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(54) ANODE FOR OXYGEN GENERATION

(57) In an insoluble anode for use in an electrolysis step accompanied by oxygen generation, by making the anode exert sufficient durability even in electrolysis accompanied by cathodic polarization besides anodic polarization, a service life of an electrode is prolonged and works of electrode repair, replacement, and the like are reduced. In order to realize this, an active material supporting member made of a porous metal sheet such as an expanded metal, a punching metal, or a bamboo blind-

like or net-shaped metal is bonded to a conductive metal as an electrode structure, to configure an electrode substrate. The electrode substrate is coated, on the side to which the supporting member is bonded, with an electrode active material consisting mainly of iridium oxide. Thus, the anode for oxygen generation, which is highly resistant to a cathodization phenomenon, is obtained.

Description

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TECHNICAL FIELD

[0001] The present invention relates to an anode for oxygen generation which is used as an insoluble anode for an electrolysis step accompanied by oxygen generation, electroplating with mainly zinc, tin or copper or a surface treatment of stainless steel, or electrowinning of a metal.

BACKGROUND ART

[0002] Conventionally, lead or a lead-based alloy has been used for electroplating of a steel plate with zinc, tin, or the like, but there have been problems such as contamination of a plating solution due to eluted lead and degradation of a film quality. As an anode substituting for such an electrode, there have been proposed various insoluble anodes in which an electrode active layer containing a platinum group metal or an oxide thereof, for example, iridium oxide, as an electrode active material is formed on an electrode substrate. However, an electrode of this type is intended for use as an anode, and in electrolysis accompanied by cathodic polarization besides anodic polarization, there is a defect that an electrode life is significantly shortened compared with electrolysis accompanied only by anodic polarization.

[0003] Usually, in electroplating of a steel plate, two pieces of anodes are placed opposite to each other in order to plate both surfaces of a steel plate, and the width (size in a direction perpendicular to the traveling direction of a steel strip) of the two pieces of anodes placed opposite to each other is set to a maximum width of the steel strip since the steel strips passing therebetween have various widths. Therefore, when a steel strip with a smaller width than the maximum width passes through (a part through which the steel strip passes is referred to a plate path), electrodes will directly face each other at the side edge parts on both sides of the anodes. When the thickness of metal plating is different between both surfaces of a steel plate, a difference in the potential to the steel plate occurs between the two pieces of anodes. It has been found that a part outside the plate path of an electrode of a lower potential side acts as a cathode (a cathodization phenomenon of an anode). In the side edge parts of the anode suffering from this cathodization phenomenon, consumption of the electrode active material proceeds rapidly compared with the central part always facing a steel strip, and this rapid consumption of the electrode active material in the side edge part dominates the life of the whole anode.

[0004] In order to prolong the life of an electrode of this type as a cathode, Patent Document 1 proposes an electrode in which two intermediate layers of a platinum layer and an oxide layer are provided between a conductive electrode substrate and an electrode active material layer. This electrode is recognized to have an effect of prolonging the life of a cathode, but the adhesion between the platinum layer and the oxide layer is inherently poor. Therefore, this electrode has not achieved a state in which the life of a plate path part of an anode is equal to that of a part outside the plate path in electroplating of a steel plate.

[0005] As another countermeasure, Patent Document 2 proposes an electrode in which a coating layer of tantalum oxide containing platinum metal is disposed on a conductive electrode substrate, a coating layer made from iridium oxide and tantalum oxide is disposed thereon as an intermediate layer, and further an overcoat layer made from platinum and iridium oxide is disposed on the intermediate layer. By disposing the overcoat layer, there is an improvement in durability, but significant consumption inherent in platinum in the case where the electrode acts as an anode cannot be suppressed, and durability in the case where the electrode acts as a cathode intermittently is insufficient.

[0006] Because of these circumstances, it has been an important technical object in an insoluble anode to effectively suppress the consumption of an electrode active material associated with a cathodization phenomenon of an anode, and one of means to achieve this the technical object is to thicken the electrode active material layer at a part where the cathodization phenomenon occurs than that at other parts (Patent Document 3). An increase in the thickness of the electrode active material layer is effective, but this increase in the layer thickness involves a large increase in cost. That is, the electrode active material layer is formed in a predetermined thickness by repeating the so-called baking finishing of applying an electrode coating solution, drying and firing the solution. In order to increase the layer thickness, it is necessary to increase the number of repetition of baking finishing operations, and not only the usage of an expensive electrode active material, but also man-hour of works significantly increase.

