United States Patent [19]

Martinsons

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[45] **Feb. 27, 1973**

[54] **RUTHENIUM COATED TITANIUM ELECTRODE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 767,281, Oct. 14, 1968, Pat. No. 3,562,008.

[52] **U.S. Cl.** .....**204/98,** 204/290 F

[51] **Int. Cl.**.....**B01r 3/04,** B01r 1/00

[58] **Field of Search**.....204/98–100, 128, 204/290 F

[56] **References Cited**

UNITED STATES PATENTS

3,616,445 10/1971 Bianchi .....204/290 F

FOREIGN PATENTS OR APPLICATIONS

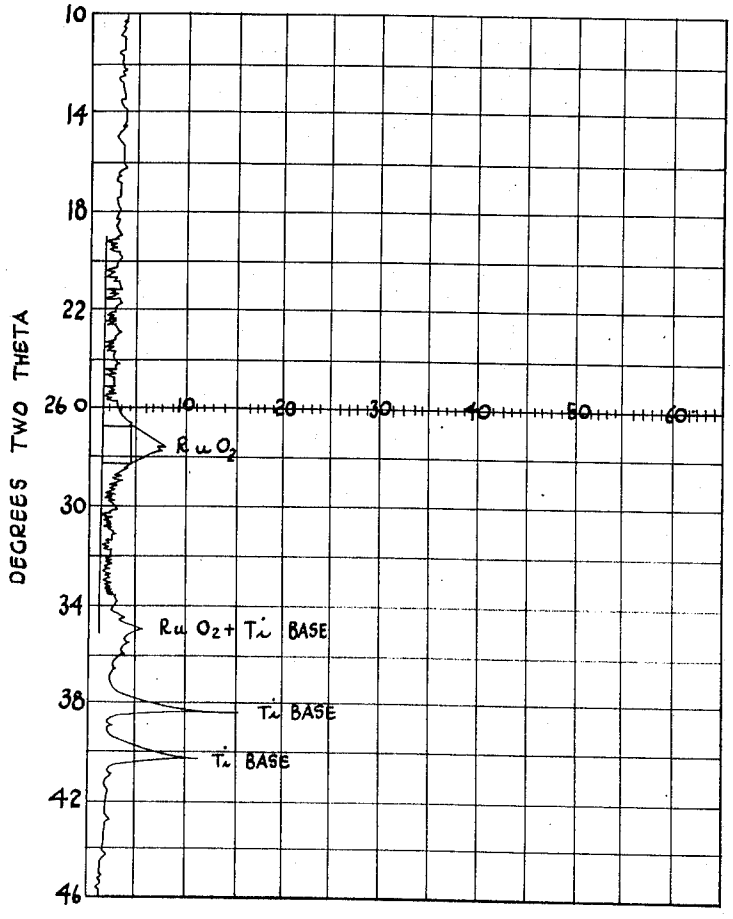
6,8/0,834 8/1968 South Africa .....204/290 F

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[57] **ABSTRACT**

An anode for the electrolysis of brines is disclosed. The anode has a titanium base member and an electroconductive coating thereon. The electroconductive coating comprises a mixture of amorphous titanium dioxide and a member of the group consisting of ruthenium and ruthenium oxide.

