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PROVISIONAL SPECIFICATION

" A PROCESS FOR THE PREPARATION OF INSOLUBLE ANODES FOR ELECTROCHEMICAL PROCESSES "
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following Specification describes the nature of this invention.

THIS IS AN INVENTION BY RAMASWAMY THANGAPPAN NADAR, SCIENTIST, HANDADY VENKATAKRISHNA UDUPA DIRECTOR, BABU RAM YADAV, SENIOR SCIENTIFIC ASSISTANT AND PERUMAL SUBBIAH, JUNIOR SCIENTIFIC ASSISTANT, ALL OF CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, TAMIL NADU, INDIA, ALL INDIANS.

This invention relates to insoluble anodes formed by thermally depositing a single platinum group metal, a combination of platinum group metals or a combination of oxides of one or more of platinum group metals and a film forming metal from suitable salts supported in an organic vehicle, over a substrate like titanium, tantalum or an alloy of film forming metals.

Hitherto it is known to employ as anodes in an electrolytic cell, particularly in cells used for the electrolysis of aqueous solutions of alkali metal halides, anodes which would be resistant to the corrosive halide electrolytes and which will keep their dimensions almost constant for long durations. Lead dioxide deposited onto graphite, titanium, tantalum etc., and magnetite, titanium electroplated with one or more of platinum group metals are known to have been used as anodes in the electrolysis of brine solutions to chlorine-caustic soda, chlorate and perchlorate of sodium etc. Lead dioxide anodes could not be used in mercury type chlor-alkali cells as the coating will get reduced to metallic lead in case of contact with mercury cathode; the high temperature operation involved in both diaphragm and mercury type cells are detrimental to the electrode. Magnetite electrodes are very massive; they possess poor mechanical strength; they are not easily machinable and their wear rate in chloride electrolysis is quite significant. Electrodeposited platinum on titanium, while used as anode, get passivated and hence require activation. The wear rate of platinum or platinumiridium coated titanium is also high which prohibits the use of such anodes in commercial installations.

The object of this invention is to obviate these disadvantages by making insoluble anodes formed by thermally depositing platinum along with traces of an activating element or a combination of platinum group metals such as rhodium, iridium, ruthenium, osmium and palladium or a combination of oxides of one or more of platinum group metals and a film forming metal like titanium, zirconium, niobium, tantalum or tungsten over a corrosion resistant substrate like titanium, tantalum or an alloy of the film forming metals.

To these ends, the invention broadly consists in the preparation of insoluble anodes by depositing platinum or a combination of platinum group metals like rhodium, iridium, ruthenium, osmium, and palladium or a combination of the oxides of one or more of platinum group metals and a film forming metal like titanium, zirconium, niobium, tantalum or tungsten over a corrosion resistant substrate like titanium, tantalum or an alloy of the film forming metal, the deposition being effected by thermal

decomposition of a paste, a mixture of the various compounds supported in an organic vehicle required to supply the metal or the metal oxide, painted over the polished and etched surface of the substrate and fired at temperature between 300 and 650°C in an atmosphere of either limited supply or forced circulation of air. The etching of the substrate is done in hydrochloric acid, sulphuric acid, a mixture of nitric acid and hydrofluoric acid or other etching solutions or by anodic etching suitable for the particular substrate and type of deposit. The coating chelate was prepared by dissolving the respective chloride of the platinum group metal in an organic solvent like ethyl alcohol or isopropyl alcohol. In certain cases a reducing agent was added to the above chelate. Similarly, a paste of the titanium tetrachloride was made separately. The etched surface was painted with the paste and dried in hot air and baked at a temperature of 300-350°C with or without a current of air circulated over the surface of the substrate. The sample was air cooled and the painting and baking operation continued till sufficient thickness of the metal or metal oxide layer formed on the surface. For making mixed oxide electrodes the above baking operation was followed by coating of titanium chloride chelate. In certain cases, both the chelates were mixed together and painted and baked. When sufficient thickness was built up, the final baking was carried out at a temperature of 300-650°C for 30 minutes to one hour and then the electrode was air cooled.

The following typical examples are given to illustrate the invention:

Example I

A titanium plate of 80 cm² was mechanically polished, degreased in trichloroethylene and etched in 20% hydrochloric acid at a temperature of 90°C for 30 minutes. A chelate was prepared by mixing the following:

chloroplatinic acid (39% metal content)	: 1.32 g.
Ethyl alcohol	: 16 mil.
Acetamide	: 1.7 g.
Antimony oxide	: 6.5 mg

The etched titanium surface was brushed with this chelate, dried in hot air and fired at 350°C for 15 minutes. The painting and firing operations were continued till all the chelate was consumed. Finally, the coated surface was baked at 400°C for 30 minutes.

Theoretically the coating thickness of platinum corresponded to 3 microns. The anode potential of this electrode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.2 volts against SCE.

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It showed a weight loss of 0.10 mg/cm² after three current reversals and 0.21 mg/cm² after three amalgam dips.

