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[54] **REMOVING OF WORN COATING FROM METAL ELECTRODES**

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[57] **ABSTRACT**

A method including immersing a coated electrode into a molten salt bath including essentially at least one bisulphate or pyrosulphate of an alkali metal or ammonium, at a temperature between 300° and 500° C, and water-rinsing the so-treated electrode after cooling thereof.

13 Claims, No Drawings

REMOVING OF WORN COATING FROM METAL ELECTRODES

BACKGROUND OF THE INVENTION

The present invention relates to a chemical method for removing worn coatings of electrodes for use in electrolysis, including (a) an electroconductive metal support resistant to corrosion under the conditions ruling in the electrochemical cell; and (b) a conductive coating, fixed on the support, which is also resistant to electrochemical attack and promotes the electron exchange between the support and ions of an electrolyte.

Lately, such metal electrodes have been used more and more, especially in the electrolysis of aqueous solutions of alkali metal halides, with the object to replace graphite anodes which, owing to their relatively rapid wear, require frequent readjustings of the anode-cathode distance and the periodical renewal of worn anodes, thus necessitating stopping the electrolysis and opening the cell.

On account of their high resistance to chemical attack in the cell, the use of metal electrodes having a support made of titanium or tantalum allows to avoid these disadvantages.

Although such metal electrodes have a very low wear rate in the cell, their useful lifetime is not infinite, owing to the progressive passivation and the slow time-wearing of their coating, by among others partial dissolution or at times local spalling. This promotes a progressive increase of the halide discharge tension on the anodic surface, so that it is, after some time, more convenient to replace or to re-coat the anodes having a worn coating, in order to maintain optimum performance.

When the metal electrodes are taken out of service, they still retain an appreciable amount of the original coating, which often comprises noble metals, their oxides or other relatively inert materials rather difficult to remove by conventional chemical or electrochemical means. If it is desired to deposit new coatings on the surface of such supports and ensure their adherence, any trace of worn coating must disappear. But if the etching of a titanium or tantalum surface does not set any problem, it is not the case with metal electrodes taken out of service on account of the important chemical inertia of the support by anodic protection, resulting from the presence of noble metal, in a quantity ever so little.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a method for the complete and rapid removing of worn coating from the support surface of a metal electrode, without substantial damage to such support.

Another object is to provide the easy recovering of the removed coating in order to provide its re-utilization and exploitation.

A further object is to give the entire metal support its initial surface condition without subsequent treatment such as a conventional etching more or less harmful to the support metal.

It is also an object of this invention to allow the further deposit of a new very adherent coating with the same electrochemical characteristics as the first one under the cell conditions.

The present invention relates to a method for rapidly and completely removing worn coatings from electrodes including an electroconductive coating fixed on an electroconductive metal support, without substantially damaging the support, such electrodes being adapted to be used in electrochemical processes and both support and coating being resistant to electrochemical corrosion under the conditions ruling in an electrochemical cell. The coating promotes an electron-exchange between the support and ions of an electrolyte in contact with the electrode. The method includes the steps of immersing the worn electrodes in a molten salt bath which includes essentially at least one bisulphate or pyrosulphate of an alkali metal or of ammonium, at a temperature between 300° and 500°C, cooling the electrodes and water-rinsing the so-treated electrodes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

By "electroconductive metal support resistant to electrochemical corrosion in the conditions ruling in the cell," we generally mean a support at least superficially made of a film-forming metal such as titanium, tantalum, niobium, zirconium and tungsten or an alloy mainly constituted at least by one of such metals. This support may optionally contain a core of a more conductive metal or alloy, such as copper, aluminum, or alloys thereof.

The nature of the conductive coating, set on the support, is not critical for the method according to the invention, which allows to remove a large range of conductive coatings and particularly coatings containing, as active material promoting the electron exchange between the support and the electrolyte, at least one metal of the platinum group in metal form, in alloy and/or in combination, especially in oxide state. By "metal of the platinum group," we mean platinum, iridium, rhodium, osmium, ruthenium and palladium. Such coatings comprise for example, ruthenium and titanium dioxides, iridium-platinum alloys or stoichiometric compositions such as $2IrO_2—WO_3$. They are rapidly removed by the method of the invention which besides allows their easy recovering: a molten salt bath containing an adequate quantity of coating material is allowed to cool and an aqueous solution is then made thereform. The coating material, generally insoluble, is easily separated by a convenient technique, such as filtration or centrifugation and may, afterwards, be re-utilized as electrode coating or assigned to any different use.

