11) Publication number:

0 082 514

**A1** 

12

## **EUROPEAN PATENT APPLICATION**

(21) Application number: 82111802.3

(22) Date of filing: 20.12.82

(5) Int. Cl.<sup>3</sup>: **C 25 B 11/06** C 25 B 11/08, C 25 B 11/12

//C25B1/46

30 Priority: 23.12.81 US 333592 23.12.81 US 333593

43 Date of publication of application: 29.06.83 Bulletin 83/26

(84) Designated Contracting States: AT BE CH DE FR GB IT LI NL SE (71) Applicant: THE DOW CHEMICAL COMPANY Dow Center 2030 Abbott Road Post Office Box 1967 Midland Michigan 48640(US)

(72) Inventor: McIntyre, James Arthur 2115 Burlington Midland Michigan 48640(US)

(72) Inventor: Phillips, Robert Floyd 649 South 8 Mile Michigan 48640(US)

(74) Representative: Weickmann, Heinrich, Dipl.-Ing. et al, Patentanwälte Dipl.-Ing. H. Weickmann Dipl.-Phys.Dr. K. Fincke Dipl.-Ing. F.A. Weickmann Dipl.-Chem. B. Huber Dr.-Ing. H. Liska Möhlstrasse 22 D-8000 München 86(DE)

(54) Electrode material.

(57) A particle suitable for use as an electrode material comprising a substrate at least partially coated with an admixture of hydrophobic material and an electrochemically active, electrically conductive catalyst.

The invention includes a method for producing the coated particles.

#### ELECTRODE MATERIAL

The invention resides in an improved electrode material and a method for producing that material.

Chlorine and alkali metal hydroxide, for example, sodium hydroxide and potassium hydroxide, are commercially prepared by the electrolysis of the corresponding alkali metal chloride brines in an electrolytic cell. In one type of cell, where the anode is separated from the cathode by an ion permeable barrier, chlorine is evolved at the anode according to the reaction:

10 · 
$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

while hydroxyl ions are produced at the cathode according to

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

which is actually a multi-step reaction in which a

15 hydrogen species is absorbed onto the surface of the
cathode and the hydrogen molecule is desorbed
therefrom.

The total hydrogen reaction, as a series of postulated adsorption and desorption steps, consumes about 0.8 volts in an alkaline solution, such that if the cathode in a chlorine cell is depolarized with 5 oxygen instead of being allowed to evolve hydrogen, a savings of about 1.2 volts is possible, since the oxygen reduction reaction can theoretically generate 0.4 V. The cathodes previously developed for utilization of oxygen as a depolarizer were characterized by a structure of a thin sandwich of a microporous separator 10 of plastic combined with a catalyzed layer, wetproofed with, e.g., polytetrafluoroethylene, and pressed onto a wire screen current collector. In the prior art depolarized cathodes, oxygen is fed into the catalyst zone 15 through the microporous backing. Such cathodes work. However, they suffered from various deficiencies, including separation or delamination of the various layers and flooding of the microporous layer.

The invention resides in an electrode

20 material comprising a substrate at least partially coated with an admixture of a binder and an electrochemically active, electrically conductive catalyst, characterized in that the electrode material is a coated particle having an average diameter of greater than 0.3 mm and less than 2.5 cm.

The invention also resides in a method for the production of an electrode material comprising forming a fluid admixture of an electrochemically active, electrically conductive catalyst and a binder, bonding the catalyst to the substrate by solidifying the fluid admixture and characterized by forming the electrode material into particles having an average diameter greater than 0.3 mm and up to 2.5 cm.

The invention further resides in a method of electrolyzing an aqueous electrolyte in an electrolytic cell having an anolyte compartment with an anode therein and a catholyte compartment with a cathode therein, which method comprises feeding said aqueous electrolyte to the cell, passing an electrical current between the anode and the cathode and recovering the products of electrolysis, at least one of the electrodes being formed of an electrode material comprising a substrate which is at least partially coated with an electrically conductive admixture of a hydrophobic material and at least one catalyst, and characterized in that the electrode material comprises a plurality of packed particles each having an average diameter of greater than 0.3 mm and up to 2.5 cm.