2 Claims, 5 Drawing Figures



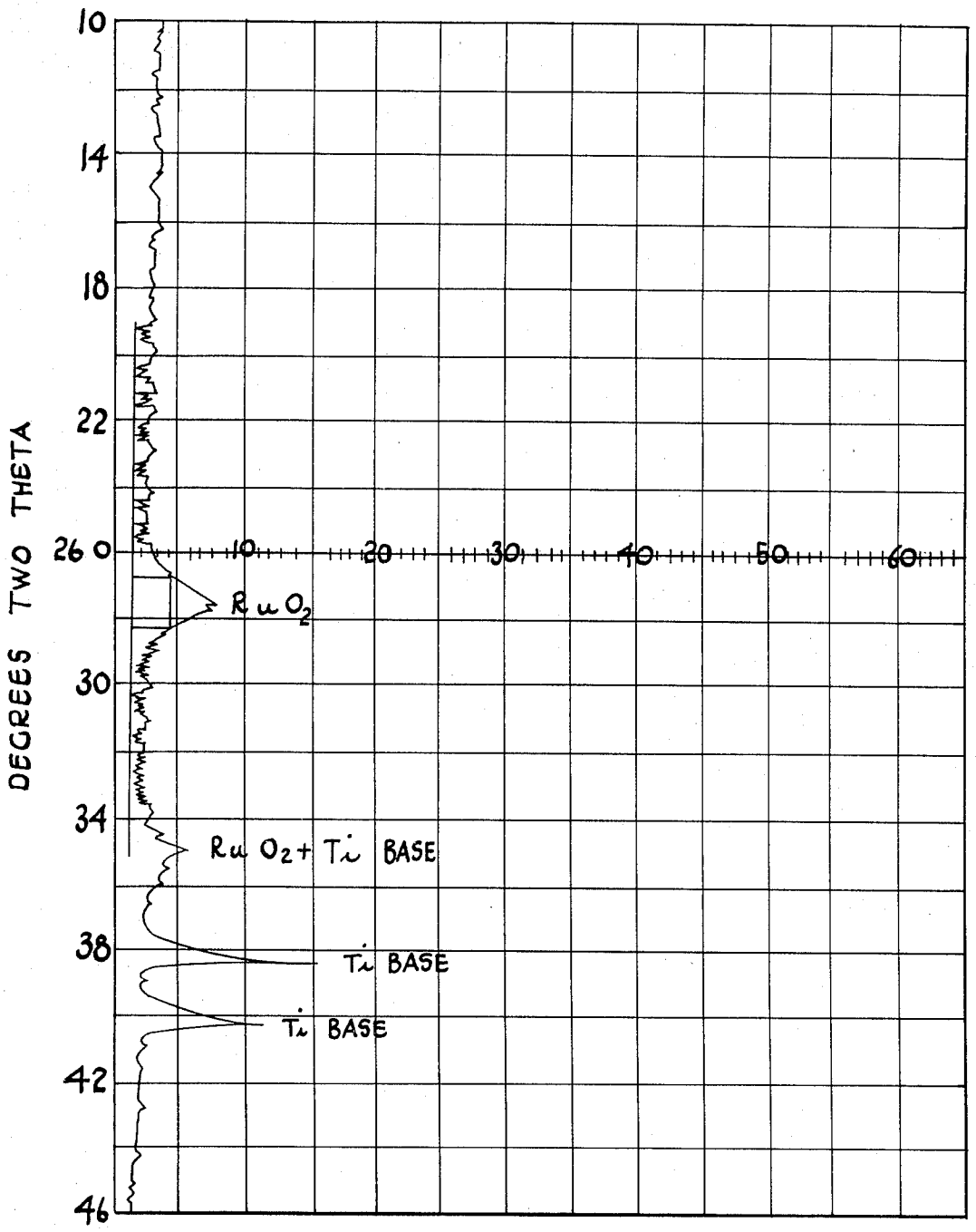


FIG. 1

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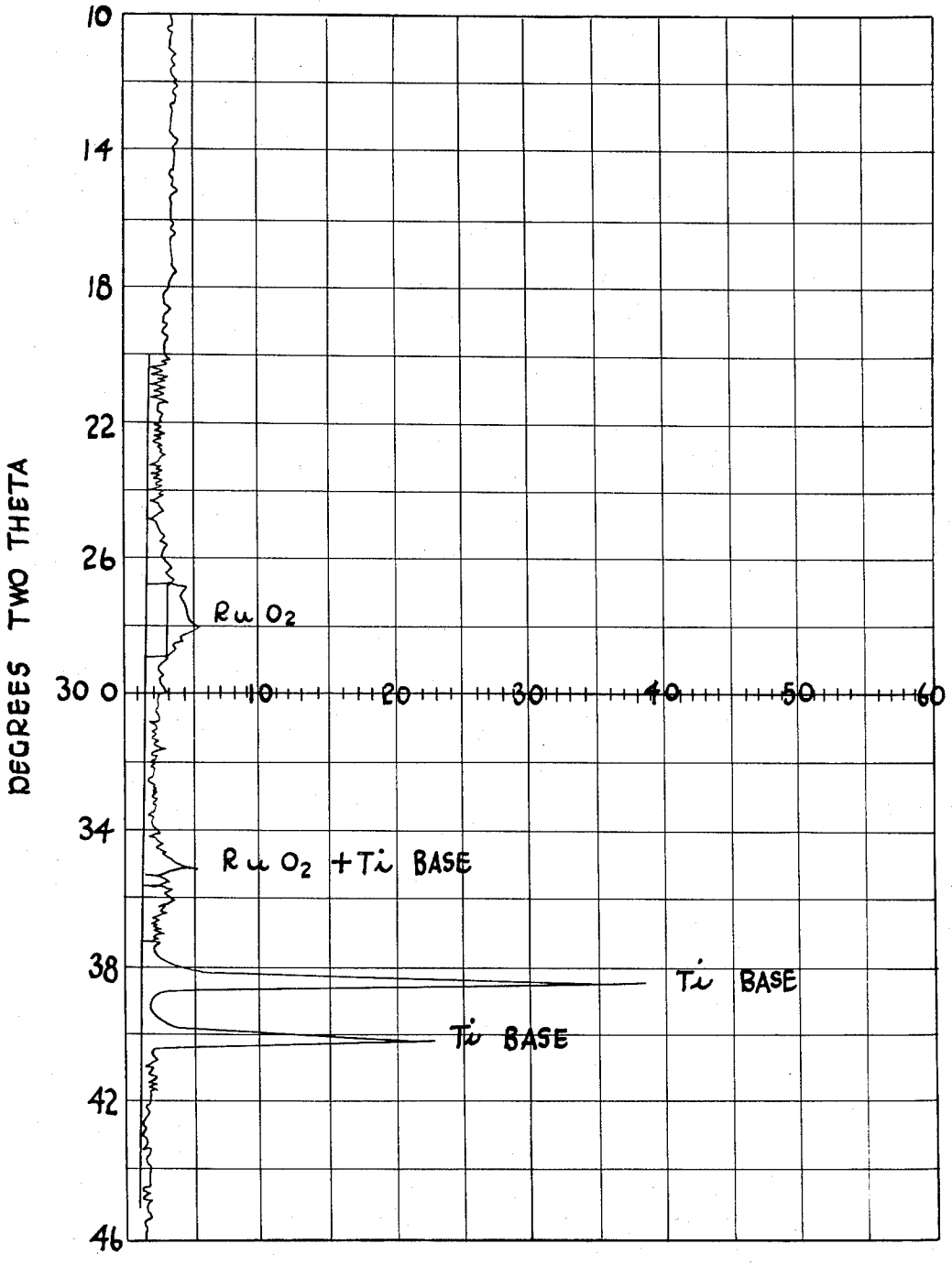


