

Description

This invention relates to a lead oxide-coated electrode for use in electrolysis suitable, for example, as an anode for generating oxygen or ozone, or for anodic oxidation in the electrolysis of, for example an aqueous acidic solution or organic-containing solution,

This invention also relates to a process for producing such an electrode.

A metal electrode coated with lead oxide has been known to be suitable as an electrode for use in electrolysis requiring corrosion resistance or high oxygen overvoltage, for instance, electrolysis for the generation of oxygen, anodic oxidation, electroplating, electrolysis of organic materials, or electrolytic treatment of waste water, and various improvements have been made in the electrode. However, since practical problems have still been present, these electrodes have not yet been generally used for industrial applications.

Lead oxide used as the electrode includes two types, that is, rhombic α -PbO₂ and tetragonal β -PbO₂ of a rutile type structure. While α -PbO₂ shows poor corrosion resistance when used as an anode for electrolysis as compared with β -PbO₂, α -PbO₂ with no substantial internal strain can be obtained by electrodepositions when it is electrolytically formed on a metal substrate such as titanium. On the other hand, while β -PbO₂ has good electroconductivity and good corrosion resistance, if β -PbO₂ is electrolytically formed, internal straining due to electrodeposition is generally increased to cause cracking or deteriorate the bondability with the metal substrate.

In addition, these PbO₂ layers are generally poor in mechanical strength, lack processability and passivate the metal substrate, such as titanium, due to the oxidizing effect of PbO₂ thereby making electroconduction difficult.

Among the problems as described above, for improving the bondability between the metal substrate and lead oxide, it has been known to adopt a countermeasure for increasing the surface area of the metal substrate, as described, for example, in Japanese Patent Publication Nos. 31396/83 and 34235/84.

Further, there has also been proposed a method of partially depositing a platinum group metal on a metal substrate by electric discharge as described in Japanese Patent Publication No. 45835/82, and a method of disposing fine noble metal portion areas in a distributed manner on the surface of the substrate as described in Japanese Patent Publication No. 32435/79, for preventing the passivation of the metal substrate. According to these methods, however, a large amount of expensive noble metal is needed, which is not practical and, in addition, they involve complicated procedures.

There have also been made proposals relating to coating a lead oxide layer on a metal substrate by way of various primary layers or intermediate layers. For example, there is a method of previously coating a titanium (IV) compound on the surface of a titanium substrate as described in Japanese Patent Publication No. 45191/78, a method of disposing a thin flash layer of a platinum group metal as described in Japanese Patent Publication No. 9236/81, a method of disposing an intermediate layer made of a platinum group metal or metal oxide as described in Japanese Patent Publication Nos. 30957/83, 31396/83, and 34235/84, a method of disposing an intermediate layer of a carbide and boride of a group IV - V element and/or silicide of a sub-group of group IV - VI elements and/or silicon carbide as described in Japanese Patent Publication No. 72878/75, and a method of disposing a semiconductor intermediate layer made of a tin compound and an antimony compound as described in Japanese Patent Application (OPI) No. 82680/77 (the term "OPI" as used herein refers to "unexamined published patent application").

Among these methods, the method of disposing the intermediate layer containing the platinum group metal or the oxide thereof is not practical since the intermediate layer itself is extremely expensive. In addition, some of these materials are usually employed as an electrode active substance and, since they show a low oxygen overvoltage as an anode as compared with lead oxide, if electrolytes intrude through pin holes in the lead oxide coating layer, the intermediate layer acts as an anode to evolve gases due to the electrolytic action at the surface of the intermediate layer to possibly result in peeling and destruction of the lead oxide layer. Further, in the method of disposing an intermediate layer not containing a platinum metal group such as an intermediate layer of a semiconductor material of tin and antimony compounds, although there is less possibility that the intermediate layer will act as an anode, the electroconductivity is insufficient leaving a problem for electric current supply. Further, since the radius of lead ions is 0.078 nm (0.78 Å) for Pb⁴⁺ (6-coordination), which is greater as compared with 0.069 nm (0.69 Å) for Sn⁴⁺ or 0.061 nm (0.61 Å) for Ti⁴⁺, it is difficult to firmly bond the intermediate layer and the lead oxide layer to each other by fusion or by forming a solid-solution. Further, since the β -PbO₂ layer has a great ion radius as described above, considerable stresses occur within β -PbO₂ being a rutile type oxide, and complete bonding is difficult even to the intermediate layer.