Example II

A titanium plate of 12.5 cm x 1cm was degreased in trichloroethylene and etched in 20% hydrochloric acid at 90°C for 30 minutes and rinsed with distilled water. 0.150 g of chloroplatinic acid was dissolved in 1.2 ml of isopropyl alcohol and 0.4 ml of 40% formaldehyde was added to this solution. Similarly, a solution of iridium compound was prepared by dissolving 0.03 g of iridium trichloride (64.33% metal content) in 5 drops of liquor ammonia diluted with 0.7 ml of isopropyl alcohol. The etched titanium base was brushed with the platinum containing paint, dried in hot air and baked in a muffle furnace at a temperature of 300°C for 10 minutes. On this a coating of iridium was provided by painting the iridium containing solution and baking as before. Seven such coatings in each of the solution were made and finally the electrode was baked at a temperature of 400°C for a period of 30 minutes.

The anode thus prepared contained 2.34 mg/cm² and 0.772 mg/cm² of platinum and iridium respectively. This anode registered an anode potential of 1.14 volt against SCE in saturated brine electrolysis in mercury cell at 60°C and at a current density of 10 kA/m². It showed a weight loss of 0.067 mg/cm² after three current reversals and a loss of 0.17 mg/cm² after three amalgam dips.

Example III

A strip of titanium plate of 25 cm² was degreased and etched in a solution containing 20% by weight of nitric acid and 40% by weight of hydrochloric acid between 60 and 90°C for 25 minutes. One part by weight of iridium trichloride was added to 6 parts by weight of liquor ammonia to form a complex of iridium chloropenta amino chloride. Isopropyl alcohol 9 parts by weight was added to the above and the mixture painted over the etched surface of the titanium strip, dried in hot air, and heated in a current of air in a furnace at 300°C for 10 minutes to form a coating. A similar paint mixture was made by adding 1 part by weight of titanium tetrachloride (25.2% metal content) to 9 parts by weight of isopropyl alcohol and brushed over the once coated titanium surface, dried, baked at 300°C for 10 minutes and air cooled. After giving 10 coatings alternately in each of the paint mixture, the anode was baked at 450°C in a current of air for one hour.

The coating thus made contained theoretical amounts of 13 g/m² of IrO₃ and 12 g/m² of TiO₂. This anode registered a potential of 1.16 volt against SCE while using it as anode in saturated brine electrolysis at 60°C in mercury cell at a current density of 10 kA/m². It showed a weight loss of 0.053 mg/cm² after three current reversals; but no weight loss was found after three amalgam dips.

Example IV

A strip of etched titanium plate of 25 cm² was coated alternately with a paste containing iridium and titanium compounds and baked as in Example III. The coating was applied several times. The applied mixture contained the following ingredients:

Iridium trichloride	: 0.03 g.
Titanium tetrachloride	: 0.05 ml
Isopropyl alcohol	: 0.6 ml
Liquor ammonia	: 4 to 5 drops

The quantities of IrO₃ and TiO₂ in the coating corresponded to a weight ratio of 1:1.622 on theoretical basis. The anode

potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.2 volt against SCE.

Example V

As in Examples III and IV, a titanium plate of 25 cm² was coated with IrO₃ and TiO₂ to give a weight ratio of 1:6.25. The total weight of the coating as oxides corresponded to 54.3 mg. The anode potential of this anode in saturated brine electrolysis at 60°C at a current density of 10 kA/m² was 1.6 volts against SCE. Coating losses of 0.06 mg/cm² and 0.01 mg/cm² occurred on three current reversals and three short circuits in the amalgam respectively.

Example VI

A strip of tantalum measuring 25 cm² was electrolytically etched in a solution containing 12 g/l ammonium bromide, 2.5 g/l water in methyl alcohol at a current density of 5 amp/dm² at 30-35°C for 40 minutes. The surface was brushed with a mixture containing the following:

Ruthenium trichloride (44.82% metal content)	: 46 mg
Titanium tetrachloride	: 0.1 ml
Isopropyl alcohol	: 0.6 ml

Dried in hot air blast and decomposed by heating in an oven at 300°C for 10 minutes. The painting and heating was repeated 13 times till all the mixture was used up. The final baking was carried out in a current of air at 400°C in a muffle furnace for 30 minutes. The theoretical amounts of RuO₃ and TiO₂ in the coating were 27.16 and 73.0 mgs respectively. The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.23 volt against SCE. No weight loss was found after three current reversals and three amalgam dips.

Example VII

A titanium sheet of total surface area 30 cm² was etched in 50% sulphuric acid at 60°C for 10 minutes. 49 mg of ruthenium trichloride was dissolved in 0.3 ml of isopropyl alcohol and a portion of this was painted over the etched surface of titanium, dried in hot air and baked at a temperature of 300°C in a furnace for 10 minutes. Subsequently the plate was coated with a mixture containing titanium tetrachloride and isopropyl alcohol in the ratio 1:8 by weight and drying and baking were done as before. The painting and baking procedure was repeated several times till the coating formed contained theoretically 28.93 mg of RuO₃ and 36 mg of TiO₂. The final baking was done at 400°C in the presence of an atmosphere of surplus air for one hour.

This anode registered an anode potential of 1.18 volt against SCE in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². It showed weight loss of 0.03 mg/cm² after three current reversals and no weight loss after three amalgam dips.

Example VIII

A titanium sheet of 30 cm² area was etched in 20% hydrochloric acid and was painted with a solution containing titanium tetrachloride and isopropyl alcohol in the ratio 1:8 by weight. The painted substrate was baked in a furnace at 300° for 10 minutes. Subsequently the substrate was painted with a solution containing 83 mg of ruthenium trichloride and 0.5 ml of isopropyl alcohol and baked in the furnace as before in an atmosphere of air. The painting and baking process was repeated till all the solution containing the precious metal compound was

used up. The final baking was done at 450°C for one hour. The coating weight corresponded to 49 mg of RuO₂ and 36 mg of TiO₂. An anode potential of 1.13 volt against SCE was observed when using it as anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². This anode gave a weight loss of 0.017 mg/cm² after three current reversals and no weight loss after three amalgam dips.

