



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 437 178 B1

(12)

EUROPEAN PATENT SPECIFICATION

(49) Date of publication of patent specification: **13.09.95** (51) Int. Cl.⁶: **C25B 11/06**

(21) Application number: **90810945.7**

(22) Date of filing: **04.12.90**

(54) **Electrode with electrocatalytic coating.**

(30) Priority: **08.12.89 US 447775**

(43) Date of publication of application:
17.07.91 Bulletin 91/29

(45) Publication of the grant of the patent:
13.09.95 Bulletin 95/37

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(56) References cited:
EP-A- 0 153 586
FR-A- 2 189 122
US-A- 4 005 004
US-A- 4 564 434

(73) Proprietor: **ELTECH SYSTEMS CORPORATION**
Town Executive Center
6100 Glades Road
Suite 305
Boca Raton
Florida 33434 (US)

(72) Inventor: **Carlson, Richard C.**
51 East 216th Street
Euclid 44123 (US)
Inventor: **Hardee, Kenneth L.**
15818 Georgia Road
Middlefield,
Ohio 44062 (US)

(74) Representative: **Cronin, Brian Harold John et al**
42, rue Plantamour
CH-1201 Genève (CH)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

BACKGROUND OF THE INVENTION

Electrodes for use in electrolytic processes have been known which have a base or core metal bearing a layer or coating of metal oxides. The core metal of the electrode may be a valve metal such as titanium, tantalum, zirconium, niobium or tungsten. Where the coating is an oxide mixture, an oxide of the core or substrate metal can contribute to the mixture. As taught for example in U.S. Patent 3,711,385, such mixture can include an oxide of the substrate metal plus at least one oxide of a metal such as platinum, iridium, rhodium, palladium, ruthenium, and osmium.

It has also been known that such mixture which can be termed a noble metal oxide mixture, can be a mixture of ruthenium oxide and iridium oxide. Such have been taught generally in U.S. Patent 3,632,498 and examples shown specifically, when combined with titanium oxide, in U.S. Patent 3,948,751. Particularly for utilization as a coating on an electrode used in an electrolysis of an aqueous alkali-metal halide, e.g., sodium chloride, it has been taught in U.S. Patent 4,005,004 that such noble metal oxide mixture can be particularly serviceable when in further mixture with both titanium oxide and zirconium oxide. Such a mixture, as taught in the patent, yields a solid solution coating that ostensibly enhances the practical utilization of the electrodes for their intended use.

More recently, it has been proposed for enhanced wear resistance of an electrode, especially when utilized in electrolysis producing oxygen and chlorine in combination, to provide the molar amount of titanium oxide equal to or greater than the moles of the total oxides of iridium and ruthenium. Such has been disclosed in U.S. Patent 4,564,434, wherein there is also taught providing the molar amount of iridium oxide about the same as, to greater than, the molar amount of ruthenium oxide.

SUMMARY OF THE INVENTION

It would however be desirable to provide an electrocatalytic coating which in electrolysis of halogen-containing solutions, e.g., chlor-alkali production from brine electrolysis, will achieve reduced oxygen evolution. It would also be particularly desirable to provide such a coating exhibiting retarded weight loss when exposed to caustic. It would be most beneficial if such characteristics could be achieved, not only in combination, but without sacrifice to other wanted features, e.g., no sacrifice in the chlorine evolution potential for the anode. It would also be advantageous to prepare

an electrode using a coating composition that is readily prepared, has a simplistic formulation, and provides ease and safety in handling and use.

The invention is broadly directed to an electrode having reduced oxygen evolution during electrolysis of halogen-containing solutions particularly at low pH, such electrode comprising an electrically conductive metal substrate having a coating of enhanced stability under alkaline conditions, which coating comprises at least 15, but less than 25, mole percent iridium oxide, 35-50 mole percent ruthenium oxide and at least 30, but less than 45 mole percent titanium oxide basis 100 mole percent of the oxides present in the coating. Thereby the coating has a molar ratio of titanium oxide to the total of the oxides of iridium and ruthenium of less than 1:1, and should have a molar ratio of ruthenium oxide to iridium oxide of greater than 1.5:1 and up to 3:1.

