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PROCESS FOR CODEPOSITING PLATINUM METAL AND A WET-PROOFING POLYMER

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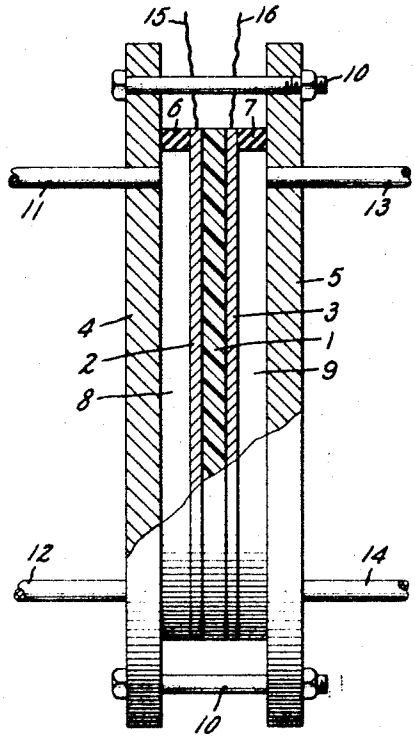

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PROCESS FOR CODEPOSITING PLATINUM METAL AND A WET-PROOFING POLYMER

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ABSTRACT OF THE DISCLOSURE

A process is disclosed for producing an intimately blended codeposit of a platinum metal and a wet-proofing polymer. A plating bath is formed containing from 0.1 to 10 percent by weight of the platinum metal and from 0.1 to 50 percent by weight of the polymer. A substrate is immersed in the plating bath and a current of from 10 to 25 ma./cm.^{2} is applied to the substrate with polarity being reversed at 10 to 60 second intervals. The so coated substrate may be utilized as an electrode in a cell such as a fuel cell.

The invention relates to molecularly blending electrocatalytic materials and polymer wet-proofing agents and to structures formed of such molecularly blended materials.

It has heretofore been recognized that electrocatalysis by platinum metals is a surface phenomenon and that electrocatalytic efficiency requires a high surface area per unit weight. For this reason, the use of platinum metals in the form of metallic structures has been largely discarded in favor of employing platinum metals in high surface area per unit weight particulate form. Typically, the platinum metal is employed in the most finely divided form obtainable such as a black, for example, and is fabricated into a unitary electrocatalytic electrode by physical blending with a particulate, polymeric wet-proofing agent which also functions as a binder. In order to improve the structural strength and electrical conductivity of the electrode, a foraminous substrate is frequently employed as an electrode core element.

While such electrodes offer the best electrocatalytic efficiency available by physical blending techniques, the inherent limitations of physical blending prevent realization of the full electrocatalytic potential. In the first instance, the blending of platinum metal and wet-proofing agent at the particle level rather than at the molecular level fails to expose the maximum electrocatalytic surface area per unit weight. Secondly, physical blending of the electrocatalyst and wet-proofing materials can be achieved with only a limited degree of uniformity. An excess of polymer at any given point within the electrode may substantially encapsulate and thereby inactivate adjacent platinum metal particles. On the other hand, too little polymer at any given point may result in the adjacent electrocatalyst particles being vulnerable to wetting and erosion. Further, manual spreading on the substrate of the platinum metal-polymer mixture, typical of electrode fabrication from physically blended materials, requires that a layer of considerable thickness be applied, since the uniformity of the layer thickness cannot be controlled with exactness.

It is an object of our invention to provide a novel plating bath.

It is another object of our invention to provide a process of electrically codepositing and molecularly blending platinum metals and polymeric wet-proofing materials.

It is still another object to provide a process for producing an electrode comprised of molecularly blended platinum metal and polymeric wet-proofing material.

