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54 **Oxygen-generating electrode and method for the preparation thereof.**

57 The electrode of the invention suitable for use in an oxygen-generating electrolytic process with durability comprises (A) a substrate of, e.g., titanium metal; (B) an undercoating layer thereon which is formed of a mixture of an iridium oxide and tantalum oxide in a limited molar proportion and (C) an overcoating layer formed of an iridium oxide. The undercoating layer can be formed by coating the substrate surface with a solution containing an iridium compound and tantalum compound each having thermal decomposability and then subjecting the coated substrate body to a heat treatment in an oxidizing atmosphere. Similarly, the overcoating layer can be formed by coating with a solution containing a thermally decomposable iridium compound followed by an oxidative heat treatment in an oxidizing atmosphere.

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OXYGEN-GENERATING ELECTRODE AND METHOD FOR THE PREPARATION THEREOF

The present invention relates to a novel oxygen-generating electrode and to a method for the preparation thereof. More particularly, the invention relates to an electrode which has an excellent durability and low oxygen overvoltage for generating oxygen by the electrolytic oxidation of an aqueous solution at an anode, as well as to a method for the preparation thereof.

Conventional metallic electrodes widely used in the electrolytic industry include those prepared by providing a coating layer of a platinum group metal or an oxide thereof on an electroconductive substrate made of titanium metal.

For example, known electrodes used as anodes for producing chlorine by the electrolysis of brine include those prepared by providing a titanium substrate with a coating layer formed from an oxide mixture of ruthenium and titanium, or an oxide mixture of ruthenium and tin (see, for example, Japanese Patent Publications 46-21884, 48-3954 and 50-11330).

Besides the above mentioned process of electrolysis of brine in which chlorine is produced as the electrolytic product, various processes are known in the electrolytic industry in which oxygen is generated at the electrode. Examples of such oxygen-generating electrolytic processes include the recovery of spent acids, alkalis or salts; electrolytic metallurgy of copper, zinc, etc; metal plating and cathodic protection.

These oxygen-generating electrolytic processes require electrodes which are different from the electrodes successfully used in the electrolytic processes accompanied by the generation of chlorine. When an electrode for the chlorine-generating electrolysis, such as the above mentioned titanium-based electrode having a coating layer of an oxide mixture of ruthenium and titanium or ruthenium and tin, is used in an oxygen-generating electrolytic process, the electrolysis must be discontinued due to the rapid corrosion of the electrode. Thus, the electrodes must be specialized for the particular electrolytic processes. The electrodes most widely used in oxygen-generating electrolysis are lead-based electrodes and soluble zinc anodes, although other known and usable electrodes include iridium oxide and platinum-based electrodes, iridium oxide and tin oxide-based electrodes and platinum-plated titanium electrodes.

These conventional electrodes are not always satisfactory due to the problems which may arise depending on the particular oxygen-generating electrolytic process. When a soluble zinc anode is used in zinc plating, for example, the anode is consumed so rapidly that adjustment of the elec-

trode distance must be frequently performed. When a lead-based insoluble electrode is used for the same purpose, a small amount of lead in the electrode is dissolved in the electrolyte solution thus affecting the quality of the plating layer. Platinum-plated titanium electrodes are also subject to rapid consumption when used in a so-called high-speed zinc plating process at a high current density of 100 A/dm² or higher.

Accordingly, it is an important technical problem in the technology of electrode manufacture to develop an electrode useful in an oxygen-generating electrolytic processes which can be used with versatility in various processes without the above mentioned drawbacks.

When an oxygen-generating electrolytic process is performed using a titanium-based electrode having a coating layer thereon, on the other hand, it is rather usual that an intermediate layer of titanium oxide is formed between the substrate surface and the coating layer thus causing a gradual increase in the anode potential which may result in the coating layer falling from the substrate surface which is in a passive state. Various attempts and proposals have been made to provide an appropriate intermediate layer between the substrate surface and the coating layer in order to prevent the subsequent formation of a layer of titanium oxide (see, for example, Japanese Patent Publications 60-21232 and 60-22074 and Japanese Patent Kokai 57-116786 and 60-184690).

