United States Patent Office 3,503,799
Patented Mar. 31, 1970

3,503,799

METHOD OF PREPARING AN ELECTRODE COATED WITH A PLATINUM METAL

Kiyoshi Aoki, Tokyo, and Seiichi Ishikawa, Kiyomi Nagaike, Shiro Honda, and Minoru Watanabe, Kanagawaken, Japan, assignors to Ajinomoto Co., Inc., Tokyo, Japan

No Drawing. Filed May 12, 1967, Ser. No. 637,918
Claims priority, application Japan, May 19, 1966, 41/31,919
Int. Cl. B44d 1/18, 1/02
U.S. Cl. 117—217 9 Claims

ABSTRACT OF THE DISCLOSURE

An anode for brine electrolysis having low chlorine overvoltage is prepared by coating titanium with an alloy of a platinum metal with a less noble metal (typically Cu, Ni, Fe, Ag, Pb, Mn, Co), dissolving the less noble metal from the alloy layer, and coating the substrate so produced with a surface layer of platinum metal. The loss of platinum metal under otherwise comparable conditions during brine electrolysis is lower than from otherwise similar conventional anodes coated with platinum metals.

BACKGROUND OF THE INVENTION

This invention relates to the production of chlorine by electrolysis of brine, and particularly to the preparation of anodes for brine electrolysis.

Titanium anodes coated with platinum metals have good resistance to the electrolyte under the conditions prevailing in commercial brine electrolysis. However, they have not found wide application because the overvoltage of chlorine at the known electrodes is relatively high, and causes an increase in power consumption too great to be economically bearable under many conditions. The cost of cell operation with the known coated electrodes is further increased by the small but significant losses of the costly platinum metal.

The object of the invention is the provision of an anode for brine electrolysis, which combines the durability of the known coated titanium electrodes with low chlorine overvoltage and with lower consumption of precious metal.

SUMMARY OF THE INVENTION

Electrodes having the desired properties are obtained by coating a conductive base material with an alloy of a platinum metal with a less noble metal (typically Cu, Ni, Fe, Ag, Pb, Mn, Co), dissolving at least a major portion of the less noble metal in a solvent which does not significantly attack the platinum component of the alloy, and coating the substrate so produced with a surface layer of a platinum metal, the latter term being employed in this specification for platinum, rhodium, iridium, palladium, osmium, ruthenium, and alloys of these metals with each other. Masurium and rhenium are not available in adequate quantities at reasonable cost to require consideration.

While the results of the method are most favorable when the base material is titanium, important advantages of the method of the invention are achieved when the base material is zirconium or magnetite, and other conductive materials benefit at least to some extent from the method of the invention.

The alloy layer may be deposited on the base material in any known manner. Cathodic codeposition of platinum metals with the less noble metals is possible in many instances. Diffusion alloys are readily prepared by sequentially depositing layers of a platinum metal and of one

or more of the less noble metals enumerated above, and heating the laminar coating until the desired alloy is formed without fusion of either layer. If needed, the surface layer may be protected in an inert atmosphere. Separation of the constituents upon cooling from the diffusion temperature may occur unless the alloy coating is quenched.

The individual metal layers may be deposited in any desired manner, and suitable electrochemical and chemical precipitation methods are commonly known. Those skilled in the art are also familiar with the preparation of diffusion alloys.

The solvents employed for removing the less noble metal component from the alloy layer are selected according to the known properties of the less noble alloy constituent. It is evident that the solvents must not attack the platinum metal. Strong aqueous solutions of the mineral acids (hydrochloric, nitric, sulfuric acid) or of strong alkali are representative solvents, but anodic dissolution of the less noble component in alkali metal chloride solutions is usually most rapid. Other solvents will readily suggest themselves to those skilled in the art.

Depending on the chemical nature of the base material and of the solvent employed in decomposing the alloy layer, it may be advisable to protect the base material by a layer of platinum metal deposited on the base material surface prior to alloy deposition or to limit the thickness of a diffusion alloy formed from an inner layer of platinum metal and an outer layer of less noble metal.

The platinum metal employed as the ultimate surface coating need not be identical with the metal used in the alloy coating. Alloys of two or more platinum metals are preferred in the surface coating because of their better resistance to anodic corrosion. The method employed in depositing the surface layer may be entirely conventional, and may be either electrochemical or chemical.

In evaluating the overvoltage characteristics of anodes, we have relied on the method of W. C. Gardiner (Electrochem. Tech. 1, 71 (1963) and H. A. Sommers (Chem. Eng. Prog. 61 (3) 94 (1965)). The overvoltage properties of an electrode are expressed by the factors α and β in the equation

$$E=\alpha+\beta\cdot D_A$$

wherein E is the observed cell voltage, α is the cell voltage extrapolated to zero current density, β is the slope of the curve of cell voltage v, current density, and D_A is the anodic current density.

