

CATHODE FOR ELECTROLYTIC EVOLUTION OF HYDROGEN

FIELD OF THE INVENTION

- 5 The invention relates to an electrode, with particular reference to a metal electrode for use as a cathode for evolution of hydrogen in industrial electrolytic processes and a method for its production.

BACKGROUND OF THE INVENTION

- 10 The electrolysis of alkali brines for the simultaneous production of chlorine and alkali and the electrochemical processes of hypochlorite and chlorate generation are the most typical examples of industrial electrolytic applications with cathodic evolution of hydrogen, but the electrode is not limited to any particular use. In the industry of the
- 15 electrolytic processes, competitiveness is associated to several factors, the main of which being the reduction of energy consumption, directly linked to process voltage; this justifies the many efforts to reduce the various components of the latter, among which cathodic overvoltage must be included. Cathodic overvoltages naturally obtainable by means of electrodes made of chemically resistant material (for example carbon steel)
- 20 with no catalytic activity have been considered acceptable for a long time. In the specific case, the market nevertheless requires increasing concentrations of caustic product, which made the use of carbon steel cathodes unfeasible due to corrosion problems; in addition, the increase in the cost of energy has made advisable to use catalysts for facilitating the cathodic evolution of hydrogen. One possible solution is to use nickel
- 25 substrates, chemically more resistant than carbon steel, and platinum-based catalytic coatings. Cathodes of this type are normally characterised by an acceptable cathodic overvoltage, presenting however limited useful lifetimes, probably due to poor adhesion of the coating to the substrate. A partial improvement in the adherence of the catalytic coating to the nickel substrate is obtainable by the addition of rare earths to the
- 30 formulation of the catalytic layer, optionally as a porous external layer that performs a protective function against the underlying platinum-based catalytic layer; this type of cathode is sufficiently durable under normal operating conditions, being liable however

to suffer serious damages following the occasional current reversals inevitably produced in case of malfunctioning of industrial plants.

A partial improvement in the resistance to current reversals is obtainable by activating the nickel cathode substrate with a coating consisting of two distinct phases, a first platinum-based catalytic phase added with rhodium and a second phase comprising palladium having a protective function. This type of formulation, however, requires high loads of platinum and rhodium in the catalytic phase, such as to determine a rather high production cost.

A less expensive catalytic coating which presents high activity combined with some resistance to current reversals is obtained from mixtures of ruthenium and rare earths, for example praseodymium; the resistance of electrodes obtained according to such a formulation can be increased by interposing a platinum-based thin layer between the cathode substrate and the catalytic coating.

The above formulations made possible to obtain electrodes capable of functioning for sufficient times in correctly operated industrial electrolyzers provided, according to a common practice in the industry, with polarisation devices actuated in case of scheduled or sudden plant shut-downs by imposing a small residual voltage which serves to protect the cell components from corrosion. With these devices, current reversals can only occur during the short period of time that elapses between the shut-down of the electrical load and the onset of the residual voltage, during which the cathodes should not undergo any appreciable damage. However, the most recent advancements in the design of industrial electrolyzers, in particular of electrolyzers for the production of chlorine and alkali from alkali brines consisting of electrolytic cells with the anodic and cathodic compartments separated by ion-exchange membranes, provide the use of materials and construction techniques which make possible to dispense with the polarisation devices, whose installation and management accounts for an important additional cost. The plant shut-down in an electrolyser free of polarising device entails, at least in an initial phase, cell voltage reversal phenomena caused by the presence of reaction product residues in the two compartments: in these conditions, the electrolysis cell can work for a short period as a battery, with the relevant cathodes being subject to

the passage of anodic current. This entails the need of providing cathodes with a much higher tolerance to current reversals, compared to the best prior art formulations.

SUMMARY OF THE INVENTION

5

Various aspects of the invention are set out in the accompanying claims.

