Abstract: The present invention aims to provide an anode for oxygen generation and a manufacturing method for the same used for industrial electrolyses including manufacturing of electrolytic metal foils such as electrolytic copper foil, aluminum liquid cast and continuously electrogalvanized steel plate, and metal extraction. The present invention features an anode for oxygen generation and a manufacturing method for the same comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate wherein the coating is baked in a low temperature region of 370°C - 400°C in an oxidation atmosphere to form the catalyst layer containing amorphous iridium oxide and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize almost all amount of iridium oxide in the catalyst layer.
DESCRIPTION

Title of Invention
ANODE FOR OXYGEN GENERATION AND MANUFACTURING METHOD FOR THE SAME

Technical Field
The present invention relates to an anode for oxygen generation used for various industrial electrolysises and a manufacturing method for the same; more in detail, it relates to a high-load durable anode for oxygen generation and a manufacturing method for the same used for industrial electrolysises including manufacturing of electrolytic metal foils such as electrolytic copper foil, aluminum liquid contact, and continuously electrogalvanized steel plate, and metal extraction.

Background Art
Mixing of lead ions in the electrolytic cell is often seen in various types of industrial electrolysis. Mixing of lead compounds in the production of electrolytic copper foil as its typical example is derived from the following two points: that is, sticking to, as a lead alloy, a scrap copper which is one of the raw materials of copper sulfate in electrolyte, and before DSE (registered trademark of Permelec Electrode Ltd.) type of electrode being used, lead-antimony electrodes were used, this time of leaching lead ions become lead sulfate particles and residue in electrolytic cell.

High purity electrolytic copper is best for raw materials, but in a practical manner, scrap copper which is recycled products is often used. Copper raw material is leached as copper ion by using concentrated sulfuric acid as an immersion liquid, or the copper raw material is compulsory eluted as anode for a short time. In an anodic dissolution, elution becomes easy from the complex
morphology of clad metals and other metal parts. In a scrap copper, wax materials such as lead soldering material is adhered, and other metals included in the wax materials or the clad is eluted with elution of copper in the electrolyte of a sulfuric acid-copper sulfate, or is mixed as floating particles. To the surface of the metal lead, a water-insoluble lead sulfate coating is formed, and so lead ion is high corrosion resistance to sulfuric acid, but a small amount of it is dissolved in a concentrated sulfuric acid, and such lead ion crystallizes as a minute particle of lead sulfate in electrolyte and floats under a lower temperature than that in dissolving and a high pH conditions.

Still more, lead sulfate, PbSO₄, is a water-insoluble salt in which a solubility product is 1.06 * 10⁻⁸ mol/L (18°C), and is extremely small in which a solubility in 10% sulfuric acid and 25°C is approximately 7mg/L.

Incidentally a standard electrode potential of copper is high after the precious metal (Cu²⁺ + 2e⁻ → Cu : +0.342V vs. SHE) and a potential difference compared with base metal such as lead and etc. is great (Pb²⁺ + 2e⁻ → Pb : -0.126V vs. SHE), and as overvoltage of copper in electro deposition is also low, there is no hydrogen evolution and no eutectoid with other base metals. That is why scrap copper can be used as raw materials.

However, an influence by floating fine particles such as lead ion, Pb²⁺, or lead compounds, PbSO₄ against an electrode for electrolysis and an electrolytic copper foil which is an electrolytic product cannot be made light of.

Namely, in an electrode for electrolysis (anode), if electrolysis occurs, lead-ion, Pb²⁺, is oxidized to lead-β-PbO₂ in acidic solution, and electrodeposited to a surface of the electrode (anode) catalyst (Pb²⁺ / PbO₂ : pH = nearly 0, E₀ = approximately 1.47V vs. SHE) (exactly 1.459 + 0.0295p (Pb²⁺) - 0.1182pH). Since oxidized lead-P-PbO₂ has a small electrode catalyst function, a total surface of an electrode is covered by it, although an electrode potential increases, an electrolysis continuously occurs and an electrode life as a coating to protect the
electrode is prolonged, but if it is partially peeled off, an original electrode catalyst layer of which catalyst activity is high, is exposed, and therefore an electrolysis current of it increases and an unevenness of a foil thickness of copper foil growing on an opposite cathode drum is caused.

Also an electrolysis stops and an electrode continues to be immersed in the electrolyte and lead oxide is easily reduced to lead sulfate, PbSO\(_4\) having no electrode catalyst activity to correspond to oxidation reaction of a trace oxygen evolution by the action of local battery (PbSO\(_4\) + 2H\(_2\)O = PbO\(_2\) + HS0\(_4\)\(^-\) + 3H\(^+\) + 2e\(^-\) : at pH = nearly 0, \(E_0\) = approximately 1.62V vs. SHE) (exactly 1.632 - 0.0886pH - 0.0295p(HSO\(_4\)\(^-\))) and so a problem that electrolysis voltage rises after electrolysis appears.