Example IX

A liquid mixture containing the following chemicals was prepared :

Ruthenium trichloride	: 46 mg
Titanium tetrachloride	: 0.07 ml
Isopropyl alcohol	: 0.8 ml

The entire solution was applied several times onto the surface of a pre-etched titanium sheet of 25 cm². Drying and baking was done as in Example VIII. The final baking was done at 450°C in the presence of a current of air for 30 minutes. Theoretical amounts of RuO₂ and TiO₂ in this electrode were 27.16 mg and 50.75 mg respectively. The anode potential of this electrode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.23 volt against SCE. No weight loss was found after three current reversals as well as in three amalgam dips.

Example X

A pre-cleaned and pre-etched titanium base of 30 cm² surface area was painted several times with the following solutions and baked as in Example IX.

Ruthenium trichloride	: 37.6 mg
Titanium tetrachloride	: 0.12 ml
Ethyl alcohol	: 1 ml

The theoretical amounts of RuO₂ and TiO₂ formed in this case were 22.19 mg and 87 mg respectively.

This anode showed an anode potential of 1.27 volts against SCE in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². No weight loss occurred during three current reversals and three amalgam dips.

Example XI

A pre-cleaned and pre-etched perforated titanium plate of 30 cm² was painted with a mixture containing the following chemicals :

Ruthenium trichloride	: 112 mg
Titanium tetrachloride	: 0.3 ml
n-Butanol	: 2 ml

The painted surface was dried in hot air and baked at 300°C for 15 minutes. The painting and baking were repeated 20 times till all the mixture was used up. The final firing was carried out at 400°C in an atmosphere of air for one hour. The theoretical amounts of RuO₂ and TiO₂ in this electrode corresponded to 66.12 mg and 217.4 mg respectively.

The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.17 volt against SCE. No weight loss occurred during three current reversals and three amalgam dips.

Example XII

An etched titanium sheet of 25 cm² was painted and baked with coatings from the following solutions :

Ruthenium trichloride	: 23.2 mg
Titanium tetrachloride	: 0.05 ml
Isopropyl alcohol	: 0.6 ml

AND

Iridium trichloride	: 14.8 mg
Ammonia	: 3-4 drops
Isopropyl alcohol	: 0.2 ml

The baking was done as in the previous example. The mixed oxide coating thus obtained corresponded to theoretical amounts of 13.69 mg, 11.11 mg and 36.5 mg of RuO₂, IrO₂ and TiO₂ respectively. The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.19 volt against SCE. It showed a weight loss of 0.18 mg/cm² after three current reversals and 0.05 mg/cm² after three amalgam dips.

Example XIII

A pre-cleaned and pre-etched titanium sheet of 25 cm² was coated separately with mixtures containing a palladium compound in one and a titanium compound in the other. The mixtures were prepared as follows :

Palladium dichloride	: 0.05 g
Isopropyl alcohol	: 0.1 ml
Sodium nitrate	: 0.05 g

AND

Titanium tetrachloride	: 0.1 ml
Isopropyl alcohol	: 0.8 ml

The coating of the former mixture was baked at 650°C and the latter at 450°C. This anode registered an anode potential of 1.3 volt against SCE in the electrolysis of saturated brine at 60°C and at a current density of 10 kA/m². No weight loss occurred during three current reversals and three amalgam dips.

Example XIV

A solution containing 39.8 mg of ruthenium trichloride 106 mg of stannic chloride and 1 ml of n-butanol was prepared and painted over an etched titanium sheet of 25 cm² and baked as in the previous example. The coating contained 23.5 mg and 45.6 mg of RuO₂ and SnO₂ respectively. This electrode registered a potential of 1.2 volt against SCE while using it as anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m².

On three current reversals the anode lost a weight of 0.4 mg/cm². The weight loss after three amalgam dips was 0.44 mg/cm².

Example XV

A titanium plate of 40 cm² was coated with compounds of platinum and titanium under identical conditions as in Example III. The applied mixture contained the following chemicals.

Chloroplatinic acid	: 0.225 g
Titanium tetrachloride	: 0.3 ml
Isopropyl alcohol	: 2 ml

This anode was used in the oxidation of sodium chloride to sodium chlorate. A current efficiency of 93% was obtained at a current density of 1.6 kA/m², the electrolyte being a mixture containing 274 g/l of sodium chloride and 92 g/l of sodium chlorate and the electrolyte pH and temperature being 6-7 and 65°C respectively. No loss in weight of the coating was observed after the passage of a current of 400 amp-hr.

A current efficiency of 85% was obtained while using the same anode for oxidising sodium chlorate to sodium perchlorate at a current density of 2.5 kA/m², the electrolyte being a solution containing 613 g/l of sodium chlorate. The pH and temperature of the electrolyte.

were maintained at 6.7—7 and 50°C respectively. No loss of weight of the anode was found after the passage of a current of 360 amp-hrs.

Example XVI

An anode made under identical condition as in Example IX was used for the oxidation of sodium chloride to sodium chlorate. The operating conditions were as in Example XV. It gave a current efficiency of 90%. This anode registered an increase in weight of 1.7 mg after the passage of a current of 950 amp-hr.