In another aspect, the invention is directed to a coating composition adapted for providing the foregoing described mixed metal oxide coating and in a still further aspect is directed to the method of making an electrode which is hereinbefore defined. The electrode will be particularly useful as an anode in a membrane cell used for the electrolysis of brine that is at a pH within the range of from about 2 to about 4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The coating composition of the present invention is broadly applicable to any electrically conductive metal substrate which will be sufficiently electrically conductive to serve as an electrode in an electrolysis process. Thus the metals of the substrate are broadly contemplated, but in view of the application of an electrocatalytic coating, the substrate metals more typically may be such as nickel or manganese, or most always the valve metals, including titanium, tantalum, aluminum, tungsten, zirconium and niobium. Of particular interest for its ruggedness, corrosion resistance and availability is titanium. As well as the normally available elemental metals themselves, the suitable metals of the substrate can include metal alloys and intermetallic mixtures. For example, titanium may generally be alloyed with nickel, cobalt, iron, manganese or copper. More specifically, Grade 5 titanium may include up to 6.75 weight % aluminum and 4.5 weight % vanadium, grade 6 up to 6% aluminum and 3% tin, grade 7 up to 0.25 weight % palladium, grade 10, from 10 to 13 weight % molybdenum plus 4.5 to 7.5 weight % zirconium and so on.

The coating composition applied to the coated metal substrate will be aqueous, which will most

always be simply water without any blending with further liquid. Preferably, deionized or distilled water is used to avoid inorganic impurities. For economy of preparation and utilization, the aqueous compositions that are serviceable will be solutions of precursor constituents in the aqueous medium, that is, precursors to the oxides that will be present in the coating. The precursor constituents utilized in the aqueous solution are those which can be solubilized in water efficiently and economically, e.g., achieve solution without extensive boiling condition. Moreover, the precursors must supply the respective metal oxide on thermodecomposition. Where they are all present in the same composition, they must also be compatible with one another. In this regard, they are advantageously non-reactive toward one another, e.g., will not react so as to form products which will lead to deleterious non-oxide substituents in the coating or precipitate from the coming solution. Usually, each precursor constituent will be a metal salt that most often is a halide salt and preferably for economy coupled with efficiency of solution preparation such will all be the chloride salt. However, other useful salts include iodides, bromides and ammonium chloro salts such as ammonium hexachloro iridate or ruthenate.

In the individual or combination solutions, in addition to the suitable precursor constituent, most always with only one exception no further solution ingredients will be present. Such exception will virtually always be the presence of inorganic acid. For example, a solution of iridium trichloride can further contain strong acid, most always hydrochloric acid, which will usually be present in an amount to supply about 5 to 20 weight percent acid. Typically, the individual or combination solutions will have a pH of less than 1, such as within the range of from about 0.2 to about 0.8.

When the coating composition is a solution of all precursor constituents, such will contain at least 15, but less than 25, mole percent of the iridium constituent, 35-50 mole percent of the ruthenium constituent, and at least 30, but less than 45, mole percent of the titanium constituent, basis 100 mole percent of these constituents. A composition containing an iridium constituent in an amount of less than 15 mole percent will be inadequate for providing an electrode coating having the best caustic stability, such as when the electrode is used in a chlor-alkali cell. On the other hand, less than 25 mole percent for the iridium precursor will be desirable for best low operating potential efficiency for the coating. In regard to the ruthenium, a constituent amount in the solution of less than about 35 mole percent will be insufficient to provide the most efficient low chlorine potential for resulting coatings, while an amount not greater than 50 mole

percent enhances coating stability. Also, for best coating characteristics, the molar ratio of ruthenium oxide to iridium oxide in the resulting coating will be from greater than 1.5:1 up to 3:1.

For the titanium precursor in the coating composition, an amount providing less than 30 mole percent titanium is uneconomical while 45 mole percent titanium or more can lead to higher operating potential for electrode coatings operating in chlor-alkali cells. Preferably for best economy, coupled with the overall most desirable coating characteristics, the coating solution will contain constituents in a proportion such as to provide from about 18-22 mole percent iridium, 35-40 mole percent ruthenium, and 40-44 mole percent titanium. The resulting coating will furthermore have a molar ratio of titanium oxide to the total of the oxides of iridium ruthenium of less than 1:1, but most always above 0.5:1.

