

ELECTRODE FOR THE ELECTROPLATING OR ELECTRODEPOSITION OF A METAL

FIELD OF THE INVENTION

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The invention relates to the field of electrodes for the electroplating or electrodeposition of a metal comprising at least one topcoating layer and at least one electrochemically active coating layer and to the method for producing the same.

10 BACKGROUND OF THE INVENTION

In electroplating and, more generally, in electrodeposition processes, a thin metal coating is formed starting from cations of the metal dissolved in an electrolytic bath and deposited over a designated cathodic surface via an electrolytic reaction. The reaction
15 is carried out within an electrolytic cell containing at least an anode-cathode pair immersed in the electrolytic bath. The cells are often equipped with dimensionally stable anodes, such as activated titanium anodes, and the electrolyte typically contains a certain amount of added organic elements. These additives, which usually comprise brighteners, levelers, surfactants and suppressors, are used for example to promote a
20 uniform deposition of the metal and to control its physical-mechanical properties, such as its tensile strength and elongation. However, during operation, these organic constituents degrade over time, mainly through oxidation occurring at the anode. The resulting additive consumption affects the quality of the metal plating/deposition and also strongly impacts on the overall costs of the process.

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Furthermore, the process conditions for electroplating and electrodeposition of metals may be very harsh on the cell components, especially on the activated anodes. The corrosive electrolytes, and in certain applications the high current densities, affect the electrode lifetime and performance by degrading the active coating layer and further
30 aggravate the amount of additive that is consumed.

Electrodes for the electroplating or electrodeposition of a metal comprising at least one topcoating layer based on tantalum oxides over an activated electrode, i.e. an electrode

provided with at least an electrochemically active coating layer, are known to the applicant to partially address the aforementioned issues.

In US6527939 and US2004031692 there is taught the use of a valve metal or tin
5 topcoating layer on an activated electrode to protect the underlying electrocatalytic coating layer in applications involving oxygen evolution, and to prevent organic elements or other oxidizable species in the electrolyte from oxidation. The valve metal topcoating layer is taught to be formed from a valve metal alkoxide in an alcohol solvent, with or without the presence of an acid, or using salts of the dissolved metals.
10 However, the preparation methods described in the art for valve metal topcoats in general, and in particular the preparation methods of Ta- or Sn-based topcoats taught in the prior art examples, were not found to work as well for other valve metal topcoating compositions, in particular for Nb-based compositions.

15 Additionally, Sn-based topcoatings are generally not desirable in applications such as copper foil, where even a small tin contamination of the electrolyte may negatively affect the quality of the deposited copper.

It would be therefore desirable to provide an alternative or improved electrode for
20 electroplating/electrodeposition processes showcasing extended service life and limited additive consumption.

It would be also desirable to provide an alternative and improved method for producing an electrode comprising a Nb-based topcoating layer for electroplating and
25 electrodeposition processes.

SUMMARY OF THE INVENTION

The present invention relates to an improved activated electrode for electroplating and
30 electrodeposition processes, and the method for producing the same. The electrode is operated in electrolyte environments containing organic additives, where it may reduce the amount of organic constituent lost via oxidation.

The activated electrode is provided with at least one topcoating layer containing niobium oxide that may induce an improved barrier effect to additive consumption, wherein the Nb-based topcoating layer is obtainable by thermal decomposition of acid precursors, namely aqueous niobium oxalate in acetic acid.

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Other benefits and advantages of the invention will become apparent to those skilled in the art based on the following detailed specification.

DETAILED DESCRIPTION OF THE INVENTION

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Under one aspect, the invention relates to an electrode suitable for the electroplating or electrodeposition of a metal from an electrolyte solution in an electrolytic cell comprising a conductive substrate, at least one topcoating layer of a first composition and at least one electrochemically active coating layer of a second composition different from the first one, the electrochemically active coating layer being positioned between the conductive substrate and the topcoating layer, the first composition containing 90-100% niobium or oxides thereof, expressed in weight percentage referred to the metal.

