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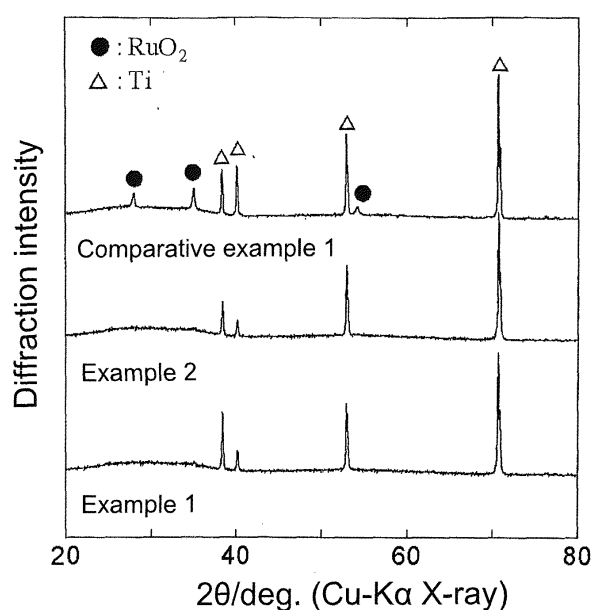
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(54) **ANODE FOR ELECTROWINNING AND ELECTROWINNING METHOD USING SAME**

(57) Provided is an anode for electrowinning in a sulfuric acid based electrolytic solution. The anode produces oxygen at a lower potential than a lead electrode, lead alloy electrode, and coated titanium electrode, thereby enabling electrowinning to be performed at a reduced electrolytic voltage and the electric power consumption

rate of a desired metal to be reduced. The anode is also available as an anode for electrowinning various types of metals in volume with efficiency. The anode is employed for electrowinning in a sulfuric acid based electrolytic solution and adopted such that a catalyst layer containing amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate.

FIG. 1



Description

Technical Field

5 **[0001]** The present invention relates to an anode employed for electrowinning a desired metal by electrolysis and to a method for electrowinning using the same. More particularly, the present invention relates to an anode employed for electrowinning in a sulfuric acid based electrolytic solution with oxygen produced by anode reaction and to a method for electrowinning using the same.

10 Background Art

[0002] Electrowinning of a metal is performed by submerging and energizing an anode and a cathode in an aqueous solution (hereafter referred to as the electrolytic solution) which contains ions of a metal to be extracted, thereby allowing the metal to be deposited on the cathode. Examples of typical electrowinning may include a method for electrowinning a metal by electrolysis in an electrolytic solution. In this case, to prepare an electrolytic solution, an ore is first crushed which contains any one or more of copper, zinc, nickel, cobalt, lead, platinum family metals (such as platinum, iridium, ruthenium, or palladium), precious metals (silver or gold), other transition metal elements, and metal elements collectively called rare metal or critical metal, etc. Subsequently, for example, metal ions are dissolved in an adequate acid, etc., and a target metal ion is then extracted, thereby preparing the electrolytic solution. Furthermore, in the electrowinning, metals may also be reproduced and extracted by electrolysis in an electrolytic solution containing target metal ions. In this case, the electrolytic solution is prepared by crushing used metal or alloy and allowing metal ions to be dissolved therein, etc. This may be performed to recycle metal or alloy used in various applications, e.g., for primary batteries, secondary batteries, fuel cells, mobile devices such as cellular phones, other electronic devices, electrical and electronic components, plated steel plates, or plated ornaments. Furthermore, in the electrowinning, metal ions may be extracted from a plating liquid waste so as to prepare an electrolytic solution containing target metal ions, etc., so that a metal is extracted by electrolysis in the electrolytic solution. Focusing on a component other than metal ions in an electrolytic solution employed for electrowinning, electrolytic solutions may include a sulfuric acid based electrolytic solution with an electrolyte component mainly composed of sulfuric acid, a chloride based electrolytic solution with an electrolyte component mainly composed of hydrochloric acid or chloride, and in addition to these solutions, various types of electrolytic solutions based on an aqueous solution with pH adjusted to acidic or basic.

[0003] The energy consumed in electrowinning is the product of electrolytic voltage and the amount of electricity used for energization, so that the amount of metal obtained on the cathode is proportional to the amount of electricity. Thus, the amount of consumed electric energy required for electrowinning a metal per unit weight of the metal to be extracted (hereafter referred to as the electric power consumption rate) decreases with decreasing electrolytic voltages. This electrolytic voltage is the potential difference between the anode and the cathode, and the cathode reaction may differ depending on the metal obtained on the cathode, so that the potential of the cathode may differ depending on the type of the reaction. On the other hand, when illustrated by the type of the electrolytic solutions mentioned above, the anode reaction is the occurrence of oxygen for the sulfuric acid based electrolytic solution and the occurrence of chlorine for the chloride based electrolytic solution. For example, in the electrowinning which is currently commercially available, the sulfuric acid based electrolytic solution is used for electrowinning a metal such as copper, zinc, nickel, or cobalt. When the sulfuric acid based electrolytic solution is used, the potential of the anode when oxygen occurs varies depending on the material of the anode. For example, a comparison between materials with a high and low catalytic activity for the occurrence of oxygen shows that the higher the catalytic activity of the material, the lower the potential of the anode. Thus, to reduce the electric power consumption rate for electrowinning in the same electrolytic solution, it is critical and necessary to employ a material of a high catalytic activity for the anode so as to reduce the potential of the anode.

[0004] Furthermore, the anode for electrowinning in the sulfuric acid based electrolytic solution is required not only to have a high catalytic activity for the occurrence of oxygen but also to have a low catalytic activity, contrary to the case of the occurrence of oxygen, for a reaction that possibly occurs on the anode (hereafter referred to as the side reaction) other than the occurrence of oxygen. For example, in the electrowinning of zinc, copper, cobalt, or nickel, etc., the electrolytic solution may contain metal ions other than an essential component therein such as zinc ions, copper ions, cobalt ions, or nickel ions. Such metal ions known include, e.g., manganese ions and lead ions. In the electrowinning in electrolytic solution containing manganese ions or lead ions, oxidation of plus divalent manganese ions occurs so as to deposit, on the anode, a manganese compound such as manganese oxyhydroxide (MnOOH) or manganese dioxide (MnO_2), or oxidation of plus divalent lead ions occurs so as to deposit lead dioxide (PbO_2) on the anode. These reactions occur on the anode at the same time as the occurrence of oxygen as the anode reaction in the sulfuric acid based electrolytic solution. However, the manganese compound or the lead dioxide have a low catalytic activity for the occurrence of oxygen and a lower electrical conductivity, thus inhibiting the reaction for the occurrence of oxygen on the anode. This will lead to an increase in the potential of the anode, causing the electrolytic voltage to be increased.

