition to form precursor droplets;
- c) heating said precursor droplets for a time not greater than about 600 seconds to form said electrocatalyst particles; and
- 10       d) collecting said electrocatalyst particles to form said powder batch.

57. A method as recited in Claim 56, wherein said heating step comprises heating for not greater than about 300 seconds.

58. A method as recited in Claim 56, wherein said heating step comprises heating for not greater than about 100 seconds.

15       59. A method as recited in Claim 56, wherein said heating step comprises heating for not greater than about 30 seconds.

60. A method as recited in Claim 56, wherein said heating step comprises heating for not greater than about 10 seconds.

20       61. A method as recited in Claim 56, wherein said active species phase comprises platinum metal.

62. A method as recited in Claim 56, wherein said active species phase comprises manganese oxide.

63. A method as recited in Claim 56, wherein said active species phase comprises cobalt.

25       64. A method as recited in Claim 56, wherein said active species phase comprises nickel.

65. A method as recited in Claim 56, wherein said electrocatalyst particles have a unimodal size distribution with a volume average particle size of from about 1 to about 10  $\mu\text{m}$ .

66. A method as recited in Claim 56, wherein said electrocatalyst particles have a bimodal size distribution with a volume average particle size of from about 1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

67. A method as recited in Claim 56, wherein said heating step  
5 comprises heating said droplets in a spray-dryer.

68. A method as recited in Claim 56, wherein said heating step comprises heating said droplets in a mixed-flow spray-dryer.

69. A method as recited in Claim 56, wherein said heating step comprises heating to a temperature of not greater than about 500°C.

10 70. A method as recited in Claim 56, wherein said heating step comprises heating to a temperature of not greater than about 400°C.

71. A method as recited in Claim 56, wherein said heating step comprises heating to a temperature of not greater than about 300°C.

72. A method as recited in Claim 56, wherein said electrocatalyst  
15 particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .

73. A method as recited in Claim 56, wherein said support phase comprises primary carbon particles having an average primary particle size of from about 10 to about 100 nanometers.

74. A method as recited in Claim 56, wherein said electrocatalyst  
20 particles have an internal porosity of at least about 40 percent.

75. A method as recited in Claim 56, wherein said active species phase has an average size less than about 4 nanometers.

76. An energy device assembly comprising at least a first electrode, said electrode comprising at least an anode, a cathode and an electrolyte separating said anode and said cathode, wherein at least one of said anode and  
5 said cathode comprises electrocatalyst layer including electrocatalyst particles, said electrocatalyst particles having been formed by heating suspended droplets of an electrocatalyst precursor composition to remove liquid from said precursor and form said electrocatalyst particles.

77. An energy device as recited in Claim 76, wherein said  
10 electrocatalyst particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .

78. An energy device as recited in Claim 76, wherein said electrocatalyst particles have a volume average particle size of not greater than about 20  $\mu\text{m}$ .

79. An energy device as recited in Claim 76, wherein said  
15 electrocatalyst particles have a volume average particle size of not greater than 10  $\mu\text{m}$ .

80. An energy device assembly as recited in Claim 76, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a  
20 support phase and an active species phase dispersed on said support phase.

81. An energy device assembly as recited in Claim 76, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and a platinum metal phase dispersed on said support phase.

82. An energy device assembly as recited in Claim 76, wherein said  
25 heating step comprises heating said suspended droplets in a spray-dryer.

83. An energy device assembly as recited in Claim 76, wherein said heating step comprises heating said suspended droplets in a mixed-flow spray-dryer.

84. An energy device assembly as recited in Claim 76, wherein said  
30 heating step comprises heating to a temperature of not greater than about 500°C.

85. An energy device assembly as recited in Claim 76, wherein said heating step comprises heating to a temperature of not greater than about 400°C.

86. An energy device assembly as recited in Claim 76, wherein said  
5 heating step comprises heating to a temperature of not greater than about 300°C.

87. An energy device assembly as recited in Claim 76, wherein said heating step comprises heating for not greater than about 600 seconds.

88. An energy device assembly as recited in Claim 76, wherein said  
10 heating step comprises heating for not greater than about 100 seconds.

89. An energy device assembly as recited in Claim 76, wherein said electrocatalyst particles comprise an active species phase dispersed on a support phase and wherein said support phase comprises primary carbon particles having an average primary particle size of from about 10 to about 100  
15 nanometers.

90. An energy device as recited in Claim 76, wherein said energy device is a fuel cell.

91. An energy device as recited in Claim 76, wherein said energy device is a proton exchange membrane fuel cell.

92. An energy device as recited in Claim 76, wherein said energy  
20 device is a direct methanol fuel cell.

93. An energy device as recited in Claim 76, wherein said energy device is an alkaline fuel cell.

94. An energy device as recited in Claim 76, wherein said energy  
25 device is a phosphoric acid fuel cell.

95. An energy device as recited in Claim 76, wherein said energy device is a battery.

96. An energy device as recited in Claim 76, wherein said electrocatalyst particles have a substantially spherical morphology.

30

97. A membrane electrode assembly comprising at least an anode, a cathode and a membrane separating said anode and said cathode, wherein at least one of said anode and said cathode comprises electrocatalyst particles fabricated by heating suspended droplets of an electrocatalyst precursor composition.

98. A membrane electrode assembly as recited in Claim 97, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and an active species phase dispersed on said support phase.

99. A membrane electrode assembly as recited in Claim 97, wherein said electrocatalyst particles are composite electrocatalyst particles comprising a support phase and a platinum metal phase dispersed on said support phase.

100. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating said suspended droplets in a spray-dryer.

101. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating said suspended droplets in a mixed-flow spray-dryer.

102. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating to a temperature of not greater than about 400°C.

103. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating to a temperature of not greater than about 300°C.

104. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating for not greater than about 600 seconds.

105. A membrane electrode assembly as recited in Claim 97, wherein said heating step comprises heating for not greater than about 100 seconds.

106. A membrane electrode assembly as recited in Claim 97, wherein said electrocatalyst particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .

107. A membrane electrode assembly as recited in Claim 97, wherein said electrocatalyst particles comprise an active species phase dispersed on a support phase and wherein said support phase comprises primary carbon

particles having an average primary particle size of from about 10 to about 100 nanometers.

108. A membrane electrode assembly comprising at least an anode, a cathode and a membrane separating said anode and said cathode, wherein at least one of said anode and said cathode comprises an electrocatalyst layer and  
5 said electrocatalyst layer comprises substantially spherical electrocatalyst particles.

109. A membrane electrode assembly as recited in Claim 108, wherein said electrocatalyst particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ .

10 110. A membrane electrode assembly as recited in Claim 108, wherein said electrocatalyst particles are composite electrocatalyst particles comprising an active species phase dispersed on a support phase.

111. A membrane electrode assembly as recited in Claim 108, wherein said electrocatalyst particles have an internal porosity of at least about 40  
15 percent.



112. A liquid vehicle comprising electrocatalyst particles, said liquid vehicle being adapted to be deposited using a direct-write tool to form an electrocatalyst layer, wherein said liquid vehicle comprises a liquid carrier and  
5 substantially spherical electrocatalyst particles having a volume average particle size of not greater than about 30  $\mu\text{m}$  dispersed in said liquid carrier.

113. A liquid vehicle as recited in Claim 112, wherein said volume average particle size is from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ .

114. A liquid vehicle as recited in Claim 112, wherein said  
10 electrocatalyst particles are secondary particles comprising an active species phase dispersed on primary support particles.

115. A liquid vehicle as recited in Claim 112, wherein said electrocatalyst particles are secondary particles comprising an active species phase dispersed on primary carbon support particles having an average primary  
15 particle size of from about 10 nanometers to about 100 nanometers.

116. A liquid vehicle as recited in Claim 112, wherein said electrocatalyst comprises a platinum metal active species phase dispersed on primary carbons support particles.

117. A liquid vehicle as recited in Claim 112, wherein said  
20 electrocatalyst comprises  $\text{MnO}_x$  active species phase dispersed on primary carbon support particles.

118. A liquid vehicle as recited in Claim 112, wherein said liquid vehicle comprises a solvent and a carboxy methyl cellulose binder.

119. A method for the deposition of an electrocatalyst layer, comprising the steps of:

- a) dispersing substantially spherical electrocatalyst particles in a liquid carrier to form a liquid vehicle, wherein said electrocatalyst particles have a volume average particle size of not greater than about 30  $\mu\text{m}$ ;
- b) depositing said liquid vehicle onto a surface using an ink-jet device; and
- c) heating said liquid vehicle to form an electrocatalyst layer.

120. A method as recited in Claim 119, wherein said volume average particle size is from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ .

121. A method as recited in Claim 119, wherein said electrocatalyst particles are secondary particles comprising an active species phase dispersed on primary support particles.

122. A method as recited in Claim 119, wherein said electrocatalyst particles are secondary particles comprising an active species phase dispersed on primary carbon support particles having an average primary particle size of from about 10 nanometers to about 100 nanometers.

123. A method as recited in Claim 119, wherein said electrocatalyst comprises a platinum metal active species phase dispersed on primary carbon support particles.

124. A method as recited in Claim 119, wherein said electrocatalyst comprises  $\text{MnO}_x$  active species phase dispersed on primary carbon support particles.

125. A method as recited in Claim 119, wherein said liquid vehicle comprises a solvent and a carboxy methyl cellulose binder.

126. A method as recited in Claim 119, wherein said heating step comprises heating to a temperature of at least about 200°C.

127. A membrane electrode assembly comprising at least an anode, a cathode and a membrane separating said anode and said cathode, wherein at least one of said anode and said cathode comprises electrocatalyst particles comprising an active species phase and a polymer phase intimately mixed with  
5 said active species phase.

128. A membrane electrode assembly as recited in Claim 127, wherein said polymer phase comprises a proton conductive polymer.

129. A membrane electrode assembly as recited in Claim 127, wherein said polymer phase comprises a hydrophobic polymer.

10 130. A membrane electrode assembly as recited in Claim 127, wherein said polymer phase comprises a hydrophilic polymer.

131. A membrane electrode assembly as recited in Claim 127, wherein said polymer phase comprises a fluorcarbon polymer.

15 132. A membrane electrode assembly as recited in Claim 127, wherein said polymer phase comprises a perfluorohydrocarbon polymer.

133. A membrane electrode assembly as recited in Claim 127, wherein said electrocatalyst particles comprise primary carbon support particles.

134. A membrane electrode assembly as recited in Claim 127, wherein said electrocatalyst particles comprise primary carbon support particles having  
20 an average primary particle size of from about 10 nanometers to about 100 nanometers.

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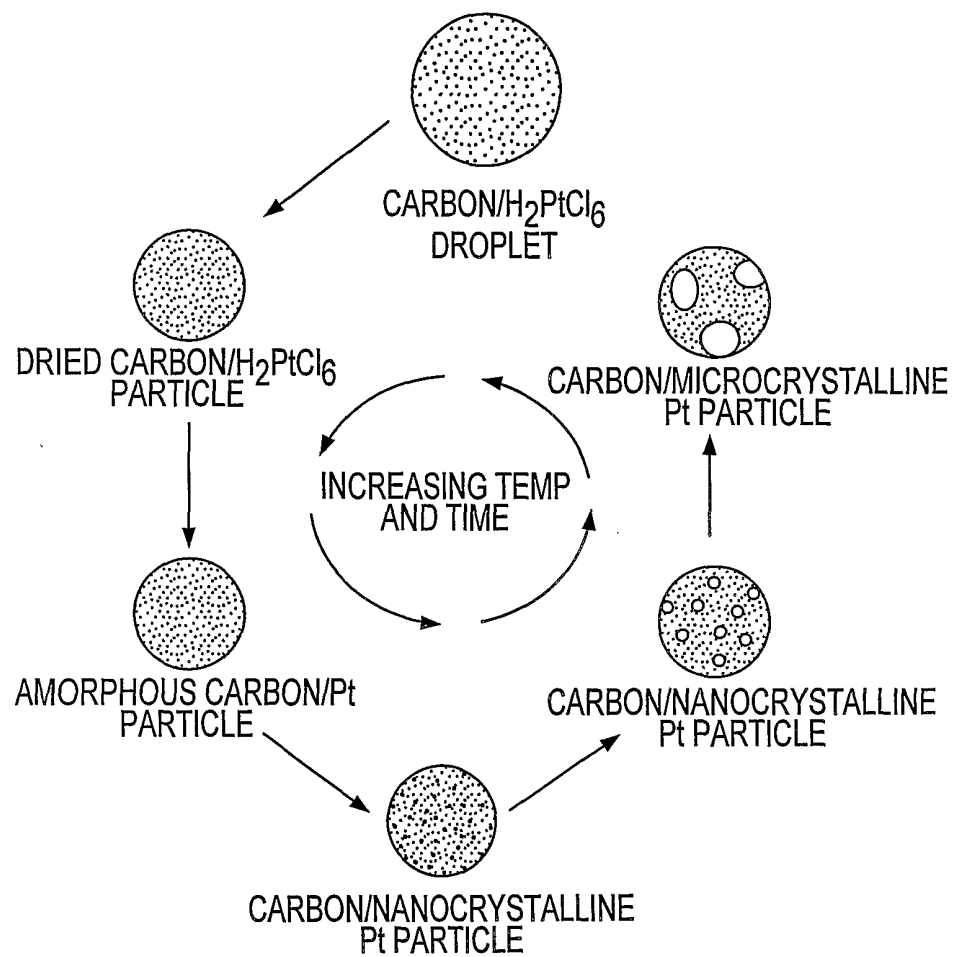