Example XVII

An anode made under identical conditions as in Example II was used for the oxidation of sodium chloride to sodium chlorate. The operating conditions were as in Example XV. It registered a current efficiency of 85%. The weight loss after the passage of a current of 630-amp-hr. was 0.5 mg.

The following are among the main advantage of the invention :

(1) The anodes prepared as described in Examples I to XIII and particularly in Examples III to XIII would withstand current reversals and immersions in sodium amalgam in mercury type chlor-alkali cells.

(2) They will give lower anode potentials at very high current densities in both mercury and diaphragm type chlor-alkali cells.

(3) The wear rate of these anodes is very small and hence will have longer life.

(4) The employment of these anodes in chlor-alkali cells will result in lower power consumption, lower capital investment, lower operating cost and purer chlorine.

(5) They could also be used in the electrolytic production of chlorates, perchlorates, hypochlorite of sodium and the like products, in sea water electrolysis, in electro dialysis, as stable anodes for cathodic protection by impressed current and as insoluble anodes in plating operations.

Sd/- R. BHASKAR PAI

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 19th day of January, 1972.

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

THIS IS AN INVENTION BY RAMASWAMY THANGAPPAN NADAR, SCIENTIST, HANDADY VENKATAKRISHNA UDUPA DIRECTOR, BABU RAM YADAV, SENIOR SCIENTIFIC ASSISTANT AND PERUMAL SUBBIAH, JUNIOR SCIENTIFIC ASSISTANT, ALL OF CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, TAMIL NADU, INDIA, ALL INDIANS.

This invention relates to the preparation and application of insoluble anodes for electrochemical processes.

Definitions :

Titanium, tantalum, zirconium, niobium and tungsten are known as valve metals as their oxides have the typical rectifying action.

Throughout this specification, by the expression 'valve metals' we mean the above metals.

Similarly, by the expression 'platinum group metals', we mean the metals platinum, iridium, ruthenium, rhodium, osmium and palladium throughout this specification.

By insoluble anode, we mean that there is no change in the dimensions of the anode with time and as such there is no dissolution or disintegration of the anode structure during electrolysis.

This invention relation relates more particularly to the preparation of insoluble anodes formed by thermally depositing a single platinum group metal, a combination of platinum group metals or a combination of oxides of one or more of platinum group metals and a film forming metal from suitable salts supported in an organic vehicle, over a substrate like titanium, tantalum, tantalum, or an alloy of film forming metals.

Hitherto it is known to employ as anodes in an electrolytic cell, particularly in cells used for the electro-

lysis of aqueous solutions of alkali metal halides, anodes which would be resistant to the corrosive halide electrolytes and which will keep their dimensions almost constant for long durations. Lead dioxide deposited onto graphite, titanium, tantalum and magnetite, titanium electroplated with one or more of platinum group metals are known to have been used as anodes in the electrolysis of brine solutions to chlorinecaustic soda, chlorate and perchlorate of sodium. Lead dioxide anodes could not be used in mercury type chlor-alkali cells as the coating will get reduced to metallic lead in case of contact with mercury cathode; the high temperature of operation in both diaphragm and mercury type cells are detrimental to the electrode. Magnetite electrodes are very massive; they possess poor mechanical strength; they are not easily machinable and their wear rate in chloride electrolysis is quite significant. Electrodeposited platinum on titanium, while used as anode, gets passivated and hence requires activation. The wear rate of platinum or platinum-iridium coated titanium is also high which prohibits the use of such anodes in commercial installations.

The object of this invention is to obviate theses disadvantages. We have found that this can be done by making insoluble anodes formed by thermally depositing platinum along with traces of an activating element like antimony or bismuth or a combination of platinum group metals such as rhodium, iridium, ruthenium, osmium and palladium or a combination of oxides of one or more of

platinum group metals and a film forming metal like titanium, zirconium, niobium, tantalum or tungsten, over a corrosion resistant substrate like titanium, tantalum or an alloy of the valve metals.

The new principle underlying the invention is the preparation and application of insoluble anodes made of corrosion resistant valve metal such as titanium, tantalum or an alloy of valve metals as the base and activation of the surface of the base by thermally depositing platinum along with traces of an activating element or a combination of platinum group metals such as platinum, iridium, ruthenium, rhodium, osmium, palladium or a combination of oxides of one or more of platinum group metals and a valve metal like titanium, zirconium, niobium, tantalum or tungsten (for use as anodes in aqueous electrolysis, especially in the electrolysis of saturated brine). The coating of a single platinum group metal like platinum, iridium or palladium makes the surface conducting and the activating element added to it prevents the passivation of the coated surface. In the case of mixed oxides, a semi-conductive coating is formed.

According to the present invention, there is provided a process for the preparation of insoluble anodes for use as anodes in aqueous electrolysis, especially in the electrolysis of saturated brine, which consists in using corrosion resistant valve metals as substrate and coating the surface of the substrate by thermally depositing platinum along with traces of an activating element like antimony or bismuth or a combination of platinum group metals such as platinum, iridium, ruthenium, rhodium, osmium, palladium or a combination of oxides of one or more of platinum group metals and a valve metal like titanium, zirconium, niobium, tantalum or tungsten, the deposition being effected by thermal decomposition of a paste or chelate which is a mixture of the platinum group metal compound and the valve metal compound supported in an organic vehicle like ethyl alcohol, isopropyl alcohol or n-Butanol, required to supply the metal or the metal oxide, painted over the polished and acid etched surface of the substrate and fired at temperatures between 300 and 650°C in an atmosphere of either limited supply or forced circulation of air.