The immersion duration in the molten salt bath, necessary to the complete removing of the conductive coating from its support, depends on the temperature and the composition of the bath, on the nature of the coating, its thickness and crystallinity. It is possible to operate in a wide range of temperatures lying between 300°C and 500°C. Even if a temperature lower than 300°C is sufficient to keep the bath in molten state, it is inconvenient to work below such temperature, if the maintenance of the required immersion term within reasonable limits is desired for removing all the coating. Likewise, it is preferred not to exceed substantially 550°C in order to avoid any ignition risk for the metal support, as well as to avoid an important reduction of the bath volume by evaporation after some hours of use. An immersion from 15 to 60 minutes allows to

treat any coating at temperatures compatible with the treatment.

At temperatures comprised between 400° and 500°C, the removing of the coating is generally carried out by keeping the pieces for 30 minutes in the bath.

As bath of molten salt, suitable for the process of the invention, any bisulphate or pyrosulphate of an alkali metal or ammonium, optionally a mixture of two or more of them, and optionally in mixture with a minor proportion of one or more salts of an alkali metal or ammonium, especially sulphate, sulphite, bisulphite, pyrosulphite, dithionite, thiosulphate, sulphide, sulfhydrate. By alkali metal, we mean lithium, sodium and potassium. Baths with low melting point such as lithium bisulphate $LiHSO_4$ (M.P. 120°C), ammonium bisulphate NH_4HSO_4 (M.P. 147°C), equimolar mixture $Na_2S_2O_7 + K_2S_2O_7$(M.P. 145°C), mixture $Na_2S_2O_7 + Na_2SO_4$ (10 moles/1 mole — M.P. 190°C), etc. can be used among others. Nevertheless, there is no direct relation between the melting point of the bath and the treatment temperature, and it is useful, in any case, to carry the bath of molten salt at a minimal temperature of about 400°C if a rapid and complete removing of the coating is desired.

The process according to the invention presents the appreciable advantage of leaving the metal support practically undamaged and ready to receive a new so adherent coating and with as favorable electrochemical properties as the former, after its emersion from a molten salt bath, cooling and water rinsing to dissolve the salt, and optionally a light etching in diluted oxalic acid. The following examples (1–4) are given by way of illustration of the results obtained carrying out the process according to the invention.

EXAMPLE 1

The molten salt bath consists of ammonium bisulphate NH_4HSO_4 (M.P. 147°C).

A titanium strip uncoated and two titanium strips coated respectively with $RuO_2 + TiO_2$ (10–12 g/m²) and with Pt + Ir (7.3g/m²), were immersed for a period of 30 minutes, in a bath kept at 400°C. Several coats of a liquid composition were painted on the titanium, each coating being followed by thermal treatment. The first coating consisted of a solution of $RuCl_3.3H_2O$ and $TiCl_4$ in isopropylic alcohol; the thermal treatments were carried out between 380° and 525°C. The second one consisted of a solution of $H_2PtCl_6.6H_2O$ and $H_2IrCl_6.xH_2O$ in isopropylic alcohol; the thermal treatments were carried out between 350° and 400°C.

After emersion from the molten salt bath, cooling, water rinsing and drying of the treated strips, the agressivity of the bath was measured with regard to titanium of the uncoated strip and to the coating of the two other strips. This agressivity is given by the penetration depth (microns) for titanium and by the elimination ratio (percent) of the initial coating for the two coated strips. The determination for the first of two strips was realized by spectrography and by fluorescence X, when only this last technique has been applied to the last strip where the elimination rates of Pt and Ir were separately determined. The results are set forth in Table 1. Under the conditions of this test, the molten bath of NH_4HSO_4 showed an unimportant agressivity with regard to Ti, whereas it removed the whole coating of $RuO_2 + TiO_2$ and an average of 90 percent of the Pt + Ir coating.

After treatment in the molten salt bath and water rinsing, the metal support presents an homogeneous and rough surface suitable for receiving a coating by painting. Four coats of a solution of $RuCl_3.3H_2O$ and $TiCl_4$ in isopropylic alcohol were applied onto the so treated titanium strips. After the fourth coating, the coated strips were heated between 380° and 525°C. The thus obtained coatings of $RuO_2 + TiO_2$ of approximately 10 grams per square meter, adhered tightly to the underlying support and passed successfully the test consisting of attempting to tear off such coating with an adhesive tape applied under pressure.

Used as anodes in a cell with mercury-cathode for the electrolysis of a brine saturated with sodium chloride and chlorine at 80°C, under an anode-cathode potential difference kept constant, the tested strips present excellent electrochemical characteristics such as shown in Table 2.

EXAMPLE 2

The molten salt bath consists of potassium pyrosulphate $K_2S_2O_7$ (M.P. higher than 300°C).

The three strips of Example 1, a W strip uncoated and a Ti strip with a coating of $2IrO_2—WO_3$ of 4.6 g/m² obtained by painting several coats of a solution of WCl_6 and H_2IrCl_6 in dimethylformamide and last thermal treatment during 5 hours at 475°C, were immersed in such bath kept at 425°C.