The invention also resids in an electrolytic cell having an anolyte compartment with an anode therein and a catholyte compartment with a cathode therein, means for feeding an aqueous electrolyte to the cell, means for passing an electrical current between the anode and the cathode, and means for recovering the products of electrolysis from the cell, at least one of the anode or cathode being formed of an electrode material comprising a substrate which is at least partially coated with an electrically conductive admixture of a hydrophobic material and at least one catalyst, characterized in that the electrode material comprises a plurality of packed particles each having an average diameter of greater than 0.3 mm and less than 2.5 cm.

10

15

20

25

Optionally, the cell may contain an ion permeable barrier located between the anode and the Optionally, the cell may include a means to feed a gas to the electrode.

5 A bed of these particles has been found to be useful as a gas electrode. The electrode may be used as a cathode or as an anode.

The substrate, upon which a coating is applied, should be a material which will hold its shape. 10 provide for a convenient method of preparing the herein--described particles, the substrate is preferably a material which will not substantially deform when heated to a temperature of 350-375°C for a period of 1 hour.

15 The substrate may be a sintered material, a solid material, or a bonded agglomeration of small particles. Suitable materials of construction include, but are not limited to steel, iron, graphite, nickel, platinum, copper, and silver. Particularly preferred 20 is graphite, because of its availability and its low cost. The substrate may be of the same composition or of a different composition than that of the coating.

The substrate may be electrically conductive or electrically nonconductive. Electrically conductive substrates are preferred because they offer less resistance to the flow of electrical energy through the particles. Nonconductive substrates are operable because they are at least partially coated with an electrically conductive coating, thus providing a 30 pathway for the flow of electrical current. However,

nonconductive substrates offer greater resistance because the electrical charge must flow around the particle through its coating, rather than through the particle.

The average diameter of the particle is 5 greater than 0.3 mm and up to as large as 2.5 cm. For use as an electrode material, it is preferred to use particles which are generally smaller than 2.5 cm. This maximizes the surface area and gives a high porosity to the bed of particles. Particles having 10 a size of from 0.7 mm to 4 mm are particularly preferred when the particles are used as an electrode material. Particles smaller than 0.3 mm tend to pack and offer a high resistance to fluid flow through the bed of particles. Substrates larger 15 than 2.5 cm are not preferred because there is a minimum amount of surface area for electrical chemical reactions to occur.

The particles may be of any shape. Irregularly shaped particles may be conveniently used. However, spherical particles are preferred because they form a bed having optimum porosity and surface area. Irregularly shaped particles tend to pack and minimize the porosity of the bed.

The substrate need not be chemically inert to the electrolyte or the products of electrolysis of the process in which the particle is used. Preferably, however, the substrate is chemically inert so the coating need not totally cover the substrate. If the substrate is not chemically inert, the coating applied thereto should be a complete coating to prevent reaction

between the substrate and the electrolyte or the products of electrolysis.

The coating on the substrate is an admixture of a binder and an electrochemically active, electrically conductive catalyst. The binder should be a material which may be put into a fluid form by melting, dispersing, or dissolving. The binder should be chemically stable to any electrolyte or products it will contact when in use in an electrolytic cell. The binder should be firmly stable at the temperature of operation for the 10 electrochemical cell in which it will be used. binder need not itself be electrically conductive, since the catalyst mixed with it is electrically conductive. The coating may be a porous coating or a · 15 nonporous coating depending on the materials of construction of the substrate. If the substrate is chemically inert to the electrolyte, the coating may be a porous coating. If, however, the substrate is not chemically inert to the electrolyte, the coating shouli be nonporous to prevent reactions between the substrate 20 and the electrolyte or electrolytic products from occurring.

Preferably, the binder is a hydrophobic material. When used as an electrode material, the hydrophobic binder will cause bubbles to form on the surface of the particles and provides maximum contact between the gas and the liquid. If the binder is now hydrophobic, the surfaces of the particles will be wetted and no bubbles will form.

Various types of hydrophobic material may be used as a binder. The hydrophobic material may be a

polyfluorocarbon, for example, polytetrafluoroethylene, polychlorotrifluoroethylene, polytrifluoroethylene, polyvinylfluoride, polyvinylidene fluoride and copolymers, including interpolymers and terpolymers having tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, vinylidene fluoride and vinyl fluoride. Particularly preferred is polytetrafluoroethylene.

