

- [54] **METHOD OF MAKING AN ELECTRODE**
- [75] Inventors: **Joseph Bernard Cotton**, Sutton Coldfield; **Peter Charles Steele Hayfeeld**, Castle Bromwich; **Ian Robert Scholes**, Sutton Coldfield, all of England
- [73] Assignee: **Imperial Metal Industries (Kynoch) Limited**, Witton Birmingham, England
- [22] Filed: **Dec. 14, 1970**
- [21] Appl. No.: **98,184**

- [30] **Foreign Application Priority Data**  
Dec. 22, 1969 Great Britain ..... 62,332/69
- [52] U.S. Cl..... 117/217, 117/215, 117/221, 204/290 F
- [51] Int. Cl..... **B44d 1/18**
- [58] Field of Search ..... 204/290 F; 117/217, 117/215, 221

- [56] **References Cited**  
**UNITED STATES PATENTS**  
3,234,110 2/1966 Beer ..... 204/290 F

|           |        |                    |           |
|-----------|--------|--------------------|-----------|
| 3,096,272 | 7/1963 | Beer .....         | 204/290 F |
| 3,562,008 | 2/1971 | Martinsons .....   | 204/290 F |
| 3,645,862 | 2/1972 | Cotton et al. .... | 204/290 F |
| 3,663,280 | 5/1972 | Lee .....          | 117/217   |

### FOREIGN PATENTS OR APPLICATIONS

|         |        |             |           |
|---------|--------|-------------|-----------|
| 661,462 | 4/1963 | Canada..... | 204/290 F |
|---------|--------|-------------|-----------|

### OTHER PUBLICATIONS

Tsvetnova, R. V. and Krasilshchikov, A. I., Passivity of Titanium in Sulfuric Acid, Chemical Abstracts. 62:12,743f

*Primary Examiner*—Cameron K. Weiffenbach  
*Attorney*—Cushman, Darby & Cushman

### [57] ABSTRACT

A method of manufacturing an electrode in which there is chemically or electrically deposited on to a film-forming metal base an oxide of a film-forming metal from a solution containing ions of the film-forming metal, followed by the application of a coating containing a platinum group metal or oxide.

**10 Claims, No Drawings**



## METHOD OF MAKING AN ELECTRODE

## BACKGROUND OF THE INVENTION

This invention relates to electrodes and is concerned with electrodes which are suitable for use in electrolytic processes, and the manufacture of such electrodes. Examples of such electrolytic processes are chloralkali electrolysis, per-salt electrolysis, electroplating and cathodic protection.

The invention is particularly concerned with electrodes in which at least the surface of an electrode base is formed of a "film-forming metal", there being applied to at least part of said surface an electrically conductive electrolyte-resistant coating. By the term "film-forming metal" is meant a metal with incidental impurities, or an alloy, which has anodic polarisation properties similar to those of titanium and titanium base alloys. The film-forming metals and alloys as referred to in this specification are titanium itself and titanium base alloys, tantalum and tantalum base alloys, niobium and niobium base alloys, and zirconium and zirconium base alloys.

There has been proposed, inter alia in British Patent Specification No. 925,080, a method of manufacturing an electrode composed of a core of titanium and a porous coating of a metal of the platinum group, in which the titanium core is provided with a barrier layer by anodising or by oxidation before the coating is applied thereto. In said specification, the advantages of such a method are said to be the avoidance of any necessity prior to coating with a metal of the platinum group to remove the oxide film naturally occurring on titanium, the certainty that the titanium will be protected from corrosion by the barrier layer, even under the coating of a metal of the platinum group, which could be significant should said coating be damaged, the avoidance of any need for removing the barrier layer when a fresh coating of a metal of the platinum group is to be applied, and ease in providing an adherent coating of the metal of the platinum group.

It is an object of the present invention to provide an improved method of applying a barrier layer on a film-forming metal, and manufacturing an electrode therefrom, whereby further benefits and advantages are attained.