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Contrary to the electrodes obtained via the preparation methods disclosed in the art, the inventor has surprisingly observed that the Nb-based topcoating layer obtained via thermal decomposition of a precursor solution comprising an aqueous solution of niobium oxalate in acetic acid provides an advantageous impact on additive consumption, thereby improving the quality of the deposited/plated metal. Additionally, the Nb-based topcoating obtainable via the aforementioned process may extend the service life of the electrode by minimizing the exposure to the electrolyte of any platinum group metal or oxide thereof that may be present in the electrochemically active coating. The foregoing can be achieved without an adverse effect on the cell electrode potential.

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Thus, the electrode according to the invention may represent a viable and advantageous alternative with respect to electrodes provided with Ta- and Sn-based topcoats described in the art.

By Nb-based topcoating layer it is meant a topcoating layer containing 90-100% niobium or oxides thereof, expressed in weight percentage referred to the metal.

5 Additionally, the electrode provided with the Nb-based topcoating according to the invention may also represent an improved alternative with respect to the electrodes provided with Nb-based topcoating layers obtained by the preparation methods described in the art. Such methods teach, for example, the use of alkoxydes or chlorides of the valve metal as precursors, dissolved in an alcohol solvent, with or without the presence of an acid. While these known methods yield suitable results when
10 the valve metal is tantalum, they are less satisfactory when the valve metal is niobium.

In general, niobium chlorides hydrolyse in the presence of moisture, even when water is present just in traces. As a result, the chloride precipitates as niobium oxide thereby hindering the coating application and causing stability issues of the coating solution.

15 The inventor found, as expected, that the tendency of these niobium precursors to hydrolyse adversely affects the performance of the resulting topcoating. Indeed, the Nb-based topcoating layers obtained starting from NbCl_5 in hydrochloric acid or in alcoholic solutions (such as butanol, isopropanol and ethanol), were found not to deliver a
20 suitable and reproducible electrode.

In particular, the high evaporation rates of the alcohols strongly affect the stability of the resulting solution, as can be observed in particular for ethanol and isopropanol.

25 Additionally, since the topcoating layers are thermally treated at temperatures well above 100°C , it is generally desirable to waive the use of inflammable solutions, such as alcohols, in the electrode preparation process.

30 The Nb-based topcoating layers obtained starting from Nb alkoxides yielded to extremely porous electrodes with a very poor barrier effect towards additive consumption.

Among all the solutions listed above, only NbCl_5 in butanol was found to produce a working electrode, however the latter underperformed in terms of additive consumption and lifetime with respect to both the Nb-based topcoats according to the present invention and the Ta-based topcoats known in the art.

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The above may explain why, to the inventor's knowledge, electrodes for the electroplating or electrodeposition of metals provided with a Nb-based topcoating are not commercially available and are not usually employed in the envisaged applications.

10 In general, the electrode according to the invention is particularly useful as a dimensionally stable anode, in particular when used in the electrodeposition of copper foil from a sulfate electrolyte, for example in the production of printed circuit boards.

The electrode according to the invention may also be advantageously used for
15 electrochemical processes where it is desirable to reduce the oxidation of oxidizable species in solutions, for instance to inhibit the production of chlorine and/or hypochlorite, in systems with low levels of chloride.

The electrode according to the invention may be used, for instance, in an undivided
20 electrolytic cell where the opposite electrodes are separated by a physical gap containing the electrolyte. The cell may include a bag of insulating material, such as a plastic material like polypropylene, surrounding the anode.

In the electroplating and electrodeposition of metals of interest, the electrolyte will
25 typically be a water-based solution where the metal to be plated/deposited is dissolved. The electrolyte will typically contain additives such as brighteners, levelers, surfactants and suppressors. The additives may include disulfide compounds such as bis(sodiumsulfopropyl)disulfide (SPS), polyethylene glycols or amines.