Under one aspect, the invention relates to an electrode suitable for use as a cathode in electrolytic processes comprising a substrate made of metal, for example nickel,
10 provided with a catalytic coating formed by at least three distinct layers: an internal layer, in direct contact with the substrate, containing platinum, at least one intermediate layer consisting of a mixture of oxides containing 40-60% by weight of rhodium referred to the elements and an external ruthenium oxide-based layer.

15 Platinum in the internal layer is present predominantly in metallic form, especially in operating conditions under cathodic hydrogen evolution, however, is not excluded, especially prior to the first use, that platinum or a fraction thereof may be present in form of oxide.

20 In one embodiment, the internal layer consists of a layer of platinum alone.

In one embodiment, the external layer consists of a layer of ruthenium oxide alone. In the present context, the term ruthenium oxide indicates that such element is present, after the preparation of the electrode, mainly in oxide form; it is not excluded, especially
25 in operating conditions under cathodic hydrogen evolution, that such oxide can be partially reduced to ruthenium metal.

In one embodiment, the mixture of oxides of the intermediate layer further contains, besides rhodium, 10-30% by weight palladium and 20-40% by weight of rare earths; in
30 one embodiment, the rare earth content consists entirely of praseodymium. In the present context, the term mixture of oxides indicates that the elements of the relative formulation are present, after the preparation of the electrode, mainly in form of oxides; is not excluded, especially in operating conditions under cathodic hydrogen evolution,

that a fraction of such oxides can be reduced to metal or even form hydrides, as in the case of palladium.

The inventors have surprisingly observed that formulations of this type impart a resistance to current reversals several times higher than the closest prior art formulations at substantially reduced specific loading of noble metal.

In one embodiment, the specific loading of platinum in the internal layer is between 0.3 and 1.5 g/m², the sum of the specific loading of rhodium, palladium and rare earths in the intermediate layer is between 1 and 3 g/m² and the specific loading of ruthenium in the external layer is between 2 and 5 g/m². The inventors have in fact observed that, in the case of the above formulations, so reduced noble metal loadings are more than sufficient to impart a high catalytic activity combined with a resistance to current reversals unprecedented in the prior art.

Under another aspect, the invention relates to a method for the preparation of an electrode which comprises the application in one or more coats of an acetic solution of Pt(NH₃)₂(NO₃)₂ (platinum diamino dinitrate) to a metallic substrate, with subsequent drying at 80-100°C, thermal decomposition at 450-600°C and optional repetition of the cycle until the desired loading is achieved (e.g., 0.3-1.5 g/m² of Pt as metal); the application in one or more coats of an acetic solution containing a rhodium nitrate and optionally nitrates of palladium and rare earths to the internal catalytic layer thus obtained, with subsequent drying at 80-100° C, thermal decomposition at 450-600° C and optional repetition of the cycle until the desired loading is achieved (e.g., 1-3 g/m² as the sum of Rh, Pd and rare earths); the application in one or more coats of an acetic solution of Ru nitrosyl nitrate to the intermediate catalytic layer thus obtained, with subsequent drying at 80-100°C, thermal decomposition at 450-600°C and optional repetition of the cycle until the desired loading is achieved (for example, 2-5 g/m² of Ru as metal).

As it is well known, Ru nitrosyl nitrate designates a commercially available compound expressed by the formula Ru(NO)(NO₃)₃, sometimes written as Ru(NO)(NO₃)_x to

indicate that the average oxidation state of ruthenium can slightly deviate from the value of 3.

5 The above application of the solutions may be carried out by brushing, spraying, dipping, or other known technique.

10 The inventors have observed that the use of the specified precursors in the adopted preparation conditions favours the formation of catalysts with a particularly ordered crystal lattice, with a positive impact in terms of activity, durability and resistance to current reversals.

The best results were obtained by adjusting the thermal decomposition temperature of the various solutions in the range between 480 and 520° C.

