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RECOATING OF ELECTRODES

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ABSTRACT OF THE DISCLOSURE

Describes a method of recoating a previously used dimensionally stable electrode having a previously applied conductive electrocatalytic coating thereon which comprises cleaning the previously used electrode without stripping the old coating therefrom and recoating the cleaned electrode with a new conductive electrocatalytic coating applied over the old coating and any exposed portions of the electrode base, and the product produced thereby.

This invention relates to methods of recoating dimensionally stable electrodes having a base of a valve metal such as titanium or tantalum or alloys of titanium or tantalum which have previously been coated with a conductive electrocatalytic coating comprising oxides of a platinum group metal or oxides of a platinum group metal mixed with oxides of valve metals such as titanium or tantalum which have previously been used in an electrolysis cell and have become inactive, and to the electrodes produced by such methods.

In recoating dimensionally stable electrodes coated with oxides of platinum group metals or oxides of platinum group metals mixed with oxides of valve metals which have become inactive after a period of use in an electrolysis cell, it has previously been considered necessary to completely strip the coating from the valve metal base, for example, by immersion of the inactive electrode in a molten salt bath comprising a mixture of an alkali metal hydroxide and an alkali metal salt of an oxidizing agent until the coating was completely removed (see for example, Belgian Pat. No. 728,860). After complete removal of the coating, recovery of the platinum group metal contained in the coating from the salt bath was not economical. The stripping of the coating by the molten salt bath resulted in some attack on the metal of the base, resulting in a loss, for example, of as much as 5% or more by weight of a titanium base with each stripping and if the temperature of the molten salt bath was too high, resulted in actual ignition of the titanium or tantalum base with loss of the entire electrode.

We have discovered that complete stripping of the electrocatalytic coating from the base is not necessary and that recoated electrodes can be produced by the methods herein described at less cost than by the use of the molten salt baths of the prior art, and that the recoated electrodes produced by our processes give performance equal to the initially coated clean electrodes or equal to recoated electrodes from which the initial coating has been completely stripped.

By applying the recoating composition over the old coating, the old coating can be reused and the platinum

group and other metals in the old coating are not wasted and need not be recovered from a molten salt bath.

The term "dimensionally stable electrodes" as used throughout the specification and claims is intended to refer primarily to titanium or tantalum structures carrying an electrically conductive electrocatalytic coating. In addition to "pure" titanium and tantalum, alloys of these metals may be used as well as other conductive metals, such as copper and aluminum, clad or coated with titanium, tantalum or alloys thereof. Other valve metals may also be used in special applications. These electrode base structures are generally in the form of a sheet, a perforated or slotted sheet, an expanded mesh or screen configuration or in rod form, although the shape of the electrode is not important to the practice of the present invention.

The term "platinum group metals" is intended to include platinum, ruthenium, iridium, palladium, osmium and rhodium, and these metals are usually deposited on the electrodes as oxides of the particular metal.

Prior to the initial coating of the electrode base structure, the base metal, such as titanium or tantalum or alloys thereof, is degreased by ultrasonic cleaning or by a solvent such as perchlorethylene vapor and is etched in azeotropic (20% by weight) $HCl\text{-}H_2O$ solution at about 100° C. to a specified weight loss, which usually requires an etch time of about 30 to 60 minutes. After etching, the bases are rinsed free of acid in cold clean tap water, dried and the desired coating applied. The etching prepares the titanium bases to receive the coating and the slight pitting of the bases by the etch promotes adherence of the initial coating to the base.

Our invention is particularly applicable to the recoating of previously used valve metal base electrodes having oxides or a ceramic coating composed of oxides of platinum group metals, mixtures of oxides of platinum group metals with oxides of valve metals (e.g., titanium, tantalum, aluminum) and mixtures of oxides of platinum group metals with oxides of valve metals and with oxides of other metals. Examples of such coatings include ruthenium oxide; ruthenium oxide-titanium oxide; ruthenium oxide-titanium oxide-iridium oxide; ruthenium oxide-titanium oxide-tantalum oxide; ruthenium oxide-titanium oxide-cobalt oxides-tin oxides and others.

OBJECTS OF THE INVENTION

One of the objects of our invention is to produce a recoated, previously used dimensionally stable electrode which will be equal in performance to the same electrode as initially coated.

