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(54) **Three-layer laminated matrix electrode.**

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Description

Background of the invention and prior art

Within the field of electrochemistry, there is a well-known type of electrolytic cell known as chlor-alkali cell. Basically this is a cell wherein chlorine gas and caustic soda, viz., sodium hydroxide, are produced by passing an electric current through a concentrated salt (brine) solution containing sodium chloride and water. A large portion of the chlorine and caustic soda for the chemical and plastic industries is produced in chlor-alkali cells.

Such cells are divided by a separator into anode and cathode compartments. The separator characteristically can be a substantially hydraulically impermeable membrane, e.g., a hydraulically impermeable cation exchange membrane such as the commercially available NAFION^R (trademark of E. I. Du Pont de Nemours and Co). Alternatively, the separator can be a porous diaphragm, e.g. asbestos, which can be in the form of vacuum deposited fibers or asbestos paper sheet as are well known in the art. The anode can be a valve metal, e.g., titanium, provided with a precious metal coating to yield what is known in the art as a dimensionally stable anode.

The cathodes employed in such chlor-alkali cells are subjected to the corrosive environment of the caustic soda and so special precautionary measures and techniques have been employed in an attempt to reduce damage and deactivation of the active layer particles contained in the cathode used in chlor-alkali cells.

One of the unwanted by-products present in a chlor-alkali cell is hydrogen which forms at the cell cathode. This hydrogen increases the power requirement for the overall electrochemical process and eliminating its production is one of the desired results in chlor-alkali cell operation. Fairly recently, attention has been directed in chlor-alkali cell technology to various forms of oxygen (air) cathodes. Such cathodes can result in significant savings in the cost of electrical energy employed to operate chlor-alkali cells. Estimates indicate that there is a theoretical savings of about 25% of the total electrical energy required to operate chlor-alkali cells provided that the formation of molecular hydrogen gas at the cathode can be prevented. In other words, about 25% of the electrical energy employed in a chlor-alkali cell is used to form hydrogen at the cathode. Hence, the prevention of hydrogen formation at the cathode can lead to significant savings in the cost of electrical power. This is one of the major benefits of and purposes for oxygen (air) cathodes. However, such cathodes, being in contact with the electrolyte caustic soda, are subjected to the corrosive action thereof.

One known form of oxygen (air) cathode involves use of an active cathode layer containing porous active carbon particles whose activity in promoting the formation of hydroxide may or may not be catalyzed (enhanced) using precious metal catalyst materials, such as silver, platinum, etc. The active carbon particles become wetted (flooded) by the caustic soda thereby significantly reducing their ability to eliminate the formation of hydrogen at the cathode and resulting in a loss of activity of the air cathode. Some attempts to overcome this difficulty involve incorporating hydrophobic materials, e.g., polytetrafluoroethylene (PTFE) in such active layers in particulate or fibrillated (greatly attenuated and elongated form) to impart hydrophobicity to the active carbon layer, per se. With the PTFE, however, comes the problem of reduced electrical conductivity in the cathode active layer in as much as PTFE, per se, in nonconductive when compared with the porous active carbon particles. Such active carbon/PTFE-containing electrode active layers are subject to loss of strength resulting in failure combined with blistering thereof when the chlor-alkali cell is operated at high current densities, viz., current densities ranging from about 250 mA/cm^2 and higher for prolonged time periods.

Some oxygen (air) cathodes contain PTFE in both the active layer and in a backing sheet laminated thereto. The PTFE has been employed in particulate or fibrillated (greatly attenuated and elongated) form to impart hydrophobicity to the desired layer. Thus it can be seen that the development of corrosion resistant oxygen (air) cathodes of improved durability for use in conjunction with chlor-alkali cells is an overall objective in the newly-developing oxygen (air) cathode field.

Field of the invention

The present invention is directed to a gas, e.g., oxygen (air) electrode containing an improved fibrillated matrix electrode active layer and a process for forming the electrode such that the active layer when laminated to a backing (wetproofing) sheet and current collector results in an oxygen (air) cathode having high durability and resistance to degradation due to the corrosive environment present in a chlor-alkali cell, fuel cell, etc. In other words, the fibrillated, matrix active layer produced in accordance with this invention is capable of long life with a lower rate of decline in operating voltage. The term "matrix" is employed herein in as much as it is believed that in an electrode of this type, the catalyzed active carbon is thoroughly involved with assisting the reduction of oxygen within the cathode active layer while the carbon black and the PTFE act in one or more ways; (a) as a hydrophobic gas path, (b) as a conductive agent, which lowers the electrical resistance of the mixture from about 2 or 3 times, resulting in a better current distribution to the current collector, and (c) as a hydrophobic binder, incorporating the wet active carbon in a matrix of PTFE/carbon black.

U.S. Patent 4 058 482 discloses a sheet material principally comprised of a polymer such as PTFE and a pore-forming material wherein the sheet is formed of co-agglomerates of the polymer and the pore former. This patent teaches mixing polymer particles with positively charged particles of a pore former, e.g., zinc oxide, to form co-agglomerates thereof followed by mixing same with a catalyst suspension so as to form co-agglomerates of catalyst and polymer-pore-former agglomerates followed by pressing, drying, and sintering these co-agglomerates. Subsequent to this sintering, the pore former can be leached out of the electrodes.

U.S. Patent 4 150 076 (a division of U.S. Patent 4 058 482) is directed to the process for forming the sheet of U.S. Patent 4 058 482, said process involving formation of polymer-pore-former co-agglomerates, distributing same as a layer on a suitable electrode support plate, for example, a carbon paper, to form a fuel cell electrode by a process which includes pressing, drying, sintering, and leaching.

U.S. Patent 4 170 540 to Lazarz et al discloses microporous membrane material suitable for electrolytic cell utilization and formed by blending particulate polytetrafluoroethylene, a dry pore-forming particulate material, and an organic lubricant. These three materials are milled and formed into a sheet which is rolled to the desired thickness, sintered, and subjected to leaching of the pore-forming material. The present invention avoids the use of lubricants and similarly avoids the necessity of removing same. Additionally, according to the present invention, when forming the sheet by passing the fibrillated mixture of PTFE-particulate pore-forming agent through the rollers, special care is taken to avoid conditions which would cause the PTFE to sinter.

