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(54) ELECTRODE BASE, NEGATIVE ELECTRODE FOR AQUEOUS SOLUTION ELECTROLYSIS USING SAME, METHOD FOR PRODUCING THE ELECTRODE BASE, AND METHOD FOR PRODUCING THE NEGATIVE ELECTRODE FOR AQUEOUS SOLUTION ELECTROLYSIS

(57) The negative electrode for aqueous solution electrolysis of the present invention includes a conductive substrate having a nickel surface, a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on the conductive substrate surface, and an electrode catalyst layer formed on the mixture layer surface, wherein the electrode catalyst layer is formed by a layer including a platinum group metal or a platinum group metal compound. The negative electrode for aqueous solution electrolysis of the present invention is preferably used in electrolysis of an aqueous solution of an alkali metal halide, and the like.

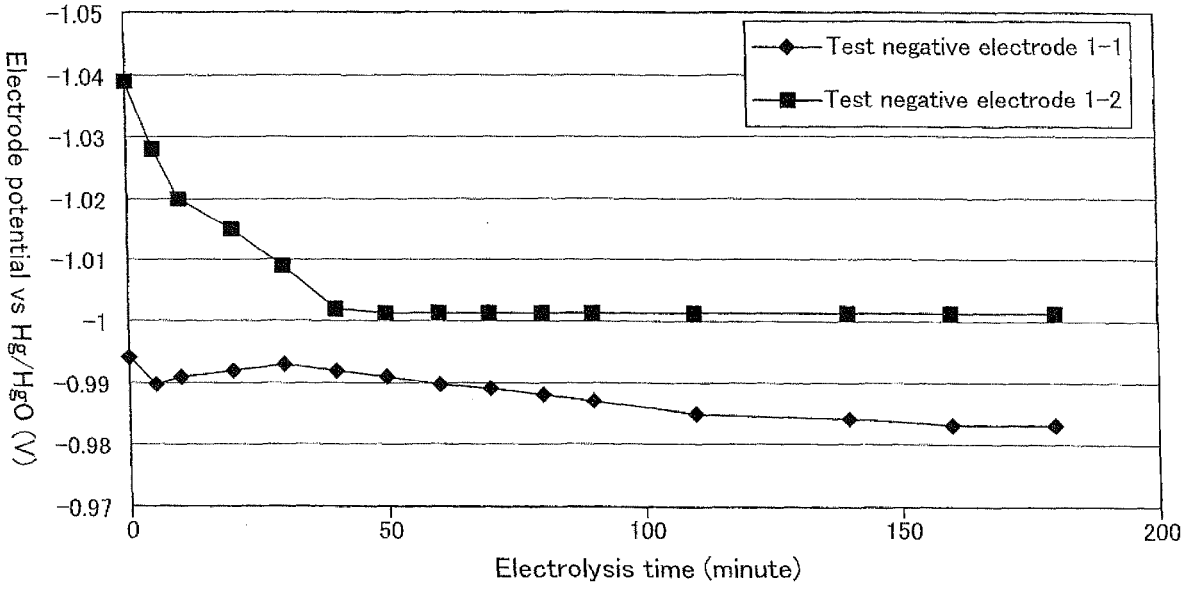

FIG. 1

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Description

Technical Field

[0001] The present invention relates to an electrode base used in an electrode for aqueous solution electrolysis. In addition, the present invention relates to a negative electrode for aqueous solution electrolysis in which an electrode catalyst layer is formed on the electrode base and which is preferably used as a negative electrode for electrolysis of an aqueous solution of an alkali metal halide, and a production method thereof.

Background Art

[0002] In an electrolysis industry consuming a large amount of electric power, reduction of energy required for production is getting to be a bigger issue, in terms of reduction of electric power consumption rate, and reduction of carbon dioxide emission as measures against global warming. In order to reduce energy required for electrolysis, an electrode, an ion-exchange membrane and an electrolytic cell are particularly getting advanced.

[0003] Negative electrodes for aqueous solution electrolysis having a low hydrogen overvoltage and a long operating life have been proposed as a negative electrode for aqueous solution electrolysis used in an aqueous solution electrolysis, which are obtained by forming, on a base made of nickel, an electrode catalyst layer including a platinum group metal or metal oxide, or an electrode catalyst layer including a rare earth metal such as a lanthanum or its compound and a platinum group metal.

[0004] These negative electrodes for aqueous solution electrolysis have a low hydrogen overvoltage, and a feature in which they have smoother surfaces of the electrode catalyst layer than that of conventional electrodes having particulate substances deposited on the surface, and thus damage caused by repetitive contact with an ion-exchange membrane can be prevented even if the electrolysis is performed with the ion-exchange membrane being in close contact with the electrode.

[0005] However, because the metal nickel, which is used as the base of the negative electrode for aqueous solution electrolysis, is brought into contact with the electrode catalyst layer showing a more noble potential than the nickel, the nickel base is easily corroded due to galvanic corrosion during a downtime of electrolysis or exposure to the atmosphere.

[0006] In addition, if a electrolytic cell is assembled from negative electrodes, positive electrodes and ion-exchange membranes and then the cell is stored in a state in which an electrolytic solution is not filled in the electrolytic cell, nickel ions generated by corrosion of the nickel base, which is caused by contact of the negative electrode with the ion-exchange membrane, permeate into the ion-exchange membrane to cause a phenomenon that the ions are deposited in the ion-exchange membrane as a nickel compound, which leads to deterioration of properties of the ion-exchange membrane and thus sometimes to a rise of an electrolysis voltage and a decrease in current efficiency.

[0007] In order to solve such defects, a method for producing a negative electrode has been proposed in which a nickel substrate surface is heated and baked at a temperature of 350 to 550°C for 5 to 60 minutes to form an intermediate layer including a nickel oxide as a main component on the conductive base surface (see, for example, Patent Document 1). The document describes that according to this method, the adhesion is strong because the intermediate layer and the base are formed from an originally integral material, and therefore peeling-off or lacking of the intermediate layer is not caused.

[0008] In addition, the present applicant has proposed a negative electrode for aqueous solution electrolysis including an electrode catalyst layer containing a platinum group metal compound and a lanthanoid, which has superior electrolysis properties (see, for example, Patent Document 2).

Patent Document

[0009]

Patent Document 1: Japanese Patent No. 4142191

Patent Document 2: Japanese Patent No. 4274489

Summary of Invention

Technical Problem

[0010] The negative electrode described in Patent Document 1 seems that elution of the nickel component from the electrode base can be prevented. However, the document also describes that the cell voltage is risen after the electrolysis

is started and then the electrolytic cell operation is shutdown.

[0011] The electrode described in Patent Document 2 has superior electrolysis properties to those of similar kinds of conventional electrodes, but resistance to reverse current is required to be more sufficient at emergency shutdown of the electrolytic cell operation, and the like.

Solution to Problem

[0012] The present invention aims to provide an negative electrode for aqueous solution electrolysis whose electrode base is a conductive substrate having nickel on its surface, which prevents elusion of nickel from the electrode base, prevents elusion of nickel from the negative electrode base during storage of an electrolytic cell integrally assembled from three components of a positive electrode, an ion-exchange membrane and the negative electrode in the atmosphere or suspension of the electrolytic cell operation, and is little affected by a reverse current generated at the time of emergency shutdown of the electrolytic cell operation. The present invention also aims to provide a negative electrode for aqueous solution electrolysis, having a low electrolytic cell voltage at the start of initial operation as well as at re-start of operation after shutdown of the electrolytic cell.

[0013] The present invention has the following constitution features [1] to [15].

[0014] [1] An electrode base including a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on a surface of a conductive substrate having a nickel surface.

[0015] [2] The electrode base according to the item 1 above, wherein the mixture layer is formed by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to the surface of the conductive substrate, and performing a thermal decomposition.

[0016] [3] The electrode base according to the item 2 above, wherein the nickel compound is either of a nickel formate and a nickel acetate.

[0017] [4] A negative electrode for aqueous solution electrolysis including:

a conductive substrate having a nickel surface;
a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on the surface of the conductive substrate; and
an electrode catalyst layer including a platinum group metal or a platinum group metal compound, formed on a surface of the mixture layer.

[0018] [5] The negative electrode for aqueous solution electrolysis according to the item 4 above, wherein the electrode catalyst layer further includes a lanthanoid compound.

[0019] [6] The negative electrode for aqueous solution electrolysis according to the item 5 above, wherein the electrode catalyst layer is formed by thermally decomposing an electrode catalyst layer-forming solution including a ruthenium nitrate and a lanthanum acetate at 400°C to 600°C in an atmosphere containing oxygen.

[0020] [7] The negative electrode for aqueous solution electrolysis according to the item 6 above, wherein the electrode catalyst layer-forming solution further includes a platinum compound.

[0021] [8] The negative electrode for aqueous solution electrolysis according to the item 5 above, wherein the electrode catalyst layer includes a cerium oxide and platinum.

[0022] [9] A method for producing an electrode base including the steps of:

applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface; and
performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms.

[0023] [10] The method for producing an electrode base according to the item 9 above, wherein the nickel compound is either of a nickel formate and a nickel acetate.

[0024] [11] A method for producing a negative electrode for aqueous solution electrolysis including the steps of:

producing an electrode base by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface, and
performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms; and
forming an electrode catalyst layer by applying an electrode catalyst layer-forming solution including a platinum group metal compound to a surface of the mixture layer of the electrode base, and performing thermal decomposition in an atmosphere containing oxygen.

