

[54] **ELECTRODES AND ELECTROCHEMICAL PROCESSES**

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[58] **Field of Search** ..... 117/217, 215, 221; 204/290 F

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[57] **ABSTRACT**

A method for manufacturing an electrode for use in electrochemical processes which comprises coating a support member made of a film-forming metal or alloy thereof with a first layer of a mixture of a platinum group metal and a film-forming metal oxide and then coating said first layer with a second layer consisting of a film-forming metal oxide.

**11 Claims, No Drawings**

## ELECTRODES AND ELECTROCHEMICAL PROCESSES

### CROSS-REFERENCE TO A RELATED APPLICATION

This is a division, of application Ser. No. 233,354 filed Mar. 9, 1972.

The present invention relates to electrodes for electrochemical processes. More particularly it relates to electrodes comprising a support member of a film-forming metal carrying a coating which is active in transferring an electric current from the support member to ions of an electrolyte and is resistant to electrochemical attack.

It is known to employ oxides of the platinum group metals as coatings on electrodes of the aforesaid type because they have a high intrinsic resistance to electrochemical dissolution in a variety of corrosive media and they are active in discharging ions from an electrolyte. The present invention provides improved electrodes incorporating coatings comprising platinum group metal oxides. The electrodes of the invention are very useful as anodes in cells for the electrolysis of alkali metal chloride solutions. They are particularly useful in cells with flowing mercury cathodes, because the electrodes have a high resistance to damage by short-circuit contact with the cathode, such as may occur accidentally even during the normal course of operation in these cells. The electrodes can also be used in other electrochemical processes, including other electrolytic processes, electrocatalysis, as for instance in fuel cells, electrosynthesis and cathodic protection.

According to the present invention we provide an electrode for use in electrochemical processes which comprises a support member made of a film-forming metal or alloy and a coating thereon consisting of a layer of a mixture of the oxide(s) of at least one platinum group metal in a proportion of 20-80 percent by weight and a film-forming metal oxide and superimposed on the said layer a layer of a film-forming metal oxide.

In a preferred form of the electrode the ratio of platinum group metal oxides:film-forming metal oxide in the layer of the said mixture is not less than 1:1 but is less than 2:1 by weight.

By a film-forming metal we mean one of the metals titanium, zirconium, niobium, tantalum and tungsten. By a film-forming alloy we mean an alloy containing a major proportion of one of these metals and having anodic polarisation properties similar to the commercially pure metal. The support member of the electrode is preferably made of titanium or a titanium alloy having anodic polarisation properties similar to those of titanium.

By the oxide(s) of at least one platinum group metal we mean the oxide(s) of at least one of the metals ruthenium, rhodium, palladium, osmium, iridium and platinum.

In a preferred form of the electrode according to the invention the layer of the said mixture consists of ruthenium dioxide and titanium dioxide and the superimposed layer consists of titanium dioxide.

The preferred method of forming the layer of mixed oxides on the support member is as follows. A coating of a paint composition comprising a thermally decomposable compound of at least one platinum group metal

and a thermally decomposable organo-compound of a film-forming metal in an organic liquid vehicle and optionally also comprising a reducing agent, e.g., linalool, is applied to the support member, the coating is dried by evaporation of the liquid vehicle and the coated support is then heated in an oxidising atmosphere, e.g., in air, at a temperature of at least 350°C and preferably in the range 400°-550°C to convert the compounds of the platinum group metals and the film-forming metal to oxides of these metals. Further coats of the paint composition may then be applied to the coated support, dried and heated in the same manner to increase the thickness of the mixed oxide layer to any desired extent. For example for electrodes that are to be used as anodes in mercury-cathode cells electrolysing alkali metal chloride solutions we prefer to build up a thickness of this layer in the range 10-15g/m<sup>2</sup> of the coated surface of the support member. This thickness is, however, in no way critical. Thinner or thicker coatings may be employed and the thickness will generally be chosen having regard to the wear to which the electrode will be submitted during use in the cell, which itself will be related inter alia to the current density at which the electrode will be required to operate.