The determination of α and β for the various anodes, to which reference will be made hereinbelow, was made in a cell having a mercury cathode containing 0.1% sodium (by weight) at a distance of 5 mm from the tested anode, and using a 300 g./l. NaCl solution at 60° C. as an electrolyte. The cell voltage was measured at anode current densities of 20, 40, 60, 80 and 100 amps/dm.^{2}, and the values of α and β were determined graphically from the measured values.

Loss of material from the anodes was determined during electrolysis of a 250 g./l. NaCl solution which additionally contained 15 g./l. Na_2SO_4 and 9 g. $NaClO_3$, and was kept at a pH of 2.5 and a temperature of 70° C. The distance between the tested anode and the mercury cathode was about 50 mm., and an applied potential of 8 volts produced an anode current density of 130 amps/dm.^{2}. Each anode was tested for a period of 10 days to three months, and the metal loss was calculated in mg./1000 amp hrs.

Under the test conditions outlined above, the anodes of the invention typically show α values of 3.05 ± 0.05 v., and β values of $(1.03\pm0.05)\times10^{-2}$ v. dm.^{2}/amp. When platinum is used as a surface coating in the known electrodes, the metal loss is about 1.4 mg./1000 amp hrs. It is about 40% lower in otherwise similar electrodes prepared by the method of the invention. The metal loss from conventional

anodes coated with alloys of platinum metals is more than 0.8 mg./1000 amp hrs., and is reduced by about 50% by the method of the invention.

DETAILED DESCRIPTION

The following examples further illustrate the invention, but it is to be understood that the invention is not limited thereto. Because titanium has obvious advantages over other base materials for anodes to be used in brine electrolysis, and in order to provide a common basis of comparison for the several examples, the base materials employed in each example were circular titanium discs of 30 mm. diameter, 1 mm. thickness and provided with five approximately uniformly spaced holes of 3 mm. diameter. Unless stated otherwise, each disc was prepared for plating either by immersion in boiling 35% hydrochloric acid for 25 minutes, or by immersion in a melt of equal weights of NaCl and KCl at 750° to 800° C. for 30 minutes, and subsequent immersion in 50% phosphoric acid for 10 minutes at 80° to 90° C. Washing with water followed each immersion step.

Example 1

Four titanium discs prepared by immersion in HCl were coated with approximately 6 mg. platinum per cm.^{2} of surface area by electrodeposition from a bath of the following composition and operating condition:

$H_2PtCl_6 \cdot 6H_2O$—5 g./l.
$NH_4H_2PO_4$—45 g./l.
$(NH_4)_2HPO_4$—240 g./l.
Temperature—80–100° C.
Current density—0.3 amp/dm.^{2}

One disc was thereafter copper plated to a thickness of 7 mg./cm.^{2}, a second disc was nickel plated (4 mg./cm.^{2}), a third disc was silver plated (3 mg./cm.^{2}), and the fourth gold plated (5 mg./cm.^{2}). Conventional acid copper and nickel plating solutions and conventional cyanide type silver and gold plating solutions were employed.

The surface layers were diffused into the platinum base coating by heat treatment in an electric furnace at 700° C. for 20 minutes, followed by cooling to room temperature, an inert atmosphere being employed during the treatment.

The less noble metal was then dissolved from each alloy layer by making the coated disc the anode in a 300 g./l. NaCl solution at 60° C. and a current density of 100 amps/dm.^{2}. The anodic treatment was interrupted from time to time to determine the weight loss of the treated disc, and anodic treatment was continued until the weight became constant. This took 30 to 120 minutes with the several discs.

The weight loss of the discs coated with copper and nickel alloys was about equal to the weight of the copper and nickel deposit. The silver diffusion alloy lost about 150% of the weight gained by silver plating, and the gold diffusion alloy lost slightly more than the added gold weight.

The substrates so formed were coated with platinum by brushing the discs with a solution prepared from 2.6 g. chloroplatinic acid (1 g. Pt), one drop each of 35% HCl and 25% boric acid in aqueous solutions, 20 ml. ethanol, 10 ml. lavender oil, and 8 ml. turpentine, and by thermally decomposing the liquid coating by heating in the flame of a gas burner. The procedure of brushing and decomposing was repeated to build up a coating having a thickness of approximately 1.5 mg. Pt per cm.^{2}.