Before applying the coating composition to the substrate metal, the substrate metal advantageously is a cleaned surface. This may be obtained by any of the treatments used to achieve a clean metal surface, including mechanical cleaning. The usual cleaning procedures of degreasing, either chemical or electrolytic, or other chemical cleaning operation may also be used to advantage. Where the substrate preparation includes annealing, and the metal is grade 1 titanium, the titanium can be annealed at a temperature of at least about 450 °C. for a time of at least about 15 minutes, but most often a more elevated annealing temperature, e.g., 600 °-875 °C. is advantageous.

After the foregoing operation, e.g., cleaning, or cleaning and annealing, and including any desirable rinsing and drying steps, the metal surface is then ready for continuing operation. Where such is etching, it will be with an active etch solution. Typical etch solutions are acid solutions. These can be provided by hydrochloric, sulfuric, perchloric, nitric, oxalic, tartaric, and phosphoric acids as well as mixtures thereof, e.g., aqua regia. Other etchants that may be utilized include caustic etchants such as a solution of potassium hydroxide/hydrogen peroxide in combination, or a melt of potassium hydroxide with potassium nitrate. For efficiency of operation, the etch solution is advantageously a strong, or concentrated, aqueous solution, such as an 18-22 weight % solution of hydrochloric acid, or a solution of sulfuric acid. Moreover, the solution is advantageously maintained during etching at elevated temperature such as at 80 °C. or more for aqueous solutions, and often at or near boiling condition or greater, e.g., under refluxing condition. Preferably, the etching will prepare a roughened surface, as determined by aided, visual inspection. Following etching, the etched metal surface can then be subjected to rinsing and

drying steps to prepare the surface for coating.

The coating composition can then be applied to the metal substrate by any means for typically applying an aqueous coating composition to a substrate metal. Such methods of application include brush, roller, and spray application. Moreover, combination techniques can be utilized, e.g., spray and brush technique. Spray application can be either conventional compressed gas or can be electrostatic spray application. Advantageously, electrostatic spray application will be used for best wrap around affect of the spray for coating the back side of an article such as a mesh electrode.

Following application of the coating, the applied composition will be heated to prepare the resulting mixed oxide coating by thermodecomposition of the precursors present in the coating composition. This prepares the mixed oxide coating containing the mixed oxides in the molar proportions as above discussed. Such heating for the thermodecomposition will be conducted at a temperature of at least about 440 °C. peak metal temperature for a time of at least about 3 minutes. More typically the applied coating will be heated at a more elevated temperature for a slightly longer time, but usually a temperature of greater than about 550 °C. is avoided for economy and to avoid detrimental effects on anode potential where the coated metal will serve as an anode. Suitable conditions can include heating in air or oxygen. Following such heating, and before additional coating as where an additional application of the coating composition will be applied, the heated and coated substrate will usually be permitted to cool to at least substantially ambient temperature. The resulting finished coating has a smooth appearance to the unaided eye, but under microscopic examination is seen to be non-homogeneous, having embedded crystallites in the field of the coating. For best overall performance of the coated substrate metal as an electrode, subsequently applied coatings will be of those compositions of the invention disclosed herein.

The following example shows a way in which the invention has been practiced, but should not be construed as limiting the invention.

EXAMPLE

A coating solution was prepared by combining 157 g of iridium, using a solution of iridium trichloride in 18% by weight HCl, 144 g of ruthenium, using a solution of ruthenium trichloride in 18% by weight HCl, 80 g of titanium, using titanium tetrachloride in 10% by weight HCl solution, 331 g HCl, using 36 weight % solution, then diluting to 10 liters with deionized water. This provided a coating composition having 21 mole % iridium; 36.3 mole % ruthenium, and 42.7 mole % titanium. Four liters

of 93 grams per liter (gpl) HCl solution were then added to make the final coating solution.