## SUMMARY OF THE INVENTION

In accordance with the invention a method of manufacturing an electrode suitable for use in electrolytic processes comprises taking an electrode base of which at least the surface is a metal selected from the group of film-forming metals consisting of titanium, tantalum, niobium, zirconium and alloys based on at least one of these metals, applying to at least part of said surface a solution containing film-forming metal ions, depositing from said solution on to said surface a layer consisting of an oxide of the film-forming metal of the solution, and applying to at least part of said surface an electrically conductive electrolyte resistant layer containing a metal of the platinum group or an oxide of a metal of the platinum group.

Preferably the method comprises depositing the layer consisting of an oxide of the film-forming metal on to said surface before applying the layer containing a metal of the platinum group or an oxide of a metal of the platinum group.

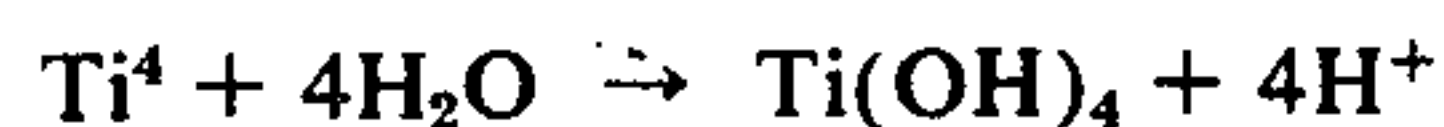
If required, a layer containing a platinum group metal or oxide may be applied to at least part of the surface of the electrode base before application of a layer of an oxide of a film-forming metal.

The surface areas over which the various layers are applied may be the same or they may differ but overlap, as required. The layer of an oxide of a film-forming metal is preferably of the same metal as that forming the surface.

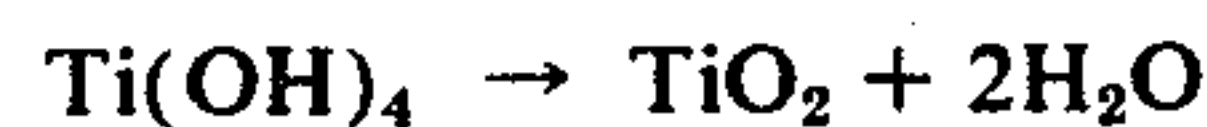
The layers mentioned above have not been specifically referred to in terms of multiple layers, but this is within the scope of the invention. Thus preferably the method of the invention also comprises depositing one or more layers each consisting of an oxide of the film-forming metal of the respective solution, at least one of said layers being deposited on top of a corresponding layer containing a metal of the platinum group or an oxide of a metal of the platinum group. As an example, an electrode base of which the surface is a film-forming metal can be provided with one or more layers containing a platinum group metal or an oxide of a platinum group metal, followed by one or more layers from solution of an oxide of a film-forming metal, followed by one or more layers containing a platinum group metal or oxide, followed by one or more layers from solution of an oxide of a film-forming metal, etc. The film-forming metal oxide need not be the same in each layer thereof, and the layers containing a platinum group metal or oxide may differ from each other, for example by containing only metals or only oxides or mixtures thereof, and by using different platinum group metals or mixtures thereof.

Preferably further the or at least one of the layers of an oxide of the film-forming metal is deposited from the solution by chemically decomposing in the solution a compound containing the film-forming metal. Alternatively the or at least one of the layers of an oxide of a film-forming metal is deposited from the solution by electrolysis of the solution.