Another object is to preserve the portions of the previous coating on the electrode so that the noble metal values in the previous coating will be preserved and not destroyed by a molten salt stripping operation.

Another object is to provide a process of cleaning and recoating previously used titanium base electrodes which will be more economical than the recoating processes previously used.

Another object is to reduce the time of recoating an electrode and reduce the cost of the equipment necessary to clean and recoat an electrode by molten salt stripping of the previous coating.

Another object of the invention is to provide a superior recoated valve metal base electrode without the loss of weight and/or weakening or destruction of the valve metal base brought about by molten salt stripping of the bases.

Various other objects and advantages of our invention will appear as this description proceeds.

BACKGROUND OF THE INVENTION

When titanium or other valve metal base electrodes are used as anodes in an electrolysis cell for the production of chlorine (for example), a bare titanium anode will develop a passivating oxide film within a few seconds and will no longer conduct current to the electrolyte at normal cell voltage. For this and other reasons, it is necessary to initially coat the titanium or other valve metal base with a conducting electrocatalytic coating which will continue to conduct current to and through the electrolyte at normal voltage for the electrolysis process being performed. In the production of chlorine, this voltage (anode potential) is about 1.35 to 1.8 v. (NHE) at a current density of 10 ka./m.^{2} and for economical production of chlorine this voltage should continue for long periods of time, such as a year or more. In addition to conducting current to the electrolyte, the coating on the valve metal base must be capable of catalyzing the anodic oxidation of the dissolved chloride ions to atomic chlorine which atoms combine to produce chlorine gas which is then released from the anode surface as molecular chlorine gas. When the potential of an anode in use in a chlorine electrolysis cell reaches or exceeds 1.8 v. (NHE) at 10 ka./m.^{2} it is consider to be passivated and must be recoated or replaced if economical chlorine production is to be continued.

Coatings of platinum group metal oxides or mixed coatings of platinum group metal oxides together with oxides of valve metals on titanium or other valve metal base anodes and other electrodes have been found satisfactory to meet the need for continued conductivity and continued catalytic activity of valve metal base electrodes over periods of a year or more of service in, for example, chlorine production. Typical examples of such coatings are found in Belgian Pats. No. 680,763; No. 710,551; No. 725,491 and No. 725,492.

However, when oxide coated valve metal base electrodes of the type described in said patents have been in use for a year or more, for example, as anodes in an electrolysis cell used in the production of chlorine and alkali metal hydroxides, they often become inactive due to passivation (that is, loss of electrocatalytic activity), partial destruction of the coating due to short circuits and other causes and will no longer produce chlorine at economically acceptable current consumption rates and must be replaced with new oxide coated valve metal base anodes or must be removed and recoated.

As described above and in Belgian Pat. No. 728,860, it has previously been considered necessary to completely strip the old coating off the valve metal base by the use of an oxidizing molten salt bath and to recoat the stripped valve metal base with a loss of the platium group metal oxide in the coating, the loss of some of the valve metal base in the stripping operation and the occasional destruction of the entire anode by ignition of the titanium or tantalum if the molten salt bath was at too high temperature.

In the process of invention, a used dimensionally stable electrode previously provided with an oxide coating which has become passivated, after removal from an electrolysis cell, is water washed and any loose material removed from the electrode by scrubbing or otherwise. The electrode is then degreased and again washed with a solvent which will clean any exposed valve metal surfaces and clean, but not remove, the previously applied adhering oxide coating, after which a new oxide coating similar in composition to the old coating is applied over the old coating and over any exposed valve metal base, in a series of coats, with drying and baking between each coat and heating for about one hour at about 450° C. after the final coat.

By the processes described in the illustrative examples given below, we have found that electrodes equal to those initially produced by coating bare or stripped valve metal bases with oxide coatings, may be produced in a more economical way, a portion of the old coating may be preserved and reactivated, and the expense and nuisance of maintaining molten salt baths in corrosion-proof vessels to strip the previously coated anodes is eliminated.