In view of the above, use of α -PbO₂ with less strain has been proposed and alternate layers of α -PbO₂

and β -PbO₂ are disclosed in Japanese Patent Publication No. 9472/80. It is also known to apply silver plating to the surface of a metal substrate and dispose α -PbO₂ further thereover as described in Japanese Patent Publication No. 23494/76. While these methods can provide a lead oxide layer with less strain, there have still been problems such as poor corrosion resistance of α -PbO₂, or solution of silver in an acidic solution, and they can not yet be said to be satisfactory.

As has been described above, known lead oxide-coated electrodes involve various problems in view of their performance and manufacture and no practically excellent electrode had been obtained yet.

US-A-4 510 034 discloses a lead-oxide electrode for use in electrolysis, with a titanium plate as substrate, which is coated with a layer of PdO or Pt. This layer is coated with a layer of α -PtO₂ and with a further layer of β -PbO₂.

It is the object of the present invention to provide a lead oxide-coated electrode having a long life time and satisfactory stability, and having β -PbO₂ coatings formed on a metal substrate which is dense and excellent in the bondability and shows less internal strain due to electrodepositions.

Said object is achieved by a lead oxide-coated electrode for use in electrolysis on a substrate comprising a corrosion resistant metal which comprises

- (1) a primary layer comprising platinum and/or palladium oxide,
- (2) an intermediate layer comprising α -PbO₂, and
- (3) a coating layer comprising β -PbO₂ and having dispersed therein a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.

The present invention also provides a process for producing the above-described lead oxide-coated electrode for use in electrolysis which comprises successively forming on a substrate comprising a corrosion resistant metal, a primary layer comprising platinum and/or palladium oxide, an intermediate layer comprising α -PbO₂, and a coating layer comprising β -PbO₂ and having dispersed therein a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.

This invention will now be described in more detail.

In the present invention, a corrosion-resistant metal is used as the substrate for the electrode, and titanium, zirconium, niobium and tantalum which are collectively referred to as valve metals or a basic alloy thereof are preferred. The metal substrate has no particular restriction on the shape, and may be a plate, apertured plate, rod-like member, expanded metal, or meshlike member. Further, since a relatively thick layer of lead oxide is subsequently coated on the substrate, it is preferred to apply a roughing treatment to the surface thereby increasing the deposition area. As the roughing treatment, a blasting treatment can be used. The blasting treatment is usually performed using grits or sand having a relatively large particle size. Also, it is desirable to form a fine unevenness on the surface of the substrate by way of pickling using, for example, oxalic acid, sulfuric acid, hydrochloric acid, for improving the adherence with the primary layer, as well as to clean or activate the surface.

A primary layer containing platinum and/or palladium oxide is formed on the surface of the thus prepared metal substrate for protecting the substrate and improving the bondability with the intermediate layer. While platinum is usually used in the form of a metal, it is necessary that palladium is used in the form of its oxide since the corrosion resistance of palladium in the form of a metal is poor.

For forming such a primary layer, heat decomposing is usually preferred and a primary coating containing platinum and/or palladium oxide can be obtained with ease by coating a solution containing a heat decomposable salt of platinum and/or palladium, drying and then heating and performing a heat decomposing treatment in air.

The platinum and/or palladium oxides are used for the primary layer in the electrode of present invention, because these materials have a sufficiently high oxygen generating over-voltage. Specifically, the lead oxide electrode is often used as an anode in an aqueous solution and the reaction mainly comprises evolution of oxygen. In this case, it has been found that since the lead oxide has a high oxygen generation overvoltage, it is necessary to increase the overvoltage of the primary layer. The above-mentioned materials have been found to sufficiently satisfy this requirement. Electroconductive oxides not using a noble metal, for example, tin oxide or titanium oxide have a sufficiently high overvoltage but have poor electroconductivity, whereas noble metals other than platinum and palladium, such as ruthenium, iridium and rhodium have good electroconductivity but have a lower oxygen overvoltage than that of lead oxide, and thus they are not suitable for use in the present invention.

Although a sufficient effect can be attained by using only platinum and/or palladium oxide in the primary layer, the platinum and/or palladium oxide may be used in admixture with other metal oxides for improving the bondability with the substrate and reducing the amount of expensive noble metal used. As such metal oxides, for example, titanium oxide, tantalum oxide-doped titanium oxide or tin oxide, can be used, by which additional effects can also be expected such as improvement in the corrosion resistance of the primary

layer itself and an increase in the oxygen overvoltage. The amount of the other metal oxide in the composition is preferably from 0 to 90 mol% based on the total amount of the primary layer.