The anodes so prepared were tested for chlorine overvoltage and showed α values of 3.08 to 3.13 v., averaging 3.10 v., and β values of 1.01 to 1.15×10^{-2} v. dm.^{2}/amp averaging 1.06×10^{-2} v. dm.^{2}/amp. By comparison, discs merely electroplated with platinum to a thickness of about 6 mg./cm.^{2} showed average values of 3.70 v. and 1.15×10^{-2} v. dm.^{2}/amp respectively. When a platinum plated disc was provided with a platinum surface coating of approximately 1.5 mg./cm.^{2} by brushing and thermal decomposition of the solution described above, the values were 3.23 and 1.18×10^{-2} respectively. The weight loss from the platinum coating during extended electrolysis was 1.40 mg./1000 amp hrs. as compared with 1.06 mg./1000 amp hrs. for the aforementioned disc which had received a copper alloy coating from which the copper was dissolved prior to surface coating.

Example 2

Additional anodes of the invention were prepared by variations of the methods described in Example 1, using the same materials unless specifically stated otherwise.

Titanium discs electroplated with platinum to a thickness of 5 mg./cm.^{2} were copper plated (7 mg./cm.^{2}) and heat treated for 30 minutes to diffuse the copper into the platinum, whereupon the copper was dissolved electrolytically. A platinum electrodeposit (1.8 mg./cm.^{2}) was applied as a surface coating on one disc, resulting in α and β values of 3.17 and 1.15×10^{-2} respectively. A platinum surface coating (1.5 mg./cm.^{2}) produced by thermal decomposition of a brushed chloroplatinic acid solution on another disc over a similar electrodeposit gave values of 3.10 and 1.13×10^{-2} respectively.

A Pt-Cu alloy coating was applied to one disc by sequential electrodeposition of platinum (6 mg./cm.^{2}) and copper (10 mg./cm.^{2}) and heat treatment for 30 minutes. The weight gained in copper plating was substantially completely lost during immersion in 62% HNO_3 for 150 minutes at 20° C. When a platinum surface layer (1.5 mg./cm.^{2}) was subsequently applied by thermal decomposition of chloroplatinic acid solution, the α and β values of the anode so obtained were 3.09 v. and 1.04×10^{-2} v. dm.^{2}/amp.

Another disc pretreated by immersion in fused salts was electroplated with platinum (5 mg./cm.^{2}) and copper (7 mg./cm.^{2}), and a diffusion alloy was formed by heating for 30 minutes. The copper was substantially completely removed by electrolysis, and a surface coating of platinum (2 mg./cm.^{2}) was applied by thermal decomposition of the chloroplatinic acid solution. When tested for chlorine overvoltage, the anode obtained yielded α and β values of 3.12 and 1.00×10^{-2} respectively. During extended electrolysis, the disc lost 0.88 mg. platinum per 1000 amp hrs.

Another disc prepared by immersion in fused alkali metals chlorides was electroplated with platinum (12 mg./cm.^{2}) and thereafter with iron (25 mg.) from a conventional ferrous chloride bath, the iron deposit was diffused into the platinum layer for 120 minutes at 700° C., and the iron was removed from the diffusion alloy by electrolysis. With a surface coating of platinum (1.8 mg./cm.^{2}) produced by thermal decomposition of chloroplatinic acid solution, the anode obtained showed α and β values of 3.05 and 1.05×10^{-2} respectively.

It is evident from Examples 1 and 2 that the manner of preparing the titanium disc for coating with platinum according to the method of this invention has no bearing on the results ultimately obtained, and the nature of the less noble metal alloyed to the platinum in the base layer and subsequently dissolved does not cause significant changes in the α and β values. It is also relatively unimportant in which manner a surface layer of platinum is applied after removal of the less noble metal. The thickness of the several layers applied also is not critical, but it will be appreciated that the coating should substantially cover the titanium base, and that the less noble metal should be removed by means of a solvent which does not affect the platinum.

Example 3

Alloy base coatings were produced by methods other than thermal diffusion of separately deposited metal layers on a series of titanium discs. The less noble alloying element was removed from each disc by anodic treatment

in NaCl, and a surface coating of platinum was applied by decomposition of chloroplatinic acid solution.

Two discs respectively pretreated with hydrochloric acid and fused alkali chlorides were respectively coated with 6 and 5 mg./cm.^{2} of a platinum-copper alloy by electrodeposition from a solution obtained by adding 0.4 g./l. $CuCl_2$ to the afore-described platinum plating solution under the same conditions of temperature and cathode current density. After removal of the copper, surface layers of platinum (1.6 and 1.4 mg.) were applied. The finished anodes gave α values of 3.14 and 3.05, and β values of 0.98 and 1.08×10^{-2}.