[0025] [12] The method for producing a negative electrode for aqueous solution electrolysis according to the item 11 above, wherein the nickel compound is either of a nickel formate or a nickel acetate.

[0026] [13] The method for producing a negative electrode for aqueous solution electrolysis according to the item 11 or 12 above, wherein the electrode catalyst layer-forming solution includes a ruthenium nitrate and a lanthanum acetate, and the electrode catalyst layer is formed by applying this electrode catalyst layer-forming solution to the surface of the mixture layer of the electrode base and then thermally decomposing it at 400°C to 600°C in an atmosphere containing oxygen.

[0027] [14] The method for producing a negative electrode for aqueous solution electrolysis according to the item 13 above, wherein the electrode catalyst-forming solution further includes a platinum compound.

[0028] [15] The method for producing a negative electrode for aqueous solution electrolysis according to the item 11 or 12 above, wherein the electrode catalyst layer-forming solution further includes a cerium nitrate.

Advantageous Effects of Invention

[0029] The electrode base of the present invention is one in which a mixture layer including metal nickel, a nickel oxide and carbon is formed on a conductive substrate having nickel on its surface by thermal decomposition of a nickel compound composed of nickel atoms, carbon atoms, oxygen atoms and hydrogen atoms such as a nickel carboxylate at a low temperature. Due to the presence of the mixture layer, even if a reverse current flows to a negative electrode in a case of, for example, emergency shutdown of electrolytic cell operation, nickel does not elute from the nickel substrate to deposit in an ion-exchange membrane. In addition, due to the presence of the mixture layer, corrosion resistance of the conductive substrate is enhanced and also adhesion between the conductive substrate and the electrode catalyst layer is increased. Furthermore, an initial potential stability is high when electrolysis is started, the electrolysis can be stably operated right from the beginning, and a negative electrode for aqueous solution electrolysis having a small hydrogen overvoltage can be provided. In particular, the effects described above is more extensive when the mixture layer is formed by thermal decomposition of a nickel carboxylate as typified by nickel formate or nickel acetate at a low temperature.

Brief Description of Drawings

[0030]

Fig. 1 is a diagram showing results of anodic polarization tests of a negative electrode of the present invention.
Fig. 2 is a diagram showing change in a negative electrode potential in one Example of the present invention.
Fig. 3 is a diagram showing change in a negative electrode potential in another Example of the present invention.
Fig. 4 is a diagram showing change in a negative electrode potential in still another Example of the present invention.
Fig. 5 is a diagram showing change in a negative electrode potential in still another Example of the present invention.

Description of Embodiments

[0031] The electrode base of the present invention is one in which a mixture layer including metal nickel, a nickel oxide and carbon atoms is provided on a surface of a conductive substrate having a nickel surface.

[0032] The electrode base of the present invention has the mixture layer including the metal nickel, nickel oxide and carbon atoms on the conductive substrate having the nickel surface, and therefore the electrode base has an advantage in which it is not broken even at the time of occurrence of anodic polarization, which is caused by reverse current occurring when electrolytic power is urgently stopped during electrolytic cell operation to shut down the operation, and after the electricity is turned on again, the operation can be performed just as the operation was performed before it was shutdown.

[0033] In the present invention, the conductive substrate having a nickel surface refers to nickel, or one in which a nickel layer is formed on a surface of a conductive material such as stainless steel, iron or copper by plating or cladding.

[0034] It is apparent that the mixture layer is a layer in which the metal nickel, the nickel oxide and the carbon atoms exist in a mixed state, from its analysis results. Though the reason why excellent properties can be obtained by providing such a mixture layer is not clear, it can be considered that the mixture layer has a good adhesion with the nickel surface of the conductive base, it has corrosion resistance even if it is subjected to an anodic polarization, and it suppresses a corrosion reaction with the conductive substrate surface.

[0035] The electrode base of the present invention may be produced by, for example, a method shown below.

[0036] The nickel compound composed of nickel atoms, carbon atoms, oxygen atoms and hydrogen atoms is applied to the surface of the conductive substrate having the nickel surface, and the resulting substrate is baked in an atmosphere containing oxygen, for example, in the atmosphere. Thus, the mixture layer including the metal nickel, the nickel oxide and the carbon atoms can be formed. The nickel compound can be applied to the conductive substrate surface by, for

example, coating the surface with a coating solution including the nickel compound. Organic acid salts of nickel can also be used as the nickel compound, and nickel carboxylates as typified by nickel formate and nickel acetate are particularly preferably used.

[0037] The mixture layer is preferably baked at a temperature of 250°C to 600°C, and more preferably 250°C to 500°C.

[0038] The baking time is preferably from 5 minutes to 60 minutes, and more preferably from 5 minutes to 30 minutes.

[0039] The thermal decomposition reaction of the nickel carboxylates such as nickel formate and nickel acetate can proceed at a lower temperature compared with the reaction of inorganic salts such as nickel nitrate and nickel sulfate, and the nickel surface of the base is not seemingly affected, because acidic gases capable of causing metal corrosion such as nitrogen oxides and sulfur oxides are not generated upon the baking. In addition, the method has features that a special removing facility is not necessary for gases exhausted from a furnace and a working environment is good.

[0040] The nickel formate and the nickel acetate, among the nickel compounds of carboxylic acid, have a high solubility in water, and therefore can be applied as an aqueous solution.

[0041] When the thickness of the mixture layer in which the metal nickel, the nickel oxide and the carbon atoms exist in a mixed state is too thick, resistance loss becomes large, whereas, when the thickness is too thin, the base protection becomes insufficient. The thickness of the mixture layer is, accordingly, preferably from 0.001 μm to 1 μm.

[0042] The negative electrode for aqueous solution electrolysis of the present invention is one in which an electrode catalyst layer is formed on the mixture layer surface of the electrode base. The electrode catalyst layer is formed of a layer including a platinum group metal or platinum group metal compound, and preferably a layer including the platinum group metal or platinum group metal compound, and a lanthanoid compound.

[0043] The components forming the electrode catalyst layer, i.e., the platinum group component including the platinum group metal or platinum group metal compound, and the lanthanoid component including the lanthanoid compound, have a low hydrogen overvoltage and a high resistance as a negative electrode used in an ion-exchange membrane electrolysis of a brine.

[0044] In the negative electrode for aqueous solution electrolysis of the present invention, owing to the mixture layer of the electrode base, the elution of the nickel from the nickel substrate can be prevented, the potential stability can be improved upon the start-up of the passage of electric current through the electrolytic cell, and the deterioration of the electrode caused by a reverse current can be effectively prevented when the electrolytic cell operation is suddenly shutdown. In addition, in the present invention, the deterioration of the electrolytic cell can be effectively prevented during storage thereof before an electric current is passed through the electrolytic cell.

[0045] The negative electrode for aqueous solution electrolysis in which the electrode catalyst layer including the platinum group metal or platinum group metal compound, and the lanthanoid compound is formed furthermore shows the properties.

[0046] The negative electrode for aqueous solution electrolysis of the present invention can be produced by, for example, a method described below.

[0047] First, the electrode base was produced in the same manner as described above. Then, the electrode catalyst layer is formed on the mixture layer surface of the electrode base.

[0048] The electrode catalyst layer can be formed by application of an electrode catalyst-forming solution in which the platinum group metal or platinum group metal compound, and optionally the lanthanoid compound are dissolved or dispersed, and then thermal decomposition in an atmosphere containing oxygen.

[0049] The elements of the platinum group may include platinum, palladium, ruthenium, iridium, and the like. When the platinum is used, it is preferable to dissolve it in the electrode catalyst layer-forming solution as a dinitrodiammine platinum salt, and when the ruthenium is used, it is preferable to dissolved it in the electrode catalyst layer-forming solution as a ruthenium nitrate. In this way, the use of a compound including no chlorine enables prevention of a negative influence on the mixture layer and the conductive substrate upon the formation of the electrode catalyst layer.

[0050] The lanthanoid elements may include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium having an atomic number of 57 to 71, and the like. In particular, the lanthanum and cerium are preferably used. When the lanthanum is used as the lanthanoid element, calboxylic acid salts thereof such as lanthanum acetate are preferably used, and when the cerium is used, cerium nitrate is preferably used.

[0051] When the electrode catalyst layer includes both the platinum component and the lanthanoid component, the atomic ratio of the platinum group atoms to the lanthanoid atoms is preferably from 30/70 to 90/10 in the electrode catalyst layer-forming solution.

[0052] The electrode catalyst layer is formed by applying the electrode catalyst layer-forming solution to the mixture layer surface of the electrode base, and drying and baking (thermal decomposition) it. The thickness may be controlled by repeating the procedure of applying, drying and baking several times. The electrode catalyst layer-forming solution applied is dried at 60 to 80°C for 10 to 20 minutes, and it is baked at a temperature of 400 to 600°C for 10 to 20 minutes in an atmosphere containing oxygen.

[0053] The thickness of the electrode catalyst layer formed is preferably from 3 to 6 μm.