A suitable coating thickness of the primary layer is from 0.05 to 3 μm . A sufficient coating for the substrate can not be obtained if the thickness of the primary layer is less than 0.05 μm , whereas electrical resistance tends to be increased if the thickness of the primary layer exceeds 3 μm .

The heat decomposing conditions for forming the primary layer are properly selected depending on the composition of the coating, and heat treatment may usually be applied in an oxidative atmosphere such as air at a temperature of from 300 to 700 °C for 5 to 30 min. The desired coating thickness can be obtained by repeating the coating and heating procedures for the coating solution. For coating the primary layer, coatings of different compositions may be applied in an adequate order thereby obtaining, as a whole, a primary layer of a desired composition, as well as repeating the coating of an identical composition. In the case of applying repeated coatings of different compositions, since the thickness of each coating is thin, ingredients are diffused between layers upon heat treatment of each layer thereby enabling a primary layer coating of sufficiently high electroconductivity as a whole to be obtained.

After forming the primary layer, an intermediate layer comprising $\alpha\text{-PbO}_2$ is formed. The $\alpha\text{-PbO}_2$ mainly serves as a joint between the substrate/primary layer and the $\beta\text{-PbO}_2$ coating layer described later. That is, since the radius of metal ions of Pb^{4+} is greater by 0.01 to 0.02 nm (0.1 to 0.2 Å) than the radius of metal ions of titanium, tin, tantalum and niobium in the primary layer or the metal substrate and, since all are rutile type oxides and thus have identical crystal configuration, misfitting between the oxides is great and can possibly worsen the bondability. This problem can be moderated by disposing $\alpha\text{-PbO}_2$ having a different crystal structure as an intermediate layer therebetween. Accordingly, the $\alpha\text{-PbO}_2$ can be thin so long as it can serve as the joint and, since excessive thickness may possibly cause problems in the corrosion resistance and electroconductivity, the appropriate thickness is from 20 to 500 μm . There is no particular restriction for the method of forming the $\alpha\text{-PbO}_2$ intermediate layer, and a method of electrolytically forming the layer from an aqueous alkaline solution containing Pb ions through anodic oxidation is usually suitable. The intermediate layer coating of a desired thickness can be obtained under typical conditions of using an electrolyte in which lead monoxide (PbO) is dissolved to saturation in an aqueous solution of 3 to 5 N NaOH and electrolysis is conducted with a current density of from 0.1 to 10 A/dm², at a temperature of from 20 to 60 °C under a voltage of from 1 to 2 V, for a time from 0.1 to 10 h using a substrate coated with the primary layer as the anode.

After coating the $\alpha\text{-PbO}_2$ intermediate layer in this way, a coating layer comprising $\beta\text{-PbO}_2$ is formed on the surface thereof. The $\beta\text{-PbO}_2$ layer has an extremely satisfactory affinity with the $\alpha\text{-PbO}_2$ intermediate layer and known methods of forming $\beta\text{-PbO}_2$ can be used to make the coating layer. The $\beta\text{-PbO}_2$ layer can be formed with ease by an electrolytic process using an acidic bath containing lead ions, such as an aqueous 30 - 35% lead nitrate solution, as the electrolyte and using a substrate coated with the primary layer and the intermediate layer as the anode. Suitably the current density is from 0.1 to 20 A/dm² and the electrolysis time is from 0.1 to 10 h. Although a slight amount of the $\alpha\text{-PbO}_2$ layer intrudes into the coating layer comprising $\beta\text{-PbO}_2$ using this method, the intrusion does not result in any problems in view of the durability.

In the electrolytically formed $\beta\text{-PbO}_2$ layer, internal strains of its own are necessarily produced in view of the crystal structure, and these internal strains can desirably be relieved by incorporating a corrosion resistant and substantially electrochemically inactive granular and/or fibrous material into the $\beta\text{-PbO}_2$ layer. That is, by incorporating the granular and/or fibrous material into the $\beta\text{-PbO}_2$ layer, continuous bonding of $\beta\text{-PbO}_2$ in the coating layer can be avoided to obtain an advantageous effect of dispersing the internal strains formed in the $\beta\text{-PbO}_2$ layer due to electrodeposition.