FIG.1

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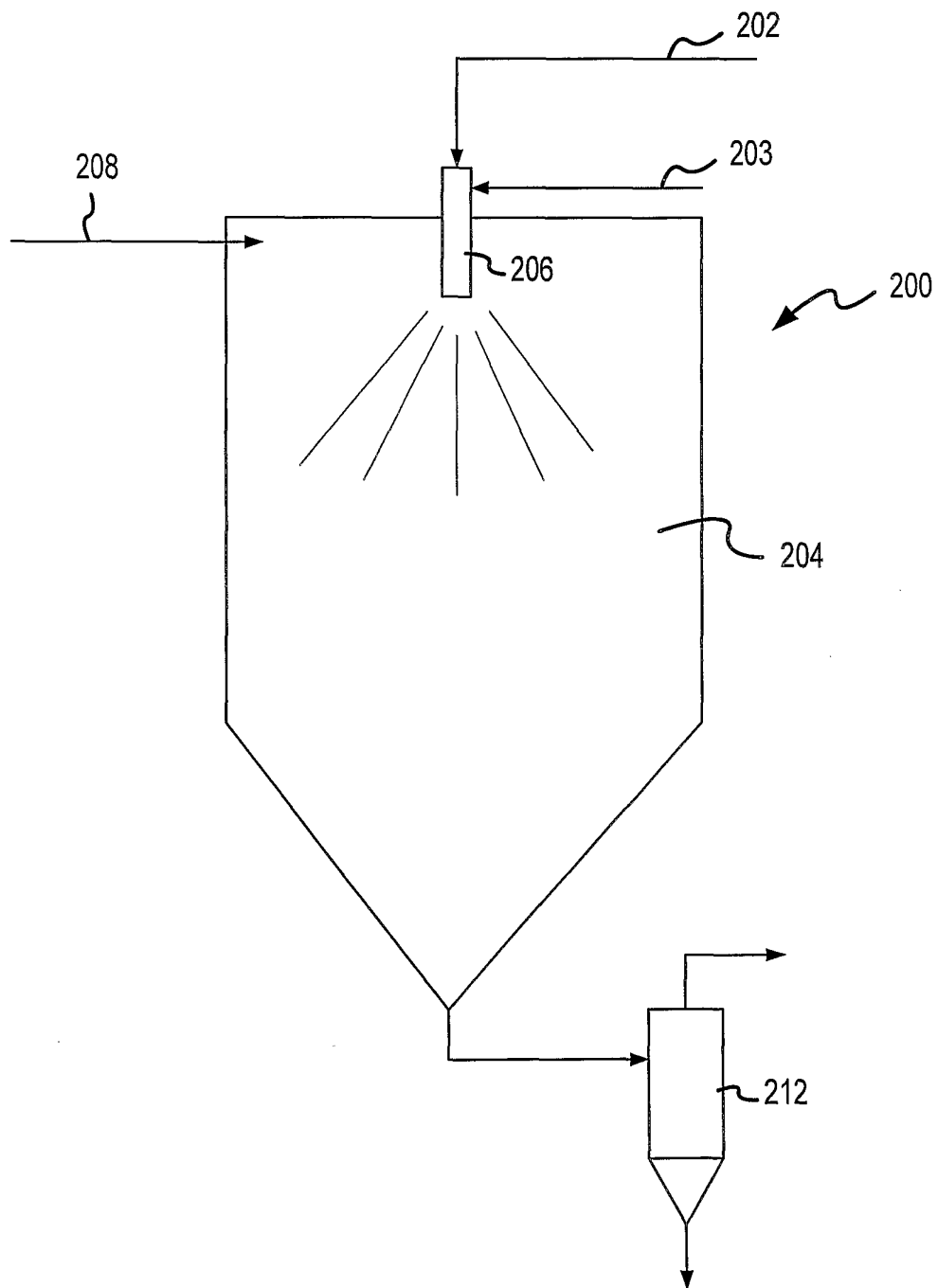


FIG.2

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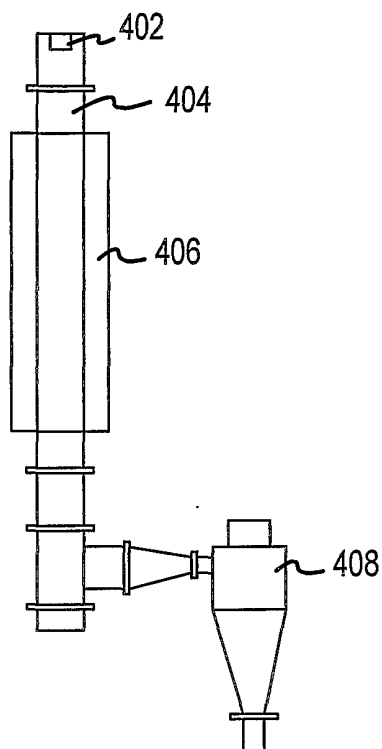


FIG. 3

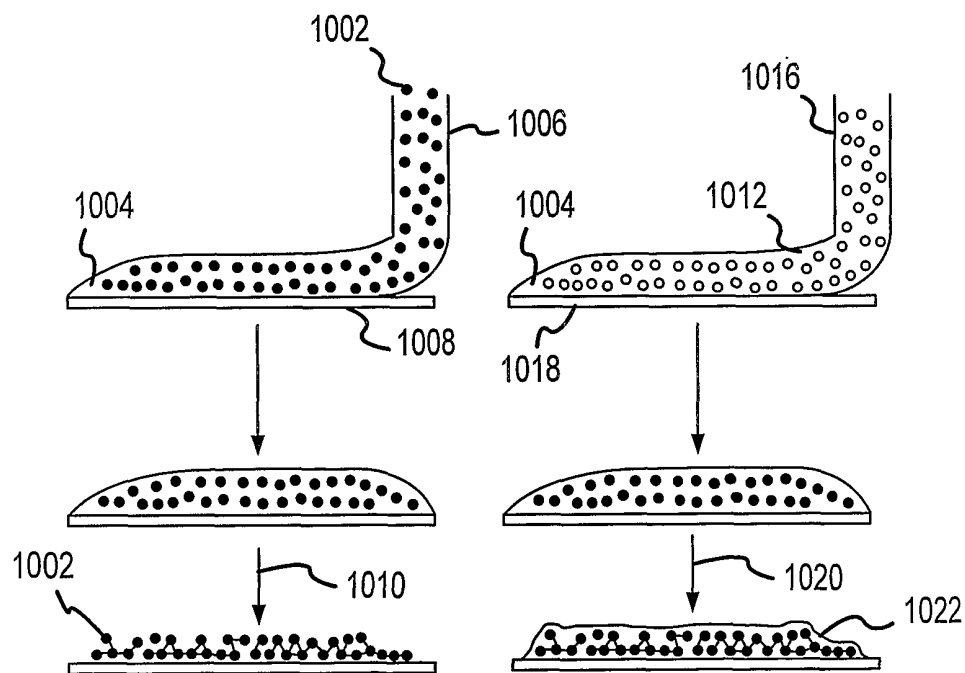


FIG. 4(a)

FIG. 4(b)

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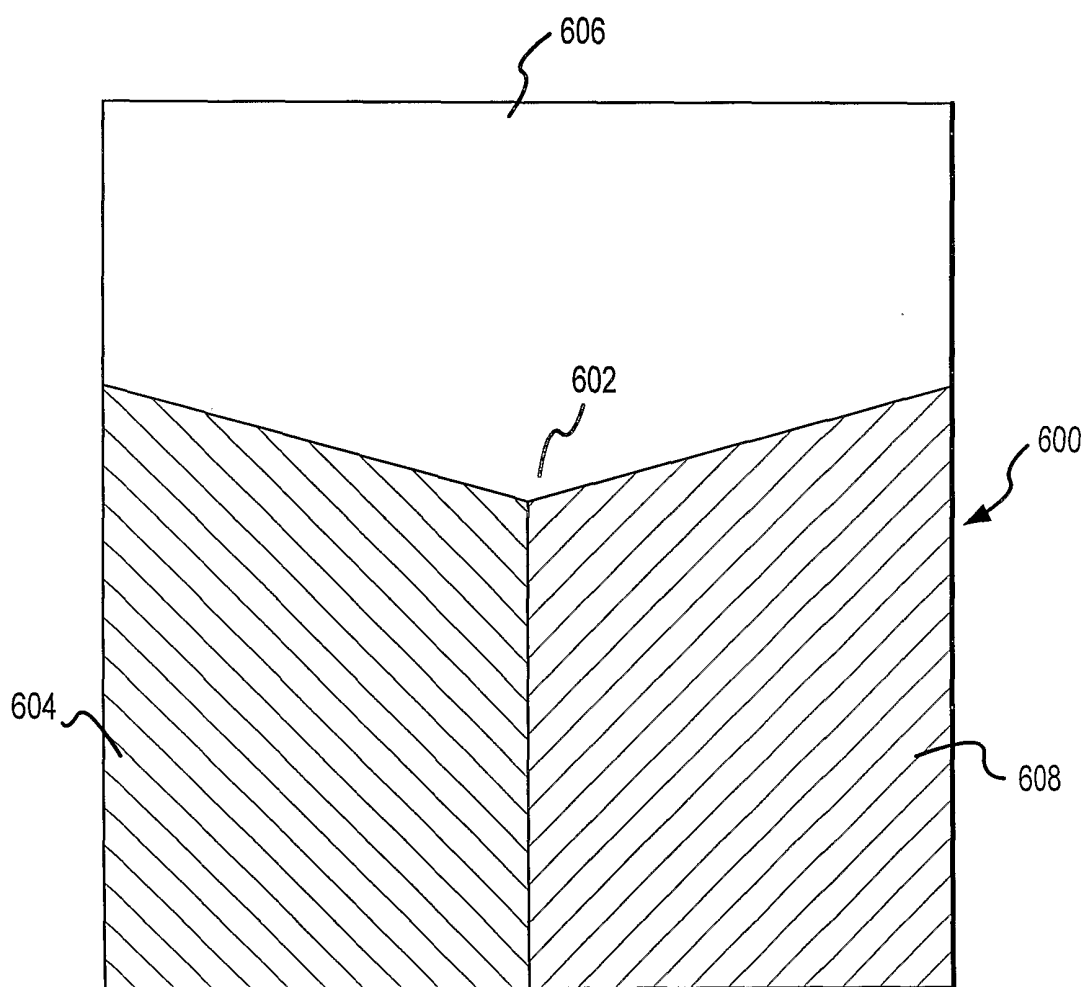


FIG.5

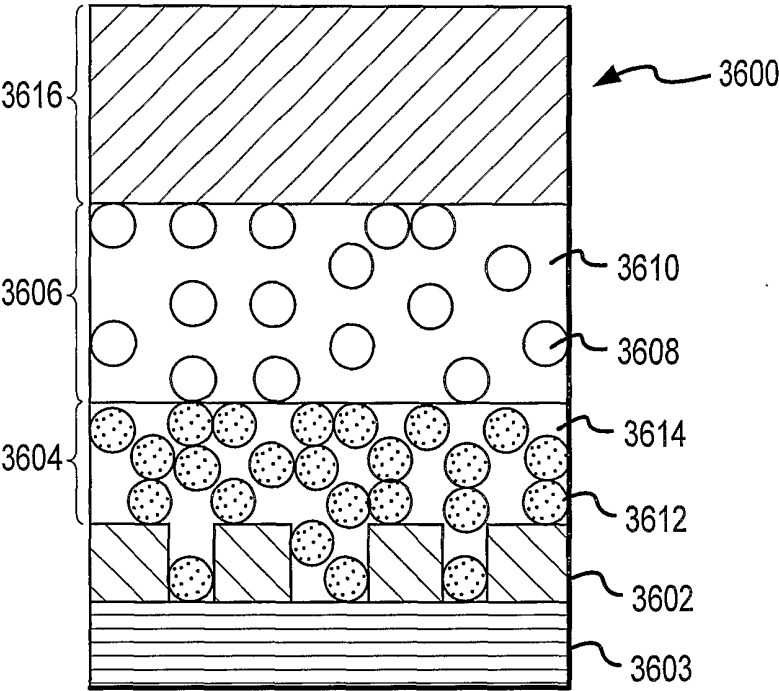


FIG.6



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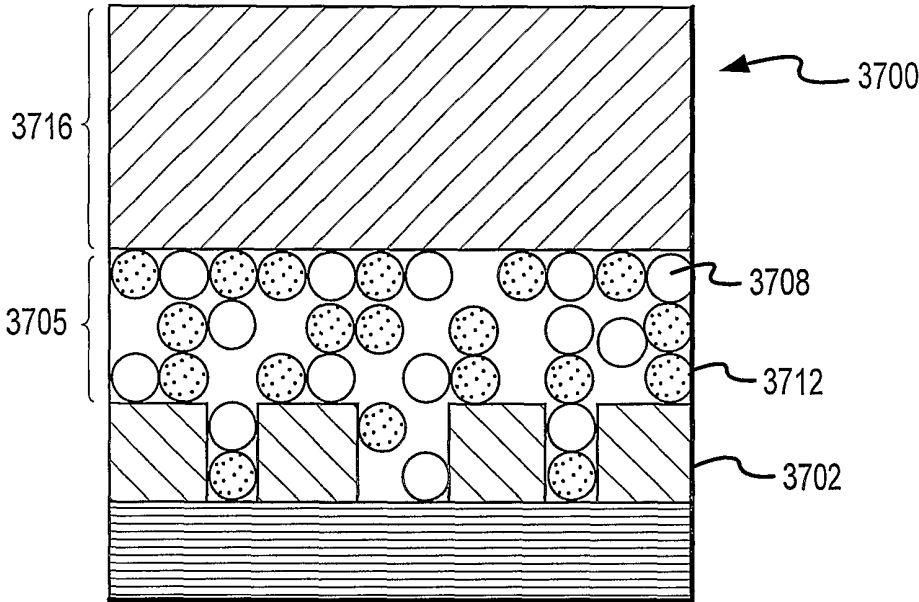