An electrode having an intermediate layer provided as mentioned above is not as effective as desired when the electrode is used in an electrolytic process at a high current density because the electroconductivity of the intermediate layer is usually lower than the overcoating layer.

It has also been proposed to provide an intermediate layer formed by dispersing platinum in a matrix of a non-precious metal oxide (see Japanese Patent Kokai 60-184691) or to provide an intermediate layer formed from an oxide of a valve metal, e.g., titanium, zirconium, tantalum and niobium, and a precious metal (see Japanese Patent Kokai 57-73193). These electrodes also possess disadvantages because platinum does not have a very high corrosion resistance in particular in the former type and, in the latter type, the valve metal oxide and the compounding amount thereof are not without inherent limitations.

Furthermore, Japanese Patent Kokai 56-123388 and 56-123389 disclose an electrode having an undercoating layer containing iridium oxide and tantalum oxide on an electroconductive metal substrate and an overcoating layer of lead dioxide. The

undercoating layer in this electrode, however, serves merely to improve the adhesion between the substrate surface and the overcoating layer of lead dioxide to exhibit some effectiveness in preventing corrosion due to pin holes. When such an electrode is used in an oxygen-generating electrolytic process, disadvantages are caused because of the insufficient effect of preventing formation of titanium oxide and the unavoidable contamination of the electrolyte solution with lead.

We have now developed a novel and improved electrode suitable for use in an oxygen-generating electrolytic process which is free from the above described problems and disadvantages in the prior art electrodes.

The electrode of the present invention suitable for use in an oxygen-generating electrolytic process is an integral body composed of:

(A) an electroconductive substrate made of a metal which is preferably titanium;

(B) an undercoating layer on the substrate surface formed of a binary mixture of iridium oxide and tantalum oxide each in a molar proportion in the range from 50% to 90% and from 50% to 10%, respectively, calculated as iridium metal and tantalum metal; and

(C) an overcoating layer of iridium oxide in an amount in the range from 0.05 to 3 mg/cm², calculated as iridium metal.

As is described above, the electrode of the invention has a basic structure in which an electroconductive substrate of a metal such as titanium is provided with an undercoating layer formed of a binary oxide mixture composed of iridium oxide and tantalum oxide and an overcoating layer of iridium oxide. Such an undercoating layer of a mixed oxide can be formed by coating the substrate surface with a coating solution containing an iridium compound and a tantalum compound each of which decomposes on heating to form the respective oxides, followed by a heat treatment in an oxidizing atmosphere to convert the thermally decomposable compounds into the respective metal oxides.

Examples of the metal from which the electroconductive substrate is formed include so-called valve metals such as titanium, tantalum, zirconium and niobium as well as alloys of these metals, of which titanium is preferred in the invention. The substrate shaped from these metals or alloys in an appropriate form of electrode is first provided as mentioned above with an undercoating layer of the binary oxide mixture. Examples of suitable thermally decomposable compounds of iridium and tantalum include chloroiridic acid $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and tantalum halides and tantalum alkoxides, e. g., tantalum pentaethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$, tantalum pentapropoxide $\text{Ta}(\text{OC}_3\text{H}_7)_5$ and tantalum pentabutox-

ide $\text{Ta}(\text{OC}_4\text{H}_9)_5$, respectively, convertible into the respective oxides. The coating solution can be prepared by dissolving these compounds in a suitable organic solvent such as butyl alcohol in a proportion to give a mixed-oxide coating layer in which the molar proportions of iridium and tantalum calculated as metals are in the ranges from 50% to 90% for iridium and from 50% to 10% for tantalum or preferably, from 50% to 70% for iridium and from 50% to 30% for tantalum. When the proportion of the tantalum oxide is too large, the undercoating layer is less effective in providing protection of the substrate surface and adhesion between the substrate surface and the undercoating layer may be somewhat decreased in addition to the disadvantage of a decreased electroconductivity of the coating layer per se. The substrate coated with the coating solution is dried and subjected to heat treatment at a temperature in the range from 400 to 500 °C in an oxidizing atmosphere containing oxygen, such as air, for a length of time of 1 to 30 minutes. When the atmosphere for the heat treatment is not fully oxidizing, the metal compounds can be oxidized into the respective oxides only incompletely to leave an amount of metallic constituents badly influencing the durability of the electrode. The thickness or coating amount of the undercoating layer is not particularly limited but it should be at least 0.2 mg/cm² calculated as iridium metal. When the coating amount is too small, insufficient protection of the substrate surface is obtained. If necessary, the cycle of coating with the coating solution and heat treatment to effect thermal oxidative decomposition of the metal compounds is repeated several times until the coating amount of the oxide mixture has reached the above mentioned preferred range.