Also the following problem occurs: Fine particles of PbSO\(_4\) floating in the electrolyte adhere to the surface of the electrolytic copper foil and are embroiled in a roll of electrolytic copper foil.

In recent years from the environmental point of view, in all aspects of raw materials of electrolyte, equipment and waste matter and etc., the consciousness that is going to make lead-free is increasing. However, after a lead-free solder penetrated, there is time lag up to replace to scrap copper of the lead-free and in the point of cost, it is predicted that the coexistence with the lead ion continues for a while now. In the electrode for electrolysis, therefore, it is necessary to reduce the influence of the lead ion such as the above as much as possible.

Furthermore, as an electrode for this kind of electrolysis, together with reducing the influence of the lead ion as much as possible, electrode with a low oxygen generation potential and a long service life is required. Conventionally, as electrode of this type, an insoluble electrode comprising a conductive metal
substrate, such as titanium, covered with a catalyst layer containing precious metal or precious metal oxide has been applied. For example, PTL 1 discloses an insoluble electrode prepared in such a manner that a catalyst layer containing iridium oxide and valve metal oxide is coated on a substrate of conductive metals, such as titanium, heated in oxidizing atmosphere and baked at a temperature of 650°C - 850°C, to crystallize valve metal oxide partially. This electrode, however, has the following drawbacks. Since the electrode is baked at a temperature of 650°C or more, the metal substrate, such as of titanium causes interfacial corrosion, and becomes poor conductor, causing oxygen overvoltage to increase to an unserviceable degree as electrode. Moreover, the crystallite diameter of iridium oxide in the catalyst layer enlarges, resulting in decreased an electrode effective surface area of the catalyst layer, leading to a poor catalytic activity.

PTL 2 discloses use of an anode for copper plating and copper foil manufacturing prepared in such a manner that a catalyst layer comprising amorphous iridium oxide and amorphous tantalum oxide in a mixed state is provided on a substrate of conductive metal, such as titanium. This electrode, however, features amorphous iridium oxide, and is insufficient in electrode durability. The reason why durability decreases when amorphous iridium oxide is applied is that amorphous iridium oxide shows unstable bonding between iridium and oxygen, compared with crystalline iridium oxide.

PTL 3 discloses an electrode coated with a catalyst layer comprising a double layer structure by a lower layer of crystalline iridium oxide and an upper layer of amorphous iridium oxide, in order to suppress consumption of the catalyst layer and to enhance durability of the electrode. The electrode disclosed by PTL 3 is insufficient in electrode durability because the upper layer of the catalyst layer is amorphous iridium oxide. Moreover, crystalline iridium oxide exists only in the lower layer, not uniformly distributed over the entire catalyst layer, resulting in
insufficient electrode durability.

PTL 4 discloses an anode for zinc electrowinning in which a catalyst layer containing amorphous iridium oxide as a prerequisite and crystalline iridium oxide, as a mixed state is provided on a substrate of conductive metal like titanium. PTL 5 discloses an anode for cobalt electrowinning in which a catalyst layer containing amorphous iridium oxide as a prerequisite and crystalline iridium oxide, as a mixed state is provided on a substrate of conductive metal like titanium. However, it is thought that electrode durability of these two electrodes is not enough because they contain a large amount of amorphous iridium oxide, as a prerequisite.

Citation List

Patent Literature

PTL 1: JP2002-275697A (JP3654204B)
PTL 3: JP2007-146215A
PTL 5: JP2010-001556A (JP4516618B)

Summary of Invention

Technical Problem

In order to solve the above-mentioned problems, the present invention aims to provide an anode for oxygen generation and a manufacturing method for the same, which can reduce the oxygen overvoltage of the anode for oxygen evolution to use for production of an electrode for industrial electrolysis to coat the electrolysis active substance layer particularly the electrolysis copper foil and
metal winning by the electrolytic method and control adhesion, coating of the lead dioxide to the anode and raise the durability.

**Solution to Problem**

As the first solution to achieve the above-mentioned purposes, the present invention provides an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the coating is baked in a low temperature region of 370°C - 400°C in an oxidation atmosphere to form the catalyst layer containing amorphous iridium oxide and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize almost all amount of iridium oxide in the catalyst layer.

As the second solution to achieve the above-mentioned purposes, the present invention provides an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the degree of crystallinity of iridium oxide in the catalyst layer after the post-baking is made to be 60% or more.

As the third solution to achieve the above-mentioned purposes, the present invention provides an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate wherein the crystallite diameter of iridium oxide in the catalyst layer is 8.0nm or less.

As the fourth solution to achieve the above-mentioned purposes, the present invention provides an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive
metal substrate, wherein an arc ion plating (hereafter called AIP) base layer containing tantalum and titanium ingredients is formed by AIP process on the conductive metal substrate before the formation of the catalyst layer.