FIG.7

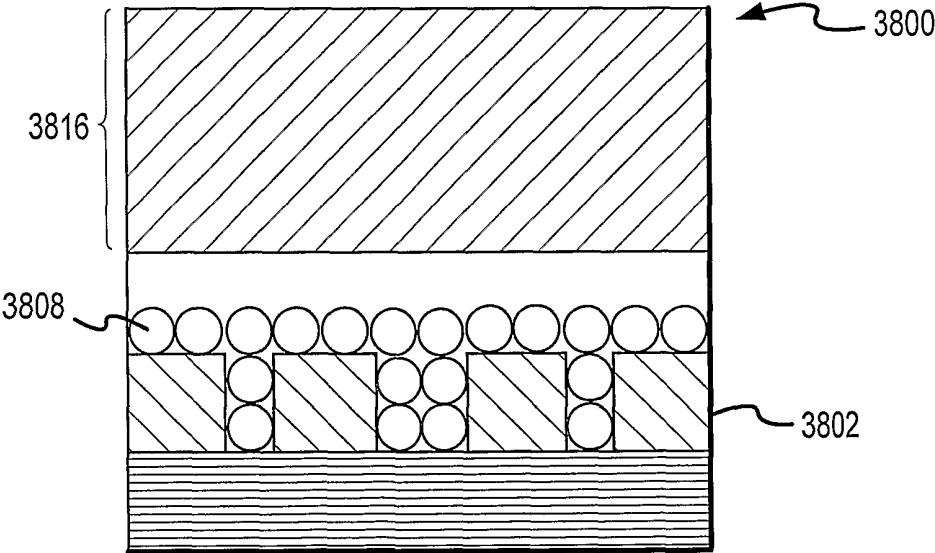


FIG.8

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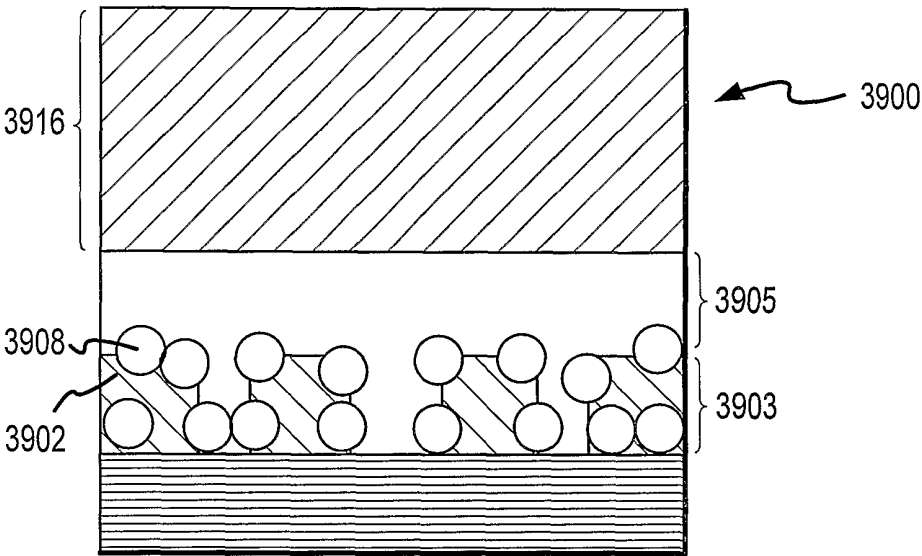


FIG.9

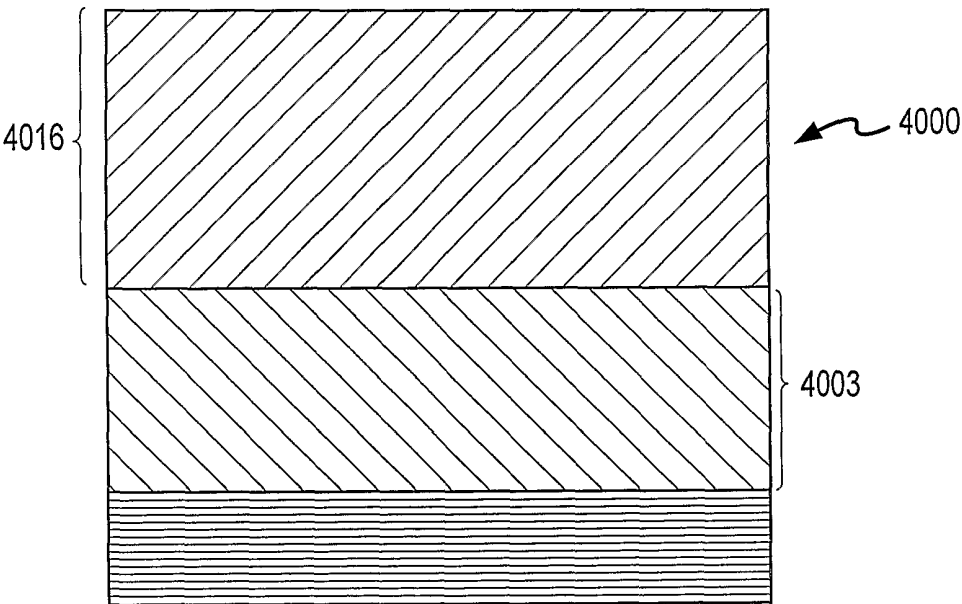


FIG.10

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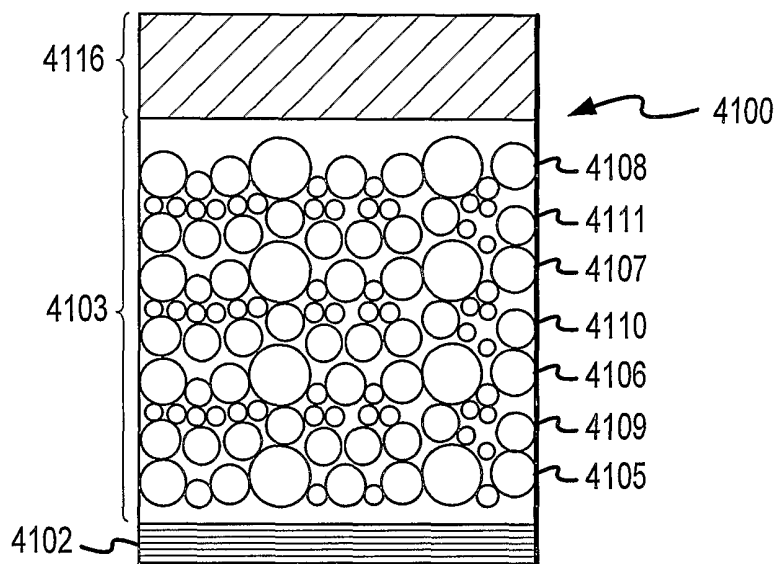


FIG. 11

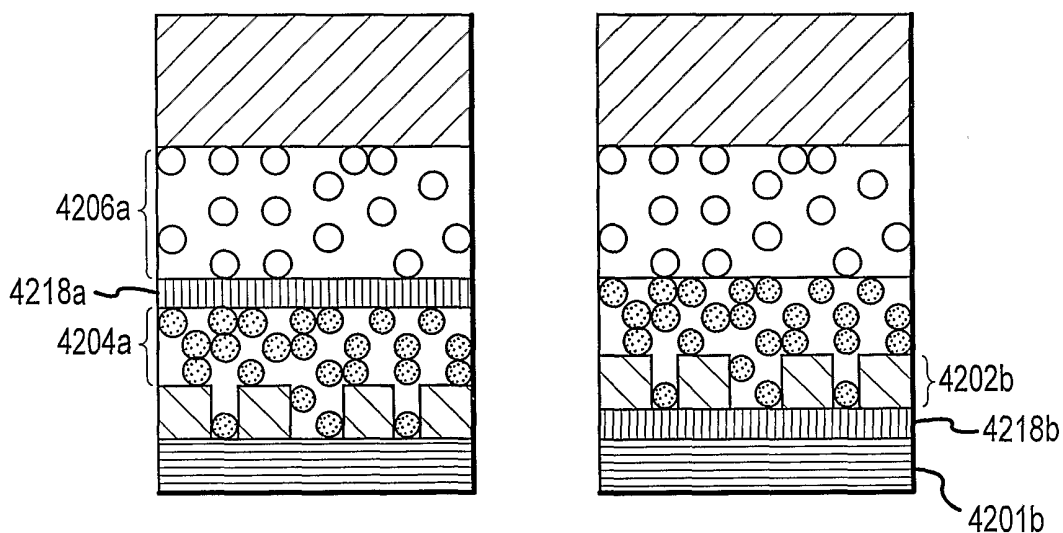


FIG. 12(a)

FIG. 12(b)

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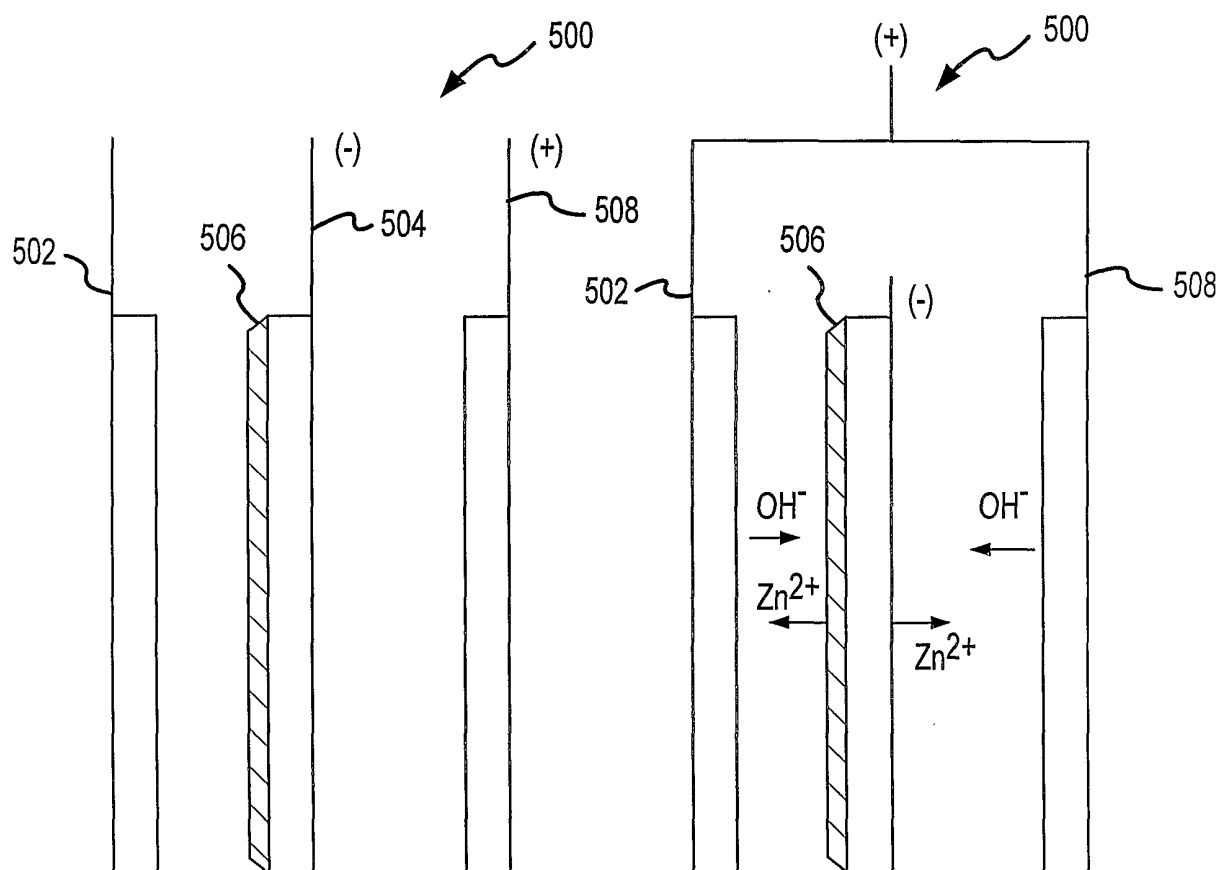


FIG.13(a)

FIG.13(b)