As the corrosion resistant and electrochemically inactive material to be incorporated and dispersed in the $\beta\text{-PbO}_2$ coating layer, any material can be used as long as the material is corrosion resistant and exerts no effect on the electrochemical activity of the $\beta\text{-PbO}_2$ layer. Metal oxides are generally suitable since they are corrosion resistant and less reactive, and oxides of metals of group IV and group V of the periodic table such as Ti, Ta, Zr, Hf, Nb and V are particularly effective. Carbides, nitrides or borides of these metals can also be used. Further, fluoro resins can also be used suitably since they are excellent in chemical resistance and show no reactivity. Those metals referred to as valve metals exemplified above among the group IV and group V elements can also be used in the form of a metal since they produce passivated corrosion resistant oxide films at the surface by the anodic oxidation and show no reactivity.

The content of these materials can properly be selected, and, suitably, it is from about 0.01 to 10% by weight based on the total amount of the coating layer. The granule or fiber diameter of these materials is preferably less than 500 μm .

There is no particular restriction for the method of forming such a coating layer and it is suitable to

employ an electrolytic forming method combined with a so-called dispersed plating method in which a β - PbO_2 layer is electrolytically formed while dispersing the granular and/or fibrous material in the electrolyte. Further, formation of the β - PbO_2 layer and the introduction of the above-mentioned material can be conducted separately in an appropriate order. That is, a coating layer comprising a β - PbO_2 layer and a layer of the fibrous and/or granular material alternately may be formed by repeating, for several times, the procedures of forming a thin β - PbO_2 layer electrolytically, coating the fibrous and/or granular material thereover and then baking. Conventional methods can be used for the electrolytic conditions and, usually, electrolysis may be conducted in a lead nitrate bath while using the intermediate-coated substrate as the anode, preferably, with a current density from 0.1 to 10 A/dm² and at a temperature of from 40 to 80 °C.

In this way, a lead oxide-coated electrode having a β - PbO_2 layer as the electrode active surface can be obtained with ease.

This invention will now be described by way of examples. Unless otherwise specified, all percents, ratios, etc. are by weight.

EXAMPLE 1 AND COMPARATIVE EXAMPLES 1 to 3

The surface of an expanded mesh made of pure titanium of 1.5 mm plate thickness was blasted by using #70 stainless steel grits (average grain size: 0.7 mm) and washed for 15 min in a boiling aqueous 25% hydrochloric acid solution. Then, using the titanium expanded mesh as the substrate, a primary layer comprising platinum and tantalum oxide in Pt-Ta = 1/1 (metal molar ratio) composition was disposed on the surface thereof to a thickness of 0.1 μm . The primary layer was formed by using platinum in the form of chloroplatinic acid and tantalum in the form of tantalum pentachloride dissolved in an aqueous 4% hydrochloric acid solution used as the coating solution for the primary layer, and repeating 4 times the procedures of coating the solution by brushing on the expanded mesh of the substrate, drying at 40 °C and then heating in a muffle furnace at 570 °C for 10 min.

Then, electrolysis was conducted using the thus formed primary layer as the anode and a titanium plate as the cathode, in an electrolyte comprising lead monoxide (PbO) dissolved to saturation in an aqueous 3.5N sodium hydroxide solution at 40 °C, with a current density of 1 A/dm² for 2 h thereby forming an α - PbO_2 coating layer as the intermediate layer. The thickness of the intermediate layer was about 100 μm .

Further, a lead dioxide layer composed of β - PbO_2 containing a fluoro resin was formed as the surface coating layer under the conditions described below. An electrolyte was prepared by adding 10 ml of a fluoro resin dispersion (trade name, "Teflon 30J" manufactured by Mitsui Du Pont Fluoro Chemical) per 1 l of an aqueous 30% solution of lead nitrate. Electric current was supplied while using a titanium plate as a cathode under stirring the solution by passing nitrogen gas therethrough at a temperature of from 65 to 70 °C with a current density of 2 A/dm² for 2 h. Thus, a lead oxide layer containing fluoro resin of about 300 μm thickness was obtained.

As comparative electrodes, specimens were prepared in the same manner as above except for deleting the platinum-tantalum oxide primary layer (Comparative Example 1), deleting the α - PbO_2 intermediate layer (Comparative Example 2) and using only the surface coating layer (Comparative Example 3).

An accelerated electrolysis test was conducted on the specimens using them as the anode in an aqueous 150 g/l sulfuric acid solution at 60 °C with a current density of 100 A/cm².

The results are shown in Table 1.