[0054] The thus formed electrode catalyst layer has a high catalytic activity in a hydrogen generation reaction as a negative electrode for aqueous solution electrolysis, and can maintain a hydrogen overvoltage low for a long time when electrolysis is performed at not only a low current density but also a high current density. In addition, the negative electrode surface has a good current uniformity, and the ion-exchange membrane can be prevented from the contamination with the heavy metals, even if the electrolysis is performed with the ion-exchange membrane being in contact with the negative electrode.

[0055] In the negative electrode for aqueous solution electrolysis having this electrode catalyst layer, the electrode catalyst layer can be prevented from the deterioration due to oxidation and the like, even if the negative electrode is exposed to the atmosphere.

[0056] The electrode catalyst layer formed by applying the electrode catalyst layer-forming solution to the electrode base, and then performing the thermal decomposition in the atmosphere containing oxygen does not include chlorine compounds as a component other than the metals forming the metal compound which forms the electrode catalyst layer, and therefore, it can be thought that any negative influence is not exerted on the conductive base, the mixture layer and the electrode catalyst layer.

[0057] Conventionally, when ruthenium oxide, which serves as the electrode catalyst, is formed by heat in an atmosphere containing oxygen, ruthenium chloride is generally used, and therefore the electrode catalyst layer formed has a chlorine compound. It is preferable to use salts from which chlorine compounds are not generated such as ruthenium nitrate as in the present invention.

[0058] In the present invention, when the lanthanoid carboxylate is used together with the ruthenium component, it is preferable to use at least one lanthanum carboxylate selected from the group consisting of, for example, lanthanum acetate, lanthanum formate and lanthanum oxalate, and more preferably lanthanum acetate having a high solubility.

[0059] In particular, it can be thought that an oxycarbonate or carbonate may be generated from the lanthanum carboxylate in the thermal decomposition step forming the electrode catalyst layer in an atmosphere containing oxygen having a temperature of 400 to 600°C.

[0060] As a result, it is confirmed that the carbon atoms uniformly exist in the electrode catalyst layer formed. In addition, it can be thought that the presence of the compound having carbon atoms in the electrode catalyst layer due to the thermal decomposition of the lanthanum carboxylate, also contributes to the electrochemical properties of the negative electrode for aqueous solution electrolysis.

[0061] The electrode properties of the negative electrode for aqueous solution electrolysis of the present invention are not deteriorated even if the electrolytic cell operation is shutdown, the electrode is taken out from the electrolytic cell, exposed to the atmosphere, and put in the electrolytic cell again, and then the operation is resumed. This may show that the properties of the electrode catalyst layer formed from the ruthenium nitrate and the lanthanum carboxylate are not changed in the atmosphere, and the conductive substrate of the electrode is covered with the dense mixture layer and electrode catalyst layer.

[0062] The deterioration due to the elution of the metal component from the conductive substrate is not caused, because the conductive substrate of the electrode is covered with the dense mixture layer and electrode catalyst layer. As a result, an advantage can be obtained in which it is not necessary to prevent the negative influence on the ion-exchange membrane caused by the elution of the metal component and the stable operation can be performed for a long term.

[0063] To the electrode catalyst layer-forming solution, which is used for forming the electrode catalyst layer, may be added a component including a platinum compound having no chlorine atom in addition to the ruthenium compound and the lanthanum carboxylate, whereby the platinum may be contained in the electrode catalyst layer.

[0064] The reason why some properties can be obtained by containing the platinum in the electrode catalyst layer in addition to the ruthenium and lanthanum is not made clear, but the electrode catalyst layer is prevented from the performance deterioration after the passage of electric current, and an effect of inhibiting abrasion of the electrode catalyst layer can be obtained.

[0065] When the platinum compound having no chlorine atom is added, the atomic ratio of Pt/La in the electrode catalyst layer-forming solution is preferably 0.005 or more. When the ratio is less than 0.005, sufficient effects cannot be obtained.

[0066] As the platinum compound having no chlorine atom, at least one of dinitrodiammine platinum and hexahydroxoplatinum acid may be used. A sufficient catalytic activity can be maintained in a hydrogen generation reaction for a long term, even if the thickness of the electrode catalyst layer is 5 μm or less, because the abrasion of the electrode catalyst layer can be more effectively inhibited due to the presence of the platinum.

[0067] The electrode catalyst layer is formed by heat-treatment in the atmosphere containing oxygen at a temperature of preferably 400°C to 600°C, and more preferably 460°C to 540°C. When the temperature is lower than 400°C, it is hard to form a coating layer having a high electrode catalytic activity in the hydrogen generation reaction; whereas when it is higher than 600°C, the conductive substrate becomes easily oxidized. The atmosphere containing oxygen may include the air, an atmosphere containing 100% by volume of oxygen, and the like.

[0068] It can be thought that when the electrode catalyst layer includes the platinum, the corrosion of the nickel base may be easily caused due to galvanic corrosion, because the platinum have a more noble oxidation-reduction potential. According to the electrode base of the present invention, however, the corrosion reaction of the electrode base can be inhibited, because it has the mixture layer including the metal nickel, nickel oxide and carbon atoms on the conductive substrate surface, and therefore it is also possible to inhibit the corrosion of nickel in the electrode base in the case where the electrode base includes the electrode catalyst layer including the platinum.

[0069] When the noble metal is used in the electrode catalyst layer of the negative electrode for aqueous solution electrolysis, it is feared that the elution of the nickel of the base, caused during the storage before the passage of electric current or during the suspension of the passage of electric current, damages the ion-exchange membrane. This phenomenon is more markedly shown in a condition in which the negative electrode is stored after the electrolysis is performed or the passage of electric current is stopped than a condition in which the negative electrode for aqueous solution electrolysis is not used in the electrolysis yet.

[0070] This may be because the nickel surface of the base is likely to give rise to the corrosion reaction after the electrolysis, though the nickel surface of the base is covered with the stable oxide layer before the electrolysis operation.

[0071] Examples and Comparative Examples described below show comparisons of a nickel contamination into an ion-exchange membrane when a negative electrode for aqueous solution electrolysis was brought into contact with an ion-exchange membrane after the start of the passage of electric current. The elusion of nickel was not observed from the unelectrolyzed sample in the mixture layer formed from the nickel carboxylate; whereas the elusion of nickel was observed in a case where nickel sulfate was used as a coating material for forming the mixture layer, despite the sample was not subjected to the electrolysis. The component analysis of this mixture layer shows that the nickel sulfate is not thermally decomposed and remains in a salt form, and therefore it can be understood that the stable mixture layer is not formed.

[0072] The nickel oxide is more easily formed when baking at a high temperature, but the initial potential stability at the start of electrolysis can be more improved when the mixture layer is formed at a lower temperature.

[0073] As shown in Examples and Comparative Examples described below, the mixture layer including the metal nickel, the nickel oxide and the carbon atoms is characterized by a higher corrosion resistance than the nickel oxide layer formed by baking the nickel base in the atmosphere when anodic polarization occurs, and characterized that the destruction of the mixture layer is not advanced even when the anodic polarization occurs.

[0074] Consequently, the destruction of the mixture layer is not advanced even when the negative electrode is anodically polarized to flow the reverse current, which occurs, for example, at emergency stop of electrolysis during the electrolytic cell operation, and the same performance as that before the operation is shutdown can be shown after the electric current is passed again.

[0075] This shows that in the present invention the nickel carboxylate, which can be formed at a low temperature, is preferably used for the mixture layer formed on the surface of the electrode base, in the negative electrode for aqueous solution electrolysis having the electrode catalyst layer including the platinum group metal or the compound thereof.

[0076] It is also shown that the mixture layer formed by the thermal decomposition of nickel carboxylate is preferable, in a case where the mixture layer is formed in low-temperature baking conditions for improving the potential stability after the start of the passage of electric current through the electrolytic cell.

Examples

[0077] The present invention will be explained below, showing Examples and Comparative Examples.

Example 1

Anodic Polarization Test of Electrode Base

[0078] A surface of a nickel expanded metal having a thickness of 0.9 mm, a length of 20 mm and a width of 20 mm was sandblasted with alumina particles having a particle size of 50 μm to roughen the surface, thereby obtaining a conductive substrate for a sample.

[0079] The conductive substrate was immersed in 30% by mass sulfuric acid having a temperature of 60°C for 10 minutes to perform etching, thereby removing the surface oxide coating film and the remaining alumina particles.

[0080] Next, an aqueous solution including 0.1 mol/L nickel formate (II) dihydrate (manufactured by Wako Pure Chemical Industries, Ltd.) was prepared to be used as a coating solution for a mixture layer. The coating solution for a mixture layer was applied to the nickel expanded metal which had been surface-treated, and the resulting metal was dried at 60°C for 3 minutes and baked in a muffle furnace (KDF-P80G manufactured by Denken Co,. Ltd.) at 300°C for 10 minutes to give a sample 1 (electrode base) for an anodic polarization test. Using the sample 1 as a negative electrode and a 20 mm x 20 mm nickel expanded metal as a positive electrode, a first pre-electrolysis was performed at a current density

of 10 kA/m^2 for one hour using an aqueous 32% by mass sodium hydroxide solution having a temperature of 90°C as an electrolytic solution.

[0081] After the pre-electrolysis was stopped, a first anodic polarization test was performed in which the direction of the passage of electric current was immediately reversed, the anodic polarization test sample 1 was subjected to anodic polarization at a current density of 10 A/m^2, a change in the electrode potential of the anodic polarization test sample 1 to a mercury/mercury oxide reference electrode in an electric quantity was determined until the electrode potential was suddenly increased from the oxidation-reduction potential of the nickel to a noble potential, and the passage of electric current was intercepted. The results are shown in Fig. 1 as Test 1.