FIG. 2

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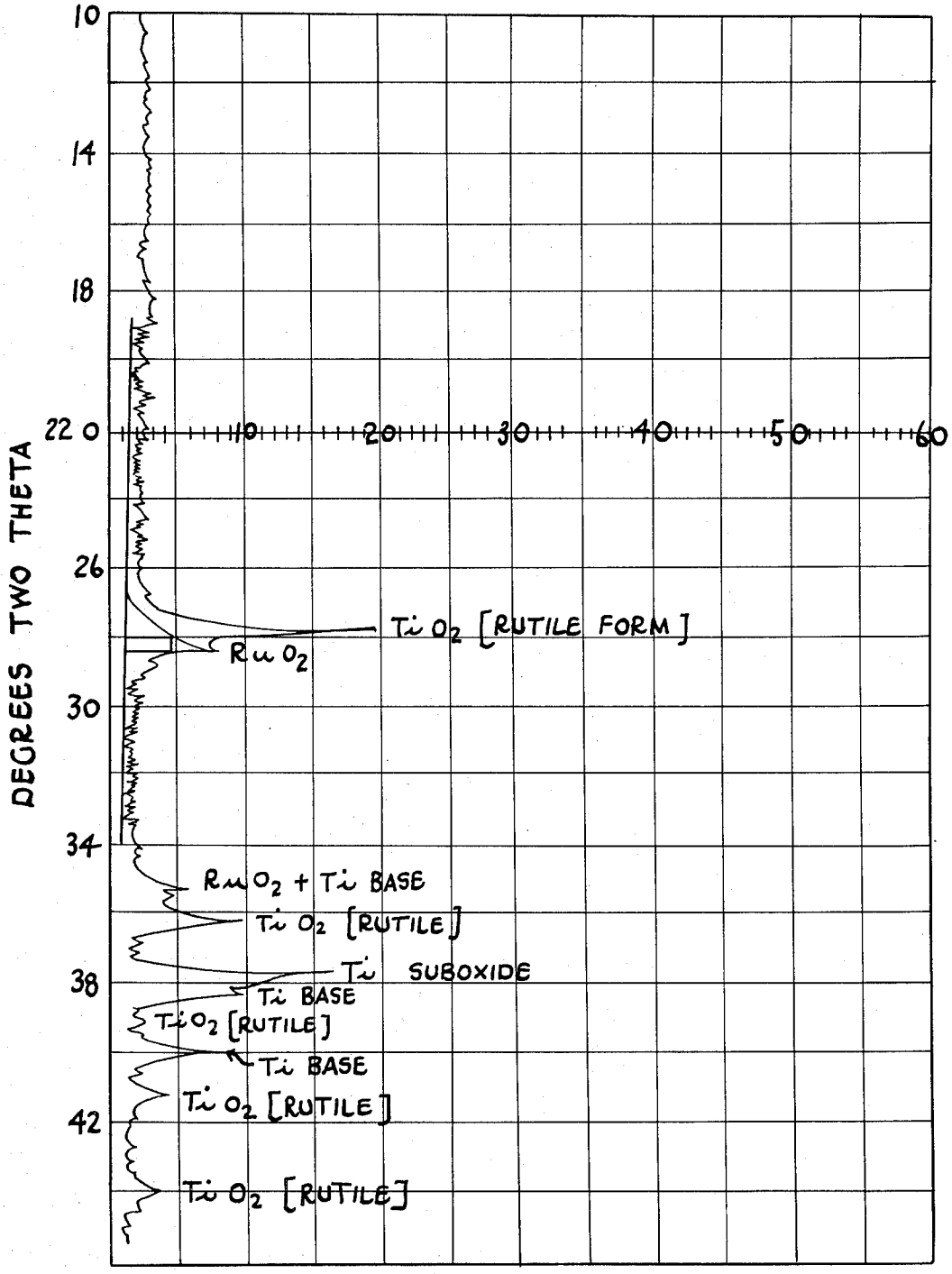


FIG. 3

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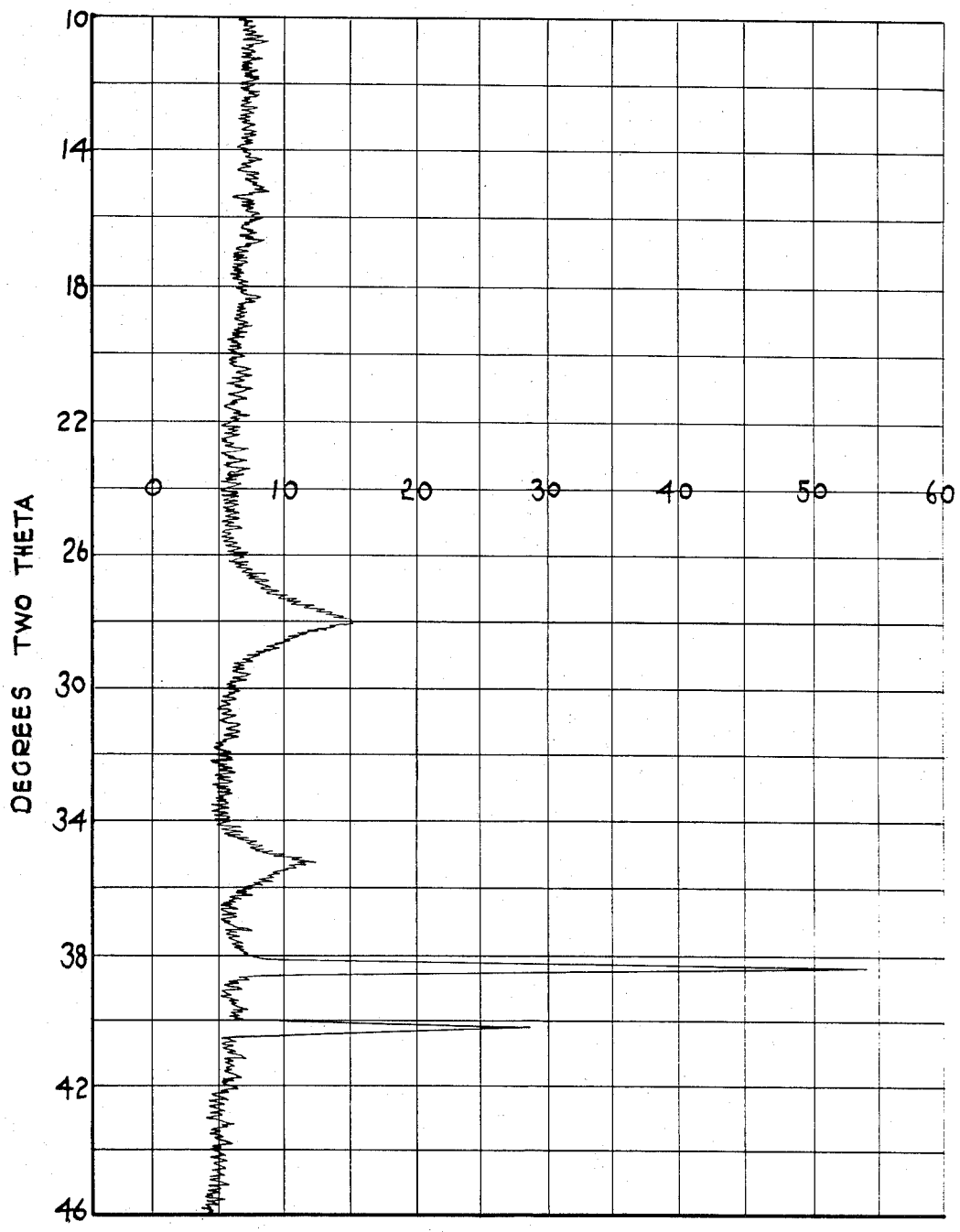


