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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 comprises (A) a substrate of, e.g., titanium metal and (B) a coating layer thereon which is formed with a mixture of iridium oxide, tantalum oxide and elementary platinum in a specified molar proportion. The coating layers can be formed by coating the substrate surface with a solution containing an iridium compound, tantalum compound and platinum compound each having thermal decomposability and then subjecting the coated substrate to a heat treatment in an oxidizing atmosphere so as to convert the iridium and tantalum compounds into respective oxides and the platinum compound into elementary platinum. Further, the coating layer is preferably provided with an overcoating layer formed of iridium oxide or of a mixture of iridium oxide and tantalum oxide in a similar manner.

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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 electrode 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/dm^2 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 cause 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; and

(B) a coating layer on the substrate surface formed of a ternary mixture of iridium oxide, tantalum oxide and platinum in the elementary form each in a molar proportion in the range from 40% to 90%, from 50% to 10% and from 0.1% to 30%, respectively, calculated as the respective metals.

It is preferable that the above defined coating layer formed of the ternary mixture is provided with an over-coating layer of iridium oxide or a mixture of iridium oxide and a minor amount, e.g., 50% by moles or less as metals, of tantalum oxide.

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 a coating layer formed of a ternary mixture composed of iridium oxide, tantalum oxide and platinum in the elementary form. Such a coating layer of a ternary mixture can be formed by coating the substrate surface with a coating solution containing an iridium compound, a tantalum compound and a platinum compound each of which decomposes on heating, followed by a heat treatment in an oxidizing atmosphere to convert the thermally decomposable iridium and tantalum compounds into the respective oxides and the platinum compound into elementary platinum.

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. Preferably, the substrate is made of titanium metal. The substrate shaped from these metals or alloys in an appropriate form of electrode is provided as mentioned above with a coating layer of the ternary mixture. Examples of suitable thermally decomposable compounds of iridium and tantalum convertible into the respective oxides include chloroiridic acid $H_2IrCl_6 \bullet 6H_2O$ and tantalum halides and tantalum alkoxides, e.g., tantalum pentaethoxide $Ta(OC_2H_5)_5$ and tantalum pentabutoxide $Ta(OC_4H_9)_5$, respectively, and suitable platinum compounds include chloroplatinic acid $H_2PtCl_6 \bullet 6H_2O$. The coating solution can be prepared by dissolving these compounds in a suitable organic solvent such as butyl alcohol in such a proportion as to give a coating layer of the ternary mixture in which the molar proportions of iridium oxide, tantalum oxide and elementary platinum calculated as respective metals are in the ranges from 40% to 90% for iridium, from 50% to 10% for tantalum and from 0.1% to 30% for platinum. When the proportion of the tantalum oxide is too large, the overvoltage on the electrode increases and adhesion between the substrate surface and the coating layer may be somewhat decreased. The substrate coated with the coating solution is dried and subjected to heat treatment for 1 to 30 minutes at a temperature in the range from 400 to 550 °C in an oxidizing atmosphere of oxygen, such as air. the atmosphere for the heat treatment is not fully oxidizing, the compounds of iridium and tantalum 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 coating layer is not particularly limited but it should be at least 0. 1 mg/cm^2 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 decomposition of the metal compounds is repeated several times until the coating amount of the oxide mixture has reached the above mentioned prefered range.

When the coating layer is formed from the ternary mixture of iridium and tantalum oxides and elementary platinum, it is preferable that the coating layer is further coated with an overcoating layer of iridium oxide optionally admixed with a minor amount of tantalum oxide in order to decrease consumption of the electrode in the electrolytic process. The coating amount of the overcoating layer should be in the range from 0.02 to 5 mg/cm^2 calculated as iridium metal. When the coating amount of the overcoating layer is too small, no desired effect as mentioned above can be obtained to affect 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.

The procedure for providing the overcoating layer of iridium oxide, optionally, admixed with tantalum oxide is similar to the procedure for forming the ternary mixed coating layer of iridium and tantalum oxides and elementary platinum. Thus, a thermally decomposable iridium compound such as chloroiridic acid and, optionally, a tantalum compound are dissolved in an organic solvent and the substrate surface provided with the undercoating layer of ternary mixture is coated with the solution, dried and subjected to a heat treatment for 1 to 30 minutes at a temperature in the range from 400 to 550 °C in an oxidizing atmosphere. The cycle of coating with the solution of the metal compound or compounds and heat treatment may be repeated several times until the coating amount has reached the desired range mentioned above. The molar proportion of tantalum oxide relative to the oxide mixture should not exceed 50% calculated as metals.

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.

Seven coating solutions were prepared for the electrodes No. 1 to No. 7 each by dissolving chloroiridic acid $H_2IrCl_6 \bullet 6H_2O$, chloroplatinic acid $H_2PtCl_6 \bullet 6H_2O$ and tantalum pentaethoxide $Ta(OC_2H_5)_5$ 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 proportion of iridium:platinum:tantalum as metals (Ir:Pt:Ta) indicated in Table 1 below.

Separately, five more coating solutions were prepared for the electrodes No. 8 to No. 12 for comparative purpose in the same manner as above excepting omission of one or two of the three metal compounds in each of the formulations of the solution. The molar ratios of Ir:Pt:Ta are also shown in Table 1.