Table 1

Electrode Coatings				
No.	Primary Layer	Intermediate Layer	Coating Layer	Life time (h)
Example 1	Pt-Ta oxide	α - PbO_2	Fluoro resin-containing β - PbO_2	more than 500
Comparative Example 1	-	α - PbO_2	Fluoro resin-containing β - PbO_2	64
Comparative Example 2	Pt-Ta oxide	-	Fluoro resin-containing β - PbO_2	145
Comparative Example 3	-	-	Fluoro resin-containing β - PbO_2	30

As can be seen from Table 1, for the specimens with no primary layer (Comparative Examples 1 and 3), current condition became impossible within a short period of time and the coating peeled from the substrate.

In the specimen in which no intermediate layer was disposed but the surface coating layer was disposed directly above the primary layer (Comparative Example 2), although a certain life time was recognized, cracking was formed soon during electrolysis. On the other hand, the electrode according to the present invention (Example 1) showed neither weight reduction nor peeling during electrolysis for more than 500 h and electrolysis could be conducted stably for a long period of time.

EXAMPLE 2

A titanium substrate was prepared in the same manner as in Example 1. A coating composed of tantalum oxide was at first formed on the surface to a thickness of about $0.1\text{ }\mu\text{m}$ and then a coating composed of an oxide mixture of palladium oxide and tantalum oxide was formed to a thickness of about $0.1\text{ }\mu\text{m}$ to form a primary layer. The primary layer was formed by coating an aqueous hydrochloric acid solution of tantalum pentachloride and an aqueous hydrochloric acid solution of palladium chloride and tantalum pentachloride on the substrate, respectively, drying and then heating them 550°C for 10 min. in air. The procedures of coating and heating were repeated three times for each of the coatings. An $\alpha\text{-PbO}_2$ layer was disposed in the same manner as in Example 1 over the primary layer. The electrolysis was conducted for 1 h to form the $\alpha\text{-PbO}_2$ layer to a thickness of about $100\text{ }\mu\text{m}$.

Then, a coating layer composed of $\beta\text{-PbO}_2$ containing niobium oxide dispersed therein was electrolytically formed on the $\alpha\text{-PbO}_2$ layer. An aqueous 35% lead nitrate solution containing 10 g of fine niobium oxide fully passing $41\text{ }\mu\text{m}$ (345 mesh) dispersed per 1 l of the solution was used as an electrolyte. Electrolysis was conducted using the electrolyte under stirring by using a magnetic stirrer with a current density of 4 A/dm^2 for 2 h to obtain a coating layer of about 1 mm thickness. The electrolysis temperature was 40°C .

When conducting an accelerated electrolysis test in the same manner as in Example 1 for the specimen in 150 g/l sulfuric acid, it was found that there was neither a voltage increase, nor peeling of the coating layer at all even for electrolysis for more than 500 h with a current density of 100 A/dm^2 .

EXAMPLE 3

A titanium substrate was prepared in the same manner as in Example 1. A primary layer composed of platinum and tin oxide was formed on the surface. The primary layer was formed by using a coating solution prepared by dissolving chloroplatinic acid in n-amyl alcohol solution of n-amyl alkoxy tin, coating the solution on the substrate by brushing, drying at 150°C and then baking at 500°C . The procedures were repeated twice to form a primary coating of $0.2\text{ }\mu\text{m}$ thickness. Then, an $\alpha\text{-PbO}_2$ layer of about $200\text{ }\mu\text{m}$ thickness was formed in the same manner as in Example 1.

A lead oxide layer composed of $\beta\text{-PbO}_2$ containing titanium dispersed therein was electrolytically formed as the coating layer on the $\alpha\text{-PbO}_2$ layer. A titanium sponge pulverized in ethanol into products fully passing 275 mesh was used as titanium. The electrolysis was conducted under the same conditions as in Example 2 for 4 h to obtain a lead oxide-coated electrode having a $\beta\text{-PbO}_2$ coating layer of about 2 mm thickness.

An accelerated electrolysis test was conducted for the specimen in the same manner as in Example 1 using an aqueous 150 g/l H_2SO_4 solution. As a result, after conducting electrolysis for 700 h, there was neither substantial weight change nor cracking in the coating layer. Only discoloration was observed at the surface.

In the present invention, since corrosion resistant metal is used for the electrode substrate and a primary layer comprising platinum and/or palladium oxide, an intermediate layer comprising $\alpha\text{-PbO}_2$ and a coating layer comprising $\beta\text{-PbO}_2$ are successively coated thereover, the layers are firmly adhered to the substrate thereby enabling the obtainment of a lead oxide-coated electrode with no strains due to electrodeposition, being strong and having high durability. In addition, passivation and the resistance increase of the electrode can be prevented, and the electrode according to the present invention can be used stably for a long period of time even during electrolysis at high current density, which is extremely useful as an electrode for various electrolysis or electrolytic treatments requiring high corrosion resistance and high oxygen overvoltage.