FIG. 4

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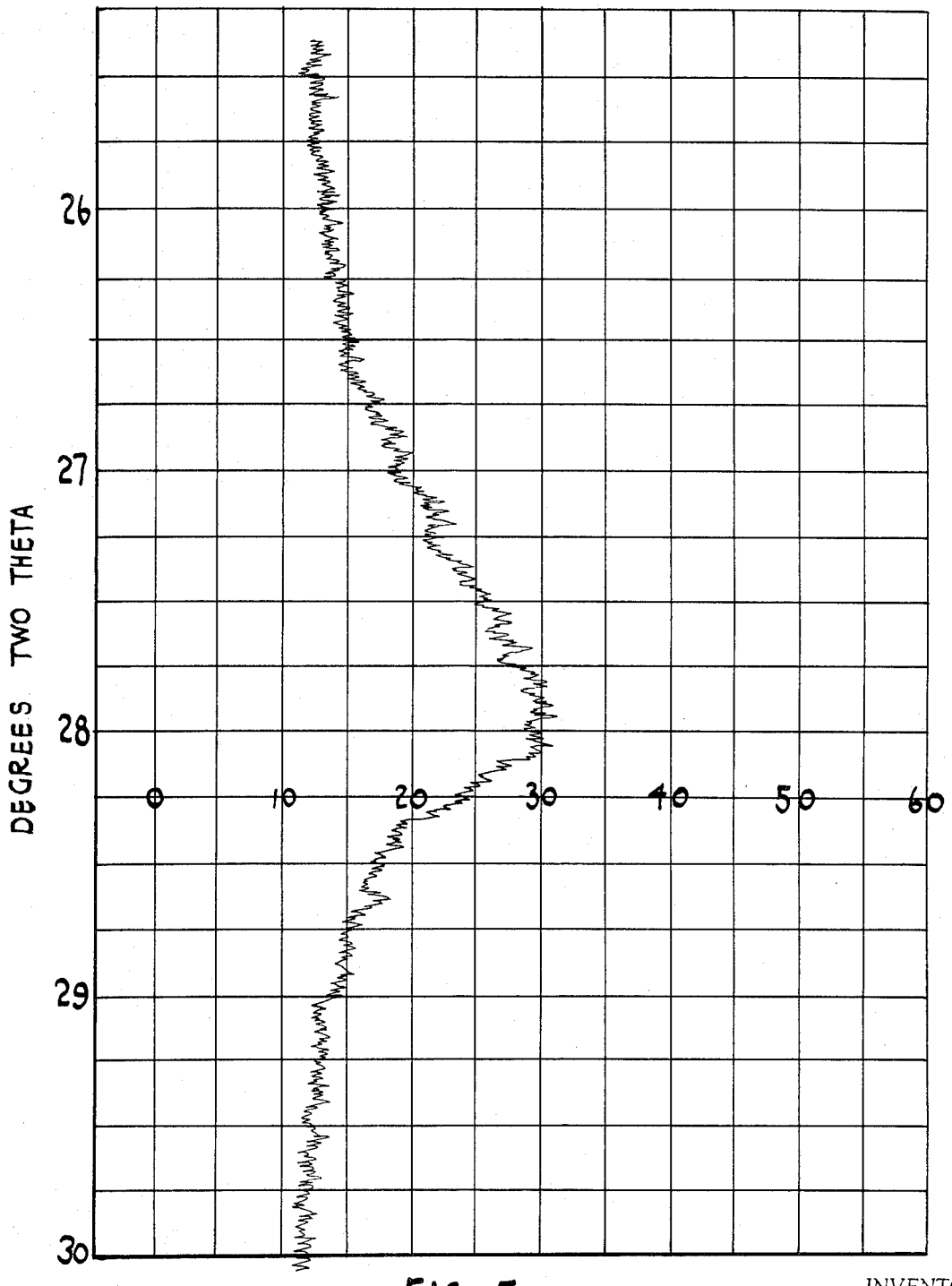


FIG. 5

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RUTHENIUM COATED TITANIUM ELECTRODE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 767,281 now U.S. Pat. No. 3,562,008, filed Oct. 14, 1968.

BACKGROUND OF THE INVENTION

This invention relates to electrodes for electrolytic cells and, more particularly, to a corrosion-resistant, dimensionally-stable anode for electrolysis of aqueous alkali metal chloride in the production of elemental chlorine or alkali metal chlorate. Such electrode has a metallic oxide coating.

The electrolysis of aqueous alkali metal chloride solutions such as solutions of sodium chloride or potassium chloride is conducted on a vast commercial scale. In the production of alkali metal chlorate, anodes and cathodes, or bipolar electrodes which when arranged in a spaced electrical series in an electrolytic cell may serve as both anode and cathode, are immersed in an aqueous solution of the sodium chloride or the like and an electric potential is established between the electrodes. In the past, graphite or carbon electrodes have been used as anodes or as the bipolar electrodes in series. In consequence of the electrochemical reactions which occur, alkali metal chlorate is produced either directly in the cell or outside the cell after the solution is allowed to stand.

The electrolysis of alkali metal chloride to produce elemental chlorine and alkali metal hydroxide is conducted in two general types of cells—the diaphragm and the mercury cathode cell. In the diaphragm cell, the cell is divided into two compartments—the anode compartment and the cathode compartment—which are separated by a porous diaphragm usually of asbestos. The cathode is of perforate metal and the asbestos diaphragm is in contact with the cathode. The anode, usually of carbon or graphite, is dispersed centrally in the anode compartment.

In the mercury cathode cell, the cathode is a flowing stream of mercury which flows along a solid metal base connected to the negative pole of a power source. The anode, again of carbon or graphite, is spaced from the mercury cathode and, as electric current flows, the sodium or like alkali metal is evolved and collected in the mercury as an amalgam which is removed from the cell. Outside the cell the mercury amalgam is contacted with water in a "denuder" to remove the sodium as sodium hydroxide solution and the mercury is then recycled.