Furthermore, for example, suppose that not metal ions to be extracted by the electrowinning but cobalt ions as an additive component to the electrolytic solution are added to the electrolytic solution. In this case, not only does oxygen occur on the anode but also oxidation of plus divalent cobalt ions occur as the side reaction, causing cobalt oxyhydroxide (CoOOH) produced thereby to be deposited on the anode. This in turn causes an increase in the electrolytic voltage in the same manner as the aforementioned deposition of the manganese compound or the lead dioxide on the anode. The aforementioned deposition and accumulation of metal oxide or metal oxyhydroxide on the anode by the side reaction cause an increase in the electrolytic voltage and at the same time, degradation in service life and durability of the anode.

[0005] For the aforementioned reasons, the anode for electrowinning in the sulfuric acid based electrolytic solution is required to be made of a material which is adopted to have the following features:

- 1) A high catalytic activity for the occurrence of oxygen;
- 2) A low catalytic activity for a side reaction of depositing metal oxide or metal oxyhydroxide on the anode and for a side reaction of allowing a deposit to be adhered or accumulated on the anode even when no metal component is contained;
- 3) Thus, a high selectivity for the occurrence of oxygen;
- 4) As a result, the anode is at a low potential, in other words, the overvoltage for the anode reaction is low, and no increase in the anode potential is caused by the effects of a side reaction even when the electrowinning is continued;
- 5) Thus, the electrolytic voltage is low and the low electrolytic voltage is maintained even when the electrowinning is continued, thereby reducing the electric power consumption rate for electrowinning a target metal;
- 6) At the same time, no degradation in the service life and durability of the anode is caused by the effects of a side reaction; and
- 7) A high durability for the occurrence of oxygen.

[0006] On the other hand, typical anodes to be used as the anode for electrowinning in the sulfuric acid based electrolytic solution may include a lead electrode, a lead alloy electrode, or an electrode (hereafter referred to as the coated titanium electrode) for which a titanium substrate is coated with a catalytic layer of a platinum family metal or a platinum family metal oxide or a mixture or a composite oxide of these metals or oxides, etc. A specific example of the coated titanium electrode is a titanium electrode coated with a catalytic layer containing iridium oxide, and in particular, a coated titanium electrode has been used which is coated with a catalytic layer of an oxide mixture of iridium oxide and tantalum oxide or a catalytic layer of the oxide mixture further mixed with another metal or metal oxide. Furthermore, taking examples of the coated titanium electrode not only for the electrowinning but also for other fields of application, disclosed in Patent Literature 1 to Patent Literature 7 are coated titanium electrodes which are used as the anode for various types of electrolytic processes in an aqueous solution, such as electroplating, manufacturing of electrolytic metal foil, common salt electrolysis, manufacturing of an electrolytic solution, or manufacturing of an electrolytic function solution. Note that the anodes disclosed in Patent Literature 1 to Patent Literature 7 include those that are employed not only for producing oxygen but also those used for producing chlorine. Furthermore, disclosed in Patent Literature 8 are a precursor solution that is used when the coated titanium electrode for electrowinning is manufactured by thermal decomposition and a method for preparing the precursor solution. The inventor of the present application discloses, in Patent Literature 9 and Patent Literature 10, an anode for electrowinning, including a coated titanium electrode, and a method for electrowinning using the anode.

Citation List

Patent Literature

[0007]

- PTL 1: Japanese Published Unexamined Patent Application No. H06-101083
- PTL 2: Japanese Published Unexamined Patent Application No. H09-87896
- PTL 3: Japanese Published Unexamined Patent Application No. 2007-246987
- PTL 4: Japanese Published Unexamined Patent Application No. 2008-050675
- PTL 5: Japanese Published Unexamined Patent Application No. 2010-507017
- PTL 6: Japanese Published Unexamined Patent Application No. 2011-017084
- PTL 7: Japanese Published Unexamined Patent Application No. 2011-503359
- PTL 8: United States Patent Application Publication No. 2009/0288958
- PTL 9: Japanese Patent No. 4516617
- PTL 10: Japanese Patent No. 4516618

Summary of Invention

Technical Problem

5 **[0008]** As described above, in Patent Literature 9, the inventor of the present application disclosed an anode for electrowinning zinc with a catalytic layer of amorphous iridium oxide formed on a conductive substrate and a method for electrowinning zinc using the same. It is thereby clearly shown that when compared with a conventional anode for electrowinning zinc and method for electrowinning, the anode potential and the electrolytic voltage may be reduced for the occurrence of oxygen at the time of electrowinning of zinc and that the deposition of manganese oxyhydroxide and manganese dioxide that occurs as a side reaction of the anode may be restrained, etc. Here, the deposition of manganese oxyhydroxide and manganese dioxide, which is a side reaction, may be restrained because the catalytic layer containing amorphous iridium oxide has a high catalytic activity for the occurrence of oxygen and thus gives a higher priority to the occurrence of oxygen than to the side reaction, thus allowing the electric current at the time of energization to be consumed not for the side reaction but for the main reaction or the occurrence of oxygen. That is, the anode for electrowinning in the sulfuric acid based electrolytic solution could restrain a side reaction by increasing the catalytic activity for the occurrence of oxygen so as to allow oxygen to occur with a higher priority over the side reaction. Meanwhile, disclosed in Patent Literature 10 are an anode for electrowinning cobalt with a catalytic layer of amorphous ruthenium oxide formed on a conductive substrate and a method for electrowinning cobalt using the same. It is thereby clearly shown that when compared with a conventional anode for electrowinning cobalt in a chloride based electrolytic solution and a method for electrowinning therein, the anode potential and the electrolytic voltage may be reduced for the occurrence of chlorine, and the deposition of cobalt oxyhydroxide that occurs as a side reaction of the anode may be restrained, etc. In these prior art techniques, it was found that in the electrowinning of zinc or cobalt in the sulfuric acid based electrolytic solution, the catalytic layer containing amorphous iridium oxide selectively has a high catalytic activity for the occurrence of oxygen on the anode, while in the electrowinning of cobalt in the chloride based electrolytic solution, the catalytic layer containing amorphous ruthenium oxide selectively has a high catalytic activity for the occurrence of chlorine on the anode.

[0009] However, the electrowinning in the sulfuric acid based electrolytic solution has been required to further increase the catalytic activity for the anode reaction, thereby further reducing the anode potential and accordingly further reducing the electrolytic voltage. In addition, in the electrowinning of a metal in the sulfuric acid based electrolytic solution, that is, the electrowinning with the occurrence of oxygen as an anode reaction, it has also been required to provide an anode and a method for electrowinning which may further reduce the electrolytic voltage even in the electrowinning of other metals, for example, copper or nickel, etc. Furthermore, it has also been required to provide a reduced electric power consumption rate for electrowinning in the sulfuric acid based electrolytic solution as well as to provide not an anode that has a catalytic layer of an expensive metal like iridium as a component but an anode with a catalytic layer less expensive than that or an anode manufactured at a lower cost. Furthermore, concerning the method for electrowinning in the sulfuric acid based electrolytic solution as well, it has been required to provide a method for electrowinning which may further reduce the electrolytic voltage and which may reduce the cost of the anode to thereby perform the electrowinning at a lower cost.