When the undercoating layer composed of the binary oxide mixture of iridium oxide and tantalum oxide is formed in the above described manner, the undercoating layer is further coated with an overcoating layer of iridium oxide. Such a coating layer of iridium oxide can be formed by coating the surface with a coating solution prepared by dissolving a thermally decomposable iridium compound in an organic solvent followed by a heat treatment in an oxidizing atmosphere. The coating amount of the overcoating layer should be in the range from 0.05 to 3 mg/cm² calculated as iridium metal. When the coating amount of the overcoating layer is too small, a disadvantage is that the consumption of the electrode in the electrolytic process is increased to effect the durability of the electrode. When the coating amount of the overcoating layer is too large, on the other hand, an adverse influence is that the adhesive strength of the active electrode film is decreased together with an eventual increase in the anode potential within a short

time in the course of the electrolytic process.

The procedure for providing the overcoating layer of iridium oxide is similar to the process for forming the binary mixed-oxide undercoating layer of iridium and tantalum oxides. Thus, a thermally decomposable iridium compound such as chloroiridic acid is dissolved in an organic solvent and the substrate provided with the undercoating layer of iridium and tantalum oxides is coated with the solution, dried and subjected to a heat treatment at a temperature in the range from 400 to 550 °C in an oxidizing atmosphere. The cycle of coating with the solution of the iridium compound and heat treatment may be repeated several times until the coating amount has reached the desired range mentioned above.

In the following, the electrode suitable for use in an oxygen-generating electrolytic process according to the invention is described in more detail by way of examples and comparative examples which should not be construed as limiting the scope of the present invention in any way.

Example 1.

A first coating solution was prepared by dissolving chloroiridic acid $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and tantalum pentabutoxide $\text{Ta}(\text{OC}_4\text{H}_9)_5$ in n-butyl alcohol each in such an amount that the molar ratio of iridium to tantalum as metals was 60:40 and the total concentration thereof corresponded to 80 g of the metals per liter.

An electrode substrate made of titanium metal after an etching treatment using a hot aqueous solution of oxalic acid was coated by brushing with the coating solution prepared above and, after drying, subjected to a heat treatment at 450 °C in an electric oven into which air was blown. The coating layer of mixed oxide thus formed on the substrate surface had a thickness corresponding to a coating amount of about 0.1 mg/cm² calculated as metals. This procedure of coating with the coating solution, drying and a heat treatment in air was repeated 2 to 10 times to prepare five undercoated electrode bodies having different coating amounts of the mixed oxides of iridium and tantalum.

A second coating solution was prepared by dissolving chloroiridic acid in n-butyl alcohol in such an amount that the concentration of the compound as iridium metal was 60 g/liter. Each of the electrode bodies having an undercoating layer of a mixture of iridium and tantalum oxides formed by twice to 8 times repetition of the procedure of coating with the first coating solution, drying and a heat treatment as well as a fresh titanium-made electrode substrate was coated with the second coating solution by brushing and, after drying, sub-

jected to a heat treatment at 450 °C in an electric oven into which air was blown. This procedure of coating with the second coating solution, drying and a heat treatment was repeated several times in such a number of repetition that the total number of the repeated procedures of coating with either the first or the second coating solution, drying and heat treatment was always 10. In this manner, six coated electrodes No. 1 to No. 6 were prepared, of which No. 1 was prepared without undercoating with the first coating solution but 10 times repeated coating with the second coating solution and No. 6 was prepared with 10 times repeated coating with the first coating solution but without coating with the second coating solution, No. 2, No. 3, No. 4 and No. 5 being prepared with 2, 4, 6 and 8 times repeated coating with the first coating solution, respectively, and with 8, 6, 4 and 2 times repeated coating with the second coating solution, respectively.

