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[54] **ANODES FOR MERCURY-CATHODE ELECTROLYTIC CELLS**

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[52] **U.S. Cl.** ..... **204/290 F**; 136/120 FC; 427/115; 427/126; 427/375; 427/376; 427/407; 427/409; 427/419

[51] **Int. Cl.**[2] **C23B 11/00**; B32B 3/02

[58] **Field of Search** ..... 117/218, 63, 45, 212; 136/120 FC; 204/290 F; 427/115, 126, 375, 379, 407, 419, 409

[56] **References Cited**

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[57] **ABSTRACT**

A process for forming on an anode an anodically-conducting oxidic coating having a porous outer layer of a chlorine resistant polymer bonded thereto, the process comprising coating the anode with the oxidic coating, applying to the said oxidic coating the polymer in admixture with a removable solid particulate material, bonding the polymer to the oxidic coating by the successive stages of drying, heating to melt the polymer and cooling, and subsequently removing the solid particular material from the coating.

Suitable chlorine-resistant polymers for the porous outer layer of the anode include polyvinylidene fluoride and low molecular weight polytetrafluoroethylene (PTFE).

The solid particulate materials include alkali metal chlorides, starch, cellulose, water-insoluble bases or carbonates.

16 Claims, No Drawings

ANODES FOR MERCURY-CATHODE ELECTROLYTIC CELLS

The present invention relates to improvements in anodes for mercury-cathode electrolytic cells. More particularly it relates to improvements in coated metal anodes used for the electrolysis of alkali-metal chloride solutions in cells having flowing mercury cathodes.

In recent years attempts have been made to replace consumable graphite anodes in mercury-cathode cells electrolysing alkali-metal chloride solutions by dimensionally stable anodes made of titanium or a titanium alloy carrying a thin anodically-conducting coating. The greatest success has been achieved with oxidic coatings. These may, for example, consist of the electrically-conducting oxides of the platinum group metals, mixtures of these with the non-conducting oxide of one of the film-forming metals, titanium, tantalum, zirconium, niobium and tungsten, and/or with other refractory oxides such as tin dioxide, sometimes referred to a semiconducting mixtures, eg a mixture of the oxides of tin and antimony, to which a proportion of a platinum group metal oxide may be added to increase the electrocatalytic activity.

The aforesaid oxidic coatings have proved to be much more resistant to dissolution and stripping from the titanium support by accidental contact with the mercury cathode in the working cell than are the earlier-proposed metallic coatings, eg platinum, iridium, rhodium and mixtures of these. Nevertheless even the oxide-coated anodes are capable of passing a large short-circuit current whenever they come into contact with the cell cathode, and this current can lead to serious overheating, which can cause erosion of both the coating and the titanium support if the short-circuit condition is not quickly corrected. Since accidental short-circuiting of anodes cannot be entirely avoided, prevention of short-circuit damage is a serious problem.

The present invention provides a method of treating an anode of the oxide-coated titanium or titanium-alloy type so that the short-circuit current between the anode and the mercury cathode at any given impressed voltage is reduced without preventing passage of the electrolysing current under normal operating conditions. The invention thus provides an anode of the oxide-coated titanium or titanium-alloy type which has improved resistance to damage by overheating under short-circuit conditions.

According to the present invention, therefore, there is provided a process for forming on an anode an anodically-conducting oxidic coating having a porous outer layer of a chlorine resistant polymer bonded thereto, the process comprising coating the anode with the oxidic coating, applying to the said oxidic coating the polymer in admixture with a removable solid particulate material, bonding the polymer to the oxidic coating by the successive stages of drying, heating to melt the polymer and cooling, and subsequently removing the solid particular material from the coating.

From another aspect the present invention is a process for forming on an anode an anodically conducting oxidic coating having a porous outer layer of chlorine resistant polymer bonded thereto, the process comprising coating the anode with the oxidic coating, coating the said oxidic coating with a discontinuous layer of solid particulate material so that a fraction of the oxidic coating is left uncovered between individual particles of the particulate material, coating with the polymer so as to fill the spaces between the particles, bonding the polymer to the oxide by heating to melt the polymer followed by cooling, and subsequently removing the solid particulate material from the coating.

Suitable chlorine-resistant polymers for the porous outer layer of the anode are polyvinylidene fluoride and low molecular weight polytetrafluoroethylene (PTFE).

By a film-forming titanium alloy we mean an alloy consisting mainly of titanium and having anodic polarisation properties through formation of a surface-film of oxide similar to those of commercially pure titanium.

The anodically-conducting oxidic coating of the electrode may be any one of those known in the art which is resistant to electrochemical dissolution when connected anodically in an aqueous alkali-metal chloride electrolyte, particularly oxides of the platinum group metals and the prior-art combinations of oxides listed hereinbefore. The preferred oxidic coatings are combinations of oxides of one or more of the platinum group metals, platinum, iridium, osmium, ruthenium, rhodium and palladium, with the oxide of one of the film-forming metals, titanium, tantalum, zirconium, niobium and tungsten, especially a combination of ruthenium dioxide and titanium dioxide. These combinations may be substantially homogeneous mixtures of which the platinum group metal oxide and the film-forming metal oxide components have been laid down together on the titanium or titanium alloy support member, or they may be coatings formed by depositing alternate layers of platinum group metal oxide and film-forming metal oxide on the support member, for instance as taught in British Patent Specifications Nos. 1,206,863 and 1,294,373. With the latter method of forming the oxidic coating the homogeneity of the finished coating is less certain, but when the coating is made by firing layers of paint compositions there is at least some interpenetration between the layers of the coating thereby deposited.