[0010] The present invention was developed to meet the aforementioned demands. It is therefore an object of the present invention to provide an anode for electrowinning in a sulfuric acid based electrolytic solution, the anode being capable of producing oxygen at a lower potential when compared with a lead electrode, a lead alloy electrode, or a coated titanium electrode, thereby allowing the electrowinning to be performed at a reduced electrolytic voltage and the electric power consumption rate of a desired metal to be reduced; being available as an anode for electrowinning of various types of metals; and at the same time, allowing the catalytic layer to be provided at a reduced cost and the electrowinning to be performed in volume with efficiency when compared with the coated titanium electrode used for electrowinning in the sulfuric acid based electrolytic solution. It is another object of the present invention to provide a method for electrowinning in the sulfuric acid based electrolytic solution, the method being capable of reducing the potential of the anode and the electrolytic voltage and thus reducing the electric power consumption rate in the electrowinning; and allowing the initial cost and the maintenance cost of the anode to be reduced, thereby reducing the cost of the entire electrowinning process.

Solution to Problem

[0011] As a result of intensive studies for solving the aforementioned problems, the inventor of the present application has completed the present invention by finding that the aforementioned problems could be solved by an anode for electrowinning with a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide formed on a conductive substrate and a method for electrowinning using the same.

[0012] That is, to solve the aforementioned conventional problems, the anode for electrowinning of the present invention

and the method for electrowinning using the same have the following arrangements.

[0013] The anode for electrowinning according to the first aspect of the present invention is an anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate.

[0014] This arrangement provides the following effects.

(1) The catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide selectively shows a high catalytic activity for the occurrence of oxygen in the sulfuric acid based electrolytic solution, allowing the potential of the anode for the occurrence of oxygen to be considerably reduced.

(2) The anode is capable of producing oxygen at a lower potential in the sulfuric acid based electrolytic solution than an electrode with a catalytic layer of crystalline iridium oxide formed on a conductive substrate or an electrode with a catalytic layer of amorphous iridium oxide formed on a conductive substrate; at the same time, restraining a side reaction and providing a high catalytic activity for the occurrence of oxygen; when compared with the case where another anode is used for electrowinning in the sulfuric acid based electrolytic solution, reducing the electrolytic voltage irrespective of the type of a metal to be extracted on the cathode.

(3) When compared with the electrowinning in the sulfuric acid based electrolytic solution using an anode with a catalytic layer of amorphous iridium oxide formed and in particular, an anode with a catalytic layer of amorphous iridium oxide and amorphous tantalum oxide formed, the anode of the present invention is provided with a very high inventive step and novelty and uniqueness that the potential of the anode may further be reduced and the electrolytic voltage may also be reduced.

(4) The potential of the anode for electrowinning is reduced for the occurrence of oxygen and the occurrence of oxygen is given a higher priority over other side reactions, thereby restraining side reactions such as the deposition and accumulation of manganese oxyhydroxide, manganese dioxide, lead dioxide, or cobalt oxyhydroxide, etc., on the anode for electrowinning.

(5) Since ruthenium is one third or less the price of iridium, a catalytic activity higher than the catalytic activity for the occurrence of oxygen in the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide may be achieved by a less expensive catalytic layer that contains amorphous ruthenium oxide and amorphous tantalum oxide.

[0015] Here, the conductive substrate may be preferably made of a valve metal such as titanium, tantalum, zirconium, niobium, tungsten, or molybdenum; an alloy predominantly composed of a valve metal such as titanium - tantalum, titanium - niobium, titanium - palladium, or titanium - tantalum - niobium; an alloy of a valve metal and a platinum family metal and/or a transition metal; or an electrically conductive diamond (e.g., boron doped diamond), but the present invention is not limited thereto. Furthermore, the conductive substrate may be formed in various shapes such as a three-dimensional porous structure in which bonded to each other are metal particles that are plate-shaped, net-shaped, bar-shaped, sheet-shaped, tubular, linear, porous plate shaped, porous, or spherical. As the conductive substrate other than the aforementioned ones, it is also acceptable to employ metals other than valve metals, such as iron or nickel, or electrically conductive ceramic which is coated with the aforementioned valve metals, alloys, or electrically conductive diamond, etc.

[0016] Note that the catalytic layer may contain other components than amorphous ruthenium oxide and amorphous tantalum oxide so long as the electrolytic voltage may be reduced in electrowinning.

[0017] Such other components may include platinum, iridium, ruthenium, tungsten, tantalum, iridium oxide, titanium oxide, and oxidation niobium; however, the present invention is not limited thereto.

[0018] The anode for electrowinning according to the second aspect of the present invention is an anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate; electrowinning may be performed at an electrolytic voltage reduced by 0.02 V or greater when compared with an anode with a catalytic layer of amorphous iridium oxide and amorphous tantalum oxide formed on a conductive substrate, or electrowinning may be performed at an electrolytic voltage reduced by 0.05 V or greater when compared with an anode with a catalytic layer of crystalline ruthenium oxide and amorphous tantalum oxide formed on a conductive substrate.

[0019] This arrangement provides the following effect.

(1) Without being affected by a third component (another component) such as iridium oxide, it is possible to increase the catalytic activity for the occurrence of oxygen with reliability and reduce the electrolytic voltage irrespective of the type of a metal to be extracted on the cathode.

[0020] The anode for electrowinning according to the third aspect of the present invention is an anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous

tantalum oxide is formed on a conductive substrate.

[0021] This arrangement provides the following effects.

(1) The catalytic layer of the anode for electrowinning is made of a mixture of amorphous ruthenium oxide and amorphous tantalum oxide, thereby providing durability that is applicable to electrowinning in the sulfuric acid based electrolytic solution.

[0022] Here, in Patent Literature 6, disclosed is one comparative example in which the coating layer having metal components of ruthenium and tantalum obtained by thermal decomposition at 480°C had a very low durability in a sulfuric acid solution. Such a result is a problem that may occur when crystalline ruthenium oxide is involved which is obtained by thermal decomposition at a temperature of at least 350°C or greater. In contrast to this, the inventor of the present application found that the anode for electrowinning with a catalytic layer of ruthenium oxide made amorphous in a mixture of amorphous tantalum oxide and the same would not cause a problem with durability to the occurrence of oxygen, like the one in Patent Literature 6, as the anode for electrowinning in the sulfuric acid based electrolytic solution. In particular, the anode for electrowinning of the present invention provides an outstanding durability in an electrolysis condition of a current density of 0.1 A/cm² or less per an electrode area, the condition being a typical electrolysis condition for the electrowinning in which the occurrence of oxygen is the anode reaction in the sulfuric acid based electrolytic solution.