Each of the thus prepared coated electrodes No. 1 to No. 6 was used as the anode for electrolysis of a 1 mole/liter aqueous solution of sulfuric acid at 60 °C with a platinum electrode as the cathode at a current density of 150 A/dm² continuously over a length of time up to 3000 hours under monitoring of the cell voltage. The figure of the accompanying drawing is a graph showing the change in the cell voltage for each electrode in the lapse of time. As is clear from this figure, the single-coated electrodes, i.e. No. 1 and No. 6, failed to serve for continued electrolysis already after about 1500 hours due to the increase of the cell voltage, which was initially about 5 volts, to exceed 10 volts. In contrast thereto, the dually coated electrodes, i.e. No. 2 to No. 5, could serve to continue the electrolysis even after about 3000 hours with little increase in the cell voltage.

The electrodes No. 1 to No. 5 were subjected to the measurement of the oxygen overvoltage by the potential scanning method in a 1 mole/liter aqueous solution of sulfuric acid at 30 °C with a current density of 20 A/dm². The results were: 440 mV, 430 mV, 430 mV, 410 mV and 380 mV for the electrodes No. 1 to No. 5, respectively.

Example 2.

Four coating solutions for undercoating were prepared each by dissolving chloroiridic acid $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and tantalum pentabutoxide $\text{Ta}(\text{OC}_4\text{H}_9)_5$ in n-butyl alcohol each in such an amount that the total concentration thereof corresponded to 80 g of the metals per liter but with varied molar proportions of iridium to tantalum as metals of 20:80, 50:50, 60:40 and 70:30.

Five titanium-made electrode substrates were

coated each with the second coating solution of tantalum pentabutoxide alone prepared in Example 1 (electrode No. 7) or one of the above prepared coating solutions of iridium:tantalum molar ratio of 20:80 (electrode No. 8), 50:50 (electrode No. 9) 60:40 (electrode No. 10) and 70:30 (electrode No. 11) followed by drying and a heat treatment at 500 °C in an electric oven into which air was blown. This procedure of coating with the coating solution, drying and heat treatment was repeated five times.

Each of the electrode bodies No. 7 to No. 11 was further coated with the second coating solution prepared in Example 1 followed by drying and a heat treatment at 500 °C in an electric oven into which air was blown. This procedure of coating with the second coating solution, drying and a heat treatment was repeated five times.

Each of the thus prepared coated electrodes No. 7 to No. 11 was used as the anode for electrolysis of a 1 mole/liter aqueous solution of sulfuric acid at 60 °C with a platinum electrode as the cathode at a current density of 200 A/dm² continuously over a length of time up to 1000 hours under monitoring of the cell voltage. The results were that the electrodes No. 9, No. 10 and No. 11 could serve to continue the electrolysis over 1000 hours while the electrolysis could no longer be continued after 200 hours and 400 hours of continued electrolysis with the electrodes No. 7 and No. 8, respectively.

Claims

1. An electrode for use in an oxygen-generating electrolytic process which is an integral body comprising:

(A) an electroconductive substrate made of a metal;

(B) an undercoating layer formed on the surface of the substrate and composed of a mixture of an iridium oxide and a tantalum oxide each in a molar proportion in the range from 50% to 90% and from 50% to 10% respectively, calculated as iridium metal and tantalum metal; and

(C) an overcoating layer formed on the undercoating layer and composed of iridium oxide in an amount in the range from 0.05 to 3 mg/cm², calculated as iridium metal.

2. An electrode as claimed in claim 1 wherein the metal forming the electroconductive substrate is titanium.

3. An electrode as claimed in claim 1 or claim 2 wherein the undercoating layer comprises at least 0.2 mg/cm² of iridium.

4. An electrode as claimed in any one of the preceding claims wherein the overcoating layer comprises from 0.05 to 3 mg/cm² of iridium.