British Patent 1 284 054 to Boden et al is directed to forming an air-breathing electrode containing an electrolyte within an air-depolarized cell. This air-breathing electrode is made by hot pressing a fluoropolymer sheet containing a pore-forming agent onto a catalyst composition (containing silver) and a metallic grid member. According to page 3 of said British patent, the PTFE-pore-forming agent-paraffin wax containing sheet, is subjected to a solvent wash to remove the paraffin wax and then sintered and while it still contains the pore-forming particles, it is then ready for application to the catalyst composition of the air electrode for the hot pressing operation. Hot pressing involves the use of pressures ranging from about 350 to about 2.05 10^8 N/m^2 in conjunction with temperatures ranging from about 94°C to 205°C.

U.S. Patent 3 385 780 to I-Ming Feng discloses a thin, porous electrode consisting of a thin layer of a polytetrafluoroethylene pressed against a thin layer of polytetrafluoroethylene containing finely divided platinized carbon, the platinum being present in amount of 1.2 to 0.1 mg/cm^2 in the electrically conductive face of the thin electrode, viz., the side containing the platinized carbon, viz., the active layer. A thermally decomposable filler material can be used, or the filler can be a material capable of being leached out by either a strong base or an acid. U.S. Patent 3 385 780 also mentions a single unit electrode involving finely divided carbon in mixture with PTFE.

U.S. Patent 4 135 995 to Cletus N. Welch is directed to a cathode having a hydrophilic portion formed of a solid intercalation compound of fluorine and carbon of the empirical formula CF_x, where x ranges from about 0.25 to 1 and preferably ranges from about 0.25 to 0.7. The intercalation compounds of carbon and fluorine are referred to as hydrophilic, fluorinated graphites and graphite fluorides characterized by an infrared spectrum showing an absorption band at 1220 cm^{-1}. A layer of hydrophobic material, such as polyperfluoroethylene (polytetrafluoroethylene) can be utilized in a hydrophobic portion of the same layer or it can be utilized in the form of a different layer which can be associated with a current carrier layer. The Welch cathode may be utilized as an oxygen (air) cathode.

U.S. Patent 3 838 064 to John W. Vogt et al is directed to a process for dust control involving mixing a finely divided fibrillatable polytetrafluoroethylene with a material which characteristically forms a dust to form a dry mixture followed by sufficient working to essentially avoid dusting. Very small concentrations of PTFE, e.g., from about 0.02 to about 3% by weight, are employed to achieve the dust control. Corresponding U.S. Patent 3 838 092 also to Vogt et al is directed to dustless compositions containing fibrous polytetrafluoroethylene in concentrations of about 0.02% to less than 1%, e.g., about 0.75% by weight, of PTFE based on total solids.

An article entitled "On the Effect of Various Active Carbon Catalysts on the Behavior of Carbon Gas-Diffusion Air Electrodes: 1. Alkaline Solutions" by I. Iliev et al appearing in the *Journal of Power Sources*, 1 (1976/1977) 35, 46. On pages 35 to 46 of said Journal there are described double layer fixed-zone, PTFE-bonded carbon electrodes having a gas supplying layer of carbon black "XC" (not further defined by the authors) wetproofed with 35% PTFE and an active layer consisting of a 30 mg/cm^2 mixture of the same wetproof material "XC-35" and active carbon "weight ratio of 1:2.5". These electrodes were sintered at 350°C under a pressure of 1.96 10^7 N/m^2 and employed as oxygen (air) cathodes in alkaline test environments.

The active layers and laminates of this invention are also readily distinguishable from the oxygen (air) cathodes described in Iliev et al. In accordance with this invention, the active layer is a "matrix" layer prepared essentially by shear blending (fibrillating) a combined mixture of two separately formed mixes which are in turn mixed, chopped and then fibrillated to result in a coherent, self-sustaining sheet having a tensile strength characteristically exceeding 6.8×10^5 N/m^2 (100 psi). Such active layers, when laminated, yield a matrix electrode having an unusual combination of high tensile strength with resistance to blistering under high current densities in use. It will be observed that the conditions employed in formation of the two separately formed mixtures and fibrillation thereof are insufficient to affect sintering of the PTFE contained in said matrix electrode.

The publication "Advances in Chemistry Series", copyright 1969, Robert F. Gould (Editor), American Chemical Society Publications, contains at pages 13 to 23 an article 3e entitled "A Novel Air Electrode" by H. P. Landi et al. The electrode described contains 2 to 8% PTFE, is produced without sintering and is composed of graphitic carbon (ACCO Graphite) or metallized graphitic carbon particles blended with a PTFE latex and a thermoplastic molding compound to form an interconnected network which enmeshes the filter particles. This blend is molded into a flat sheet and the thermoplastic is then extracted.

British Patent 1 222 172 discloses use of an embedded conductive metal mesh or screen 35 with a formed electrode 30 containing a particulate matrix 34 of polytetrafluoroethylene polymer particles 21 in which there are located dispersed electrically conductive catalyst particles 24 which can be silver-coated nickel and silver-coated carbon particles, viz., two different types of silver-coated particles in the PTFE particulate matrix in an attempt to overcome an increase in resistance as silver is consumed in the gas diffusion fuel cells to which said British Patent is directed.

The US patent No. 3,943,006 discloses a method of making an electrode structure for fuel cells comprising blending of noble metal black particles, particules of dry polytetrafluoroethylene (PTFE) and particles of soluble bulking agent in a liquid. The electrode bulking agent is insoluble in the liquid. Polytetrafluoroethylene constitutes at least 10% of the combined weight of the noble metal black and PTFE. After blending the liquid is filtered from the blend to form a filtered mixture. The filtered mixture is then subjected to rolling to form a sheet of fibrillated PTFE containing noble metal black and bulking agent. Upon rolling the remainder of the blending liquid is removed and the electrode sheet sintered at 325°C to allow the PTFE in the electrode to set.

Brief summary of the invention

The active layer of this invention is comprised of active carbon particles present within an unsintered network (matrix) of fibrillated carbon black/PTFE. The laminated gas electrode of this invention are comprised of said active layer laminated on the electrode working surface to a current distributor and on its opposite surface to a porous coherent, hydrophobic, polytetrafluoroethylene-containing wetproofing layer.

The active carbon particles of the active layer preferably are catalyzed to contain silver or platinum and range in size from about 1 to 30 micrometers. The unsintered network (matrix) contains from about 25 to 35 weight parts of polytetrafluoroethylene and about 75 to 65 weight parts of carbon black having a surface area ranging from about 25 to 300 m^2 per gram and particle size ranging from about 0.005 to 0.3 micrometers. The active layer contains a pore-forming agent and the concentration of active carbon therein ranges from about 40 to 80% by weight.