[0023] Here, the present invention will be described in more detail below. The catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide may be formed on the conductive substrate by thermal decomposition, in which a precursor solution containing ruthenium and tantalum is applied to the conductive substrate and then heated at a predetermined temperature. Other than the thermal decomposition, it is also possible to employ various types of physical vapor deposition and chemical vapor deposition methods, etc., such as sputtering and CVD. In particular, among those methods for making the anode for electrowinning of the present invention, the method for making the anode by thermal decomposition will be described in more detail. For example, a precursor solution containing ruthenium and tantalum in a variety of forms such as an inorganic compound, organic compound, ion, or complex is applied to a titanium substrate, which is then thermally decomposed at temperatures in a range lower than at least 350°C, thereby forming a catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide on the titanium substrate. For example, a butanol solution in which ruthenium chloride hydrate and tantalum chloride are dissolved is employed as a precursor solution, which is then applied to the titanium substrate and thermally decomposed. At this time, for example, if the molar ratio between ruthenium and tantalum in the butanol solution is 30:70, the catalytic layer of a mixture of amorphous ruthenium oxide and amorphous tantalum oxide is formed at a thermal decomposition temperature of 280°C. Furthermore, by thermal decomposition at 260°C after the application of the aforementioned precursor solution, the catalytic layer of a mixture of amorphous ruthenium oxide and amorphous tantalum oxide may also be formed in the same manner.

[0024] When the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate by thermal decomposition, it varies whether amorphous ruthenium oxide and amorphous tantalum oxide are contained in the catalytic layer, depending on the molar ratio between ruthenium and tantalum contained in the precursor solution to be applied to the titanium substrate and the thermal decomposition temperature. Furthermore, when a metal component other than ruthenium and tantalum is contained in the precursor solution, it also varies depending on the type of the metal component and the molar ratio of the metal component to all metal components contained in the precursor solution, etc. For example, when the same components other than metal components are contained in the precursor solution and only ruthenium and tantalum are contained as metal components, a lower molar ratio of ruthenium in the precursor solution would tend to show a greater range of thermal decomposition temperatures in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide is obtained. Furthermore, the conditions for forming the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide also vary depending not only on the molar ratio between such metal components but also on the method for preparing and the material of the precursor solution, for example, raw materials of ruthenium and tantalum used to prepare the precursor solution, the type of a solvent, and the type and concentration of an additive that may be added to accelerate thermal decomposition.

[0025] Thus, for the anode for electrowinning of the present invention, the conditions for forming, by thermal decomposition, the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide are not limited to the use of the butanol solvent in the thermal decomposition method mentioned above, the molar ratio between ruthenium and tantalum, and the range of thermal decomposition temperatures associated therewith. The aforementioned conditions are only an example, and the method for manufacturing the anode for electrowinning of the present invention may include any methods other than those mentioned above so long as the methods are available to forming the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide on the conductive substrate. For example, as a matter of course, such methods may include one which is disclosed in Patent Literature 8 that involves a heating step in the preparation process of the precursor solution. Note that the formation of the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide may be known from the fact that by a typically employed X-ray diffraction

method, the diffraction peak corresponding to ruthenium oxide is not observed and the diffraction peak corresponding to tantalum oxide is not observed.

[0026] The invention according to the fourth aspect is the anode for electrowinning according to any one of the first to third aspects, wherein the molar ratio between ruthenium and tantalum in the catalytic layer is 30:70.

[0027] This arrangement provides the following effect in addition to those obtained by any one of the first to third aspects. (1) When the same components other than metal components are contained in the precursor solution and only ruthenium and tantalum are contained as metal components, a lower molar ratio of ruthenium in the precursor solution would tend to show a greater range of thermal decomposition temperatures in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide is obtained, thus providing an outstanding mass productivity.

[0028] The invention according to the fifth aspect is the anode for electrowinning according to any one of the first to fourth aspects, wherein an intermediate layer is formed between the catalytic layer and the conductive substrate.

[0029] This arrangement provides the following effects in addition to those obtained in any one of the first to fourth aspects.

(1) The intermediate layer is formed between the catalytic layer and the conductive substrate and at the same time, the surface of the conductive substrate is coated, thereby preventing the electrolytic solution from reaching the conductive substrate even when the electrolytic solution penetrates into the catalytic layer. Thus, the conductive substrate will never be corroded by the acidic electrolytic solution, thereby preventing an unsmooth current flow caused by corrosion between the conductive substrate and the catalytic layer.

(2) When an intermediate layer is formed which is made of oxide or composite oxide and which is different from the catalytic layer of the anode for electrowinning of the present invention, the catalytic activity for the occurrence of oxygen is low when compared with the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide. Thus, even when the electrolytic solution penetrates the catalytic layer and reaches the intermediate layer, the intermediate layer has a higher durability than the catalytic layer and thus protects the conductive substrate because oxygen does not occur on a priority basis in the intermediate layer as compared to the catalytic layer. At the same time, the conductive substrate is coated with such an oxide or composite oxide having a higher durability, thereby further preventing the corrosion of the conductive substrate by the electrolytic solution when compared with the case of no intermediate layer provided.

[0030] Here, the intermediate layer has a low catalytic activity for the occurrence of oxygen when compared with the catalytic layer, but sufficiently coats the conductive substrate, thus restraining the corrosion of the conductive substrate. The intermediate layer may be made of, for example, metal, alloy, a carbon based material such as boron doped diamond, a metal compound such as an oxide and sulfide, or a composite compound such as a metal composite oxide. For example, the intermediate layer would be formed of a metal, in the case of which a thin film of tantalum or niobium, etc., may be preferably employed. The intermediate layer would also be formed of an alloy, in the case of which preferably employed are, for example, tantalum, niobium, tungsten, molybdenum, titanium, or platinum. Furthermore, an intermediate layer made of a carbon based material such as boron doped diamond also has the same effects. The intermediate layer made of the aforementioned metal, alloy, or carbon based material may be formed by various types of physical vapor deposition or chemical vapor deposition methods such as thermal decomposition, sputtering, and CVD, etc., or by a variety of methods such as hot dipping or electroplating, etc. For example, the intermediate layer made of a metal compound such as an oxide or sulfide or a metal composite oxide may be preferably an intermediate layer made of an oxide containing crystalline iridium oxide, etc. In particular, when the catalytic layer is made by thermal decomposition, it is advantageous, from the viewpoint of simplifying the manufacturing process of the anode for electrowinning, to form the intermediate layer of an oxide or composite oxide in the same manner by thermal decomposition.

[0031] The invention according to the sixth aspect is the anode for electrowinning according to the fifth aspect and is adopted such that the intermediate layer is made of tantalum, niobium, tungsten, molybdenum, or titanium, platinum or any one of alloys of these metals. This arrangement provides the following effect in addition to those obtained in the fifth aspect. (1) The intermediate layer may be formed in volume with efficiency by various types of physical vapor deposition or chemical vapor deposition methods such as thermal decomposition, sputtering, and CVD or by a variety of methods such as hot dipping and electroplating.

[0032] The invention according to the seventh aspect is the anode for electrowinning according to the fifth aspect, wherein the intermediate layer contains crystalline iridium oxide and amorphous tantalum oxide.

[0033] This arrangement provides the following effect in addition to those obtained in the fifth aspect.

(1) Since ruthenium oxide in the catalytic layer and iridium oxide in the intermediate layer belong to the same crystalline family and have a close interatomic distance, the catalytic layer and the intermediate layer formed thereon have a good adhesion therebetween, thus providing a distinctively improved durability.