[0082] Subsequently, the direction of the passage of electric current was reversed, and a second pre-electrolysis was performed in the same manner as in the first electrolysis. After that, a second anodic polarization test was performed. The results are shown in Fig. 1 as Anodic polarization test 2.

[0083] Furthermore, a third pre-electrolysis and anodic polarization was performed in the same manner as above, and the results are shown in Fig. 1 as Anodic polarization test 3.

Comparative Example 1

Comparative Anodic Polarization Test of Oxide Layer

[0084] Instead of the anodic polarization test sample 1 in Example 1, a comparative anodic polarization test sample 1 was made by baking a conductive substrate at 500°C for 10 minutes to form a nickel oxide coating film. A first comparative anodic polarization test, a second comparative anodic polarization test and a third comparative anodic polarization test were performed in the same manner as in Example 10.

[0085] The results are shown in Fig. 1 as Comparative anodic polarization test 1, Comparative anodic polarization test 2 and Comparative anodic polarization test 3.

[0086] The results show that the electrode base of the present invention has a higher resistance to an electric current generated by the anodic polarization and oxidizing the negative electrode than that of the oxide coating film formed by the oxidation of the substrate nickel formed in the atmosphere.

Example 2

Confirmation of Thermal Decomposition Products of Nickel Formate

[0087] The aqueous nickel formate solution prepared in Example 1 was applied to a nickel plate and a procedure of baking at 300°C in the atmosphere was repeated ten times to produce a sample 1 for confirmation of thermal decomposition products.

[0088] Ten portions on the surface coated with nickel formate and baked of the sample 1 for confirmation of thermal decomposition products were measured using an energy dispersive X-ray analyzer (Genesis-XM 2 manufactured by EDAX Inc.).

[0089] The abundance ratio of nickel, oxygen and carbon was 45.5 : 39.8 : 14.7 by atom on an average of the ten portions.

[0090] After that, a sample 2 for confirmation of thermal decomposition products was produced in the same manner as above except that the baking temperature was changed to 500°C, and the measurement was performed in the same manner as above. The abundance ratio of nickel, oxygen and carbon was 51.4 : 36.7 : 11.9 by atom on an average of the ten portions.

[0091] The presence of carbon could be confirmed on all of the samples.

Comparative Example 2

[0092] A comparative sample 1 for confirmation of thermal decomposition products was produced by repeating the procedure of baking at 300°C in the atmosphere ten times in the same manner as in Example 2 , except that the aqueous nickel formate solution was not applied to the nickel plate. The products on the surface were measured in the same manner as in Example 2. The abundance ratio of nickel, oxygen and carbon was 91.1 : 8.9 : 0 by atom.

[0093] After that, a comparative sample 2 for confirmation of thermal decomposition products was produced in the same manner as above except that the baking temperature was changed to 500°C, and the same measurement as above was performed. The abundance ratio of nickel, oxygen and carbon was 80.9 : 19.1 : 0 by atom on an average of ten portions.

[0094] It was found that there was no carbon on all of the comparative samples for confirmation of thermal decomposition products.

Examples 3 and 4, and Comparative Example 3

[0095] Each of samples of nickel acetate, nickel formate and nickel nitrate which were heated at 300°C and 500°C in the atmosphere for 10 minutes was measured using an X-ray diffractometer (X'Pert PRO MPD manufactured by PANalytical, target: copper, accelerating voltage: 45 kV). The measurement results are shown in Table 1 as an atomic ratio of nickel oxide (NiO) or nickel metal (Ni).

[0096]

[Table 1]

	Nickel compound	Thermal decomposition temperature (°C)	Nio (%)	Ni (%)	Undecomposed salt (%)
Example 3	Nickel acetate	300	65	35	0
	Nickel acetate	500	83	17	0
Example 4	Nickel formate	300	69	31	0
	Nickel formate	500	96	4	0
Comparative example 3	Nickel nitrate	300	84	0	16
	Nickel nitrate	500	100	0	0

Example 5

[0097] The nickel formate powder used in Example 1 was heated at 300°C and 500°C in the atmosphere to perform thermal decomposition. The resulting sample was measured for an X-ray absorption fine structure (XAFS) using beam line BL-12C in Radiation Science Research Facility (Photon Factory) of High Energy Acceleration Research Organization.

[0098] The measurement was performed under conditions described below. Spectrometer: an Si (111) two crystal spectrometer. Mirror: a focusing mirror. Absorption edge: a transmission method.
Detector used: Ionization chamber. The abundance ratio was obtained using XANES spectra.

[0099] The measured results were obtained according to a general analysis method of XANES spectra in which a computation process was performed so that a difference between a synthesized peak which was synthesized from the standard peaks of the metal nickel and the nickel oxide which could be thought as the components based on the measured peak, and a measured peak becomes the minimum in a least squares method. The percentage was shown as the abundance ratio of each component.

[0100] The nickel formate which had been thermally decomposed at 300°C had 31.6% of metal nickel and 68.4% of nickel oxide.

[0101] The nickel formate which had been thermally decomposed at 500°C had 18.6% of metal nickel and 81.4% of nickel oxide.

Example 6

[0102] A surface of a nickel expanded metal having a thickness of 0.9 mm, a length of 20 mm and a width of 20 mm was sandblasted with alumina particles having a particle size of 50 μm to roughen the surface, thereby obtaining a conductive substrate for a sample.

[0103] The conductive substrate was immersed in 30% by mass sulfuric acid having a temperature of 60°C for 10 minutes to perform etching, thereby removing the surface oxide coating film and the remaining alumina particles.

[0104] Next, an aqueous solution including 0.1 mol/L nickel acetate (II) tetrahydrate (manufactured by Wako Pure Chemical Industries, Ltd.) was prepared to be used as a coating solution for a mixture layer. The coating solution for a mixture layer was applied to the nickel expanded metal which had been surface-treated, and the resulting metal was dried at 60°C for 3 minutes and baked in a muffle furnace (KDF-P80G manufactured by Denken Co,. Ltd.) at 300°C for 10 minutes to give a sample 1-1 (electrode base) on which the mixture layer was formed, or baked at 500°C for 10 minutes to give a sample 1-2 (electrode base) on which the mixture layer was formed.

[0105] After that, an electrode catalyst layer-forming solution 1 which was a solution of ruthenium nitrate-lanthanum acetate-dinitrodiammine platinum nitrate in an atomic ratio of Ru : La : Pt = 1: 1 : 0.05 using a solution of ruthenium nitrate in nitric acid (manufactured by Tanaka Kikinzoku Kogyo Co., Ltd.), a lanthanum acetate n-hydrate (manufactured by Wako Pure Chemical Industries, Ltd.) and a dinitrodiammine platinum nitrate solution (manufactured by Tanaka

Kikinzoku Kogyo Co., Ltd.).

[0106] The electrode catalyst layer-forming solution 1 was coated to the mixture layer-formed sample 1-1 or 1-2 previously produced and was dried, and a procedure of baking at 500°C for 10 minutes was repeated five times to produce test negative electrodes 1-1 and 1-2.

[0107] Electrolysis was performed in an aqueous solution including 30% by mass of sodium hydroxide at 90°C at a current density of 10 kA/m^2 for one hour using the test negative electrode 1-1 or 1-2 produced and the same nickel expanded metal as that used in the base of the test negative electrode 1-1 as a positive electrode, and electrolysis was continued at a current density of 20 kA/m^2 for further one hour.

[0108] The surfaces of the test negative electrodes 1-1 and 1-2 were observed after the electrolysis by using a scanning electron microscope (JSM-6490 manufactured by JEOL Ltd.) about peeling-off of the coating film, and the like. The results are shown in Table 2.

Elution Test of Nickel after Electrolysis

[0109] The test negative electrode 1-1 or 1-2 after the electrolysis was brought into close contact with a positive ion-exchange membrane (N-2030 manufactured by Du Pont), which had been immersed in an aqueous sodium hydroxide solution having a pH of 11, and a pressure of 981 Pa was applied thereto, which was sealed in a polyethylene bag and allowed to stand for 24 hours.

[0110] After that, nickel in the positive ion-exchange membrane taken out was detected using an ICP emission spectrophotometric analyzer (ICPS-8100 manufactured by Shimadzu Corporation). The results are shown in Table 2 as a nickel deposition amount per 4 cm^2 area.

Example 7

[0111] A test negative electrode 2-1 whose mixture layer was formed at 300°C and a test negative electrode 2-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 6, except that nickel formate was used as the mixture layer-forming material instead of the nickel acetate, and the evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Example 8

[0112] A mixture layer-formed sample 3-1 whose mixture layer was formed at 300°C and a mixture layer-formed sample 3-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 6.

[0113] Then, cerium nitrate and a dinitrodiammine platinum salt were dissolved in 8% by mass nitric acid so that the atomic ratio of Pt : Ce was 1:1 to prepare an electrode catalyst layer-forming solution 2 having a total concentration of cerium and platinum of 5% by mass.

[0114] The electrode catalyst layer-forming solution 2 was applied and dried, and a procedure of baking at 500°C for 10 minutes was repeated five times to produce test negative electrodes 3-1 and 3-2. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Example 9

[0115] A mixture layer-formed sample 4-1 whose mixture layer was formed at 300°C and a mixture layer-formed sample 4-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 7.