[0007] From the viewpoint that the very fast consumption of the electrode active material at the time of cathodic polarization results from selective dissolution of a valve metal oxide added as a binder, for example, tantalum oxide, there is proposed a method of preventing the dissolution at the time of cathodic polarization by improving the crystallinity of tantalum oxide or another valve metal oxide as a binder to make the tantalum oxide more robust by changing a heating temperature at the time of forming an electrode active material layer from 650°C to 850°C (Patent Document 4). However, when a valve metal, for example, titanium, is exposed to an elevated temperature of 650°C or higher for a long time in the air, the titanium substrate is oxidized and the electrode becomes unusable.

[0008] As another countermeasure, Patent Document 5 proposes a method in which an electrode active material layer

is formed on an electrode substrate in which fine titanium particles are bonded to a titanium plate by sintering them in a vacuum or an inert atmosphere as an electrode to stand cathodic polarization, but this method needs strict temperature control at elevated temperatures and atmosphere control for sintering, and production cost of a sintered substrate is very high.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

10 [0009]

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Patent Document 1: Japanese Patent Laid-open Publication No. 5-230682
Patent Document 2: Japanese Patent Laid-open Publication No. 11-302892
Patent Document 3: Japanese Patent Laid-open Publication No. 10-287998
Patent Document 4: Japanese Patent Laid-open Publication No. 2002-275697
Patent Document 5: Japanese Patent Laid-open Publication No. 2006-188742

DISCLOSURE OF THE INVENTION

20 PROBLEMS TO BE SOLVED BY THE INVENTION

[0010] It is an object of the present invention to provide an anode for oxygen generation which has sufficient durability even in electrolysis accompanied by cathodic polarization besides anodic polarization, thereby prolonging the service life of an electrode, reducing loads of works of electrode repair, replacement, and the like, and reducing production cost of the anode for oxygen generation.

SOLUTIONS TO THE PROBLEMS

[0011] Here, when an insoluble anode is used in electrolysis accompanied only by anodic polarization, the electrode develops symptoms that iridium oxide as an electrode active material is gradually consumed and the consumption of iridium oxide becomes severe in the late stage of the electrode life. The life of the electrode in this case is determined by an embrittlement rate of an electrode active layer rather than the consumption of the electrode active material. On the other hand, it was found that when the insoluble anode is used in electrolysis accompanied by cathodic polarization besides anodic polarization, the consumption of the electrode active material is very fast compared with electrolysis accompanied only by anodic polarization, and the electrode reaches the end of its life before the electrode active layer becomes brittle.

[0012] Based on such a fact, the present inventors made earnest investigations concerning a method of suppressing the consumption of the electrode active material in the case of using the insoluble anode in electrolysis accompanied by cathodic polarization. Consequently, it was found that, from the viewpoint of an electrode structure, it is effective for prolonging a life of a part where cathodic polarization occurs to use an electrode substrate formed by bonding a porous metal sheet such as an expanded metal or a punching metal as a physical supporting member of an electrode active material on a conductive metal as an electrode structure.

[0013] More specifically, when the insoluble anode is used in electrolysis accompanied only by anodic polarization, the porous metal sheet on the conductive metal as an electrode structure does not have any effect on an anode life. That is, the porous metal sheet does not contribute to the prolongation of a life of the electrode active material and does not function as a physical supporting member. However, when the insoluble anode is used in electrolysis accompanied by cathodic polarization, the porous metal sheet contributes to the prolongation of the anode life. This fact means that when the insoluble anode is used in electrolysis accompanied by cathodic polarization, the porous metal sheet contributes to the prolongation of the life of the electrode active material, and functions as a physical supporting member or a support accelerating member.

[0014] The anode for oxygen generation of the present invention has been completed based on such findings, and is an anode for oxygen generation exhibiting resistance to a cathodization phenomenon, formed by coating a surface of an electrode substrate with an electrode active material, wherein the electrode substrate is configured by bonding an active material supporting member made of a porous metal sheet or an active material support accelerating member to a surface of a conductive metal as an electrode structure, and the electrode substrate is coated, on the side to which the supporting member is bonded, with an electrode active material predominantly composed of iridium oxide.