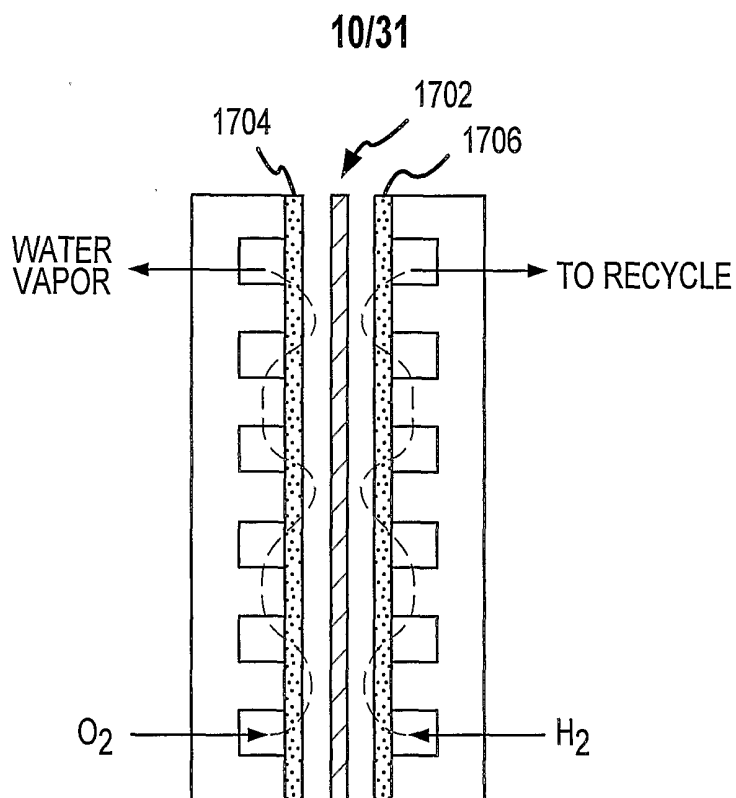


FIG.14

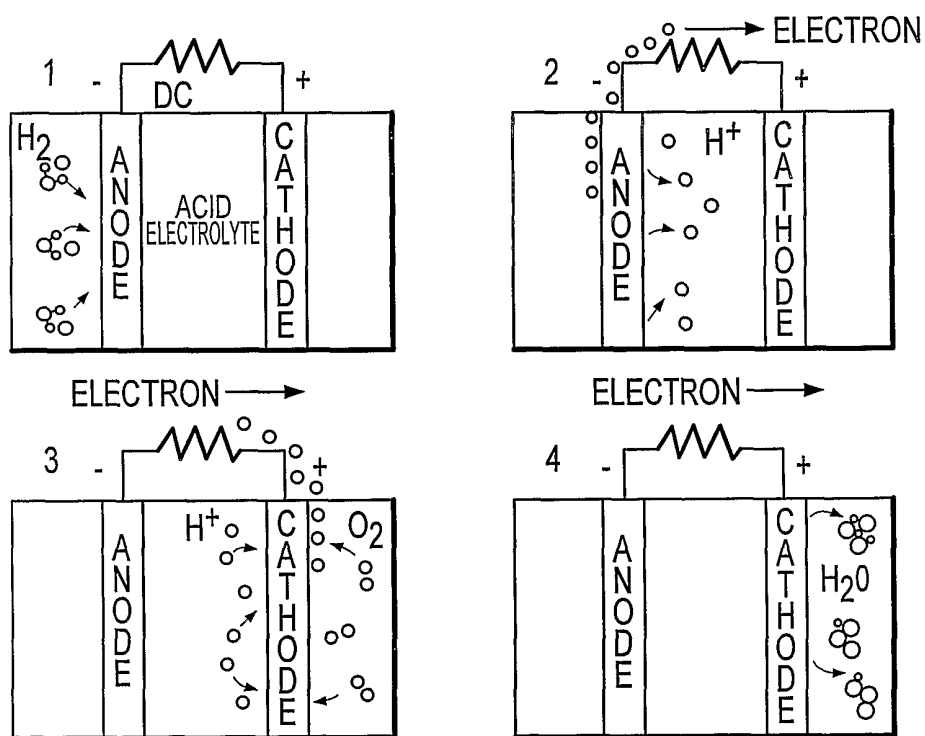


FIG.15

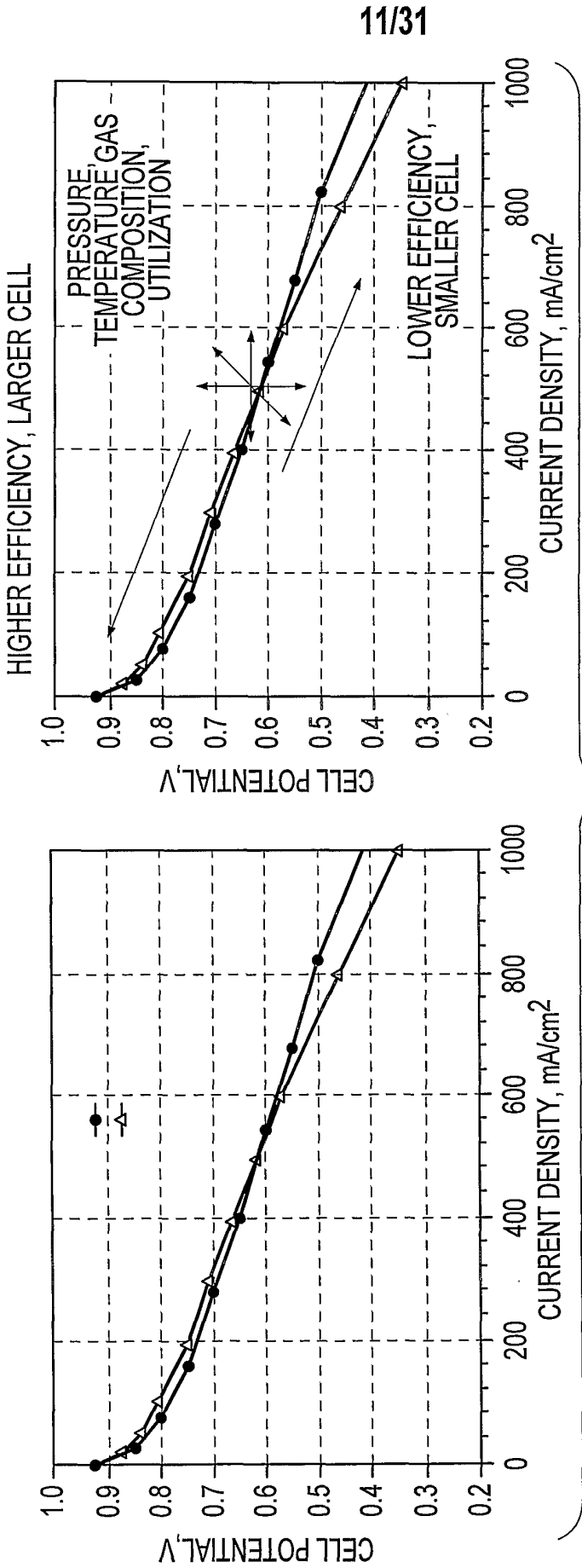


FIG.16

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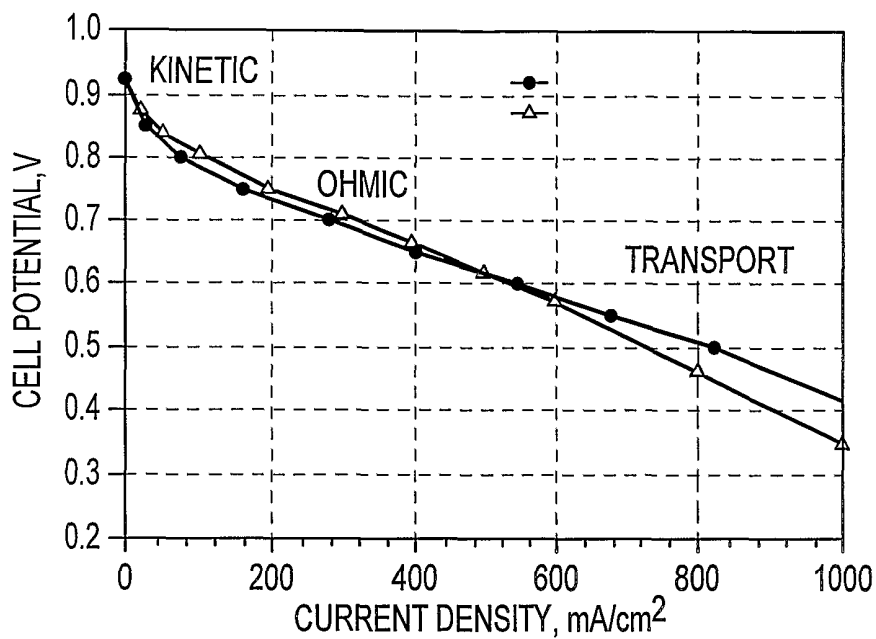


FIG. 17

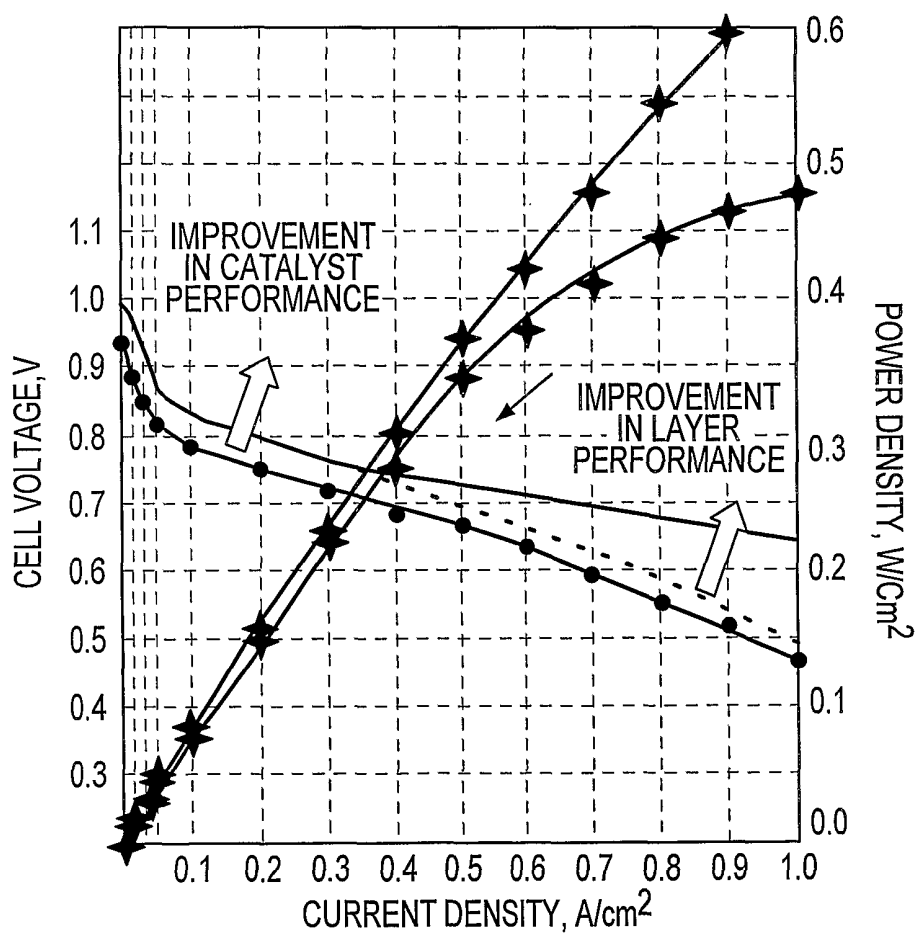


FIG. 18

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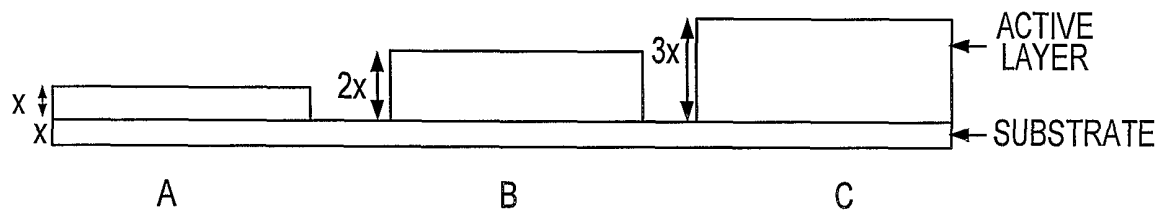


