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[54] **STRIPPING OF COATED TITANIUM ELECTRODES FOR RE-COATING**

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[58] **Field of Search**.....134/2, 3, 27, 28, 29; 252/79.5, 103, 156

[56] **References Cited**

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[57] **ABSTRACT**

Stripping a coating comprising a platinum group metal oxide from a titanium support member of a coated titanium electrode ready for re-coating, by immersing the electrode in molten alkali metal hydroxide containing a small amount of alkali metal hydride, washing the treated electrode in water and then, preferably, dipping in hot dilute mineral acid.

10 Claims, No Drawings

STRIPPING OF COATED TITANIUM ELECTRODES FOR RE-COATING

The present invention relates to stripping of coated titanium electrodes for re-coating. More particularly it relates to a method for the removal of a coating comprising one or more platinum group metal oxides from a titanium support which carries the coating, in a manner which renders the titanium surface suitable for re-coating and without excessive loss of titanium from the support.

It has recently been proposed to employ as electrodes, particularly as anodes in cells electrolyzing aqueous solutions of alkali metal chloride, a combination of a film-forming metal support and a coating thereon comprising oxides of one or more of the platinum group metals, the coating optionally also containing one or more oxides of non-noble metals, for example an oxide of one of the film-forming metals, especially titanium dioxide (see for instance British Pat. Specifications No. 1,147,442 and No. 1,195,871), or other oxides that are resistant to anodic attack, for instance oxides of tin, antimony and germanium as taught in Belgian Pat. Specification No. 740,242. In electrodes of this type the film-forming metal of the support is most suitably titanium.

Electrodes of the aforesaid type have advantages over prior art electrodes when employed as anodes in the electrolysis of alkali metal chloride solutions in that they have both low chlorine overpotential characteristics and high resistance to electrochemical attack in use.

Although the electrodes have a very low wear rate in the cell, their useful lives are not infinite and in time they must be replaced or re-coated in order to maintain optimum performance. When the electrodes are taken out of service they still retain an appreciable amount of the original coating and if the titanium support is to be used as a support for a new coating it is preferable first to remove the remains of the old coating. This presents the problem of removing the old coating cheaply and easily without at the same time removing an unacceptable amount of titanium metal from the support.

According to the present invention we provide a method for stripping the coating from an electrode comprising a titanium support and a coating comprising a platinum group metal oxide thereon, which comprises immersing the electrode for at least 10 seconds, preferably at least 30 seconds, in a bath of molten alkali metal hydroxide containing at least 0.1 percent by weight of alkali metal hydride and then washing the treated electrode in water.

For economic reasons the alkali metal hydroxide is most suitably sodium hydroxide, and the alkali metal hydride is most suitably sodium hydride.

The desired concentration of alkali metal hydride may suitably be established in a bath of molten alkali metal hydroxide by suspending in the molten hydroxide a sufficient amount of alkali metal and passing a stream of hydrogen or cracked ammonia gas into the bath. Baths prepared in this way may be used in the method of the invention whether or not all the added alkali metal has been converted to hydride, i.e., they are suitable for use whether or not they contain some free alkali metal as well as the required amount of alkali metal hydride.

The bath of molten alkali metal hydroxide containing alkali metal hydride may be used at any convenient temperature upwards of a minimum of approximately 10° C. above the temperature at which the bath begins to freeze on cooling but we have found no advantage in working at temperatures more than about 100° C. above the freezing range of the bath. Moreover, we have found that with bath temperatures above 450° C. the rate of attack on the titanium substrate of the electrode can become unacceptably high. The preferred temperature range for baths based on sodium hydroxide is 345°–380° C. Preferably also the alkali metal hydride content of these baths is in the range 0.5–2 percent sodium hydride by weight. The treatment time in these preferred baths is most suitably in the range 1–3 minutes.

After treatment of the electrode in the bath of molten alkali metal hydroxide containing alkali metal hydride the washing step in water may most suitably be carried out by immediately quenching the hot electrode in water.

Furthermore, within the scope of the invention, after the said washing step in water it is preferred to give the electrode a dip for a few seconds in hot dilute mineral acid, suitably sulphuric acid of about 10 N concentration, followed by again washing in water. Most suitably the electrode is immersed in the acid until effervescence begins and is then immediately withdrawn and washed in water. We have found that this acid dip improves the condition of the titanium surface for re-coating.

The electrodes to be treated in accordance with the invention may have coatings in which the whole of the platinum group metal content is in the form of platinum group metal oxides. The method of the invention is, however, also applicable to coatings wherein a minor amount of the platinum group metal content is in the form of free platinum group metals, the remainder and major amount being in the form of oxides. The platinum group metal content thus defined may consist of any one or more of the metals platinum, iridium, rhodium, osmium, ruthenium and palladium.

The invention is applicable to electrodes in which the coating consists entirely of platinum group metals, mainly in the oxidized state, and also to electrodes in which the coating consists of platinum group metals, mainly in the oxidized state, in association with oxides of other metals, e.g., oxides of the film-forming metals titanium, zirconium, niobium, tantalum and tungsten, tin dioxide, germanium dioxide and oxides of antimony. Specific examples of the latter type of coating are coatings of ruthenium dioxide in association with titanium dioxide and coatings of ruthenium dioxide in association with mixtures of tin dioxide and oxides of antimony.