It should be understood that so long as the active layer is incorporated therein, the present laminates can incorporate any backing layer and any current distributor, respectively, including those of the prior art disclosed herein. Of course, then such laminates will not posses the specific desirable characteristics obtainable in the specific laminates formed and referred to herein. Nevertheless, the present invention in its broadest aspects embraces the active layer with any wetproofing (backing) .layer and any current distributor.

Detailed description of the invention

The backing (wetproofing layer)

The three-layer laminated electrodes produced in accordance with this invention contain an outer wetproofing or backing layer the purpose of which is to prevent electrolyte from coming through the active layer and wetting the gas side of the active layer and thereby impeding access of the oxygen (air) gas to the active layer. Such backing layer can be made porous by incorporating a pore former in polytetrafluoroethylene and can be made conductive by incorporating carbon black particles, per se, or carbon black particles which have been partially fluorinated to certain extents of fluorination, as will be pointed out in more detail hereinafter.

When it is desired to employ a porous PTFE backing layer made by the single-pass procedure and containing chiefly only a pore former and PTFE, the backing layer can be prepared using the PTFE particles in the form of a nonaqueous dispersion (eg. the PTFE DuPont Teflon® 6A series) which, consists of coagulates or agglomerates having a particle size of about 500 to 550 micrometers which were made by coagulating PTFE dispersed particles of about 0.05 to 0.5 micrometers and having an average particle size of about 0.2 micrometers. These agglomerates are dispersed in an organic liquid medium, usually a lower alkyl alcohol, such as isopropanol, and broken down by beating, e.g., in a high speed blender for about 3 minutes to redisperse same and break up the larger particles into smaller PTFE particles in isopropanol.

Then pulverized sodium carbonate particles, having particle sizes ranging from about 1 to about 40 micrometers, and more usually from about 5 to 20 micrometers, and preferably having an average particle size of 3 to 4 micrometers added to the alcohol dispersion of the blended PTFE particles in a weight ratio ranging from about 30 to 40 weight parts of PTFE to about 60 to about 70 weight parts of sodium carbonate to result in an intimate dispersion of PTFE with pore former. Then the alcohol is removed and the PTFE-Na_2Co_3 mix particles are dried.

Subsequent to drying, the particulate PTFE-sodium carbonate mixture is subjected to mixing under conditions which mildly fibrillate the PTFE. The mixing is conducted in a mixer with a charge of approximately 140 g of mix. This fibrillation is performed for approximately 10 to 20, e.g., 15, minutes at 100 rpm and 15° to 25°C. e.g., 20°C.

After fibrillating and before passing the mix between rolls, the fibrillated PTFE-pore former mix is chopped for 1 to 20 seconds, e.g., 5 to 10 seconds.

The mildly fibrillated mixture of PTFE-sodium carbonate is then dry rolled into sheet form using a single pass through one or more sets of metal, e.g., chrome plated steel rolls. Temperatures of about 70° to about 90°C and roll gaps ranging from about 0.13 to about 0.4 mm (5 to about 15 mils) are customarily employed. The conditions employed in the dry rolling are such as to avoid sintering of the PTFE particles.

On the other hand, when the laminate has a backing layer containing carbon particles to enhance the conductivity thereof, either unmodified carbon black particles, can be utilized to impart conductivity to the backing layer.

When utilizing unfluorinated carbon black particles to impart the conductivity to the PTFE-containing porous backing layer, carbon blacks can be employed which are electrically conductive. The term carbon black is used generically as defined in an article entitled "Fundamentals of Carbon Black Technology" by Frank Spinelli appearing in the August 1970 edition of *American Print Maker* to include carbon blacks of a particulate nature within the size range of 5 to 300 nanometers which includes a family of industrial carbons such as lampblacks, channel blacks, furnace blacks, thermal blacks, etc.

A preferable form of unmodified (unfluorinated) carbon black is acetylene carbon black, e.g., made from acetylene by continuous thermal decomposition, explosion, by combustion in an oxygen-deficient atmosphere, or by various electrical processes. Characteristically, acetylene black contains 99.5+ weight percent carbon and has a particle size ranging from about 0.005 to about 0.2 micrometers. The true density of the acetylene black material is approximately 1.95 g/cm^2. Preferably, the acetylene black is a commercially available acetylene black with a mean particle size of 0.0425 micrometers with a standard deviation of about 0.025 micrometers. Such acetylene blacks are somewhat hydrophobic, e.g., as demonstrated by the fact that the particles thereof float on cold water but quickly sink in hot water.

Hydrophobic electroconductive electrode backing layers can be prepared by combining the PTFE in particulate form as a dispersion with the carbon black particles as described above. According to a preferred embodiment of this invention, the acetylene carbon black employed is that having an average particle size of approximately 0.0425 micrometers with the remainder having a standard deviation of 0.025 micrometers. The range of particle size is from about 0.005 to about 0.2 micrometers.

These acetylene black particles are mixed with PTFE particles by adding a commercially available aqueous dispersion of PTFE, (e.g. DuPont "Teflon® 30") to the carbon black, also dispersed in water to form an intimate mixture thereof. The mix can contain from about 50 to about 80 weight % carbon black and from about 20 to about 50 weight % PTFE. Water is removed and the mix is dried. The dried mix can then be heated at 275° to 300°C for 10 to 80 minutes to remove a substantial portion of the wetting agent used to disperse the PTFE in water. Approximately 50 weight % of this mix is fibrillated (as described above in relation to the "one-pass" process) and then mixed with the remaining unfibrillated mix. A water soluble pore-forming agent, e.g., sodium carbonate, can be added thereto and the carbon black mixture with polytetrafluorethylene and pore former mixed.

Such conductive PTFE/carbon black-containing backing layers characteristically have thickness of 0.13 to 0.4 mm (5 to 15 mils) and may be produced by filtration of by passing the afore mentioned actylene black-PTFE mixes through heated rollers at temperatures of 65° to 90°C or by any other suitable technique.

Then these backing layers are laminated with a current distributor and the active layer as disclosed herein.

Resistivity of this wetproofing layer was measured and found to be 0.53 ohm-cm. The resistivity of pure PTFE is greater than 10 ohm-cm by way of comparison.

The resistivity of the PTFE/SB carbon black wetproofing layer illustrates that it is still low enough to be useful in forming electrodes when in intimate contact with a current distributor.

Permeability is an important factor in high current density operation of a gas electrode having hydrophobic (conductive or non-conductive) backing, viz., a wetproofing or liquid barrier layer.