EXAMPLE I

After removal from a flowing mercury cathode electrolysis cell, any mercury trapped in the anode risers is removed and the anode is water washed and scrubbed to remove loose material and is then degreased in perchlorethylene vapor or other degreasing medium, cooled and weighed. The still adhering previous oxide coating is tested for adherence and any loose portions mechanically removed. The tightly adhering portions of the previous oxide coating are permitted to remain on the anode and the anode is mildly etched for 5 minutes in a hydrochloric acid etch bath containing a 20% solution by weight of HCl in water at a temperature of about 100° C., or in 36% HCl plus 10% of isopropanol solution at 30 to 40° C. for about 5 minutes. This treatment is sufficient to clean any exposed titanium surface and to clean, but not remove, the previous adhering oxide coating. It does not cause material loss of titanium metal as caused by the previously used etching and molten salt stripping procedures. The cleaned anode base with portions of the prior oxide coating thereon, is then rinsed with water, dried and cooled and is then recoated by any of the procedures described in the above-identified Belgian patents.

A typical recoating procedure is as follows:

The coating solution for each 50 cm.^{2} of projected anode area to contain the following materials:

Ru as $RuCl_3.H_2O$—20 mg. (metal)
Ir as $(NH_4)_2IrCl_6$—20 mg. (metal)
Ti as $TiCl_3$—48 mg. (metal)
$HCONH_2$—10 to 12 drops
H_2O_2 30%—3 to 4 drops

The coating is prepared by first blending or mixing the ruthenium and iridium salts in the required amount of Ru and Ir in a 2 molar solution of hydrochloric acid (5 ml. are sufficient for the above amounts) and allowing the mixture to dry until a dry precipitate is formed. Formamide is then added to the dry salt mixture to dissolve the mixture. The titanium chloride, $TiCl_3$, dissolved in hydrochloric acid (15% strength commercial solution) is added to the dissolved Ru-Ir salt mixture and a few drops of hydrogen peroxide (30% H_2O_2) are added, sufficient to make the solution turn from the blue color of the commercial solution of $TiCl_3$ to a brown, reddish color.

The coating mixture thus prepared is applied to the cleaned electrode to be recoated, by brush, roller, electrostatic spraying, dipping or other coating methods in a series of 5 to 15 coats with drying and baking at 300° to 460° C. for about 15 minutes between each coat until the required coating weight has been applied and after the final coat has been applied, the anode is heated to about 450° C. for about 60 minutes.

The quantities of the three metals in this mixture correspond to the weight ratios of 22.6% Ir, 22.6% Ru and 54.8% Ti, and the amount of noble metal oxide in the active coating corresponds to 0.4 mg. Ir, 0.4 mg. Ru per square centimeter of the active electrode area in addition to the Ir and Ru in the previous coating which adheres to the anode after the cleaning operation for recoating.

The coating composition used to recoat a previously coated anode, prepared for recoating as described above, should in general correspond in composition to the initial coating on the electrode, although it need not correspond exactly with the previously used coating composition. Any coating composition and any recoating procedure meeting these requirements may be used.

The coating composition applied in this manner to a cleaned and previously used anode having a portion of a previously applied coating thereon adheres as well as the initial coating and preserves the metal values of the previous coating which adhere to the electrode after the cleaning for recoating. Standardized adherence tests show that the adherence of the recoated coating to the base equals the adherence of the coating on initially coated etched electrodes, and the recoated electrodes or anodes have a longer useful life than initially coated etched anodes. The cost of completely removing the old coatings is avoided, the entire recoating operation is simplified, and the recoated anodes can be put back into operation with less "down time" than if the old coating is completely stripped from the anodes. In comparative tests, the recoated unstripped anodes showed the same voltage as the anodes with the original coating when this was new.

The reasons for the superiority of the recoated coating over the initial coating are not precisely known, but it is believed that the procedure used in preparing the previously used electrodes to receive the new coating gives a better surface to the electrode base and the old coating thereon to receive the new coating, so that the new coating adheres to the base and the previous coating as well as when the base has been stripped of the old coating and subjected to a drastic etching procedure.

EXAMPLE II

After removal from an electrolysis cell, the anode is washed with water and scrubbed to remove loose material. The thickness of the old coating is measured and if the ruthenium amount in the old coating is over 5.0 g./m.^{2} and with a uniform distribution and the anode potential is 1.35–1.50 v. (NHE) at 1 amp. per square centimeter, the anode may be degreased, washed with demineralized water and recoated by any of the methods described in said Belgian Pats. No. 680,763; No. 710,551; No. 725,491 and No. 725,492, or the method described in Example I.