This solution was applied using a hand roller to a titanium mesh substrate having a diamond-patterned mesh, with each diamond pattern having about 8 millimeters (mms.) long way of design plus about 4 mms. short way of design. The titanium mesh had been annealed at 600 °C. for 30 minutes and etched in 25 wt % sulfuric acid at 85-90 °C., then water rinsed and air dried. The applied coating was air dried then baked at 470 °C. Eighteen (18) coats were applied in this manner. After the final coat, the anode was postbaked at 525 °C. for 4 hours.

Operation of eight samples of the resulting coated titanium substrate, when utilized as an anode in 12 normal NaOH at 95 °C. for 4 hours at 25 kA/m² resulted in an average weight loss of 5.27 g/m². Use of a sample as an anode in a chlor-alkali membrane cell operating at 3.3 kA/m² resulted in 0.06%, 0.22%, and 0.38%, by volume, oxygen produced in the chlorine cell product at an electrolyte pH of 2, 3 and 4, respectively. The operating potential of this anode in the membrane cell was 1.09 volts vs. a standard calomel reference electrode.

The average caustic weight loss of 5.27 g/m² was especially noteworthy since a comparative coating having 7.8 mole percent iridium oxide, 15 mole percent ruthenium oxide and 77.2 mole percent titanium oxide exhibited such weight loss of 8.9 g/m² when tested under the same conditions. Moreover, again comparatively, but as the mole percent changed to more closely approach the invention composition, but still in a comparative coating, the caustic weight loss increased to 19.2 g/m²

Claims

1. An electrode having reduced oxygen evolution during electrolysis of halogen-containing solutions at low pH, said electrode comprising an electrically conductive metal substrate having a coating of enhanced stability under alkaline conditions, which coating comprises at least 15, but less than 25, mole percent iridium oxide, 35-50 mole percent ruthenium oxide and at least 30, but less than 45, mole percent titanium oxide, basis 100 mole percent of these oxides present in the coating, whereby the coating has a molar ratio of titanium oxide to the total of the oxides of iridium and ruthenium of less than 1:1, with the molar ratio of ruthenium oxide to iridium oxide being from greater than 1.5:1 and up to 3:1.

2. The electrode of claim 1, wherein said conductive metal substrate comprises a metal selected from titanium, tantalum, zirconium, niobium, aluminum, tungsten and alloys and intermetallic mixtures thereof. 5
3. The electrode of claim 1, wherein said conductive metal substrate comprises titanium, or an alloy or intermetallic mixture containing titanium. 10
4. The electrode of claim 3, wherein said conductive metal substrate comprises an annealed and etched titanium substrate. 15
5. The electrode of claim 1, wherein said coating is a non-homogeneous but smooth coating of mixed oxides and consists essentially of 18-22 mole percent iridium oxide, 35-40 mole percent ruthenium oxide and 40-44 mole percent titanium oxide, with a molar ratio of ruthenium oxide to iridium oxide of from 1.7:1 to 2.2:1. 20
6. The electrode of claim 1, wherein said electrode is an anode in a membrane cell used for the electrolysis of brine that is at a pH within the range of from about 2 to about 4. 25
7. A coating composition adapted for providing a mixed metal oxide coating on a metal substrate, which composition comprises an acidic aqueous medium containing soluble constituents of iridium, ruthenium and titanium in proportion providing at least 15, but less than 25, mole percent iridium, 35-50 mole percent ruthenium and at least 30, but less than 45, mole percent titanium, basis 100 mole percent of such constituents, whereby the composition has a molar ratio of titanium to the total of the iridium and ruthenium of less than 1:1, with the molar ratio of ruthenium to iridium being from greater than 1.5:1 up to 3:1. 30 35 40
8. The coating composition of claim 7, wherein said acidic aqueous medium contains strong inorganic acid in water and is at a pH within the range of from about 0.2 to about 0.8. 45
9. The coating composition of claim 8, wherein said strong inorganic acid is hydrochloric acid. 50
10. The coating composition of claim 7, wherein said soluble constituents are compatible and are selected from chlorides, bromides, iodides and ammonium chloro salts. 55
11. The coating composition of claim 10, wherein all said soluble constituents are chlorides and said aqueous medium contains hydrochloric acid.
12. The coating composition of claim 7, wherein said proportions provide 18-22 mole percent iridium, 35-40 mole percent ruthenium and 40-44 mole percent titanium, basis 100 mole percent of these constituents, with a molar ratio of ruthenium to iridium being from 1.7:1 to 2.2:1.
13. The coating composition of claim 7, wherein said composition provides an electrocatalytic coating of said mixed metal oxides on an electrically conductive valve metal substrate.
14. The method of making an electrode having an electrocatalytic coating of enhanced performance in a chlor-alkali cell when said coating is present in said electrode on an electrically conductive metal substrate, which method comprises:
 - annealing a titanium substrate at a temperature of at least about 450 ° C. for a time of at least about 0.25 hour;
 - etching the resulting annealed surface with strong etching agent to produce a roughened surface;
 - applying to the resulting etched surface an aqueous coating composition comprising constituents that are thermally decomposable to provide a mixed oxide coating of the constituents in the amount of at least 15, but less than 25 mole percent iridium oxide, 35-50 mole percent ruthenium oxide and at least 30, but less than 45, mole percent titanium oxide, basis 100 mole percent of these oxides present in the coating, whereby the coating has a molar ratio of titanium oxide to the total of the oxides of iridium and ruthenium of less than 1:1, with the molar ratio of ruthenium oxide to iridium oxide being from greater than 1.5:1 and up to 3:1; and
 - heating the resulting coated substrate at a temperature of at least about 440 ° C. for a time of at least about 3 minutes.
15. The method of claim 14, wherein said annealed substrate is cooled to about room temperature and the resulting cooled substrate is then etched.
16. The method of claim 14, wherein said annealed substrate is etched with strong inorganic acid etching agent.
17. The method of claim 14, wherein said etched surface is water rinsed prior to application of said coating composition.

