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(54) METHOD OF MANUFACTURING ELECTROCATALYSTS FOR USE IN FUEL CELL ELECTRODES

(71) We, UOP INC. a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement—:

The present invention relates to electrocatalysts which may be utilized in electrodes which form an element of an electrochemical cell such as is described in U.S. Patent No.3,651,386.

An electrochemical cell is basically comprised of an anode and a cathode positioned in an electrolyte and connected in an external circuit, although many variations of the physical arrangement of the three components are possible. An electrochemical cell is a device which permits the performance of oxidation or reduction reactions electrochemically, that is, by way of an electron transfer reaction at an electrode electrolyte interface. Oxidation reactions take place at the anode while reduction reactions take place at the cathode.

Electrochemical cells can be classified according to their use. Some produce energy and are called batteries. Others are used to produce chemicals under the use of energy and are called electrolysis cells.

There are a great many different types of energy producing electrochemical cells, such as primary batteries, secondary batteries, fuel cells and batteries which are combinations where one electrode may be a fuel cell electrode, the other a conventional battery electrode, such as is the case in the zinc-air battery.

If the cell is a fuel cell, fuel is supplied from an external source to the anode where it is oxidized, thereby freeing electrons which flow in the external circuit. The oxidation of the fuel also results in the production of hydrogen ions at the anode. These hydrogen ions pass through the electrolyte to the cathode, where they combine with oxygen and electrons to form water. Electrodes of a fuel cell may be of the diffusion type, and usually are porous and have at least one surface impregnated with a catalyst, such as the catalyst substance of this invention. Chemical and catalytic action takes place only at the interface between the electrolyte, the reacting gas, and an electrode.

As it is desirable to design an electrochemical cell so as to increase the surface of this interface, the electrodes are often constructed with at least one surface of a porous material and with possibly a hollow interior. The reacting fuel gas and the oxygen are forced into the interior of the pores of the respective electrodes where the gases meet the electrolyte. The electrochemical reactions take place at a three phase boundary area. It is at this boundary area of the anode or cathode that oxidation of the fuel and reduction of the oxygen takes place, thereby producing electricity in the external circuit, and it is this boundary area that has to have catalytic activity.

Fuel cells are often classified on the basis of their mode of operation. Typical high temperature fuel cells which operate at 800° to 1200 °C use solid electrolytes and gaseous fuels. Molten salt electrolytes are used in fuel cells operating at temperatures from 400° to 800 °C. They use gaseous fuels also. Low temperature fuel cells operate at temperatures from ambient to 200° or 300 °C use liquid, dissolved or gaseous fuels. The oxidizing agent in most fuel cells is air, although others such as chlorine gas may be used as well. The range of available fuels is much larger. Examples are hydrogen, alcohols, hydrazine, hydrocarbons, and many more. The power which can be obtained from a battery is given by the current which can be drawn under a given voltage. It is characteristic of all chemical energy conversion devices that the voltage difference between the anode and cathode decreases as the current goes up. This voltage decrease is called polarization. Since one always attempts to obtain the highest power output possible, one is constantly striving to reduce the polarization of the fuel cell electrodes. This is achieved by increasing the temperature of operation or by the use of an electrocatalyst such as is claimed in this invention.

The electrodes are often composed of a structural base section and a catalyst material mounted on the base. The structural base section usually takes the form of conductive screens or gauzes. The electrode is held in place by an electrically conductive holder having an opening. It is upon this opening that the electrode is mounted. The holder is made of electroconductive material, such as copper, silver, carbon and the like. The holder is directly connected to the electric terminal of the external circuit and is hollow with an inlet opening through which fuel or oxygen (air) may be supplied to one side of the electrode. The electrode assembly is located below the surface of the electrolyte such that the other surface of the electrode is in contact with this electrolyte.

A typical gas diffusion electrode used in the manner described above permits the fuel gas or oxygen or air to diffuse into the interior of the pores of the electrode from one side while the electrolyte penetrates the pores from the electrolyte side. In this manner, an extended area or interface for three phase contact is achieved.

This is often brought about by incorporating a certain hydrophobicity into the electrolyte by compacting the catalyst material with hydrophobic powderous plastic material or by such techniques as spraying one surface with a solution of polytetrafluoroethylene, oil, or other polymeric materials, or any other suitable means. Appropriate plastic polymers include porous polytetrafluoroethylene, porous polyethylene, porous polyurethane foams, polystyrene, regenerated cellulose (as sold under the Registered Trade Mark CELLOPHANE), polyvinylidene chloride, polyvinyl chloride, polyvinyl ethyl ether, polyvinyl alcohol, polyvinyl acetate, polypropylene cellulose, polymethyl methacrylate, butadiene-styrene copolymers, styrenated alkyd resins, some poly-exoxide resins, and chlorinated rubber.

The success of an electrochemical cell using a catalyst is fundamentally measured by the cost of producing electricity in the cell. Factors which are determinative of this cost include the temperature at which for example a fuel cell must be maintained during operation, the coulombic efficiency at which the fuel is oxidized, the cost of the fuel used, the cost of the catalyst used, and the life or stability of the catalyst, and finally the thermodynamic efficiency.

An important object of fuel cell development is to obtain high discharge voltage at current rates which produce a good watt/pound ratio. This can be achieved if the current-voltage characteristic of the electrode is close to the theoretical Tafle slope and exhibits a minimum of overvoltage.