[0116] Next, the electrode catalyst layer-forming solution 2 was applied to the sample and dried, and a procedure of baking at 500°C for 10 minutes was repeated five times in the same manner as in Example 8 to produce test negative electrodes 4-1 and 4-2. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 4

[0117] A comparative negative electrode 2-1 whose mixture layer was formed at 300°C and a comparative negative electrode 2-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 6, except that nickel sulfate was used for the mixture layer instead of nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 5

[0118] A comparative negative electrode 2-1 whose mixture layer was formed at 300°C and a comparative negative electrode 2-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 6, except that nickel nitrate was used for the mixture layer instead of the nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 6

[0119] A comparative negative electrode 3 was produced in the same manner as in Example 6, except that the mixture layer was not formed. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 7

[0120] A comparative negative electrode 4 was produced in the same manner as in Example 6, except that a mixture layer was formed by baking the conductive substrate at 500°C in the atmosphere without applying a nickel salt such as nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 8

[0121] A comparative negative electrode 5-1 whose mixture layer was formed at 300°C and a comparative negative electrode 5-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 8, except that nickel sulfate was used for the mixture layer instead of the nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 9

[0122] A comparative negative electrode 6-1 whose mixture layer was formed at 300°C and a comparative negative electrode 6-2 whose mixture layer was formed at 500°C were produced in the same manner as in Example 8, except that nickel nitrate was used for the mixture layer instead of the nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 10

[0123] A comparative negative electrode 7 was produced in the same manner as in Example 8, except that the mixture layer was not formed. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

Comparative Example 11

[0124] A comparative negative electrode 8 was produced in the same manner as in Example 8, except that a mixture layer was formed by baking the conductive substrate at 500°C in the atmosphere without applying a nickel salt such as nickel acetate. The evaluation test was performed in the same manner as in Example 6. The results are shown in Table 2.

[0125]

[Table 2]

		Intermediate layer			Ni deposition amount (μg/4cm^2)	Elements contained in electrode catalyst	Presence or absence of surface peeling-off
		Coating solution	concentration of coating solution	Baking temperature			
Example 6	Test negative electrode 1-1	Nickel acetate	0.1 mol/L	300ºC	4.7	Ru La Pt	Absence
	Test negative electrode 1-2	Nickel acetate	0.1 mol/L	500 ºC	4.0	Ru La Pt	Absence
Example 7	Test negative electrode 2-1	Nickel formate	0.1 mol/L	300 ºC	7.5	Ru La Pt	Absence
	Test negative electrode 2-2	Nickel formate	0.1 mol/L	500 ºC	7.0	Ru La Pt	Absence
Example 8	Test negative electrode 3-1	Nickel acetate	0.1 mol/L	300ºC	9.0	Ce Pt	Absence
	Test negative electrode 3-2	Nickel acetate	0.1 mol/L	500 ºC	7.0	Ce Pt	Absence
Example 9	Test negative electrode 4-1	Nickel formate	0.1 mol/L	300 ºC	8.0	Ce Pt	Absence
	Test negative electrode 4-2	Nickel formate	0.1 mol/L	500 ºC	9.0	Ce Pt	Absence
Comparative example 4	Comparative test negative electrode 1-1	Nickel sulfate	0.1 mol/L	300ºC	14.3	Ru La Pt Ru	Absence
	Comparative test negative electrode 1-2	Nickel sulfate	0.1 mol/L	500 ºC	10.0	Ru La Pt	Absence
Comparative example 5	Comparative test negative electrode 2-1	Nickel nitrate	0.1 mol/L	300 ºC	29.0	Ru La Pt	Absence
	Comparative test negative electrode 2-2	Nickel nitrate	0.1 mol/L	500ºC	6.0	Ru La Pt	Absence
Comparative example 6	Comparative test negative electrode 3	No formation			15.3	Ru La Pt	Absence
Comparative example 7	Comparative test negative electrode 4	Oxidation in the atmosphere		500 ºC	4.0	Ru La Pt	Absence
Comparative example 8	Comparative test negative electrode 5-1	Nickel sulfate	0.1 mol/L	300 ºC	23.0	Ce Pt	Absence
	Comparative test negative electrode 5-2	Nickel sulfate	0.1 mol, L	500 ºC	18.0	Ce Pt	Absence

(continued)

		Intermediate layer			Ni deposition amount (μg/4cm^2)	Elements contained in electrode catalyst	Presence or absence of surface peeling-off
		Coating solution	concentration of coating solution	Baking temperature			
Comparative example 9	Comparative test negative electrode 6-1	Nickel nitrate	0.1 mol/L	300 ºC	19.0	Ce Pt	Absence
	Comparative test negative electrode 6-2	Nickel nitrate	0.1 mol/L	500 ºC	13.0	Ce Pt	Absence
Comparative example 10	Comparative test negative electrode 7	No formation			18.0	Ce Pt	Absence
Comparative example 11	Comparative test negative electrode 8	Oxidation in the atmosphere		500 ºC	9.0	Ce Pt	Absence

Example 10

[0126] A mixture layer was formed at 300°C in the same manner as in Example 6 except that a nickel expanded metal having a thickness of 0.15 mm was used as the conductive substrate. The same electrode catalyst layer-forming solution 1 as in Example 6 was applied thereto, and a test negative electrode 5 was produced in the same manner as in Example 6.

Evaluation of Electrode Performance

[0127] On a test electrolytic cell were mounted the test negative electrode 5 produced above as the negative electrode and an electrode for generating chlorine whose base was a titanium expanded metal (DSE JP-202 manufactured by Permelec Electrode Ltd.) as a positive electrode, and a negative electrode room and a positive electrode room were divided with a positive ion-exchange membrane (N-2030 manufactured by Du Pont) treated with an aqueous solution of 2% by mass sodium hydroxide. A zero-gap ion-exchange membrane in which the negative electrode, the ion-exchange membrane and the positive electrode were integrally touched was assembled. The electrolytic cell was stored for 15 hours after the assembly without filling an electrolytic solution therein.

[0128] Then, while a brine having a concentration of 200 g/L as an anolyte and an aqueous sodium hydroxide solution having a concentration of 32% by mass as a catholyte were circulated, electrolysis was performed at an operation temperature of 90°C at a current density of 6 kA/m^2.

[0129] In a 100-day electrolysis term, electrolysis was stopped for two days of the 51st day and 52nd day, and the electrolytic cell was disassembled and stored under exposure to the atmosphere. After the storage, the electrolysis was performed, but the increase of the electrolytic cell voltage was not observed and the current efficiency was kept at 97%.

[0130] After the 100-day electrolysis, the electrolytic cell was disassembled, and the ion-exchange membrane was observed. The deposition of nickel was not found.

Evaluation of Short-Circuit Performance

[0131] Only ion-exchange membrane was exchanged in the test electrolytic cell which was disassembled for the evaluation of electrode performance, and the electrolysis was performed again. After it was confirmed that the flowing current was stabled at a current density of 6 kA/m^2, an electrolysis current was stopped, and supply and discharge of the anolyte and the catholyte was stopped in a state in which the positive electrode and the negative electrode were short circuited, and the electrolytic cell was allowed to stand at 70°C for 2 hours.

[0132] After that, the electrolysis operation was restarted at a current density of 6 kA/m^2, and a test for determining degradation of performances after 10 days was repeated twice.

[0133] After the first short-circuit test, the electrolytic cell voltage was increased by 0.004 V and the hydrogen over-voltage was increased by 0.7 mV.

[0134] After the second short-circuit test, the electrolytic cell voltage was increased by 0.004 V and the hydrogen overvoltage was increased by 2.4 mV. That is to say, the increase of the electrolytic cell voltage was only 0.008 V and the increase of the hydrogen overvoltage was only 3.1 mV after the second short-circuit test, compared to those before the first short-circuit test.

Comparative Example 12

[0135] A comparative test negative electrode 9 was produced in the same manner as in Example 10, except that a mixture layer was formed by baking a conductive substrate at 500°C for 10 minutes instead of formation of a mixture layer by the application of the nickel salt and the thermal decomposition, and the electrolysis was performed in the same manner as in Example 10. The initial electrolytic cell voltage showed a voltage 0.010 V higher than that in Example 10. In a 100-day electrolysis term, electrolysis was stopped for two days of the 51st day and 52nd day, and the electrolytic cell was disassembled and stored under exposure to the atmosphere, in the same manner as in Example 10. The increase of the electrolytic cell voltage was not observed in the subsequent electrolysis, and the current efficiency was kept at 97%. However, the electrolytic cell voltage was increased by 0.010 V. In addition, the nickel deposition to the ion-exchange membrane was not confirmed after the electrolytic cell was disassembled.

[0136] The short-circuit test was performed twice in the same manner as in Example 10.

[0137] After the first short-circuit test, the electrolytic cell voltage was increased by 0.007 V, and the hydrogen overvoltage was increased by 7.0 mV.

[0138] After the second short-circuit test, the electrolytic cell voltage was increased by 0.018 V, and the hydrogen overvoltage was increased by 6.2 mV. That is to say, the electrolytic cell voltage was increased by 0.025 V and the hydrogen overvoltage was increased by 13.2 mV after the second short-circuit test, compared to those before the first short-circuit test.