As the fifth solution to achieve the above-mentioned purposes, the present invention provides a manufacturing method for an anode for oxygen generation, wherein the catalyst layer containing amorphous iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize almost all amount of iridium oxide in the catalyst layer.

As the sixth solution to achieve the above-mentioned purposes, the present invention provides a manufacturing method for an anode for oxygen generation, wherein the catalyst layer containing amorphous iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a high temperature region of 520°C - 600°C in an oxidation atmosphere to make the degree of crystallinity of iridium oxide in the catalyst layer to be 60% or more.

As the seventh solution to achieve the above-mentioned purposes, the present invention provides a manufacturing method for an anode for oxygen generation, wherein the catalyst layer containing amorphous iridium oxide is formed by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a high temperature region of 520°C - 600°C in an oxidation atmosphere to make the crystallite diameter of iridium oxide in the catalyst layer to be 8.0nm or less.
As the eighth solution to achieve the above-mentioned purposes, the present invention provides a manufacturing method for an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the AIP base layer containing tantalum and titanium ingredients is formed by the AIP process on the conductive metal substrate before the formation of the catalyst layer.

**Advantageous Effects of Invention**

In the formation for the electrode catalyst layer containing iridium oxide by the present invention, baking is conducted, instead of the conventional repeated baking operations at 500°C or more, which are the perfect crystal deposition temperature, by two steps: baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere to form a catalyst layer containing amorphous iridium oxide and post-baking in a high temperature region of 520°C - 600°C in an oxidation atmosphere to suppress the crystallite diameter of iridium oxide in the electrode catalyst layer preferably to 8.0nm or less and to crystallize most of the iridium oxide preferably to 60% or more in crystallinity. Thus, the growth of crystallite diameter of iridium oxide and coexistence of amorphous and crystalline iridium oxides was able to be suppressed and the electrode effective surface area of the catalyst layer was able to be increased. Thus, according to the present invention, the growth of crystallite diameter of iridium oxide can be suppressed. As the reasons, the following are considered. The baking is conducted by two stages: first, coating and baking is repeated in a low temperature region of 370°C - 400°C in an oxidation atmosphere and then post-baking in a high temperature of 520°C - 600°C in an oxidation atmosphere. Compared with the baking at a high temperature from the beginning by the conventional method, crystallite diameter under the present invention will not enlarge beyond a certain degree. If the growth of crystallite diameter of iridium oxide is suppressed, the smaller the crystallite
diameter is, the larger the electrode effective surface area of the catalyst layer will be. Then, the oxygen generation overvoltage of the electrode can be decreased, oxygen generation is promoted, and the reaction to form PbO₂ from lead ion can be suppressed. In this way, PbO₂ attachment and covering on the electrode were suppressed.

Furthermore, according to the present invention, by increasing the electrode effective surface area of the catalyst layer, the current distribution is dispersed at the same time and the current concentration is suppressed and also wear rate of the catalyst layer by electrolysis can be suppressed, and then the durability of the electrode is improved.

**Brief Description of Drawings**

[Fig. 1] Fig. 1 is a graph indicating the change of degree of crystallinity of iridium oxide (IrO₂) of the catalyst layer by baking temperature and post-bake temperature.

[Fig. 2] Fig. 2 is a graph indicating the change of crystallite diameter of iridium oxide (IrO₂) of the catalyst layer by baking temperature and post-bake temperature.

[Fig. 3] Fig. 3 is a graph indicating the change of the electrostatic capacity of the electrode by baking temperature and post-bake temperature.

[Fig. 4] Fig. 4 is a graph indicating the dependence of oxygen overvoltage on baking conditions.

**Description of Embodiments**

The following explains embodiments of the present invention, in detail, in reference to the figures. In the present invention, it is found that if the electrode effective surface area of the electrode catalyst layer is increased to suppress adhesive reaction of lead oxide to the electrode surface, oxygen generation overvoltage can be reduced and then, oxygen generation is promoted and at the
same time the adhesive reaction of lead oxide can be suppressed. In addition, the present invention has been completed from the idea that it is necessary that iridium oxide of the catalyst layer is mainly crystalline in order to improve the electrode durability at the same time, and experiments were repeated.

In the present invention, a two-step baking is performed, first, in a low temperature region of 370°C - 400°C in an oxidation atmosphere to form a catalyst layer containing amorphous IrO$_2$ in the baking, then, in a high temperature region of 520°C - 600°C in an oxidation atmosphere to post-bake, through which the iridium oxide of the catalyst layer is almost crystallized.