An electrode substrate made of titanium metal after an etching treatment using a hot aqueous solution of oxalic acid was coated by brushing with either one of the coating solutions prepared above and, after drying, subjected to 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 a heat treatment in air was repeated several times until the coating amount of the coating layer had reached 0.05 to 10 mg/cm^2 calculated as iridium metal to give 12 electrodes No. 1 to No. 12.

These electrodes 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/dm^2. The results are shown in Table 1. Further, the electrodes were subjected to the durability test as the anode for electrolysis of a 1 mole/liter aqueous solution of sulfuric acid at 60 °C using a platinum electrode as the cathode with a current density of 200 A/dm^2 to give the results that the durability or the serviceable life was at least 2000 hours for each of the electrodes No. 1 to No. 7 while the life was between 1000 and 2000 hours for the electrode No. 11 and less than 1000 hours for the electrodes No. 8, No. 9, No. 10 and No. 12.

Table 1

Electrode No.	Ir:Pt:Ta	Oxygen overvoltage, mV
1	68 : 2:30	395
2	65: 5:30	380
3	60: 10:30	380
4	20: 20:30	375
5	40:30:30	415
6	50: 10:40	380
7	70: 10:20	380
8	30: 0:70	450
9	0: 50:50	670
10	100: 0: 0	430
11	50: 50: 0	450
12	0:100: 0	650

Example 2.

Nine titanium-made electrode substrates for electrodes No. 13 to No. 21 were coated each with either one of the coating solutions prepared in Example 1 indicated in Table 2 below to be provided with the undercoating layer of a ternary mixture in the same manner as in Example 1.

Separately, several coating solutions for overcoating were prepared each by dissolving chloroiridic acid $H_2IrCl_6 \bullet 6H_2O$ alone or chloroiridic acid and tantalum pentabutoxide $Ta(OC_4H_9)_5$ or tantalum pentaethoxide $Ta(OC_2H_5)_5$ in n-butyl alcohol each in such an amount that the molar ratio of iridium to tantalum as metals (Ir:Ta) was as indicated in Table 2 and the total concentration thereof ccrresponded to 80 g of the metals per liter.

The electrode bodies provided with the undercoating layer were each coated with either one of the above prepared overcoating solutions, dried and subjected to a heat treatment at 500 °C in an electric oven into which air was blown. The procedure of coating with the coating solution, drying and a heat treatment was repeated several times to give an overcoating layer of iridium oxide or a mixture of iridium oxide and tantalum oxide in a coating amount of 0.01 to 8 mg/cm^2 as iridium metal.

The thus prepared dually coated electrodes were subjected to the measurement of the oxygen overvoltage in the same manner as in Example 1 to give the results shown in Table 2. Further, they were subjected to the durability test for electrolysis in the same manner as in Example 1 to give the results that the durability or serviceable life was at least 2000 hours for each of the electrodes No. 13 to No. 18 and between 1000 and 2000 hours for each of the electrodes No. 19 to No. 21.

Table 2

Electrode No.	Undercoating, the same as in electrode No.	Ir:Ta in overcoating	Oxygen overvoltage, mV
13	3	70:30	385
14	3	90:10	385
15	4	80:20	385
16	7	80:20	385
17	3	60:40	390
18	3	100:0	400
19	8	70:30	430
20	3	30:70	430
21	10	70:30	420

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; and

(B) a coating layer formed on the surface of the substrate and composed of a mixture comprising iridium oxide, tantalum oxide and platinum in the elementary form in molar proportions in the range of from 40% to 90% iridium oxide, 50% to 10% tantalum oxide and 0.1% to 30% platinum, the percentages being calculated as the respective metals.

2. An electrode as claimed in claim 1 which further comprises an overcoating layer of iridium oxide, or a mixture of iridium oxide and tantalum oxide in which the content of iridium oxide is at least 50% by mole calculated as the metal.

3. An electrode as claimed in claim 1 or claim 2 wherein the coating layer is applied in an amount of at least 0.1 mg/cm^2 calculated as iridium metal.

4. An electrode as claimed in claim 2 or claim 3 wherein the overcoating layer is applied in an amount of from 0.02 to 5 mg/cm^2 calculated as iridium metal.

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 thermally decomposable compounds of iridium, tantalum and platinum; and

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

6. A method as claimed in claim 5 which includes the additional steps of

(c) overcoating the surface of the substrate with a solution of a thermally decomposable compound of iridium or a combination of thermally decomposable compounds of iridium and tantalum; and

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

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

8. A method as claimed in any one of claims 5 to 7 wherein the decomposable compound of tantalum is a tantalum halide or a tantalum alkoxide.

9. A method as claimed in any one of claims 6 to 8 wherein the heat treatment in steps (b) and (d), are carried out at a temperature in the range of from 400 to 550 °C.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 8794

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.4)
A	GB-A-2 099 019 (PERMELEC ELECTRODE LTD) * Page 4, table I, run 5; page 5, claims * ---	1	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	
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	
A	GB-A-2 134 544 (PERMELEC ELECTRODE LTD) * Page 4, table I, runs 1,2,3; claims * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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

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