The prior art has disclosed various fuel cell electrode catalysts which may be used in an electromechanical cell. For example, U.S. Patent No.3,857,737 discloses a fuel cell electrode catalyst comprising a noble metal catalyst such as platinum deposited on particles of an inert carrier such as carbon, the catalyst being prepared by admixing the carbon powder with a salt of platinum to form a slurry followed by concentration and drying. Likewise, U.S. Patent No.3,364,074 discloses a carbon containing electrode which is contacted with an organic solution containing a wetproofing agent for the electrode and an organometallic compound, the electrode then being heated at a temperature sufficient to decompose the organic portion of the organometallic compound to form the desired electrode. Another U.S. Patent which discloses an electrochemical cell is U.S. Patent No.3,881,957 in which a support such as an inorganic refractory oxide may be preimpregnated with a metal and thereafter the inorganic refractory oxide containing a coating of the catalytic metal is heated in an atmosphere containing an organic pyrolyzable material whereby a pyropolymer is deposited on the surface of the support. However, the electrocatalyst thus prepared possesses a drawback or defect in that the temperature which is required to pyrolyze the organic pyrolyzable substance is of the magnitude of from 400° to 900 °C, the preferred range being from 850° to 900 °C. The use of a temperature of this magnitude will agglomerate the metal crystallites and increase the size of the crystal. This increased crystal size may be deleterious to the function of the electrocatalyst due to the fact that the surface of the catalytic metal will be minimized and will therefore decrease the activity of the electrocatalyst. As will hereinafter be shown in greater detail, in contradistinction to this method of preparing an electrocatalyst, the process of the present invention will permit the preparation of an electrocatalyst wherein the catalytic metal is impregnated on the surface of the carbonaceous pyropolymer at temperatures which will not disturb the crystallite size of the metal and therefore the crystallite size will remain in a desired range.

The present invention seeks to provide a method for the preparation of an electrocatalyst suitable for use in an electrochemical cell whereby the electrodes of which the electrocatalyst is one element will function in an efficient manner for a relatively long period of time in a stable manner.

According to the invention there is provided a method for the preparation of an electrocatalyst which comprises treating an inorganic refractory oxide having a surface area of from 1 to 500 square meters per gram with a pyrolyzable organic compound at pyrolysis conditions to form at least a monolayer of a carbonaceous pyropolymer on the surface of said inorganic refractory oxide, thereafter impregnating the resultant composition with a solution containing at least one compound of a catalytically active metal, heating the composite to a temperature sufficient to remove the solvent, reducing said composite in a reducing atmosphere at reducing conditions, and recovering the resultant electrocatalyst.

In one embodiment of the method the polymer-containing composite is impregnated with a complex of a soluble salt of at least one catalytically active metal and a sulfur-containing carboxylic acid, e.g. a complex of a soluble salt of platinum and thiomalic acid.

The invention also provides an electrochemical fuel cell having an electrode of which one element is an electrocatalyst comprising an inorganic refractory oxide having a surface area of from 1 to 500 square meters per gram and a carbonaceous pyropolymer forming at least a monolayer on said refractory oxide, the surface of said pyropolymer having at least one catalytically active metal impregnated thereon, as well as the electrocatalyst and electrode themselves.

In a specific embodiment of such a fuel cell one element of an electrode is an electrocatalyst which comprises gamma-alumina and a carbonaceous pyropolymer forming at least a monolayer on said gamma-alumina, the surface of said pyropolymer containing from 0.5 to 20% by weight of platinum (based on the weight of the electrocatalyst) impregnated thereon.

A preferred method according to the invention for the preparation of an electrocatalyst comprises treating gamma-alumina with benzene in a reducing atmosphere at a temperature in the range of from 400° to 1200 °C to form at least a monolayer of a carbonaceous pyropolymer on the surface of said gamma-alumina, thereafter impregnating the resultant composition with a solution containing platinum, heating the composite at a temperature in the range of from 100° to 400 °C to remove the solvent, reducing the composite in the presence of hydrogen at a temperature in the range of from 200° to 600 °C, and recovering the resultant electrocatalyst.

As hereinbefore set forth, the present invention is concerned with a method for the preparation of electrocatalysts which may be used in electrodes. The performance of fuel cell electrocatalysts of the type hereinafter set forth in greater detail is in general substantially improved when both the particle size of the catalyst particulate and the crystallite size of the promoter metal or combination of metals are at a minimum value. In order to produce high performance fuel cell electrocatalysts which contain the catalytic metal in small-sized crystallites with minimum of metal crystallite agglomeration, the electrocatalysts must be prepared in such a manner that on deposition of the catalytically active metal on the surface of the carbonaceous pyropolymer coated refractory inorganic oxide the metal crystallites are prevented from agglomerizing. In order to effect this particular type of deposition, and in accordance with a preferred embodiment of the invention, the catalytically active metal is complexed with a compound which is present, preferably in a molar excess over the metal, whereby the crystallite size of the metal and the agglomeration are at a minimum.

The electrocatalyst which is prepared according to the process of this invention comprises a refractory inorganic oxide possessing a surface area of from 1 to 500 square meters per gram and a carbonaceous pyropolymer forming at least a monolayer on said refractory oxide, the surface of said carbonaceous pyropolymer having at least one catalytically active metal impregnated thereon. The electrocatalyst in general possesses a conductivity at room temperature of from 10^{-8} to 10^{+2} inverse ohm-centimeters. This electrocatalyst can form one element of an electrode for an electrochemical cell such as a phosphoric acid electrolyte fuel cell, replacing the noble-metal-impregnated carbon electrocatalysts which have been used in the prior art.

