ELECTRODE FOR ELECTROLYTIC CELL

FIELD OF THE INVENTION

The invention relates to an electrode suitable for operating as anode in electrolysis cells, for instance as chlorine-evolving anode in chlor-alkali cells.

BACKGROUND OF THE INVENTION

The use of metal electrodes equipped with catalytic coatings in electrolytic applications is known in the art: electrodes consisting of a metal substrate equipped with a coating based on noble metals or oxides thereof are for instance utilised as cathodes for hydrogen evolution in water or alkali chloride electrolysis processes, as anodes for oxygen evolution in electrometallurgical processes of various kinds or for chlorine evolution in alkali chloride electrolysis. Electrodes of such kind can be produced via thermal route, i.e. by suitable thermal decomposition of solutions containing the precursors of metals to be deposited; by galvanic electrodeposition from suitable electrolytic baths; by direct metallisation via flame or plasma spraying processes or chemical or physical phase vapour deposition.

The electrolysis of sodium chloride brine directed to the production of chlorine and caustic soda, for instance, is often carried out with anodes consisting of a titanium or other valve metal substrate activated with a superficial layer or ruthenium dioxide (RuO_2) in order to lower the overvoltage of the anodic chorine evolution reaction. For this type of electrolysis, catalyst formulations based on mixtures of oxides of ruthenium, iridium and titanium are also known, all capable of lowering the overvoltage of the anodic chorine evolution reaction.

Electrodes of such kind are generally produced via thermal route.

Catalytic formulations can be deposited on the substrate by phase vapour deposition techniques, having the advantage of allowing an extremely accurate control of coating deposition parameters. However, these are fundamentally characterised by being

batch-type processes, requiring the loading of the substrate in a suitable deposition chamber, which has to undergo a slow depressurisation process, lasting several hours, in order to be able to treat a single piece. Besides the remarkable duration of the process (several hours being usually necessary, depending on the required noble metal loading), the application of high amounts of catalytic coatings leads to coatings having a very limited lifetime.

SUMMARY OF THE INVENTION

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

Under a first aspect, the present invention relates to an electrode for evolution of gaseous products in electrolysis cells consisting of a valve metal substrate coated with at least one first catalytic composition and with an outer catalytic composition, said at least one first catalytic composition comprising a mixture of oxides of a valve metal or of tin and of noble metals selected from the group of platinum metals (PM) or oxides thereof taken alone or in admixture, said at least one first catalytic composition obtained by thermal decomposition of precursors, said outer catalytic composition comprising noble metals selected from the group of platinum metals or oxides thereof taken alone or in admixture, said outer catalytic composition being deposited by means of a chemical or physical phase vapour deposition technique, the amount of noble metal on said first catalytic composition being higher than 5 g/m² of surface and the amount of noble metal in said outer catalytic composition ranging between 0.1 and 3.0 g/m² of surface.

The inventors have surprisingly found out that the deposition of one last catalytic layer, with the specified characteristics, through chemical or physical phase vapour allows obtaining an electrode with unexpected features both in terms of duration and of potential decrease.

In one embodiment, the first catalytic composition of the electrode according to the invention comprises titanium, iridium, ruthenium in form of metals or oxides.

In one embodiment, the outer catalytic composition comprises ruthenium and/or iridium in form of metals or oxides.

In one embodiment, the specific noble metal loading in the first catalytic composition ranges between 6 and 8 g/m² and the specific metal loading in the outer catalytic composition ranges between 1.5 and 2.5 g/m².

Under another aspect, the invention relates to a method of manufacturing an electrode comprising the deposition of an outer catalytic composition by chemical or physical phase vapour deposition, preferably by reactive sputtering of noble metals selected in the group of platinum metals.
Under a further aspect the invention relates to the reactivation of a used electrode comprising the chemical or physical phase vapour deposition of an outer catalytic composition including noble metals selected from the group of platinum metals or oxides thereof taken alone or in admixture.

Under a further aspect, the invention relates to an electrolysis cell of alkali chloride solutions, for instance a sodium chloride brine electrolysis cell directed to producing chlorine and caustic soda, which effects the anodic evolution of chlorine on an electrode as hereinbefore described.

