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(19)



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(54) ELECTRODES FOR ELECTROCHEMICAL PROCESSES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrodes for electrochemical processes. More particularly it relates to electrodes of the type wherein an electrochemically active coating is carried on a support member made from a corrosion-resistant metal.

In British Patent Specification Serial No. 1,244,650 it has been proposed to employ as an electrode in electrochemical processes a structure in which an electrochemically active coating consisting of a minor amount of a platinum group metal oxide and a major amount of the oxides of one or more of tin, antimony and germanium is carried on a support made of a film-forming metal, e.g. titanium. The present invention provides an improved electrode of the coated film-forming-metal type wherein the coating comprises a platinum group metal oxide and oxides of one or more of tin, antimony and germanium, as defined in the following paragraph.

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 which consists of a mixture of the following three components: (a) ruthenium dioxide, (b) titanium dioxide and (c) one or more of tin dioxide, germanium dioxide and oxides of antimony, and in the said mixture the amount of component (a) is not less than 1% by weight, the amount of component (b) is not more than 50% by weight, the amount of component (c) is in the range 1% to 80% by weight and the weight ratio of component (a): component (b) is less than 2:1.

By a film-forming metal or alloy we mean titanium, zirconium, niobium, tantalum or tungsten or an alloy based on one of these metals and having anodic polarisation properties similar to those of the commercially pure metal. The preferred metal for construction of the support member is titanium or a titanium alloy having anodic polarisation properties similar to those of titanium.

Electrodes according to the invention are very useful as anodes in cells for the electrolysis of alkali metal chloride solutions, especially in cells having flowing mercury cathodes, because the electrode coating has excellent adhesion to the film-forming metal support, it has a suitably low overpotential for the liberation of chlorine and it has high resistance to damage by accidental contact with the cathode amalgam, such as can occur even during normal operation of mercury-cathode cells. The electrode can also be used in other electrochemical processes, including other electrolytic processes, electrocatalysis, as for instances in fuel cells, electrosynthesis and cathodic protection.

Preferred electrodes within the scope of the invention for use as anodes in the electrolysis of alkali metal chloride solutions comprise a titanium or titanium alloy support member carrying a coating consisting by weight of 25% to 50% ruthenium dioxide, 40% to 50% titanium dioxide and 5% to 25% tin dioxide.

An electrode according to the invention is suitably manufactured by applying to a support member made of a film-foaming metal or alloy a coating of a paint composition comprising a thermally-decomposable compound of ruthenium, a thermally-decomposable organo-compound of titanium and at least one compound selected from thermally-decomposable organo-compounds and thermally-oxidisable inorganic compounds of tin, germanium and antimony in an organic liquid vehicle, drying the coating by evaporation of the liquid vehicle and then heating the coated support member in an oxidising atmosphere, e.g. air,

[Price 25p]

at a temperature of at least 350°C and preferably in the range 400°C to 550°C to convert the said compounds of ruthenium, titanium, tin, germanium and antimony to oxides of these elements. Further coats of the paint composition may then be applied to the coated support member, dried and heated in the same manner to increase the thickness of the mixed oxide layer to any desired extent.

A preferred paint composition consists of compounds of ruthenium, titanium and tin in an organic liquid vehicle.

The thickness of the finished coating is in no way critical and will generally be chosen having regard to the wear to which the electrode will be submitted during use in the electrochemical cell, which itself will be related inter alia to the current density at which the electrode will be required to operate. For electrodes that are to be used as anodes in the electrolysis of alkali metal chloride solutions, for example, a thickness corresponding to a weight of finished coating in the range 5 to 40 g/m² of the coated surface of the support member is generally suitable. Thinner or thicker coatings may, however, be employed if desired.

In the paint compositions used for depositing the electrode coatings in accordance with the preceding paragraph, the thermally-decomposable ruthenium compound may suitably be ruthenium trichloride or a ruthenium resinate. Suitable thermally-decomposable organo-compounds of titanium are titanium alkoxides, titanium alkoxy-halides in which the halogen is chlorine, bromine or fluorine and titanium resinates. The preferred titanium compounds are the alkoxides and the said alkoxy-halides, alternatively known as alkyl titanates and alkyl halotitanates. Most preferred are the alkyl titanates and halotitanates wherein the alkyl groups contain two to four carbon atoms each. Suitable thermally-decomposable organo-compounds of tin, germanium and antimony are alkoxides and alkoxy-halides of these elements. Alternatively the thermally-oxidisable inorganic halides, especially the chlorides, of these elements may be employed. The organic liquid vehicle is most suitably a lower alkanol or a mixture of lower alkanols, particularly those containing three to six carbon atoms per molecule.