In order to produce the required porous outer layer of chlorine-resistant organic polymer on the anode according to the invention it is necessary to fix a coating of the polymer in the molten state to the oxide layer on the anode support member. This may be done by preheating the oxide-coated support member to about 250°C, spraying the molten polymer on to the oxide layer and then allowing the coated electrode to cool. Alternatively a coating of the polymer in a liquid vehicle may be applied to the oxide layer, the liquid vehicle than being removed by evaporation, the coated anode heated to about 250°C to melt the polymer coating and allowed to cool.

Thus an aqueous emulsion of low-molecular-weight PTFE may be brushed or sprayed on to the oxide coating, the coating then dried by heating in air at about 160°C, after which the coated anode is heated at a temperature not higher than 280°C for about 10 minutes to melt the polymer and is allowed to cool. The molecular weight of the PTFE must be restricted so that it can be melted satisfactorily on the anode surface. A coating of polyvinylidene fluoride may suitably be applied in a similar manner starting with a solution or suspension of the polymer or a low-molecular-weight precursor in an organic solvent, eg in a mixture of dimethyl phthalate and di-isopropyl ketone.

When the polymer coating is applied by one of the aforesaid procedures, the optimum thickness of the coating corresponds to a weight of about 5 g/m² of the coated surface. Substantially thicker layers may interfere to an unacceptable extent with passage of the normal electrolysing current when the anode is in use, while layers less than about 3 g/m² usually have an adequate effect in limiting the short-circuit current in the cell. As aforesaid, the porosity of the polymer coating may be usefully increased by adding a removable particulate filler to an emulsion or solution of the chlorine-resistant organic polymer that is used for coating the anode so that, after drying the coating, heating the dried coating to melt the polymer and cooling, the particles of filler remain in the coating but are removed by water-washing or by reaction in the electrolytic cell soon after the anode is put into service. Examples of suitable removable particulate fillers are alkali metal chlorides, eg potassium chloride, starch, cellulose or a water insoluble base or carbonate, for example calcium carbonate. The particle size of the filler is most suitably in the range 5 to 500 micron.

Another way of employing a removable particulate material to increase the porosity of a polymer coating is first to coat the anode with a discontinuous layer of the particulate material so that between the individual particles a fraction of the anode surface remains uncovered, then to apply the polymer coating so as to fill the spaces between the particles and then to bond the polymer coating to the anode surface by heating to melt the polymer. For example, a discontinuous layer of potassium chloride crystals may be formed on the anode surface by coating the anode with a saturated aqueous solution of potassium chloride and evaporating the aqueous medium. Then after applying and melting the polymer coating the potassium chloride crystals may be removed by water-washing before the anode is put to use or they may be allowed to dissolve in the electrolyte shen the anode is installed in the electrolytic cell.

Coatings of increased porosity produced in accordance with either of the two preceding paragraphs have the advantage of being slightly thicker for the same weight of polymer, although of reduced electrical resistance, and the total weight of polymer may also be increased with the advantage of reducing the short-circuit current still further without interfering to an unacceptable extent with passage of the normal electrolysing current through the anode.

The invention is further illustrated by the following Example:

EXAMPLE

A strip of titanium 70 mm × 6 mm × 1 mm was etched in 10% oxalic acid solution, washed, dried and then provided with an anodically-conducting electrocatalytic coating consisting of approximately 40% RuO_2 and 60% TiO_2 by weight, by applying to it eight layers of a paint composition prepared by dissolving ruthenium trichloride and tetrabutyl orthotitanate in n-pentanol, each paint layer being dried in air at 180°C and then heated in air for 15 minutes at 450°C. The coated titanium strip was then dipped into a saturated aqueous solution of potassium chloride and withdrawn. The layer of solution remaining on the coated strip was allowed to dry out leaving a film of small potassium chloride crystals covering about 80% of the coated surface. The cracks between the crystals were filled by brushing on a suspension of low-molecular-weight polyvinylidene fluoride in an organic solvent (sold as 'Kynar' 500). The coated strip was then heated at 250°C for about 4 minutes to cause further polymerisation of the polyvinylidene fluoride and bonding of the polymer to the coating of RuO_2/TiO_2 between the potassium chloride crystals. The coated strip was then washed in water to remove the potassium chloride crystals and was afterwards used as an anode to electrolyse sodium chloride brine in a laboratory-scale mercury-cathode cell.