The chemically decomposing method is exemplified with reference to titanium in which an aqueous solution is prepared containing a trivalent titanium ion. This is oxidised, for example by bubbling air through the liquid, whereby titanium in the quadrivalent state is obtained. When the electrode base has been immersed in the solution, the solution is heated to near its boiling point which has the effect of hydrolysing the titanium to deposit titanium dioxide on the titanium surface. Without prejudice to the present invention, it is thought that the reactions concerned are those symbolised in the following simplified reaction equations:



followed by



Using a solution of 10wt.% sulphuric acid containing 1,000 p.p.m. of titanium in the quadrivalent state, the rate of weight gain of the titanium dioxide film is steady and is approximately 5 g/m<sup>2</sup>/day. This rate can be varied by rapid boiling of the solution, or by use of the solution at a temperature slightly below its boiling point, but the titanium dioxide must be applied at too fast a rate since a non-adherent deposit can be formed. The maximum weight of the titanium dioxide film which can usefully be obtained is in the region 20-30 g/m<sup>2</sup>,



after which a white non-adherent film is formed and spalling may occur.

When the desired weight of titanium dioxide has been deposited, preferably in the range  $2\frac{1}{2}$  to  $20\text{ g/m}^2$ , an associated deposit of oxidised platinum group metal is applied. In the instance of ruthenium oxide this involves use of a paint which is stoved in air at  $500^\circ\text{C}$  for 20 minutes. An optimum paint composition is obtained by dissolving  $60\text{ g/l}$  of  $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$  in a suitable alcohol saturated with ammonium chloride. The paint may be applied, for example, using a brush such that the paint dries off within a few minutes of deposition.

The electrolysing method is exemplified within reference to titanium in which there is again prepared an aqueous solution containing a trivalent titanium ion. An electrode base is immersed in the solution and is connected as an anode with respect to a cathode of a suitable material also in the solution. With the solution near its boiling point a voltage of typically 12 volts produces a strongly adhering coating on the electrode base. There can be achieved a coating rate of about  $2\text{ g/m}^2/\text{hr}$ .

Preferably the layer containing a metal of the platinum group or an oxide of a metal of the platinum group is applied by thermal decomposition of a paint coating. Typically the paint coating is decomposed by being fired at  $450\text{--}700^\circ\text{C}$  in an oxygen-containing atmosphere for 5 minutes to 1 hour. The coating may be given a subsequent heat treatment in an oxygen-containing atmosphere for up to 20 hours. If the coating contains ruthenium the temperature may be up to and including  $700^\circ\text{C}$ .

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical examples of the invention will now be more particularly described.

##### Example 1

An electrode base consisting of commercial quality titanium of low impurity content in the annealed and chemically descaled condition, is coated, without chemical etching in this example, with a titanium oxide layer of  $10\text{ g/m}^2$  loading. On top of this layer is deposited  $15\text{ g/m}^2$  of oxidised ruthenium.

The chemical deposition of titanium dioxide is achieved in the following way. Commercial purity titanium is dissolved in heated 10wt.% sulphuric acid to give a purple/blue solution typical of  $\text{Ti}^{3+}$  solution. This solution is diluted to a concentration of 1,000 p.p.m. titanium per litre and the titanium ions are oxidised to the tetravalent state by bubbling air through the solution until the purple coloration disappears and the solution becomes colourless. With this solution near boiling point, or gently boiling, the titanium electrode base is suspended vertically for a period during which chemical deposition of the titanium oxide takes place. An immersion period of 24 to 48 hours results in deposition of from  $5$  to  $10\text{ g/m}^2$ . At the end of the coating period the electrode base is washed in water, gently scrubbed with a nylon brush to remove any loose coating, and then dried.

The oxidised ruthenium is derived from a paint consisting of  $60\text{ g/l}$  of  $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$  dissolved in an alcohol and saturated with ammonium chloride. The paint is applied by a nylon brush on to the titanium in a number of coatings. Stoving is effected for every two coats, the

procedure consisting of exposure to circulating air at  $500^\circ\text{C}$  for 20 minutes.

The electrode of Example 1 was subjected to an electrolytic test in which a coated blade edge  $30 \times 1\text{ mm}$  was located 2mm above a mercury surface. Brine of  $22\text{ g/l}$  concentration at  $70^\circ\text{C}$  was passed between the electrodes, and the test surface made anodic with respect to the mercury at a real current density of  $40\text{ kA/m}^2$ . The length of electrolysis time at a low cell voltage exceeded that obtainable by depositing the same quantity of oxidised ruthenium on an etched titanium surface without application of the chemically deposited titanium dioxide layer. This is a severe test with a short anode-to-mercury gap and a high current density.