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, 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.

COUNTEREXAMPLE 1

A sample of titanium mesh of 10 cm x 10 cm size was blasted with corundum, cleaning the residues with a jet of compressed air. The sample was then degreased using acetone in a ultrasonic bath for about 10 minutes. After drying, the sample was dipped into an aqueous solution containing 250 g/l of NaOH and 50 g/l of KNO_3 at about 100°C for 1 hour. After the alkaline treatment, the sample was rinsed in deionised water at 60°C for three times, changing the liquid every time. The last rinse was carried out adding a small quantity of HCl (about 1 ml per litre of solution). An air drying was effected, observing the formation of a brown hue due to the growth of a thin film of TiO_x. 100 ml of a hydroalcoholic solution containing $RuCl_3*3H_2O$, $H_2IrCl_6*6H_2O$, $TiCl_3$ in a mixture of water and 2-propanol acidified with HCl were then prepared, having a molar composition of 36% Ru, 20% Ir, 44% Ti referred to the metals.

The solution was applied to the sample of titanium mesh by brushing in five coats; after each coat, a drying at 100-110°C for about 10 minutes was carried out, followed by a thermal treatment of 15 minutes at 450°C. The sample was cooled in air each time prior to applying the subsequent coat.

At the end of the whole procedure, a total noble metal loading of 9 g/m², expressed as the sum of Ru and Ir referred to the metals, was obtained.

The thus obtained electrode was identified as sample No. 1.

COUNTEREXAMPLE 2

A sample of titanium mesh of 10 cm x 10 cm size was blasted with corundum, cleaning the residues with a jet of compressed air. The sample was then degreased using acetone in a ultrasonic bath for about 10 minutes. After drying, the sample was dipped into an aqueous solution containing 250 g/l of NaOH and 50 g/l of KNO_3 at about 100°C for 1 hour. After the alkaline treatment, the sample was rinsed in deionised water at 60°C for three times, changing the liquid every time. The last rinse was carried out

adding a small quantity of HCl (about 1 ml per litre of solution). An air drying was effected, observing the formation of a brown hue due to the growth of a thin film of TiO_x.

The mesh sample was then introduced into the vacuum chamber of the reactive sputtering equipment.

Upon establishing a dynamic vacuum of about 50 E-4 mbar feeding an oxygen mixture with 20% argon, the sputtering targets were polarised at the following powers: ruthenium 35 W, iridium 24 W, titanium 250 W. The target-electrode substrate gap was about 10 centimetres.

The process of deposition was carried out, at the same conditions, alternatively on the two sides of the titanium mesh for an overall duration of 220 minutes. The thus obtained electrode presented a catalytic coating of about 1 micron and a total noble metal loading of about 9 g/m², expressed as the sum of Ru and Ir referred to the metals.

The thus obtained electrode was identified as sample No. 2.

EXAMPLE 1

A sample of titanium mesh of 10 cm x 10 cm size was blasted with corundum, cleaning the residues with a jet of compressed air. The sample was then degreased using acetone in a ultrasonic bath for about 10 minutes. After drying, the sample was dipped into an aqueous solution containing 250 g/l of NaOH and 50 g/l of KNO_3 at about 100°C for 1 hour. After the alkaline treatment, the sample was rinsed in deionised water at 60°C for three times, changing the liquid every time. The last rinse was carried out adding a small quantity of HCl (about 1 ml per litre of solution). An air drying was effected, observing the formation of a brown hue due to the growth of a thin film of TiO_x.

100 ml of a hydroalcoholic solution containing $RuCl_3*3H_2O$, $H_2IrCl_6*6H_2O$, $TiCl_3$ in a mixture of water and 2-propanol acidified with HCl were then prepared, having a molar composition of 36% Ru, 20% Ir, 44% Ti referred to the metals.

The solution was applied to the sample of titanium mesh by brushing in five coats; after each coat, a drying at 100-110°C for about 10 minutes was carried out, followed by a thermal treatment of 15 minutes at 450°C. The sample was cooled in air each time prior to applying the subsequent coat.