Claims

1. A lead oxide-coated electrode for use in electrolysis on a substrate comprising a corrosion resistant metal which comprises



In the specimen in which no intermediate layer was disposed but the surface coating layer was disposed directly above the primary layer (Comparative Example 2), although a certain life time was recognized, cracking was formed soon during electrolysis. On the other hand, the electrode according to the present invention (Example 1) showed neither weight reduction nor peeling during electrolysis for more than 500 h and electrolysis could be conducted stably for a long period of time.

EXAMPLE 2

A titanium substrate was prepared in the same manner as in Example 1. A coating composed of tantalum oxide was at first formed on the surface to a thickness of about 0.1 μm and then a coating composed of an oxide mixture of palladium oxide and tantalum oxide was formed to a thickness of about 0.1 μm to form a primary layer. The primary layer was formed by coating an aqueous hydrochloric acid solution of tantalum pentachloride and an aqueous hydrochloric acid solution of palladium chloride and tantalum pentachloride on the substrate, respectively, drying and then heating them 550°C for 10 min. in air. The procedures of coating and heating were repeated three times for each of the coatings. An $\alpha\text{-PbO}_2$ layer was disposed in the same manner as in Example 1 over the primary layer. The electrolysis was conducted for 1 h to form the $\alpha\text{-PbO}_2$ layer to a thickness of about 100 μm .

Then, a coating layer composed of $\beta\text{-PbO}_2$ containing niobium oxide dispersed therein was electrolytically formed on the $\alpha\text{-PbO}_2$ layer. An aqueous 35% lead nitrate solution containing 10 g of fine niobium oxide fully passing 41 μm (345 mesh) dispersed per 1 l of the solution was used as an electrolyte. Electrolysis was conducted using the electrolyte under stirring by using a magnetic stirrer with a current density of 4 A/dm² for 2 h to obtain a coating layer of about 1 mm thickness. The electrolysis temperature was 40°C.

When conducting an accelerated electrolysis test in the same manner as in Example 1 for the specimen in 150 g/l sulfuric acid, it was found that there was neither a voltage increase, nor peeling of the coating layer at all even for electrolysis for more than 500 h with a current density of 100 A/dm².

EXAMPLE 3

A titanium substrate was prepared in the same manner as in Example 1. A primary layer composed of platinum and tin oxide was formed on the surface. The primary layer was formed by using a coating solution prepared by dissolving chloroplatinic acid in n-amyl alcohol solution of n-amyl alkoxy tin, coating the solution on the substrate by brushing, drying at 150°C and then baking at 500°C. The procedures were repeated twice to form a primary coating of 0.2 μm thickness. Then, an $\alpha\text{-PbO}_2$ layer of about 200 μm thickness was formed in the same manner as in Example 1.

A lead oxide layer composed of $\beta\text{-PbO}_2$ containing titanium dispersed therein was electrolytically formed as the coating layer on the $\alpha\text{-PbO}_2$ layer. A titanium sponge pulverized in ethanol into products fully passing 275 mesh was used as titanium. The electrolysis was conducted under the same conditions as in Example 2 for 4 h to obtain a lead oxide-coated electrode having a $\beta\text{-PbO}_2$ coating layer of about 2 mm thickness.

An accelerated electrolysis test was conducted for the specimen in the same manner as in Example 1 using an aqueous 150 g/l H₂SO₄ solution. As a result, after conducting electrolysis for 700 h, there was neither substantial weight change nor cracking in the coating layer. Only discoloration was observed at the surface.

In the present invention, since corrosion resistant metal is used for the electrode substrate and a primary layer comprising platinum and/or palladium oxide, an intermediate layer comprising $\alpha\text{-PbO}_2$ and a coating layer comprising $\beta\text{-PbO}_2$ are successively coated thereover, the layers are firmly adhered to the substrate thereby enabling the obtainment of a lead oxide-coated electrode with no strains due to electrodeposition, being strong and having high durability. In addition, passivation and the resistance increase of the electrode can be prevented, and the electrode according to the present invention can be used stably for a long period of time even during electrolysis at high current density, which is extremely useful as an electrode for various electrolysis or electrolytic treatments requiring high corrosion resistance and high oxygen overvoltage.