[0034] Here, the intermediate layer containing crystalline iridium oxide and amorphous tantalum oxide may be manufactured by thermal decomposition, in which a precursor solution containing iridium and tantalum is applied to the conductive substrate and then heated at a predetermined temperature. The intermediate layer may also be manufactured by, for example, various types of physical vapor deposition or chemical vapor deposition methods such as by sputtering or CVD. For example, in the case of the thermal decomposition, preferable is such an intermediate layer which is made of crystalline iridium oxide and amorphous tantalum oxide that are obtained by thermally decomposing the precursor solution containing iridium and tantalum at a temperature from 400°C to 550°C.

[0035] The invention according to the eighth aspect is the anode for electrowinning according to any one of the first to seventh aspects, wherein a metal extracted by electrowinning is any one of copper, zinc, nickel, cobalt, platinum, gold, silver, indium, lead, ruthenium, rhodium, palladium, and iridium.

[0036] This arrangement provides the following effect in addition to those obtained in any one of the first to seventh aspects. (1) Since oxygen is produced at a lower potential, the electrolytic voltage in electrowinning may be lowered so as to reduce the electric power consumption rate of a metal. Thus, the anode is available as an anode for electrowinning of various types of metals, thus enabling outstanding general-purpose use.

[0037] The method for electrowinning according to the ninth aspect of the present invention is a method for electrowinning in the sulfuric acid based electrolytic solution, wherein a desired metal is extracted using the anode for electrowinning according to any one of the first to eighth aspects.

[0038] This arrangement provides the following effect.

(1) In the method for electrowinning in the sulfuric acid based electrolytic solution, the potential of the anode for electrowinning and the electrolytic voltage are reduced, and thus the electric power consumption rate for electrowinning may be reduced. Furthermore, the initial cost and the maintenance cost for the anode for electrowinning are also reduced, thus reducing the cost of the entire electrowinning process.

[0039] The invention according to the tenth aspect is the method for electrowinning according to the ninth aspect, wherein a metal extracted by electrowinning is any one of copper, zinc, nickel, cobalt, platinum, gold, silver, indium, lead, ruthenium, rhodium, palladium, and iridium.

(1) The electrolytic voltage is reduced and the reduced electrolytic voltage is maintained even when the electrowinning is continued. Thus, the electric power consumption rate for electrowinning a target metal is reduced, and nodegradation in the service life and durability of the anode for electrowinning is caused by the effects of a side reaction, so that the target metal may be extracted by electrowinning with stability for a long period of time. This allows electrowinning to be performed with outstanding efficiency and stability.

Advantageous Effects of Invention

[0040] The present invention provides the effects listed below.

1) In the electrowinning of a metal in a sulfuric acid based electrolytic solution, the potential at which oxygen is produced on the anode for electrowinning may be lowered when compared with a conventional one. Thus, irrespective of the type of the metal to be extracted, the electrolytic voltage for the electrowinning may be reduced, thereby significantly reducing the electric power consumption rate.

2) Furthermore, since the potential at which oxygen is produced on the anode for electrowinning may be lowered when compared with a conventional one, various side reactions that would otherwise possibly occur on the anode for electrowinning may be restrained. Thus, in long-term electrowinning, the electrolytic voltage may be prevented from being increased.

3) In addition to the aforementioned effects, the present invention provides the effect to eliminate or alleviate the need for removing oxide, oxyhydroxide, and other compounds which would be otherwise deposited or accumulated by a side reaction on the anode for electrowinning. Thus, damage to the anode for electrowinning which would be caused by such work is restrained, thus providing an elongated service life to the anode for electrowinning.

4) In addition to the aforementioned effects, the present invention provides the effect to eliminate or reduce the need for removing oxide, oxyhydroxide, and other compounds which would be otherwise deposited or accumulated by a side reaction on the anode for electrowinning. Thus, maintenance or replacement of the anode for electrowinning may be restrained or alleviated in electrowinning. Furthermore, such removal work restrains the necessity of suspending the electrowinning, thereby enabling electrowinning to be performed continuously with an improved stability.

5) In addition to the aforementioned effects, the present invention provides the effect in which the deposits would never restrict the effective surface area of the anode for electrowinning, or the area of the anode available for electrowinning may be prevented from being unevenly formed, since the deposits on the anode for electrowinning

are restrained. It is thus possible to prevent a metal from being unevenly deposited on the cathode and an unsmooth metal from being produced thereon, thereby restraining the difficulty of reproducing the metal or degradation in the quality of the metal to be extracted.

6) Furthermore, since metal is not grown unevenly on the cathode for the aforementioned reasons, the metal grown on the cathode may be prevented from reaching and short-circuiting the anode for electrowinning. It is thus possible to prevent unavailability of electrowinning. Furthermore, since the uneven growth and dendritic growth of a metal on the cathode are restrained, the inter-electrode distance between the anode for electrowinning and the cathode may be reduced, and an increase in the electrolytic voltage to be caused by an ohmic loss in the electrolytic solution may be restrained.

7) Furthermore, since various problems that would be otherwise caused by deposits resulting from a side reaction on the anode for electrowinning are resolved as described above, it is possible to continuously perform electrowinning with stability and reduce maintenance and management work in electrowinning, allowing the product management of the extracted metal to be performed with ease. Furthermore, the cost of the anode for electrowinning for a long-term electrowinning may be reduced.

8) Furthermore, according to the present invention, when compared with a conventional coated titanium electrode with a catalytic layer containing iridium oxide, use of ruthenium oxide alleviates the cost of the catalytic layer; and a reduced thermal decomposition temperature reduces the cost of the step of forming the catalytic layer as well.

9) In addition to the aforementioned effects, the present invention provides the effect to reduce the manufacturing cost of the entire electrowinning in the electrowinning of various metals in a sulfuric acid based electrolytic solution.

Brief Description of Drawings

[0041]

Fig. 1 is a graph of an X-ray diffraction image obtained from the anodes for electrowinning according to Example 1, Example 2, and Comparative Example 1.

Description of Examples

[0042] Hereinafter, the present invention will be described in more detail in accordance with the Examples and Comparative Examples; however, the present invention is not limited to the following Examples. For example, the present invention is also applicable to electrowinning of other metals than zinc, copper, and cobalt.

[Electrowinning of zinc]

Example 1

[0043] A commercially available titanium plate (5 cm in length, 1 cm in width, 1 mm in thickness) was immersed and etched in a 10% oxalic acid solution at 90°C for 60 minutes and then washed and dried. Next, prepared was an application liquid which was obtained by adding ruthenium trichloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) and tantalum pentachloride (TaCl_5) to a butanol ($\text{n-C}_4\text{H}_9\text{OH}$) solution containing 6 vol% concentrated hydrochloric acid so that the molar ratio between ruthenium and tantalum is 3 : 0 : 70 and the total of ruthenium and tantalum is 50 g/L in terms of metal. This application liquid was applied to the titanium plate dried as mentioned above, dried at 120°C for 10 minutes, and then thermally decomposed for 20 minutes in an electric furnace that was held at 260°C. This series of application, drying, and thermal decomposition was repeated five times in total in order to prepare an anode for electrowinning according to Example 1, the anode having a catalytic layer formed on the titanium plate that was a conductive substrate.