The new coating is applied in multiple coats, with intermediate baking at 350 to 460° C. between each coat until a recoated layer from 8 to 16μ average thickness has been formed, containing 10 to 15 grams of ruthenium (or other platinum group metal) per square meter of anode surface.

The amount of ruthenium in the old coating may be measured in any desired way. We have found measurement by metallographic analysis, atomic adsorption analysis, X-ray or β-ray back-scatter analyses and anode potential satisfactory to determine the amount of ruthenium in the old coating. Visual inspection for uniform distribution of the old coating after the anode has been cleaned is also used.

The recoated anode shows all the advantages given in Example I, the platinum group metal oxide, usually ruthenium oxide, in the old coating is preserved and there is no loss of metal from the titanium base.

EXAMPLE III

After removal from an electrolysis cell, the anode is washed with water and scrubbed to remove loose material and treated as in Example II, except that after degreasing it is washed with isopropyl alcohol in place of demineralized water, and then recoated by the method of Example I or any of the methods described in said Belgian patents.

EXAMPLE IV

If the anode, after determining the amount of ruthenium in the old coating and the anode potential, is found suitable for recoating but has iron oxide precipitated on the surface of the anode, the anode is degreased and is treated with a 3 to 6% solution of cold HCl for 5 to 15 minutes until the precipitates are removed and it is then recoated as described above.

EXAMPLE V

When the amount of ruthenium in the coating is less than 5.0 g./m.^{2} and the anode potential is over 1.75 to 1.85 v. (NHE) at 1 a./cm.^{2} or when a substantial percentage of the anode surface has been damaged by short circuits and the anode performance has deteriorated to the extent indicated by the above tests, precipitates of iron or manganese salts (oxides) are often found. In order to remove these and other precipitates, the anode after degreasing is etched with a 16 to 24% HCl solution for several minutes until the precipitate is removed, with a minimum removal of the old coating, after which the anode with a portion of the old coating thereon is recoated by any of the procedures described above.

While we have referred more particularly to ruthenium in the coating, other platinum group metals and oxides having electrocatalytic properties, such as those given in the Belgian patents referred to, are to be conseidered as included within the recoating procedure herein described.

The procedures described and the sequence of steps may be varied without departing from the principles of the invention herein described.

What is claimed is:

1. The method of recoating previously used dimensionally stable electrodes having a valve metal base and a conductive electrocatalytic coating thereon containing oxides of the group consisting of platinum group metal oxides and oxides of platinum group metals with oxides of valve metals which comprises removing loose material and foreign matter from the electrode base and the previous adhering coating by cleaning any exposed valve metal surfaces of the electrode base and cleaning but not removing the previous adhering oxide coating thereon, applying a new coating similar in composition to the old coating over the old coating and over any exposed valve metal base in a series of coats with drying and baking between each coat at about 300° to 460° C. for about 5 to 15 minutes and after the final coat, heating to about 450° C. for about one hour.

2. The method of claim 1, in which the cleaning is by degreasing and etching the electrode base with a portion of the previous adhering coating thereon.

3. The method of claim 1, in which the electrode is an anode for an electrolysis cell for the production of chlorine.

4. The method of claim 1, in which the valve metal base is titanium and the old and new coating contain titanium oxide and ruthenium oxide.

5. As a product of manufacture, a valve metal electrode base having a conductive electrocatalytic coating thereon which has previously been used in an electrolysis cell and has become passivated, having a new conductive electrocatalytic coating applied over the previous coating and to any exposed surfaces of the valve metal electrode base.

6. The product of claim 5, in which the valve metal electrode base is titanium having an old coating containing titanium oxide and ruthenium oxide thereon and the new coating applied over the old coating also contains titanium oxide and ruthenium oxide.

7. As a product of manufacture, a previously used titanium base anode having a portion of a previously used conductive electrocatalytic coating thereon and a new conductive electrocatalytic coating applied over the old coating and any exposed portions of the titanium base.

8. The product of claim 7, in which the previously used coating contains titanium dioxide and ruthenium dioxide and the new coating contains titanium dioxide and ruthenium dioxide.

9. As a product of manufacture, a cleaned previously used titanium base electrode having a portion of a previous conductive electrocatalytic coating thereon and a new conductive electrocatalytic coating over the old coating and over any exposed portions of the titanium base, said new coating being in several coats baked on said previously used coated titanium base.

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