[0015] Since the consumption rate of the electrode active material increases if the cathodization phenomenon occurs, conventionally there is a method in which a thickness of the electrode active material layer is increased, or strength of

a binder to be added to the active material is increased by elevating the sintering temperature. However, in the anode for oxygen generation of the present invention, resistance to the cathodization phenomenon is improved by adopting a mechanism of physically supporting the electrode active material, which is different from conventional methods. As described above, the mechanism is found to be inherent in electrolysis accompanied by cathodic polarization, but details of active material supporting are unclear. With respect to this point, the present inventors think that as follows. For example, in an electrode substrate formed by bonding an expanded metal to a plate-shaped conductive metal, since a catalyst coating solution is unevenly distributed in a gap at a bonding portion or an intersecting part of the expanded metal, the thickness of the electrode active material layer is partially increased, and therefore this electrode substrate is more resistant to cathodization than a plate-shaped electrode substrate to which a catalyst coating solution is uniformly applied, and this contributes to the prolongation of the anode life in electrolysis accompanied by cathodic polarization.

[0016] Examples of the porous metal sheet bonded to a surface of a conductive metal as an electrode structure include an expanded metal, a punching metal, and a bamboo blind-like or net-shaped metal, and the expanded metal and the punching metal are particularly preferable from the viewpoint of the ability to bond to a surface of a conductive metal, availability and mechanical strength.

[0017] As the materials of a conductive metal constituting the electrode substrate and the porous metal sheet bonded thereto, valve metals, for example, titanium, tantalum, niobium, tungsten, and zirconium are preferable, and further titanium alloys such as titanium-tantalum, titanium-tantalum-niobium, and titanium-palladium, and titanium coated with tantalum are preferable, and the surface of a metal substrate may be oxidized, nitrided, borided, or carbonized. The shape of the conductive metal as an electrode structure may be a desired shape such as a flat plate-shape, a net-shape, a rod-shape or a porous sheet-shape, but a flat plate-shape and a porous sheet-shape are particularly preferable.

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[0018] The thickness of the porous metal sheet is desirably 0.2 mm or more and 4.0 mm or less. When the thickness of the porous metal sheet is too small, there is a problem of a property of supporting an electrode active material. On the contrary, even when the thickness of the porous metal sheet is increased, the effect is small and it is just economically disadvantageous.

[0019] In the porous metal sheet, a thickness as well as an opening ratio are important. This opening ratio, that is, a ratio of an opening area to the whole area, is preferably 5 to 85%, and particularly preferably 30 to 50%. When the opening ratio is too small, an ability of supporting an electrode active material, and hence the effect of prolonging an anode life is deteriorated. Similarly, when the opening ratio is too large, an ability of supporting an electrode active material, and hence the effect of prolonging an anode life is deteriorated. In addition to this, there is a problem of workability of bonding to the conductive metal as an electrode structure. Specifications by the type of the porous metal sheet are as follows.

[0020] With respect to dimensions of an expanded metal, LW (center-to-center distance in a longer direction of a mesh) and thickness are important, and LW: 4 to 40 mm and thickness: 0.5 to 4.0 mm are preferable, and LW: 8 to 20 mm and thickness: 1.0 to 2.5 mm are more preferable. Openings in the punching metal may have a staggered arrangement of 45°, 60°, or 90°, a ratio of the opening area to the whole area is preferably 5 to 85%, and a hole diameter of the opening is preferably 1.5 to 25 mm, and particularly preferably 2 to 10 mm.

[0021] As a method of bonding an expanded metal, a punching metal, or a bamboo blind-like or net-shaped metal as a porous metal sheet to a conductive metal, welding, securing by screws, or the like is used. When a large current density is applied, a welding method such as spot welding or TIG welding is preferable. Two or more pieces of the expanded metals, the punching metals, or the bamboo blind-like or net-shaped metals may be bonded to the surface of the conductive metal. Further, two or more types of metals having different shapes may be bonded to the conductive metal. [0022] The porous metal sheet which is a supporting member of an electrode active material has been described above. Next, the electrode active material will be described. The present inventors made earnest investigations concerning a method of suppressing the consumption of the electrode active material in the case of using the insoluble anode in electrolysis accompanied by cathodic polarization, and consequently, found from the viewpoint of an electrode active material that as for an oxygen generating catalyst as a main material, an oxide of a platinum group metal, particularly iridium oxide, is desired, and as for a binder added to the main material, it is effective from the viewpoint of giving priority to suppression of the consumption over the prevention of the embrittlement to reduce the amount of a valve metal oxide, e.g., tantalum oxide to increase the relative amount of iridium oxide as a main material.