In operating each of the above-described cells, one is confronted with a common problem; namely, that during the course of the electrolysis the carbon or graphite electrode erodes and/or decomposes. Consequently, as the electrodes wear away or erode, the spacing between the electrodes increases with resulting increase in voltage between electrodes. This, together with the reactions which cause degradation of the anode, results in a loss of current efficiency for the production of the desired product. The graphite anodes ultimately must be replaced. In all these cells this erosion increases as the temperature of the electrolyte rises or as the anode current density is increased. At the same time, the trend of operation is toward high current density to increase the amount of product produced per unit cell. Thus it has become necessary to resort to anodes or bipolar electrodes which remain dimensionally stable and do not erode appreciably over long periods of cell operation.

The present invention is directed to an improved stable electrode, the electrolysis of alkali metal chloride solutions in cells having the improved electrode, and to electrolytic cells, particularly to cells of the type described above which contain such electrodes as the anode or anodic surface thereof.

Electrodes herein contemplated normally should possess a certain degree of rigidity and, in any event, they must have surfaces which exhibit good electrolytic characteristics. These characteristics, particularly in the case of anodes, include low oxygen and chlorine overvoltage, resistance to corrosion and decomposition in the course of use as anodes in the electrolytic cell, and minimum loss of coating during such use. It is well known that certain metals, metallic oxides, and alloys are stable during electrolysis and have other superior properties when used as anodes. Such metals typically include the members of the platinum group; namely, ruthenium, rhodium, palladium, osmium, iridium, and platinum. These metals are not satisfactory for construction of the entire electrode since, for example, their cost is prohibitive. Therefore, these metals, metallic oxides, and alloys are commonly applied as a thin layer over a strength or support member such as a base member comprising titanium, tantalum, niobium, and alloys thereof. These support members have good chemical and electrochemical resistance but may be lacking in good surface electroconductivity because of their tendency to form on their surface an oxide having poor electroconductivity. Even when the platinum metals are applied in a thin layer, the cost is still substantial. Therefore, it is highly desirable to provide a coating having good electrolytic characteristics as is typical of the platinum metals and yet a coating which is less expensive.

Various methods have been proposed for applying the layers of metal to the base member. In the development of this invention, it has been found that the procedure used in applying the layer of metal, metallic oxide, or alloy affects the electrolytic characteristics of the electrode as well as does the particular metal, metallic oxide, or alloy selected. For example, if platinum is electrolytically deposited on a titanium electrode, the operating voltage of a cell containing such electrode as an anode operated at a particular current density is reduced when the electrode is heated following the final coating in an attempt to improve adhesion between the platinum and the titanium.

Furthermore, it has been found that the procedure used in applying the layer of noble metal, metal oxide, or alloy materially affects the adhesion between the layer and the titanium base member, thus affecting the durability and life span of the electrode. One approach to improving the adhesion between the layer and the base member is that of etching the base member prior to coating. Another approach is that of oxidizing the surface of the titanium base member, thereby forming a porous titanium oxide layer. The adhesion is greater between the noble metal and titanium oxide than between the noble metal and the titanium metal. Irregular results can be obtained with either method.

DESCRIPTION OF THE INVENTION

The present invention provides an electrode having superior electrolytic characteristics and superior bonding of the noble metal or noble metal oxide coating on the titanium base member as well as providing a more economical coating. According to this invention, a thermally-decomposable organic mixture containing a noble metal compound and a titanium compound is applied to the base member. The electrode is heated to decompose and/or to volatilize the organic matter and other components, leaving a deposit of amorphous titanium oxide and the noble metal or noble metal oxide. The titanium oxide being mixed with the noble metal or noble metal oxide serves to bond the noble metal or noble metal oxide to the titanium base member. The electrode of the present invention has a low chlorine and oxygen overvoltage.

IN THE DRAWINGS

FIG. 1 shows an X-ray diffraction pattern made at 35 kilovolts and 15 milliamperes of an electrode of the present invention produced as described in Example III.

FIG. 2 shows an X-ray diffraction pattern also made at 35 kilovolts and 15 milliamperes of the electrode of Example IV prior to final heating.

FIG. 3 shows an X-ray diffraction pattern also made at 35 kilovolts and 15 milliamperes of another electrode of Example IV following final heating.

FIG. 4 shows an X-ray diffraction pattern made at 40 kilovolts, 20 milliamperes, and a detector rotation of two degrees two theta per minute of another electrode of the present invention produced as described in Example III.

FIG. 5 shows an X-ray diffraction pattern in the range of 26 to 30 degrees two theta of the same electrode shown in FIG. 4. The diffraction pattern was made at 40 kilovolts, 20 milliamperes, and a detector rotation of one quarter degree two theta per minute.

The present invention provides an electrode having a layer or coating which exhibits improved electrolytic characteristics and improved adhesion. The invention also includes the steps of applying to the titanium electrode base one or a plurality of layers of a mixture of certain thermally-decomposable metal organic compounds such as organic salts and esters of both titanium and a platinum group metal. Especially useful for this purpose are mixtures of ruthenium resinate and titanium resinate, or a mixture of titanium resinate with other platinum resinates. The resulting coating, if comprising a mixture of ruthenium oxide and titanium oxide, should have a ruthenium oxide to titanium oxide ratio of at least 1 to 1 and preferably at least 1.8 to 1 by weight. Resinates of this type are manufactured by the Hanovia Division of Engelhard Industries. The metallic resinates may be mixed with an organic solvent or diluent, such as terpenes and aromatics, typically, oil of turpentine, xylene, and toluene, before being applied to the base member for further increasing adhesion.

As a general rule, the coating is applied as a series of thin layers in order to promote maximum adhesion of the coating to the base. The layers are then heated between coating operations to volatilize or drive off the organic matter, solvent, decomposition products, etc., and to form the oxides of the metals as a thin film on the base member.

It has been found that if the electrode is heated to a proper temperature while volatilizing or driving off the organic matter, a coating is produced comprising an evenly dispersed mixture of amorphous or essentially noncrystalline titanium oxide and the noble metal or noble metal oxide. Furthermore, the titanium oxide extends throughout the coating. The type titanium oxide having only a minor amount or no crystallinity not only serves to bond the noble metal or noble metal oxide to the titanium base member but also provides an exposed surface of high electroconductivity and low or even substantially no chlorine overvoltage. The electrode produced has excellent electrolytic characteristics and greatly improved adhesion. On the other hand, if the electrode is heated to an unduly high temperature, the titanium is converted to highly crystalline titanium oxide and a very unsatisfactory electrode is produced having high chlorine overvoltage and a surface which does not conduct electricity satisfactorily.