Through the experiments conducted by inventors of the present invention, it has been proved that the catalyst layer containing amorphous iridium oxide, which can greatly increase the electrode effective surface area, consumes amorphous iridium oxide quite rapidly by electrolysis and durability is reduced relatively. In other words, it is considered that the electrode durability cannot be improved unless iridium oxide of the catalyst layer is crystallized. Therefore, in order to achieve the purpose of the present invention that the electrode effective surface area of the electrode catalyst layer is increased and the overvoltage of the electrode is reduced, the present invention applies two-step baking: low temperature baking plus high temperature post-baking in order to control the crystallite diameter of iridium oxide of the catalyst layer, through which iridium oxide crystal, smaller in size than the conventional product precipitates, resulting in increased the electrode effective surface area of the electrode catalyst layer and reduced overvoltage. In addition, it was found that in the catalyst layer of the electrode manufactured by the baking method of the present invention, a small amount of an amorphous iridium oxide exists, but that such a small amount of an amorphous iridium oxide is effective for an increase of the electrode effective surface area and does not give a big influence on the electrode durability (by the electrolysis evaluation in the pure sulfuric acid).
In the present invention, a catalyst layer containing amorphous Iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere; thereafter, the catalyst layer of amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize the almost iridium oxide in the catalyst layer.

The coating amount of iridium oxide by the present invention is preferable to control to 2.0g/m² or less per time as a metal. This amount is determined by electrolytic conditions and an ordinal electrolysis is performed at a current density of 50A/dm² - 130A/dm² and in this case, a coating amount of iridium oxide of 1.0 - 2.0g/m² per time as a metal is used, and a coating times is ordinarily 10 - 15 times and a total amount is 10 - 30g/m².

The baking temperature in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the post-baking temperature in a high temperature region of 520°C - 600°C in an oxidation atmosphere are determined by the crystal particle size and the degree of crystallinity of iridium oxide to be formed in the catalyst layer, and the catalyst layer with a low oxygen overvoltage and a high corrosion resistance is formed in the above-mentioned temperature region.

In the present invention, the degree of crystallinity of the iridium oxide of the catalyst layer is preferably to 60% or more and if it being less than this value, the amorphous iridium oxide of the catalyst layer becomes more and the iridium oxide of the catalyst layer become unstable and a sufficient durability is not obtained. Also the crystallite diameter of iridium oxide in the catalyst layer is preferably equal to or less than 8.0nm and if it being more than this value, the electrode effective surface area iridium oxide of the catalyst layer becomes smaller and the oxygen generation overvoltage of the electrode increases and a reaction of
generation of PbO₂ from lead ions is not suppressed.

Prior to forming the catalyst layer, it is preferable to form the AIP base layer comprising a valve metal base alloy containing crystalline tantalum and titanium components by AIP process on the conductive metal substrate. If the AIP base layer is provided on the conductive metal substrate, it is possible to prevent further interfacial corrosion of the metal substrate. The base layer consisting of TiTaOₓ oxide layer may be applied instead of the AIP base layer.

The catalyst layer was formed in such a manner that hydrochloric acid aqueous solution of IrCl₃/Ta₂Cl₅ as a coating liquid was coated on the AIP coated titanium substrate at 1.1g - Ir/m² per time and baked in a low temperature region of 370°C - 400°C. After repeating the coating and baking process until the necessary support amount of the catalyst was obtained, one hour post-bake was conducted in a high temperature region of 520°C - 600°C. In this way, the electrode sample was prepared. The prepared sample was measured for IrO₂ crystalline of the catalyst layer by X-ray diffraction, oxygen generation overvoltage, electrostatic capacity of electrode, etc. and evaluated for sulfuric acid electrolysis and gelatin-added sulfuric acid electrolysis and lead adherence test.

As a result, it has been found that in case iridium oxide of the catalyst layer was formed by a baking in a temperature region of 370°C - 400°C and the post-baking in a temperature region of 520°C - 600°C, the most of the IrO₂ of the formed catalyst layer was crystalline, the crystallite diameter became smaller, and the electrode effective surface area increased. The oxygen generation overvoltage was reduced up to approximately 50mV by conventional products at the same time, too. After examining lead adhesion, a quantity of lead adhesion became 1/10 of conventional products on the lowest mark, and a suppressant effect of good lead adhesion was recognized. In addition, sulfuric acid electrolysis life was at the same class that of conventional products, proving improvement in
durability.

The experimental conditions and methods by the present invention are as follows.

The sample manufacturing procedures were as follows.

(1) Preparation of AIP substrate

- Ultrasonic cleaning: Detergent + alcohol, 15 minutes
- Drying: 60°C, more than 1 hour
- Etching: 20% HCl aq. 60°C, 20 minutes

(2) AIP Coating

The cleaned metal substrate of the electrode was set to the AIP unit applying Ti-Ta alloy target as a vapor source and a coating of tantalum and titanium alloy was applied as the base layer on the surface of the metal substrate of the electrode. Coating condition is shown in Table 1.

(3) Catalyst layer coating

Coating solution: Ir / Ta = 65:35, it is a hydrochloric acid water solution.