Thus titanium, tantalum or any other valve metal base is given a coating of platinum with traces of an activating element like antimony or bismuth or a combination of platinum group metals such as platinum, iridium, ruthenium, rhodium, osmium, palladium or a combination of oxides of one or more of platinum group metals and valve metals.

The conducting coating is deposited by thermal decomposition of a paste or chelate which is a mixture of the platinum group metal compound and the valve metal compound supported in an organic vehicle like ethyl alcohol, isopropyl alcohol or n-Butanol, required to supply the metal or the metal oxide.

Anodes prepared as described above are light and possess good mechanical strength and they could withstand temperatures that normally prevail in anodic oxidation in aqueous electrolytes, especially in the electrolysis of saturated brine to chlorine and alkali. The wear rates of these anodes are very insignificant and hence have longer life. As the dimensions of the anodes are remaining constant throughout its use, the interelectrode distance also remains constant which in turn eliminates the necessity of frequent adjustment of anodes to keep the cell voltage at a minimum. Thus, in

saturated brine electrolysis in mercury cell at 90°C and at a current density of 10 kA/m², these anodes, particularly the one with mixed oxide coating, showed a weight loss of 0.1 to 0.12 mg/cm² after 1280 hours of operation. In brine electrolysis in diaphragm cell at 70°C and at a current density of 3 kA/m², these anodes showed a weight loss of 0.06 to 0.09 mg/cm² after 1920 hours of operation. A commercial diaphragm cell equipped with this type of insoluble anode (strip type anodes without any welded structure) registered a voltage of 3.7 volts at an anode current density of 1.6 kA/m² (calculated on the basis of the surface facing the cathode) compared to 3.7 volts with graphite anode at a current density of 0.8 kA/m² (calculated on the basis of the surface facing the cathode). While no increase in cell voltage was noticed in the former case, the cell voltage in the latter one started increasing gradually within two months time. The chlorine gas purity in the same diaphragm cell was 98.5% with the new insoluble anode while it was 97.2% with graphite anodes. The cell with the new titanium substrate insoluble anode is in continuous operation and has not showed any change in the operating characteristics in the past five months and is being continued. A similar anode installed in a mercury type chlor-alkali cell is in continuous operation for the past four months and it has registered a cell voltage of 3.6 volts at an interelectrode distance of 3 mm and at a current density of 5 kA/m². It showed no change in the operating characteristics throughout and is being continued. These anodes withstand current reversals and immersions in sodium amalgam in mercury type chlor-alkali cell. The weight loss on three current reversals and three amalgam dips varied between 0 and 0.18 mg/cm² and 0 and 0.21 mg/cm² respectively.

To these ends, the present invention broadly consists in the preparation of insoluble anodes by depositing platinum or a combination of platinum group metals like rhodium, iridium, ruthenium, osmium and palladium or a combination of the oxides of one or more of platinum group metals and a film forming metal like titanium, zirconium, niobium, tantalum or tungsten over a corrosion resistant substrate like titanium, tantalum or an alloy of the film forming metal, the deposition being effected by thermal decomposition of a paste, a mixture of the various compounds supported in an organic vehicle required to supply the metal or the metal oxide, painted over the polished and etched surface of the substrate and fired at temperatures between 300 and 650°C in an atmosphere of either limited supply or forced circulation of air. The etching of the substrate is done in hydrochloric acid, sulphuric acid, a mixture of nitric acid and hydrofluoric acid or other etching solutions or by anodic etching suitable for the particular substrate and type of deposit. The coating chelate was prepared by dissolving the respective chloride of the platinum group metal in an organic solvent like ethyl alcohol or isopropyl alcohol. In certain cases a reducing agent was added to the above chelate. Similarly, a paste of the titanium tetrachloride was made separately. The etched surface was painted with the paste and dried in hot air and baked at a temperature of 300-350°C with or without a current of air circulated over the surface of the substrate. The sample was air cooled and the painting and baking operation continued till sufficient thickness of the metal or metal oxide layer formed on the surface. For making mixed oxide electrodes the above baking operation was followed by coating of titanium chloride chelate. In certain cases, both the chelates were mixed together and painted and baked,

When sufficient thickness was built up, the final baking was carried out at a temperature of 300-650°C for 30 minutes to one hour and then the electrode was air cooled.

The following typical examples are given to illustrate the invention:

Example I

A titanium plate of 80 cm² was mechanically polished, degreased in trichloroethylene and etched in 20% hydrochloric acid at a temperature of 90°C for 30 minutes. A chelate was prepared by mixing the following:

Chloroplatinic acid (39% metal content)	1.32 g.
Ethyl alcohol	16 ml.
Acetamide	1.7 g.
Antimony oxide	6.5 mg.

The etched titanium surface was brushed with this chelate, dried in hot air and fired at 350°C for 15 minutes. The painting and firing operations were continued till all the chelate was consumed. Finally, the coated surface was baked at 400°C for 30 minutes.

Theoretically the coating thickness of platinum corresponded to 3 microns. The anode potential of this electrode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.2 volts against SCE. It showed a weight loss of 0.10 mg/cm² after three current reversals and 0.21 mg/cm² after three amalgam dips.