These and other objects of our invention are accomplished by providing an aqueous plating bath containing from 0.1 to 10 percent by weight, preferably 0.5 to 5 percent by weight, platinum metal in the form of a soluble salt and from 0.1 to 50 percent by weight, preferably from 0.5 to 15 percent by weight, of a dispersed polymer having a critical surface tension less than the surface tension of water. Plating onto an electrically conductive substrate is conducted at a current density of from 10 to 25 ma./cm.^{2} and the polarity of the substrate is reversed each 10 to 60 seconds. The structure so formed is sintered briefly to remove volatile impurities. The electrode formed is comprised of a molecular blend of platinum metal and wet-proofing polymer.

Our invention may be better understood by reference to the following detailed description taken in conjunction with the drawing, which is a vertical section of a fuel cell.

The term "platinum metal" as herein employed refers to metals of the light and heavy platinum triads with the exception of osmium. These metals are platinum, iridium, palladium, rhodium, and ruthenium. These metals may be employed either singly or in combination in a concentration range of from 0.1 to 10 percent by weight, and preferably from 0.5 to 5 percent by weight. The platinum metal may be placed in solution in an aqueous plating bath through the use of any one of a variety of well-known water soluble platinum metal salts. Exemplary water soluble platinum metal compounds include chloroplatinic acid, tetraplatinic bromide, platinic sulfate, iridium tri-bromide, iridium di-chloride, iridium tetra-chloride, iridium hexa-fluoride, iridium sulfate, palladium chloride, palladium sulfate, diamminepalladium hydroxide, dichlorodiamminepalladium, tetramminepalladium chloride, rhodium tri-chloride, rhodium nitrate, rhodium sulfate, rhodium sulfite, ruthenium tri-chloride, ruthenium tetra-oxide, etc. In order to improve the electrocatalytic properties of the deposited platinum metal, it may be desired to also include a material such as lead acetate capable of causing smaller platinum metal crystallites to form—i.e., capable of increasing lattice defects. Such materials may be employed in concentrations up to one percent by weight.

In addition to platinum metal, the aqueous plating bath must also include a polymer wet-proofing agent. The polymer is employed in the form of aqueous dispersion. In order to impart wet-proofing properties, the polymer must have a critical surface tension less than the surface tension of water. A preferred maximum critical surface tension is 32 dynes/cm. Critical surface tension is defined as the value of the liquid surface tension at which liquids spread on a given polymer surface. A full discussion of critical surface tension is provided at page 240, "Surface Chemistry Theory and Industrial Application," by Lloyd I. Osipow, Reinhold Publishing Corporation, New York, 1962. A preferred polymer for use in the invention is polytetrafluoroethylene sold under the trademark "T–30," which is an aqueous dispersion containing 65 percent by weight of the polymer. Another polymer having a critical surface tension less than 32 dynes/cm. is polychlorotrifluoroethylene. The aqueous bath may contain from 0.1 to 50 percent by weight, preferably from 0.5 to 15 percent by weight, of dispersed polymer.

A substrate is immersed within the aqueous bath to receive the plate. The substrate may take the form of any conventional current collector, including expanded and woven metal screens, meshes, mats, plates, strips or any other convenient structural form. The substrate may be formed of any electrically conductive material that is not readily chemically attacked in the environ

ment of intended use. For fuel cell applications, the substrate is preferably foraminous and formed of a relatively corrosion-resistant material, such as nickel, stainless steel, titanium-palladium alloy, etc. It is, of course, contemplated that plating may be conducted onto a platinum metal containing substrate such as a conventional electrode in order to impart or improve wet-proofing. Alternately, the substrate need not form any part of the finished electrode, but may merely serve as a convenient plating surface from which the electrode may be stripped after deposition as disclosed, for example, in commonly assigned application, Ser. No. 411,693, filed Nov. 17, 1964.