The electrocatalyst is prepared according to the present invention by treating an inorganic refractory oxide of the type hereinbefore set forth, that is, an inorganic refractory oxide possessing a surface area of from 1 to 500 square meters per gram, with a pyrolyzable organic compound at temperature conditions which are sufficient to pyrolyze the inorganic compound to form a carbonaceous pyropolymer i.e. a polymer containing carbon and hydrogen atoms in recurring units. Examples of refractory inorganic oxides which may be treated with the pyrolyzable organic compound include alumina such as gamma-alumina, eta-alumina and theta-alumina, silica and alumina-silica. In one method of preparing the composite, the inorganic refractory oxide is heated to a temperature of from 400° to 1200 °C in a reducing atmosphere containing an organic pyrolyzable compound. The organic pyropolymer precursors most commonly and preferably used for the purposes of this invention are aliphatic hydrocarbons, aliphatic halogen derivatives, aliphatic oxygen derivatives, aliphatic sulfur derivatives, aliphatic nitrogen derivatives, organometallic compounds, alicyclic compounds, aromatic compounds and heterocyclic compounds. Of the aliphatic hydrocarbons, the more common classes which may be utilized to perform this invention are alkanes, alkenes, alkynes and alkadienes. Ethane, propane, butane and pentane are among the alkanes that may be used in the performance of this invention. Similarly, alkenes which suffice include ethene, propene, 1-butene, 2-butene and 1-pentene. Alkynes which may be used include ethyne, propyne, 1-butyne, 2-butyne, 1-pentyne and 1-hexyne. 1,3-Butadiene and isoprene are included among the alkadienes which may be utilized. Among the aliphatic halogen derivatives which suffice for the purposes of this invention are monohaloalkanes, polyhaloalkanes and unsaturated halo compounds. In the monohaloalkane subgroup, chloromethane, bromoethane, 1-iodopropane and 1-chlorobutane may be used. Polyhaloalkanes such as carbon tetrachloride, chloroform, 1,2-dichloroethane and 1,2-dichlorobutane may also be utilized. One unsaturated halo compound which may be utilized is chloroprene.

The aliphatic oxygen derivatives for use as pyropolymer precursors include alcohols, ethers, halohydrins and alkene oxides, saturated aldehydes and ketones, unsaturated aldehydes and ketones, ketenes, acids, esters, organic salts and carbohydrates. Alcohols which may be utilized include ethanol, 2-butanol, 1-propanol, glycols (e.g. 1,3-propanediol) and glycerol. Ethers which may be utilized include ethyl ether, and isopropyl ether. Appropriate halohydrins and alkene oxides include ethylene chlorohydrin, propylene chlorohydrin, ethylene oxide and propylene oxide. Suitable saturated aldehydes and ketones include formaldehyde, acetaldehyde, acetone and ethyl methyl ketone. Unsaturated aldehydes and ketones which may be used include propenal, trans-2-butenal and butenone. Ketene has also been successfully used as an organic pyrolyzable substance. Likewise, formic acid, acetic acid, oxalic acid, acrylic acid, chloroethanoic acid, formic anhydride and formyl chloride may also be utilized. Esters such as methyl formate, ethyl formate and ethyl acetate may also be used. Salts such as sodium formate, potassium acetate and calcium propionate may be utilized, as may a variety of carbohydrates. The broad classification of aliphatic sulfur derivatives may be broken down into the subclasses of alkanethiols, alkylthioalkanes, sulfonic acids and alkyl sulfates and alkyl metallic sulfates. Suitable among the alkanethiols are ethyl mercaptan and *n*-propyl mercaptan. Among the alkylthioalkanes usable are the thioethers, alkyl sulfides, methyl sulfide, ethyl sulfide and methyl propyl sulfide. Ethyl sulfonic acid and *n*-propyl sulfonic acid are sulfonic acids which may also be successfully used. Ethyl sulfate and sodium laurel sulfate are also appropriate for use.

The broad class of aliphatic nitrogen derivatives may be broken down into the subclasses of nitroalkanes, amides, amines, nitriles, and carbylamines. Nitroethane and 1-nitropropane are exemplary of suitable nitroalkanes while acetamide and propionamide are among the appropriate amides. Amines such as dimethylamine and ethylmethylamine, nitriles such as acetonitrile and propionitrile, and carbylamines such as ethyl isocyanide may also be used for the organic pyrolyzable substance of this invention. Organometallic compounds such as tetraisopropyl titanate, tetrabutyl titanate, and 2-ethylhexyl titanate may also be used.

Particularly appropriate and preferred for use as the organo pyrolyzable substance of this invention are the alicyclic compounds. Foremost among these are cyclohexane and cyclohexene. Aromatic compounds include the subclasses of hydrocarbons, halogen compounds, oxygen derivatives, ethers, aldehydes, ketones, quinones and aromatic acids. Aromatic sulfur derivatives and aromatic nitrogen compounds may also be utilized. Among the hydrocarbons, benzene, naphthalene, anthracene and toluene may be utilized. Benzyl chloride and benzal chloride are appropriate halogen compounds, while phenol, *o*-cresol, benzyl alcohol and hydroquinone are among the suitable oxygen derivatives. Ethers such as anisole and phenetole, and aldehydes, ketones and quinones, such as benzaldehyde, acetophenone, benzophenone, benzoquinone and anthraquinone, may also be used. Aromatic acids such as benzoic acid, phenylacetic acid, and hydrocinnamic acid may be utilized while the aromatic sulfur derivative of benzenesulfonic acid will also serve successfully. The aromatic nitrogen compounds of nitrobenzene, 1-nitronaphthalene, aminobenzene and 2-amine toluene may also be successfully used as the organic pyrolyzable substance of this invention. Among the heterocyclic compounds, five member ring compounds such as furan, proline, coumarone, thionaphthene, indole, indigo and carbozole may be utilized. Six member ring compounds such as pyran, coumarin and acridine may also be utilized.