18. The method of claim 14, wherein said etched surface is a roughened, etched surface.
19. The method of claim 14, wherein said coating composition is applied to said titanium substrate by electrostatic spray application. 5
20. The method of claim 14, wherein said titanium substrate is annealed at a temperature within the range of from about 600°C. to about 875°C. 10
21. An electrode having reduced oxygen evolution during electrolysis of halogen-containing solutions at low pH, while having a coating of enhanced stability under alkaline conditions, which electrode is produced by the method of claim 14. 15

Patentansprüche 20

1. Elektrode mit verringerter Sauerstoffentwicklung während der Elektrolyse von halogenhaltigen Lösungen bei niederem pH-Wert, welche einen elektrisch leitenden Metallträger mit einem Überzug erhöhter Stabilität unter alkalischen Bedingungen aufweist, wobei der Überzug mindestens 15 aber weniger als 25 Mol-% Iridiumoxid, 35 bis 50 Mol-% Rutheniumoxid und mindestens 30 aber weniger als 45 Mol-% Titanoxid bei einer Basis von 100 Mol-% dieser in dem Überzug anwesenden Oxide enthält, wodurch der Überzug ein Molverhältnis von Titanoxid zu der Gesamtheit von Iridium- und Rutheniumoxiden von weniger als 1 : 1 hat, wobei das Molverhältnis von Rutheniumoxid zu Iridiumoxid größer als 1,5 : 1 und bis 3 : 1 ist. 25 30 35
2. Elektrode nach Anspruch 1, in welcher der leitende Metallträger ein Metall ausgewählt aus Titan, Tantal, Zirkon, Niob, Aluminium, Wolfram und Legierungen und intermetallischen Mischungen derselben enthält. 40 45
3. Elektrode nach Anspruch 1, in welcher der leitende Metallträger Titan oder eine Legierung oder eine titanhaltige intermetallische Mischung enthält. 50
4. Elektrode nach Anspruch 3, in welcher der leitende Metallträger einen ausgeglühten und geätzten Titanträger enthält. 55
5. Elektrode nach Anspruch 1, in welcher der Überzug ein nicht-homogener aber glatter Überzug aus gemischten Oxiden ist und im wesentlichen aus 18 bis 22 Mol-% Iridiumoxid, 35 bis 40 Mol-% Rutheniumoxid und 40 bis 44 Mol-% Titanoxid bei einem Molverhältnis von Rutheniumoxid zu Iridiumoxid von 1,7 : 1 bis 2,2 : 1 besteht.
6. Elektrode nach Anspruch 1, in welcher die Elektrode eine Anode in einer Membranzelle ist, die zur Elektrolyse von Kochsalzlösung bei einem pH-Wert in dem Bereich von etwa 2 bis etwa 4 verwendet wird.
7. Zur Bildung eines gemischten Metallüberzugs auf einem Metallträger geeignete Überzugszusammensetzung, welche ein saures wäßriges Medium umfaßt, das lösliche Bestandteile von Iridium, Ruthenium und Titan in Mengenanteilen enthält, welche mindestens 15 aber mehr als 25 Mol-% Iridium, 35 bis 50 Mol-% Ruthenium und mindestens 30 aber weniger als 45 Mol-% Titan bei einer Basis von 100 Mol-% dieser Bestandteile gewährleisten, wodurch die Zusammensetzung ein Molverhältnis von Titan zu der Gesamtmenge von Iridium und Ruthenium von weniger als 1 : 1 hat, wobei das Molverhältnis von Ruthenium zu Iridium größer als 1,5 : 1 bis zu 3 : 1 ist.