Plating is accomplished utilizing current densities of from 10 to 25 ma./cm.^{2} and by reversing the polarity of the substrate each 10 to 60 seconds. When the substrate is cathodically polarized, the principal deposit on the substrate is platinum metal, although a certain amount of polymer may be occluded by the depositing metal ions. Additionally, a certain amount of polymer will deposit onto the substrate in the complete absence of an electric field, merely by physical adherence. Neither the quantity of the polymer occluded by the depositing platinum metal ions nor the quantity physically adhering, however, is sufficient in itself to completely wet-proof the substrate. The principal amounts of wet-proofing polymer are anodically deposited. Some quantity of platinum metal may be occluded by the polymer during anodic deposition. Since the polymer molecules exhibit low mobility, polarity reversal at less than 10-second intervals is generally unproductive. By reversing polarity at least once every 60 seconds, an intimate molecular blend of the wet-proofing polymer and platinum metal is maintained in the deposit. Current densities above 25 ma./cm.^{2} are generally undesirable, since an uneven deposit is obtained. A preferred procedure of electrodeposition consists of immersing two substrates in the aqueous bath simultaneously so that by reversing polarity at even time intervals, two identical electrodes may be simultaneously formed. It is, of course, contemplated that it may be desired to vary the proportion of polymer or platinum metal deposited on a substrate by selectively varying the time interval during which the substrate is maintained at a given polarity. For example, a minimum polymer deposit may be obtained by cyclically anodically depositing for 10-second intervals and cathodically depositing for 60-second intervals. Upon removal from the aqueous bath, the deposit is sintered on the substrate for a brief period, approximately 30 seconds to 4 minutes, in order to drive out any water or other volatile impurities which may be present. Preferred sintering temperatures range from 640° F. to 700° F. Higher temperatures may decompose the polymer wet-proofing agent while lower temperatures may not produce a completely hydrophobic surface.

The electrode formed according to our invention is comprised of a platinum metal electrocatalyst blended at a molecular level with a polymer wet-proofing agent so that a maximum surface area per unit weight of the platinum metal is obtained. The electrode may include a substrate to improve its structural strength and electrical conductivity. Electrodes for use in fuel cells typically include a foraminous, noncorrosive substrate. As previously noted, the electrode may, however, be formed entirely of the platinum metal-polymer deposit by being transferred from the substrate, which serves only as a plating surface. The electrode dimensions are not critical. The thickness may vary from 1 to 25 mils or more, and the areal extent of the electrode may be varied to suit the geometric requirements of use.

While it is preferred to form an electrode by codeposition of platinum metal and a wet-proofing polymer onto a substrate, it is contemplated that the platinum metal may be first deposited by conventional techniques. In order to wet-proof the electrode so formed, it may be

immersed into an aqueous bath consisting essentially of 0.1 to 50 percent by weight, preferably 0.5 to 15 percent by weight, wet-proofing polymer and water. A completely hydrophobic electrode may be obtained by this technique, although molecular blending of the platinum metal and wet-proofing polymer is not obtained, as in the preferred procedure.

An illustrative fuel cell configuration is shown in the drawing. An ion exchange membrane **1** is mounted between electrodes **2** and **3** formed according to our invention. The membrane and electrodes together form a membrane-electrode assembly. Fixtures **4** and **5**, separated from electrodes **2** and **3**, respectively, by insulating shims **6** and **7** form reactant chambers **8** and **9** adjacent the electrodes. The fixtures, shims, and membrane-electrode assembly are held together by tie-bolt assemblies **10**. Conduits **11** and **12** in fixture **14** and conduits **13** and **14** in fixture **5** allow ingress and egress of fluent reactants and products to and from the fuel cell. Electrical energy may be obtained from the fuel cell through electrical leads **15** and **16** attached to electrodes **2** and **3**, respectively. It is appreciated that electrodes formed according to our invention may also be employed in a fuel cell utilizing a liquid electrolyte. The fuel cell shown in the drawing could, for example, be converted to a liquid electrolyte fuel cell merely by replacing the ion exchange membrane **1** with a shim similar to shims **6** and **7**. Electrolyte could be admitted to and removed from the area occupied by the ion exchange membrane merely by providing conduits in the additional shim.