[0023] Based on such findings, as an electrode active material with which the electrode substrate is coated, a main material being an oxygen generating catalyst is used as a main component, and a mixture obtained by adding a binder to the main material is used. More specifically, iridium oxide superior in the ability as an oxygen generating catalyst is used as a main material. As the binder, one or more metal oxides selected from the group consisting of valve metals such as titanium, tantalum, niobium, tungsten, and zirconium; and tin are suitable. Typical examples of the electrode active material include a mixture of iridium oxide and tantalum oxide, a mixture of iridium oxide, and titanium oxide, and a mixture of iridium oxide, tantalum oxide, and niobium oxide.

[0024] With respect to the specific composition of the electrode active material, from the viewpoint of giving priority to suppression of the consumption over the prevention of the embrittlement, the content of the binder is reduced and the

content of the oxygen generating catalyst as a main material is increased. Specifically, a mixture of metal oxides, which contains iridium in an amount of 50 to 95 wt% on the metal equivalent basis, and contains one or more valve metals in an amount of 50 to 5 wt% on the metal equivalent basis, is preferable. A more preferable electrode active material is a mixture of metal oxides in which one valve metal is tantalum, and which contains iridium in an amount of twice or more the amount (wt%) of tantalum on the metal equivalent basis. A particularly preferable electrode active material is a mixture of iridium oxide and tantalum oxide, which contains iridium in an amount of 70 wt% or more on the metal equivalent basis and tantalum as the rest.

[0025] When the content of iridium oxide in the electrode active material is small, there is a disadvantage that the ability of an electrode active layer to generate oxygen is insufficient and the electrode active layer becomes porous. Further, the content of the binder is relatively increased and resistance to a cathodization phenomenon is deteriorated. On the contrary, when the content of iridium oxide in the electrode active material is excessive, the content of the binder is relatively decreased and detachment of the electrode active material caused by the reduction and reduction in performance caused by the detachment become remarkable.

[0026] As a method of coating the electrode substrate with an electrode active material, the conventionally used thermal decomposition method, powder sintering method and the like can be applied, and the thermal decomposition method is preferable. That is, solutions of these metal salts are applied, dried, and fired at a temperature of 410 to 550°C in the air. Operations of application, drying and firing are performed from several times to several tens of times to form a required amount of an electrode active layer.

20 ADVANTAGES OF THE INVENTION

[0027] By configuring an electrode substrate by bonding, as a supporting member of an electrode active material, a porous metal sheet such as an expanded metal or a punching metal to a conductive metal as an electrode structure, and coating the electrode substrate with an electrode active material predominantly composed of a platinum group metal, particularly iridium, the anode for oxygen generation of the present invention can effectively solve the problem that a life of a part outside the plate path of an anode is shorter than that of a central part always facing a steel plate due to a cathodization phenomenon when zinc metal or the like is plated in different amounts of coatings on both sides of a steel plate for various widths of plates. Further, since it is not necessary to particularly increase a coating amount of an electrode active material or to elevate a firing temperature at the time of forming an electrode active material layer, the production cost can be kept low.

[0028] Accordingly, the anode for oxygen generation of the present invention is particularly suitable for use in an insoluble anode for electroplating suffering from a cathodization phenomenon, or for use in a part of the insoluble anode for electroplating where the cathodization phenomenon occurs.

35 EMBODIMENT OF THE INVENTION

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[0029] Hereinafter, an embodiment of the present invention will be described.