The exact temperature to which the electrode coating should be heated depends upon the time of heating and temperature at which the titanium and platinum compounds decompose. It should be high enough to cause formation of the titanium oxide, normally as TiO_2, and of the platinum group metal or oxide thereof. At the same time, crystallinity of the titanium oxide should be low although it is not necessary that the titanium oxide be completely noncrystalline. If materials such as silicon, aluminum and boron are present in the coating, the electrode may be heated to a higher temperature without adversely affecting the overvoltage characteristics of the electrode.

The effect on crystallinity of heating is illustrated in the drawings. The charts are drawings of an X-ray diffraction pattern obtained by analyzing the particular electrode on a Phillips Diffractometer. For FIGS. 1, 2, and 3, the X-ray tube was operated at 35 kilovolts and 15 milliamperes. For FIGS. 4 and 5 the X-ray tube was operated at 40 kilovolts and 20 milliamperes. Copper radiation was used and the Phillips Diffractometer was adjusted as follows: 1° divergence slit, 0.006 inch receiving slit, and 1° scatter slit. For FIGS. 1, 2, 3, and 4, the detector was rotated at one quarter degree two theta per minute. For FIGS. 1, 2, 3, and 4, the X-ray tube was operated at 1,000 counts per second full scale and a time constant of 2 seconds. For FIG. 5 the X-ray tube was operated at 500 counts per second full scale and a time constant of 5 seconds.

Referring to FIGS. 1, 4, and 5, it will be noted that the charts show background signal over the entire chart and that there is a small peak at an angle of about 27.2 to 28.5 degrees two theta and another at about 34.8 to 36 degrees two theta. These peaks reflect a ruthenium oxide having a small degree of crystallinity.

Referring to FIG. 1, it is noted that the peak between about 26 to 30 degrees two theta and, more particularly, between about 27.2 and 28.5 degrees two theta, exhibits a median number of counts per second above background at about 27.80 degrees two theta.

Referring specifically to FIG. 5, it is noted that the peak between about 27.2 and 28.5 degrees two theta exhibits a median number of counts per second above background at 27.80 degrees two theta, and the median number of counts per second above one half maximum intensity is at 27.85 degrees two theta. The peak itself has a height above background of about two hundred

per cent of background and a breadth at half maximum intensity of about 1.85 degrees two theta.

Turning now to the peak between 34 and 38 degrees two theta and, more particularly, between about 34.8 and 36.0 degrees two theta, and referring specifically to FIG. 1, it is noted that this peak exhibits a maximum height above background in the range of about 35.0 to 35.4 degrees two theta and, more particularly, at about 35.2 degrees two theta. This peak exhibits a median number of counts per second above background at about 35.4 degrees two theta.

Referring specifically to FIG. 4, it is noted that this peak exhibits a maximum height above background in the range of about 35.0 to 35.4 degrees two theta, and, more particularly, at about 35.2 degrees two theta, and a median number of counts per second above background at about 35.4 degrees two theta.

There are also peaks at about 38 to 38.8 and 39.6 to 40.4, both of which reflect the crystallinity of the titanium metal base. The chart of FIG. 2 is quite similar to that of FIGS. 1 and 4.

In contrast, however, a very high peak appears at an angle of about 26.8 to 28.4 of FIG. 3. Note that FIG. 3 shows the graph of an X-ray diffraction pattern of an electrode coated in the same way as the electrode of FIG. 2 except that whereas the electrode of FIG. 2 was heated only to 550°C. the electrode of FIG. 3 was heated to 700°C. for 15 minutes after its last coating was applied. Thus the high peak referred to in FIG. 3 shows higher (and unduly high) crystallinity. As shown below in the Examples, the anode of FIG. 3 was substantially poorer in electrical properties than the anodes of FIGS. 1, 2, and 4.

It is to be noted that the ruthenium oxide shows a small but detectible degree of crystallization in the electrodes of FIGS. 1, 2, and 4 and masks to a degree a small amount of crystallinity of TiO_2. However, the TiO_2 crystallinity was raised substantially by the 700°C. heat treatment as shown by FIG. 3.

While completely amorphous ruthenium oxide coatings have some value, best results have been obtained in accordance with this invention when the ruthenium oxide possesses a small amount of crystallinity which, in general, should correspond to that shown by the above-described X-ray test method in the range of about 100 to 400 percent above background, and, in any event, less than 700 percent above background in the range of 26 to 30 degrees two theta, and in the range of about 75 to 300 percent above background, and, in any event, less than 600 percent above background in the range of 34 to 38 degrees two theta.

Similarly, the titanium oxide crystallinity, when so measured, should not be above 700 percent above background and generally should be below 200 to 400 percent above background. However, rarely is it below 100 percent above background with the best bonded electrodes. Such titanium oxide, having a crystallinity as described above, is referred to herein as being amorphous or essentially non-crystalline, which terms are used interchangeably.

To achieve these results and unless heating is conducted for extremely short periods, the temperature of heating should not exceed about 650°C. and generally should be 600°C. or below. In order to obtain decomposition of the titanium and ruthenium compounds, it is rare that heating below 120°C. is suitable particularly because of the unduly long periods of heating which are required and, preferably, heating is conducted at 200°C. to 600°C.

The heating step described above is most advantageously conducted in an atmosphere containing elemental oxygen such as air or other oxygen-inert gas mixtures or even in an atmosphere of pure oxygen. With easily decomposable compounds and at relatively high temperatures the heating may be conducted in an inert atmosphere. However, in such a case the tendency is to produce a coating containing ruthenium metal rather than ruthenium oxide.

The organic compounds may, if desired, be applied by brushing a coating on the titanium base member or alternatively by any other method of application such as spraying or dipping. The electrode must then be heated to a temperature sufficient to drive off the organic material and to form the ruthenium oxide and the type of titanium oxide described above.

The temperature of the electrode may be raised at a continuous, steady rate or raised in a series of incremental steps. For example, a coating of the metal organic compound may be applied to the titanium base member while at room temperature. The temperature may be raised between 25°C. and 75°C. and held at that point for between 2 and 10 minutes. The temperature may then be raised a similar increment and held for a like period of time and repeating until the ultimate temperature is reached. The following examples are illustrative.

