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Lee

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[54] **ELECTRODES FOR ELECTROCHEMICAL PROCESSES**

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Related U.S. Application Data

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[51] **Int. Cl.²** **B01K 1/00;** C25B 11/08

[58] **Field of Search** ..... 204/290 R, 290 F

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

An electrode for use in electrochemical processes which comprises a support of a film-forming metal carrying a coating of smooth vitreous appearance which coating comprises a layer of an operative electrode material and superimposed thereon a layer of an oxide of a film-forming metal. The electrode is made by a process which comprises forming on the surface of a support of a film-forming metal a layer of an operative electrode material, applying over the layer a coating comprising a thermally decomposable organo-compound of a film-forming metal in a liquid vehicle and heating the coating so as to convert the organo-compound of the film-forming metal to an oxide of the film-forming metal.

8 Claims, No Drawings

ELECTRODES FOR ELECTROCHEMICAL PROCESSES

This is a division of application Ser. No. 807,993, filed Mar. 17, 1969 now U.S. Pat. No. 3,663,280.

The present invention relates to electrodes for electrochemical processes. More particularly it relates to improvements in the durability of electrodes comprising a layer of operative electrode material on a support formed from a film-forming metal, especially titanium.

It is known to employ as an anode in an electrochemical cell, particularly in a cell wherein an aqueous solution of an alkali metal chloride is electrolysed, an electrode comprising a film-forming support, particularly a titanium support, which carries on at least a part of its surface a coating of an operative electrode material. The titanium support is resistant to anodic attack even in the highly corrosive chloride electrolytes. The operative electrode material must be resistant to anodic attack and must also be active in transferring electrons to the electrode from the ions of the electrolyte. The operative electrode material is usually one or more of the platinum group metals and/or the oxides of these metals, but it may be any other electroconducting material which has adequate resistance to anodic dissolution in the cell and which will function as an anode.

Although the above-mentioned operative electrode materials are very resistant to electrochemical attack in a variety of corrosive media, they do wear away at an appreciable rate or even break away from the film-forming metal support in use. The present invention provides a method of anchoring the operative electrode material more securely to the support in an electrode of the aforesaid type while at the same time presenting the operative electrode surface in a form which has a low over-potential for the liberation of chlorine when the electrode is used as an anode in the electrolysis of alkali metal chloride solutions.

The improved electrodes of the invention are manufactured by first preparing an electrode of the type comprising a film-forming metal support carrying a coating of an operative electrode material by a method as known in the art, or by a simple variant thereof as will appear hereinafter, then applying over the layer of operative electrode material a coating of a thermally decomposable organo-compound of a film-forming metal and heating the thus coated electrode so as to convert the organo-compound of the film-forming metal to an oxide of the film-forming metal.

According to the present invention, therefore, we provide a method for the manufacture of an electrode for use in electrochemical processes, which comprises forming on the surface of a support of a film-forming metal a layer of an operative electrode material, applying over the said layer a coating comprising a thermally decomposable organo-compound of a film-forming metal in a liquid vehicle and heating the coating so as to convert the organo-compound of the film-forming metal to an oxide of the film-forming metal.

The finished coating has a smooth vitreous appearance and excellent adhesion to the metal of the support. The two-stage coating method of the invention enables this coating containing a film-forming metal oxide to be produced at a temperature below the melting point of the film-forming metal oxide and in fact at temperatures below the melting points of glasses that oxides of film-forming metals form with other oxides.

This is important since it enables high temperatures at which the metal of the support would react appreciably with the coatings or with oxygen of the atmosphere to be avoided during the coating operation.

The present invention also provides, therefore, an electrode for use in electrochemical processes which comprises a support of a film-forming metal carrying a coating of smooth vitreous appearance which coating comprises a layer of an operative electrode material and superimposed thereon a layer of an oxide of a film-forming metal.

Although the electrodes of the invention are produced by forming two distinct coating layers on the film-forming metal support — first a layer of operative electrode material and afterwards a film-forming metal oxide — we do not exclude from the scope of the invention electrodes in which there is some interpenetration between the two coating layers. Indeed it seems likely that at the temperatures employed to form the coating of film-forming metal oxide by decomposition of an organo-compound of the metal some interdiffusion of the layers will take place, and this may be the explanation of the high mechanical strength of the electrodes of the invention.