Example II

A titanium plate of 12.5 cm x 1 cm was degreased in trichloroethylene and etched in 20% hydrochloric acid at 90°C for 30 minutes and rinsed with distilled water. 0.150 g of chloroplatinic acid was dissolved in 1.2 ml of isopropyl alcohol and 0.4 ml of 40% formaldehyde was added to this solution. Similarly, a solution of iridium compound was prepared by dissolving 0.03 g of iridium trichloride (64.33% metal content) in 5 drops of liquor ammonia diluted with 0.7 ml of isopropyl alcohol. The etched titanium base was brushed with the platinum containing paint, dried in hot air and baked in a muffle furnace at a temperature of 300°C for 10 minutes. On this a coating of iridium was provided by painting the iridium containing solution and baking as before. Seven such coatings in each of the solution were made and finally the electrode was baked at a temperature of 400°C for a period of 30 minutes.

The anode thus prepared contained 2.34 mg/cm² and 0.772 mg/cm² of platinum and iridium respectively. This anode registered an anode potential of 1.14 volt against SCE in saturated brine electrolysis in mercury cell at 60°C and at a current density of 10 kA/m². It showed a weight loss of 0.067 mg/cm² after three current reversals and a loss of 0.17 mg/cm² after three amalgam dips.

Example III

A strip of titanium plate of 25 cm² was degreased and etched in a solution containing 20% by weight of nitric acid and 40% by weight of hydrofluoric acid between 60 and 90°C for 25 minutes. One part by weight of iridium trichloride was added to 6 parts by weight of liquor ammonia to form a complex of iridium chloropenta amino chloride. Isopropyl alcohol 9 parts by weight was added to the above and the mixture painted over the etched surface of the titanium strip, dried in hot air, and heated in a current of air in a furnace at 300°C for 10 minutes to form a coating. A similar paint mixture

was made by adding 1 part by weight of titanium tetrachloride (25.2% metal content) to 9 parts by weight of isopropyl alcohol and brushed over the once coated titanium surface, dried, baked at 300°C for 10 minutes and air cooled. After giving 10 coatings alternately in each of the paint mixture, the anode was baked at 450°C in a current of air for one hour.

The coating thus made contained theoretical amounts of 13 g/m² of IrO₂ and 12 g/m² of TiO₂. This anode registered a potential of 1.16 volt against SCE while using it as anode in saturated brine electrolysis at 60°C in mercury cell at a current density of 10 kA/m². It showed a weight loss of 0.053 mg/cm² after three current reversals; but no weight loss was found after three amalgam dips.

Example IV

A strip of etched titanium plate of 25 cm² was coated alternately with a paste containing iridium and titanium compounds and baked as in Example III. The coating was applied several times. The applied mixture contained the following ingredients:

Iridium trichloride	0.03 g
Titanium tetrachloride	0.05 ml
Isopropyl alcohol	0.6 ml
Liquor ammonia	4 to 5 drops

The quantities of IrO₂ and TiO₂ in the coating corresponded to a weight ratio of 1:1.622 on theoretical basis. The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.2 volts against SCE.

Example V

As in Examples III and IV, a titanium plate of 25 cm² was coated with IrO₂ and TiO₂ to give a weight ratio of 1:6.25. The total weight of the coating as oxides corresponded to 54.3 mg. The anode potential of this anode in saturated brine electrolysis at 60°C at a current density of 10 kA/m² was 1.6 volts against SCE. Coating losses of 0.06 mg/cm² and 0.01 mg/cm² occurred on three current reversals and three short circuits in the amalgam respectively.

Example VI

A strip of tantalum measuring 25 cm² was electrolytically etched in a solution containing 12 g/l ammonium bromide, 2.5 g/l water in methyl alcohol at a current density of 5 amp/cm² at 30-35°C for 40 minutes. The surface was brushed with a mixture containing the following:

Ruthenium trichloride (44.82% metal content)	46 mg
Titanium tetrachloride	0.1 ml
Isopropyl alcohol	0.6 ml

Dried in hot air blast and decomposed by heating in an oven at 300°C for 10 minutes. The painting and heating was repeated 13 times till all the mixture was used up. The final backing was carried out in a current of air at 400°C in a muffle furnace for 30 minutes. The theoretical amounts of RuO₂ and TiO₂ in the coating were 27.16 and 73.0 mg respectively. The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.23 volt against SCE. No weight loss was found after three current reversals and three amalgam dips.

Example VII

A titanium sheet of total surface area 30 cm² was etched in 50% sulphuric acid at 60°C for 10 minutes. 49 mg of ruthenium trichloride was dissolved in 0.3 ml of isopropyl alcohol and a portion of this was painted over the etched surface of titanium, dried in hot air and baked at a temperature of 300°C in a furnace for 10 minutes. Subsequently the plate was coated with a mixture containing titanium tetrachloride and isopropyl alcohol in the ratio 1:8 by weight and drying and baking were done as before. The painting and baking procedure was repeated several times till the coating formed contained theoretically 28.93 mg of RuO₃ and 36 mg of TiO₂. The final baking was done at 400°C in the presence of an atmosphere of surplus air for one hour.

This anode registered an anode potential of 1.18 volt against SCE in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². It showed weight loss of 0.03 mg/cm² after three current reversals and no weight loss after three amalgam dips.