[0139] The present application claims benefit of priority of Japanese Patent Application No. 2010-032578 filed on February 17, 2010, the contents of which are hereby incorporated by reference.

Industrial Applicability

[0140] The negative electrode for aqueous solution electrolysis of the present invention has a low hydrogen overvoltage; nickel on the conductive substrate surface does not elute even when the passage of electric current is stopped; only a small amount of nickel is deposited in the ion-exchange membrane when it is used as a negative electrode in the ion-exchange membrane electrolytic cell; the operation can be stably performed for a long term; the electrolysis voltage is kept stable from the beginning of the electrolysis even when the platinum electrode catalyst layer is formed; and it is possible to stably operate the electrolytic cell. The negative electrode for aqueous solution electrolysis of the invention having the effects described above is preferably used for the electrolysis of an aqueous solution of an alkali metal halide, and the like.

Claims

1. An electrode base comprising a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on a surface of a conductive substrate having a nickel surface.

2. The electrode base according to claim 1, wherein the mixture layer is formed by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to the surface of the conductive substrate, and performing a thermal decomposition.

3. The electrode base according to claim 2, wherein the nickel compound is either of a nickel formate and a nickel acetate.

4. A negative electrode for aqueous solution electrolysis comprising:

   a conductive substrate having a nickel surface;
   a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on the surface of the conductive substrate; and
   an electrode catalyst layer including a platinum group metal or a platinum group metal compound, formed on a surface of the mixture layer.

5. The negative electrode for aqueous solution electrolysis according to claim 4, wherein the electrode catalyst layer

further includes a lanthanoid compound.

6. The negative electrode for aqueous solution electrolysis according to claim 5, wherein the electrode catalyst layer is formed by thermally decomposing an electrode catalyst layer-forming solution including a ruthenium nitrate and a lanthanum acetate at 400°C to 600°C in an atmosphere containing oxygen.

7. The negative electrode for aqueous solution electrolysis according to claim 6, wherein the electrode catalyst layer-forming solution further includes a platinum compound.

8. The negative electrode for aqueous solution electrolysis according to claim 5, wherein the electrode catalyst layer includes a cerium oxide and platinum.

9. A method for producing an electrode base comprising the steps of:

applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface; and
performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms.

10. The method for producing an electrode base according to claim 9, wherein the nickel compound is either of a nickel formate and a nickel acetate.

11. A method for producing a negative electrode for aqueous solution electrolysis comprising the steps of:

producing an electrode base by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface, and performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms; and
forming an electrode catalyst layer by applying an electrode catalyst layer-forming solution including a platinum group metal compound to a surface of the mixture layer of the electrode base, and performing thermal decomposition in an atmosphere containing oxygen.

12. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11, wherein the nickel compound is either of a nickel formate or a nickel acetate.

13. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11 or 12, wherein the electrode catalyst layer-forming solution includes a ruthenium nitrate and a lanthanum acetate, and the electrode catalyst layer is formed by applying this electrode catalyst layer-forming solution to the surface of the mixture layer of the electrode base and then performing thermal decomposition at 400°C to 600°C in an atmosphere containing oxygen.

14. The method for producing a negative electrode for aqueous solution electrolysis according to claim 13, wherein the electrode catalyst-forming solution further includes a platinum compound.

15. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11 or 12, wherein the electrode catalyst layer-forming solution further includes a cerium nitrate.

Amended claims under Art. 19.1 PCT

1. (Amended) An electrode base for forming an electrode catalyst layer comprising a mixture layer including metal nickel, a nickel oxide and carbon atoms formed on a surface of a conductive substrate having a nickel surface.

2. The electrode base according to claim 1, wherein the mixture layer is formed by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to the surface of the conductive substrate, and performing a thermal decomposition.

3. The electrode base according to claim 2, wherein the nickel compound is either of a nickel formate and a nickel

acetate.

4. A negative electrode for aqueous solution electrolysis comprising:

a conductive substrate having a nickel surface;
a mixture layer including metal nickel, a nickel oxide and carbon atoms, formed on the surface of the conductive substrate; and
an electrode catalyst layer including a platinum group metal or a platinum group metal compound, formed on a surface of the mixture layer.

5. The negative electrode for aqueous solution electrolysis according to claim 4, wherein the electrode catalyst layer further includes a lanthanoid compound.

6. The negative electrode for aqueous solution electrolysis according to claim 5, wherein the electrode catalyst layer is formed by thermally decomposing an electrode catalyst layer-forming solution including a ruthenium nitrate and a lanthanum acetate at 400°C to 600°C in an atmosphere containing oxygen.

7. The negative electrode for aqueous solution electrolysis according to claim 6, wherein the electrode catalyst layer-forming solution further includes a platinum compound.

8. The negative electrode for aqueous solution electrolysis according to claim 5, wherein the electrode catalyst layer includes a cerium oxide and platinum.

9. (Amended) A method for producing an electrode base for forming an electrode catalyst layer, the method comprising the steps of:

applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface; and
performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms.

10. The method for producing an electrode base according to claim 9, wherein the nickel compound is either of a nickel formate and a nickel acetate.

11. A method for producing a negative electrode for aqueous solution electrolysis comprising the steps of:

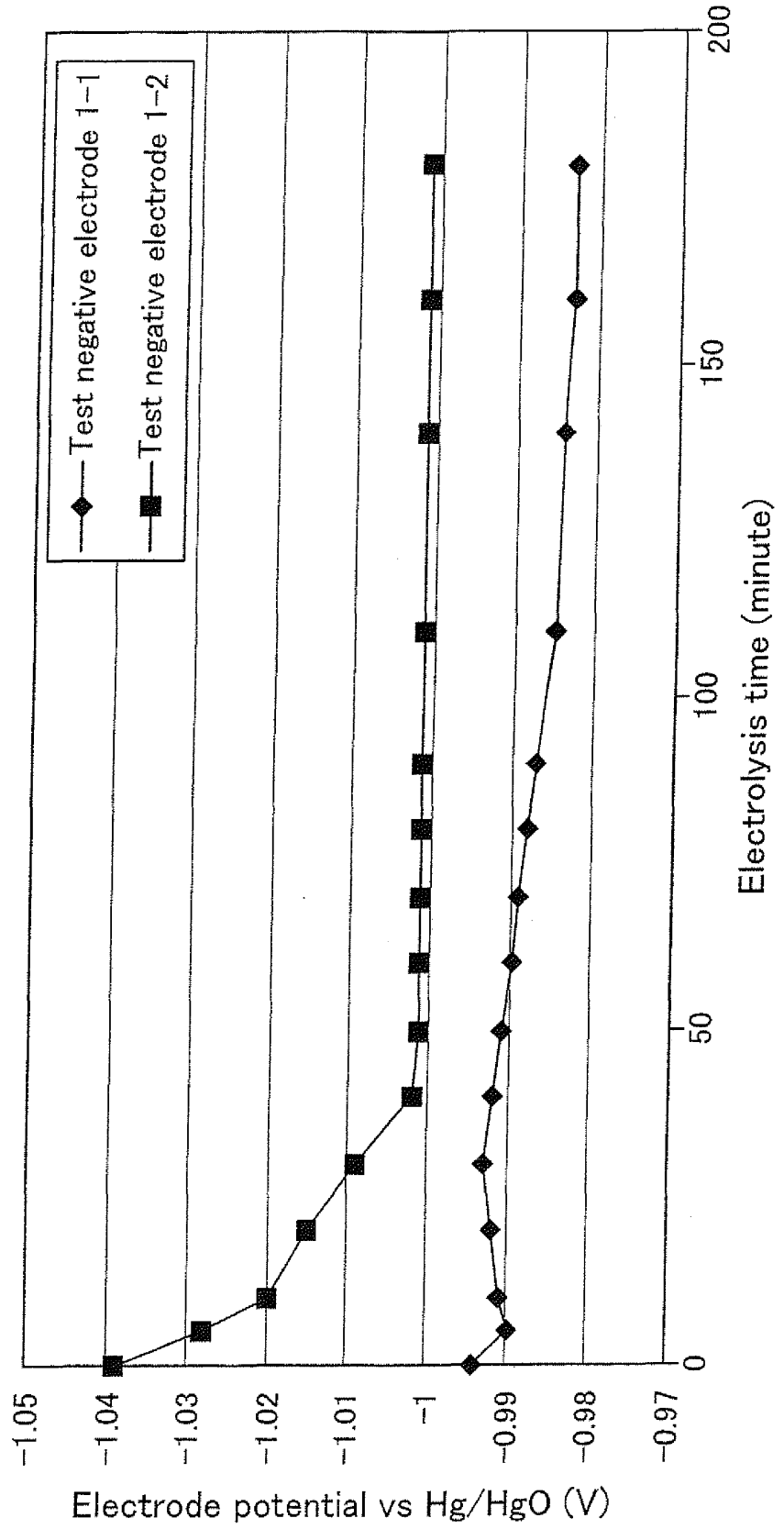
producing an electrode base by applying a nickel compound including a nickel atom, a carbon atom, an oxygen atom and a hydrogen atom to a surface of a conductive substrate having a nickel surface, and performing thermal decomposition at 250°C to 600°C in an atmosphere containing oxygen, thereby forming a mixture layer including metal nickel, a nickel oxide and carbon atoms; and
forming an electrode catalyst layer by applying an electrode catalyst layer-forming solution including a platinum group metal compound to a surface of the mixture layer of the electrode base, and performing thermal decomposition in an atmosphere containing oxygen.

12. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11, wherein the nickel compound is either of a nickel formate or a nickel acetate.

13. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11 or 12, wherein the electrode catalyst layer-forming solution includes a ruthenium nitrate and a lanthanum acetate, and the electrode catalyst layer is formed by applying this electrode catalyst layer-forming solution to the surface of the mixture layer of the electrode base and then performing thermal decomposition at 400°C to 600°C in an atmosphere containing oxygen.

14. The method for producing a negative electrode for aqueous solution electrolysis according to claim 13, wherein the electrode catalyst-forming solution further includes a platinum compound.

15. The method for producing a negative electrode for aqueous solution electrolysis according to claim 11 or 12, wherein the electrode catalyst layer-forming solution further includes a cerium nitrate.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100
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0
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-1.04
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-1.01
-1
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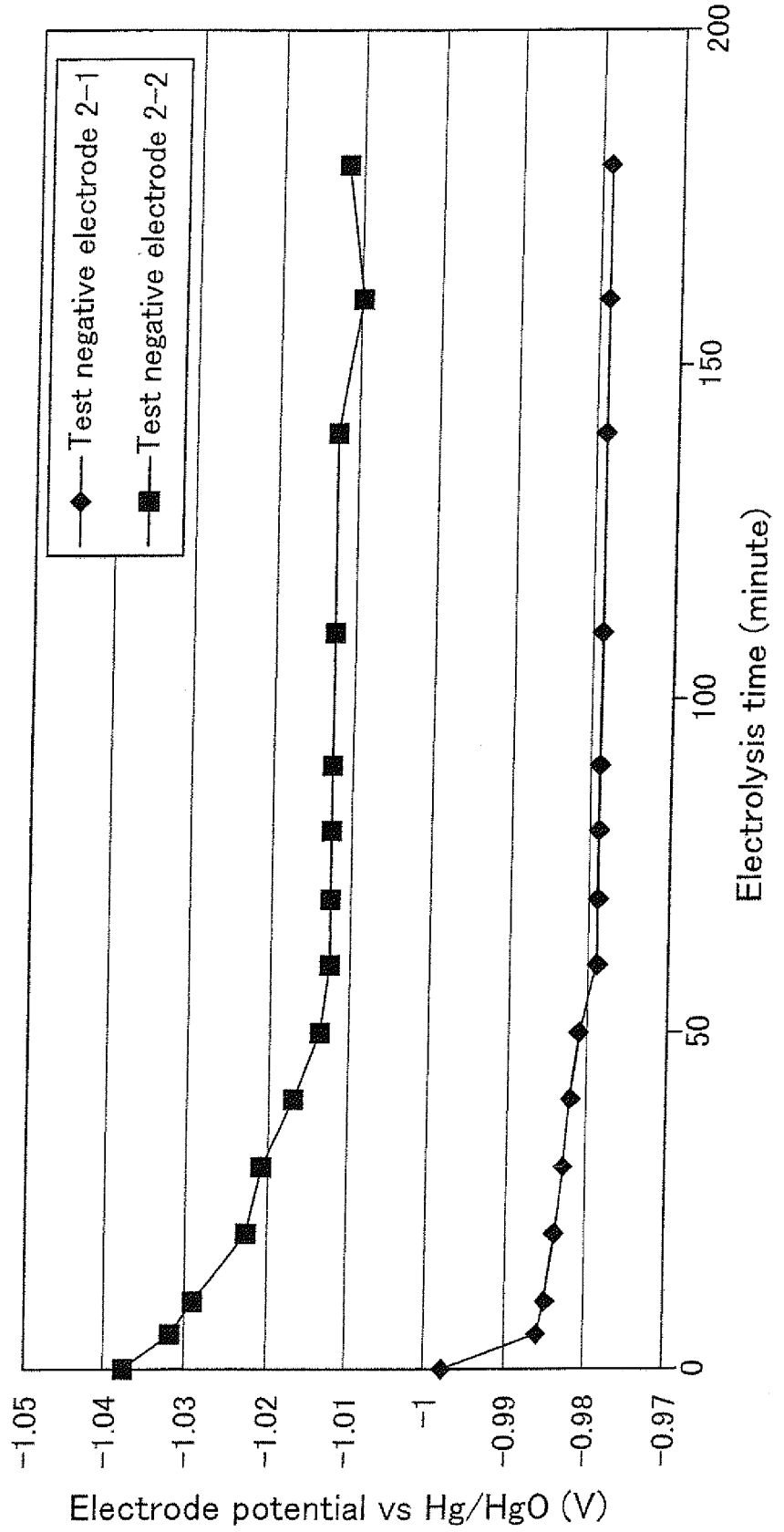
Electrode potential vs Hg/HgO (V)

FIG. 1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Test negative electrode 2-2
200
150
100
50
0
Electrolysis time (minute)
-1.05
-1.04
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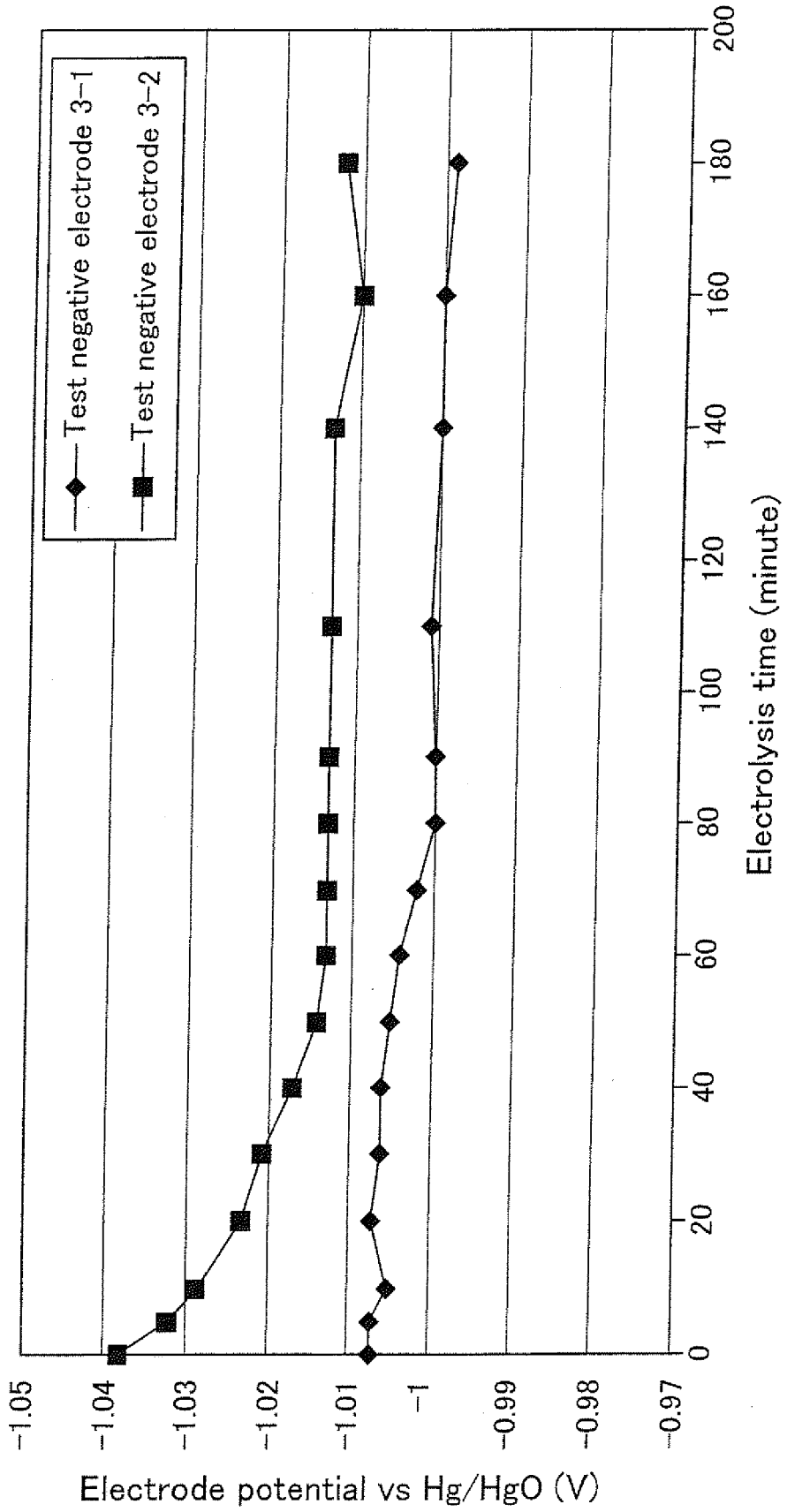
Electrode potential vs Hg/HgO (V)