The wetproofing layers employed in forming laminates according to this invention have adequate permeability to be comparable to that of pure PTFE backings (even when pressed at up to 7.6 10^7 N/m^2) yet have far superior electroconductivity.

The testing of air electrodes employing such backing layers in the corrosive alkaline environment present in a chlor-alkali cell has revealed a desirable combination of electroconductivity with balanced hydrophobicity and said layers are believed to have achieved a desired result in the oxygen (air) cathode field.

Conductive backing layer containing partially fluorinated carbon black

When in conjunction with the active layer according to the invention conductive backing layers are employed, it is also contemplated to use partially fluorinated carbon black backing layers. Partially fluorinated carbon blacks are preferably acetylene blacks which are subjected to partial fluorination to arrive at compounds having the formula CF_x, wherein x ranges from about 0.1 to about 0.18.

The hydrophobicity of the already hydrophobic acetylene black particles is enhanced by such partial fluorination as was observed from comparative experiments wherein the unfluorinated acetylene black particles floated on cold water but quickly sank in hot water versus the partially fluorinated acetylene blacks, fluorinated to the extent of x being about 0.1 to about 0.18, which floated on hot water virtually indefinitely and could not be made to pierce the meniscus of the water.

Such hydrophobic electrode backing layers (containing $CF_{x=0.1 \text{ to } 0.18}$ partially fluorinated carbon black) were prepared by combining the PTFE in particulate form as a dispersion with the partially fluorinated acetylene black particles. According to the preferred embodiment, the acetylene black employed is that having an average particle size of approximately 0.0425 micrometers with a standard deviation of 0.025 micrometers. The range of particle size is from about 0.005 to about 0.2 micrometers.

The partially fluorinated carbon black particles are suspended in isopropylalcohol and a dilute aqueous dispersion of PTFE (2 weight % PTFE) is added gradually thereto. This dilute dispersion is made from PTFE dispersion of 60 weight parts of PTFE in 40 weight parts of water to form an intimate mixture of $CF_{x=0.1 \text{ to } 0.18}$/PTFE. The PTFE/$CF_{x=0.1 \text{ to } 0.18}$ mix was the filtered, dried, treated to remove the PTFE wetting agent (by heating at 300°C for 20 minutes in air or extracting it with chloroform), a and briefly chopped to form a grannular mix and then fabricated into sheet form either by (a) passing between heated rollers (65° to 90°C), or (b) by dispersion of said PTFE/$CF_{x=0.1 \text{ to } 0.18}$ particles in a liquid dispersion medium capable of wetting said particles and filtration on a salt (NaCl) bed previously deposited on filter paper or like filtration media, or (c) by spraying the $CF_{x=0.1 \text{ to } 0.18}$/PTFE mix in a mixture of water and alcohol, e.g., isopropyl alcohol, on an electrode active layer/current distributor composite assembly and drying to yield a fine-pore wetproofing layer. The mix can contain from about 50 to 80 weight % $CF_{x=0.1 \text{ to } 0.18}$ and about 20 to 50 weight % PTFE.

In any case, a pore former can be incorporated into the $CF_{x=0.1 \text{ to } 0.18}$/PTFE mix prior to forming the wetproofing layer or sheet. The pore former can be of the soluble type, e.g., sodium carbonate or the like, or the volatile type, e.g., ammonium benzoate or the like.

Whether the wetproofing sheet is formed by rolling, filtration or spraying, the pore former can be removed by washing (if a soluble one) or heating (if a volatile one) either prior to laminating the wetproofing layer to the current distributor (with the distributor on the gas side) and active layer, or after lamination thereof. In cases where a soluble pore former is used, the laminate is preferably given a hot (50° to about 100°C) soak in an alkylene polyol, e.g., ethylene glycol or the like, prior to water washing for 10 to 60 minutes. The ethylene glycol hot soak combined with water washing imparts enhanced resistance of such laminated electrodes to blistering during water washing.

When the wetproofing layer is formed by filtration, it can be released from the filter media by washing with water to dissolve the salt bed, drying and pressing lightly to consolidate same, followed by laminating to the current distributor and active layer. Alternatively, the filter paper/salt/wetproofing layer can be laminated to the current distributor and active layer (with the filter paper side away from the current distributor and the wetproofing layer side in contact with the current distributor) followed by dissolving the salt away.

The testing of such partially fluorinated backing layers in the corrosive alkaline environment of use in a chlor-alkali cell has revealed a desirable combination of electroconductivity with balanced hydrophobicity and said layers are believed to have achieved a desired result in the oxygen (air) cathode field.

The active layer

In forming the three-layer laminate electrode of this invention, there is employed a "matrix" active layer as an essential component. This matrix active layer comprises active carbon particles present within an unsintered network (matrix) of fibrillated carbon black/polytetrafluoroethylene.

One stream (mixture), the matrixing mix component, is obtained by adding a dilute dispersion containing polytetrafluoroethylene (PTFE), having a particle size of about from 0.05 to 0.5 micrometers in water to mix of a carbon black, e.g., an acetylene black, and water ink a weight ratio of from about 25 om 35 weight parts of PTFE to from about 65 to 75 weight parts of carbon black to form an intimate mix of PTFE/carbon black particles, drying the aforementioned mixture heat treating it to remove the PTFE wetting agent thereby resulting in a first component mix.

The second component, the active carbon-containing catalyst component, is comprised of an optionally catalyzed, preferably previously deashed and optionally particle size classified active carbon, having a particle size ranging from about 1 to about 30 micrometers and more usually from about 10 to about 20 micrometers.

Deashing can be done by pretreatment with caustic and acid to remove a substantial amount of ash from the active carbon prior to catalyzing same. The term ash refers to oxides principally comprised of silica, alumina, and iron oxides. The deashed, classified, active carbon particles can then be catalyzed with a precious metal, e.g., by contacting with a silver or platinum precursor, followed by chemical reduction with or without heat to deposit silver, platinum or other respective precious metal on the active carbon.

The catalyzed carbon can be filtered, dried at temperatures ranging from about 80 to 150°C, with or without vacuum, to produce a second (active carbon catalyst) component or mixture.