As can be seen, an extremely wide latitude can be exercised in the selection of the organic pyrolyzable substance since virtually any organic material that can be vaporized, decomposed and polymerized on the refractory oxide by heating will suffice.

In another embodiment the composite may be prepared by impregnating the inorganic refractory oxide with a solution of a carbohydrate material such as dextrose, sucrose, fructose or starch, thereafter drying the impregnated support and then subjecting it to pyrolysis temperatures in the range hereinbefore set forth whereby a carbonaceous pyropolymer similar in nature to those hereinbefore described is formed in at least a monolayer on the surface of the inorganic refractory oxide support.

It has been found that the specific carbon concentration corresponding to a particular conductivity is a function of the pyrolyzable substance used to build the carbonaceous pyropolymer as well as of the temperature which is utilized to effect the pyrolysis. For example, a carbon concentration of 31.7% by weight with a pyropolymer produced from cyclohexane results in a conductivity of about 4×10^{-3} inverse ohm-centimeters, while a carbon concentration of 21.1% by weight with a pyropolymer produced from benzene results in a conductivity of about 4×10^{-2} inverse ohm-centimeters. This indicates a difference in the pyropolymer structure as between the pyropolymers produced from different pyrolyzable substances. This difference is due to organic residues not included in the extended, conjugated double-bond structure. Such a difference indicates that extraneous carbon structures may be eliminated from the pyropolymer by a proper choice of starting materials. One particularly advantageous choice is a mixture of benzene and *o*-oxylene. Demethylation of the xylene to produce the benzyl radical or diradical promotes the formation of large aromatic polynuclear networks without extraneous, non-conjugated network elements by providing a large concentration of nucleation radicals. This results in an organic semiconducting material having a high conductivity with a relatively low carbon concentration. Similar results can be achieved using mixtures of *o*-xylene and naphthalene, *o*-xylene and anthracene and halogenated or dihalogenated benzene and benzene, naphthalene or anthracene. It has also been found that the greater the temperature of pyrolysis which is employed, the greater will be the conductivity of the resulting product.

The inorganic refractory oxide support which is utilized as one component of the electrocatalyst of the present invention may be ground to the desired size prior to treatment with the organic pyrolyzable compound using conventional means such as ball mills, or if so desired, the semiconducting material comprising the inorganic refractory oxide containing at least a monolayer of a carbonaceous pyropolymer which consists of recurring carbon and hydrogen atoms on the surface thereof, may be ground to the desired size upon completion of the pyrolysis step of the process. In a preferred embodiment of the invention the particle sizes which are utilized for treatment with the catalytically active metal range from 0.5 or less to 50 microns in diameter, the preferred size for use in the preparation of an electrode for fuel cells being 1 micron or less.

Following the preparation of the pyropolymer composite it is then impregnated with a solution of at least one compound of a catalytically active metal to form the desired electrocatalyst material. The impregnation is preferably effected by treating the composite with an aqueous or organic solution of the desired metal or combination of metals in an amount sufficient to deposit at least one catalytically active metal in compound form on the surface of the carbonaceous pyropolymer in an amount ranging from 0.5 to 20% by weight, calculated as elemental metal based on the weight of the final catalytic composite. Examples of catalytically active metals and mixture of metals include platinum, platinum and rhenium, platinum and rhodium, platinum and tungsten, platinum and nickel, platinum and ruthenium, platinum and lead, platinum and germanium, palladium, palladium and rhenium, palladium and rhodium, palladium and tungsten, palladium and nickel, palladium and ruthenium, palladium and lead, and palladium and germanium. It is to be understood that the aforementioned list of catalytically active metals are only representative of the type of metals which may be impregnated on the surface of the carbonaceous pyropolymer and that the present invention is not limited thereto.

Preferably, in order to provide an electrocatalyst in which the catalytically active metal or combination of metals which are impregnated on the surface of the carbonaceous pyropolymer fall within the optimum size range as well as being present in a minimum of metal crystallite agglomeration, the impregnation is effected by forming a complex of a soluble salt of the catalytically active metal or a combinnation of soluble salts of catalytically active metals with a sulfur-containing carboxylic acid. The complex may be formed by admixing a soluble salt of the catalytically active metal, usually in aqueous form, with the sulfur-containing carboxylic acid, the latter suitably being present in an amount of from 1 to 3 moles of sulfur-containing carboxylic acid per gram atom of catalytically active metal. Examples of water-soluble salts of catalytically active metals which may be employed include chloroplatinic acid, chloroplatinous acid, platinous chloride, platinic chloride, chloropalladic acid, chloropalladous acid, palladic chloride, palladous chloride, rhenic chloride, rhenous chloride, chlororhenic acid, chlororhenous acid, chlororuthenic acid, chlororuthenous acid, ruthenium chloride, tin chloride, germanium chloride and rhodium chloride, as well as the corresponding nitrates, sulfates, chlorates and carbonates. The aforementioned water-soluble salts of the catalytically active metals are admixed with sulfur-containing carboxylic acids, and preferably a thio- or mercaptocarboxylic acid, specific examples of these compounds being thiomalic acid, thioglycolic acid, thiocarbonic acid, thiolactic acid, thioglyoxylic acid, thioglyceric acid, thiotartronic acid, thiotartaric acid, mercaptoacetic acid, mercaptopropionic acid, mercaptobutyric acid and mercaptovaleric acid. It is to be understood that the aforementioned water-soluble salts of catalytically active metals and sulfur-containing carboxylic acids are only representative of the type of compounds and that the present invention is not limited thereto.