In this specification, by "a film-forming metal" we mean one of the metals titanium, zirconium, niobium, tantalum or tungsten or an alloy consisting principally of one of these metals and having anodic polarisation properties in the electrolyte where the electrode is to be used which are comparable to those of the pure metal. It is preferred to use as support material in the electrode titanium alone or an alloy based on titanium and having anodic polarisation properties comparable with those of titanium. Examples of such alloys are titanium-zirconium alloys containing up to 14% of zirconium, alloys of titanium with up to 5% of a platinum metal such as platinum, rhodium or iridium and alloys of titanium with niobium or tantalum containing up to 10% of the alloying constituent.

The operative electrode material of the electrode may be one or more of the platinum group metals, i.e. platinum, rhodium, iridium, ruthenium, osmium and palladium, and/or the oxides thereof, or another metal or a compound which is resistant to electrochemical dissolution in the cell where it is to be employed and will function as an electrode, for instance rhenium, rhenium trioxide, manganese dioxide, magnetite, titanium nitride and the borides, phosphides and silicides of the platinum group metals. The preferred operative electrode materials are the oxides of the platinum group metals, particularly ruthenium dioxide, and mixtures of one or more platinum group metals with the oxides thereof. The invention will be further described by reference to the use of these preferred operative electrode materials but is not limited thereto.

The method employed for forming the layer of a platinum metal oxide or a mixture of a platinum metal and the oxides thereof on a support of a film-forming metal may suitably be one of those known in the art. According to the British Pat. Specification No. 984,973 for example, a coating of a platinum metal may be formed on a titanium support by applying to the chemically-cleaned support a plurality of coatings of a platinum-bearing preparation comprising a platinum metal compound in an organic vehicle and containing a reducing agent, e.g. an essential oil, and heating each coating in an oxidising atmosphere, e.g. air, at a temperature be-

tween 350° and 550°C. The platinum metal compounds may be thermally decomposable inorganic compounds, resinates or sulphoresinates of the platinum metals. It can be shown that coatings produced in this manner contain at least a proportion of the platinum metal in the form of its oxides and that with the more easily oxidised platinum metals, e.g. ruthenium, and a firing temperature in the upper half of the said temperature range, the resultant coating consists substantially of the oxides of the platinum metal.

The method of the aforesaid British specification is suitable for use with the present invention. The method may, however, be varied if desired by heating each coating of the platinum-bearing preparation first at a lower temperature to reduce the platinum metal compounds and produce a layer consisting substantially of the platinum metal and then in an oxidising atmosphere at a higher temperature, suitably at least 350°C, to convert the platinum metal at least in part to its oxides. For example a ruthenium chloride composition containing a reducing agent may first be heated at approximately 300°C to reduce the chloride substantially to ruthenium metal and the ruthenium coating may then be converted substantially completely to ruthenium dioxide by heating in air at approximately 450°C.

For the purpose of the present invention a coating of the oxides of one or more platinum metals on a film-forming metal support may also be formed directly from thermally decomposable compounds of the platinum metals, i.e. without intermediate reduction to the metals, by coating the support with a composition comprising compounds of the platinum metals and an organic vehicle but containing no reducing agent and heating in an oxidising atmosphere at a temperature higher than 300 °C, preferably at least 350°C and most preferably about 450°C. For example, as taught in French Pat. Specification No. 1,479,762, a coating of palladium oxide is formed directly on a film-forming metal support, e.g. titanium, by heating a coating consisting of an acidified solution of palladium chloride in isopropyl alcohol at 400°–500°C in an oxidising atmosphere, e.g. air, and a coating of the mixed oxides of palladium and iridium is formed directly on a tantalum support from a similar solution of the chlorides of palladium and iridium by heating in air at 300°–600°C.

For the purpose of the present invention the preformed oxides of the platinum metals may also be employed to produce the layer of operative electrode material. The preformed oxides may be applied to the film-forming metal support for example by any of the methods described in the aforesaid French patent specification, for instance by application in the molten state, by coating with a dispersion of the oxide in a liquid vehicle or by electrophoresis on to the film-forming metal support from a colloidal solution of the oxide. If desired to increase the initial adhesion the platinum metal oxide coating may be rolled or pressed into the support.