At the end of the whole procedure, a total noble metal loading of 7 g/m², expressed as the sum of Ru and Ir referred to the metals, was obtained.
The semi-finished electrode was then introduced into the vacuum chamber of the reactive sputtering equipment.

Upon establishing a dynamic vacuum of about 100 E-4 mbar feeding an oxygen mixture with 20% argon, the sputtering targets were polarised at the following powers: ruthenium 30 W, iridium 35 W. The target-electrode substrate gap was about 10 centimetres. To confer optimal properties to the resulting coating, the substrate was also subjected to a residual polarisation of about 150 V.

The process of deposition was carried out, at the same conditions, alternatively on the two sides of the electrode for an overall duration of 40 minutes. The thus obtained electrode had an outer catalytic coating about 0.1 µm thick and a total noble metal loading of about 9 g/m², expressed as the sum of Ru and Ir referred to the metals.

The thus obtained electrode was identified as sample No. 3.

The samples of the previous examples were characterised as anodes for chlorine evolution in a lab cell fed with a sodium chloride brine at a concentration of 200 g/l, strictly controlling the pH at 3. Table 1 reports chlorine overvoltage measured at a current density of 4 kA/m² and the volume percentage of oxygen in product chlorine.

TABLE 1

Sample No.	ηCl_2 (mV)
1	73
2	63
3	44

The samples of the previous examples were also subjected to a duration test. Said duration test is the simulation in a separated cell of industrial electrolysis conditions as regards electrolyte concentration and temperature, but at a current density conveniently increased up to a value 2-3 times higher than the nominal one for the sake of accelerating the experimental response. Table 2 reports the precious metal lost per unit current.

TABLE 2

Sample No.	Loss of precious metal per unit current (mg_{PM}/kAh)
1	0.016
2	0.5
3	0.005

The previous description is not intended to limit the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is univocally 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 exclude the presence of other elements or additives.

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 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 for evolution of gaseous products in electrochemical cells consisting of a valve metal substrate coated with at least one first catalytic composition and an outer catalytic composition, said at least one first catalytic composition comprising a mixture of a valve metal or tin or an oxide thereof and noble metals chosen in the platinum group metals or oxides thereof taken alone or in admixture, said at least one first catalytic composition obtained by thermal decomposition of precursors, said outer catalytic composition deposited by a chemical or physical vapor deposition technique, the amount of noble metal in said at least one first catalytic composition being above 5 g/m² and the amount of noble metal in said outer catalytic composition ranging between 0.1 and 3.0 g/m².

2. The electrode according to claim 1, wherein said mixture of said at least one first catalytic composition comprises titanium, iridium and ruthenium.

3. The electrode according to claim 1, wherein said outer catalytic composition comprises ruthenium and/or iridium.

4. The electrode according to any one of claims 1 to 3, wherein the specific noble metal loading of said at least one first catalytic composition is 6 to 8 g/m² and the specific noble metal loading of said outer catalytic composition is 1.5 to 2.5 g/m².

5. Method for manufacturing an electrode according to any one of claims 1 to 4 comprising the deposition of said outer catalytic composition by a chemical or physical vapor deposition technique.

6. Method for manufacturing an electrode according to any one of claims 1 to 4 comprising the deposition of said outer catalytic composition as a mixture of oxides by reactive sputtering of noble metals selected from the group of platinum metals.

7. Method for the reactivation of an exhausted electrode consisting of a metal substrate and an exhausted catalytic coating, comprising the deposition of an outer catalytic composition as a mixture of oxides by reactive sputtering of iridium and ruthenium onto said exhausted catalytic coating.

8. Method for the reactivation of an exhausted electrode according to claim 7 comprising the deposition by a chemical or physical vapor deposition technique of an outer catalytic composition comprising noble metals selected from the group of platinum metals or oxides thereof taken alone or in admixture.

9. Electrolysis cell comprising a cathodic compartment containing a cathode and an anodic compartment containing an anode separated by a membrane or diaphragm, said anodic compartment being fed with an alkali chloride brine, wherein said anode of said anodic compartment is an electrode according to any one of claims 1 to 4.