The preferred method of forming the superimposed layer of film-forming metal oxide is by applying over the mixed oxide layer a coating of a thermally decomposable organo-compound of the film-forming metal in an organic liquid vehicle, drying the coating by evaporation of the liquid vehicle and then heating the coating in an oxidising atmosphere, e.g., air, to convert the organo-compound of the film-forming metal to the oxide of the metal. The preferred thickness of this superimposed layer of film-forming metal oxide is in the range 2-10g/m<sup>2</sup> of the coated surface. The desired thickness of this layer may be obtained by adjusting the viscosity of the coating composition by adding more or less of the organic liquid vehicle and/or by repeated application of thinner layers of coating composition, drying and heating each coating, to build up the desired thickness.

The thermally decomposable organo-compounds of the film-forming metals employed in forming the superimposed layer of film-forming metal oxide in accordance with the preceding paragraph are most suitably the alkyl titanates, the alkyl halotitanates wherein the halogen is chlorine, bromine or fluorine (alternatively known as titanium alkoxides and alkoxy-halides) and the corresponding alkyl compounds of other film-forming metals. Other suitable thermally decomposable organo-compounds are resinates of the film-forming metals. The preferred compounds are the alkyl titanates and halotitanates, especially those in which the alkyl groups contain 2-4 carbon atoms each. Coatings of these preferred compounds applied in an organic liquid vehicle as aforesaid are suitably dried at a temperature of 100°-200°C and then heated in an oxidising atmosphere at 250°-800°C, preferably at 350°-550°C, to convert the titanate compounds to titanium dioxide.

Any of the thermally decomposable compounds of the film-forming metals listed in the preceding paragraph may also be employed in the paint compositions used for forming the under-layer of mixed oxides on the electrode support member. Again the alkyl titanates and the alkyl halotitanates wherein the halogen is chlorine, bromine or fluorine, especially those in which the

alkyl groups contain 2-4 carbon atoms each, are preferred. The thermally decomposable compounds of the platinum group metals used in these paint compositions may suitably be halides, e.g., ruthenium trichloride, halo-acid complexes, e.g., hexachloroplatinic acid, or resins of these metals. The preferred platinum group metal compound is ruthenium trichloride.

The invention is further illustrated by the following Example 5.

#### EXAMPLE 1

A strip of titanium 35 cm long, cross section 6 mm  $\times$  1 mm was etched in oxalic acid solution, washed, dried and then painted with a mixture of 4.3g partly hydrated ruthenium trichloride, 12.0g n-pentanol and 6.4g tetrabutyl ortho titanate. The paint layer was dried at 180°C and then fired by heating in air at 450°C for 15 minutes. A total of six layers of this paint was applied, each layer being dried and heated in the same manner, to give a loading on the titanium surface of 14g/m<sup>2</sup> of a coating consisting of 60 percent ruthenium dioxide and 40 percent titanium dioxide by weight. Over this mixed oxide coating was painted a mixture of 5g tetrabutyl ortho titanate in 5g n-pentanol. This paint was also dried at 180°C and then fired by heated in air at 450°C for 15 minutes. A total of three layers of this second paint was applied, each layer being dried and heated in the same manner, to give a loading of 4g/m<sup>2</sup> of titanium dioxide over the mixed oxide layer.

Samples cut from the coated strip were tested as anodes for chlorine production in sodium chloride brine containing 21.5% NaCl at pH 2-3 and a temperature of 65°C. The samples operated with low overpotential (50 mV at a current density of 8 kA/m<sup>2</sup>) and they also showed excellent resistance to damage when contacted with the cathode amalgam in a mercury cell electrolyzing sodium chloride brine.

#### EXAMPLE 2

An anode whose working surface was in the form of a grid made up of titanium strips and having a projected area of 0.1 m<sup>2</sup> was in oxalic acid solution for 16 hours, washed and dried. The anode grid was then sprayed with a paint composition consisting of 60.5 g ruthenium trichloride and 90.0 g tetra-n-butyl ortho titanate in 300 g n-pentanol. The paint layer was dried in an oven at 180°C and was then converted to a layer of composition 60% RuO<sub>2</sub>/40% TiO<sub>2</sub> by weight by heating in air in a furnace at 450°C for 20 minutes. A further five layers of the same paint composition were then sprayed on to the anode, each layer being dried and then fired by heating in air as was the first layer. An outer layer consisting of titanium dioxide alone was then applied to the anode grid by spraying on to it three coats of a paint composition consisting of 25 g tetra-n-butyl titanate in 75 g n-pentanol, each being dried at 180°C and then fired in air at 450°C for 20 minutes. The total loading of oxides deposited on the titanium grid was then 32 g/m<sup>2</sup> projected area.