15 The following examples are included to demonstrate particular embodiments of the invention, whose practicability has been largely verified in the claimed range of values. It should be appreciated by those of skill in the art that the compositions and techniques disclosed in the examples which follow represent compositions and techniques discovered by the inventors to function well in the practice of the invention; however,
20 those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

EXAMPLE

25

An amount of Pt diamino dinitrate, $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$ corresponding to 40 g of Pt was dissolved in 160 ml of glacial acetic acid. The solution was stirred for 3 hours while maintaining the temperature at 50° C, and then brought to the volume of one litre with 10% by weight acetic acid (platinum solution).

30

An amount of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ corresponding to 200 g of Ru was dissolved in 600 ml of glacial acetic acid with addition of a few ml of concentrated nitric acid. The solution was

stirred for three hours while maintaining the temperature at 50° C. The solution was then brought to a volume of 1 l with 10% by weight acetic acid (ruthenium solution).

Separately, amounts of $\text{Rh}(\text{NO}_3)_3$, $\text{Pd}(\text{NO}_3)_2$ and $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ corresponding to 4.25 g of Rh, 1.7 g of Pd and 25.5 g of Pr expressed as metals were mixed under stirring (rhodium solution).

A mesh of nickel 200 of 100 mm x 100 mm x 0.89 mm size was subjected to a process of blasting with corundum, etching in 20% HCl at 85°C for 2 minutes and thermal annealing at 500°C for 1 hour.

The platinum solution was applied by brushing in a single cycle, carrying out a drying treatment for 10 minutes at 80-90°C and a thermal decomposition for 10 minutes at 500°C, obtaining a specific loading of 0.8 g/m² of Pt.

The rhodium solution was then applied by brushing in three coats carrying out a drying treatment for 10 minutes at 80-90°C and a thermal decomposition for 10 minutes at 500°C after each coat, obtaining a specific loading of 1.4 g/m² of Rh, 0.6 g/m² of Pd and 0.84 g/m² of Pr.

The ruthenium solution was then applied by brushing in four coats carrying out a drying treatment for 10 minutes at 80-90°C and a thermal decomposition for 10 minutes at 500°C after each coat, obtaining a specific loading of 3 g/m² of Ru.

The sample was subjected to a performance test, showing an ohmic drop-corrected initial cathodic potential of -930 mV/NHE at 3 kA/m² under hydrogen evolution in 33% NaOH, at a temperature of 90°C.

The same sample was then subjected to cyclic voltammetry in the range from -1 to +0.5 V/NHE at a 10 mV/s scan rate; after 25 cycles, the cathodic potential was -935 mV / NHE, which indicates a resistance current reversal perfectly suitable for operation in industrial electrolyzers free of polarisation devices.

COUNTEREXAMPLE

An amount of Pt diamino dinitrate, $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$ corresponding to 40 g of Pt was dissolved in 160 ml of glacial acetic acid. The solution was stirred for 3 hours while
5 maintaining the temperature at 50° C, and then brought to the volume of one litre with 10% by weight acetic acid (platinum solution).

An amount of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ corresponding to 200 g of Ru was dissolved in 600 ml of glacial acetic acid with addition of a few ml of concentrated nitric acid. The solution was
10 stirred for three hours while maintaining the temperature at 50° C. The solution was then brought to a volume of 1 l with 10% by weight acetic acid (ruthenium solution).

Separately, an amount of $\text{Pr}(\text{NO}_3)_3$ corresponding to 200 g of Pr was dissolved in 600 ml of glacial acetic acid with addition of a few ml of concentrated nitric acid. The solution
15 was stirred for three hours while maintaining the temperature at 50°C. The solution was then brought to a volume of 1 l with 10% by weight acetic acid (rare earth solution). 480 ml of ruthenium solution were blended with 120 ml of rare earth solution and left under stirring for five minutes. The solution thus obtained was brought to 1 litre with 10% by weight acetic acid (ruthenium and praseodymium solution).