A pair of discs, differently pretreated as described above, were coated with platinum-nickel alloy (3 and 5 mg.) by electrodeposition from a solution obtained by adding 0.8 g./l. $NiCl_2\cdot6H_2O$ to the basic platinum plating solution. The platinum surface coatings of the two discs were of approximately equal thickness (1.5 mg./cm.^{2}). The values characteristic of chlorine overvoltage were low and closely similar at 3.09, 3.08 and 1.06×10^{-2}.

Yet another pair of titanium discs was pre-treated in hydrochloric acid and coated (approx. 4 mg./cm.^{2}) with platinum-copper and platinum-nickel alloys respectively by thermal decomposition of brushed-on solutions which differed from the afore-described chloroplatinic acid solution by the addition of 0.21 g. $CuCl_2$ and 0.1 g. $NiCl_2\cdot6H_2O$ respectively. When coated with 2.0 and 1.7 mg./cm.^{2} platinum respectively, the two anodes had α and β values of 3.10, 0.99×10^{-2} and 3.09, 1.05×10^{-2}.

The manner in which the alloy of platinum and a less noble metal is deposited on the titanium discs thus has no bearing on the properties of the ultimate anode disc.

Example 4

The effect of alloying the platinum surface layer with another platinum group metal, and the independence of this effect from other processing variables are illustrated by the following tests.

A titanium disc pretreated in hydrochloric acid was coated with successive layers of platinum (6 mg./cm.^{2}) and copper (5 mg./cm.^{2}). The copper was diffused into the platinum by heat treatment for 20 minutes, and about 95% of the weight gained in copper plating was lost in subsequent anodic treatment in brine. A surface coating of platinum-rhodium alloy (1.6 mg./cm.^{2}) was deposited by thermal decomposition of a solution which differed from the afore-described chloroplatinic acid solution by the addition of 0.26 g. $RhCl_3\cdot3H_2O$ (0.1 g. Rh). The coated disc when tested for chlorine overvoltage yielded α and β values of 3.10 and 1.02×10^{-2} respectively, and it lost only 0.43 mg./1000 amp hours during extended use as an anode.

Another disc pretreated in fused alkali metal chlorides was coated sequentially with 6.5 mg./cm.^{2} platinum by electrodeposition, 1.8 mg./cm.^{2} by thermal decomposition of chloroplatinic acid, and 5.9 mg./cm.^{2} of copper. A diffusion alloy was produced by heating for 30 minutes to 700° C., and the copper was removed again by electrolysis. A platinum-rhodium alloy coating (1.1 mg./cm.^{2}) was formed as described above. The finished anode had α and β values of 3.09 and 1.02×10^{-2}. It lost 0.26 mg./1000 amp hrs. during extended electrolysis of brine.

For control purposes, a titanium disc prepared for plating by immersion in fused alkali metal chlorides was electroplated with platinum (5.4 mg./cm.^{2}), heated 30 minutes, and coated with platinum-rhodium alloy (1.6 mg./cm.^{2}). When used as an anode, the disc coated with platinum group metals gave α and β values of 3.19 v. and 1.16×10^{-2} v. dm.^{2}/amp. which are significantly higher than those produced by the method of the invention under otherwise closely analogous conditions. The platinum group metal was lost during electrolysis at a rate of 0.82 mg./1000 amp hrs.

A similar control disc carrying a platinum electrodeposit (6.3 mg./cm.^{2}) and a platinum-iridium alloy surface coating (1.4 mg./cm.^{2}) gave α and β readings of 3.17, 1.13×10^{-2}, and lost 1.29 mg./1000 amp hrs.

Example 5

That the manner in which the basic alloy layer is produced has no effect on the properties of an anode of the invention was further confirmed.

A titanium disc was immersed in the afore-described fused alkali metal chlorides for only 15 minutes, and was thereafter immersed in boiling 40% phosphoric acid for 5 minutes. It was coated with platinum by immersion in 20 ml. of an aqueous solution containing 0.2 g. $Pt(NH_3)_2(NO_2)_2$ and 1.0 g. EDTA, and mixed with enough 28% ammonia water to make the pH 10. The solution was heated to a boil, and 24 ml. of a 3% hydrazine solution were added in 2 ml. batches at 5 minute intervals. When recovered from the solution, the disc was coated with 6.8 mg./cm.^{2} platinum.

It was thereafter copper plated (7.2 mg./cm.^{2}), and the copper coating was alloyed with the platinum layer by heating to 700° C. for 30 minutes. After removal of the copper by electrolysis a platinum surface layer of 2.1 mg./cm.^{2} was formed by thermal decomposition of the afore-mentioned chloroplatinic acid solution.