The following examples are illustrative of the practice of our invention:

EXAMPLE 1

A bright platinum strip having a surface area of 1 cm.^{2} on a side was immersed in an aqueous plating bath. The bath consisted essentially of 0.75 percent by weight platinum in the form of chloroplatinic acid, 0.5 percent by weight polytetrafluoroethylene (PTFE) in the form of a dispersion sold under the trademark "T–30," 0.025 weight percent lead acetate, and the remainder water. A current density of 10 ma./cm.^{2} was established using the platinum strip alternately as a cathode and an anode, with the polarity being reversed at 30-second intervals. Plating was continued for four minutes. After plating, the platinum strip was sintered in an oven maintained at 660° F. for two minutes to drive out volatile components. Upon examination, the electrode formed was noted to exhibit a molecularly blended deposit of platinum metal and wet-proofing polymer. The thickness of the deposit was uniform. The hydrophobicity of the electrode was tested by partially immersing the electrode in a body of distilled water. The electrode was held perpendicular to the surface of the water and lowered into the water. The meniscus was noted to be convex upwardly indicating that the electrode was not wetted. Quantitatively stated, a contact angle of greater than 90° was noted.

EXAMPLE 2

The procedure of Example 1 was repeated except that a mixture of 5 percent by weight ruthenium tri-chloride and 95 percent by weight chloroplatinic acid was substituted for the chloroplatinic acid previously employed. The total concentration of the substituted salt mixture was 5 percent by weight. The properties of the electrode formed were generally similar to those of the electrode of Example 1.

EXAMPLE 3

The procedure of Example 1 was repeated, except that the current density was increased to 25 ma./cm.^{2}. The properties of the electrode formed were generally similar to those of the electrode formed by the procedure of Example 1.

EXAMPLE 4

The procedure of Example 1 was repeated, except that the weight percent of platinum was increased to 7.5. The

properties of the electrode formed were generally similar to those of the electrode formed by the procedure of Example 1.

EXAMPLE 5

The procedure of Example 1 was repeated, except that the PTFE content was increased to 15 percent by weight. The properties of the electrode formed were generally similar to those of the electrode formed by the procedure of Example 1.

EXAMPLE 6

The procedure of Example 1 was repeated using first a polished platinum metal substrate and then a substrate having a film of platinum black deposited thereon. No electric field was employed to facilitate deposition. Some PTFE was observed to adhere to the surface of the substrates; however, upon partially immersing the substrates in distilled water, it was noted that a meniscus was obtained which was concave upwardly, thereby indicating wetting of the electrode surfaces. In other words, a contact angle of less than 90° was observed.

EXAMPLE 7

The procedure of Example 6 was repeated, except that only a cathodic current was used. While platinum was deposited and some PTFE was observed to adhere to the surface of the substrates, the surfaces of the electrodes were readily wetted by distilled water.

EXAMPLE 8

The procedure of Example 6 was repeated, except that only an anodic current was used. A uniform deposit of PTFE was noted. Upon partial immersion in distilled water a meniscus was obtained which was convex upwardly, indicating hydrophobicity.

EXAMPLE 9

An ion exchange membrane formed of "Aclar 22A," a trademark for a copolymer of 3.5 percent by weight vinylidene fluoride and chlorotrifluoroethylene, and a sulfonated copolymer of styrene and divinylbenzene, of the type disclosed in commonly assigned application, Ser. No. 414,011, filed Nov. 25, 1964, was placed in a 50 ml. beaker filled approximately two-thirds full with distilled water. Ten drops (0.5 cc.) of a saturated solution of platinum sulfate (0.0366 gm. of platinum per gram of solution) was added, and the solution stirred until well mixed. Next 10 drops of a solution containing 5 gm. of sodium borohydride and 300 gm. of potassium hydroxide per liter were added. In approximately 10 minutes the surfaces of the membrane were mirrored with metallic platinum. The mirroring procedure is disclosed in commonly assigned application Ser. No. 441,921, filed Mar. 22, 1965. The ion exchange membrane was removed from the mirroring bath, rinsed in distilled water, and trimmed for mounting in a fuel cell.