##### Example 2

An electrode base consisting of commercial purity titanium of low impurity content is used in the air annealed and chemically descaled condition. With the surface of the electrode base degreased in trichlorethylene vapour, but unetched, two layers of oxidised ruthenium are applied by painting and stoving using the procedure described in Example 1. On to this surface is deposited  $10\text{ g/m}^2$  of titanium dioxide using the technique described in Example 1. To complete the coating, a further  $4\text{ g/m}^2$  of oxidised ruthenium are applied by the method used to deposit the initial two layers. A coating of such sandwich construction gave good performance on electrolytic testing by the route described above in relation to Example 1.

##### Example 3

In this example, a process route very similar to that of Example 2 is used, except that the initial noble metal paint applied to the titanium consists of 70/30 platinum/iridium. A single layer of "Hanovia Ir1" paint is applied, and this is dried for 15 minutes at  $250^\circ\text{C}$  followed by stoving for 20 minutes at  $450^\circ\text{C}$ , all in air. On to this layer is deposited  $10\text{ g/m}^2$  of titanium oxide by the sulphuric acid route, and finally  $4\text{ g/m}^2$  of ruthenium metal as oxidised ruthenium. This coating also gave good electrolysis characteristics.

Electrodes manufactured by Examples 1, 2 and 3 were found to have a chlorine overpotential with current density in the region of  $10\text{ kA/m}^2$  which is at least comparable to that of a titanium base electrode which has several layers thereon of ruthenium oxide only.

In modifications of Examples 1, 2 and 3, other film-forming metals than titanium can be used for the electrode base, for example niobium, tantalum and, when the chlorine environment is avoided, zirconium. In addition, the applied layer of titanium dioxide can be replaced by layers of oxides of others of the film-forming metals. It is not necessary for the same film-forming metal to be used in the applied oxide layer as in the electrode base. Thus, a layer of titanium dioxide may be applied to an electrode base of tantalum.

Furthermore, the film-forming metal oxide may be applied from a paint composition by the stoving in air of a paint containing an appropriate organo-compound. For titanium a paint containing isopropyl titanate can be used.

In addition, the electrode base may either solely consist of the film-forming metal, or it may be provided with a core of a different metal, for example copper in order to improve its electrical conductivity.

##### Example 4



An electrode base of commercial purity titanium is etched in 10wt./vol. % oxalic acid between 8 and 16 hours. The base is then supplied with a positive potential of 12 volts with respect to a lead cathode and the base and cathode are immersed in a 7wt.% sulphuric acid solution containing 5g/l of titanium as  $Ti^{3+}$  ions. The solution is heated to and maintained at 90°C. A coating of a titanium dioxide layer is deposited upon the electrode base at a rate of approximately 2g/m<sup>2</sup>/hr. A coating of 15g/m<sup>2</sup> was produced.

After coating, the electrode base is washed in water and dried. The titanium dioxide coating was found to be firmly adherent to the titanium substrate.

The electrode base is then given an electrically conductive coating by dissolving iridium chloride and ruthenium chloride in n-butyl alcohol to produce a paint composition, applying the paint composition in a number of layers to the electrode base over the titanium dioxide, drying each layer and firing each two layers in air at 500°C for 20 minutes. The electrically conductive coating was found to adhere well to the titanium dioxide and was a mixture of iridium metal or oxide and ruthenium oxide present in the amount of about 15g/m<sup>2</sup>. The ratio between the iridium and ruthenium is varied between 3:1, 1:1 and 1:3 as regards metal content by using different paint compositions from different sample electrode bases. Satisfactory electrodes were obtained.