The invention is further illustrated by the following Examples:

Example 1

A titanium strip 35 cm long and 6 mm × 1 mm cross section was etched in oxalic acid solution, washed and dried. A paint composition was made by dissolving 3.9 g of partly hydrated ruthenium trichloride and 9.6 g of tetrabutyl orthotitanate in 19.5 g of *n*-pentanol and adding 5 g of a solution made by dissolving 20.8 g of stannic chloride in 60 g of *n*-pentanol. Nine coats of this paint were applied to the titanium strip, each coat being dried at 180°C and then fired by heating in air for 15 minutes at 450°C, thus providing a finished coating amounting to 20 g/m² of the coated titanium surface and consisting by weight of 40% ruthenium dioxide, 45% titanium dioxide and 15% tin dioxide.

Samples cut from the coated strip were tested as anodes for chlorine production in sodium chloride brine containing 21.5% NaCl at pH 2 to 3 and a temperature of 65°C. The samples operated with low overpotential (50 to 70 mV at a current density of 8 kA/m²) and they also showed good resistance to damage when contacted with the cathode amalgam in a mercury cell electrolysing 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 m² (the area that would be covered by an orthogonal projection of the grid on to a plane surface, excluding the spaces between the strips, i.e., the area of only the strip edges that form a face of the grid) was etched in oxalic acid solution for 16 hours, washed and dried. The anode grid was then sprayed with a paint composition consisting of 55 g ruthenium trichloride, 136 g tetra-*n*-butyl orthotitanate and 29.5 g stannous octoate in 264 g *n*-pentanol. The paint layer was dried in an oven at 180°C for 15 minutes and was then fired by heating in air in a furnace at 450°C for 20 minutes to produce a coating of composition 40% RuO_2/45% TiO_2/15% SnO_2 by weight on the titanium surface. A further seven coats of the same paint composition were then sprayed on to the anode, each coat being dried and fired in the same manner as the first coat, to give a total loading of mixed oxides on the titanium grid amounting to 32 g/m² projected area.

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

Example 3

A titanium grid anode of 0.1 m² projected area (see Example 2) was coated as in Example 2 except that the paint composition consisted of 62.5 g ruthenium trichloride, 136 g tetra-*n*-butyl orthotitanate and 20.1 g stannous octoate in 266 g *n*-pentanol. This composition, after drying and firing, produced a coating of composition 45% RuO_2/45% TiO_2/10% SnO_2, and the eight layers of paint gave a total loading of mixed oxides on the titanium grid amounting to 32 g/m² projected area. This anode was also operated in a mercury-cathode cell electrolysing sodium

chloride brine and also showed no signs of wear no decline in performance after six months' use with an anode current of up to 900 amp.

WHAT WE CLAIM IS:—

1. An electrode for use in elecrochemical processes which comprises a support member made of a film-forming metal or alloy as hereinbefore defined and a coating thereon which consists of a mixture of the following three components: (a) ruthenium dioxide, (b) titanium dioxide and (c) one or more of tin dioxide, germanium dioxide and oxides of antimony, and in the said mixture the amount of component (a) is not less than 1% by weight, the amount of component (b) is not more than 50% by weight, the amount of component (c) is in the range of 1% to 80% by weight and the weight ratio of component (a): component (b) is less than 2:1.

2. An electrode 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. An electrode according to claim 2, wherein the said coating consists by weight of 25% to 50% ruthenium dioxide, 40% to 50% titanium dioxide and 5% to 25% tin dioxide.

4. An electrode according to any one of the preceding claims, wherein the weight of the said coating is in the range 5 to 40 g/m² of the coated surface.

5. A method for the manufacture of an electrode according to claim 1, which comprises applying on a support member made of a film-forming metal or alloy a coating of a composition comprising a thermally-decomposable compound of ruthenium, a thermally-decomposable organo-compound of titanium and at least one compound selected from thermally-decomposable organo-compounds and thermally-oxidisable inorganic compounds of tin, germanium and/or antimony in an organic liquid vehicle, drying the coating by evaporation of the liquid vehicle and then heating the coated support member in an oxidising atmosphere at a temperature of at least 350°C to convert the said compounds of ruthenium, titanium, tin, germanium and antimony to oxides of these elements.

6. A method according to claim 5, wherein the said support member is made of titanium or a titanium alloy having anodic polarisation properties similar to those of titanium.

7. A method according to either of claims 5 or 6, wherein the sequence of applying and drying the said coating and then heating the coated support member is repeated at least once to build up a thicker layer of the said oxides.

8. A method according to any one of claims 5 to 7, wherein the total amount of the said coating which is applied on the support member is sufficient to produce a layer of the said oxides amounting to 5 to 40 g/m² of the coated surface of the support member.

9. A method according to any one of claims 5 to 8, wherein each said coating after drying is heated in an oxidising atmosphere at a temperature in the range 400°C to 550°C.