These mixtures are then chopped together, with or without the addition of a particulate, subsequently removable (fugitive) pore-forming agent and then shear blended (fibrillated) at temperatures ranging from about 40° to about 60°C for 2 to 10 minutes, e.g., 4 to 6 minutes, in the presence of a processing aid or lubricant, e.g., a 50:50 mixture (by weight) of isopropylalcohol and water, viz., when no pore former is used as bulking agent. When a water-soluble pore former is used, the lubricant can be isopropyl alcohol. The previously chopped mixture can be fibrillated using a mixer. During this fibrillation step, the chopped mixture of the two-component mixes is subject to shear blending forces, viz., a combination of compression and attenuation which has the effect of substantially lengthening the PTFE in the presence of the remaining components. This fibrillation is believed to substantially increase the strength of the resulting sheets formed from the fibrillated mixed components. After such fibrillating, the mixture is noted to be fibrous and hence the term "fiberizing" is used herein as synonymous with fibrillating.

Subsequent to fibrillation, the mixture is dried, chopped for from 1 to 10 seconds into a fine powder and formed into a sheet by rolling at 50°C to 100°C or by deposition on a filter. A pore former, if one is employed as a bulking agent, can be then removed prior to electrode fabrication. In the event no pore former is employed, the matrix active layer sheet can be used (as is) as the active catalyst-containing layer of an oxygen (air) cathode, e.g., for use in a chlor-alkali cell fuel cell, etc.

In forming the active layers and laminates of the present invention, the aforementioned blistering and structural strength problems encountered at high current densities in the active layers of gas electrodes can be substantially overcome by a process involving: forming two separate components, one a matrixing mix component containing carbon black with polytetrafluoroethylene particles and heat treating this PTFE-carbon black mix at given temperature conditions; separately forming an active carbon-containing catalyst component; combining these two separate components into a mix; chopping the mix and shear-blending the chopped mix (fibrillating same) in order to arrive at a readily formable matrix which can be formed, e.g., pressed between rolls, or deposited upon a filter paper as a forming medium, pressed and then used as the active layer in an oxygen (air) cathode. Such process results in active layers having reduced carbon corrosion, higher conductivity and air-transport combined with strength when compared with prior structures. This results in electrodes which can be used longer and are more stable in use.

Tensile strength tests of the coherent, self-sustaining active layer sheets rolled from the fiberized material characteristically displayed approximately 50% greater tensile strength than unfiberized sheets. Life testing of electrodes employing the fibrillated (fiberized) active layer sheets of this invention resulted in approximately 8900 hours life at 300 mA/cm^2 in 30% hot (60° to 80°C) aqueous sodium hydroxide before failure. In addition to the advantages of longevity and strength, this process is easy to employ in making large batches of active layer by continuous rolling of fibrillated mix resulting in a material uniform in thickness and composition. Furthermore, the process is easy to administer and control.

In accordance with one preferred embodiment of this invention, a water-soluble pore-forming agent, e.g., sodium carbonate, is employed in the mixing step wherein the polytetrafluoroethylene dispersion is mixed with carbon black. Alternatively, the pore-forming agent can be added later, when the carbon black-PTFE mix and the catalyzed active carbon particles are mixed together and chopped.

In forming an initial mixture of carbon black and polytetrafluoroethylene, the usual particle size of the carbon black ranges from about 0.50 to about 300 micrometers and it has a surface area ranging from about 25 to about 300 m^2/g. The PTFE is preferably employed in aqueous dispersion form and the mixture of carbon black and polytetrafluoroethylene can contain from about 65 to about 75 weight parts of carbon black and about 35 to about 25 weight parts of PTFE. After mixing, the carbon black and PTFE are dried and then the dried initial mix is heated in air at temperatures ranging from about 250° to 325°C, and more preferably 275° to 300°C, for time periods ranging from 10 minutes to 1.5 hours and more preferably from 20 minutes to 60 minutes. This heating removes the bulk of the PTFE wetting agent.

The other component of the matrix electrode, viz., the active carbon, preferably "RB" carbon manufactured by Calgon, a division of Merck., is deashed by contact with an aqueous alkali, e.g., sodium hydroxide, or equivalent alkali, and more usually aqueous sodium hydroxide having a sodium hydroxide concentration of about 28 to about 55 weight % for 0.5 to 25 hours. After washing, the active carbon is then contacted with an acid, which can be hydrochloric acid, phosphoric acid, sulfuric acid, hydrobromic acid, etc., at ambient temperatures using aqueous acid solutions having from about 10 to about 30 weight % acid, based on total solution for comparable time periods. Subsequent to the contact with acid, the deashed active carbon particles are preferably catalyzed. The deashed particles are preferably catalyzed as by contact with a precursor of a precious metal catalyst. In the event that silver is desired to be deposited within the pores of the active carbon, it is preferred to use silver nitrate as the catalyst precursor followed by removal of excess silver and chemical reduction with alkaline formaldehyde.

On the other hand, in the event that it is desired to deposit platinum within the pores of the active carbon material, chloroplatinic acid can be used as a precursor followed by removal of excess chloroplatinic acid and chemical reduction using sodium borohydride or formaldehyde as a reducing agent. According to a preferred embodiment, the platinum is derived from $H_3Pt(SO_3)_2OH$. The reduction can be accompanied with the use of heat or it can be done at ambient room temperatures. After catalysis, the active carbon particles are filtered and vacuum dried as the active carbon-containing catalyst component in preparation for combination with the acetylene black/PTFE matrixing component mix.

The carbon black/PTFE matrixing component mix preferably in a weight ratio ranging from about 65 to 75 weight parts of carbon black to 25 to 35 weight parts of PTFE is mixed with the catalyzed deashed active carbon-containing component and subjected to chopping to blend the carbon black/PTFE matrixing component with the catalyst component in the manner set forth above. This mix is then subjected to fibrillation (shear blending or fiberizing), for example, in a mixer with appropriate blades at approximately 50°C. This shear blended material has a combination of good conductivity and high tensile strength with low PTFE content resulting in extraordinarily long life in use at high current densities in the corrosive alkaline environment present in a chlor-alkali cell.

The active layers are employed in this invention can contain (after removal of any pore-forming bulking agent therefrom) from about 40 to 80 weight % of active carbon, the remainder being the matrixing materials, carbon black and PTFE.

Subsequent to the fibrillation step, the fibrillated material is dried, chopped and rolled at approximately 75°C yielding the resulting coherent, self-sustaining and comparatively high tensile strength active layer sheet. Active carbon-containing active layer sheets produced in accordance with this invention characteristically have thicknesses of 0.3 to 0.6 millimeters with corresponding tensile strengths ranging from about 5.25 to 10.5 kg/cm^2 measured after pressing in a hydrualic press at 1.3 10^8 N/m^2 and 112°C for 3 minutes).