#### Example 5

The method of Example 4 is repeated with the modification that there was used as a paint composition ruthenium chloride alone dissolved in n-butyl alcohol. This paint composition is also fired at 500°C for 20 minutes and sufficient layers were applied to provide 15g/m<sup>2</sup> of ruthenium oxide. The resulting electrode was found to have excellent resistance to loss when used as an anode in the electrolysis of brine in a mercury cell to produce chlorine.

#### Example 6

The method of Example 4 is repeated with the modification that there is used as a paint composition a mixture of platinum and iridium chlorides dissolved in n-butyl alcohol. This paint composition is also fired at 500°C for 20 minutes and sufficient layers are applied to provide about 15g/m<sup>2</sup> of a mixture of platinum and iridium firmly adherent to the titanium dioxide coating. An electrode manufactured according to this example had excellent properties in the electrolysis of chlorine in a diaphragm cell.

#### Example 7

The method of Example 4 was repeated with the modification that there was used as a paint composition iridium chloride dissolved in n-butyl alcohol. This paint composition was also fired at 500°C for 20 minutes and sufficient layers were applied to provide about 10g/m<sup>2</sup> of iridium metal content as a coating firmly adherent to the titanium dioxide. Whether the iridium was present in the metallic or oxide form, or a mixture of both, was not determined. The electrode was very useful in the electro-chemical manufacture of sodium chlorate from brine solutions.

#### Example 8

The method of Example 7 is followed with the modification that the paint composition also contains some tetra-n-butyl titanate. This produces an electrode in which the top layer is a mixture of oxides of titanium and iridium. The mixture of the paint composition is

arranged to produce equal weights of titanium dioxide and iridium oxide on the assumption that the iridium will fully oxidise. This example can be modified by replacing iridium by ruthenium.

#### Example 9

The method of Example 4 is repeated with the modification that the titanium electrode base is replaced by an electrode base of tantalum. The titanium dioxide layer is applied to the tantalum base in the way described, but the tantalum is mechanically roughened instead of etched. The resulting electrode was found to be highly resistant to wear when used as an anode in the electrolytic production of chlorine in a mercury cell.

#### Example 10

The method of Example 9 is repeated but modified in that the electrically conductive coating applied to the titanium dioxide layer is that described in Example 5. This also produced a highly satisfactory electrode.

#### Example 11

The method of Example 5 is repeated with the additional modification that the electrode base is vaqua-blasted tantalum. This also produced a very useful electrode.

The tantalum was then replaced by niobium and the process of this example repeated to produce another very useful electrode, although some difficulty was encountered in preventing undue oxidation of the niobium during firing the ruthenium chloride paint composition in air at 500°C.

This method was repeated again using an etched zirconium electrode base. There were produced thin layers of titanium dioxide which were adherent to the zirconium substrate and which served as a satisfactory base for the ruthenium oxide deposited from the paint composition.

This method was repeated again with the modification that the electrode base was the titanium alloy containing 6wt.% aluminium 4wt.% vanadium, balance titanium. This also produced a satisfactory electrode.

In yet a further modification, the titanium alloy just described was replaced by the alloy titanium 0.2wt.% palladium. This also produced a satisfactory electrode.

#### Example 12

An electrode base of commercial purity titanium is vaqua-blasted. The base is then coated with a tantalum-containing paint composition dried at 250°C for 15 minutes and fired in air at 500°C for 20 minutes. The painting with the tantalum-containing paint composition and firing was repeated as many times as necessary to produce 10g/m<sup>2</sup> of tantalum oxide on the electrode base.

The electrode base was then given an electrically conductive coating by the method described in Example 5. This produced a satisfactory electrode.

#### Example 13

An electrode base of commercial purity titanium is etched in 10wt./vol. % oxalic acid for about 10 hours. The base is then supplied with a positive potential of 12 volts with respect to a lead cathode and the base and cathode immersed in a 15.4 wt.% solution of phosphoric acid containing 4.3g/l of trivalent titanium ions. The solution is heated to and maintained at 90°C for about 7 hours. This produced a titanium dioxide coating on the electrode base of 13.3 g/m<sup>2</sup> with good adhesion.