20 A mesh of nickel 200 of 100 mm x 100 mm x 0.89 mm size was subjected to a process of blasting with corundum, etching in 20% HCl at 85°C for 2 minutes and thermal annealing at 500°C for 1 hour.

25 The platinum solution was applied by brushing in a single cycle, carrying out a drying treatment for 10 minutes at 80-90°C and a thermal decomposition for 10 minutes at 500°C, obtaining a specific loading of 1 g/m² of Pt.

30 The ruthenium and praseodymium solution was then applied by brushing in 4 successive coats, carrying out a drying treatment for 10 minutes at 80-90°C and a thermal decomposition for 10 minutes at 500°C after each coat, until obtaining the deposition of 4 g/m² of Ru and 1 g/m² Pr

The sample was subjected to a performance test, showing an ohmic drop-corrected initial cathodic potential of -930 mV/NHE at 3 kA/m² under hydrogen evolution in 33% NaOH, at a temperature of 90°C.

- 5 The same sample was then subjected to cyclic voltammetry in the range from -1 to +0.5 V/NHE at a 10 mV/s scan rate; after 25 cycles, the cathodic potential was -975 mV / NHE, which indicates a resistance current reversal suitable for operation in industrial electrolyzers only if equipped with polarisation devices.
- 10 The previous description shall not be intended as limiting the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

- Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to
15 exclude the presence of other elements, components or additional process steps.

- The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present
20 invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention before the priority date of each claim of this application.

CLAIMS

1. Electrode suitable for use as cathode in electrolytic processes comprising a metal substrate equipped with a catalytic coating, said catalytic coating comprising a platinum-containing internal layer directly contacting the substrate, at least one
5 intermediate layer consisting of an oxide mixture containing 40-60% by weight of rhodium referred to the elements, an external layer of ruthenium oxide.
2. The electrode according to claim 1 wherein said metal substrate is made of nickel.
3. The electrode according to claim 1 or 2 wherein said at least one intermediate layer contains 10-30% by weight of palladium and 20-40% by weight of rare earths referred to the elements.
4. The electrode according to claim 3 wherein said rare earths consist of
15 praseodymium.
5. The electrode according to claim 3 or 4 wherein the specific loading of platinum in said internal layer is 0.3 to 1.5 g/m², the sum of specific loadings of rhodium,
20 palladium and rare earths in said intermediate layer is 1 to 3 g/m² and the specific loading of ruthenium in said external layer is 2 to 5 g/m².
6. Method for manufacturing an electrode according to one of the preceding claims comprising the following steps:
 - 25 a) application of an acetic solution of $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$ to a metal substrate, with subsequent drying at 80-100°C and thermal decomposition at 450-600°C;
 - b) optional repetition of step a) until obtaining an internal catalytic layer with a specific loading of 0.3-1.5 g/m² of Pt;
 - 30 c) application of an acetic solution containing a rhodium nitrate with optional addition of nitrates of palladium and of rare earths on said internal catalytic layer, with subsequent drying at 80-100°C and thermal decomposition at 450-600°C;

- d) optional repetition of step c) until obtaining an intermediate catalytic layer with a specific loading of 1-3 g/m² as sum of Rh, Pd and rare earths;
- e) application of an acetic solution containing Ru nitrosyl nitrate on said intermediate catalytic layer, with subsequent drying at 80-100°C and thermal decomposition at 450-600°C;
- f) optional repetition of step e) until obtaining an external catalytic layer with a specific loading of 2-5 g/m² of Ru.

7. The method according to claim 6 wherein the temperature of said thermal decomposition of steps a), c) and e) ranges from 480 to 520°C.

8. Electrolysis cell comprising an anodic compartment and a cathodic compartment separated by an ion-exchange membrane wherein the cathodic compartment is equipped with an electrode according to any one of claims 1 to 5.

9. Electrolyser for production of chlorine and alkali from alkali brine free of protecting polarisation devices comprising a modular arrangement of cells according to claim 8.