Rotary coating: 650rpm, 1 minute

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target(vapor source)</td>
</tr>
<tr>
<td>Vacuum pressure</td>
</tr>
<tr>
<td>Metal substrate temperature</td>
</tr>
<tr>
<td>Coating pressure</td>
</tr>
<tr>
<td>Vapor source charge power</td>
</tr>
<tr>
<td>Coating time</td>
</tr>
<tr>
<td>Coating thickness</td>
</tr>
</tbody>
</table>
Room temperature drying: 10 minutes
Dryer drying: 60°C, 10 minutes
Muffle furnace: 15 minutes
Cooling: Electric ian, 10 minutes
Coting times: 12 times
Post Baking: 1 hour

Manufacturing conditions of samples, degree of crystallinity, crystallite diameter, electrostatic capacity and oxygen generation overvoltage are shown in Table 2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Base</th>
<th>Top coating temperature (°C)</th>
<th>Post-baking temperature (1h) (°C)</th>
<th>Degree of crystallinity (%)</th>
<th>Crystallite diameter (nm)</th>
<th>Electrostatic capacity (C/m²)</th>
<th>Oxygen generation overvoltage (V vs. SSE @100A/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>none</td>
<td>370</td>
<td>0</td>
<td>0.0</td>
<td>37.1</td>
<td>0.891</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>520</td>
<td>78</td>
<td>7.9</td>
<td>12.1</td>
<td>1.019</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>560</td>
<td>70</td>
<td>7.3</td>
<td>8.5</td>
<td>1.044</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>600</td>
<td>67</td>
<td>7.3</td>
<td>7.4</td>
<td>1.066</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ti/AIP 530°C x 180min</td>
<td>none</td>
<td>390</td>
<td>0</td>
<td>0.0</td>
<td>35.8</td>
<td>0.888</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>520</td>
<td>75</td>
<td>6.9</td>
<td>11.3</td>
<td>1.019</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>560</td>
<td>95</td>
<td>6.8</td>
<td>9.0</td>
<td>1.030</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>600</td>
<td>77</td>
<td>8.0</td>
<td>8.5</td>
<td>1.039</td>
<td></td>
</tr>
<tr>
<td>9 (Conventional product)</td>
<td></td>
<td>520</td>
<td>none</td>
<td>100</td>
<td>10.7</td>
<td>5.4</td>
<td>1.066</td>
</tr>
</tbody>
</table>

Experimental items for evaluation
(1) Degree of crystallinity and measurement of crystallite diameter

IrO₂ crystallinity and crystallite diameter of the catalyst layer were measured by X-ray diffractometry.

The degree of crystallinity was estimated from the X-ray diffraction peak intensity.
(2) Electrostatic capacity of electrode
Method: Cyclic voltammetry
Electrolyte: 150g/L $\text{H}_2\text{SO}_4$ aq.
Electrolysis temperature: 60°C
Electrolysis area: $10 \times 10$ mm$^2$

Counter electrode: Zr plate (20 mm $\times$ 70 mm)
Reference electrode: Mercurous sulphate electrode (SSE)

(3) Measurement of oxygen overvoltage
Method: Current interrupt method
Electrolyte: 150g/L $\text{H}_2\text{SO}_4$ aq.
Electrolysis temperature: 60°C
Electrolysis area: $10 \times 10$ mm$^2$
Counter electrode: Zr plate (20 mm $\times$ 70 mm)
Reference electrode: Mercurous sulphate electrode (SSE)

(4) Lead adhesion examination evaluation
Evaluation by consecutive electrolysis in flow cells was carried out.
Electrolyte: 100g/L $\text{H}_2\text{SO}_4$ aq.
Additive: 7ppm Pb$^{2+}$ ($\text{PbCO}_3$), 150ppmSb$^{3+}$ ($\text{Sb}_2\text{O}_3$), 40ppmCo$^{2+}$ ($\text{CoSO}_4$), 10ppm gelatin
Electrolysis temperature: 60°C
Current density: 80A/dm$^2$
Electrolysis area: $20 \times 20$ mm$^2$
Cathode: Zr plate (20 $\times$ 20 mm)
Electrolysis time: 130 hours
The measurement of the adhesion amount: An anode regularly was taken out and adhesion amount was calculated by the anodic weight change.

(5) Acceleration life evaluation (sulfuric acid solution)
An electrolyte: 150g/L $\text{H}_2\text{SO}_4$ aq.
Electrolysis temperature: 60°C
Current density: 500A/dm$^2$ (in pure sulfuric acid solution)
Electrolysis area: 10 × 10mm²

The results of the above experiment are as follows.

Fig. 1 is a graph showing the degree of crystallinity based on the data in Table 2 and Fig. 2 is a graph showing crystallite diameter based on the data in Table 2. As is clear from Table 2 and Figs. 1 and 2, the degree of crystallinity of samples of iridium oxide samples 2 - 4 and 6 - 8 by examples of the present invention after being post baked was more than 60%. On the other hand, a clear peak of IrO₂ belonging to an electrode catalyst layer by baking of 370°C and 390°C without post baking (samples 1 and 5) is not found and it is confirmed that the electrode catalysts of these examples are formed composed of amorphous IrO₂. Also, sample 9 which is conventional product is completely crystalized a degree of the crystallinity of the iridium oxide is 100% and the crystallite diameter became large and was 10.7nm.