EXAMPLE I

An electrode was prepared starting with a titanium metal strip 5¾ /4 × ⅜ × 1/16 inch and brushing on a first coating of a mixture comprising 5 grams ruthenium resinate (4.0 percent ruthenium), 2 grams titanium resinate (4.2 percent titanium), and 3 grams toluene, thus providing a RuO_2/TiO_2 ratio of 1.87 by weight. The electrode was then heated to 400°C. by starting at room temperature and sequentially raising the temperature 50°C. every 5 minutes. The electrode was held at 400°C. for 10 minutes and then cooled to room temperature. In like manner, a total of 13 coatings were applied to the titanium base member. The final layer was further raised to 450°C. and retained at that temperature for 10 minutes. X-ray investigation indicated a satisfactory electrode coating.

EXAMPLE II

An electrode was prepared having 23 coats of the mixture used in Example I. The electrode was heated to 400°C. following each of the first 22 coatings and then heated to 500°C. following the final coating. The electrode was 1½ × 1½ × 1/16 inch and the total thickness of ruthenium was a little over 23 micro-inches. The electrode was placed as an anode in series with other platinum metal surfaced or ruthenium oxide surfaced electrodes in a cell in which the anode-cathode spacing was one-half inch. A brine solution having a concentration of 100 to 125 grams per liter NaCl and 500 to 600 grams per liter $NaClO_3$ was added to the cell. The cell was operated, maintaining the above NaCl concentration, at a current density of 500 amps per square foot.

The voltage between the anode and the cathode spaced next to it the first day was 3.18; the 12th day, 3.45; and after 17 days it was 3.54. This compares with 3.19, 3.49, and 3.64 volts, respectively, for a platinized titanium anode operated in an identical cell.

EXAMPLE III

An electrode was prepared by brushing onto a 1½ × 1-½ × 1/16 inch titanium base member **11** layers of a mixture comprising 5 grams ruthenium resinate containing 4 per cent by weight Ru, 2 grams titanium resinate containing 4.2 per cent by weight Ti, and 3 grams toluene. The electrode was heated to a temperature of 400°C. following the application of each of the layers **1** through **6**, **8** and **9**. The electrode was heated to 500°C. following the application of layers **7** and **10** and then heated to 550°C. following application of layer **11**. An X-ray analysis disclosed that the apparent ruthenium oxide thickness was 12 micro-inches or 3.8 grams per square meter.

The electrode had an X-ray diffraction pattern as shown by the chart of FIG. **1**. The X-ray diffraction pattern had a broad main peak for ruthenium dioxide at about 27.2 to about 28.5 degrees two theta with a breadth at half maximum of approximately 1.3 degrees two theta. This peak possibly may include some crystalline titanium dioxide (rutile form), such being hidden in the ruthenium dioxide peak. No substantial amount of crystalline titanium oxide was shown. The peak height above background for this main ruthenium dioxide peak is at about **600** per cent above background.

The X-ray diffraction pattern had a broad second-ary peak at about **34.8** to about **36.0** degrees two theta with a breadth at half maximum intensity of approximately **1.4** degrees two theta. This peak may also possibly include some crystalline titanium dioxide (rutile form), such being hidden in the ruthenium dioxide peak. No substantial amount of crystalline titanium oxide was shown. The peak height above background for this secondary ruthenium di-oxide peak is at about **450** per cent above background.

The other peaks on the chart are ruthenium di-oxide and titanium. The electrode was tested in a small, high-temperature chlorate cell, identical to that described in Example II, where it was compared with a standard plat-inum coated electrode.

The following table shows a comparison of voltages in the cell using the ruthenium-coated anode and the standard platinum electrode which is a titanium metal strip coated with platinum.

	cell Voltage After 1 day	3 days	49 days
Cell with ruthenium coated anode	3.070	3.193	3.670
Cell with standard platinum metal coated anode	3.260	3.271	3.690

Both electrodes were tested by X-ray for loss of coating after 49 days. The ruthenium-coated anode was found to have lost 3.8 micro-inches whereas the platinum-coated anode lost 13.4 micro-inches.

EXAMPLE IV

An electrode was prepared by applying 10 layers of a mixture comprising 5 grams ruthenium resinate, 2 grams titanium resinate, and 3 grams toluene. The electrode was heated to a temperature of 400°C. following each of the layers **1** through **6**, **8** and **9**. The electrode was then heated to a temperature of 500°C. following layers **7** and **10** and further heated to 700°C. following layer **11**. An X-ray analysis disclosed that the apparent thickness of ruthenium was 11.1 micro-inches or 3.5 grams per square meter. The X-ray diffraction pattern for this electrode following layer **10**, thus prior to heating to 700°C. (FIG. **2**), shows a moderate crystalline peak for ruthenium oxide at 28 degrees two theta. This peak has a breadth at half-maximum intensity of approximately 2.1 degrees two theta. The peak height above background for this peak is about 400 per cent of background. The other peaks in FIG. **2** are for ruthenium oxide and titanium. The X-ray diffraction pattern for this electrode following heating to 700°C. (FIG. **3**) shows several changes. The main ruthenium oxide peak indicates more crystallinity with a half-maximum intensity of approximately 0.5 degrees two theta. The peak height above background for this peak is at about 640 per cent of background. Also, a strong pattern for titanium oxide (rutile form) has developed of approximately 1,430 per cent. This electrode was also tested in the above-described, high-temperature chlorate cell and, after two hours of testing, the electrode was disconnected because of an excessively-high voltage of 7.02.

In the above description and examples, emphasis has been laid upon the production of anodes having a titanium dioxide-ruthenium dioxide coating on a titanium metal base particularly using a coating composition comprising a mixture of a titanium resinate and a ruthenium resinate. The composition is very effective in producing a coated anode or electrode in which the exposed or outside surface thereof is a mixture of these oxides with a minimum degree of crystallinity desired as described above. However, other compounds (usually solids or high body liquids) of titanium and ruthenium which form a solid or essentially nonvolatile residue when applied to the base and which decompose or hydrolyze upon heating in oxygen including inert air to produce the corresponding metal oxide may be used in lieu of the resinate in the above examples or in other procedures.