FIG.2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Electrolysis time (minute)
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20
40
60
80
100
120
140
160
180
200
Electrode potential vs Hg/HgO (V)
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-1.03
-1.02
-1.01
-1
-0.99
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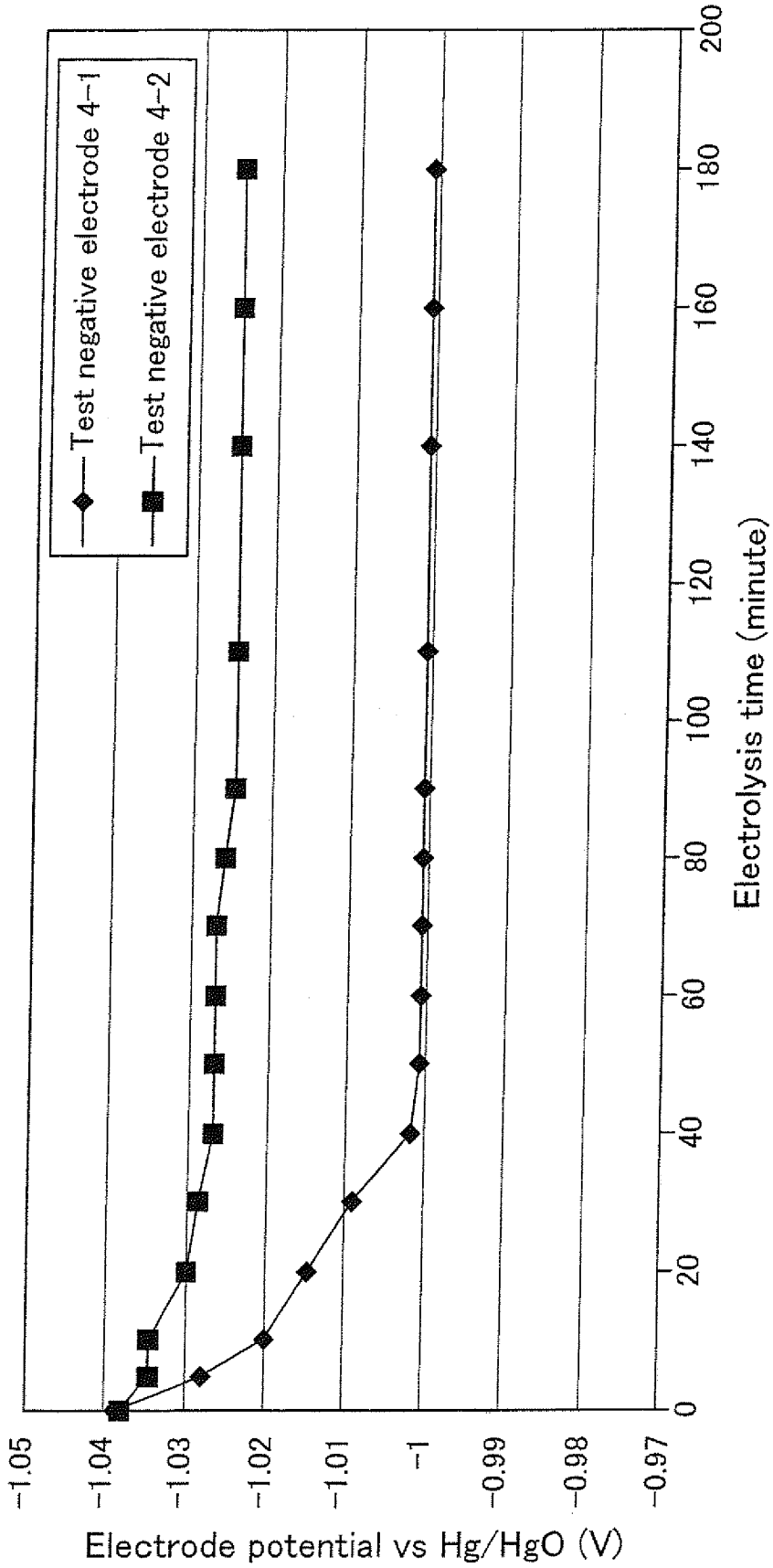
-0.97

FIG.3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Test negative electrode 4-2
Electrolysis time (minute)
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20
40
60
80
100
120
140
160
180
200
Electrode potential vs Hg/HgO (V)
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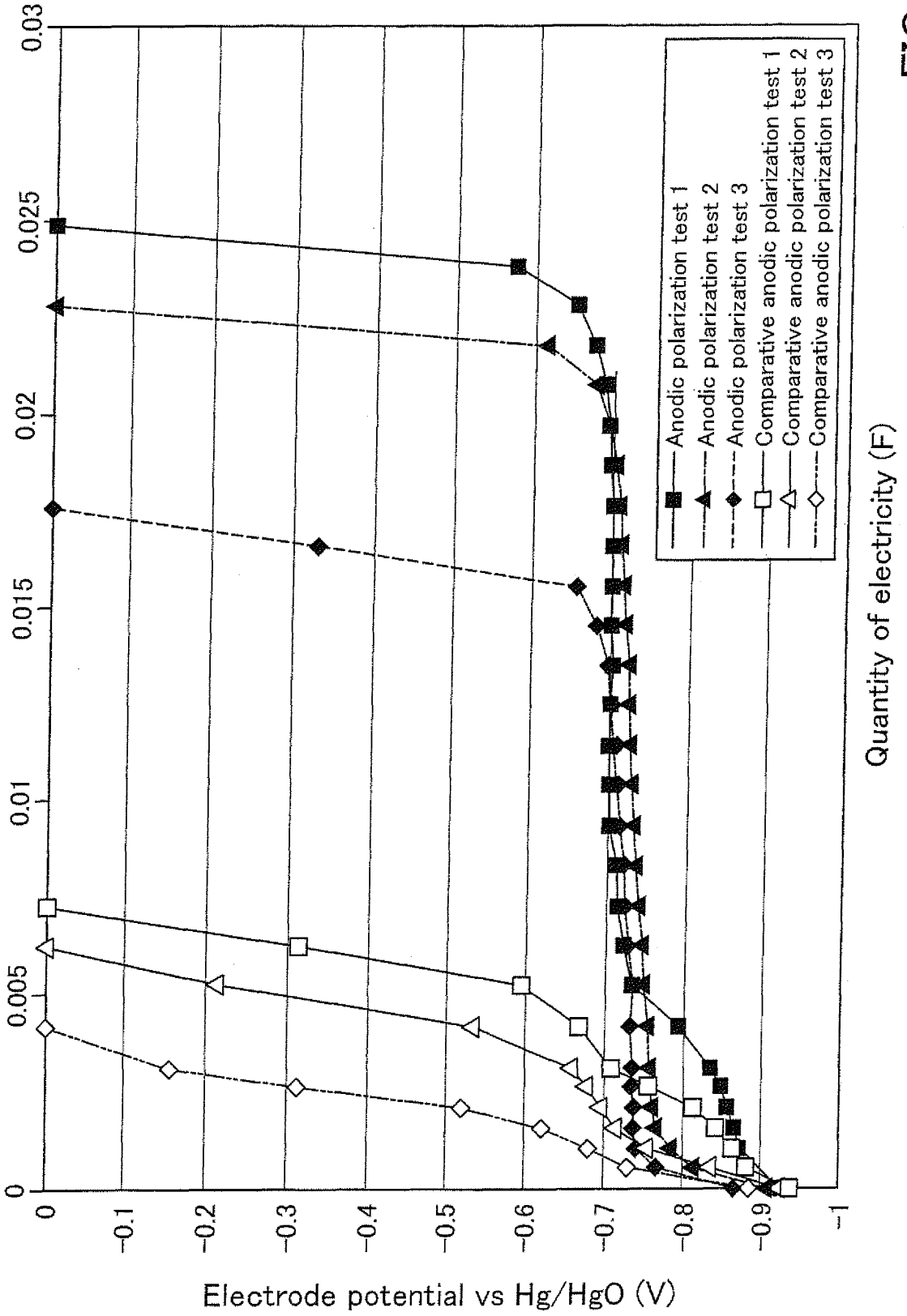
-1.03
-1.02
-1.01
-1
-0.99
-0.98
-0.97

FIG.4


Anodic polarization test 1
Anodic polarization test 2
Anodic polarization test 3
Comparative anodic polarization test 1
Comparative anodic polarization test 2
Comparative anodic polarization test 3
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0.025
0.02
0.015
0.01
0.005
0
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Electrode potential vs Hg/HgO (V)

FIG.5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/053418

A. CLASSIFICATION OF SUBJECT MATTER
C25B11/04(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)
C25B11/04

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
X Y	JP 56-020181 A (Solvay et Co.), 25 February 1981 (25.02.1981), claims; column 9, line 7 to column 11, line 14 & US 4394231 A & EP 23368 A1 & FR 2460343 A & PT 71423 A	1-3,9,10 4-8,11-15
X Y	JP 03-044154 B2 (Asahi Chemical Industry Co., Ltd.), 05 July 1991 (05.07.1991), column 7, lines 10 to 28 & US 4605484 A & EP 126189 A1 & DE 3370833 D	1-3,9,10 4-8,11-15

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

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" 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
"X" 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
"Y" 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 member of the same patent family

Date of the actual completion of the international search 05 April, 2011 (05.04.11)	Date of mailing of the international search report 12 April, 2011 (12.04.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/053418

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 62-086187 A (Asahi Chemical Industry Co., Ltd.), 20 April 1987 (20.04.1987), page 4, lower right column, line 8 to page 5, upper left column, line 7 & US 4839015 A & CN 86107530 A	1-3,9,10 4-8,11-15
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REFERENCES CITED IN THE DESCRIPTION

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- JP 4142191 B **[0009]**
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