As for the estimation of degree of crystallinity, the intensity of the crystal X-ray diffraction peak (2θ=28 degrees) of each sample is expressed as a ratio when compared with the intensity of the crystal X-ray diffraction peak (2θ=28 degrees) of the conventional product which is assumed as 100%. By baking of 370°C and 390°C without post baking, IrO₂ crystal is not formed and the degree of the crystallinity of the iridium oxide was zero. It was found that an amorphous IrO₂ formed by baking on a low temperature of 370°C and 390°C were converted to crystallize almost all amount of iridium oxide by post baking, but that a small amount of an amorphous IrO₂ was remained in the catalyst layer.

The change in crystallite diameter of IrO₂ by baking conditions was as shown in Table 2. It was found that the crystallite diameter of the sample after post baking was not changed due to the increase of post-baking temperature and it became smaller, compared with conventional products. That is, amorphous IrO₂ of the
catalyst layer formed at a low temperature baking was crystallized by post-baking, but the growth of the crystallite diameter could be suppressed as compared with conventional products. In addition, Fig. 2 shows the graph that was created based on data for the crystallite diameter shown in Table 2. The amorphous IrO₂ was formed by baking at 370°C and 390°C without post-baking and the crystallite diameter was set to "0". It was also found that in case of a baking at more than 410°C without post baking, with increasing baking temperature, the crystallite diameter of IrO₂ was increased.

If subjected to post-baking, amorphous IrO₂ formed by the baking of 370°C and 390°C was found to be crystallized, but the crystallite diameter was found to be smaller, with conventional products. However, the change of the crystallite diameter of IrO₂ due to an increase of post baking temperature was not nearly recognized. As is apparent from Table 2 and Fig. 2, the crystallite size of the iridium oxide after post-baking of samples 2 - 4 and 6 - 8 according to the examples of the present invention, was 8.0nm or less. On the other hand, clear peaks of IrO₂ attributable to the electrode catalyst layer by the baking of 370°C and 390°C without post-baking (samples 1 and 5) was not observed, and it was confirmed that the catalyst layer of the sample is comprised of the amorphous IrO₂. In addition, the crystallite diameter of the iridium oxide in the sample 9 which is a conventional product is a large, it was 10.7nm.

Then, measurements were made about the change of the electrode effective surface area of the electrode catalyst layer prepared by a low temperature baking plus a high temperature post baking.

Electrostatic capacity of the electrode calculated by the cyclic voltammetry method is shown in Table 2 and Fig. 3. Consequently, it is found that electrostatic capacity of the electrode (samples 2 - 4 and 6 - 8) formed by low temperature baking plus high post baking temperature electrostatic are increased, compared with the conventional product (sample 9), that is, the electrode effective surface
area is also increased. On the other hand, Table 2 and Fig. 3 show that the
degree of crystallinity and the crystallite diameter of the iridium oxide were not
changed with the increase of the post baking temperature, but the electrode
effective surface area of the electrode was decreased with the increase of the
post baking temperature. The reason is considered that if a catalytic layer is
post-baked at a high temperature, the catalytic layer became fine.

As shown in Fig. 4 and Table 2, according to increase in the electrode effective
surface area, oxygen generation overvoltage of the electrode, it can be reduced
compared with the conventional product (sample 9) and was reduced degree
50mV up by low-temperature baking plus high temperature post-baking. The
relationship between the capacitance of the catalyst layer and the baking
conditions shown in Fig. 3, based on the data on the capacitance of Table 2.
Since IrO₂ of the catalyst layer formed by baking at 370°C and 390°C without
post-baking was amorphous, it showed a maximum the electrode effective
surface area. The product in which a baking was carried out at 370°C and 390°C
and post baking was carried out, the electrode effective surface area was reduced,
because of crystallization of IrO₂, but it was increased, compared with
conventional products. The reason is that the crystallite diameter of the deposited
IrO₂ was smaller, compared with conventional products and due to the small
amount of residual amorphous IrO2. In other words, the electrode effective
surface area of the electrode baked at 370°C and 390°C and post baked, was
increased, compared with the conventional products and it was found that it is
desirable for the goal of lowering the oxygen overvoltage.

Further, it was found that since the degree of crystallinity of IrO₂ was increased
according to increase of the baking temperature, in the baking condition at 410°C
or higher without a post baking, the electrode effective surface area is reduced.
Further even though to be subjected to post-baking, but it was found a tendency
that the electrode effective surface area is reduced further, there was no change
in the electrode effective surface area due to post-baking temperature increase. It is considered that this is because the degree of crystallinity and crystallite diameter IrO_2 does not change greatly by increasing of the post-baking temperature as described above. On the other hand, in the case of baking at 480°C, with or without post-baking, the electrode effective surface area of the electrodes was found that it was equivalent to conventional products.