30 The conductive substrate of the electrode may be a valve metal, for example titanium, tantalum, zirconium, niobium, and tungsten. Alternatively, tin or nickel may be used. The suitable metals of the conductive substrate can include, besides the aforementioned elemental metals themselves, their alloys and intermetallic mixtures. A preferred

material for the conductive substrate is titanium because of its sturdiness, corrosion-resistance properties and general availability.

The conductive substrate may be in any form suitable to perform its purpose; in particular, it may be in form of a plate, mesh, sheet, blade, tube or wire.

As customary in the field, before application of any of the coating layer over the substrate, the latter is preventively cleaned and optionally treated for enhanced adhesion by any conventional technique known in the art, such as intergranular etching, blasting or plasma spraying, followed by surface treatment to clean the substrate and remove any residues attached thereto.

The substrate surface may be optionally subject to other preparation steps, such as pretreatment before application of the coating layers. For example, the surface may be subjected to a hydriding or nitriding, or it may be provided with an oxide layer by heating the substrate in air or by anodic oxidation.

The electrode according to the invention is activated with an electrochemically active coating comprising at least one electrochemically active coating layer having a composition different than the composition of the topcoating layers.

The electrochemically active coating is placed between the topcoating and the conductive substrate. The topcoating likely hinders the larger additive molecules in the electrolyte from reaching the electrochemically active coating and oxidizing thereon, while still ensuring adequate access of other components of the electrolyte to the underlying electrochemically active coating.

The electrochemically active coating layer composition may be a mixture of valve metals, such as magnesium, thorium, cadmium, tungsten, tin, iron, silver, silicon, tantalum, titanium, aluminium, zirconium and niobium, and platinum group metals, such as iridium, osmium, palladium, platinum, rhodium, ruthenium.

A mixture of iridium and tantalum has been found to work very well in the execution of the invention; preferably said mixture contains 50-80% iridium and 20-50% tantalum expressed in weight percentage referred to the elements.

- 5 The electrochemically active coating layer may be applied directly on the conductive substrate or over an optional underlayer, which may promote adhesion of the electrochemically active coating layer to the electrode substrate and/or prevent passivation of the conductive substrate.
- 10 It is understood that the underlayer will have a composition different from the composition of the electrochemically active coating.

The underlayer may comprise a mixture of valve metal oxides, such as a mixture of tantalum and titanium oxides. The latter has been found to work well in the execution of the invention. In particular, a composition of 10-40% Ta and 60-90% Ti has been observed to provide very good adhesion of the electrochemically active coating layer to the electrode substrate and to prevent passivation.

Each electrochemically active coating layer, and each optional underlayer, may be formed according to the methods known in the art.

Preferably, the electrochemically active coating is formed by thermal decomposition of precursors. Preferably, the precursors are decomposed at a temperature of 400-600°C. Optionally, the thermally decomposed coating may be further baked at a temperature of 430 - 600°C after the application of the last layer.

The Nb-based topcoat according to the invention is applied in at least one layer over the electrochemically active coating; each topcoating layer is dried according to standard procedures known in the art and is then thermally decomposed.

30 The skilled person will apply as many topcoating layers as required to achieve the desired loading. The inventor has found that in general, a total amount of Nb in the

topcoating between 2-18 g/m² gives good results. In order to reduce the number of cycles, a reduced loading of 2-12 g/m², preferably 7-10 g/m², may be used.

5 A higher loading, for instance between 12-18 g/m² may provide further improved additive consumption.

Such loadings may be achieved in a number of layers, i.e. preparation cycles, that will depend on the pick up of each topcoating layer. A number of 3-20 cycles, and a pick-up of 0.5-2 gNb/m² per layer, has been found to work well in the execution of the invention.

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It is to be understood that any of the coating layers utilized in the electrode according to the invention may be applied by any of those means known in the art to be suitable for the application of a liquid composition to an electrode substrate, such as application by brush or roller coater, dip spin and dip drain methods, spraying, electro-spraying or any

15 combination of the afore mentioned techniques.