8. Überzugszusammensetzung nach Anspruch 7, in welcher das saure wäßrige Medium eine starke anorganische Säure in Wasser enthält und einen pH-Wert in dem Bereich von etwa 0,2 bis etwa 0,8 aufweist.
9. Überzugszusammensetzung nach Anspruch 8, in welcher die starke anorganische Säure Chlorwasserstoffsäure ist.
10. Überzugszusammensetzung nach Anspruch 7, in welcher die löslichen Bestandteile kompatibel sind und ausgewählt aus Chloriden, Bromiden, Jodiden und Ammoniumchlorsalzen sind.
11. Überzugszusammensetzung nach Anspruch 10, in welcher alle löslichen Bestandteile Chloride sind und das wäßrige Medium Chlorwasserstoffsäure enthält.
12. Überzugszusammensetzung nach Anspruch 7, in welcher die Anteile 18 bis 22 Mol-% Iridium, 35 bis 40 Mol-% Ruthenium und 40 bis 44 Mol-% Titan liefern, wobei die Basis 100 Mol-% dieser Bestandteile ist und wobei das Molverhältnis von Ruthenium zu Iridium 1,7 : 1 bis 2,2 : 1 ist.
13. Überzugszusammensetzung nach Anspruch 7, wobei die Zusammensetzung einen elektrokatalytischen Überzug aus den gemischten Me-

talloxiden auf einem elektrisch leitenden Ventilmetallträger schafft.

14. Verfahren zum Herstellen einer Elektrode mit einem elektrokatalytischen Überzug erhöhter Leistung in einer Chloralkalizelle, wenn der Überzug in der Elektrode auf einem elektrisch leitenden Metallträger anwesend ist, durch:

Ausglühen eines Titanträgers bei einer Temperatur von mindestens etwa 450 °C während einer Zeit von mindestens etwa 0,25 Stunden;

Ätzen der erhaltenen ausgeglühten Oberfläche mit einem starken Ätzmittel zur Bildung einer aufgerauhten Oberfläche;

Aufbringen einer wäßrigen Überzugszusammensetzung enthaltend Bestandteile, die thermisch zersetzbar sind, auf die erhaltene geätzte Oberfläche, um einen Überzug aus gemischtem Oxid der Bestandteile in der Menge von mindestens 15 aber weniger als 25 Mol-% Iridiumoxid, 35 bis 50 Mol-% Rutheniumoxid und mindestens 30 aber weniger als 45 Mol-% Titanoxid auf der Basis von 100 Mol-% dieser in dem Überzug anwesenden Oxide zu schaffen, wodurch der Überzug ein Molverhältnis von Titanoxid zu der Gesamtheit der Oxide von Iridium und Ruthenium von weniger als 1 : 1 hat, wobei das Molverhältnis von Rutheniumoxid zu Iridiumoxid größer 1,5 : 1 und bis zu 3 : 1 ist; und

Erhitzen des erhaltenen beschichteten Trägers auf eine Temperatur von mindestens etwa 440 °C während einer Zeit von mindestens etwa 3 Minuten.