The dependency of a baking condition and an oxygen generation overvoltage are shown in Table 2 and Fig. 4. The dependence of the oxygen generation overvoltage on baking conditions is shown in Fig. 4. The trend of changing in the graph of Fig. 4 was reverse to that of Fig. 3. With increase of the electrode effective surface area, the oxygen generation overvoltage of the samples tended to decrease. It was found that the oxygen generation overvoltage of the products formed by baking at 370°C and 390°C with post-baking was decreased by 30 - 50 mV, compared with conventional products. It is considered that these low oxygen generation overvoltage electrodes has a suppression effect to Pb adhesion.

Examples

The following describes examples by the present invention; provided, however, the present invention is not limited to these examples.

<Example 1>

The surface of titanium plate (JIS-I) was subjected to the dry blast with iron grit (G120 size), followed by pickling in an aqueous solution of concentrated hydrochloric acid for 10 minutes at the boiling point for cleaning treatment of the metal substrate of the electrode. The cleaned metal substrate of the electrode is set to the AIP unit applying Ti-Ta alloy target as a vapor source and a coating of tantalum and titanium alloy was applied as the AIP base layer on the surface of the metal substrate of the electrode. Coating condition is shown in Table 1.
The coated metal substrate was treated at 530°C in an electric furnace of air circulation type for 180 minutes.

Then, the coating solution prepared by dissolving iridium tetrachloride and tantalum pentachloride in concentrated hydrochloric acid is applied on the coated metal substrate. After drying, the thermolysis coating was conducted for 15 minutes in the electric furnace of air circulation type at 370°C to form an electrode catalyst layer comprising mixture oxides of iridium oxide and tantalum oxide. The amount of coating solution was determined so that the thickness of coating per time of the coating solution corresponds to approx. 1.1g/m², as iridium metal. This coating-baking operation was repeated twelve times to obtain the electrode catalyst layer of approx. 13.2g/m², as iridium metal.

The X-ray diffraction was carried out for this sample. A clear peak of iridium oxide attributable to the electrode catalyst layer was not observed, and the catalytic layer of this sample was composed of amorphous IrO₂.

Next, an electrode for electrolysis was manufactured in such a manner that the sample coated with the catalyst layer is post-baked in an electric furnace of air circulation type at 520°C for one hour.

The X-ray diffraction was carried out for the sample after post-baking. A clear peak of iridium oxide attributable to the electrode catalyst layer was observed. From this, it has been found that an amorphous IrO₂ was crystallized by a high temperature post baking. However, the intensity of the peak was smaller than that of Comparative Example 1, and it was considered that an amorphous IrO₂ was remained. Also the crystallite diameter calculated from X-ray diffraction peak was found to be smaller than that of Comparative Example 1.

About the electrode for electrolysis prepared in the above-mentioned manner, the lead adhesion test and the accelerated life evaluation test were conducted. Results are shown in Table 3. When compared with Comparative Example 1 in Table 3, the amount of lead adhesion was one-tenth and the life for electrolysis
was similar level and then it was made clear that a suppression of a lead adhesion to the electrode and a durability have been improved.

<table>
<thead>
<tr>
<th>Example</th>
<th>Baking temperature °C</th>
<th>Post-bake temperature °C</th>
<th>Accelerated life of electrolysis (hr)</th>
<th>Amount of a lead adhesion (g/m²·Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>370</td>
<td>520</td>
<td>1554</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>370</td>
<td>560</td>
<td>2685</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>370</td>
<td>600</td>
<td>2786</td>
<td>30</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>520</td>
<td>—</td>
<td>1506</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>370</td>
<td>—</td>
<td>1</td>
<td>Electrolysis impossible</td>
</tr>
</tbody>
</table>

<Example 2>

The electrode for evaluation was manufactured in the same manner as with Example 1 except that post-bake was conducted in an electric furnace of air circulation type for one hour at 560°C and the same electrolysis evaluation was performed.

The X-ray diffraction performed after post-bake showed the degree of crystallinity and crystallite diameter of IrO₂ in the catalyst layer equivalent to Example 1.

As shown in Table 3, an amount of a lead adhesion to the electrode of Example 2 is one-fourth to that of the Comparative Example 1 and a suppression effect of the lead adhesion was confirmed. In addition, the accelerated electrolysis life was increased to 80% and their durability has also have been improved.

<Example 3>

The electrode for evaluation was manufactured in the same manner as with Example 1 except that post-bake was conducted in an electric furnace of air circulation type for one hour at 560°C and the same electrolysis evaluation was performed.
circulation type for one hour at 600°C and the same electrolysis evaluation was performed.