In general, the capacity of an electrode to minimize additive consumption depends, among other parameters, on the thickness of the topcoating, which in turn, for a given metal pick-up per layer, may be linked to the number of preparation cycles. The inventor

20 observed that the Nb-based topcoating of the electrode according to the invention may reach the same thickness of Ta-based topcoats with half the number of topcoating layers, when using the same pick-up per layer.. While topcoating thickness is not the only parameter affecting the capacity of the coating to prevent additive consumption, it is noted that it contributes to such effect by introducing a physical separation between

25 the electrode active layer and the organic constituents in the electrolyte.

The inventor observed that the barrier effect of the Nb-based topcoat according to the invention, per g/m² of total metal loading of the topcoat, is improved of more than 51% with respect to the barrier effect of the same electrode without topcoat.

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The improvement in barrier effect was measured via cyclic voltammogram, determining the effect of the topcoating on the oxidation of ferrous ions in an electrolytic cell according to the procedure set out in COMPARISON TEST 3.

In general, the characteristic cyclic voltammogram peak of the electrochemically and chemically reversible reaction $\text{Fe(II)} \rightarrow \text{Fe(III)} + e^-$ changes according to the type of topcoating applied, as a function of its thickness and porosity.

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At fixed experimental conditions (such as temperature, redox reaction, scan rate, redox probe of the referenced experiment), the peak height of the cyclic voltammogram of the electrode will result proportional to the number of iron (II) ions able to penetrate the “barrier” provided by the topcoating and to get oxidized at the active layer of the electrode.

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The higher the peak height, the lower the barrier effect of the topcoating to iron (II) ions consumption, and therefore the lower the barrier effect of the topcoating to brightener consumption, though the latter will also be partly affected by other parameters, such as the specific brightener molecules used.

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The inventors have quantitatively calculated the improvement in barrier effect provided by the topcoating by dividing the peak height of the cyclic voltammogram of the electrode without the topcoating by the peak height of the cyclic voltammogram of the same electrode with the topcoating. The result is then adjusted to the total metal load in g/m^2 present in the topcoating.

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Under one embodiment, the topcoating layer of the electrode according to the invention contains substantially 100% Nb or oxides thereof.

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With the expression “substantially 100% Nb or oxides thereof” it is meant a topcoating layer consisting of niobium, save for possible traces of the elements that diffuse from the coating underneath or traces of impurities in the precursor solution.

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The topcoating of the electrode according to the present embodiment is such as may be obtained via thermal decomposition of the niobium precursor solution according to the invention, i.e. an aqueous solution of niobium oxalate in acetic acid, where the acetic acid may be diluted in deionised water.

The electrode according to this embodiment has been found to exhibit an improved barrier effect to additive consumption with respect to electrodes provided with Ta-based topcoating with same number of layers and same loading.

- 5 Additionally, the electrode according to this embodiment has been found to exhibit a strongly improved barrier effect with respect to electrodes provided with Nb-based topcoating layers prepared according to the methods described in the art.

10 In particular, in connection with the present embodiment, the inventors observed that the barrier effect of the Nb topcoating, per gNb/m^2 , is improved above 85%, and even above 100%, with respect to the barrier effect of the electrochemically active coating alone, as measured according to the procedure set out in COMPARISON TEST 3.

15 Under an alternative embodiment, the Nb-based topcoating layer is provided with at least one doping agent suitable to be incorporated as doping agent precursors into the precursor solution of the first composition, such as antimony, indium, molybdenum, tungsten, bismuth or tantalum. Such doping agents may typically be present in an amount from about 0.01% to about 10%, by weight in the topcoating layer, preferably in an amount from about 0.01% to about 5%. The doping agent may be in the form of the
20 metal or its oxides, including suboxides.