For example, the titanium esters or alcoholates or organic acid salts thereof or other organo titanates which can be readily oxidized in air or oxygen at temperatures of 300°C. to 650°C. or below may be used. Such compounds include tetraethyl titanate, tetra or butyl titanate, tetra stearyl titanate, tetra (2 ethyl hexyl) titanate, polyoctylene glycol titanate, diethylene glycol titanates or other titanates or polytitanates or titanium acylates such as hydroxyl titanium stearate, isopropoxy titanium stearate, titanium diphthalate, hydroxyl titanium linseed acylate, isopropoxy titanium oleate, or polymers of titanium esters such as polymeric tetra-n-butyl titanate, polymeric tetra isopropyl titanate, and like polymers including those which may be formed by partial hydrolysis of alkyl tetracycloalkyl or tetra aryl-titanates may be mixed with ruthenium resinate and the mixture applied to a titanium electrode base with the

resulting coating being heated in oxygen-containing atmosphere such as air to form the desired oxide coating containing both ruthenium oxide and titanium oxide. If desired, the oxygen-containing atmosphere may contain moisture to promote hydrolysis of the titanium compound and consequent generation of an oxide coating.

Also, other ruthenium compounds which decompose or hydrolyze on heating in an oxygen atmosphere in the presence or absence of air can be applied as a coating to leave a residue or deposit which on heating converts to oxide, preferably ruthenium dioxide, may be used in lieu of ruthenium resinate. Such compounds include ruthenium nitroso bromide, ruthenium trichloride, ruthenium amino nitride $[Ru(NH_3)_2(NO_2)_2]$ disulfide, $RuO(OH)_2$, calcium ruthenate or ruthenite or ruthenium diiodide, ruthenium triiodide like ruthenate or ruthenate of an alkaline earth metal, ruthenium titanate, or titanium ruthenium oxalate, the ruthenium salts of organic acid such as ruthenium acetate, ruthenium butyrate, ruthenium diphthalate, or the like may be used in the above examples or in other procedures in lieu of ruthenium resinate.

It will also be understood that other conductive coatings can be applied on a titanium anode so long as such coatings comprise a mixture of titanium oxide, preferably titanium dioxide and the platinum group metal or platinum group metal oxide. Of special value are the platinum group resinates including the resinates of platinum, palladium, osmium, rhodium, and iridium since these readily form a well bonded coating of excellent conductivity and electrochemical resistance. However, other platinum group compounds may be applied with the titanium organic compound including palladium dichloride, palladium trichloride, platinum di-n-butylamine nitride, $Pt(NH_3)_2NO$, pallidium amine, palladium iodide, palladium selenide, palladium disulfide, and the organic salts and esters or alcoholates and amino or nitro compounds of platinum group compounds corresponding to the ruthenium or titanium compounds listed above may be used in lieu of part or all of the ruthenium resinate in the above examples.

Where platinum compounds are used, the resulting coating after heating in air or oxygen at 300°C. to 650°C. generally contains platinum in metallic state and, in such a case, the coating is a mixture or intimate mosaic of platinum metal and titanium dioxide. Where it is desirable to convert the platinum to oxide, this may be done by immersing the thus-formed electrode in molten potassium nitrate at 400°C. for 1 to 10 hours.

Typical of formulations which may be used in lie of those set forth in the above examples include

A	B
15 grams isopropyl alochol	5 grams palladium resinate
2 grams titanium resinate	2 grams titanium resinate
4 grams palladium chlorate	3 grams toluene
10 grams toluene	

The ratio of titanium oxide to platinum group metal oxide in the coating applied to the titanium base should be sufficiently high to insure good adhesion of the coating to the titanium but not so high as to impair the electroconductivity of the coating. Poor conductibility is achieved when the film contains 60 per cent or more by weight of titanium (as oxide) based on the total metal content of the coating or coating composition. However, the titanium content should, in any event, not be less than 10 per cent thereof and, in general, best coatings contain 15 to 50 per cent of Ti as oxide, substantially the entire balance being a platinum group metal as oxide. Small amounts of other oxides (up to 20 per cent by weight compacted as the metal of the oxide and based on the total metal content of the coating) may be incorporated for example by adding to the coating composition (such as identified above, particularly in the examples hereof) a resinate of rhenium, lead, silicon, tantalum, tungsten, molybdenum, calcium, and zirconium, and heating the coating as described above.

Although the present invention has been described with reference to the specific details of particular embodiments thereof, it is not intended thereby to limit the scope of the invention except insofar as the specific details are recited in the appended claims.

I claim:

1. In a process for the electrolysis of brine comprising

causing an electrical current to pass from an anode to a cathode, the improvement wherein the anode has a coating consisting essentially of titanium oxide and ruthenium oxide wherein the coating shows an X-ray diffraction pattern comprising:

in the range of 26 to 30 degrees two theta a peak having a breadth at half-maximum intensity of between 1.3 to 2.0 degrees two theta, said peak having its maximum intensity between 27.80 and 28.00 degrees two theta, and a peak height above background of less than 600 percent of background;

in the range of 34.00 to 38.00 degrees two theta a peak having a breadth at half -maximum intensity of between 1.3 and 2.0 degrees two theta, said peak having its maximum intensity between 35.0 and 35.4 **degrees two theta, and a peak height above background of less than** 600 per cent of background; and wherein said anode is prepared by the method comprising applying a mixture of titanium resinate and ruthenium resinate to a titanium base and heating the coated base between 300°C and 650°C.

2. An anode having a coating consisting essentially of titanium oxide and ruthenium oxide wherein the coating shows an X-ray diffraction pattern comprising:

in the range of 26 to 30 degrees two theta a peak having a breadth at half-maximum intensity of between 1.3 and 2.0 degrees two theta, said peak having its maximum intensity between 27.80 and 28.00 degrees two theta, and a peak height above background of less than 700 per cent of background; and

in the range of 34.00 to 38.00 degrees two theta a peak having a breadth at half-maximum intensity of between 1.3 and 2.0 degrees two theta, said peak having its maximum intensity between 35.0 and 35.4 degrees two theta, and a peak height above background of less than 600 per cent of background, prepared by the method comprising applying a mixture of titanium resinate and ruthenium resinate to a titanium base and heating the coated base to between 300°C. and 650°C.

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