Example 1

(A matrix active layer containing silver-catalyzed active carbon particles).

Commercially available ball milled "RB carbon" was found to have an ash content of approximately 1% as received. This "RB carbon" was treated in 38% KOH for 16 hours at 115°C and found to contain 5.6% ash content after a subsequent furnace operation. The alkali treated "RB carbon" was then treated (immersed) for 16 hours at room temperature in 1:1 aqueous hydrochloric acid (20% concentration). The resulting ash content had been reduced to 2.8%. "RB carbon", deashed as above, was silvered in accordance with the following procedure:

20 grams of deashed "RB cabon" were soaked in 500 ml of 0.161 N (normal) aqueous $AgNO_3$ with stirring for 2 hours. The excess solution was filtered off to obtain a filter cake. The retrieved filtrate was 460 ml of 0.123 N $AgNO_3$. The filter cake was rapidly stirred into an 85°C alkaline formaldehyde solution, prepared using 300 cm^3 (cubic centimeters) water, and 30 cm^3 of 30% aqueous NaOH and 22 cm^3 of 37% aqueous CH_2O, to ppt. Ag in the pores of the active carbon.

Calculation indicated that 79% of the 2.58 grams of retained silver in the catalyst was derived from adsorbed silver nitrate.

Separately, a commercially available acetylene carbon black was mixed with polytetrafluoroethylene dispersion (DuPont "Teflon® 30") using an ultrasonic generator to obtain intimate mixture. 7.2 grams of the carbon black/PTFE mix was high speed chopped, spread in a dish, and then heat treated at 274°C for 20 minutes. Upon removal and cooling, it was once again high speed chopped, this time for 10 seconds. Then 18 grams of the classified silvered active carbon was added to the 7.2 grams of carbon black-PTFE mix, high speed chopped for 15 seconds, and placed into a mixer. The mixture was added to the cavity of the mixer using 50 cm^3 of a 30/70 (by volume) mixture of isopropyl alcohol in water as a lubricant to aid in fibrillating. The mixer was then run for 5 minutes at 30 rpm at 50°C, after which the material was removed as a fibrous coherent mass. This mass was then oven dried in a vacuum oven and was high speed chopped in preparation for rolling.

The chopped particulate material was then passed through a rolling mill. The resulting matrix active layer sheet had an area density of 22.5 mg/cm^2 and was ready for lamination.

Example 2

(A matrix active layer containing platinum-catalyzed active carbon particles).

The procedure of Example 1 was repeated except that platinum was deposited on the deashed active ("RB") carbon instead of silver. The 10 to 20 micrometers classified deashed "RB" carbon had platinum applied thereto using $H_3Pt(SO_3)_2OH$ to deposit 1 weight part platinum per 34 weight parts of deashed active carbon.

After fibrillation and upon rolling, the area density of the active layer was determined to be 22.2 mg/cm^2. This matrix active layer was then ready for lamination.

Example 3

(A matrix active layer containing silver-catalyzed active carbon particles without heat treatment before fibrillation).

An active layer containing deashed, silvered "RB" active carbon was prepared as in Example 1 with the exception that the 70/30 (by weight) acetylene carbon black/PTFE matrixing material was not heat treated before fibrillating. This matrix active layer was heavier than those prepared according to Example 1 and 2. It has an area density of 26.6 mg/cm^2 and was ready for lamination.

Example 4

(A matrix active layer containing platinum-catalyzed active carbon particles incorporating a pore former and heat treated, as in Examples 1 and 2, before fibrillation)

This matrix active layer was made according to the basic procedure of Example 1 using deashed "RB" active carbon platinized by the method of U.S. Patent 4 044 193 to a level of 19 weight parts of deashed "RB" active carbon per weight part platinum. Six grams of ultrasonically treated (70:30, acetylene carbon black: PTFE) carbon black were heat treated for 20 minutes at 274°C prior to addition thereto of 15 grams of said active carbon along with 9 grams of sodium carbonate, which had been classified to the particle size range of +5 to −10 micrometers. This material was fibrillated and rolled out as in Example 1 and extracted by water (to remove the sodium carbonate) after first hot soaking it in ethylene glycol at 75°C for 20 minutes. The resulting active layer sheet was a very porous and lightweight material.

The current distributor layer

The current distributor layer, which is usually positioned next to and laminated to the working surface of the active layer of the three-layer laminate, can be an asymmetric woven wire mesh wherein the material from which the wire is made is selected from the group consisting of nickel, nickel-plated copper, nickel-plated iron, silver-plated nickel, and silver-plated, nickel-plated copper and like materials. In such asymmetric woven wire mesh current distributors, there are more wires in one direction than in the other direction.

The current distributor or collector utilized can be a woven or nonwoven, symmetrical or asymmetric wire mesh or grid. Generally there is a preferred current carrying direction. When the current distributor is a copper wire mesh, there should be as few wired feasible in the noncurrent carrying direction. There will be found to be a minimum required for fabrication of a stable wire cloth. A satisfactory asymmetric wire cloth configuration may consist of, e.g. 20 wires/cm in the warp direction but only about 10 wires/cm in the fill, thus enhancing the economy and utility of the wire cloth, simultaneously.

Such asymmetric, woven wire mesh current distributors are useful as the current distributor in the three-layer laminates of this invention which are useful as oxygen cathodes in chlor-alkali cells.

Alternatively the current distributor can be of the plaque type, viz., a comparatively compact yet porous layer, having porosities ranging from about 30 to about 80% and made of powders of Ni, Ag or the like.

Forming the three-layer laminates

The three-layer laminates produced in accordance with this invention usually have the active layer centrally located, viz., positioned in the middle between the backing layer on the one side and the current distributor (collector) layer on the other side. The three layers arranged as described are laminated using heat and pressure at temperatures ranging from about 100° to about 130°C and pressures of 7.6 10^5 to 1.5 10^8 N/m^2. The laminates are preferably then subjected to a hot soaking step in ethylene glycol or equivalent polyol to enhance removal of the pre-forming agent(s) employed to form the aforementioned backing (wetproofing) layer and any bulking and/or pore-forming agent optionally included in the active layer, upon subsequent washing(s) with water.

The laminating pressures used will depend on whether or not electroconductive (carbon black) particles have been included in the backing layer along with the PTFE. Thus when using pure PTFE, viz., PTFE with pore former only, pressures of 6.1 10^7 to 1.21 10^8 N/m^2 have been determined to be adequate to effect the bonding of the conductive backing to the active layer. Of course, higher laminating pressures can be employed so long as the porosity of the structure is not destroyed.