Although coatings consisting of platinum group metals at least in part in the form of their oxides are preferred, especially for electrodes that are to be used as anodes under the arduous conditions ruling in mercury-cathode cells electrolysing alkali metal chloride solutions, for less arduous conditions coatings consisting substantially of platinum group metals in the unoxidised state may be emloyed. Such coatings may be prepared by thermal decomposition of compounds of platinum group metals under reducing conditions throughout, for instance by applying to the support metal a solution of a platinum group metal salt in an organic solvent containing a reducing agent, e.g. linalool, and heating the coating in an atmosphere of a gas having alkaline reaction, e.g. ammonia, and a reducing gas e.g. methane, carbon monoxide, hydrogen or town gas as taught in British Pat. Specification No. 964,913.

It should be understood that with any of the coating methods described herein the coating steps may be repeated as necessary to build up the desired thickness of the operative electrode material. Furthermore, when a final heating step in an oxidising atmosphere is employed to oxidise a coating of platinum group metal formed by thermal decomposition of a platinum group metal compound and the layer of operative electrode material is built up by superimposing a plurality of coatings, the oxidising step may be carried out in a single stage after all the coatings have been applied or if desired, particularly when building up relatively thick layers, the oxidising step may be carried out on each coating before applying the next or each time after applying a fraction of the total number of coatings greater than one coating, for instance after each second or third coating.

In general the coating of operative electrode material is applied to a chemically-cleaned surface of the film-forming metal support. The support is degreased if necessary and then pickled, for instance in hot oxalic solution or in hot or cold hydrochloric acid. It is, however, possible to coat the operative electrode material on to a support which has been given an oxidising treatment to produce a very thin surface layer of the film-forming metal oxide after the aforesaid cleaning treatment, and this oxide layer may even be beneficial in providing a better initial key for the operative electrode material, for instance when this is a preformed platinum group metal oxide in particulate form.

For use in the second coating step of the method according to the invention the thermally-decomposable organo-compound of a film-forming metal must be one that is decomposable by heat alone, optionally in an oxidising atmosphere, e.g. air, or by heating after partial hydrolysis as for instance by exposure to moisture in the atmosphere during the coating operation, to form an oxide of the film-forming metal. Particularly suitable compounds are the alkyl titanates, alkyl polytitanates and alkyl halotitanates in which the halogen is chlorine, bromine or fluorine, and the corresponding compounds of the other film-forming metals. The titanium compounds are preferred when the support metal of the electrode is titanium or a titanium alloy. Very suitable compounds are those in which the alkyl groups contain 2–4 carbon atoms each.

Methods of preparing alkyl titanates and preparing alkyl polytitanates (sometimes referred to as condensed alkyl titanates) by partial hydrolysis of alkyl titanates are disclosed in a paper by T. Boyd in Journal of Polymer Science, Vol. VII, No. 6, 1951, pages 591–602. An alkyl chlorotitanate in the form of an alcoholic solution suitable for use in the method of the invention may be prepared by heating titanium tetrachloride with the chosen alcohol without employing any chemical means to remove the hydrogen chloride formed from the reaction mixture and using an excess of alcohol, suitably 2–5 times the amount theoretically required to remove all the chlorine atoms from the tita-

nium tetrachloride. Alkyl bromotitanates and alkyl fluorotitanates may be prepared in similar manner starting with titanium tetrabromide and titanium tetrafluoride respectively.

The thermally decomposable compound of a film-forming metal (exemplified hereinafter for simplicity by reference to alkyl titanates or halotitanates) in a liquid vehicle, suitably a volatile alcoholic solvent, may be applied by dipping, brushing or spraying on to the surface of the layer of operative electrode material which has previously been formed on the film-forming metal support. The coating is then suitably dried by heating in an oven at a moderate temperature, e.g. 100°–200°C, to evaporate the solvent, after which the coated electrode is heated at a higher temperature, for instance 250°–800°C to convert the organo-compound of the film-forming metal in the coating substantially to an oxide of the metal. Additional coats may be applied, dried and then decomposed by stronger heating in the same way, if necessary to obtain good coverage of the underlying operative electrode material.

