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MANUFACTURE OF ELECTRODE

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ABSTRACT OF THE DISCLOSURE

The method of manufacturing an electrode comprising mechanically cleaning a titanium surface in the absence of oxygen or nitrogen such as by buffing with sandpaper in benzene, immediately transferring to a vacuum container still avoiding contact with oxygen or nitrogen and then vapor plating a first platinum group metal coat on the cleaned surface to a thickness of 100–3000 angstroms and subsequently electroplating a second coating of platinum or rhodium to a thickness of 0.1 to 5 microns. The electrode is suitable for electrolysis of chlorides and sulfates.

This invention relates to an improved electrode and to the preparation of the same. Particularly, this invention relates to an improvement in an electrode used for the electrolysis of aqueous chlorides and sulfates.

In accordance with the present invention, there is provided an electrode comprising a plate of titanium or tantalum as a substratum, a platinum group metal coating deposited thereon by vacuum evaporation, and a layer of platinum or rhodium layer electroplated thereon.

In the conventionally known art for the electrolysis of an aqueous solution containing sodium chloride, a graphite electrode can primarily be used as the anode. As a general rule, anode materials suited for such electrolysis should meet the following requirements:

(1) It should be resistant against nascent chlorine,
(2) It has good electroconductivity,
(3) It should be resistant against nascent oxygen,
(4) It should be inexpensive.

In practice, however, there has never been obtained any anode material which can realize fully or substantially all of these requirements. For example, platinum suffers from substantial corrosion by nascent chlorine and is expensive, although it can meet the second and third requirements as above.

As previously mentioned, graphite is the outstanding anode material but it is still unsatisfactory in the following respects:

(1) Graphite is substantially inferior in its electroconductivity to metals.

(2) It has only poor resistance against nascent oxygen and tends to be consumed gradually in response to the progress of the electrolysis, with an adverse influence on the purity of the resulting electrolytic product.

(3) It has no plasticity and accordingly it has to be used as an electrode having a large size.

(4) It is porous.

(5) It has poor mechanical strength and it is likely to contaminate both the electrolyte and the resulting product when the graphite is scraped out or consumed.

Besides graphite and platinum, magnetic iron oxide and

lead peroxide are used in practice but these have considerable disadvantages.

Titanium and tantalum have good electroconductivity, sufficient plasticity to make foils, wires, etc., and high chlorine-resistance. However, where titanium or tantalum is used as an anode for the electrolysis of saline water, it can initially conduct well, but after a short time, an oxidized thin layer having a high resistance is formed on the anode surface, until electrolytic reaction can not proceed due to the increased electric resistance resulting from the so-called passive state.

On the other hand, metals of the platinum group, including platinum, rhodium and iridium also are outstanding as anti-corrosive materials. These metals have good electroconductivity and high corrosion resistance. They are resistant to oxygen and chlorine attack, and iridium and rhodium particularly are so. However, platinum group metals are very expensive so that they can not be used as such in the commercial scale electrolytic operation. Furthermore, iridium and rhodium are difficult to be formed to an appropriate shape for electrodes. Thus, the platinum group metals have to be used in the form of a thin layer on a different metallic substratum.

It is not difficult to effect electrochemical deposition of a platinum group metal on the surface of a titanium or tantalum plate. For example, a titanium plate the surface of which is cleaned with an aqueous hydrogen fluoride solution is plated with platinum by using a solution of $Pt(NH_3)_2(NO_2)_2$ or $H_2Pt(NO_2)_2SO_4$, both of which are the known compounds in the art. Further, electrodeposition of rhodium by using a rhodium sulfate solution is also known in the art.

In spite of the prior knowledge mentioned above, a titanium or tantalum plate coated with any one of the platinum group metals has never been brought into practical use. The reason for this is found to be the fact that the titanium or tantalum plate coated with a platinum group metal suffers from exfoliation and disolution of its coating within several weeks after the initiation of the electrolysis of saline water. Upon the occurrence of said exfoliation and dissolution, the titanium or tantalum surface is exposed whereby the electrical resistance is increased, and it becomes difficult to conduct the electrolysis. I have found that undesired exfoliation of the layer of a platinum group metal mainly is due to the existence of a small amount of oxides, nitrides or other absorbed matter on the surface of the titanium or tantalum substratum, said oxides, nitrides and other absorbed matters preventing a close contact between the substratum and platinum group metal layer.

In accordance with the present invention, an improved electrode can be prepared as follows: A platinum group metal is deposited by evaporation in vacuo (10^{-4} mm. Hg or more) to a thickness of about 100–3000 A. onto the cleaned surface of a titanium or tantalum plate. Formation of any oxides and other impure compounds on the plate can be avoided because of all the procedures being conducted in the absence of air or other oxidizing or nitriding media. A platinum group metal coating having a thickness of less than 100 A. is ineffective so that it will readily suffer from oxidation or other undesired effects in the atmosphere. Although it is possible to have platinum or rhodium electrodeposited thereon, the resulting platinum or rhodium coating tends to suffer from exfoliation during the intended electrolytic operation. On

the contrary, if the platinum group metal coating is too thick, its surface will be coarse, with an increased tendency of corrosion or consumption during the electrolytic operation. Furthermore, this is disadvantageous from the economical viewpoint.