Claims

1. A lead oxide-coated electrode for use in electrolysis on a substrate comprising a corrosion resistant metal which comprises



- (1) a primary layer comprising platinum and/or palladium oxide,
 - (2) an intermediate layer comprising α -PbO₂, and
 - (3) a coating layer comprising β -PbO₂ and having dispersed therein a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.
2. The electrode of claim 1, wherein the corrosion resistant metal of the substrate is titanium, zirconium, niobium, tantalum or a base alloy thereof.
 3. The electrode of claim 1, wherein the primary layer comprises platinum and/or palladium oxide and at least one of the oxides of titanium, tantalum or tin.
 4. The electrode of claim 1, wherein the thickness of the intermediate layer is from 20 to 500 μ m.
 5. The electrode of claim 1, wherein the granular and/or fibrous material is a metal selected from Ti, Ta, Zr, Hf, Nb and V or oxides, carbides, nitrides or borides of said metals.
 6. The electrode of claim 2, wherein the granular and/or fibrous material comprises a fluoro resin.
 7. A process for producing a lead oxide-coated electrode for use in electrolysis, which comprises successively forming, on a substrate comprising a corrosion resistant metal, a primary layer comprising platinum, palladium oxide or mixtures thereof, an intermediate layer comprising α -PbO₂ and a coating layer comprising β -PbO₂ and having dispersed therein a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.
 8. The process of claim 7, wherein the surface of the corrosion resistant metal substrate is subjected to blasting and/or pickling prior to forming the primary layer.
 9. The process of claim 7, wherein the primary layer is formed by coating a solution containing a heat decomposable salt of platinum and/or palladium on the substrate and then subjecting the coated solution to heat treatment.
 10. The process of claim 7, wherein the intermediate layer is electrolytically formed from an alkaline bath containing lead ions.
 11. The process of claim 7, wherein the coating layer is electrolytically formed from an acidic bath containing lead ions and having dispersed therein a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.
 12. The process of claim 7, wherein the coating layer is formed by repeating the step of forming a β -PbO₂ layer and the step of coating a corrosion resistant and substantially electrochemically inactive granular material, fibrous material or mixtures thereof.

Revendications

1. Une électrode à revêtement d'oxyde de plomb pour l'électrolyse sur un support comprenant un métal résistant à la corrosion qui comprend :
 - (1) une couche primaire comprenant du platine et/ou de l'oxyde de palladium,
 - (2) une couche intermédiaire comprenant du PbO₂ α et
 - (3) une couche de revêtement comprenant du PbO₂ β et contenant, à l'état dispersé, une matière granulaire ou une matière fibreuse résistant à la corrosion et pratiquement inactive du point de vue électrochimique ou un de leurs mélanges.
2. L'électrode selon la revendication 1, dans laquelle le métal du support résistant à la corrosion est le titane, le zirconium, le niobium, le tantale ou l'un des alliages à base de ceux-ci.
3. L'électrode selon la revendication 1, dans laquelle la couche primaire comprend du platine et/ou de l'oxyde de palladium et au moins l'un des oxydes de titane, de tantale et d'étain.



4. L'électrode selon la revendication 1, dans laquelle l'épaisseur de la couche intermédiaire est de 20 à 500 μm .
5. L'électrode selon la revendication 1, dans laquelle la matière granulaire et/ou la matière fibreuse est un métal choisi parmi Ti, Ta, Zr, Hf, Nb et V ou les oxydes, carbures, nitrures ou borures desdits métaux.
6. L'électrode selon la revendication 2, dans laquelle la matière granulaire et/ou la matière fibreuse comprend une résine fluorée.
7. Un procédé pour produire une électrode à revêtement d'oxyde de plomb pour l'électrolyse, qui consiste à former successivement, sur un support comprenant un métal résistant à la corrosion, une couche primaire comprenant du platine ou de l'oxyde de palladium ou leurs mélanges, une couche intermédiaire comprenant du $\text{PbO}_2 \alpha$ et une couche de revêtement comprenant du $\text{PbO}_2 \beta$ et contenant à l'état dispersé une matière granulaire ou une matière fibreuse résistant à la corrosion et pratiquement inactive du point de vue électrochimique ou un de leurs mélanges.
8. Le procédé selon la revendication 7, dans lequel la surface du support de métal résistant à la corrosion est soumise au grenaillage et/ou au décapage avant de former la couche primaire.
9. Le procédé selon la revendication 7, dans lequel la couche primaire est formée en appliquant sur le support une solution contenant un sel de platine et/ou un sel de palladium décomposable par la chaleur et en soumettant ensuite la solution déposée à un traitement thermique.
10. Le procédé selon la revendication 7, dans lequel la couche intermédiaire est formée par voie électrolytique à partir d'un bain alcalin contenant des ions plomb.
11. Le procédé selon la revendication 7, dans lequel la couche de revêtement est formée par voie électrolytique à partir d'un bain acide contenant des ions plomb et contenant à l'état dispersé une matière granulaire ou une matière fibreuse résistant à la corrosion et pratiquement inactive du point de vue électrochimique ou un de leurs mélanges.
12. Le procédé selon la revendication 7, dans lequel la couche de revêtement est formée en répétant l'étape de formation de la couche de $\text{PbO}_2 \beta$ et l'étape d'application de la matière granulaire ou de la matière fibreuse résistant à la corrosion et pratiquement inactive du point de vue électrochimique ou de leur mélange.