10. A method according to any one of claims 5 to 9, wherein the said composition consists of the said compounds of ruthenium, titanium and tin in an organic liquid vehicle and the proportions of the said compounds of ruthenium, titanium and tin in the composition are chosen so that after drying and heating the coating thereof in an oxidising atmosphere the oxides produced are in the ranges 25% to 50% ruthenium dioxide, 40% to 50% titanium dioxide and 5% to 25% tin oxide by weight of the converted coating.

11. A method according to any one of claims 5 to 11, wherein the thermally-decomposable organo-compound of titanium is an alkyl titanate or an alkyl halotitanate wherein the halogen is chlorine, bromine or fluorine.

12. A method according to claim 12, wherein the alkyl groups of the said alkyl titanate or alkyl halotitanate contain two to four carbon atoms each.

13. An electrode for use in electrochemical processes, as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the foregoing Examples.

14. A method for the manufacture of an electrode for use in electrochemical processes, as claimed in claim 5 and substantially as hereinbefore described with reference to any one of the foregoing Examples.

15. A cell for the electrolysis of alkali metal chloride solutions, wherein electrodes according to any one of claims 1 to 4 and 14 constitute the anodes of the cell.

16. A cell according to claim 16, wherein the cathode is a flowing mercury cathode.

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chloride brine and also showed no signs of wear no decline in performance after six months' use with an anode current of up to 900 amp.

WHAT WE CLAIM IS:—

1. An electrode for use in elecrochemical processes which comprises a support member made of a film-forming metal or alloy as hereinbefore defined and a coating thereon which consists of a mixture of the following three components: (a) ruthenium dioxide, (b) titanium dioxide and (c) one or more of tin dioxide, germanium dioxide and oxides of antimony, and in the said mixture the amount of component (a) is not less than 1% by weight, the amount of component (b) is not more than 50% by weight, the amount of component (c) is in the range of 1% to 80% by weight and the weight ratio of component (a): component (b) is less than 2:1.

2. An electrode 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. An electrode according to claim 2, wherein the said coating consists by weight of 25% to 50% ruthenium dioxide, 40% to 50% titanium dioxide and 5% to 25% tin dioxide.

4. An electrode according to any one of the preceding claims, wherein the weight of the said coating is in the range 5 to 40 g/m² of the coated surface.

5. A method for the manufacture of an electrode according to claim 1, which comprises applying on a support member made of a film-forming metal or alloy a coating of a composition comprising a thermally-decomposable compound of ruthenium, a thermally-decomposable organo-compound of titanium and at least one compound selected from thermally-decomposable organo-compounds and thermally-oxidisable inorganic compounds of tin, germanium and/or antimony in an organic liquid vehicle, drying the coating by evaporation of the liquid vehicle and then heating the coated support member in an oxidising atmosphere at a temperature of at least 350°C to convert the said compounds of ruthenium, titanium, tin, germanium and antimony to oxides of these elements.

6. A method according to claim 5, wherein the said support member is made of titanium or a titanium alloy having anodic polarisation properties similar to those of titanium.

7. A method according to either of claims 5 or 6, wherein the sequence of applying and drying the said coating and then heating the coated support member is repeated at least once to build up a thicker layer of the said oxides.

8. A method according to any one of claims 5 to 7, wherein the total amount of the said coating which is applied on the support member is sufficient to produce a layer of the said oxides amounting to 5 to 40 g/m² of the coated surface of the support member.

9. A method according to any one of claims 5 to 8, wherein each said coating after drying is heated in an oxidising atmosphere at a temperature in the range 400°C to 550°C.

10. A method according to any one of claims 5 to 9, wherein the said composition consists of the said compounds of ruthenium, titanium and tin in an organic liquid vehicle and the proportions of the said compounds of ruthenium, titanium and tin in the composition are chosen so that after drying and heating the coating thereof in an oxidising atmosphere the oxides produced are in the ranges 25% to 50% ruthenium dioxide, 40% to 50% titanium dioxide and 5% to 25% tin oxide by weight of the converted coating.

11. A method according to any one of claims 5 to 11, wherein the thermally-decomposable organo-compound of titanium is an alkyl titanate or an alkyl halotitanate wherein the halogen is chlorine, bromine or fluorine.

12. A method according to claim 12, wherein the alkyl groups of the said alkyl titanate or alkyl halotitanate contain two to four carbon atoms each.

13. An electrode for use in electrochemical processes, as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the foregoing Examples.

14. A method for the manufacture of an electrode for use in electrochemical processes, as claimed in claim 5 and substantially as hereinbefore described with reference to any one of the foregoing Examples.

15. A cell for the electrolysis of alkali metal chloride solutions, wherein electrodes according to any one of claims 1 to 4 and 14 constitute the anodes of the cell.

16. A cell according to claim 16, wherein the cathode is a flowing mercury cathode.

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