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" AN IMPROVED PROCESS FOR THE PREPARATION OF RUTHENISED TITANIUM ELECTRODES".

Council of Scientific and Industrial Research, Rafi Marg, New Delhi-110001, 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.

PRICE: TWO RUPEES

This is an invention by Kummattithidal Senthanam Rajagopalan, Subbiah Guruviah, Ramesh Arghode, Gopalacnari Venkatachari, Scientists, Kunjumani Chandran and Mrs Marikkannu viswanathan, Scientific Assistants, all from CECRI, Karaikudi and Indian citizens.

This invention relates to improvements in or relating to preparation of Ruthenised Titanium Electrodes.

Hitherto, graphite, platinum, pt = Ir alloy, metal oxide coated titanium, lead dioxide, palladium coated titanium etc. are used as anode in Chemical industries. These electrodes are having the following defects or limitation (1) large powder consumption in the case of metal anodes (2) Fast disintegration in the case of graphite (3) instability in the case of graphite (4) Poor adhesion (5) Porosity in the case of oxide coated titanium.

The object of the present invention is to obviate the above disadvantages by preparing a stable ruthenium coated titanium by plating and subsequently annealing.

The main objective of the invention is to give (1) suitable pre-treatment to the titanium surface, (2) Deposition of ruthenium on pre-treated titanium from ruthenium nitroso chloride bath (3) Annealing the rughenium deposited titanium
(4) Testing the electrode's efficiency by anodic polarisation in hydrochloric acid and acidified sodium chloride.
(5) Measurements of physical properties of the electrodes.
400 -600°C for 1 hour -2 hours.

The following are the main advantages of this invention.

1. It can be used as stable anode in electrochemical industries, such as chlor-alkali, electrowinning of metal.

2. Ruthenium diffused into the titanium substrate and there by increase the adhesion.

3. This type of anode eliminates entirely the product contamination

4. The noble metal coating increases the electrolytic activity of the anode and there by cell voltage is dicreased.

Dated this 5th day of Oct 1984.

(S. Kumar)
ASSISTANT PATENT OFFICER
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

This is an invention by Kummattithidal Senthanam Rajagopalan, Subbiah Guruviah, Ramesh Arghode, Gopalachari Venkatachari, ~~Scientists~~, Kunjumani Chandran and Mrs Marikkannu Viswanathan, all from CECRI, Karaikudi and Indian citizens and relates to ~~Improvements in or relating to~~ an improved [the] Process for the preparation of Ruthenised Titanium Electrodes which can be used as anodes in chemical industries. Hitherto, graphite, metal oxide coated titanium, lead dioxide, palladium coated titanium are used as anode in Chemical industries.

These electrodes have either one of the following defects or limitations (1) large power consumption (2) Fast disintegration (3) instability (4) Poor adhesion (5) Porosity.

The object of the present invention is to obviate the above disadvantages by preparing a Stable ruthenium coated titanium. The main objective of the invention is to give (1) suitable pre-treatment to the titanium surface (2) deposition of ruthenium on pretreated titanium from ruthenium nitroso chloride bath (3) annealing the ruthenium deposited titanium in a furnace (4) testing the electrode's efficacy by anodic polarisation in hydrochloric acid and acidified sodium chloride solution, (5) measurements of physical properties of the elctrodes and (6) measurements of anode potential and cell voltage of the electrode in acidified NaCl at 20 NA/m^2.

To these ends the present invention broadly consists of pretreating the titanium substrate with a mixture of sulfuric acid, phosphoric acid, ammonium fluride and water and depositing

ruthenium on the substrate from a ruthenium nitroso chloride bath and annealing the coated substrate.

The annealing is preferably done at a temperature between 400°-600°C in the presence of air. The coating of ruthenium is preferably done at 75°C.

Accordingly the present invention, provides an improved process for the preparation of ~~a stable~~ ruthenium ~~coated~~ titanium electrode which comprises pretreating the titanium substrate with a mixture of sulphuric acid, phosphoric acid, ammonium fluoride and water, electrolytically depositing ruthenium on the substrate from a ruthenium nitrosochloride bath using a current density of 20 ASF-30ASF, a voltage of 20-25V for a period ranging from 20-40 minutes at a temperature in the range of 70-80°C and annealing by heating the coated substrate.

The mixture used for the pre-treatment of titanium substrate may have the following composition in wt. percent of

H_2SO_4	25 g -30 g
H_3PO_4	40 g -50 g
NH_4F	2.5 g - 3.8 g and the balance being
Water in the range of	32.5 g - 35 g

The treatment period may range from 2-5 minutes and the temperature many range from 80°C-90°C.

The amount of ruthenium nitroso chloride used in the electroplating bath may be 4g/l.

The ruthenium coated titanium electrode is annealed at 400-600°C in the presence of air for one to two hours.

In the following examples given to illustrate the invention which should not be considered as to limit the scope of the invention.

		Example I	Example II
Depositition thickness		1μ	1μ
Period of annealing		1 hr.	1.5hr.
Temperature		400°C	400°C
Exchange current density for chlorine evolution reaction in saturated acidified sodium chloride solution (310-315 gpl)	30°C	4 mA/cm^2	
	70°C	3mA/Cm^2	3 mA/cm^2
Anode potential (v vs SCE) at 20 KA/m^2 in saturated acidified sodium chloride solution (310-315 gpl) (ph 3-4) at	30°C	1.4 - 1.47V	-
Cell voltage (V) at 20 KA/m^2 in saturated acidified sodium chloride solution at	30°C	3.5 - 3.7 V	-

The surface of the ruthenium coated titanium substrate after annealing was examined in scanning electron microscope and metallurgical microscope. The coating is found to be a mixture of TiO_2-RuO_2.

It was observed from the examples 1 and 2 that exchange current density of its electrode is higher which shows it has very good electrocatalystic surface which could be used as anode.

The following are the main advantages of this invention.

1. It can be used as stable anode in electrochemical industries, such as chlor-alkali, electrowinning of metal.

2. Ruthenium diffused into the titanium substrate and thereby increases the adhesion.

3. This type of anode eliminates entirely the product contamination.

4. The noble metal coating increases the electrocatalytic activity of the anode and thereby cell voltage is decreased.

We claim: 162352

1. An improved process for the preparation of ~~a stable ruthenium~~ ruthenised coated/titanium electrode which comprises pretreating the titanium substrate with a mixture of sulphruric acid, phosphoric acid, ammonium fluoride and water, electrolytically depositing ruthenium on the substrate from a ruthenium nitroso chloride bath using a current density of 20 ASF-30ASF, a Voltage of 20-25V for a period ranging from 20-40 minutes at a temperature in the range of 70-90°C and annealing by heating the coated substrate.

2. An improved process as claimed in claim 1 wherein the mixture for pretreating has the composition in wt/percent of

H_2SO_4	25 g -30 g
H_3PO_4	40 g -50 g
NH_4F	2.5 g - 3.8 g and the balance being
Water in the range of	32.5 g - 35 g

3. An improved process as claimed in claims 1, & 2 wherein the pretreatment is done for a period of 2-5 minutes.

4. An improved process as claimed in claims 1,2 & 3 wherein the pretreatment is done at a temperature in the range of 80° to 90°C.

5. An improved process as claimed in claims 1 to 4 wherein the amount of ruthenium in the bath is 4g/l.

6. An improved process for the preparation of Stable ruthenium coated titanium electrode substantially as hereindescribed with reference to the Examples.

Dated this 7th day of November 1985.

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