[0030] An active material supporting member made of a porous metal sheet is bonded to one side or both sides being working surface(s) of a flat plate-shaped conductive metal as an electrode structure to configure an electrode substrate. The active material supporting member is a member for physically supporting an electrode active material on the surface of the electrode substrate as an electrode structure, and more precisely, in electrolysis accompanied by cathodic polarization, a member for physically supporting the electrode active material on the surface of the electrode substrate and thereby contributes to the prolongation of the anode life. The porous metal sheet is specifically composed of an expanded metal, a punching metal, or a bamboo blind-like or net-shaped metal, and bonded to the surface of the conductive metal by welding or the like. A material of the sheet is a valve metal, and titanium is preferable in view of price and performance. [0031] When the electrode substrate is prepared, the electrode substrate is coated, on the side to which the active material supporting member has been bonded, with an electrode active material. The electrode active material is a mixture of an oxygen generating catalyst being a main material and a binder, and specifically a mixture of oxides predominantly composed of iridium of an oxygen generating catalyst. The content of iridium is specifically 50 wt% or more, and preferably 70 wt% or more on the metal equivalent basis. A metal component of the binder is a valve metal and tantalum is preferable. A metal is coated with an electrode active material by a conventional method.

[0032] The produced anode for oxygen generation is used in an insoluble anode in an electroplating line of a steel strip, particularly an insoluble anode suffering from a cathodization phenomenon in the side edge part of the anode, or used in the side edge part of the insoluble anode where the cathodization phenomenon occurs. The durability of the anode for oxygen generation against a cathodization phenomenon is outstandingly excellent compared with conventional insoluble anodes not having an active material supporting member.

EXAMPLES

[0033] Next, the present invention will be described in more detail by way of examples and a comparative example.

5 Example 1

[0034] An expanded metal made of titanium (a square plate with a size of 30 mm \times 30 mm, LW: 8.0 mm, SW (center-to-center distance in a shorter direction of a mesh): 3.6 mm, thickness: 1.2 mm) as a porous metal sheet for an active material supporting member was bonded to an electrode structure made of a titanium flat plate with a size of 30 mm \times 30 mm \times 10 mm by a spot welding method to form a titanium substrate material. A titanium round bar of 8 mm in diameter was welded perpendicularly to the center of a backside of the titanium substrate material to prepare a feed lead for energization. This was degreased by ultrasonic cleaning in acetone, and then a surface of the expanded metal was blasted at a pressure of 0.6 MPa for about 10 minutes using No. 24 Alundum. The blasted titanium substrate material was washed in flowing water all night and all day, and dried to be used as an electrode substrate.

[0035] An electrode active material coating solution having the following liquid composition was prepared, and applied onto the surface of the prepared electrode substrate, to which an expanded metal has been bonded. After the application, the coating solution was dried at 100°C for 10 minutes, and then fired in an electric furnace maintained at 450°C for 20 minutes. The coating operation (application, drying, and firing) of the electrode active material was repeated ten times to prepare an anode for oxygen generation having iridium oxide on the surface of the electrode substrate as an electrode active material. A weight compositional ratio of metals in the electrode active material coating layer was Ir/Ta = 7/3, and the content of iridium was 70 wt%, which was twice or more the content (30 wt%) of tantalum. An amount of iridium metal was 30 g/m².

[0036]

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 $TaCl_5$: 3.2 g $H_2IrCl_6.6H_2O$: 10.0g 35% HCI: 10 mI n-CHs(CH₂)sOH: 100 mI

[0037] This anode for oxygen generation, which was sealed leaving a surface (30 mm \times 30 mm) of the electrode active material coating layer formed, was used as an anode for a polarity reversal life test.

[0038] In an electrolysis bath used for the polarity reversal life test, a 100 g/l aqueous solution of Na₂SO₄ having a pH of 1.2 (pH was adjusted with sulfuric acid) was used, and the temperature and velocity of flow were set at 60°C and 2 m/sec, respectively. Further, a platinum plate was used as an opposite electrode. As an electrolysis method, a combination of normal-reversal energization, in which normal energization (anodic polarization) at a current density of 100 A/dm² for 10 minutes and reverse energization (cathodic polarization) at a current density of 30 A/dm² for 10 minutes was repeated, and a time point at which a tank voltage at the time of normal energization reached a point higher than the starting voltage by 5 V was taken as an electrode life. By the polarity reversal electrode life acceleration test, electrode durability against the cathodization phenomenon is evaluated. The test results are shown in Table 1.