After emersion from the molten salt bath, cooling, water rinsing and drying of the 5 treated strips, the agressivity of the bath was measured with regard to titanium and W on the two uncoated strips and to the coating of the three other strips. This agressivity is given (see Table 1) by the penetration depth (microns) for titanium and W, and by the elimination ratio (percent) of the intial coating for the three coated strips. The elimination ratio of W and Ir were determined separately (by fluorescence X) for the last strip.

The molten bath of $K_2S_2O_7$ is practically inactive with regard to Ti and its agressivity with regard to W is unimportant. Moreover, it removes the whole coating of $RuO_2 + TiO_2$, more than 70 percent (average) of the coating of Pt + Ir and some 92 percent of noble metal included in the coating $2IrO_2—WO_3$.

After treatment in the molten salt bath and water rinsing, the metal support presents an homogeneous and rough surface suitable for receiving a coating by painting. Four coats of the solution of $RuCl_3 + TiCl_4$ were painted, in the same manner as in Example 1, on the Ti strips so obtained in order to achieve, after a thermal treatment, coatings of $RuO_2 + TiO_2$ of approximately 10 g/m². The thus obtained coatings showed a very good adhesion during the tearing off test.

Used as anodes, under the same conditions as in Example 1, the so treated and coated strips of Ti also present excellent electrochemical characteristics, as shown in Table 2.

EXAMPLE 3

The molten salt bath consists of sodium pyrosulphate $Na_2S_2O_7$ (M.P. 401°C).

The four Ti strips of Example 2 were immersed for 30 minutes in this bath kept at 450°C. After emersion from the bath of molten salt, cooling, water rinsing and drying, the agressivity of the bath was determined with regard to Ti, on the uncoated strip and to the coating on the three other strips. This agressivity is given (see

Table 1) by the depth of penetration (microns) for Ti and the elimination ratio (in percent) of initial coating on the three coated strips, as in the preceding example. While its agressivity is unimportant with regard to Ti, the molten bath of $Na_2S_2O_7$ removes all the coating of $RuO_2 + TiO_2$, 89 percent (average) of the coating Pt + Ir and near to 89 percent of noble metal contained in the coating $2IrO_2—WO_3$.

After treatment in the bath of molten salt and water, rinsing the metal support presented a homogeneous and rough surface, which promotes the coating by painting. Four coats of the solution $RuCl_3 + TiCl_4$ were applied as in Example 1, on Ti strips so treated, in order to obtain, after a thermal treatment, coatings of $RuO_2 + TiO_2$ of approximatively 10 g/m². The thus obtained coatings showed a very good adhesion during the tearing off test.

Used as anodes under the same conditions as in Example 1, the so treated and coated strips of Ti also present excellent electrochemical characteristics as shown in Table 2.

EXAMPLE 4

The bath of molten salt consists of potassium bisulphate $KHSO_4$ (M.P. 210°C).

The three Ti strips of Example 1 were immersed for 30 minutes in that bath kept at 550°C. After emersion from the bath of molten salt, cooling, water-rinsing and drying of said strips, the agressivity of bath was determined with regard to Ti on the uncoated strip and with regard to coating on the two other strips. That agressivity is given (see Table 1) by the depth of penetration (microns) for Ti and by the elimination ratio (percent) of initial coating on the two coated strips as in Example 1.

Although higher than those for the baths of preceding examples, the agressivity of the molten salt of $KHSO_4$ with regard to Ti remains in allowable limits, while permitting the complete elimination of the coating of $RuO_2 + TiO_2$ and the elimination of 90 percent (average) of coating Pt + Ir.

After treatment in the bath of molten salt and water rinsing, the metal support presents a homogeneous and rough support promoting the depositing of a coating by painting. Four coats of the solution of $RuCl_3 + TiCl_4$ were applied on the Ti strips so treated, as indicated in Example 1, in order to obtain, after thermal treatment, coats of $RuO_2 + TiO_2$ of approximatively 10 g/m². The thus obtained coatings showed a very good adhesion during the tearing off test.

Used as anodes, under the same conditions as in Example 1, the so treated and coated Ti strips also present excellent electrochemical characteristics as shown in Table 2.

COMPARATIVE EXAMPLE

By way of comparison, a Ti strip coated by 10–12 g/m² of $RuO_2 + TiO_2$ according to the technique of Example 1, was subjected to etching, under similar conditions, by immersion, for 30 minutes, in a molten bath kept at 450°C and consisting of a mixture of ⅓ KOH + ⅔ KNO_3 (parts by weight). As shown in Table 1 hereinafter, the elimination rate is comprised between 59 and 71 percent of the initial coating, following the determination technique, this being clearly below the 99–100 percent elimination obtained for this type of coating, under the same conditions, with regard to the baths of molten salts constituting the object of the present invention.