The particles also contain in the coating an electrochemically active, electrically conductive catalyst. The selection of the catalyst will depend upon the type of process to which the electrode material will be put. Examples of such processes include the reduction of oxygen and the oxidation of hydrogen. For the reduction of oxygen, the preferred catalysts include such things as carbon blacks, platinum, silver and activated carbon. Carbon black is particularly preferred because of its good physical characteristics and its availability. Preferred are carbon black catalysts having surfaces areas of from 100 to 1,000 square meters per gram of catalyst. Particularly preferred are those having a surface area from 150 to 500 square meters per gram of catalyst.

The substrate may be partially or fully coated with the binder catalyst mixture. Preferably, the coating covers substantially the entire surface of the particle. The coating may be of any convenient thickness. Thicknesses of about 1 mil are particularly preferred. This provides an adequate coating to cover substantially the entire surface of the particle, yet is sufficiently thin to conserve the catalyst-binder mixture required to cover the particle. Thickness in excess of 5 to 6 mils are wasteful in that a substantial

10

15

20

25

portion of the catalyst is unavailable for reaction since it is covered by additional catalyst and binder.

Optionally, the coating may include a peroxide decomposition catalyst. As is herein-contemplated, the peroxide decomposition catalyst may be both on the exterior surface of the particle as well as in the internal surface of the particle. Preferred is a particle in which the peroxide decomposition catalyst is on the exterior surface of the substrate because no catalyst is wasted since unexposed catalyst is ineffective.

The peroxide decomposition catalyst are known in the art and are typically a transition metal having hydrogen adsorption properties. Preferred peroxide decomposition catalysts include copper, silver, platinum, gold, and mixtures or compounds thereof. Silver and platinum and mixtures or compounds thereof mixed with carbon black are especially preferred.

Another particularly desirable class of known peroxide decomposition catalysts are compounds of (1) alkali metals, alkaline earth metals, and metals of Group IIIB, with (2) transition metals, which compounds are further characterized by electrocatalytic or surface catalytic properties. Especially preferred are the perovskites.

25 The invention includes within its scope a method for the production of coated particles suitable for use as an electrode material. The coated particles are prepared by forming a fluid admixture of a particulated substrate, an electrochemically active, electrically conductive catalyst and a binder. The catalyst

10

15

is bonded to the substrate by solidifying the fluid admixture. This forms a particle having a substrate at least partially coated with a binder and a catalyst.

The fluid admixture is initially formed by

blending a particulated substrate with a catalyst and a
binder. The admixture may be made fluid in one of
several ways. The binder, itself, may be heated to a
temperature at which it is softened or melted. It may
be softened or melted prior to being mixed with the

catalyst and the substrate or in situ with the catalyst
and substrate. The softening point or melting point of
various materials suitable as binders are well known to
those skilled in the art. They can be found in many
reference books or handbooks of chemistry.

An alternative method of forming the fluid admixture is to disperse the binder, catalyst and substrate in a liquid medium. Various liquid mediums which are nonreactive with the three components of the admixture may be used. Particularly preferred are

20 water or other liquid materials which are not solvents for any of the components of the admixture. The dispersion may be made after the components have been admixed or any one of the components may be dispersed in a liquid prior to being blended with the other

25 components. It is important to have the components adequately dispersed in the liquid medium.

A third way of forming the liquid admixture is to dissolve the binder in a solvent. The dissolved binder may then be admixed with the catalyst and the substrate. The solvent should not have the ability to dissolve neither the substrate nor the catalyst. The

binder may be dissolved after or before the components have been blended.

After the fluid admixture has been formed, it is solidified to bind the catalyst to the substrate. The admixture may be solidified in one of several different ways. The solidification method is somewhat dependent upon the method initially used to form the fluid admixture. If the fluid admixture was formed by melting or softening the binder, mere cooling of the admixture will cause the binder to solidify. 10 fluid admixture was formed by dispersing one or more of the components into a liquid medium, solidification may be caused by removing the liquid medium from the admixture. The liquid medium may be removed by heating the admixture 15 to evaporate the liquid medium or by subjecting the admixture to a vacuum to vaporize the liquid medium. If the method used to form the liquid admixture was dissolving the binder in a solvent, solidification may be accomplished by removing the solvent. The solvent 20 may be removed by heating to vaporize the solvent, by vacuum to remove the solvent, or by reacting the solvent with another component.

Optionally, the admixture, during solidification may be treated in a manner to prevent the coated particles

25 from adhering together to form one, single mass.