The present invention also relates to an electrode suitable for the electroplating or electrodepositing of a metal from an electrolyte solution in an electrolytic cell comprising a conductive substrate, a topcoating comprising at least one topcoating layer of a first
25 composition containing 90-100% niobium or oxides thereof and at least one electrochemically active coating layer of a second composition different from the first one, wherein the adjusted barrier effect of the topcoating is 51-200% the barrier effect of the underlying electrochemically active coating, as measured by means of cyclic voltammetry in the presence of the redox probe $\text{Fe(II)}|\text{Fe(III)}$. The measurement of the
30 adjusted barrier effect shall be carried out as described in COMPARISON TEST 3, by dividing the peak height of the cyclic voltammogram of the electrode without topcoating with the peak height of the electrode with the Nb-based topcoating, and adjusted for the total metal loading of the topcoating (in g/m^2).

The Nb-based topcoating according to the present embodiment can be obtained via thermal decomposition of a precursor solution comprising a Nb precursor solution of aqueous niobium oxalate in acetic acid. Said precursor solution corresponds to the precursor solution described in the present document, alone or in connection with all preferred or alternative embodiments concerning the invention.

Nb-based topcoatings prepared with the Nb precursors solutions described in the art exhibit, at best, an adjusted barrier effect which does not reach an improvement of 51% with respect of the uncoated electrode.

According to a preferred embodiment of the above electrode, the first composition of the electrode above contains substantially 100% Nb or oxides thereof and the improvement in barrier effect of the electrode with said topcoating is 85-200% times the barrier effect of the electrode without topcoating, and may reach 100-200%, measured per total gNb/m².

Under a further aspect, the invention relates to a method for manufacturing the electrode hereinbefore described. The method comprises coating a conductive substrate with an electrochemically active coating comprising at least one layer, and subsequently forming a topcoating over the electrochemically active coating. The topcoating comprises at least one topcoating layer containing 90-100% niobium or oxides thereof. Each topcoating layer is formed by performing the following sequential steps:

- (i) applying over the activated conductive substrate a precursor solution comprising a Nb precursor solution;
- (ii) drying the precursor solution at a temperature of 50-100°C for 5-20 minutes, preferably at a temperature of 50-70°C for 7-15 minutes;
- (iii) thermally decomposing the dried precursor solution at a temperature of 320-600°C for 5-20 minutes.

Preferably, the above thermal decomposition step is carried out at 350-550°C for 5-20 minutes, even more preferably at a temperature of 470-550°C for 7-15 minutes.

Steps (i)-(iii) may be repeated as many times as necessary to achieve the desired metal loading, in cyclic fashion.

5 The skilled person understands that after each cycle, at the end of the thermal decomposition step (iii) of the precursor solution, the electrode will be allowed to cool until reaching room temperature before proceeding with the subsequent cycle.

10 A number of cycles between 3-20 has been found to yield a topcoating thickness that provides a suitable barrier effect. In some embodiments, a number of cycles between 4-16 has been found to work without detriment to the increase in overpotential, thus maintaining a relatively low number of thermal cycles with consequent cost savings.

The above mentioned Nb precursor solution is obtained by mixing an aqueous solution of niobium oxalate in diluted acetic acid.

15 The concentration of Nb in the Nb precursor solution may be chosen between 20-50 g/l. This range has been observed to ensure a particularly compact topcoating layer structure, which is beneficial for reducing additive consumption.

20 By diluted acetic acid it is meant CH_3COOH diluted in water, preferably deionised water, preferably at a concentration of 5-20%, even more preferably at a concentration of 7-13% to provide particularly good wettability.

25 According to the claimed method, the formation of at least one topcoating layer occurs over an activated substrate, i.e. a substrate provided with at least one electrochemically active coating layer. The latter may be formed directly over the clean or pretreated substrate, or above at least one optional underlayer coated over the substrate.

30 The electrochemically active coating layer, the optional underlayer and the electrode substrate may be according to any of the embodiments hereinbefore described.

According to one embodiment, the precursor solution consists of a Nb precursor solution. The resulting electrode will be therefore provided with a topcoating containing

substantially 100% Nb or oxides thereof, save for traces of the elements of the electrochemically active coating that may partly diffuse into the topcoating, or traces of other metals in the Nb precursor solution.