In a preferred method, by utilizing a composite of the salt of the catalytically active metal and the sulfur-containing compound it is possible to impregnate the surface of the carbonaceous pyropolymer in such a manner that the crystallite size of the catalytically active metal will be maintained as small as possible, the mean diameter of the crystals being in a range of from 10 to 50 Angstroms. In addition, by utilizing a sulfur-containing carboxylic acid, it is possible to minimize the crystallite agglomeration of the catalytically active metal, thereby affording a greater surface area of the metal, which will enable the electrocatalyst to operate in a more efficient manner for a longer period of time when utilized as a component in an electrode.

In this preferred method, the impregnation of the carbonaceous pyropolymer composite is effected by admixing the complex with the composite in any suitable manner in order that the composite be thoroughly impregnated with the solution. In one embodiment of the invention the impregnation of the composite is effected in a series of steps, the number of steps ranging from 2 to 4 or more. When this type of operation is employed, the solution of the complex is divided into equal portions, the first portion being used to impregnate the composite which is thereafter dried and reduced in the presence of hydrogen at elevated temperatures ranging from 100° to 600 °C for a period of time ranging from 0.5 to 4 hours or more. The impregnation step is then repeated followed by further drying and further reduction until the predetermined amount of catalytically active metal is impregnated on the surface of the carbonaceous pyropolymer.

After impregnation of the composite, the solvent is removed by heating to a temperature, usually in the range of from 100° to 400 °C, which is sufficient to evaporate said solvent and leave the metal compound or mixture of metal compounds impregnated on the surface of the carbonaceous pyropolymer. Thereafter the electrocatalyst may then be dried, e.g. at elevated temperatures ranging from 100° to 200 °C for a period of time ranging from 2 to 6 hours or more. The final step in the preparation of the electrocatalyst according to the present invention is effected by subjecting the metal-impregnated carbonaceous pyropolymer-inorganic refractory oxide composite to a reducing step, which is suitably carried out in the presence of a reducing atmosphere or medium such as hydrogen at elevated temperatures of from 200° to 600 °C for a period of time ranging from 0.5 to 4 hours or more, whereby the metal compound is reduced to the metal in the form of particles. The resulting catalytically active metal impregnated carbonaceous pyropolymer-inorganic refractory oxide composite generally contains the catalytic metal or mixture of metals with metal loadings in a range of from 0.025 to 1.00 mg/cm^2, the mean particle size of the metal being in a range of from 10 to 25 Angstroms or more.

The electrocatalyst obtained according to the present invention may be utilized as a component of an electrode for an electrochemical cell such as a fuel cell by admixing the electrocatalyst with a support. The electrode may be prepared by any manner known in the art. For example, the electrocatalyst of the present invention which has been prepared in a manner hereinbefore set forth may be blended with a powder of polytetrafluoroethylene and the resulting mixture may be suspended in a suitable solvent such as water or an alcohol to form a co-suspension which is then deposited in any manner so desired on a substrate. The substrate may comprise any desired compound such as a tantalum screen or a porous graphite, the deposition being accomplished or achieved by any convenient method such as screen printing, spraying or a filter transfer process. The composite consisting of the substrate with the co-suspension deposited thereon may then be heated at an elevated temperature ranging from 300° to 400 °C for a period of time sufficient to sinter the polytetrafluoroethylene which will cause the polytetrafluoroethylene to diffuse and allow the electrocatalyst to adhere to the carrier or substrate. While this is one example of how an electrode for a fuel cell may be prepared, it is contemplated that any other method known in the art may also be employed to prepare the desired composite.

The electrodes thus prepared may be utilized in either alkaline or acid fuel cells. For example, the electrode may be used in an alkaline fuel cell comprising a housing formed of a suitable insulating material, such as the material sold under the Registered Trade Mark PLEXIGLAS, provided with openings for the insertion of conducting wire leads. The housing is provided with a central hollow portion which forms a containment well for the electrolyte material, e.g. sodium hydroxide or ammonium chloride. A zinc anode may be cemented to one interior wall of the containment well. In addition, an air well which possesses a communicating air inlet formed on the top portion of the housing and a communicating air vent formed on the lower portion of the housing is formed within said housing. A cathode comprising an electrode of the type of the present invention may be pressed between the electrolyte well and the air well. Another type of fuel cell which may be employed comprises the acid type fuel cell in which the electrode of the type herein described is affixed to a tantalum screen or a porous graphite current collector which is then placed on each side of a composite matrix. In addition, plates configured for the passage of air, oxygen and hydrogen and containing leads are pressed to the current collector to form the desired fuel cell. Air or oxygen may be passed through the plates to the electrodes which act as cathodes while hydrogen is passed through the plates to the electrodes which are utilized as fuel cell anodes.