5. A method for the preparation of an electrode as claimed in any one of the preceding claims which comprises the successive steps of:

(a) coating the surface of the substrate with a solution of a thermally decomposable iridium compound and a thermally decomposable tantalum compound;

(b) subjecting the thus coated substrate to heat treatment in an oxidizing atmosphere to convert the thermally decomposable iridium compound and the thermally decomposable tantalum compound into oxides of the respective metals;

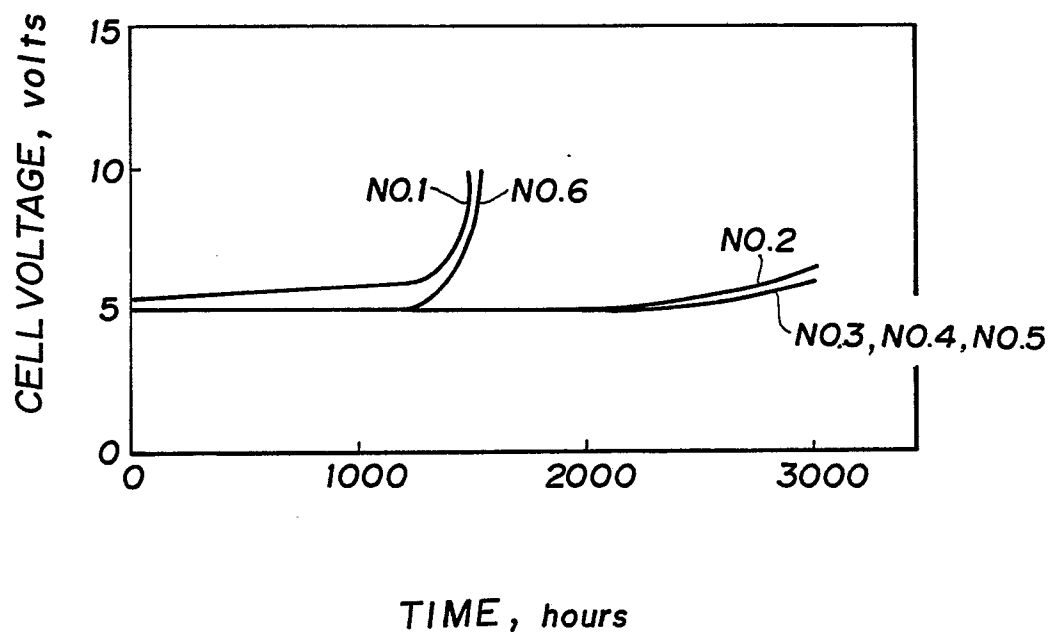
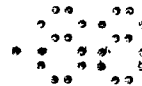
(c) coating the surface of the substrate after step (b) with a solution of a thermally decomposable iridium compound; and

(d) subjecting the thus coated substrate to heat treatment in an oxidizing atmosphere to convert the thermally decomposable iridium compound into an iridium oxide.

6. A method as claimed in claim 5 wherein the decomposable compound of iridium is chloroiridic acid.

7. A method as claimed in claim 5 or claim 6 wherein the decomposable compound of tantalum is a tantalum halide or a tantalum alkoxide.

8. A method as claimed in any one of claims 5 to 7 wherein the heat treatment in steps (b) and (d) is carried out at a temperature in the range of from 400 to 550 °C.



Neu eingereicht / Newly filed
Nouvellement déposé



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
D,Y	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 204 (C-85)[876], 24th December 1981; & JP-A-56 123 388 (ASAHI KASEI KOGYO K.K.) 28-09-1981 * Abstract * ---	1,2	C 25 B 11/10 C 25 C 7/02
Y	EP-A-0 243 302 (ELTECH SYSTEMS CORP.) * Page 4, lines 10-28; pages 6,7, claims * ---	1,2	
A	GB-A-2 099 019 (PERMELEC ELECTRODE LTD) * Page 5, claims 1-18 * ---	1	
A	GB-A-2 134 544 (PERMELEC ELECTRODE LTD) * Page 4, table 1, runs 1-3; claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.3)
			C 25 B 11 C 25 C 7
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	12-05-1989	GROSEILLER PH.A.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			