A stainless steel sheet having a thickness of 0.006 inch and an areal extent of 1 in.^{2} was immersed in a plating bath and plated according to the procedure of Example 1. The molecularly blended platinum-PTFE deposit on one side of the stainless steel sheet was mounted adjacent one surface of the ion exchange membrane. Adjacent the remaining surface of the ion exchange membrane was mounted a Niedrach-Alford electrode formed of platinum black and 15 percent by weight PTFE, of the type disclosed in commonly assigned application, Ser. No. 232,689, filed Oct. 29, 1962. The membrane-electrode assembly was placed in a platen press and subjected to a pressure of 5 tons/in.^{2} at a temperature of 250° F., according to the procedure disclosed in commonly assigned application, Ser. No. 400,228, filed Sept. 29, 1964, now U.S. Patent No. 3,356,538. The electrodes were bonded to the ion exchange membrane and the molecularly blended platinum-PTFE deposit released completely from the stainless steel sheet.

Tantalum screen current collectors were mounted adjacent the exposed faces of the electrodes and the resulting assembly was mounted in a fuel cell fixture of the same general configuration shown in the drawing. The molecularly blended platinum-PTFE electrode was first tested as a fuel electrode and was supplied with hydrogen. The Niedrach-Alford type electrode was supplied with oxygen. Both the fuel and oxidant feeds were dead-ended into the cell so that only sufficient hydrogen and oxygen were supplied to maintain a constant pressure within the fuel cell fixture—i.e., to replace the reactant depleted in cell operation.

The following performance characteristics were noted:

TABLE I

Current density (ma./cm.^{2})	Potential (volts)
3.96	0.971
5.28	0.963
7.92	0.944
13.2	0.923
26.3	0.892
52.8	0.841
65.9	0.811
79.2	0.784
92.2	0.761
105.0	0.731
132.0	0.664

Next, the fuel and oxidant feeds to the cell were reversed, so that the molecularly blended platinum-PTFE electrode became the oxygen electrode. After purging, the following test results were obtained:

TABLE II

Current density (ma./cm.^{2})	Potential (volts)
0	0.965
0.263	0.939
1.32	0.888
2.63	0.860
5.28	0.825
10.50	0.785
15.8	0.759
21.1	0.735
39.6	0.689
65.9	0.622
105.0	0.475

While we have described our invention in terms of certain prepared embodiments, it is apparent that numerous modifications will be apparent to those skilled in the art. For this reason, it is intended that the scope of the invention be interpreted by reference to the following claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A process of intimately blending a platinum metal and a wet-proofing polymer as a codeposit on a substrate comprising

forming an aqueous plating bath containing from 0.1 to 10 percent by weight of a platinum metal in the form of a soluble salt and from 0.1 to 50 percent by weight of a dispersed polymer having a critical surface tension less than the surface tension of water,

immersing the substrate in the aqueous plating bath, and

applying a current density of from 10 to 25 ma./cm.^{2} to the substrate and reversing the polarity of the substrate at 10 to 60-second intervals to form on the substrate an intimately blended codeposit of platinum metal and wet-proofing polymer.

2. A process according to claim 1 additionally including the steps of removing the codeposited platinum metal and wet-proofing polymer from the aqueous plating bath and subsequently heating the codeposit to remove volatile impurities.

3. A process according to claim 2 in which the codeposit is sintered in a temperature range of from 640° F. to 700° F.

4. A process according to claim 1 additionally including the step of stripping the codeposit from the substrate.

5. A process according to claim 1 in which the platinum metal is present in the plating bath in a concentration of from 0.5 to 5 percent by weight.

6. A process according to claim 1 in which the dispersed polymer is present in the plating bath in a concentration of from 0.5 to 15 percent by weight.

7. A process according to claim 1 in which the dispersed polymer is polytetrafluoroethylene.

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