The X-ray diffraction performed after post-bake showed the degree of crystallinity and crystallite diameter of IrO$_2$ in the catalyst layer equivalent to Example 1.

As a result of an electrolysis evaluation, as shown in Table 3, an amount of a lead adhesion and an electrolysis life was equivalent to Example 2 and a suppression effect of the lead adhesion was confirmed.

**<Comparative Example 1>**

The coating solution similar to Example 1 is coated on the tantalum and titanium alloy base coating layer and the heat-treated metal substrate similar to Example 1, and after drying, the thermal decomposition is performed at the baking temperature in the electric furnace of circulation air type to 520°C and the baking time to fifteen minutes and then an electrode catalyst layer comprising a mixture oxide of iridium oxide and tantalum oxide is formed. The repeating time and an amount of coating were performed similar to Example 1. The electrode thus manufactured without post-bake was subjected to electrolysis evaluation and the X-ray diffraction as with Example 1.

The X-ray diffraction was performed on this sample, from which a clear peak of iridium oxide attributable to the electrode catalyst layer was observed, verifying that IrO$_2$ in the catalyst layer is crystalline.

From a result of a lead adhesion test as similar to the Example 1, an amount of a lead adhesion was 120g/m$^2$. From this result, it was made clear that a suppression effect of the lead adhesion by the method of the present invention was largely improved.

**Comparative Example 2>**

In the same manner as with Example 1 except that post-bake was not carried
out, the electrode for evaluation was manufactured and electrolysis evaluation was carried out in the same manner with Example 1.

As shown in Table 3, an electrolysis life of the electrode baked at 370°C without post baking was found to be only 1 hour, and from the results of this, it was made clear that the electrolysis durability of a catalyst layer of amorphous IrO₂ was extremely low.

As shown in the above experimental results, by the present invention, the crystallite diameter of IrO₂ in the catalyst layer is small, the electrode surface area increased and an oxygen generation overvoltage decreased, compared with the conventional product, by means of a baking in a relatively low temperature region of 370°C - 400°C and a post baking in a further high temperature region of 520°C - 600°C. Accordingly, by promoting the oxygen generation reaction, a suppression effect of a lead adhesion were performed simultaneously. Furthermore, since iridium oxides of the catalyst layer mainly exist as a crystalline, a durability of the electrode was performed.

**Industrial Applicability**

The present invention relates to an anode for oxygen generation used for various industrial electrolyses and a manufacturing method for the same; more in detail, it is applicable to an anode for oxygen generation used for industrial electrolyses including manufacturing of electrolytic metal foils such as electrolytic copper foil, aluminum liquid contact, continuously electrogalvanized steel plate and metal extraction.
CLAIMS

[Claim 1]
An anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the coating layer is baked in a low temperature region of 370°C - 400°C in an oxidation atmosphere to form the catalyst layer containing amorphous iridium oxide and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize almost all amount of iridium oxide in the catalyst layer.

[Claim 2]
The anode for oxygen generation as in Claim 1, comprising the conductive metal substrate and the catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the degree of crystallinity of iridium oxide in the catalyst layer after the post-bake is made to be 60% or more.

[Claim 3]
The anode for oxygen generation, as in Claim 1 or 2, comprising the conductive metal substrate and the catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the crystallite diameter of iridium oxide in the catalyst layer after the post-baking is made to be 8.0nm or less.

[Claim 4]
The anode for oxygen generation, as in any one of Claims 1-3, comprising the conductive metal substrate and the catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein an arc ion plating base layer containing tantalum and titanium ingredients is formed by the arc ion plating process on the conductive metal substrate before the formation of the catalyst.
layer.

[Claim 5]
A manufacturing method for an anode for oxygen generation comprising a conductive metal substrate and a catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the catalyst layer containing amorphous iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to crystallize almost all amount of iridium oxide in the catalyst layer.

[Claim 6]
The manufacturing method for the anode for oxygen generation, as in Claim 5, wherein the catalyst layer containing amorphous iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to make the degree of crystallinity of iridium oxide in the catalyst layer to be 60% or more.

[Claim 7]
The manufacturing method for the anode for oxygen generation, as in Claim 5 or 6, wherein the catalyst layer containing amorphous iridium oxide is formed on the surface of the conductive metal substrate by baking in a low temperature region of 370°C - 400°C in an oxidation atmosphere and the catalyst layer containing amorphous iridium oxide is post-baked in a further high temperature region of 520°C - 600°C in an oxidation atmosphere to make the crystallite diameter of iridium oxide in the catalyst layer to be 8.0 nm or less.
[Claim 8]

The manufacturing method for the anode for oxygen generation, as in any one of Claims 5-7, comprising the conductive metal substrate and the catalyst layer containing iridium oxide formed on the conductive metal substrate, wherein the arc ion plating base layer containing tantalum and titanium ingredients is formed by the arc ion plating process on the conductive metal substrate before the formation of the catalyst layer.