The coated titanium anode was installed in a mercury-cathode cell electrolyzing sodium brine, as a replacement for a graphite anode, and after operating satisfactorily for six months with an anode current of up to 900 amp. there was no apparent wear nor decline in performance.

#### EXAMPLE 3

A titanium grid anode of 0.1 m<sup>2</sup> projected area was coated as in Example 2 except that the paint composition used for the first six coats consisted of 55 g ruthenium trichloride and 101 g tetra-n-butyl ortho titanate in 300 g n-pentanol. This composition, after drying and firing, produced an underlayer on the titanium grid of composition 55% RuO<sub>2</sub>/45% TiO<sub>2</sub> by weight. The outer layer consisting of titanium dioxide alone was then deposited as in Example 2. This anode was also operated in a mercury-cathode cell electrolyzing sodium chloride brine and also showed no signs of wear nor decline in performance after six months' use with an anode current of up to 900 amp.

We claim:

1. A method for manufacture of an electrode for use in electrochemical processes wherein said electrode comprises a support member made of a film-forming metal or an alloy thereof having a coating thereon consisting of at least one layer of a mixture of the oxide of at least one platinum group metal in a proportion of 20-80 percent by weight and a film-forming metal oxide and superimposed on the said layer a layer consisting of a film-forming metal oxide which comprises the steps of (1) applying on said support member at least one coating of a composition comprising a thermally-decomposable compound of at least one platinum group metal and a thermally-decomposable organo-compound of a film-forming metal in an organic liquid vehicle, drying each coating by evaporation of the liquid vehicle and then heating each coating in an oxidizing atmosphere at a temperature of at least 350°C to convert the compounds of the platinum group metals and the film-forming metal to mixed oxides of these metals, and (2) applying over the layer of mixed oxides thus produced on the support member at least one coating of a thermally decomposable organo-compound of a film-forming metal in an organic liquid vehicle, said last-mentioned coating being free from any platinum group metal or compound thereof, drying each coating by evaporation of the liquid vehicle and then heating each coating in an oxidizing atmosphere to convert the organo-compound of the film-forming metal to the oxide of the metal.

2. A method according to claim 1, wherein the said support member is made of titanium or a titanium alloy having anodic polarisation properties similar to those of titanium.

3. A method according to claim 1, wherein in step (1) the thermally decomposable compound of at least one platinum group metal is ruthenium trichloride.

4. A method according to claim 1, wherein in step (1) the temperature at which each coating is heated in an oxidising atmosphere is in the range 400°-550°C.

5. A method according to claim 1, wherein in step (1) the number of coatings of the said composition applied, dried and heated on the support member is sufficient to build up a layer of mixed oxides amounting to 10-15 g/m<sup>2</sup> of the coated surface of this support member.

6. A method according to claim 1, wherein in step (1) the thermally-decomposable organo-compound of a film-forming metal is an alkyl titanate or an alkyl halotitanate wherein the halogen is chlorine, bromine or fluorine.

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7. A method according to claim 1, wherein the proportions of platinum group metal compounds and film-forming metal compound in the said composition employed in step (1) are chosen so that the ratio of platinum group metal oxides:film-forming metal oxide in the said layer of mixed oxides produced in step (1) is not less than 1:1 but is less than 2:1 by weight.

8. A method according to claim 1, wherein the total amount of coating which is applied over the said layer of mixed oxides is sufficient to produce in step (2) a layer of film-forming metal oxide amounting to 2-10 g/m<sup>2</sup> of the coated surface.

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9. A method according to claim 1, wherein in step (2) the thermally decomposable organo-compound of a film-forming metal is an alkyl titanate or an alkyl halotitanate wherein the halogen is chlorine, bromine or fluorine.

10. A method according to claim 9, wherein in step (2) each coating is dried at 100°-200°C and is then heated at 250°-800°C in an oxidising atmosphere.

11. A method according to claim 10, wherein in step (2) each coating after drying is heated at 350°-550°C in an oxidising atmosphere.

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