15. Verfahren nach Anspruch 14, bei welchem der ausgeglühte Träger auf etwa Zimmertemperatur abgekühlt wird und der erhaltene abgekühlte Träger dann geätzt wird.
16. Verfahren nach Anspruch 14, bei welchem der ausgeglühte Träger mit einer starken anorganischen Säure als Ätzmittel geätzt wird.
17. Verfahren nach Anspruch 14, bei welchem die geätzte Oberfläche vor dem Aufbringen der Überzugszusammensetzung mit Wasser gespült wird.
18. Verfahren nach Anspruch 14, bei welchem die geätzte Oberfläche eine aufgerauhte geätzte Oberfläche ist.
19. Verfahren nach Anspruch 14, bei welchem die Überzugszusammensetzung auf den Titanträger durch elektrostatisches Besprühen aufgebracht wird.

20. Verfahren nach Anspruch 14, in welchem der Titanträger bei einer Temperatur in dem Bereich von etwa 600 °C bis etwa 875 °C ausgeglüht wird.

21. Elektrode mit verringerter Sauerstoffentwicklung während der Elektrolyse von halogenhaltigen Lösungen bei niederem pH-Wert, welche einen Überzug erhöhter Stabilität unter alkalischen Bedingungen aufweist, wobei die Elektrode nach dem Verfahren von Anspruch 14 hergestellt ist.

Revendications

1. Electrode à dégagement réduit d'oxygène pendant l'électrolyse de solutions contenant un halogène à bas pH, ladite électrode comprenant un substrat en métal électriquement conducteur ayant un revêtement de stabilité améliorée sous des conditions alcalines, lequel revêtement comprend au moins 15, mais moins de 25, mole pourcent d'oxyde d'iridium, 35-50 mole pourcent d'oxyde de ruthénium et au moins 30, mais moins de 45, mole pourcent d'oxyde de titane sur la base de 100 mole pourcent de ces oxydes présents dans le revêtement, le revêtement ayant un rapport molaire d'oxyde de titane sur le total des oxydes d'iridium et de ruthénium inférieur à 1:1, et un rapport molaire d'oxyde de ruthénium sur l'oxyde d'iridium de plus de 1,5:1 et jusqu'à 3:1.
2. L'électrode de la revendication 1, dans laquelle ledit substrat en métal conducteur comprend un métal sélectionné parmi le titane, le tantale, le zirconium, le niobium, l'aluminium, le tungstène et leurs alliages et les mélanges intermétalliques de ceux-ci.
3. L'électrode de la revendication 1, dans laquelle ledit substrat en métal conducteur comprend le titane, ou un alliage ou un mélange intermétallique contenant du titane.
4. L'électrode de la revendication 3, dans laquelle ledit substrat en métal conducteur comprend un substrat en titane recuit et attaqué.
5. L'électrode de la revendication 1, dans laquelle ledit revêtement est un revêtement non-homogène mais lisse d'oxydes mélangés, et consiste essentiellement de 18-22 mole pourcent d'oxyde d'iridium, 35-40 mole pourcent d'oxyde de ruthénium et 40-44 mole pourcent d'oxyde de titane, avec un rapport molaire d'oxyde de ruthénium sur l'oxyde d'iridium de

1,7:1 à 2,2:1.