FIG.19

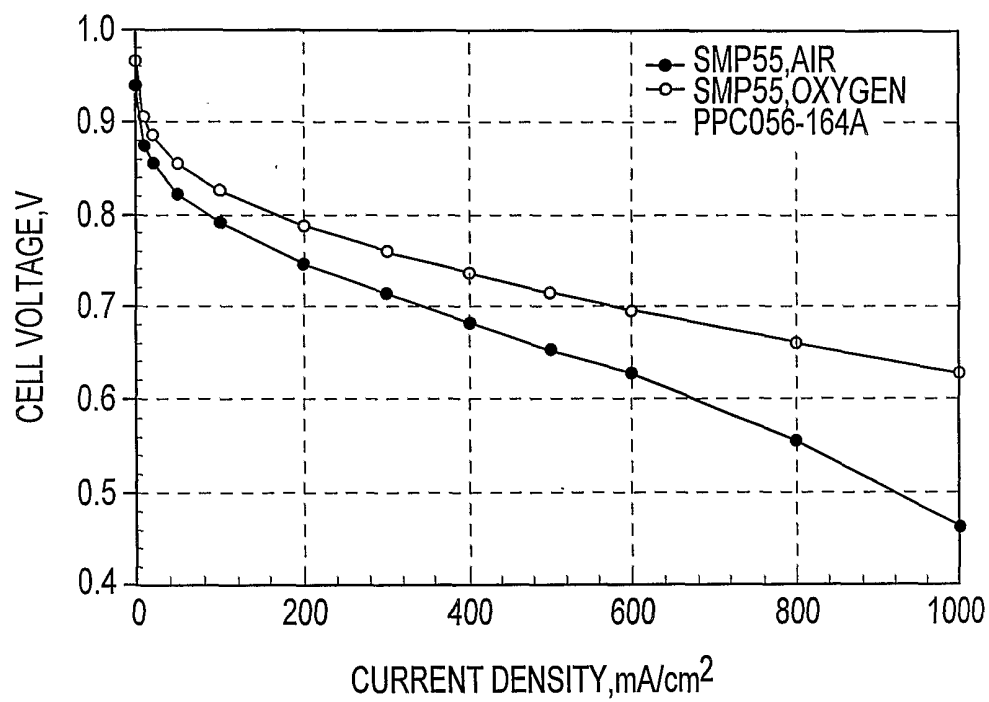


FIG.20



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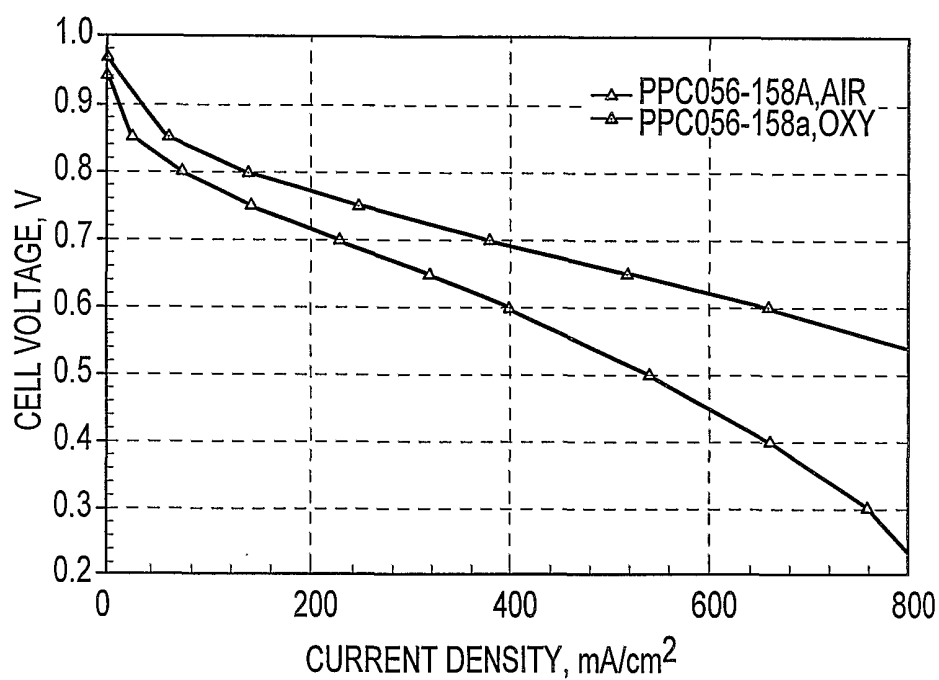


FIG.21

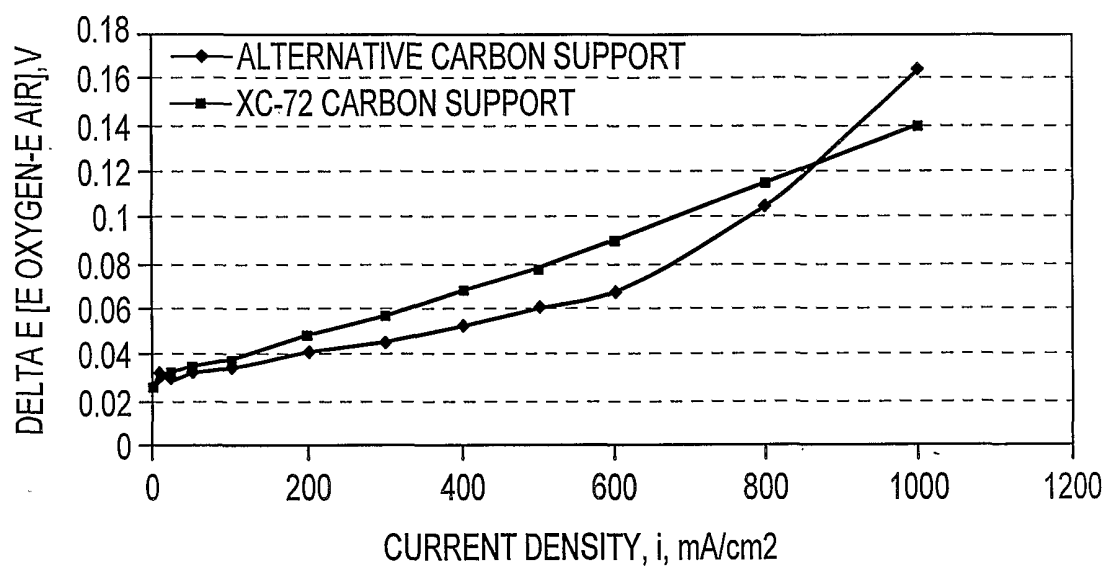


FIG.22

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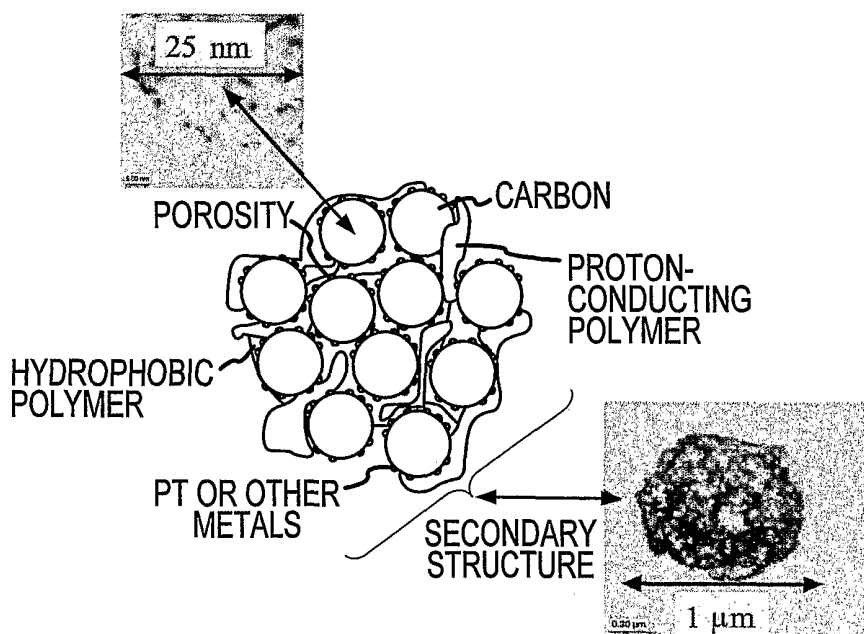


FIG.23

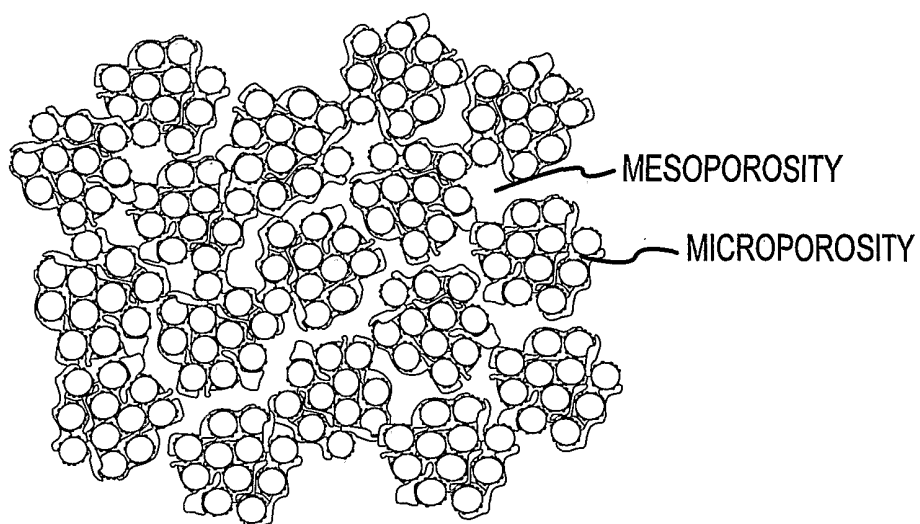


FIG.24

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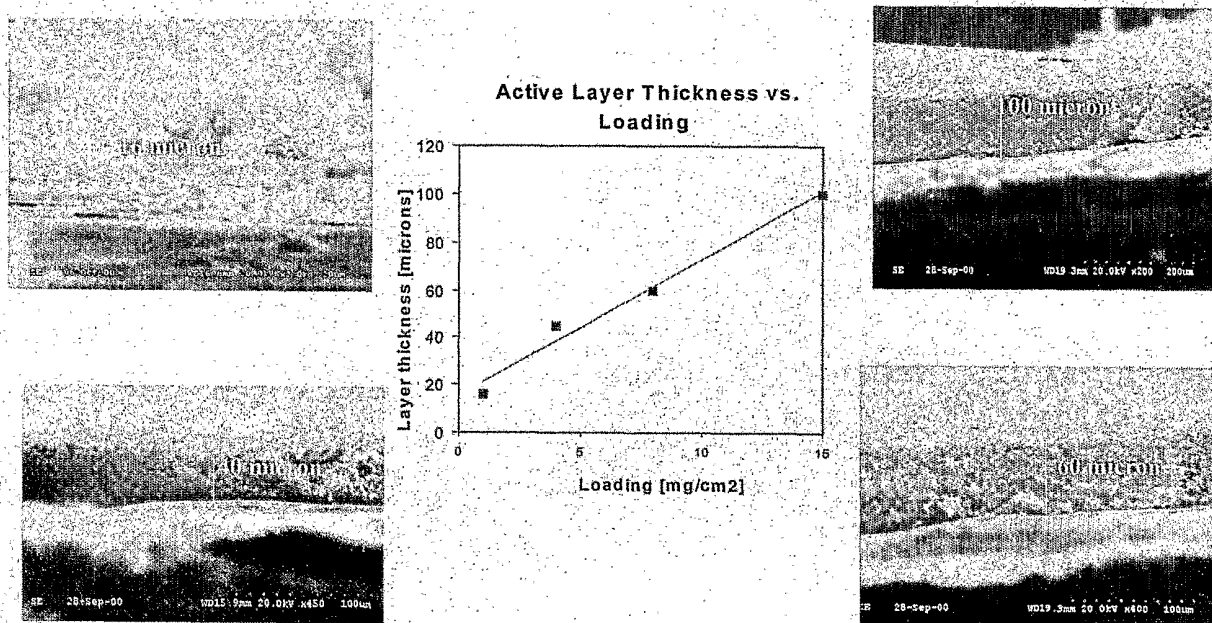


FIG.25

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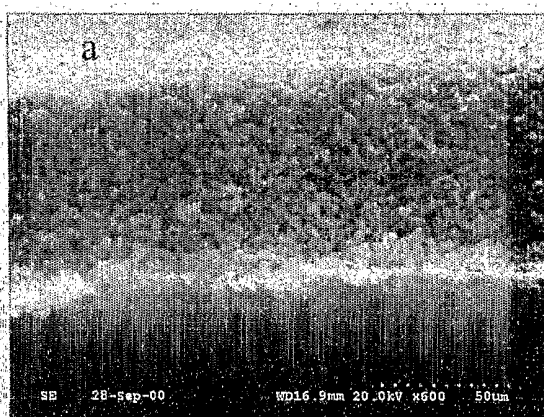


FIG.26(a)

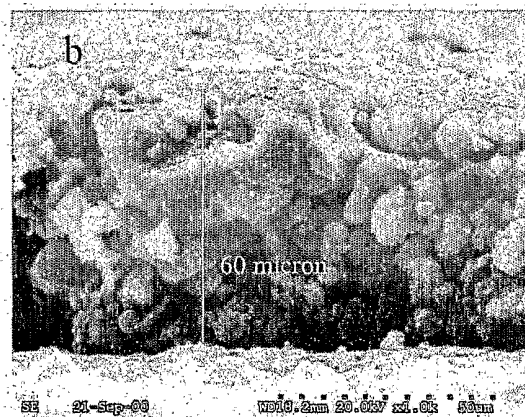


FIG.26(b)