When alkyl titanates and halotitanates are applied in thin coatings, it appears that some condensation takes place by hydrolysis caused by moisture in the atmosphere. When the condensed titanates are strongly heated they decompose substantially completely to leave a residue of titanium dioxide of vitreous appearance which serves to knit the operative electrode material securely to the underlying surface of the film-forming metal support. The time of heating to decompose the titanate should be shorter the higher the temperature employed, so as to avoid excessive reaction between the film-forming metal support and the coating or oxygen of the atmosphere. For example at a temperature of 500°C the time should not exceed about 15 minutes and at 800°C it should not exceed about 15 seconds. In this connection it should be noted that when the operative electrode material contains or consists of a platinum metal oxide, the final heating step to decompose the titanate should be carried out in an oxidising atmosphere, e.g. air.

Electrodes produced according to the invention are useful in electrolytic cells, electrodialysis cells, fuel cells and in cathodic protection systems. Specific embodiments of these electrodes wherein the film-forming metal support is titanium and the coating on the titanium comprises one or more platinum group metal oxides and titanium dioxide have special advantages when used as anodes in the electrolysis of an alkali metal chloride solution.

The invention is further illustrated by the following working examples in which all parts are by weight.

EXAMPLE 1

A strip of titanium was immersed overnight in hot oxalic acid solution to etch the surface of the metal and was then washed and dried. A mixture containing ruthenium chloride one part, isopropyl alcohol four parts and linalool 1.3 parts was painted on to the titanium, the coating of paint was allowed to dry in air for 10 minutes and was then heated in a furnace in air at 300°C of 10 minutes to form a coating consisting substantially of ruthenium. Two further coats of the paint were applied, dried and heated in the same manner. The ruthenium-coated titanium was then heated in air at 450°C for 1 hour to oxidise at least the outermost part of the ruthenium layer and was allowed to cool. A solution of ethyl chlorotitanate in ethyl alcohol was prepared by heating one part of titanium tetrachloride with five parts of absolute ethyl alcohol at 70°C for 15 minutes. Three coats of this solution were applied to the prepared titanium strip over the ruthenium oxide coating, each coating being dried in an oven at 150°C for 10 minutes and then heated in air in a furnace at 450°C for 15 minutes to form a surface layer of smooth vitreous appearance.

EXAMPLE 2

A coating of ruthenium was formed on a strip of titanium and the coating was then oxidised in air at 450°C for one hour, all as in Example 1. The weight of the coating then amounted to about 6 g/m² of the titanium surface, calculated as ruthenium metal. 8 coats of a solution consisting of 5 parts of tetra-n-butyl titanate in 5 parts of n-pentanol were then painted on to the coated titanium, each coat being dried in an oven at 200°C for 10 minutes and then heated in air at 450°C for 15 minutes. The theoretical weight of titanium dioxide thus formed on the electrode was 25 g/m².

EXAMPLE 3

A ruthenium coating was formed on a strip of titanium and oxidised in air at 450°C, all as in Example 1 to give a coating amounting to about 6 g/m² of the titanium surface, calculated as ruthenium metal. A solution of isopropyl chlorotitanate in isopropyl alcohol was prepared by heating one part of titanium tetrachloride with 5 parts of isopropyl alcohol for 1 hour at 70°C. 4 coats of this solution were then painted on to the coated titanium, each coat being dried in an oven at 200°C for 10 minutes and then heated in air in a furnace at 450°C for 15 minutes. The theoretical weight of titanium dioxide thus formed on the electrode was about 8 g/m².

EXAMPLE 4

A strip of titanium was etched, washed and dried as in Example 1 and was then coated with the same ruthenium chloride paint composition as in that Example, i.e. ruthenium chloride one part, isopropyl alcohol 4 parts, linalool 1.3 parts. Three coats of the paint composition were applied (equivalent coating weight about 6 g/m² calculated as ruthenium metal) but this time after being allowed to dry for 10 minutes in air each coat was heated once only, in air at 350°C for 1 hour, to form a coating consisting substantially of ruthenium dioxide. 4 coats of a solution of isopropyl chlorotitanate were then applied and converted to titanium dioxide as in Example 3.

EXAMPLE 5

A strip of titanium was pretreated and given three coats of a ruthenium chloride paint composition as described in Example 4 except that after being allowed to dry each coat was converted substantially to ruthenium dioxide by heating once only, in air at 450°C for 1 hour. 8 coats of a solution of tetra-n-butyl titanate in n-pentanol were then applied, each coat being dried in an oven at 200°C for 10 minutes and then heated in air in a furnace at 450°C for 15 minutes. The theoretical weight of titanium dioxide thus formed on the electrode was 35 g/m².