As will hereinafter be shown in greater detail in the Examples, the electrodes containing the electrocatalysts of the present invention may be utilized in fuel cells, the performance of the electrodes after a relatively lengthy period of time exhibiting an efficiency which may slightly decrease during the duration of the period in which the electrodes are in use, but not to the point which would impair cell performance.

The following examples are given to illustrate the preparation of the electrocatalysts of the present invention and to their use in electrodes. However, these examples are given merely for purposes of illustration and are not intended to limit the scope of the present invention.

EXAMPLE I

A gamma-alumina which had been ground to a particle size possessing a mean of about 2 microns was calcined at a temperature of about 550 °C for a period of 3 hours. Following this the alumina powder was placed in a fluidized bed reactor and treated with benzene by passage of benzene over the alumina at a temperature of 900 °C for a period of 1.5 hours. The semiconducting carbonaceous pyropolymeric inorganic refractory oxide material was stabilized for an additional period of 1.5 hours at 900 °C and atmospheric pressure.

The semiconducting carbonaceous pyropolymeric inorganic refractory oxide material comprising 53.9 grams was commingled with 4.90 grams of a chloroplatinic acid solution containing 24.7% platinum admixed with 110 grams of de-ionized water. The above mixture was stirred in an evaporating dish for 0.5 hours at ambient temperature and thereafter the water was evaporated from the chloroplatinic acid impregnated semiconducting carbonaceous pyropolymeric inorganic refractory oxide material and after evaporation the impregnated composite was dried in an oven at 110 °C for a period of 6 hours. After drying, the material was reduced by treatment with hydrogen at a temperature of 535 °C for 1.6 hours in a vertical reactor. The physical characteristics of the composite included 2.24 wt. % of platinum, 40.35 wt. % of carbon, a surface area of about 82 square meters per gram (m^2/g) and a resistance at room temperature of 0.018 ohm-centimeters.

EXAMPLE II (Comparative)

As a comparison another electrocatalyst was prepared in which the catalytic metal was impregnated on a substrate and thereafter the metal impregnated substrate was subjected to the deposition of a pyropolymer on the surface thereof. In this example a gamma-alumina powder was calcined at a temperature of 550 °C for a period of 3 hours and thereafter 100 grams of this alumina base was commingled with 15.75 grams of 24.7% platinum admixed with 110 grams of de-ionized water solution in an evaporating dish at 25 °C for a period of 0.5 hours. Thereafter the solvent was evaporated on a steam bath followed by oven drying at a temperature of 110 °C for a period of 1.5 hours. The dried platinum impregnated alumina powder was then reduced by treatment with hydrogen at a temperature of 543 °C for a period of 2 hours.

The platinum impregnated alumina was coated with a pyropolymer by placing 35 grams of the platinum impregnated alumina in a fluidized bed reactor and subjecting it to the deposition of a carbonaceous pyropolymer on the surface thereof utilizing 33.6 grams of benzene at a temperature of 901 °C for a period of 1.5 hours at atmospheric pressure. After a stabilization period of an additional 1.5 hours at 901 °C had passed, the composite was recovered. This composite had a platinum content of 2.21 wt. %, a carbon content of 40.62 wt. %, a surface area of 68 m^2/g, and had a resistivity at room temperature of 0.010 ohm-centimeters.

EXAMPLE III

The two electrocatalysts which were prepared according to Examples I and II above were utilized to prepare electrodes for use in fuel cells. The electrocatalysts were wet blended with a polytetrafluoroethylene powder in an organic medium and after filtration a catalyst layer was formed by a calendering operation. The layer was then pressed onto a tantalum screen current collector and sintered in a nitrogen atmosphere at a temperature of about 335 °C. The catalyst layer was about 0.012 centimeters thick with a 5 milligram per cubic centimeter loading of the catalyst material.

The electrode evaluation was accomplished by forming a fuel cell in which the cell plates comprised a composite material molded from graphite and an acid resistant resin. The cell matrix consisted of a composite structure of Kynol fibers and a phenolic binder, said cell matrix being filled with phosphoric acid pretreated with hydrogen peroxide. The electrodes were placed on each side of the cell matrix and tested as fuel cell cathodes operating on air or oxygen and as fuel cell anodes operating on pure hydrogen. The electrocatalyst which was prepared according to Example I when tested in a fuel cell in air showed a current density of about 50 milliamps per square centimeter (ma/cm^2) and a voltage of 0.24 volts (voltage having been corrected to eliminate internal and lead resistance effects). When the electrode was used as an oxygen cathode, the current density was 155 ma/cm^2 at a voltage of 0.45 volts. In contradistinction to this, the electrocatalyst prepared according to Example II (that is, when the catalytically active metal was impregnated on the surface of the substrate prior to deposition of the carbonaceous pyropolymer thereon), when used as an air cathode in a fuel cell, had only a current density of 16 ma/cm^2 at a voltage of 0.21 volts and a current density of 42 ma/cm^2 at a voltage of 0.28 volts when used as an oxygen cathode.