The electrode base is then given an electrically conductive coating by the method described in Example 5.



When the resulting electrode was used as an anode in the electrolysis of brine in a mercury cell to produce chlorine, it was found to be as resistant to loss as the electrode of Example 5.

#### Example 14

The method of Example 13 is repeated except that the solution containing trivalent titanium ions is replaced firstly by a 10wt.% sulphamic acid solution containing 1g/l titanium. In 5 hours at 90°C, there were produced 5.6g/m<sup>2</sup> of highly adherent titanium dioxide. The resulting electrode was satisfactory.

This example was repeated with the use of 20wt.% sulphamic acid containing 5g/l of titanium. In 7 hours, there was produced an adherent titanium dioxide coating of 3g/m<sup>2</sup>.

#### Example 15

The method of Example 13 is repeated with the use of titanium containing solution of 20wt./vol.% oxalic acid solution containing 5g/l of titanium in the Ti<sup>3+</sup> state. With 12 volts potential between the electrode base and a lead cathode, and the solution boiling, there was produced in 24 hours a titanium dioxide coating which was highly adherent to the electrode base and was present in an amount of about 35g/m<sup>2</sup>.

#### Example 16

An electrode base of commercial purity titanium is etched in 10wt./vol.% oxalic acid for about 8 hours. The base is then given an electrically conductive coating by using a paint composition of ruthenium chloride dissolved in n-butyl alcohol. The paint is applied to the etched titanium surface in a number of layers, each layer being dried and every 2 layers being fired in air at 500°C for 20 minutes. This is continued until the titanium surface carried 10g/m<sup>2</sup> of ruthenium oxide.

The electrode is then given a coating of titanium dioxide by being inserted as an anode in a 7wt.% sulphuric acid solution containing 5g/l of titanium in the trivalent state. The electrode base was subjected to a positive potential of 2 volts at 90°C with respect to a lead cathode in the solution. After 7 hours, a tightly adherent titanium dioxide layer of 12g/m<sup>2</sup> had formed on the ruthenium oxide surface. The resulting electrode showed exceptional resistance to wear when used in the electrolysis of brine in a mercury cell to produce chlorine.

#### Example 17

An electrode base of commercial purity titanium was etched at 80–90°C in a 20wt./vol.% oxalic acid solution. The period of etching was 16 hours.

At the end of the etching period, the oxalic acid solution contained the required level of about 5g/l of titanium dissolved from the electrode base. If the solution is deficient in titanium after adequate etching, adjustment can be made by adding titanium powder or titanium oxalate to bring the titanium content to about 5g/l. Without removing the electrode base from the solution, the base is connected as an anode to a lead cathode in the solution and with a potential applied to the anode of about 12 volts, the solution is boiled. This causes deposition of a titanium dioxide coating on to the etched electrode base, and, after 24 hours, there was about 30g/m<sup>2</sup> of tightly adherent titanium dioxide.

This method combines a method of etching the titanium surface with a method of depositing the titanium dioxide coating, and can be modified for use with sulphuric acid and hydrochloric acid etching solutions.

The electrode is then provided with an electrically conductive coating of a mixture of iridium and ruthenium oxide as described in Example 4.

One of the major advantages of the electrodes according to this invention is the excellent durability of the coating. This is always important, but is critically so in chlor-alkali electrolysis with a mercury cathode. The electrodes of the invention withstand mercury and mercury amalgam contact very satisfactorily. Without prejudice to the invention this durability is considered to stem from the layer or layers of oxide of film-forming metal, the method of application thereof producing such a layer or layers which will have a strongly protective effect and also provide excellent adhesion and electro-chemical properties.