Table 1

Agressivity of molten salt baths with regard to the support and the coating

Example No.			1	2	3	4	comparative example
Nature of the bath			NH_4HSO_4	$K_2S_2O_7$	$Na_2S_2O_7$	$KHSO_4$	⅓ KOH + ⅔ KNO_3
Melting point			147° C	> 300° C	401° C	210° C	235° C
Immersion duration			30 min	30 min	30 min	30 min	30 min
Bath temperature			400° C	425° C	450° C	500° C	450° C
Attack of Ti (in μ)			7.2	2.3	7.2	69.1	—
Attack of W (in μ)			—	6.2	—	—	—
$RuO_2 + TiO_2$ removed (spectro)			99.86 %	99.41 %	99.83 %	98.60 %	71 %
Id.	(by fluorescence X)		100 %	100 %	100 %	100 %	59 %
Pt + Ir removed	(do.)	Pt	94 %	75 %	94 %	94 %	—
		Ir	84 %	67 %	84 %	85 %	—
$2IrO_2–WO_3$ removed	(do.)	Ir	—	91.6 %	88.9 %	—	—
		W	—	100 %	100 %	—	—

Table 2

Anodic behaviour, in a mercury-cathode cell, of Ti strips, which coating was removed by immersion in a bath of molten salt (see Table 1) and a new coating of $RuO_2 + TiO_2$ thereon

Example No.	1	2	3	4
Nature of the etching bath used	NH_4HSO_4	$K_2S_2O_7$	$Na_2S_2O_7$	$KHSO_4$
Thickness of the new coating (g/m²)	10.87	9.73	10.87	10.27
Initial anodic current density (kA/m²)	37	41	39	37
Idem - After 21 days (kA/m²)	34	37	34	35
Idem - After 157 days (kA/m²)	22	22	22	26
Quantity of chlorine produced after 157 days (metric tons by m² of active anodic surface)	127	137	127	138

After 157 days of continuous service, the utilization limit was not yet reached and the test continued.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptions, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

We claim:

1. A method for rapidly and completely removing, without substantially damaging the support, worn coatings from electrodes which include an electroconductive coating fixed on an electroconductive metal support, said electrodes being adapted to be used in electrochemical processes and both support and coating being resistant to the electrochemical corrosion under the conditions ruling in an electrochemical cell, said coating promoting an electron exchange between the support and ions of an electrolyte in contact with the electrode, said method comprising the steps of immersing the worn electrodes in a molten salt bath which consists essentially of at least one bisulphate or pyrosulphate of an alkali metal or ammonium, at a temperature between 300° and 500°C, cooling said electrodes, and water-rinsing the so-treated electrodes.

2. A method according to claim **1,** wherein said bath of molten salt comprises substantially ammonium bisulphate as active substance.

3. A method according to claim **1,** wherein said bath of molten salt is substantially constituted by potassium bisulphate.

4. A method according to claim **1,** wherein said bath of molten salt is substantially constituted by potassium pyrosulphate.

5. A method according to claim **1,** wherein said bath of molten salt is substantially constituted by sodium pyrosulphate.

6. A method according to claim **1,** wherein said bath of molten salt is substantially constituted by an equimolar mixture of potassium and sodium pyrosulphates.

7. A method according to claim **1,** wherein the duration of immersion in the bath of molten salt is from 15 to 60 minutes.

8. A method according to claim **1,** wherein said bath of molten salt contains further at least one sulphate of an alkali metal or ammonium.

9. A method according to claim **1,** wherein the duration of immersion is 30 minutes and the temperature of the molten salt bath is comprised between 400° and 500°C.

10. A method according to claim **1,** wherein at least an outer layer of the electroconductive support is made of a film-forming metal.

11. A method as claimed in claim **10,** wherein said film-forming metal is titanium, tantalum, niobium, zirconium, or tungsten or an alloy mainly constituted by at least one of said metals.

12. A method according to claim **1,** wherein said conductive coating contains at least one metal of the platinum group, and/or an alloy, and/or a compound of at least one metal of this group.

13. A process for recoating a worn electrode, which electrode includes an electroconductive coating fixed on an electroconductive metal support having at least its outer layer made of a film-forming metal or a film-forming metal alloy, said electrode being adapted to be used in electrochemical processes and both support and coating being resistant to the electrochemical corrosion under the conditions ruling in an electrochemical cell, said coating promoting an electron exchange between the support and ions of an electrolyte in contact with the electrode, said method comprising

1. rapidly and completely removing, without substantially damaging the support, the coating on the support by
   a. immersing the worn electrode in a molten salt bath which consists essentially of at least one bisulphate or pyrosulphate of an alkali metal or ammonium, at a temperature between 300° and 500°C,
   b. cooling said electrode, and
   c. water rinsing the so-treated electrode; and
2. then depositing an electroconductive coating on the electroconductive support.

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