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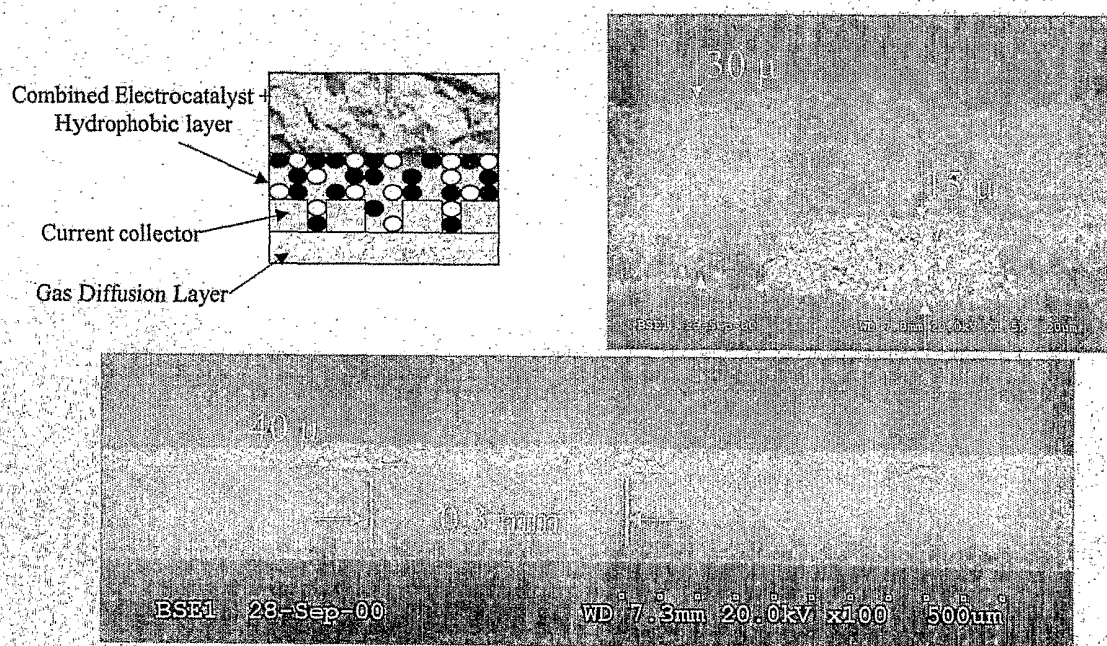


FIG.27

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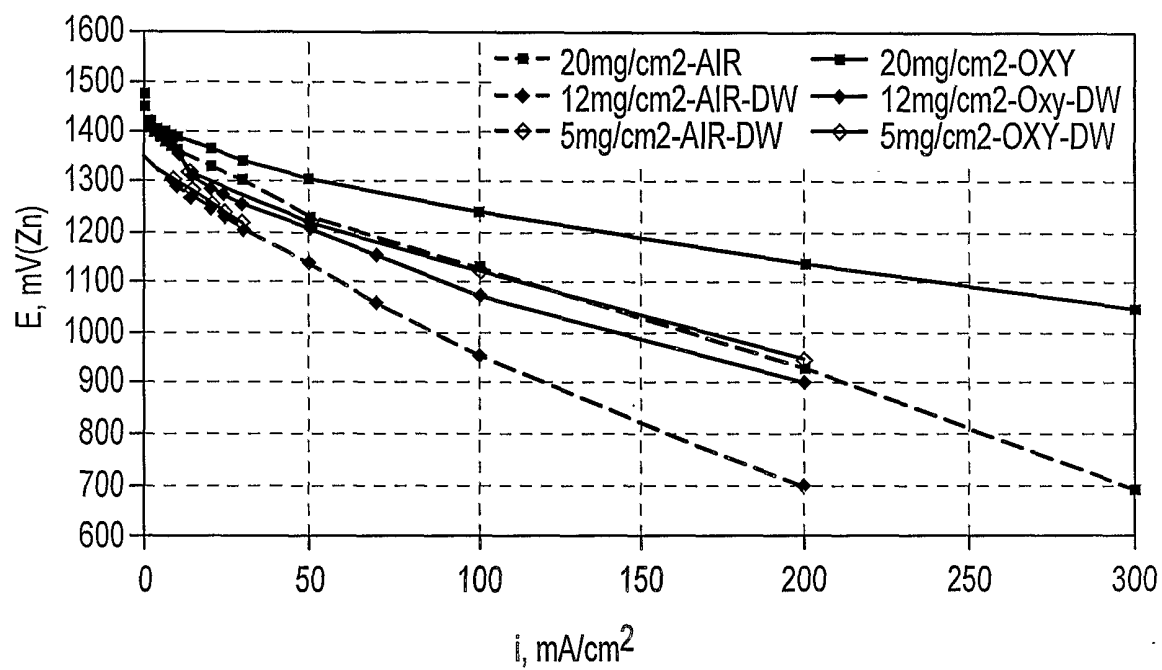


FIG.28

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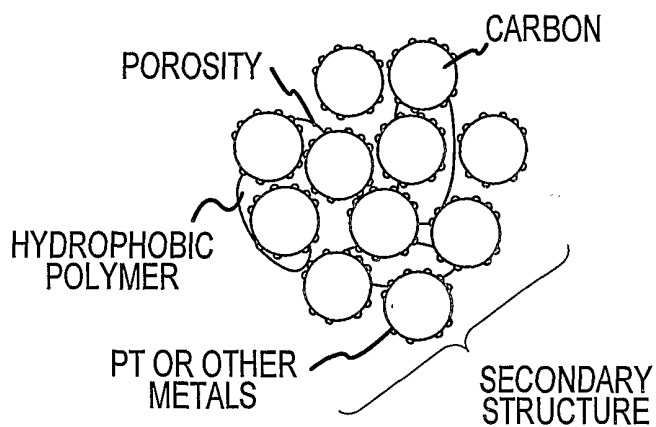


FIG.29

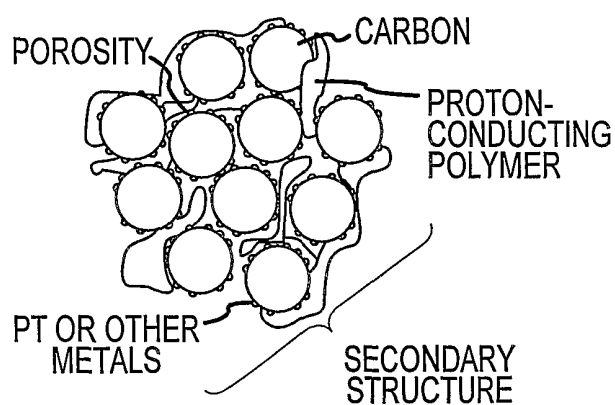


FIG.30

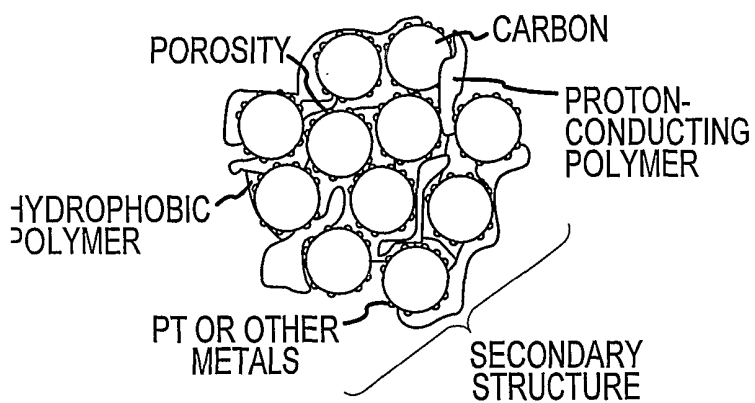


FIG.31

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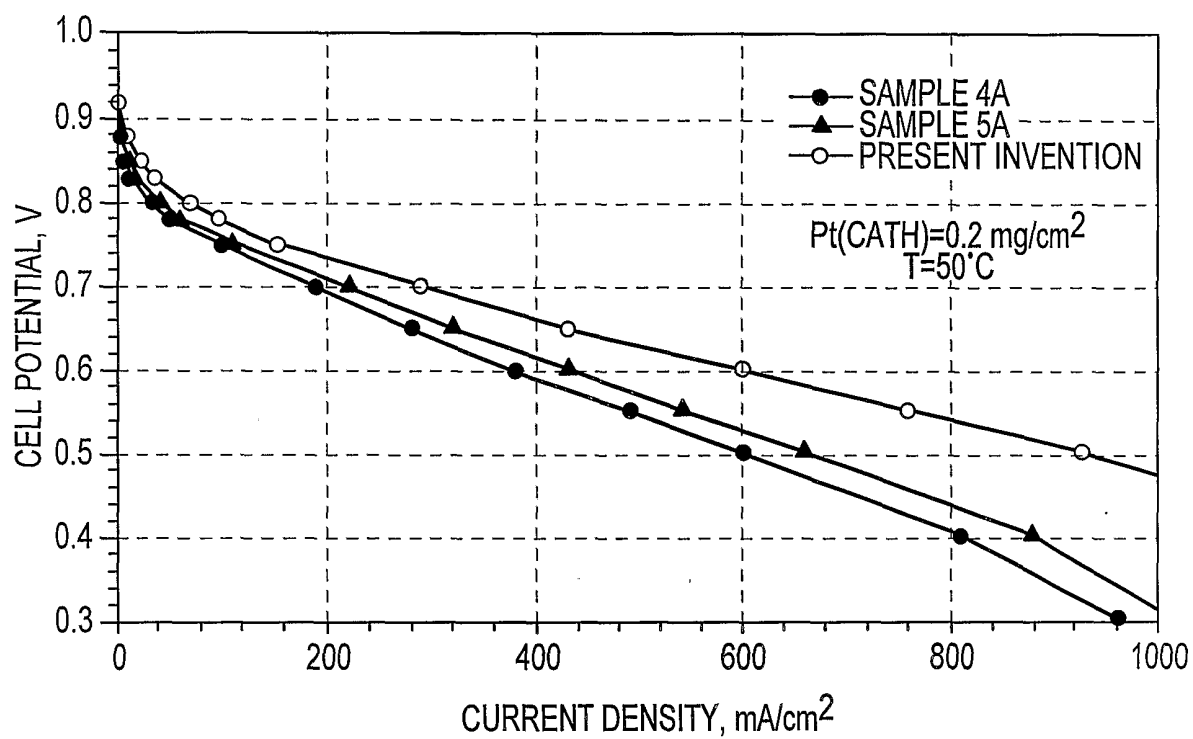


FIG.32



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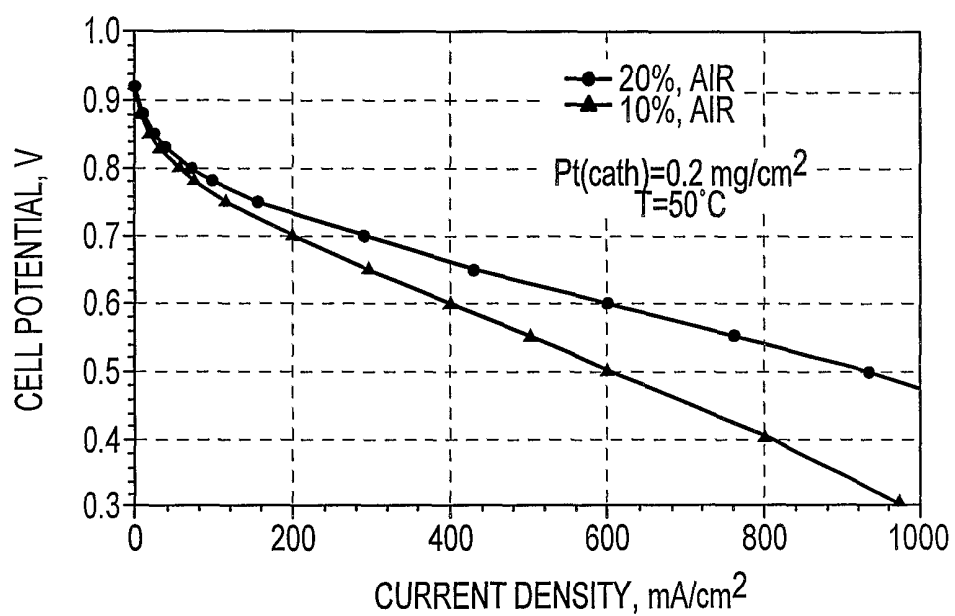


FIG.33

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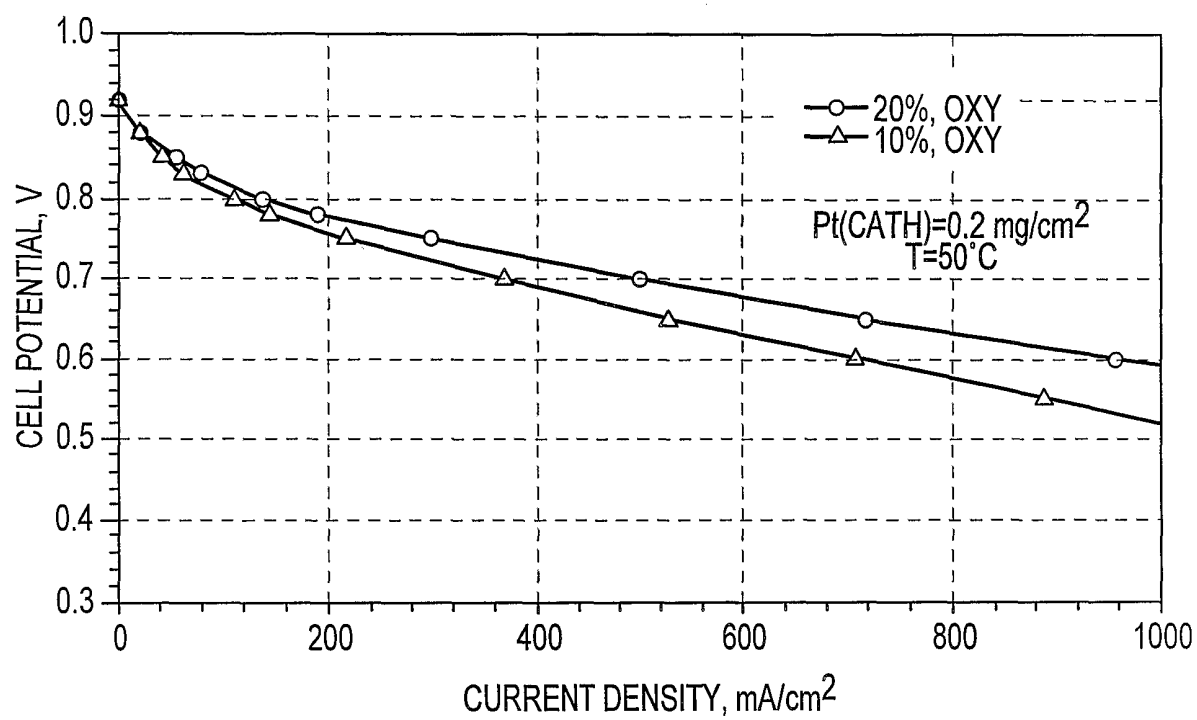