Agitation is a convenient way to prevent the particles from adhering to each other during the solidification process. The amount and severity of agitation used is minimal and can be accomplished by merely stirring or rolling the material during solidification. Agitation during solidification also helps enhance the uniformity of the coating onto the substrate.

Optionally, after solidification, the coated particles may be heated to a temperature near or above the softening point of the binder to enhance the bonding of the material to the substrate. Heating to this temperature causes the binder to soften and become more intermixed with the catalyst and better bonded to the substrate.

Optionally, the steps of coating the particle may be repeated a plurality of times. In this manner, the amount and thickness of the coating may be controlled depending on the number of times the process is repeated. The thickness of the coating is not critical to the invention.

Optionally, a surfactant may be added to the 15 fluid admixture to enhance wetting of the substrate and the catalyst by the binder. This assures better contact and a more even distribution of the admixture. preferred that a type of surfactant be used that may be removed from the particle after the bonding has occurred. 20 This is preferred because, when in use as an electrode material, the coated particle preferably is not wetted by the electrolyte. As was discussed earlier, the formation of gas bubbles on the surface of the particle is desired. The presence of a surfactant at this point 25 would minimize the formation of gas bubbles since the wetting of the particles by an electrolyte would be enhanced. As a result, the preferred surfactants are the non-ionic surfactants which may be thermally decomposed leaving only a carbon residue. Such surfactants 30 are well-known in the art and need no further elaboration. Optionally, the particles may be washed after bonding to remove any catalyst which has not been bonded to the substrate. Water and other liquids which are not solvents for any of the components of the coating are suitable. Water is particularly preferred because of its convenience.

The weight or volume ratio of the catalyst and binder to the substrate depends on the degree of coating desired on the substrate. If a small amount of coating is desired, obviously only a small amount of catalyst and binder should be blended with the substrate to form a fluid admixture. Conversely, if a thick coating is desired, the amount of catalyst and binder should be increased.

The ratio of the amount of catalyst to the amount of binder may be varied over a rather wide range. For example, if carbon black is used as the catalyst, and polytetrafluoroethylene is used as the binder, weight ratios of from 4:1 to 1:4 may be used.

Preferred ratios of carbon black to PTFE are from 1:1.5 to 1.5:1 by weight. Other catalyst and binders should also be used within this same general ratio.

If a metal powder is used as the catalyst, such as silver, platinum or other metals, it is convenient to express the proportion in terms of volume as opposed to weight. The metal powder to binder may be in the range of from 4:1 to 1:4, by volume. Preferably, the ratio should be from 1:1.5 to 1.5:1, by volume.

Optionally, various types of additional 30 catalysts may be added to the fluid admixture. One of

10

the preferred embodiments of the herein-described invention includes the addition of a peroxide decomposition catalyst, in conjunction with a carbon black catalyst. When both of these types of catalyst are used from 1 to 35 weight percent of the total catalyst 5 used should be a peroxide decomposition catalyst and from 65 and 99 percent of the total amount of catalyst used should be the carbon black catalyst. Preferably, from 3 to 10 percent of the catalyst should be the peroxide decomposition catalyst and from 90 to 97 percent of the catalyst should be the carbon black catalyst. This catalyst mixture should be used in the ratios discussed earlier concerning the catalyst to binder ratio.

Commonly, the peroxide decomposition catalyst 15 used to form the fluid admixture is a precursor catalyst. In other words, the material used in the fluid admixture is a compound of the catalyst, which must be thermally or chemically decomposed in order to form the catalyst itself. This thermal or chemical decomposition may be 20 accomplished at any stage of the process of forming the coated particles. Preferably, the material is thermally or chemically decomposed prior to being mixed with the binder and the substrate. This allows better control of the thermal or chemical decomposition of the catalyst 25 precursor. Additionally, it provides the maximum contact between the carbon black and the peroxide decomposition catalyst. If the two are blended and decomposed prior to being mixed with the substrate and the binder, maximum contact is obtained between the 30 carbon black and the peroxide decomposition catalyst.

The herein-described coated particles are suitable for use as an electrode material, since they are electrically conductive and catalytically active.

Conveniently, they may be used as a packed bed electrode.

As such, they are formed into a bed and supported in some convenient manner within the cell. They are electrically connected with a power supply associated with the cell. Optionally, a current collector may be used. The current collector may be a wire mesh bag,

wire mesh container or the like, surrounding the catalyzed particles and containing them therein.