Example VIII

A titanium sheet of 30 cm² area was etched in 20% hydrochloric acid and was painted with a solution containing titanium tetrachloride and isopropyl alcohol in the ratio 1:8 by weight. The painted substrate was baked in a furnace at 300°C for 10 minutes. Subsequently the substrate was painted with a solution containing 83 mg of ruthenium trichloride and 0.5 ml of isopropyl alcohol and baked in the furnace as before in an atmosphere of air. The painting and baking process was repeated till all the solution containing the precious metal compound was used up. The final baking was done at 450°C for one hour. The coating weight corresponded to 49 mg of RuO₃ and 36 mg of TiO₂. An anode potential of 1.13 volt against SCE was observed when using it as anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². This anode gave a weight loss of 0.017 mg/cm² after three current reversals and no weight loss after three amalgam dips.

Example IX

A liquid mixture containing the following chemicals was prepared :

Ruthenium trichloride	46 mg
Titanium tetrachloride	0.07 ml
Isopropyl alcohol	0.8 ml

The entire solution was applied several times onto the surface of a pre-etched titanium sheet of 25 cm². Drying and baking was done as in Example VIII. The final baking was done at 450°C in the presence of a current of air for 30 minutes. Theoretical amounts of RuO₃ and TiO₂ in this electrode were 27.16 mg and 50.75 mg respectively. The anode potential of this electrode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.23 volt against SCE. No weight loss was found after three current reversals as well as in three amalgam dips.

Example X

A pre-cleaned and pre-etched titanium base of 30 cm² surface area was painted several times with the following solutions and baked as in Example IX.

Ruthenium trichloride	37.6 mg
Titanium tetrachloride	0.12 ml
Ethyl alcohol	1 ml

The theoretical amounts of RuO₃ and TiO₂ formed in this case were 22.19 mg and 87 mg respectively.

This anode showed an anode potential of 1.27 volts against SCE in saturated brine electrolysis at 60°C and at a current density of 10 kA/m². No weight loss occurred three current reversals and three amalgam dips.

Example XI

A pre-cleaned and pre-etched perforated titanium plate of 30 cm² was painted with a mixture containing the following chemicals :

Ruthenium trichloride	112 mg
Titanium tetrachloride	0.3 ml
n-Butanol	2 ml

The painted surface was dried in hot air and baked at 300°C for 15 minutes. The painting and baking were repeated 20 times till all the mixture was used up. The final firing was carried out at 400°C in an atmosphere of air for one hour. The theoretical amounts of RuO₃ and TiO₂ in this electrode corresponded to 66.12 mg and 217.4 mg respectively.

The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.17 volt against SCE. No weight loss occurred during three current reversals and three amalgam dips.

Example XII

An etched titanium sheet of 25 cm² was painted and baked with coatings from the following solutions :

Ruthenium trichloride	23.2 mg
Titanium tetrachloride	0.05 ml
Isopropyl alcohol	0.6 ml
and	
Iridium trichloride	14.8 mg
Ammonia	3-4 drops
Isopropyl alcohol	0.2 ml

The baking was done as in the previous example. The mixed oxide coating thus obtained corresponded to theoretical amounts of 13.69 mg., 11.11 mg and 36.5 mg of RuO₃, IrO₃ and TiO₂ respectively. The anode potential of this anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m² was 1.19 volt against SCE. It showed a weight loss of 0.18 mg/cm² after three current reversals and 0.05 mg/cm² after three amalgam dips.

Example XIII

A pre-cleaned and pre-etched titanium sheet of 25 cm² was coated separately with mixtures containing a palladium compounds in one and a titanium compound in the other.

The mixtures were prepared as follows :

Palladium dichloride	0.05 g
Isopropyl alcohol	0.1 ml
Sodium nitrate	0.05 g
and	
Titanium tetrachloride	0.1 ml
Isopropyl alcohol	0.8 ml

The coating of the former mixture was baked at 650°C and the latter at 450°C. This anode registered an anode potential of 1.3 volt against SCE in the electrolysis of saturated brine at 60°C and at a current density of 10 kA/m². No

weight loss occurred during three current reversals and three amalgam dips.

Example XIV

A solution containing 39.8 mg of ruthenium trichloride, 106 mg of stannic chloride and 1 ml of n-butanol was prepared and painted over an etched titanium sheet of 25 cm² and baked as in the previous example. The coating contained 23.5 mg and 45.6 mg of RuO₂ and SnO₂ respectively. This electrode registered a potential of 1.2 volt against SCE while using it as anode in saturated brine electrolysis at 60°C and at a current density of 10 kA/m².

On three current reversals the anode lost a weight of 0.4 mg/cm². The weight loss after three amalgam dips was 0.44 mg/cm².

Example XV

A titanium plate of 40 cm² was coated with compounds of platinum and titanium under identical conditions as in Example III. The applied mixture contained the following chemicals:

Chloroplatinic acid	0.225 g
Titanium tetrachloride	0.3 ml
Isopropyl alcohol	2 ml

This anode was used in the oxidation of sodium chloride to sodium chlorate. A current efficiency of 93% was obtained at current density of 1.6 kA/m², the electrolyte being a mixture containing 274 g/l of sodium chloride and 92 g/l of sodium chlorate and the electrolyte pH and temperature being 6.7 and 65°C respectively. No loss in weight of the coating was observed after the passage of a current of 400 amp. hr.