[0044] An X-ray diffraction analysis of the structure of the anode for electrowinning according to Example 1 shows that as shown in Fig. 1, the diffraction peak equivalent to RuO_2 was not observed in the X-ray diffraction image, and the diffraction peak equivalent to Ta_2O_5 was not observed, either. Note that the diffraction peak of Ti was observed; however, this was caused by the titanium plate. That is, the anode for electrowinning according to Example 1 had the catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide formed on the titanium plate.

[0045] Prepared was an electrolytic solution of a 0.80 mol/L of ZnSO_4 and 2.0 mol/L of sulfuric acid, and a zinc plate (2 cm × 2 cm) was immersed as the cathode in this electrolytic solution. Furthermore, the anode for electrowinning according to Example 1 above was buried in a polytetrafluoroethylene holder, and then, with the electrode area in contact with the electrolytic solution restricted to 1 cm², was disposed in the same electrolytic solution so as to be opposed to the aforementioned cathode with a predetermined inter-electrode distance. Then, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of zinc by flowing, between the anode for electrowinning and the cathode, an electrolysis current at a current density of either

10 mA/cm² or 50 mA/cm² with respect to the electrode area of the anode for electrowinning. Note that the electrolytic solution was at 40°C.

Example 2

[0046] An anode for electrowinning according to Example 2 was manufactured by the same method as that of Example 1 except that the catalytic layer was formed at a thermal decomposition temperature of not 260°C but 280°C. An X-ray diffraction analysis of the structure of the anode for electrowinning according to Example 2 shows that as shown in Fig. 1, the diffraction peak equivalent to RuO₂ was not observed, and the diffraction peak equivalent to Ta₂O₅ was not observed, either. Note that the diffraction peak of Ti was observed; however, this was caused by the titanium plate. That is, the anode for electrowinning according to Example 2 had the catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide formed on the titanium plate.

[0047] Prepared was an electrolytic solution of a 0.80 mol/L of ZnSO₄ and 2.0 mol/L of sulfuric acid, and a zinc plate (2 cm × 2 cm) was immersed as the cathode in this electrolytic solution. Furthermore, the anode for electrowinning according to Example 2 above was buried in a polytetrafluoroethylene holder, and then, with the electrode area in contact with the electrolytic solution restricted to 1 cm², was disposed in the same electrolytic solution so as to be opposed to the aforementioned cathode with a predetermined inter-electrode distance. Then, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of zinc by flowing, between the anode for electrowinning and the cathode, an electrolysis current at a current density of either 10 mA/cm² or 50 mA/cm² with respect to the electrode area of the anode for electrowinning. Note that the electrolytic solution was at 40°C.

(Comparative Example 1)

[0048] An anode for electrowinning according to Comparative Example 1 was manufactured by the same method as that of Example 1 except that the catalytic layer was formed at a thermal decomposition temperature of not 260°C but 360°C. An X-ray diffraction analysis of the structure of the anode for electrowinning according to Comparative Example 1 shows that as shown in Fig. 1, the diffraction peak equivalent to RuO₂ was observed, but the diffraction peak equivalent to Ta₂O₅ was not observed. Note that the diffraction peak of Ti was observed; however, this was caused by the titanium plate. That is, the anode for electrowinning according to Comparative Example 1 had the catalytic layer of crystalline ruthenium oxide and amorphous tantalum oxide formed thereon.

[0049] Prepared was an electrolytic solution of a 0.80 mol/L of ZnSO₄ and 2.0 mol/L of sulfuric acid, and a zinc plate (2 cm × 2 cm) was immersed as the cathode in this electrolytic solution. Furthermore, the anode for electrowinning according to Comparative Example 1 above was buried in a polytetrafluoroethylene holder, and then, with the electrode area in contact with the electrolytic solution restricted to 1 cm², was disposed in the same electrolytic solution so as to be opposed to the aforementioned cathode with a predetermined inter-electrode distance. Then, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of zinc by flowing, between the anode for electrowinning and the cathode, an electrolysis current at a current density of either 10 mA/cm² or 50 mA/cm² with respect to the electrode area of the anode for electrowinning. Note that the electrolytic solution was at 40°C.

(Comparative Example 2)

[0050] A commercially available titanium plate (5 cm in length, 1 cm in width, 1 mm in thickness) was immersed and etched in a 10% oxalic acid solution at 90°C for 60 minutes and then washed and dried. Next, prepared was an application liquid which was obtained by adding hexachloroiridic acid hexahydrate (H₂IrCl₆ · 6H₂O) and tantalum chloride (TaCl₅) to a butanol (n-C₄H₉OH) solution containing 6 vol% concentrated hydrochloric acid so that the molar ratio between iridium and tantalum was 80:20 and the total of iridium and tantalum was 70 g/L in terms of metal. This application liquid was applied to the titanium plate dried as mentioned above, dried at 120°C for 10 minutes, and then thermally decomposed for 20 minutes in the electric furnace that was held at 360°C. This series of application, drying, and thermal decomposition was repeated five times in total in order to prepare an anode for electrowinning according to Comparative Example 2, the anode having a catalytic layer formed on the titanium plate that was a conductive substrate.

[0051] An X-ray diffraction analysis of the structure of the anode for electrowinning according to Comparative Example 2 shows that, in the X-ray diffraction image, the diffraction peak equivalent to IrO₂ was not observed, and the diffraction peak equivalent to Ta₂O₅ was not observed, either. That is, the anode for electrowinning according to Comparative Example 2 had the catalytic layer of amorphous iridium oxide and amorphous tantalum oxide formed on the titanium plate.

[0052] Prepared was an electrolytic solution of a 0.80 mol/L of ZnSO₄ and 2.0 mol/L of sulfuric acid, and a zinc plate (2 cm × 2 cm) was immersed as the cathode in this electrolytic solution. Furthermore, the anode for electrowinning

according to Comparative Example 2 above was buried in a polytetrafluoroethylene holder, and then, with the electrode area in contact with the electrolytic solution restricted to 1 cm², was disposed in the same electrolytic solution so as to be opposed to the aforementioned cathode with a predetermined inter-electrode distance. Then, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of zinc by flowing, between the anode for electrowinning and the cathode, an electrolysis current at a current density of either 10 mA/cm² or 50 mA/cm² with respect to the electrode area of the anode for electrowinning. Note that the electrolytic solution was at 40°C.

[0053] The inter-terminal voltages for electrowinning using the anode for electrowinning according to Example 1, Example 2, Comparative Example 1 and Comparative Example 2 above are as shown in Table 1 to Table 4.