If the coated particles include a peroxide decomposition catalyst, the particles may be used in a cell to produce a hydroxide. If the coated particles do not contain a peroxide decomposition catalyst, the particles may be used in a cell to produce a peroxide.

According to a preferred embodiment of the method of using the herein-described particles, an aqueous alkali metal halide brine is fed to an electrolytic cell having an anolyte compartment with an anode 20 therein, and a catholyte compartment with cathode means therein, and, optionally an ion permeable barrier therebetween. Typically, the anode is a valve metal, for example, titanium, tantalum, tungsten, columbium, 25 or the like, with a suitable electrocatalytic surface thereon. Suitable anodic electrocatalytic surfaces are well known in the art and include transition metals, oxides of transition metals, compounds of transition metals, especially platinum group metals, oxides of platinum group metals and compounds of platinum groups 30 metals. Especially preferred are compounds of oxides of platinum groups metals with oxides of the valve

metals, that is, titanium, tantalum, tungsten, columbium and the like.

The ion permeable barrier may be an electrolyte permeable diaphragm, for example, a deposited asbestos diaphragm, a preformed asbestos diaphragm, or 5 a microporous synthetic diaphragm. Alternatively, the ion permeable barrier may be ion permeable but electrolyte impermeable as a cation selective permionic Typically, cation selective permionic membranes are fluorocarbon polymers having pendent acid groups thereon. Typical pendent acid groups include sulfonic acid groups, carboxylic acid groups, phosphonic acid groups, phosphoric acid groups, precursors thereof, and reaction products thereof.

15 The anolyte liquor is typically an aqueous brine containing from 120 to 250 grams per liter of sodium chloride or from 180 to 370 grams per liter of potassium chloride, and is typically at a pH of from 1.5 to 5.5. The brine feed is typically a saturated or 20 substantially saturated brine, containing from 300 to 325 grams per liter of sodium chloride or from 450 to 500 grams per liter of potassium chloride. The catholyte liquor recovered from the electrolytic cell may be a catholyte liquor containing approximately 10 to 12 weight percent sodium hydroxide and 15 to 25 weight 25 percent sodium chloride, or approximately 15 to 20 weight percent potassium hydroxide and approximately 20 to 30 weight percent potassium chloride, as where an electrolyte permeable barrier is utilized. Alterna-30 tively, the catholyte product may contain from 10 to 45 weight percent sodium hydroxide, or from 15 to 65 weight percent potassium hydroxide, as where the ion

permeable barrier is a cation selective permionic membrane interposed between the anode and the cathode.

An oxidant, for example, oxygen, air or oxygen-enriched air, is preferably fed to the catholyte compartment as an electrical current is fed from the cathode compartment to the anode compartment, to provide an anode product of chlorine and a cathode product of alkali metal hydroxide, characterized by the substantial absence of gaseous hydrogen product. The invention is particularly directed to a preferred packed bed cathode including coated particles as herein described.

According to a further exemplification of the invention, there is provided an electrolytic cell having an anolyte compartment fabricated of a material resistant to concentrated, chlorinated alkali metal chloride brines, an anode in the anolyte compartment, a catholyte compartment that is fabricated of a material resistant to concentrated alkali metal hydroxide solutions, cathode means in said cathode compartment, and an ion permeable barrier interposed between the anode and the cathode means. The electrolytic cell herein contemplated is characterized by the catholyte compartment having means for feeding an oxidant to the electrolyte within the cathode compartment and cathode means which comprise individual particles.

In another preferred embodiment of the method of using the herein described particles to produce a peroxide aqueous hydroxide solution is fed to the electroytic cell already described except no ion exchange membrane is used. The anolyte feed is typically an aqueous solution containing from 15 to 100 grams per

5

10

15

20

25

liter of sodium hydroxide. The catholyte liquor recovered from the electrolytic cell may be a catholyte liquor containing approximately 0.5 to 3 weight percent hydrogen peroxide and 15 to 100 grams per liter sodium hydroxide.

As herein contemplated, an oxidant, for example, oxygen, air or oxygen-enriched air, is fed to the catholyte compartment as an electrical current is fed from the cathode compartment to the anode compartment, whereby to provide an anode product of oxygen and water and a cathode product of an alkali metal hydroxide and a peroxide, characterized by the substantial absence of gaseous hydrogen product. The invention is particularly directed to the cathode means for carrying out the reaction, which cathode means comprise coated particles as herein described.