EXAMPLE IV

An electrode was fabricated from an electrocatalyst consisting of a semiconductor carbonaceous pyropolymeric inorganic refractory oxide material consisting of a gamma-alumina substrate having a carbonaceous pyropolymer resulting from the pyrolysis of benzene at a temperature of 900 °C. The material had a carbon content of 34 wt. %, a surface area of 75 m^2/g, a mean particle size of 2 microns and a resistivity at 25 °C of 0.014 ohm-centimeters. The material was impregnated with an aqueous solution of chloroplatinic acid in an amount sufficient so that the electrocatalyst, after drying and reduction, had a platinum loading of 10 wt. %. After fabricating an electrode with a 0.5 m^2/g platinum loading using this electrocatalyst, the electrode was used in a fuel cell which was evaluated at a temperature of 140 °C. The electrode was tested as an air cathode, an oxygen cathode and a hydrogen anode. When used as an air cathode, the electrode had a voltage of 0.63 volts (voltage having been corrected to eliminate internal and lead resistance effects) at 100 ma/cm^2. The oxygen cathode had a voltage of 0.75 volts at 100 ma/cm^2 and the hydrogen had a voltage of 0.62 at 100 ma/cm^2.

EXAMPLE V

To illustrate the stability of electrodes formed from the electrocatalyst obtained according to the present invention, electrodes formed from electrocatalysts which possessed properties similar in nature to those set forth in Example IV above with the exception that the platinum loading of the electrode was 0.25 m^2/g was utilized in a fuel cell in which results were taken at the end of 24 hours and 2000 hours after start up. The test was run at 140 °C in a manner similar to that of Example IV. The results indicated that the air cathode performance increased steadily over the entire period thus indicating that the composite electrocatalyst possessed a good stability in the phosphoric acid fuel cell environment. A comparison of the voltage after having been corrected to eliminate internal and lead resistance effects is set forth in Table 1 below:

Table 1

	Hours	Current Density	Voltage
Oxygen Cathode	24	100 ma/cm^2	0.645
Oxygen Cathode	2000	100 ma/cm^2	0.630
Air Cathode	24	100 ma/cm^2	0.500
Air Cathode	2000	100 ma/cm^2	0.515

In like manner when the electrodes were tested as air cathodes utilizing a temperature of 180 °C in place of the 140 °C, the performance showed a 15% increase in the voltage maintained at 100 ma/cm^2 current density.

EXAMPLE VI

In this example a gamma-alumina base was ground to a particle size of from 1.3 to 2.5 microns. The alumina substrate had an apparent bulk density of 0.30, a surface area of from 70—75 square meters per gram (m^2/g) and a pore diameter of about 100 Angstroms. The base was calcined at a temperature of about 550 °C for a period of about 3 hours following which the powder was placed in a fluidized bed reactor and treated with benzene by passing said benzene over the alumina at a temperature of about 900 °C for a period of 1.5 hours. Following this, the semiconducting carbonaceous pyropolymeric refractory inorganic oxide material was stabilized for an additional period of 1.5 hours at atmospheric pressure. The material had a carbon content of 34.1 wt. % and a resistivity at room temperature of 0.02 ohm-centimeters.

A complex of chloroplatinic acid and thiomalic acid was prepared by admixing 3 moles of thiomalic acid per 1 gram atoms of platinum in an aqueous system. This complex was prepared by admixing 10.32 grams of an aqueous chloroplatinic acid solution containing 27.19% platinum with 6.47 grams of thiomalic acid and 60 grams of de-ionized water. After admixing the solution it was allowed to stand for 18 hours at room temperature in order to insure formation of the complex and was thereafter divided into two equal portions. Twenty-five grams of the semiconducting carbonaceous pyropolymeric refractory inorganic oxide base was treated with one-half of the complex in an impregnation step which consisted in admixing the two components with stirring for a period of 0.5 hours at 25 °C. At the end of this period, the impregnated base was dried in a static oven at a temperature of 110 °C for a period of 3.5 hours. Following this the dried base was then reduced in a stream of hydrogen at a temperature of 260 °C for a period of 2 hours. Analysis of this electrocatalyst showed that there was 4.9 wt. % platinum present, the crystallite size of said platinum having a nominal diameter of less than 25 Angstroms with only 1% agglomeration.

The preceding electrocatalyst was then treated with the remaining half portion of the chloroplatinic acid-thiomalic acid complex, dried at a temperature of 110 °C for a period of 3.5 hours and reduced for a period of 2 hours in a stream of hydrogen at a temperature of 260 °C. Analysis of the electrocatalysts which had been impregnated two times with the complex disclosed that said electrocatalyst contained 9.84 wt. % platinum, the crystallite size of said platinum having a nominal diameter of 34 Angstroms with a 3% agglomeration.

EXAMPLE VII

In a manner similar to that set forth in Example VI above, a semiconducting carbonaceous pyropolymeric refractory inorganic oxide material was prepared using the same technique. Following the preparation of the material it was impregnated with an aqueous chloroplatinic acid solution which did not contain any thiomalic acid. After drying and reducing the impregnated base it was found that said base contained 9.73 wt. % platinum in which the crystallite size of said platinum was 76 Angstroms and the agglomeration was 49%.

EXAMPLE VIII

An electrocatalyst which was prepared in a manner similar to that set forth in Example VI above was utilized to prepare an electrode for use in fuel cells. The electrocatalyst which, after impregnation of a gamma-alumina substrate containing carbonaceous pyropolymer thereon with a complex of chloroplatinic acid and thiomalic acid, was analyzed and found to contain 9.84 wt. % of platinum, the crystallite size of said platinum having a nominal diameter of 34 Angstroms with a 3% agglomeration. The electrocatalyst was wet blended with a polytetrafluoroethylene powder in an organic medium and after filtration a catalyst layer was formed by a calendering operation. The layer was then pressed onto a tantalum screen current collector and admixed in a nitrogen atmosphere at a temperature of about 330 °C. The catalyst layer was about 0.005 cm thick with a 0.50 mg/cm^2 loading of the catalyst material.