[Table 1]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 1	Comparative Example 1	Comparative Example 1 - Example 1
10 mA/cm ²	2.28 V	2.45 V	0.17 V
50 mA/cm ²	2.41 V	2.60 V	0.19 V

[Table 2]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 1	Comparative Example 2	Comparative Example 2 - Example 1
10 mA/cm ²	2.28 V	2.34 V	0.06 V
50 mA/cm ²	2.41 V	2.46 V	0.05 V

[Table 3]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 2	Comparative Example 1	Comparative Example 1 - Example 2
10 mA/cm ²	2.30 V	2.45 V	0.15 V
50 mA/cm ²	2.40 V	2.60 V	0.20 V

[Table 4]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 2	Comparative Example 2	Comparative Example 2 - Example 2
10 mA/cm ²	2.30 V	2.34 V	0.04 V
50 mA/cm ²	2.40 V	2.46 V	0.06 V

[0054] As shown in Table 1, in the electrowinning of zinc, when the anode for electrowinning according to Example 1 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 260°C, the electrolytic voltage was lower by 0.17 V to 0.19 V when compared with the case where the anode for electrowinning according to Comparative Example 1 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 2, when the anode for electrowinning according to Example 1 was used, the electrolytic voltage was lower by 0.05 V to 0.06 V when compared with the case where the anode for electrowinning according to Comparative Example 2 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide

was formed. That is, when the anode for electrowinning (Example 1) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was significantly reduced when compared with the case where the anode for electrowinning (Comparative Example 1) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 2) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

[0055] Furthermore, as shown in Table 3, in the electrowinning of zinc, when the anode for electrowinning according to Example 2 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 280°C, the electrolytic voltage was lower by 0.15 V to 0.20 V when compared with the case where the anode for electrowinning according to Comparative Example 1 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 4, when the anode for electrowinning according to Example 2 was used, the electrolytic voltage was lower by 0.04 V to 0.06 V when compared with the case where the anode for electrowinning according to Comparative Example 2 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed. That is, when the anode for electrowinning (Example 2) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was significantly reduced when compared with the case where the anode for electrowinning (Comparative Example 1) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 2) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

[Electrowinning of copper]

Example 3

[0056] The electrolytic solution of Example 1 was replaced with an electrolytic solution of 0.60 mol/L of CuSO_4 and 0.90 mol/L of sulfuric acid, and with other conditions kept the same as those of Example 1, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of copper.

Example 4

[0057] The electrolytic solution of Example 2 was replaced with an electrolytic solution of 0.60 mol/L of CuSO_4 and 0.90 mol/L of sulfuric acid, and with other conditions kept the same as those of Example 2, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of copper.

(Comparative Example 3)

[0058] The electrolytic solution of Comparative Example 1 was replaced with an electrolytic solution of 0.60 mol/L of CuSO_4 and 0.90 mol/L of sulfuric acid, and with other conditions kept the same as those of Comparative Example 1, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of copper.

(Comparative Example 4)

[0059] The electrolytic solution of Comparative Example 2 was replaced with an electrolytic solution of 0.60 mol/L of CuSO_4 and 0.90 mol/L of sulfuric acid, and with other conditions kept the same as those of Comparative Example 2, the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of copper.

[0060] The inter-terminal voltages for electrowinning using the anode for electrowinning according to Example 3, Example 4, Comparative Example 3 and Comparative Example 4 above are as shown in Table 5 to Table 8.

[Table 5]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 3	Comparative Example 3	Comparative Example 3 - Example 3
10 mA/cm ²	1.17 V	1.28 V	0.11 V
50 mA/cm ²	1.30 V	1.46 V	0.16 V

[Table 6]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 3	Comparative Example 4	Comparative Example 4 - Example 3
10 mA/cm ²	1.17 V	1.22 V	0.05 V
50 mA/cm ²	1.30 V	1.37 V	0.07 V

[Table 7]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 4	Comparative Example 3	Comparative Example 3 - Example 4
10 mA/cm ²	1.18 V	1.28 V	0.10 V
50 mA/cm ²	1.30 V	1.46 V	0.16 V

[Table 8]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 4	Comparative Example 4	Comparative Example 4 - Example 4
10 mA/cm ²	1.18 V	1.22 V	0.04 V
50 mA/cm ²	1.30 V	1.37 V	0.07 V

[0061] As shown in Table 5, in the electrowinning of copper, when the anode for electrowinning according to Example 3 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 260°C, the electrolytic voltage was lower by 0.11 V to 0.16 V when compared with the case where the anode for electrowinning according to Comparative Example 3 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 6, when the anode for electrowinning according to Example 3 was used, the electrolytic voltage was lower by 0.05 V to 0.07 V when compared with the case where the anode for electrowinning according to Comparative Example 4 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed. That is, when the anode for electrowinning (Example 3) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was significantly reduced when compared with the case where the anode for electrowinning (Comparative Example 3) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 4) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

[0062] Furthermore, as shown in Table 7, in the electrowinning of copper, when the anode for electrowinning according to Example 4 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 280°C, the electrolytic voltage was lower by 0.10 V to 0.16 V when

compared with the case where the anode for electrowinning according to Comparative Example 3 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 8, when the anode for electrowinning according to Example 4 was used, the electrolytic voltage was lower by 0.04 V to 0.07 V when compared with the case where the anode for electrowinning according to Comparative Example 4 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed. That is, when the anode for electrowinning (Example 4) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was significantly reduced when compared with the case where the anode for electrowinning (Comparative Example 3) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 4) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

[Electrowinning of cobalt]

Example 5

[0063] The electrolytic solution of Example 1 was replaced with an electrolytic solution of 0.30 mol/L of CoSO_4 and 2.0×10^{-3} mol/L of sulfuric acid, and with the conditions kept the same as those of Example 1 except for a current density of 10 mA/cm², the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of cobalt.

Example 6

[0064] The electrolytic solution of Example 2 was replaced with an electrolytic solution of 0.30 mol/L of CoSO_4 and 2.0×10^{-3} mol/L of sulfuric acid, and with the conditions kept the same as those of Example 2 except for a current density of 10 mA/cm², the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of cobalt.

(Comparative Example 5)

[0065] The electrolytic solution of Comparative Example 1 was replaced with an electrolytic solution of 0.30 mol/L of CoSO_4 and 2.0×10^{-3} mol/L of sulfuric acid, and with the conditions kept the same as those of Comparative Example 1 except for a current density of 10 mA/cm², the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of cobalt.

(Comparative Example 6)

[0066] The electrolytic solution of Comparative Example 2 was replaced with an electrolytic solution of 0.30 mol/L of CoSO_4 and 2.0×10^{-3} mol/L of sulfuric acid, and with the conditions kept the same as those of Comparative Example 2 except for a current density of 10 mA/cm², the inter-terminal voltage (electrolytic voltage) was measured between the anode for electrowinning and the cathode while performing electrowinning of cobalt.

[0067] The inter-terminal voltages for electrowinning using the anode for electrowinning according to Example 5, Example 6, Comparative Example 5 and Comparative Example 6 above are as shown in Table 9 to Table 12.