Example 2

[0039] An anode for oxygen generation was prepared in the same manner as in Example 1 except for changing the composition of the electrode active material coating solution to the following composition. A weight compositional ratio of metals in the electrode active material coating layer was Ir/Ta/Nb = 6.3/2.6/1.1, and the content of iridium was 63 wt%, which was twice or more the content (26 wt%) of tantalum. An amount of iridium metal was 30 g/m². A polarity reversal electrode life acceleration test similar to Example 1 was carried out. The results of the test are shown in Table 1. [0040]

50 TaCl $_5$: 9.9 g H $_2$ lrCl $_6$ -6H $_2$ O: 32.5 g NbCl $_5$: 6.3 g 35% HCl: 15 ml n-CHs(CH $_2$) $_3$ OH: 240 ml

Example 3

[0041] A punching metal made of titanium (a square plate with a size of 30 mm \times 30 mm, opening: staggered ar-

rangement of 60° , hole diameter: 3.0 mm, center pitch of hole: 5.5 mm, thickness: 1.5 mm) as a porous metal sheet for an active material supporting member was bonded to a titanium flat plate with a size of 30 mm \times 30 mm \times 10 mm of an electrode structure by a spot welding method to form a titanium substrate material. A titanium round bar of 8 mm in diameter was welded perpendicularly to the center of a backside of the titanium substrate material to prepare a feed lead for energization. Subsequent treatments for the titanium substrate material and formation of the electrode active material coating layer were performed in the same manner as in Example 1. A weight compositional ratio of metals in the electrode active material coating layer was Ir/Ta = 7/3, and the content of iridium was 70 wt%, which was twice or more the content (30 wt%) of tantalum. An amount of iridium metal was 30 g/m². A polaity reversal electrode life acceleration test similar to Example 1 was carried out. The results of the test are shown in Table 1.

Example 4

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[0042] A titanium electrode substrate was prepared by subjecting the material to the same treatment as in Example 1 except for bonding an expanded metal made of titanium (a square plate with a size of 30 mm \times 30 mm, LW: 10.0 mm, SW: 5.0 mm, thickness: 0.5 mm) as a porous metal sheet for an active material supporting member to a titanium flat plate with a size of 30 mm \times 30 mm \times 10 mm of an electrode structure by a spot welding method. A coating layer of an electrode active material having the same composition and the same coating amount as in Example 1 was formed on the surface of the prepared electrode substrate, and then a polarity reversal electrode life acceleration test similar to Example 1 was carried out. The results of the test are shown in Table 1.

Example 5

[0043] A titanium electrode substrate was prepared by subjecting the material to the same treatment as in Example 1 except for bonding an expanded metal made of titanium (a square plate with a size of $30 \text{ mm} \times 30 \text{ mm}$, LW: 10.0 mm, SW: 5.0 mm, thickness: 1.5 mm) as a porous metal sheet for an active material supporting member to a titanium flat plate with a size of $30 \text{ mm} \times 30 \text{ mm} \times 10 \text{ mm}$ of an electrode structure by a spot welding method. A coating layer of an electrode active material having the same composition and the same coating amount as in Example 1 was formed on the surface of the prepared electrode substrate, and then a polarity reversal electrode life acceleration test similar to Example 1 was carried out. The results of the test are shown in Table 1.

Comparative Example 1

[0044] A titanium electrode substrate was prepared by subjecting the material to the same treatment as in Example 1 except for using a titanium flat plate with a size of $30 \text{ mm} \times 30 \text{ mm} \times 10 \text{ mm}$ alone as a titanium substrate material. A coating layer of an electrode active material having the same composition and the same coating amount as in Example 1 was formed on the surface of the prepared electrode substrate, and then a polarity reversal electrode life acceleration test similar to Example 1 was carried out. The results of the test are shown in Table 1.

[Table 1]

Polarity reversal, electrode life test		
	Electrode life (hour)	
Example 1	614	
Example 2	593	
Example 3	557	
Example 4	474	
Example 5	738	
Comparative Example 1	232	

[0046] The anodes for oxygen generation in Examples 1 to 5, in which an electrode substrate prepared by bonding an expanded metal or punching metal made of titanium to a titanium plate as an electrode structure is used, exhibited an extremely excellent electrode life in the polarity reversal electrode life acceleration test compared with the anode for oxygen generation using mere plate-shaped titanium as an electrode substrate.

Reference Examples 1 to 6

[0047] Anodes for oxygen generation similar to those prepared in Examples 1 to 5 and Comparative Example 1 were prepared, and an electrode life acceleration test was carried out on each of these anodes. The cases are respectively designated as Reference Examples 1 to 6.