A current efficiency of 85% was obtained while using the same anode for oxidising sodium chlorate to sodium perchlorate at a current density of 2.5 kA/m², the electrolyte being a solution containing 613 g/l of sodium chlorate. The pH and temperature of the electrolyte were maintained at 6.7-7 and 50°C respectively. No loss of weight of the anode was found after the passage of a current of 360 amp. hr.

Example XVI

An anode made under identical conditions as in Example IX was used for the oxidation of sodium chloride to sodium chlorate. The operating conditions were as in Example XV. It gave a current efficiency of 90%. This anode registered an increase in weight of 1.7 mg after the passage of a current of 950 amp. hr.

Example XVII

An anode made under identical conditions as in Example II was used for the oxidation of sodium chloride to sodium chlorate. The operating conditions were as in Example XV. It registered a current efficiency of 85%. The weight loss after the passage of a current of 630 amp. hr was 0.5 mg.

The advantages of the invention are:

1. The anodes prepared as described in Examples I to XIII and particularly in Examples III to XIII withstand current reversals and immersions in sodium amalgam in mercury type chlor-alkali cells.

2. They give lower anode potentials at very high current densities in both mercury and diaphragm type chlor-alkali cells.

3. The wear rate of these anodes is very small and hence have longer life. The anodes maintain their dimensions stable throughout their period of long life. The active coating has a long life with comparatively lower cell potentials.

4. The employment of these anodes in chlor-alkali cells results in lower power consumption, lower capital investment, lower operating cost and purer chlorine.

5. They could also be used in the electrolytic production of chlorates, perchlorates, hypochlorite of sodium and the like products, in sea water electrolysis in electro-dialysis, as stable anodes for cathodic protection by impressed current and as insoluble anodes in plating operations.

Summarising, the present invention affords a method for preparing titanium substrate insoluble anode by activating the titanium surface by thermally depositing a coating of a single platinum group metal, a combination of platinum group metals or a combination of oxides of one or more of platinum group metals and a film forming metal, suitable for use as anodes in the electrolysis of aqueous solution, especially in the electrolysis or saturated brine to chlorine-caustic soda.

WE CLAIM:—

1. A process for the preparation of insoluble anodes for use as anodes in aqueous electrolysis, especially in the electrolysis of saturated brine which consists in using corrosion resistant valve metals as substrate and coating the surface of the substrate by thermally depositing platinum along with traces of an activating element like antimony or bismuth or a combination of platinum group metals such as platinum, iridium, ruthenium, rhodium, osmium, palladium or a combination of oxides of one or more of platinum group metals and a valve metal like titanium, zirconium, niobium, tantalum or tungsten, the deposition being effected by thermal decomposition of a paste or chelate which is a mixture of the platinum group metal compound and the valve metal compound supported in an organic vehicle like ethyl alcohol, isopropyl alcohol or n-Butanol, required to supply the metal or the metal oxide, painted over the polished and acid etched surface of the substrate and fired at temperatures between 300 and 650°C in an atmosphere of either limited supply or forced circulation of air.

2. A process as claimed in claim 1 wherein the titanium, tantalum or any other valve metal base is given a coating of platinum with traces of an activating element like antimony or bismuth or a combination of platinum group metals such as platinum, iridium, ruthenium, rhodium, osmium, palladium or a combination of oxides of one or more of platinum group metals and valve metals.

3. A process as claimed in claim 1 wherein the conducting coating is deposited by thermal decomposition of a paste or chelate which is a mixture of the platinum group metal compound and the valve metal compound supported in an organic vehicle like ethyl alcohol, isopropyl alcohol or n-Butanol, required to supply the metal or the metal oxide.

4. A process as claimed in any of the preceding claims wherein the deposition is carried out in an oxidising atmosphere.

5. A process as claimed in any of the preceding claims wherein the coating of the activating chelate is applied in

successive layers baking the painted substrate at a temperature of 300-350°C after each coating.

6. A process as claimed in claim 1 wherein the mixed oxide coatings are done from chelates of a single compound or a mixture of all the compounds required to provide the oxides.

7. A process as claimed in claim 1 wherein the final baking is done at a temperature of 300 to 650°C for 30 minutes to one hour before air-cooling the anodes.

8. A process as claimed in claim 1 wherein the coating is platinum, iridium or platinum and iridium in the ratio 7:3.

9. A process as claimed in claims 1 and 6 wherein the mixed oxide coatings consists of iridium oxide, ruthenium oxide or both along with oxides of titanium tantalum or both.

10. A process as claimed in claims 1 and 6 wherein the ratio of the platinum group metal oxide to valve metal oxide is between 1:50 and 1:1.

11. A process as claimed in any of the preceding claims wherein the thickness of the coating is between 0.5 and 20 microns.

12. A process as claimed in any of the preceding claims wherein a liquid chelate containing the various compounds supported in an organic vehicle, is applied on the substrate and baking is done in a furnace at a temperature of 300-350°C, repeating the procedure to build up the thickness of the coating in multiple layers before the final baking is done at a temperature of 300 to 650°C for 30 minutes to one hour.

13. A process for the preparation of anodes suitable for employment in the preparation of chlorine-alkali; chlorate and prechlorate of sodium, in sea water electrolysis, in electro dialysis as stable anodes in cathodic protection, and insoluble anodes in plating operations, substantially as described hereinbefore in the Examples I to XVII.

Sd/- R. BHASKAR PAI

Patents Officer,
Council of Scientific & Industrial Research

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