The invention is further illustrated by the following examples on the stripping of coatings consisting substantially of ruthenium dioxide in admixture with titanium dioxide (Examples 1–8), with tin dioxide (Example 9) and with a mixture of tin dioxide and oxides of antimony (Example 10), all on titanium supports.

EXAMPLES 1–6

A molten bath of sodium hydroxide containing sodium hydride was prepared by suspending sodium metal

in molten sodium hydroxide and passing a stream of hydrogen into the bath. For each example a section from a coated titanium electrode blade (composition of coating approximately 40% RuO_2:60% TiO_2 by weight) was immersed in the molten bath for the time shown in the following table. The section was then removed from the bath, immediately quenched in cold water and then immersed in 10 N sulphuric acid held at a temperature of 80° C. After an induction period varying from 30 seconds to 90 seconds effervescence began and thereupon the electrode section was immediately removed from the acid and washed in water. In each case this sequence of treatment removed the coating and left the surface of the titanium support in a suitable condition for re-coating. The temperature of the molten bath, its sodium hydride content, weight of original coating and weight loss of the titanium support are shown in the following table.

Ex. No.	Bath Temp. °C.	Sodium Hydride Concentration % w/w	immersion Time Minutes	Wt. of Original Coating of RuO_2/TiO_2 g/m²	Weight Loss of Titanium Support g/m²
1	345	1.6	1	17.5	8.6
2	350	0.6	1	39.5	15.2
3	370	0.8	0.5	22.7	4.6
4	370	0.8	1	17.8	1.5
5	370	0.8	1	17.8	3.8
6	375	2.5	6	38.8	21.6

EXAMPLES 7 AND 8

Two mercury-cell anodes having the active coating carried on a grid of parallel titanium blades spaced apart by welding at one edge to transverse titanium members and having a projected working area of 0.1 m² were stripped in a molten bath of sodium hydroxide containing sodium hydride, made up as in Examples 1–6. The active coating consisted of approximately 40% RuO_2:60% TiO_2 by weight. After immersion in the molten bath for the times shown in the following table, the anodes were quenched in cold water. The bath conditions and the results of this treatment are shown in the table.

		Example 7	Example 8
Bath temperature	°C	360	360
Sodium hydride concentration	% w/w	1.5	1.5
Immersion time	min	2	1
Initial weight	g	1202.5	1298.1
Total weight loss	g	6.0	5.9
Titanium metal loss	g	2.5	2.5
Appearance		all coating removed	all coating removed

After this treatment the titanium substrate appeared to be clean enough for re-coating. It was, however, given a short etching treatment in sulphuric acid before applying a new coating.

EXAMPLE 9

A strip of titanium coated with a mixture of ruthenium dioxide and tin dioxide (approximate composition 40% RuO_2:60% SnO_2 by weight) was immersed for one minute in a bath of molten sodium hydroxide containing 1.5 percent by weight sodium hydride held at a temperature of 360° C. and was then quenched in water. The strip was then immersed in 10 N sulphuric acid at 80° C. until effervescence began and was then washed in water. This treatment removed all the coating and left the titanium surface in a suitable condition for re-coating.

EXAMPLE 10

A strip of titanium coated with a mixture of ruthenium dioxide, tin dioxide and oxides of antimony (approximate composition by weight 5% RuO_2:85% SnO_2:10% oxides of antimony calculated as Sb_2O_4) was treated in the manner of Example 9. This treatment removed all the coating and left the titanium surface in a suitable condition for re-coating.

We claim:

1. A method for stripping the coating from an electrode comprising a titanium support and a coating comprising a platinum group metal oxide thereon, which comprises immersing the electrode for at least 10 seconds in a bath of molten alkali metal hydroxide containing at least 0.1 percent by weight of alkali metal hydride and then washing the treated electrode in water.

2. A method according to claim 1, wherein the electrode is immersed in the said bath for at least 30 seconds before washing in water.

3. A method according to claim 1, wherein the said molten alkali metal hydroxide is sodium hydroxide and the said alkali metal hydride is sodium hydride.

4. A method according to claim 3, wherein the temperature of the said bath is in the range 345°–380° C.

5. A method according to claim 4, wherein the said bath contains 0.5–2 percent by weight of sodium hydride.

6. A method according to claim 5, wherein the electrode is immersed in the said bath for 1–3 minutes before washing in water.

7. A method according to claim 1, wherein the said step of washing the treated electrode in water is carried out by immediately quenching the hot electrode in water.

8. A method according to claim 1, wherein after the said step of washing the treated electrode in water the electrode is immersed in hot dilute mineral acid for a few seconds and is then washed in water.

9. A method according to claim 8, wherein the electrode is immersed in the said acid until effervescence begins and is then washed in water.

10. A method according to claim 1, wherein the coating of the electrode is a mixture of ruthenium dioxide and titanium dioxide.

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