FIG.34

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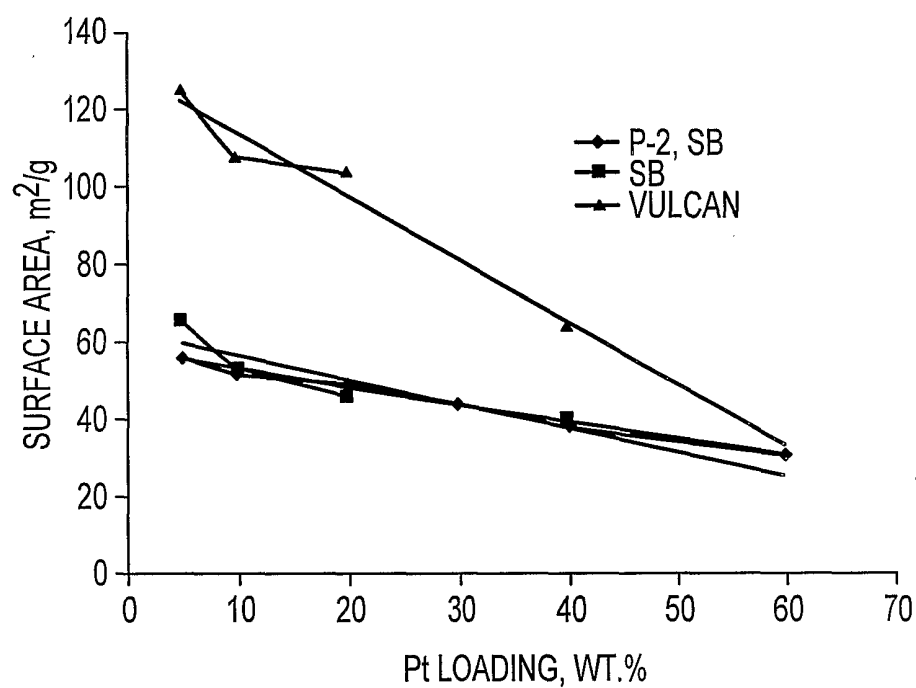


FIG.35

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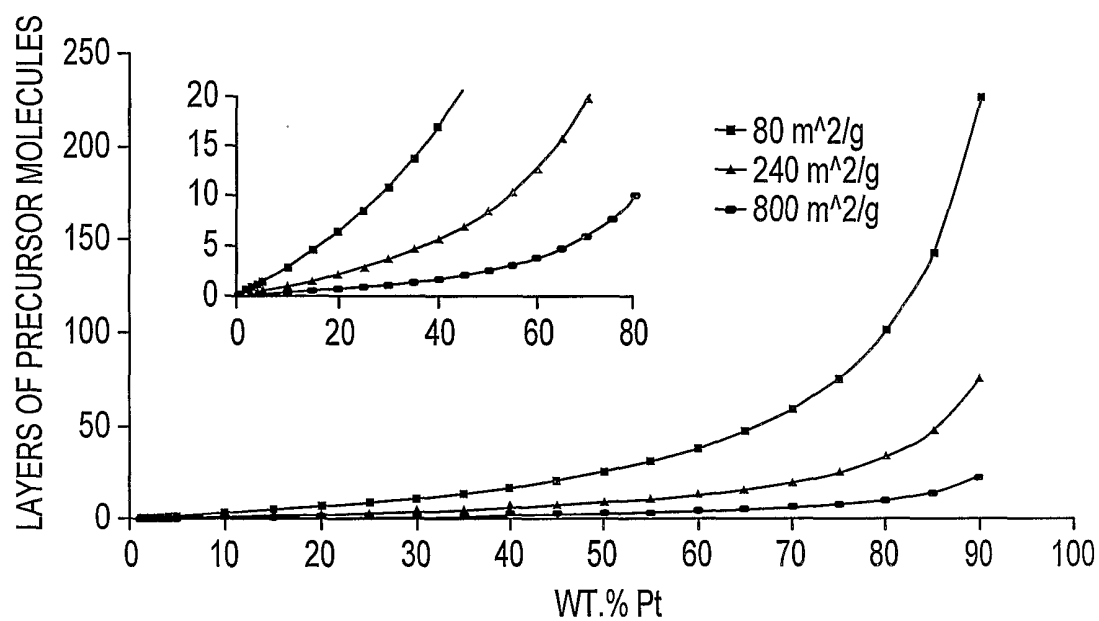


FIG.36

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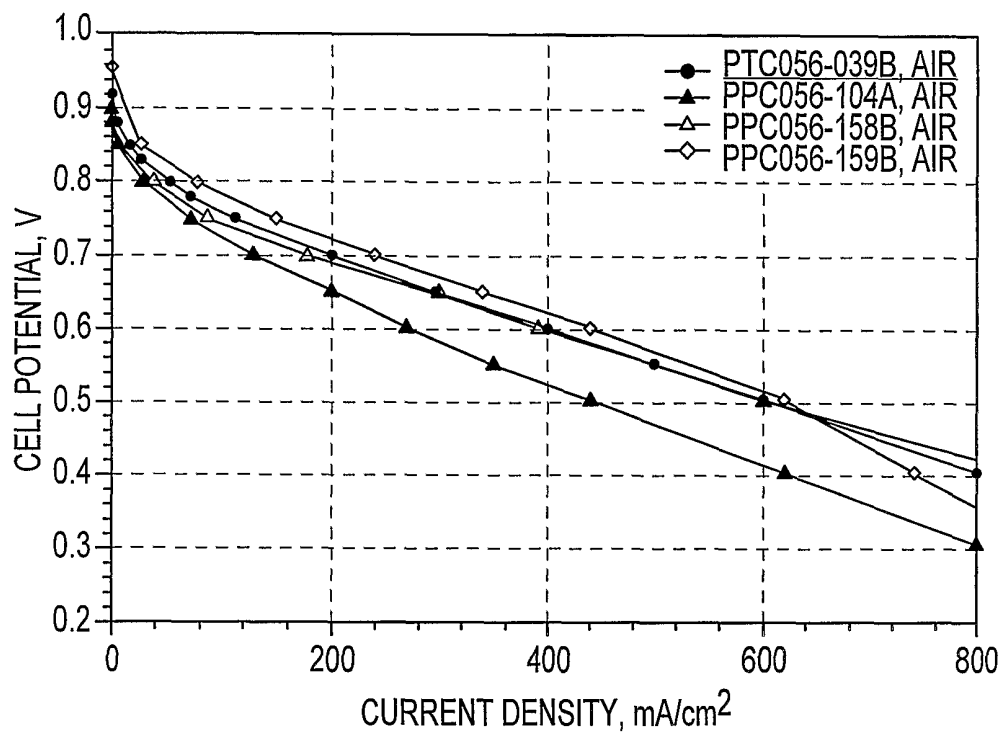


FIG.37

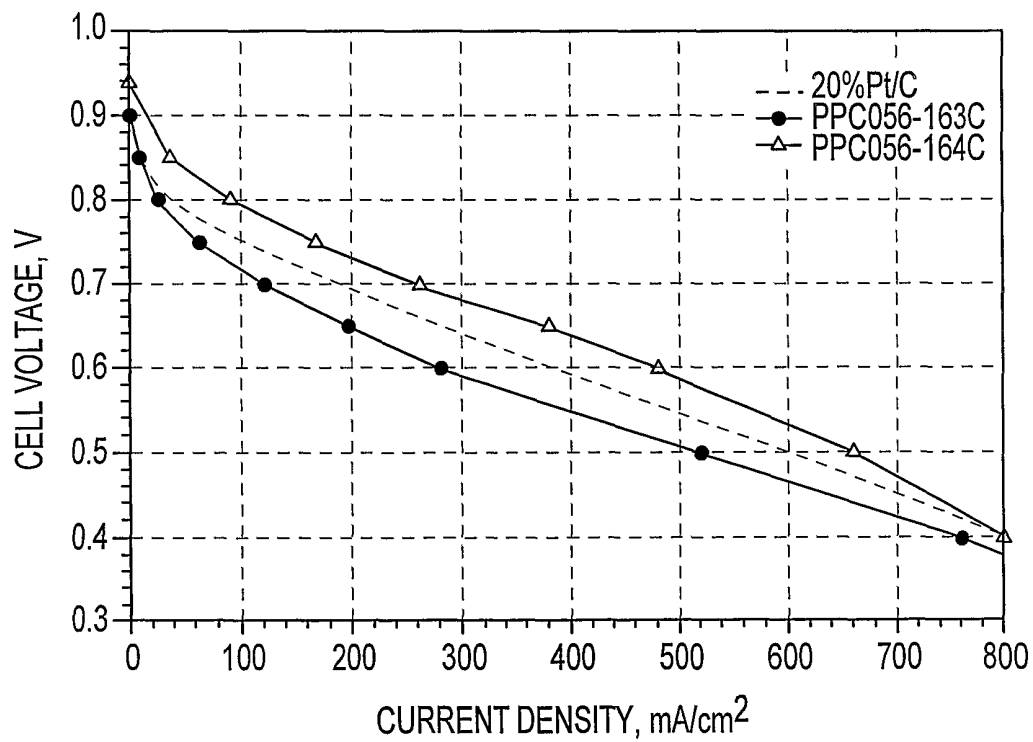


FIG.38

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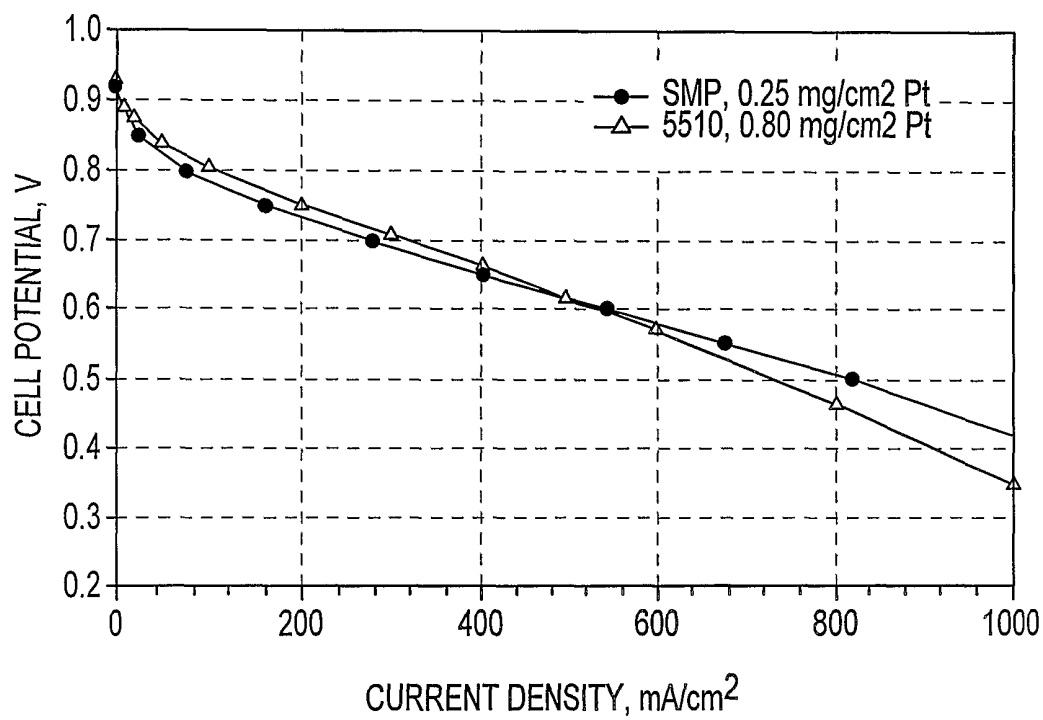