The evaluation of the electrode was accomplished by forming a fuel cell in which the cell plates comprised a composite material molded from graphite and an acid resistant resin. The cell matrix consisted of a composite structure of Kynol fibers and a phenolic binder, said cell matrix being filled with phosphoric acid which had been pretreated with hydrogen peroxide. The electrodes were pressed on each side of the cell matrix and tested as fuel cell cathodes operating on air or oxygen. The electrocatalyst when tested in a fuel cell in air at a temperature of 140 °C showed a current density of about 100 milliamps per cubic centimeter (ma/cm^2) and a voltage of 0.63 volts (voltage having been corrected to eliminate internal and lead resistance effects). When the electrode was used as an oxygen cathode, the current density was 120 ma/cm^2 at a voltage of 0.73 volts.

Other electrocatalysts prepared by impregnating gamma-alumina which contains at least a monolayer of a carbonaceous pyropolymer on the surface thereof and which has been impregnated by utilizing aqueous solutions of chloropalladic acid, or mixtures of aqueous solutions of chloroplatinic acid and rhenium chloride or chloroplatinic acid and rhodium chloride which have been complexed with from 1 to 3 moles (per gram atom of catalytically active metal) of thioglycolic acid, mercaptoacetic acid, mercaptopropionic acid or mercaptobutyric acid and thereafter dried and reduced in the presence of hydrogen at elevated temperatures of from 100° to 600 °C may exhibit polarization curves similar in nature to the hereinbefore described electrocatalyst.

WHAT WE CLAIM IS:—

1. A method for the preparation of an electrocatalyst which comprises treating an inorganic refractory oxide having a surface area of from 1 to 500 square meters per gram with a pyrolyzable organic compound at pyrolysis conditions to form at least a monolayer of a carbonaceous pyropolymer on the surface of said inorganic refractory oxide, thereafter impregnating the resultant composition with a solution containing at least one compound of a catalytically active metal, heating the composite to a temperature sufficient to remove the solvent, reducing said composite in a reducing atmosphere at reduction conditions, and recovering the resultant electrocatalyst.

2. The method of claim 1 in which said pyrolysis conditions include a temperature in the range of from 400° to 1200 °C in a reducing atmosphere.

3. The method of claim 1 or 2 in which said temperature sufficient to remove the solvent is in a range of from 100° to 400 °C.

4. The method of any of claims 1 to 3 in which said reducing conditions include a temperature in the range of from 200° to 600 °C.

5. The method of any of claims 1 to 4 in which said inorganic refractory oxide is an alumina.

6. The method of claim 5 in which said alumina is gamma-alumina.

7. The method of any of claims 1 to 6 in which said catalytically active metal is platinum.

8. The method of any of claims 1 to 6 in which said catalytically active metal is palladium.

9. The method of any of claims 1 to 6 in which said catalytically active metal is a mixture of platinum and rhenium.

10. The method of any of claims 1 to 6 in which said catalytically active metal is a mixture of platinum and rhodium.

11. The method of any of claims 1 to 10 further characterized in that the impregnating solution comprises a complex of a soluble salt of at least one catalytically active metal and a sulfur-containing carboxylic acid.

12. The method of claim 11 in which said sulfur-containing carboxylic acid is thiomalic acid.

13. The method of claim 11 in which said sulfur-containing carboxylic acid is thioglycolic acid.

14. The method of claim 11 in which said sulfur-containing carboxylic acid is mercaptoacetic acid.

15. The method of claim 11 in which said sulfur-containing carboxylic acid is mercaptopropionic acid.

16. The method of claim 11 in which said sulfur-containing carboxylic acid is mercaptobutyric acid.

17. The method of preparing an electrocatalyst claimed in claim 1 and carried out substantially as hereinbefore described or exemplified.

18. An electrocatalyst when prepared by the method of any of claims 1 to 17.

19. An electrocatalyst comprising an inorganic refractory oxide having a surface area of from 1 to 500 square meters per gram and a carbonaceous pyropolymer forming at least a monolayer on said refractory oxide, the surface of said pyropolymer having at least one catalytically active metal impregnated thereon.

20. An electrode for an electrochemical cell comprising an electrocatalyst as claimed in claim 18 or 19.

21. An electrochemical fuel cell having an electrode of which one element is an electrocatalyst comprising an inorganic refractory oxide having a surface area of from 1 to 500 square meters per gram and a carbonaceous pyropolymer forming at least a monolayer on said refractory oxide, the surface of said pyropolymer having at least one catalytically active metal impregnated thereon.

22. An electrochemical fuel cell in which at least one of the electrodes comprises an electrocatalyst prepared by the method of any of claims 1 to 17.

23. A cell as claimed in claim 21 or 22 in which, in the electrocatalyst, the refractory inorganic oxide is gamma-alumina and the catalytically active metal is platinum in an amount of from 0.5 to 20% by weight based on the electrocatalyst.

24. A cell as claimed in any of claims 21 to 23 wherein at least one electrode comprises a composite of the electrocatalyst with a sinterable carrier deposited on a support substrate.

25. A cell as claimed in any of claims 21 to 24 which is an alkaline fuel cell having a zinc anode and a cathode of which one element is the electrocatalyst.

26. A cell as claimed in any of claims 21 to 24 which is an acid fuel cell having anode and cathode of each of which the electrocatalyst forms an element.

27. An electrochemical fuel cell as claimed in claim 21 or 22 and substantially as hereinbefore described or exemplified.

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