The three-layer laminates of this invention can be formed using a variety of the afore mentioned backing layers and current distributors. The following examples further illustrate their preparation and actual testing in corrosive alkaline environments and at current densities such as are employed in chlor-alkali cells, fuel cells, batteries, etc.

Example 5

(Forming laminated electrodes from the matrix active layers of Examples 1 to 3 and testing them in alkaline media at current densities of 250 mA/cm^2 and higher)

The active layers prepared in accordance with Examples 1 to 3 respectively, were each laminated to a current distributor and a backing sheet of sodium carbonated-loaded PTFE prepared as follows:

Two hundred cubic centimeters of isopropyl alcohol were poured into blender. Then 49 grams of DuPont 6A polytetrafluoroethylene were placed in the blender and the PTFE-alcohol dispersion was blended for approximately one minute. The resulting slurry had a thick, pasty consistency. Then another 100 cm^3 of isopropyl alcohol were added in the blender and the mixture was blended for an additional two minutes.

Then 91 grams of particulate sodium carbonate in isopropanol having an average particle size of approximately 3.5 micrometers were added to the blender. This PTFE-sodium carbonate mixture was then blended in the blender for 3 minutes followed by a higher speed blending for an additional one minute. The resulting PTFE-sodium carbonate slurry was then poured from the blender onto a Buchner funnel, filtered and then placed in an oven at 80°C where it was dried for 3 hours resulting in 136.2 grams yield of PTFE-sodium carbonate mixture. This mixture contained approximately 35 weight parts of PTFE and 65 weight parts of sodium carbonate.

This mixture was mildly fibrillated as described above.

After fibrillating, which compresses and greatly attenuates the PTFE, the fibrillated material is chopped to a fine dry powder. The extent of chopping can be varied as long as the material is finely chopped.

The chopped PTFE-$NaCO_3$ mix is fed to approx. 15 cm diameter chrome-plated steel rolls heated to about 80°C. Typically these rolls are set at a gap of 0.2 millimeters for this operation. The sheets are formed directly in one pass and are ready for use as backing layers in forming electrodes, e.g., oxygen cathodes, with no further processing beyond cutting, trimming to size and the like.

The current distributor was 0.1 to 0.13 mm diameter nickel woven wire mesh having about 10 micrometers thick silver plating and the woven strand arrangement tabulated below. The distributor was positioned on one active layer side while the backing layer was placed on the other side of the active layer.

The lamination was performed in a hydraulic press at 100°C to 130°C and using pressures of 6.1 10^7 to 1.21 10^8 N/m^2 for several minutes. These laminates were then hot soaked in ethylene glycol at 75°C for 20 minutes before water washing at 65°C for 18 hours and then dried.

The laminates were then placed in respective half cells for testing against a counter electrode in 30% aqueous sodium hydroxide at temperatures of 70° to 80°C with an air flow of 4 times the theoretical requirement for an air cathode and a current density of 300 mA/cm^2. The testing results and other pertinent notations are given below.

Active layer example	Type of AC plated Ni mesh	Init. Voltage vs.Hg/HgO Ref. Electr.	Useful life of matrix electrode (hrs)	Voltage at failure
1	58×60×0.004	−0.265 volt	8,925	−0.395 volt(1)
2	50×50×0.005	−0.201 volt	3,512+	N.A.(2)
3	58×60×0.004	−0.282 volt	3,861	−0.509 volt(3)

(1) Shortly after 8,925 hours, there was steep decline in potential, and the electrode was judged to have failed.

(2) After 188 days, its voltage was −0.246 volts compared to the HgHgO reference electrode (a very slight decline in potential), and this matrix electrode is still on life testing. After being started at 300 mA/cm^2, the test current density was changed to 250 mA/cm^2.

(3) The final failure was caused by separation of the current distributor from the face of the electrode.

It should be noted here that in each of these "matrix" electrodes the approximate concentration of PTFE in the active layer mix is only about 12% by weight while still achieving the combined requirements of conductivity, strength, permeability and longevity, long sought in air-breathing electrodes.

Example 6

A laminated electrode was formed using the PTFE sodium carbonate one pass backing layer, the active layer of Example 1 and a prior art type porous sintered nickel plaque current distributor (Dual Porosity Lot No. 502—62—46). The matrix active layer was positioned on the coarse side of said plaque and the PTFE/sodium carbonate backing layer was placed on top of the other surface of the active layer. This sandwich was pressed at 1.21 10^8 N/m^2 and 115°C for 3 minutes after which it was hot soaked in ethylene glycol at 75°C for 20 minutes followed by water washing at 65°C for 18 hours. This air electrode was operated at 4 times theoretical air and 250 mA/cm^2 in 30% NaOH at 70°C and operated satisfactorily for 17 days before failure.

Several of the features mentioned above as being useful in conjunction with the electrode active layer of the invention to form gas diffusion electrodes are individually claimed in concurrent European patent applications. In particular, European patent application No. 81 305 086.1 (EP 0 052 446), European patent application No. 81 305 092.9 (EP 0 051 438), European patent application No. 81 305 093.7 (EP 0 051 439), and European patent application No. 81 305 094.5 (EP 0 051 440).

Claims

1. A gas-diffusion electrode having a hydrophobic backing layer laminated to an active layer containing active carbon particles and polytetrafluoroethylene characterized in that the active carbon particles are present within an unsintered fibrillated network or matrix of polytetrafluoroethylene and carbon black material.

2. The gas diffusion electrode according to claim 1, wherein the active carbon particles contain silver or platinum.

3. The gas diffusion electrode according to

claim 1 or 2 wherein the active carbon particles range in size from about 1 to 30 micrometers.

4. The gas diffusion electrode according to claim 3 wherein said active carbon particles have an ash content of less than 4% by weight and a B.E.T. surface area of about 500 m^2g or more.

5. The gas diffusion electrode according to any of claims 1 to 4, wherein the carbon black comprises particles which range in size from 0.005 to 0.3 micrometers.

6. The gas diffusion electrode according to claim 5, wherein the carbon black particles have a surface area ranging from 25 to 300 m^2/g.

7. The gas diffusion electrode according to any of claims 1 to 6, which contains a pore-forming bulking agent.

8. The gas diffusion electrode according to any of claims 1 to 7, wherein the unsintered network contains by weight 25 to 35 parts of polytetrafluoroethylene and 75 to 65 parts of carbon black.

9. The gas diffusion electrode according to any of claims 1 to 8, wherein the concentration of active carbon ranges from 40 to 80 weight %, based on the total weight of the active layer.