Patentansprüche

1. Mit Bleioxid beschichtete Elektrode zur Verwendung in der Elektrolyse, auf einem Substrat, umfassend ein korrosionsbeständiges Metall, die
 - (1) eine Primärschicht, umfassend Platin- und/oder Palladiumoxid,
 - (2) eine Zwischenschicht, umfassend $\alpha\text{-PbO}_2$, und
 - (3) eine Deckschicht, umfassend $\beta\text{-PbO}_2$, die ein korrosionsbeständiges und im wesentlichen elektrochemisch inaktives, granuliertes Material, faseriges Material oder Mischungen daraus darin dispergiert enthält,
 umfaßt.
2. Elektrode nach Anspruch 1, worin das korrosionsbeständige Metall des Substrats Titan, Zirkonium, Niob, Tantal oder eine Grundlegierung daraus ist.
3. Elektrode nach Anspruch 1, worin die Primärschicht Platin- und/oder Palladiumoxid und wenigstens ein Oxid von Titan, Tantal oder Zinn umfaßt.
4. Elektrode nach Anspruch 1, worin die Dicke der Zwischenschicht 20 bis 500 μm beträgt.
5. Elektrode nach Anspruch 1, worin das granuliertes und/oder faserige Material ein Metall, gewählt aus Ti, Ta, Zr, Hf, Nb und V, oder Oxiden, Carbiden, Nitriden oder Boriden dieser Metalle ist.



6. Elektrode nach Anspruch 2, worin das granuliertes und/oder faserige Material ein Fluorharz umfaßt.
7. Verfahren zur Herstellung einer mit Bleioxid beschichteten Elektrode zur Verwendung in der Elektrolyse, bei dem aufeinanderfolgend auf einem Substrat, umfassend ein korrosionsbeständiges Metall, eine Primärschicht, umfassend Platin-, Palladiumoxid oder Mischungen daraus, eine Zwischenschicht, umfassend α -PbO₂, und eine Deckschicht, umfassend β -PbO₂, die darin dispergiert ein korrosionsbeständiges und im wesentlichen elektrochemisch inaktives, granuliertes Material, faseriges Material oder Mischungen daraus enthält, gebildet werden.
8. Verfahren nach Anspruch 7, worin die Oberfläche des korrosionsbeständigen Metalls substrats einer Gebläse-und/oder Säuerungsbehandlung vor der Bildung der Primärschicht ausgesetzt wird.
9. Verfahren nach Anspruch 7, worin die erste Schicht durch Aufbringen einer Lösung, enthaltend ein wärmezersetzbares Salz von Platin und/oder Palladium, auf das Substrat und anschließende Wärmebehandlung der aufgetragenen Lösung gebildet wird.
10. Verfahren nach Anspruch 7, worin die Zwischenschicht elektrolytisch aus einem alkalischen Bad, enthaltend Bleionen, gebildet wird.
11. Verfahren nach Anspruch 7, worin die Deckschicht elektrolytisch aus einem sauren Bad, enthaltend Bleionen, worin ein korrosionsbeständiges und im wesentlichen elektrochemisch inaktives, granuliertes Material, faseriges Material oder Mischungen daraus dispergiert sind, gebildet wird.
12. Verfahren nach Anspruch 7, worin die Deckschicht durch Wiederholen der Stufe der Bildung einer β -PbO₂-Schicht und der Stufe der Beschichtung eines korrosionsbeständigen und im wesentlichen elektrochemisch inaktiven, granulierten Materials, faserigen Materials oder Mischungen daraus gebildet wird.