The plate with a platinum group metal layer deposited thereon is then moved into the air and electroplated with platinum or rhodium to provide a thin film with an appropriate thickness (e.g. 0.1–5 microns). It is essential that the platinum or rhodium electrolplating and the platinum group metal coating have a total thickness of 4000 A. In the other words, the electroplating alone should have a thickness of at least 1000 A. If the above-indicated total thickness is less than 4000 A., the resulting electrode will not be able to have a satisfactorily long service life because of dissolution due to chlorine attack and exfoliation or corrosion during the electrolysis. Platinum- or rhodium-plating can be carried out in the manner known per se in the art of electroplating. As the electrode thus prepared has a double layer (platinum group metal coating as the first layer and platinum or rhodium plating as the second one) on the substratum, it is entirely safe from corrosion by nascent chlorine or oxygen generated during the electrolysis of saline water and it does not suffer from the formation of an oxidized film on the electrode surface.

The following examples describe the manner in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

An iridium block (10 g.) is heated to incandescence and vaporized under vacuum (approximately 10^{-4}–10^{-5} mm. Hg) to be deposited on the well cleaned surface of a tantalum plate (2 cm. wide x 15 cm. long x 0.3 mm. thickness) until the plate has an increase of about 1000 A. in thickness. The iridium-coated tantalum plate is electroplated with rhodium from an aqueous solution containing rhodium sulfate (10 g./l.), sulfuric acid (d=1.8, 20 ml./l.) and sulfamic acid (2 g./l.). Temperature used is 60° C. A platinum anode is used with said tantalum plate, on which the current density is 0.5 a./dm.^{2}. By this electroplating procedures, rhodium coatings of a thickness of about 2 microns are obtained.

The thus prepared electrode is used as an anode for the electrolysis of saline water under the following conditions.

NaCl aq.: Saturated solution. The solution is replenished at an interval of about 3 hours, because its concentration is gradually reduced in response to the progress of the electrolysis.
Temperature: 40–60° C.
Anodic current density: About 100 a./dm.^{2}
Cathode: Platinum foil
Vessel: 500 cc. beaker; no diaphragm used; with agitation

The anode (rhodium-plated, iridium-coated tantalum plate) is dipped in the electrolyte to have an available area of 2 cm. wide x 3 cm. long. After electrolysis for two months, the anode surface is examined and no damage, exfoliation and corrosion are observed.

EXAMPLE 2

Platinum is heated to incandescence and deposited by vaporization under vacuo (about 10^{-4}–10^{-5} mm. Hg) onto the well cleaned surface of a titanium plate of 2 cm. wide, 15 cm. long and 0.3 mm. thick. The deposition of the platinum is continued until a layer of a thickness of about 1000 A. is obtained. The platinum-coated titanium plate is used as a cathode with a platinum anode in an aqueous rhodium sulfate solution as electrolyte. Electroplating is conducted in the same manner as in Example 1, thereby to provide a rhodium plating of about 2 microns in thickness.

The rhodium-plated, platinum-coated titanium plate is used as an anode for the electrolysis of saline water under the following conditions.

NaCl aq.: Saturated solution. The solution is replenished for every 12 hours, because its concentration is gradually decreased in response to the progress of the electrolysis.
Temperature: 40–60° C.
Anodic current density: About 10–12 a./dm.^{2}
Cathode: Platinum foil
Vessel: Same as in Example 1

The anode is dipped in the electrolyte to have an available area of 2 cm. wide x 3 cm. long. After electrolysis for one month, the anode surface is examined, and no injury, exfoliation and corrosion are observed.

EXAMPLE 3

A titanium plate (2 cm. wide x 12 cm. long x 0.1 mm. thick) is buffed with a sandpaper No. 4–0 in benzene. The plate is then removed from the benzene and immediately placed in an apparatus which is in turn evacuated to high vacuum (about 10^{-5} mm. Hg or more). Then, a platinum mass (about 10 g.) previously placed in said apparatus is heated to incandescence and deposited by vaporization onto the cleaned surface of the titanium plate to provide a coating of about 1000 A. in thickness. Then, the apparatus is vented and the platinum-coated titanium plate is used as a cathode with a platinum anode in an electroplating bath containing $Pt(NH_3)_2(NO_2)_2$. The formulation of the electroplating bath and other electroplating conditions are shown below.

Formulation:

$Pt(NH_3)_2(NO_2)_2$ (platinum "P" salt)	16 g./l.
NH_4NO_3	100 g./l.
$NaNO_2$	10 g./l.
Ammonia water (28% NH_4OH)	50 g./l.
Bath temperature	95° C. or higher.
Current density at the cathode	0.5 a./dm.^{2}

During the electroplating operation, ammonia water is added intermittently. A platinum coating of about 3 microns in thickness is obtained.

The platinum-coated, platinum-deposited titanium plate is used as an anode for the electrolysis of saline water under the following conditions.

NaCl aq.: Saturated solution
Cathode: Platinum foil
Anodic current density: 10 a./dm.^{2}
Vessel: Same as in Example 1

The electrolyte is intermittently replenished during the electrolysis. After one month, the anode surface is examined, and no damage, exfoliation and corrosion are observed. It should be understood that the term "titanium" used herein is intended to include a commercially pure titanium having a purity of not less than 98% and the term "tantalum" used herein is also intended to include a commercially pure tantalum having a purity of not less than 98%.

What I claim is:

1. A method of making an electrode which comprises mechanically cleaning the surface of a metal plate consisting of titanium or tantalum in an inactive medium free from oxygen and nitrogen, immediately thereafter placing the metal plate in a vacuum container while still avoiding contact with oxygen and nitrogen, depositing a platinum group metal onto the cleaned surface of the metal plate by evaporation in a vacuum, and then electrolytically plating the coated plate with a metal selected from the group consisting of platinum and rhodium.

2. A method as claimed in claim **1** wherein said platinum group metal is platinum, rhodium or iridium.

3. A method as claimed in claim **1**, wherein the plati-

num group metal coating is 100–3000 A. in thickness and the platinum or rhodium plating is 0.1–5 microns in thickness.

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