The anode obtained had α and β values of 3.10 and 1.10×10^{-2} respectively.

Closely analogous results were obtained when platinum was replaced in the anodes of the invention entirely or in part by the other platinum metals, namely rhodium, iridium, palladium, osmium, or ruthenium, as has been partly illustrated above. Because of its availability and desirable chemical and electrochemical properties, platinum is the preferred coating material either alone or in alloys with the other platinum metals in which platinum is the major constituent.

As has been shown above with specific reference to copper, silver, gold, nickel, and iron, the nature of the less noble metal temporarily alloyed with a platinum metal in the method of the invention is without much influence on the properties of the ultimate product. The same lack of significant effects is found when lead, manganese, or cobalt are employed as the alloying elements, and other metals capable of forming alloys with the several platinum metals may be used in an obvious manner.

When anodes for brine electrolysis are prepared by the method of the invention from base materials other than titanium, their chlorine overvoltage characteristics are determined by the surface layer of platinum metal and are equal to those indicated above, but their useful life in the electrolysis cell is affected by the chemical nature of the base material. Anodes prepared according to this invention and having a core of zirconium or magnetic iron oxide may thus find industrial applications while other conductive base materials, though operative for limited periods, are not attractive at this time.

The nature of the platinum metal coatings prepared by the method of the invention is not fully known, and the exact mechanism which causes the observed significant reduction in chlorine overvoltages and metal loss has not yet been elucidated. It may be pertinent, however, that the overvoltage characteristics of the anodes of the invention are similar, though superior, to those found in electrodes coated with platinum black. The last-mentioned coating, however, is relatively quickly lost during electrolysis.

It may further be pertinent to an understanding of the facts underlying this invention that platinum surface coatings produced by thermal decomposition of chloroplatinic acid have superior overvoltage properties as compared to platinum electrodeposits, when formed over titanium surfaces or those of platinum electrodeposits, but the difference is much reduced when the coatings are applied as surface layers in the method of the invention.

Chemically prepared surface coatings are, therefore, preferred in the method of the invention. However, most advantages of forming an alloy of a less noble metal with a platinum group metal, and of thereafter selectively dissolving the less noble metal component are retained when the surface layer of an anode of the invention consists of an electrodeposited platinum metal or platinum metal alloy.

What is claimed is:

1. A method of preparing an electrode having a surface coating of a platinum group metal which comprises:

(a) forming a coating of an alloy of platinum metal and a less noble metal on the surface of a conductive base material,

(b) removing said less noble metal from the alloy coating until a layer consisting essentially of platinum metal is formed,

(c) coating said layer with a surface coating of a metal selected from the group consisting of platinum, rhodium, iridium, palladium, osmium, ruthenium and alloys thereof.

2. A method as set forth in claim 1, wherein said conductive base material consists essentially of titanium.

3. A method as set forth in claim 1, wherein said less noble metal is copper, silver, gold, iron, nickel, cobalt, manganese, or lead.

4. A method as set forth in claim 1, wherein said surface coating consists of platinum.

5. A method as set forth in claim 1, wherein said layer is coated with said surface coating by contacting said layer with a solution of a decomposable platinum-metal inorganic compound, and by decomposing said compound to the platinum metal.

6. A method as set forth in claim 1, wherein said less noble metal is removed from said alloy coating by dissolving the less noble metal in a solvent which does not significantly attack the platinum metal component of said alloy coating.

7. A method as set forth in claim 1, wherein said conductive base material consists essentially of titanium, zirconium, or magnetic iron oxide.

8. A method as set forth in claim 7, wherein said less noble metal is removed from said alloy by dissolving the less noble metal in a strong aqueous mineral acid, in strong alkali, or by anodic dissolution in an electrolyte.

9. A method as set forth in claim 8, wherein said less noble metal is dissolved anodically in an electrolyte containing chloride ions.

References Cited

UNITED STATES PATENTS

3,177,131	4/1965	Angell.	
3,236,706	2/1966	Kuchek	156—18 X
3,236,756	2/1966	Beer.	
3,318,792	5/1967	Cotton et al.	
3,364,018	1/1968	Kirkpatrick	156—2 X

FOREIGN PATENTS

627,679	9/1961	Canada.

OTHER REFERENCES

H. H. Willard, L. L. Merritt, Jr., J. A. Dean: Instrumental Methods of Analysis, Van Nostrand Co., Inc., New York; (1958), p. 478.

ALFRED L. LEAVITT, Primary Examiner

C. K. WEIFFENBACH, Assistant Examiner

U.S. Cl. X.R.

117—8, 62, 71, 102; 156—2, 18; 204—290