FIG.39

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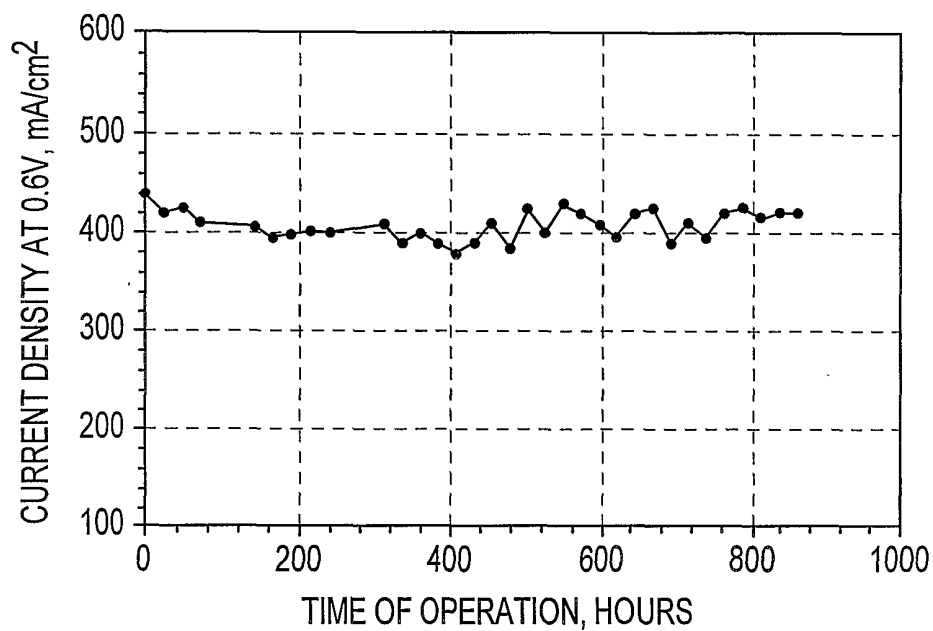


FIG.40

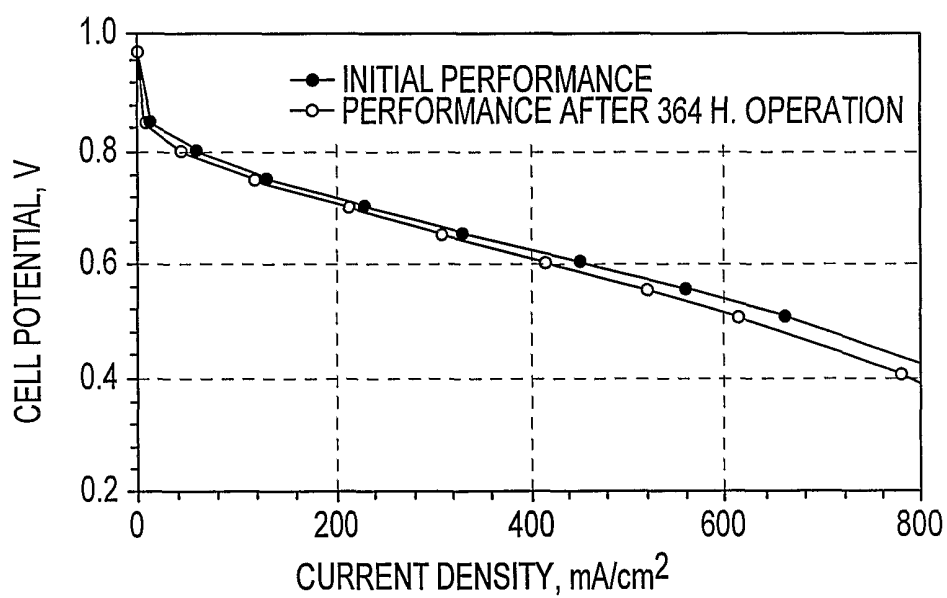


FIG.41

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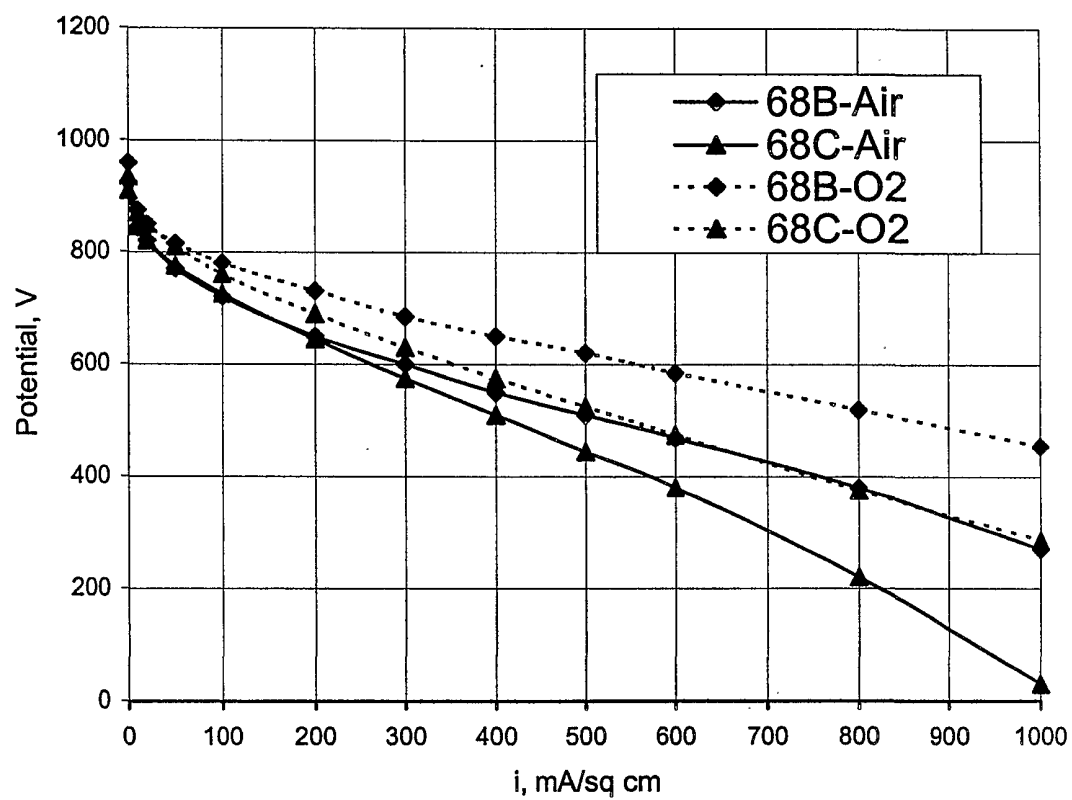


FIG.42



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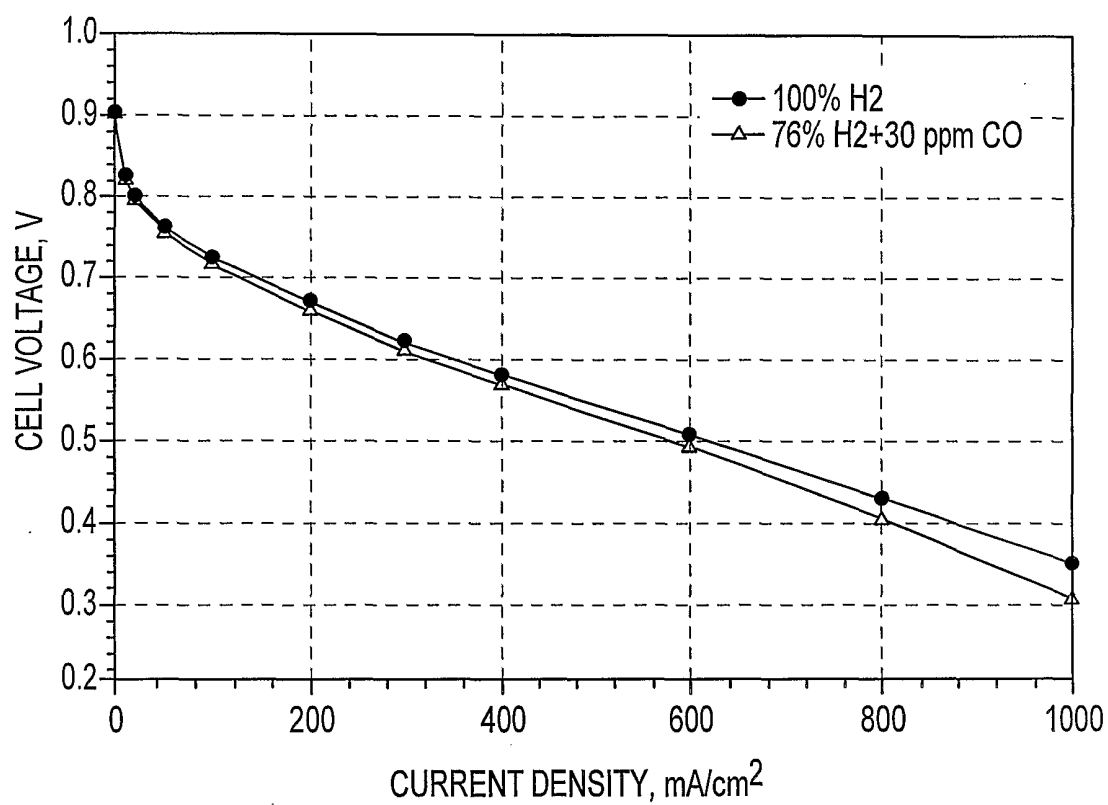


FIG.43

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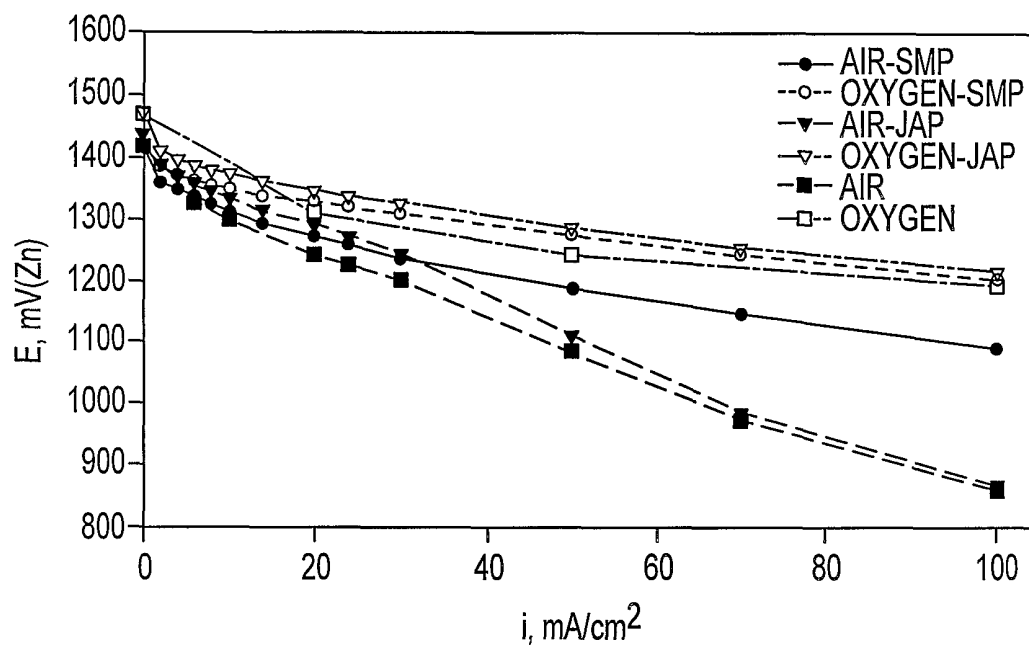


FIG.44

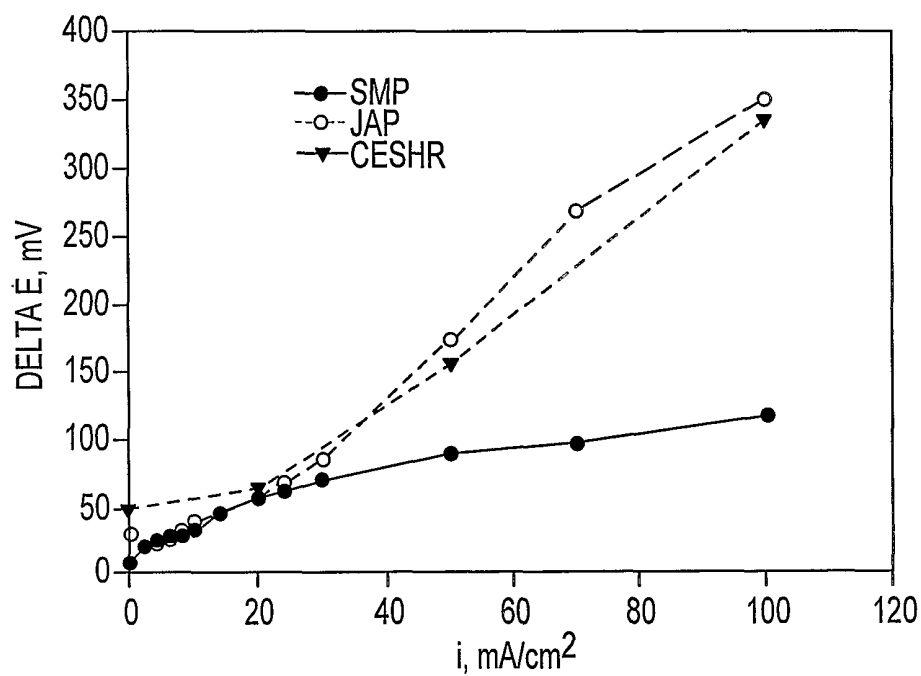


FIG.45