[0048] In an electrolysis bath used for the electrode life acceleration test, a 100 g/l aqueous solution of Na_2SO_4 having a pH of 1.4 (pH was adjusted with sulfuric acid) was used, and the temperature and velocity of flow were set at 70°C and 2 m/sec, respectively. Further, a zirconium plate was used as an opposite electrode. As an electrolysis method, continuous normal energization (anodic polarization) was carried out at a current density of 200 A/dm², and a time point at which a tank voltage reached a point higher than the starting voltage by 5 V was taken as an electrode life. The results are shown in Table 2.

[0049]

[Table 2]

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Continuous normal energization, electrode life test Electrode life (hour) Note Reference Example 1 843 Electrode in Example 1 Reference Example 2 791 Electrode in Example 2 Reference Example 3 824 Electrode in Example 3 Reference Example 4 763 Electrode in Example 4 Reference Example 5 859 Electrode in Example 5 Reference Example 6 732 Electrode in Comparative Example 1

[0050] As is apparent from Reference Examples 1 to 6, when the acceleration test accompanied only by anodic polarization was conducted under continuous normal energization, there was no large difference in electrode life between the anodes for oxygen generation in Examples 1 to 5 and the anode for oxygen generation in Comparative Example 1. As is evident from this result, the active material supporting members in the anodes for oxygen generation in Examples 1 to 5 exert an effect on an improvement of electrode durability in electrolysis accompanied by cathodic polarization in cooperation with an electrode active material predominantly composed of iridium.

Claims

- 1. An anode for oxygen generation exhibiting resistance to a cathodization phenomenon, formed by coating a surface of an electrode substrate with an electrode active material, wherein the electrode substrate is configured by bonding an active material supporting member made of a porous metal sheet to a surface of a conductive metal as an electrode structure, and the electrode substrate is coated, on the side to which the supporting member is bonded, with an electrode active material predominantly composed of iridium oxide.
- 2. The anode for oxygen generation according to claim 1, wherein the porous metal sheet is an expanded metal, a punching metal, or a bamboo blind-like or net-shaped metal.
- 3. The anode for oxygen generation according to claim 1 or 2, wherein the electrode active material is a mixture of metal oxides containing iridium in an amount of 50 to 95 wt% on the metal equivalent basis, and containing one or more valve metals in an amount of 50 to 5 wt% on the metal equivalent basis.

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- **4.** The anode for oxygen generation according to claim 3, wherein one valve metal is tantalum, and the content (wt%) of iridium on the metal equivalent basis is twice or more the content (wt%) of tantalum.
- 5. The anode for oxygen generation according to claim 4, wherein the content of iridium oxide in the electrode active material is 70 wt% or more on the metal equivalent basis and the rest of the metal oxides is tantalum oxide.
 - **6.** The anode for oxygen generation according to any one of claims 1 to 5, used as an insoluble anode for electroplating in which a cathodization phenomenon occurs.

	7.	The anode for oxygen generation according to any one of claims 1 to 5, used in a part causing the cathodization phenomenon of the insoluble anode for electroplating.
5	8.	The anode for oxygen generation according to any one of claims 1 to 7, wherein the conductive metal and the porous metal sheet are made of a valve metal.
	9.	The anode for oxygen generation according to claim 8, wherein the valve metal is a metal selected from titanium, tantalum, niobium, tungsten, and zirconium.
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INTERNATIONAL SEARCH REPORT International application No. PCT/JP2010/057562 A. CLASSIFICATION OF SUBJECT MATTER C25D17/12(2006.01)i, C25B11/03(2006.01)i, C25C7/02(2006.01)i, C25D17/10 (2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C25D17/12, C25B11/03, C25C7/02, C25D17/10 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuvo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2010 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DOCUMENTS CONSIDERED TO BE RELEVANT Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Χ JP 59-200781 A (Ishifuku Metal Industry Co., 1,6-7 Ltd.), 14 November 1984 (14.11.1984), page 1, lower left column, line 1 to lower right column, line 13; page 3, upper right column, line 19 to lower right column, line 19 (Family: none) JP 2006-188742 A (Daiso Co., Ltd.), Χ 1,6-9 20 July 2006 (20.07.2006), claims; paragraphs [0015] to [0045] & US 2009/0272646 A & EP 1857573 A1 & WO 2006/073163 A1 X Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 04 June, 2010 (04.06.10) 15 June, 2010 (15.06.10)

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