The anode strip was suspended in the cell with its faces in a vertical plane and its longest axis horizontal. When a short circuit was caused by raising the level of the mercury cathode until the bottom 4 mm of the strip were immersed in the mercury, a short-circuit current of only 3 amp/cm length of the anode strip flowed between the anode and cathode. This may be compared with a short-circuit current of 10 to 15 amp/cm length observed under the same operating conditions with a coated titanium anode strip of the same size carrying the same electrocatalytic coating of RuO_2/TiO_2 but without the superimposed layer of polyvinylidene fluoride.

What I claim is:

1. A process for forming improved anodes for mercury-cathode electrolytic cells, by forming on an anode an anodically-conducting oxidic coating having a porous outer layer of a chlorine resistant polymer bonded thereto, said polymer being polyvinylidene fluoride or low molecular weight polytetrafluoroethylene, the process comprising coating the anode with the oxidic coating, wherein the oxidic coating comprises a platinum group metal oxide; applying to said oxidic coating the polymer in admixture with a removable solid particulate material, wherein said solid particulate material is an alkali metal chloride, starch, cellulose, a water insoluble base or carbonate thereof; bonding the polymer to the oxidic coating by successive stages of drying by heating in air at about 160°C, heating to melt the polymer at temperatures of up to 280°C, and cooling; and subsequently removing the solid particulate material from the coating by dissolving the particulate material by dissolving in water or dilute acid, whereby the short-circuit current between the anode and the mercury cathode at any given impressed voltage is reduced without preventing passage of the electrolyzing current under normal operating conditions.

2. A process as claimed in claim **1** wherein the solid particulate material is an alkali metal chloride, starch or cellulose.

3. A process as claimed in claim **1** wherein the solid particulate material is removed by reaction in the electrolytic cell soon after the anode is put on service.

4. A process as claimed in claim **1** wherein the solid particulate material is a water-insoluble inorganic base or carbonate.

5. A process as claimed in claim **4** wherein the solid particulate material is calcium carbonate.

6. A process as claimed in claim **4** the solid particulate material is removed by dissolving in acid or by reaction in the electrolytic cell soon after the anode is put in service.

7. A process as claimed in claim **1** wherein the oxidic coating comprises a platinum group metal or oxide thereof in admixture with an oxide of a film forming metal.

8. A process as claimed in claim **7** wherein the oxidic coating comprises ruthenium dioxide and titanium di-

oxide.

9. The process of claim **1**, wherein the thickness of the polymer coating is up to 5 g/m².

10. An anode for a mercury cathode electrolytic cell, comprising a support member made of titanium or a film-forming titanium alloy and bonded thereto an anodically-conducting oxidic coating, said coating being a platinum group metal or an oxide thereof, having a porous outer layer of a chlorine-resistant organic polymer bonded thereto, said polymer being polyvinylidene fluoride or low molecular weight polytetrafluoroethylene, and wherein the anode is coated by the process claimed in claim **1**.

11. A process for producing an improved anode for mercury-cathode electrolytic cells, by forming on an anode anodically-conducting oxidic coating having a porous outer layer of a chlorine resistant polymer bonded thereto, said polymer being polyvinylidene fluoride or low molecular weight polytetrafluoroethylene, the process comprising coating the anode with the oxidic coating, wherein the oxidic coating comprises a platinum group metal oxide; coating the said oxidic coating with a discontinuous layer of solid particulate material, wherein said solid particulate material is an alkali metal chloride, starch, cellulose, a water insoluble base or carbonate thereof, so that a fraction of the oxidic coating is left uncovered between individual particles of the particulate material; coating with the polymer so as to fill the spaces between the particles; bonding the polymer to the oxide by heating at temperatures up to 280°C to melt the polymer, followed by cooling; and subsequently removing the solid particulate material from the coating by dissolving in water or dilute acid, whereby the short-circuit current between the anode and the mercury cathode at any given impressed voltage is reduced without preventing passage of the electrolyzing current under normal operating conditions.

12. A process as claimed in claim **11** wherein the anodically-conducting oxidic coating comprises a platinum group metal oxide.

13. The process of claim **11**, wherein the thickness of the polymer coating is up to 5 g/m².

14. A process as claimed in claim **11**, wherein the oxidic coating comprises ruthenium dioxide and titanium dioxide.

15. A process for forming on an anode an anodically conducting oxidic coating have a porous outer layer of a chlorine-resistant polymer bonded thereto said polymer being polyvinylidene fluoride or low molecular weight polytetrafluoroethylene, the process comprising coating the anode with the oxidic coating said oxidic coating being a platinum group metal oxide, heating the coated anode to about 250°C, spraying molten polymer on to the oxide layer and allowing the coated anode to cool.

16. A process for forming on an anode an anodically conducting oxidic coating having a porous outer layer of a chlorine-resistant polymer bonded thereto said polymer being polyvinylidene fluoride or low molecular weight polytetrafluoroethylene, the process comprising coating the anode with the oxidic coating said oxidic coating being a platinum group metal oxide, applying to the said coating the polymer in a liquid vehicle, removing the liquid vehicle by evaporation, and heating the coated anode to about 250°C to melt the polymer coating, and allowing the coated anode to cool.

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