10. The gas diffusion electrode according to any of claims 1—9, wherein said active layer is laminated on its working surface to a current distributor and on its opposite surface to a porous coherent hydrophobic polytetrafluoroethylene-containing wet-proofing layer.

11. A method of preparing a gas diffusion electrode active layer for the electrode according to any of claims 1—9 comprising the steps of:

a) mixing carbon black particles with an aqueous dispersion of polytetrafluoroethylene particles to form an intimate blend of particulate polytetrafluoroethylene and carbon black,

b) distributing active carbon particles through the intimate blend to produce a composite mixture,

c) fibrillating said mixture and

d) forming the fibrillated mixture into said active layer.

Patentansprüche

1. Eine Gasdiffusions-Elektrode mit einer auf eine aktive Kohlenstoffteilchen und Polytetrafluoroethylen enthaltende aktive Schicht auflaminierten hydrophoben Rückseitenschicht, dadurch gekennzeichnet, daß die aktiven Kohlenstoffteilchen innerhalb einer ungesinterten verfaserten Netzwerkschicht oder Matrix aus Polytetrafluorethylen und Ruß vorliegen.

2. Die Gasdiffusions-Elektrode gemäß Anspruch 1, bei der die aktiven Kohlenstoffteilchen Silber oder Platin enthalten.

3. Die Gasdiffusions-Elektrode gemäß den Ansprüchen 1 oder 2, bei welcher die aktiven Kohlenstoffteilchen im Teilchengrößenbereich von etwa 1 bis 30 µm liegen.

4. Die Gasdiffusions-Elektrode gemäß Anspruch 3, bei welcher die genannten aktiven Kohlenstoffteilchen einen Aschegehalt von weniger als 4 Gew.% und eine BET-Oberfläche von etwa 500 m^2/g oder darüber aufweisen.

5. Die Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 4, bei welcher der Ruß Teilchen enthält, welche im Größenbereich von 0,005 bis 0,3 µm liegen.

6. Die Gasdiffusions-Elektrode gemäß Anspruch 5, bei welcher die Rußteilchen eine Oberfläche im Bereich von 25 bis 300 m^2/g aufweisen.

7. Die Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 6, welche einen porenbildenden Volumenvergrößerer enthält.

8. Die Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 7, bei welcher das ungesinterte Netzwerk 25 bis 35 Gewichtsteile Polytetrafluorethylen und 75 bis 65 Gewichtsteile Ruß enthält.

9. Die Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 8, bei welcher die Konzentrtion an aktivem Kohlenstoff bezogen auf das Gesamtgewicht der aktiven Schicht zwischen 40 und 80 Gew.% liegt.

10. Die Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 9, bei welcher die genannte aktive Schicht mit ihrer Arbertsfläche auf einen Stromverteiler und mit ihrer anderen Oberfläche auf eine poröse zusammenhängende hydrophobe Polytetrafluorethylen enthaltende wasserabstoßende Schicht auflaminiert ist.

11. Verfahren zur Herstellung einer aktiven Schicht für eine Gasdiffusions-Elektrode gemäß einem der Ansprüche 1 bis 9 bestehend aus den Schritten

a) Mischen von Rußteilchen mit einer wässrigen Dispersion von Polytetrafluoroethylenteilchen unter Bildung einer innigen Mischung von teilchenförmigem Polytetrafluorethylen und Ruß,

b) Verteilen von aktiven Kohlenstoffteilchen in der innigen Mischung unter Bildung eines zusammengesetzten Gemisches,

c) Verfasern der Mischung und

d) Verformen der zerfaserten Mischung zu der genannten aktiven Schicht.

Revendications

1. Electrode à diffusion de gaz comprenant une couche hydrophobe formant support amenée à adhérer à une couche active contenant des particules de charbon actif et du polytétrafluoroéthylène, caractérisé en ce que les particules de charbon actif sont présentes à l'intérieur d'un réseau ou matrice fibrille non fritté de polytétrafluoroéthylène et de matière formée de noir de carbone.

2. Elektrode à diffusion de gaz selon la revendication 1, caractérisée en ce que les particules de charbon actif contiennent de l'argent ou du platine.

3. Electrode à diffusion de gaz selon la revendication 1 ou 2, caractérisé en ce que les particules de charbon actif s'étant en grosseur entre environ 1 et 30 micromètres.

4. Electrode à diffusion de gaz selon la revendication 3, caractérisé en ce que les particules de charbon actif présentent une teneur en cendres inférieure à 4% en poids et une surface spécifique B.E.T. d'environ 500 m^2/g ou plus.

5. Electrode à diffusion de gaz selon l'une quelconque des revendications précédentes, caractérisée en ce que le noir de carbone comprend des particules dont la grosseur est comprise entre 0,005 et 0,3 micromètre.

6. Electrode à diffusion de gaz selon la revendication 5, caractérisée en ce que les particules de noir de carbone présentent une surface spécifique comprise entre 25 et 300 m^2/g.

7. Electrode à diffusion de gaz selon l'une quelconque des revendications précédentes, caractérisée en ce qu'elle contient un agent gonflant porogène.

8. Electrode à diffusion de gaz selon l'une quelconque des revendications précédentes, caractérisée en ce que le réseau non fritté contient 25 à 35 parties en poids de polytétrafluoroéthylène et 75 à 65 parties en poids de noir de carbone.

9. Electrode à diffusion de gaz selon l'une quelconque des revendications précédentes, caractérisé en ce que la concentration de charbon actif est comprise entre 40 et 80% en poids calculés sur la base du poids total de la couche active.

10. Electrode à diffusion de gaz selon l'une quelconque des revendications précédentes, caractérisée en ce que la couche active est amenée à adhérer avec sa surface agissante à un distributeur de courant et avec son autre surface à une couche poreuse cohérente et hydrophobe qui contient du polytétrafluoroéthylène et est étanche à l'humidité.

11. Procédé de fabrication d'une couche active d'électrode à diffusion de gaz pour l'électrode selon l'une quelconque des revendications 1 à 9, caractérisé en ce qu'il consiste à:

a) mélanger des particules de noir de carbon avec une dispersion aqueuse de particules de polytétrafluoroéthylène pour former un mélange intime de polytétrafluoroéthylène et de noir de carbone particulaires;

b) répartir des particules de charbon actif au sein du mélange intime afin de produire un mélange composite;

c) fibriller ce mélange; et

d) transformer le mélange fibrillé en la couche active précitée.