The two principal methods of this invention, as set out above, include the chemical deposit of an oxide of a film-forming metal for the first method, and the electrolysis of a solution of a film-forming metal for the second method. When these are compared it is evident that the second method is instrumental in producing electrodes that have a longer life in electrolysis and a resistance to immersion in mercury and mercury amalgam that will withstand about twice as many immersions as electrodes for the first method. Also manufacture is facilitated with the oxide being deposited only upon the positive potential electrode base and with a better rate of deposition. Thus we prefer to deposit the oxide of the film-forming metal by electrolysis a solution containing that metal.

A further benefit which obtains when a titanium oxide layer is deposited on titanium by the methods of the invention is a higher anodic breakdown voltage in chloride solutions than uncoated titanium. This is a considerable attribute for anodes operated in chlorine cells at elevated temperature. The obtained results are given in the following table.

TABLE 1

Anodic Breakdown Voltages for Commercial Purity Titanium in 22% Brine at 80°C  
(With applied constant current of 30 mA/cm<sup>2</sup>)

| Method of Preparation                         | Breakdown Voltage |
|---|-------------------|
| Annealed and descaled (Control Material)      | 8.1               |
|   | 8.2               |
|   | 7.9               |
| Annealed and descaled + filming for 8 hours*  | 19.3              |
|   | 19.0              |
|   | 19.2              |
| Annealed and descaled + filming for 17 hours* | 18.5              |
|   | 18.5              |
|   | 18.2              |
| Annealed and descaled + filming for 24 hours* | 46                |
|   | 36                |
|   | 50                |

\* Filming in gentle boiling 10% sulphuric acid containing 1000 p.p.m. titanium in the quadrivalent state.

This benefit can be put to the maximum use by applying the layer of titanium dioxide not only to the part of the surface of the electrode base at which electrical conductivity is required, but also to the remainder of the surface.

The invention also consists in an electrode for use in electrolytic processes manufactured in accordance with the method of the present invention.

We claim:

1. A method of manufacturing an electrode suitable for use in electrolytic processes comprising taking an electrode base of which at least the surface is a metal selected from the group of film-forming metals consist-



ing of titanium, tantalum, niobium, zirconium and alloys based on at least one of these metals, separately applying to at least part of said surface at least two superimposed layers of which at least one is a layer consisting of a film-forming metal oxide formed by immersing said base in a prepared aqueous solution containing film-forming metal ions and depositing from said solution said oxide, and at least one other layer is an electrically conductive electrolyte resistant layer consisting of at least one member of the class consisting of a metal of the platinum group and an oxide of a metal of the platinum group, said resistant layer being formed by applying a solution of a heat-decomposable compound of a platinum group metal, drying and firing to decompose said compound and deposit said resistant layer.

2. A method according to claim 1 comprising depositing the layer consisting of an oxide of the film-forming metal onto said surface before applying the layer containing a metal of the platinum group or an oxide of a metal of the platinum group.

3. A method according to claim 1 comprising depositing said oxide of the film-forming metal on top of a previously deposited electrically conductive electrolyte resistant layer.

4. A method according to claim 1 wherein said oxide is deposited from the solution by chemically decompos-

ing in the solution a compound containing the film-forming metal.

5. A method according to claim 1 wherein said oxide is deposited from the solution by electrolyzing the solution.

6. A method according to any claim 1 wherein the surface of the electrode base is etched before applying any layer thereto.

7. A method according to claim 1 wherein the said firing takes place in an oxygen-containing atmosphere at 450-700°C.

8. A method according to claim 7 wherein said platinum group metal comprises ruthenium.

9. A method according to claim 1 wherein said oxide is titanium dioxide.

10. A method according to claim 1 which comprises immersing a titanium electrode base in heated sulphuric acid containing titanium ions until a coating of titanium oxide is chemically deposited on said base, withdrawing the base from said solution, removing any loose coating and drying the base, then applying a paint containing a decomposable ruthenium salt on said titanium oxide layer and baking until a layer of ruthenium oxide is deposited on said coating.

\* \* \* \* \*

30

35

40

45

50

55

60

65