EXAMPLE 6

A strip of titanium was etched, washed and dried as in Example 1 and was then given three coats of a ruthenium chloride paint composition containing no reducing agent (composition: ruthenium trichloride one part, isopropyl alcohol 4 parts). Each coat was allowed to dry in air for 10 minutes and was then heated in air at 350°C for 1 hour to form a coating consisting substantially of ruthenium dioxide. 6 coats of a solution of isopropyl chlorotitanate in isopropyl alcohol was then applied to the coated titanium, each coat being dried in air in an oven at 200°C and then heated in air in a furnace at 450°C for 15 minutes. The theoretical weight of titanium dioxide thus formed on the electrode was 15 g/m^2.

EXAMPLE 7

A suspension of ruthenium dioxide particles, mostly of size less than 4 microns diameter, in n-pentanol was brushed on to a strip of titanium which had been etched, washed and dried as in Example 1 and the solvent was evaporated from the coating in an oven at 150°–200°C. Two further coats were applied and dried in the same manner to give a total loading of 7 g ruthenium dioxide/m^2 of the coated titanium surface. A solution of tetra-n-butyl titanate in n-propyl alcohol was then sprayed on to the ruthenium dioxide coating and the titanium coating was dried in air in an oven for 10 minutes at 200°C and then heated in air in a furnace for 15 minutes at 450°C. Seven further coats of the titanate solution were applied, each one being dried at 200°C and heated at 450°C as for the first coat. The theoretical amount of titanium dioxide thus formed on the electrode was 35 g/m^2.

Electrodes produced according to each one of the foregoing Examples were tested as anodes in sodium chloride brine containing 21.5% NaCl by weight at 65°C in an electrolysis cell with a mercury cathode, and at an anodic current density of 8 kA/m^2 they showed chlorine overpotentials in the range 25–76 mV. Each anode was also dipped into the sodium amalgam cathode with a potential of about 5 volts still applied between the anode and the amalgam. The short-circuit current was found to be relatively small — less than 10 amps compared with an anode of the same size consisting of titanium coated by firing thereon a coating of a platinum-bearing preparation according to the prior art but with no further treatment, which passed a current of 400 amps under the same short-circuit conditions. This demonstrates a further advantage of an electrode prepared according to the invention, in that such an electrode develops a resistance to short-circuit currents in the cell and provides its own protection against damage by accidental short-circuit in use.

What we claim is:

1. An electrode for use in an electrochemical process which comprises a support of a film-forming metal carrying a coating of smooth vitreous appearance which coating comprises a layer of an operative electrode material and superimposed thereon a layer of an oxide of a film-forming metal, said operative electrode material comprising at least one member of the group consisting of metals and metal compounds which are resistant to electrochemical dissolution in said electrochemical process and which will function as an electrode therein.

2. An electrode according to claim **1** wherein said operative electrode material is selected from the class consisting of platinum group metals and oxides thereof.

3. An electrode according to claim **2,** wherein the support consists of titanium or an alloy based on titanium and having anodic polarisation properties comparable with those of titanium.

4. An electrode according to claim **2,** wherein the operative electrode material consists of a mixture of at least one platinum group metal and oxides thereof.

5. An electrode according to claim **2,** wherein the operative electrode material consists of oxides of at least one platinum group metal.

6. An electrode according to claim **2,** wherein the operative electrode material consists substantially of ruthenium dioxide.

7. An electrode according to claim **2,** wherein the said layer of oxide of a film-forming metal consists of titanium dioxide.

8. An electrode according to claim **1** wherein said support comprises a film-forming metal selected from the group consisting of titanium, zirconium, niobium, tantalum and tungsten or an alloy consisting principally of one of these metals, a layer of an operative electrode material resistant to electrochemical dissolution on said support, and an oxide of said film-forming metal superimposed on said layer, said operative electrode material being at least one member of the class consisting of the platinum group metals and oxides thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,915,838 Dated October 28, 1975

Inventor(s) Denis Lee

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading of the patent, add:

--[30] Foreign Application Priority Data

April 2, 1968 Great Britain....15786/68--

Signed and Sealed this

thirteenth Day of *April 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

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Commissioner of Patents and Trademarks