6. L'électrode de la revendication 1, dans laquelle ladite électrode est une anode dans une cellule à membrane utilisée pour l'électrolyse de saumure à un pH dans l'intervalle d'environ 2 à environ 4. 5
7. Composition de revêtement adaptée pour donner un revêtement en oxyde de métal mélangé sur un substrat en métal, laquelle composition comprend un milieu aqueux acide contenant des constituants solubles d'iridium, de ruthénium et de titane dans des proportions dominant au moins 15, mais moins de 25, mole pourcent d'iridium, 35-50 mole pourcent de ruthénium et au moins 30, mais moins de 45, mole pourcent de titane sur la base de 100 mole pourcent de ces composants, le revêtement ayant un rapport molaire de titane sur le total d'iridium et de ruthénium inférieur à 1:1, avec le rapport molaire du ruthénium sur l'iridium de plus de 1,5:1 et jusqu'à 3:1. 10 15 20
8. La composition de revêtement de la revendication 7, dans laquelle le milieu aqueux acide contient un acide inorganique fort dans l'eau, à un pH dans l'intervalle d'environ 0,2 à environ 0,8. 25 30
9. La composition de revêtement de la revendication 8, dans laquelle l'acide inorganique fort est l'acide chlorhydrique. 35
10. La composition de revêtement de la revendication 7, dans laquelle lesdits constituants solubles sont compatibles et sont sélectionnés parmi les sels de chlorure, bromure, iodure et chloro-ammonium. 40
11. La composition de revêtement de la revendication 10, dans laquelle lesdits constituants solubles sont les chlorures, et ledit milieu aqueux contient de l'acide chlorhydrique. 45
12. La composition de revêtement de la revendication 7, dans laquelle les proportions donnent 18-22 mole pourcent d'iridium, 35-40 mole pourcent de ruthénium et 40-44 mole pourcent de titane, sur la base de 100 mole pourcent de ces composants, avec un rapport molaire d'oxyde de ruthénium sur l'oxyde d'iridium de 1,7:1 à 2,2:1. 50
13. La composition de revêtement de la revendication 7, dans laquelle ladite composition donne un revêtement électrocatalytique desdits oxydes de métaux mélangés sur un substrat en 55

métal d'arrêt électriquement conducteur.

14. Méthode pour fabriquer une électrode ayant un revêtement électrocatalytique avec des performances améliorées dans une cellule chloro-alcaline, lorsque ledit revêtement est présent dans ladite électrode sur un substrat en métal électriquement conducteur, laquelle méthode comprend:
 - la recuite d'un substrat en titane à une température d'au moins environ 450 °C pour une durée d'au moins 0,25 heure;
 - l'attaque de la surface recuite résultante avec un agent attaquant fort pour produire une surface rugueuse;
 - l'application, sur la surface attaquée résultante, d'une composition de revêtement aqueuse comprenant des constituants qui sont thermiquement décomposables pour donner un revêtement en oxydes mélangés avec des constituants dans la quantité d'au moins 15, mais moins de 25, mole pourcent d'oxyde d'iridium, 35-50 mole pourcent d'oxyde de ruthénium et au moins 30, mais moins de 45, mole pourcent d'oxyde de titane sur la base de 100 mole pourcent de ces oxydes présents dans le revêtement, le revêtement ayant un rapport molaire d'oxyde de titane sur le total des oxydes d'iridium et de ruthénium inférieur à 1:1, et le rapport molaire d'oxyde de ruthénium sur l'oxyde d'iridium étant de plus de 1,5:1 et jusqu'à 3:1; et
 - réchauffer le substrat résultant revêtu à une température d'environ 440 °C pendant une durée d'environ au moins 3 minutes.
15. La méthode de la revendication 14, dans laquelle ledit substrat recuit est refroidi jusqu'à environ la température ambiante et le substrat refroidi résultant est alors attaqué. 40
16. La méthode de la revendication 14, dans laquelle ledit substrat recuit est attaqué avec un agent attaquant qui est un acide inorganique fort. 45
17. La méthode de la revendication 14, dans laquelle ladite surface attaquée est rincée avant l'application de ladite composition de revêtement. 50
18. La méthode de la revendication 14, dans laquelle ladite surface attaquée est une surface rugueuse, attaquée.
19. La méthode de la revendication 14, dans laquelle ladite composition de revêtement est appliquée audit substrat en titane par l'applica-

tion par giclage électrostatique.

- 20.** La méthode de la revendication 14, dans laquelle ledit substrat en titane est recuit à une température dans l'intervalle d'environ 600 °C à environ 875 °C. 5

- 21.** Une électrode ayant un dégagement réduit d'oxygène pendant l'électrolyse de solutions contenant un halogène à un bas pH, tout en ayant un revêtement avec une stabilité améliorée sous des conditions alcalines, laquelle électrode est produite par la méthode de la revendication 14. 10

15

20

25

30

35

40

45

50

55