[Table 9]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 5	Comparative Example 5	Comparative Example 5 - Example 5
10 mA/cm ²	1.89 V	1.94 V	0.05 V

[Table 10]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 5	Comparative Example 6	Comparative Example 6 - Example 5
10 mA/cm ²	1.89 V	1.91 V	0.02 V

[Table 11]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 6	Comparative Example 5	Comparative Example 5 - Example 6
10 mA/cm ²	1.82 V	1.94 V	0.12 V

[Table 12]

Current density	Electrolytic voltage		Difference in electrolytic voltage (Degree of improvement)
	Example 6	Comparative Example 6	Comparative Example 6 - Example 6
10 mA/cm ²	1.82 V	1.91 V	0.09 V

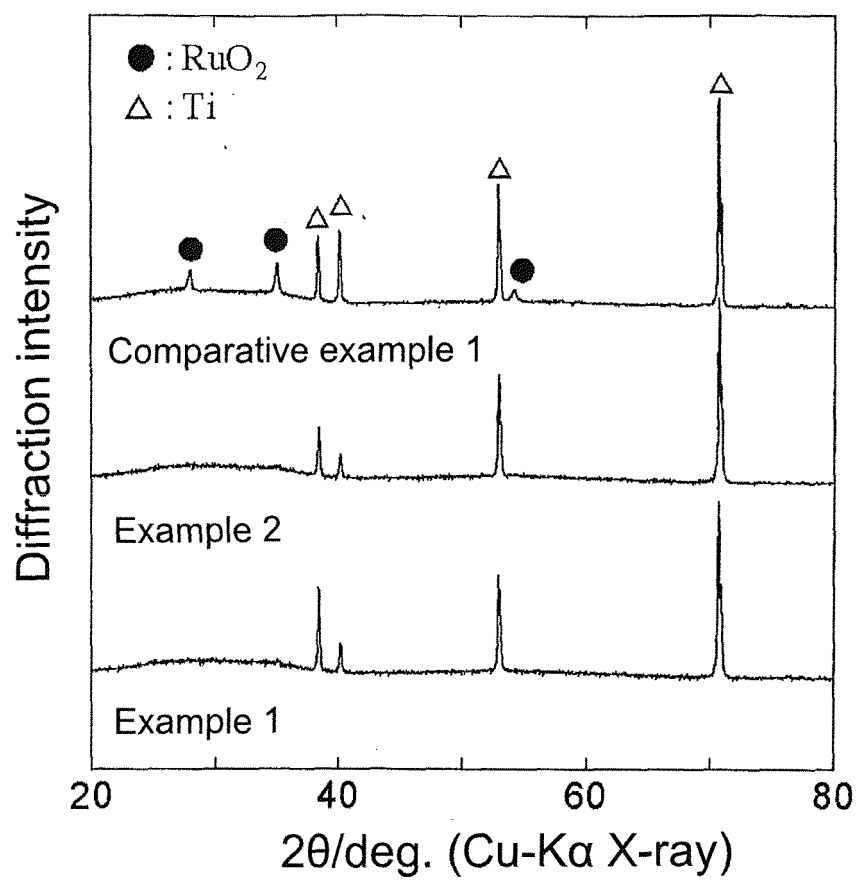
[0068] As shown in Table 9, in the electrowinning of cobalt, when the anode for electrowinning according to Example 5 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 260°C, the electrolytic voltage was lower by 0.05 V when compared with the case where the anode for electrowinning according to Comparative Example 5 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 10, when the anode for electrowinning according to Example 5 was used, the electrolytic voltage was lower by 0.02 V when compared with the case where the anode for electrowinning according to Comparative Example 6 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed. That is, when the anode for electrowinning (Example 5) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was reduced when compared with the case where the anode for electrowinning (Comparative Example 5) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 6) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

[0069] Furthermore, as shown in Table 11, in the electrowinning of cobalt, when the anode for electrowinning according to Example 6 was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 280°C, the electrolytic voltage was lower by 0.12 V when compared with the case where the anode for electrowinning according to Comparative Example 5 was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed by thermal decomposition at 360°C. Furthermore, as shown in Table 12, when the anode for electrowinning according to Example 6 was used, the electrolytic voltage was lower by 0.09 V when compared with the case where the anode for electrowinning according to Comparative Example 6 was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed. That is, when the anode for electrowinning (Example 6) was used in which the catalytic layer containing amorphous ruthenium oxide and amorphous tantalum oxide was formed, the electrolytic voltage was reduced when compared with the case where the anode for electrowinning (Comparative Example 5) was used in which the catalytic layer containing crystalline ruthenium oxide and amorphous tantalum oxide was formed. Furthermore, the electrolytic voltage was further reduced when compared with the case where the anode for electrowinning (Comparative Example 6) was used in which the catalytic layer containing amorphous iridium oxide and amorphous tantalum oxide was formed.

Claims

1. An anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate.
2. An anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate; and electrowinning may be performed at an electrolytic voltage reduced by 0.02 V or greater when compared with an anode with a catalytic layer of amorphous iridium oxide and amorphous tantalum oxide formed on a conductive substrate, or electrowinning may be performed at an electrolytic voltage reduced by 0.05 V or greater when compared with an anode with a catalytic layer of crystalline ruthenium oxide and amorphous tantalum oxide formed on a conductive substrate.
3. An anode for electrowinning in a sulfuric acid based electrolytic solution, wherein a catalytic layer of amorphous ruthenium oxide and amorphous tantalum oxide is formed on a conductive substrate.
4. The anode for electrowinning according to any one of claims 1 to 3, wherein the molar ratio between ruthenium and tantalum in the catalytic layer is 30:70.
5. The anode for electrowinning according to any one of claims 1 to 4, wherein an intermediate layer is formed between the catalytic layer and the conductive substrate.
6. The anode for electrowinning according to claim 5, wherein the intermediate layer is made of tantalum, niobium, tungsten, molybdenum, titanium, or platinum, or any one of alloys of these metals.
7. The anode for electrowinning according to claim 5, wherein the intermediate layer contains crystalline iridium oxide and amorphous tantalum oxide.
8. The anode for electrowinning according to any one of claims 1 to 7, wherein a metal extracted by electrowinning is any one of copper, zinc, nickel, cobalt, platinum, gold, silver, indium, lead, ruthenium, rhodium, palladium, and iridium.
9. A method for electrowinning in a sulfuric acid based electrolytic solution, wherein a desired metal is extracted using the anode for electrowinning according to any one of claims 1 to 8.
10. The method for electrowinning according to claim 9, wherein a metal extracted by electrowinning is any one of copper, zinc, nickel, cobalt, platinum, gold, silver, indium, lead, ruthenium, rhodium, palladium, and iridium.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/057426

A. CLASSIFICATION OF SUBJECT MATTER

C25C7/02 (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)

C25C7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012

Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-1556 A (the Doshisha), 07 January 2010 (07.01.2010), & US 2011/0079518 A1 & EP 2287364 A1 & WO 2009/151044 A1 & AU 2009258626 A & CN 102057081 A	1-10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

12 April, 2012 (12.04.12)

Date of mailing of the international search report

24 April, 2012 (24.04.12)

Name and mailing address of the ISA/
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REFERENCES CITED IN THE DESCRIPTION

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