According to a further exemplification of the invention, there is provided an electrolytic cell having an anolyte compartment fabricated of a material resistant to concentrated, alkali metal hydroxide 20 solutions, an anode in the anolyte compartment, a catholyte compartment that is fabricated of a material resistant to concentrated alkali metal hydroxide solutions, cathode means in said cathode compartment, and 25 an ion permeable barrier interposed between the anode and the cathode means. The electrolytic cell herein contemplated is characterized by the catholyte compartment having means for feeding an oxidant to the electrolyte within the cathode compartment and cathode means which comprise individual porous particles. 30

10

### Example 1

To prepare a catalytically active coating, 0.7 gram of carbon black was blended with 20 milliliters of an aqueous silver acetate solution having a concentration of 10 grams of silver acetate per liter of solution. A drop of surfactant (Triton® X-100 a product manufactured by Rohm and Haas Co.) was added to enhance the wetting of the carbon black. The mixture was then oven dried at about 100°C. Thereafter, the 10 mixture was heated for 1 hour at 350°C in a nitrogen atmosphere to thermally decompose the silver acetate. This material was then blended with 3.5 grams of a 1:10 aqueous emulsion (1 part Teflon<sup>®</sup> 30B, a product manufactured by E. I. duPont de Nemours & Co., fluoropolymer to 10 parts water). A slurry was formed therebetween. To 15 the slurry, 10 grams of -10 +20 U.S. Mesh graphite particles were added. After mixing, the material was dried at about 100°C. Thereafter, the material was heated for 1 hour at 350°C in a nitrogen atmosphere. 20 The particles produced were graphite particles having a carbon-fluorocarbon-silver coating on their surfaces.

## Example 2

25

30

An electrolytic cell was assembled as described herein. The cell had an anode and a cathode separated by a porous asbestos diaphragm. The cathode was a packed bed of the particles produced in Example 1. The anode was ruthenium oxide coated titanium.

A sodium chloride brine solution having a concentration of about 300 grams per liter of NaCl was flowed into a compartment containing the anode. Oxygen gas was flowed into the openings between the particles comprising the cathode. Electrical current at a voltage

**OTrademark** 

of about 2 volts and at a current density of about 1 amp per square inch, was passed between the anode and the cathode to cause electrolysis of the brine solution to occur. Chlorine gas was produced at the anode and sodium hydroxide was produced at the cathode.

- 1. An electrode material comprising a substrate at least partially coated with an admixture of a binder and an electrochemically active, electrically conductive catalyst, characterized in that the electrode material is a coated particle having an average diameter of greater than 0.3 mm and less than 2.5 cm.
- 2. The electrode material of Claim 1, characterized in that the substrate is selected from a sintered material, a solid material or a bonded agglomoration of small particles.
- 3. The electrode material of Claim 2, characterized in that the substrate is selected from steel, iron, nickel, platinum, copper, silver or graphite.
- 4. The electrode material of Claims 1, 2 or 3, characterized in that the coating comprises a binder of a hydrophobic polymeric material and a catalyst having a surface area of from 100 to 1000  $\rm m^2/\rm g$  of catalyst.

- 5. The electrode material of Claim 4, characterized in that the catalyst is an oxygen reaction catalyst selected from carbon black, activated carbon, platinum or silver.
- 6. The electrode material of Claim 5, characterized in that the catalyst is carbon black and has a surface area from 150 to 500  $m^2/g$  of catalyst.
- 7. The electrode material of Claim 4, characterized in that the catalyst is a peroxide decomposition catalyst selected from silver and platinum and mixtures or compounds thereof mixed with carbon black.
- 8. The material of any one of the preceding claims, characterized in that the particle has an average diamater of from 0.7 mm to 4 mm.
- 9. The material of Claim 1 characterized in that the substrate is an admixture of a solid fluorocarbon binder and a catalyst selected from the group consisting of silver, carbon black, platinum and activated carbon.
- 10. The material of Claim 1 characterized in that the substrate is electrically conductive and is completely coated with the admixture.
- 11. A method for the production of an electrode material comprising forming a fluid admixture of an electrochemically active, electrically conductive catalyst and a binder, bonding the catalyst to the substrate by solidifying the fluid

admixture, and characterized by forming the electrode material into particles having an average diameter greater than 0.3 mm and up to 2.5 cm.

- 12. The method of Claim 11 characterized by forming the fluid admixture by heating the binder to a temperature at least as high as its softening temperature, and cooling the admixture to a temperature below the softening temperature of the binder to bond the catalyst to the substrate.
- 13. The method of Claim 11 characterized by forming the fluid admixture by dispersing the catalyst, binder and substrate in a liquid, and heating the admixture to evaporate the liquid to bond the catalyst to the substrate.
- 14. The method of Claim 11 characterized by forming the fluid admixture by dissolving the binder in a solvent, and heating the admixture to evaporate the solvent to bond the catalyst to the substrate.
- 15. The method of Claim 11 characterized in that the catalyst is carbon black and the binder is polytetrafluoroethylene, and wherein the weight ratio of carbon black to binder is from 4:1 to 1:4.
- 16. The method of Claim 11 characterized by adding a surfactant to the admixture.
- 17. The method of Claim 11 characterized by adding a second catalyst which is a peroxide decomposition catalyst, and wherein the total amount of catalyst in the admixture is from 1 to 35 weight percent

peroxide decomposition catalyst and from 65 to 99 weight percent carbon black.

- electrolyte in an electrolytic cell having an anolyte compartment with an anode therein and a catholyte compartment with a cathode therein, which method comprises feeding said aqueous electrolyte to the cell, passing an electrical current between the anode and the cathode and recovering the products of electrolysis, at least one of the electrodes being formed of an electrode material comprising a substrate which is at least partially coated with an electrically conductive admixture of a hydrophobic material and at least one catalyst, and characterized in that the electrode material comprises a plurality of packed particles each having an average diameter of greater than 0.3 mm and up to 2.5 cm.
- 19. The method of Claim 18 characterized by positioning an ion permeable barrier between the anode and the cathode.
- 20. The method of Claim 18 or 19, characterized by feeding an oxygen containing gas to the cathode.
- 21. An electrolytic cell having an anolyte compartment with an anode therein and a catholyte compartment with a cathode therein, means for feeding an aqueous electrolyte to the cell, means for passing an electrical current between the anode and the cathode, and means for recovering the products of electrolysis from the cell, at least one of the

anode or cathode being formed of an electrode material comprising a substrate which is at least partially coated with an electrically conductive admixture of a hydrophobic material and at least one catalyst, characterized in that the electrode material comprises a plurality of packed particles each having an average diameter of greater than 0.3 mm and less than 2.5 cm.

- 22. The cell of Claim 20 characterized in that the substrate comprises graphite, the catalyst is selected from the group consisting of carbon black, silver and platinum, and the hydrophobic binder material is polytetrafluoroethylene.
- 23. The cell of Claim 21 characterized in that the catalyst is a mixture of carbon black and a peroxide decomposition catalyst.



# **EUROPEAN SEARCH REPORT**

DOCUMENTS CONSIDERED TO BE RELEVANT				EP 82111802.3	
Category	Citation of document wi of rele	th indication, where ap vant passages	propriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Ci. <sup>2</sup> )
A	EP - A2 - O O1 LOGY LIMITED T BANK) * Claims 1, 9-24 *	HAMES HOUS	E MILL-	1-3, 11	C 25 B 11/06 C 25 B 11/08 C 25 B 11/12// C 25 B 1/46
A	GB - A - 2 074 MATTHEY & CO., * Claims 1,	LIMITED) (28-10	SON D-1981)	1,3,5	•
A	DE - A - 2 928  * Claims 1,3 1-14 *	BOVE	RIE & CIE)	1-3,5	
		نون ميت شنه ۳۰۰			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			-		C 25 B 11/06 C 25 B 11/08 C 25 B 11/00 C 25 B 11/12 C 25 B 1/46
The present search report has been drawn up for all claims					
		tion of the search	Examiner HEIN		
A: tec O: nor	CATEGORY OF CITED DOCU ticularly relevant if taken alone ticularly relevant if combined w sument of the same category hnological background newritten disclosure termediate document	JMENTS	T: theory or pri E: earlier pater after the filir D: document c L: document c	nt document, I ng date ited in the app ited for other	ying the invention but published on, or