- 5 According to an alternative embodiment, the precursor solution contains a Nb precursor solution and a doping agent precursor solution, where the doping agent is chosen from the group consisting of antimony, indium, molybdenum, tungsten, bismuth, tantalum and the weight ratio of Nb versus the doping agent in said precursor solution is 90-99,999:10-0,001; preferably 95-99,999:5-0,001.

10 Under a different aspect, the present invention relates to an unseparated electrolytic cell for the electroplating or electrodeposition of a metal from an electrolyte solution comprising at least one anode and at least one cathode partly or completely immersed in the electrolyte solution. The electrolyte solution contains the metal to be
15 deposited/plated in solution and at least one organic substituent.

The anode used in the cell is the electrode hereinbefore described.

The cell may be used in printed circuit board applications.

20 For example, the cell according to the invention may be used in the electrodeposition of copper foil from an aqueous electrolyte containing copper sulfate.

The organic substituent may be an organic additive.

25 Under a different aspect, the present invention relates to a process for the electroplating or electrodeposition of a metal from an electrolyte solution, wherein the process is carried out in any electrolytic cell as hereinbefore described and at least one anode in said cell is operated so that the consumption of the organic substituent present in the
30 electrolyte is reduced without detriment to the anode potential in the cell.

The following examples are included to demonstrate particular ways of reducing the invention to practice, whose practicability has been largely verified in the claimed range of values.

- 5 It should be appreciated by those of skill in the art that the equipment, compositions and techniques disclosed in the following represent equipment, compositions and techniques discovered by the inventor 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
10 still obtain a like or similar result without departing from the scope of the invention.

EXPERIMENT PREPARATION

- In all the electrode samples used in the following EXAMPLES, COUNTEREXAMPLES
15 and COMPARISON TESTS, the electrode substrate was manufactured starting from a titanium grade 1 mesh of 100 mm x 100 mm x 1 mm size, degreased with acetone in an ultrasonic bath for 10 minutes. The mesh was then subjected to steel grit sandblasting, and was subsequently etched in HCl 20% weight at boiling point.

20 EXAMPLE 1

A clean electrode substrate sample was coated with an electrochemically active coating solution containing a mixture based on oxides of iridium and tantalum at a 65:35 weight ratio.

- 25 The electrochemically active coating precursor solution was applied in 10 layers, with a total loading of 15 g/m² of iridium.

- Each electrochemically active coating layer was applied by brush and dried at a
30 temperature of 50°C for 10 minutes. Each electrochemically active coating layer was then thermally decomposed at a temperature of 510°C for 15 minutes and finally was allowed to cool down to room temperature before proceeding with the next layer.

The activated electrode was then coated with a topcoating solution of Nb precursors.

The Nb precursor solution consisted of an aqueous solution of niobium oxalate at 45 g/l in 13% aqueous CH₃COOH.

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The topcoating was applied in 9 layers, with a total loading of Nb of 9 g/m².

Each topcoating layer was applied by brush and dried at a temperature of 55°C for 10 minutes. Each topcoating layer was then thermally decomposed at a temperature of
10 500°C for 10 minutes and allowed to cool down to room temperature before proceeding with the next layer.

The electrode thus obtained was labelled S1.

15 COUNTEREXAMPLE 1

A sample electrode was prepared according to the procedure outlined in Example 1, except that the Nb precursor solution consisted of NbCl₅ dissolved in butanol, the concentration of niobium in the Nb precursor solution being 45 g/l.

20 The electrode thus obtained was labelled CS1.

COUNTEREXAMPLE 2

A clean electrode substrate sample was coated with the electrochemically active
25 coating described in Example 1, according to the procedure described therein.

The activated electrode was then coated with a topcoating solution of Ta precursor. The Ta precursor solution consisted of an aqueous solution of TaCl₅ at 45 gTa/l in butanol.

30 The topcoating solution was applied in 9 layers, with a total loading of Ta of 9 g/m². Each topcoating layer was applied by brush and dried at a temperature of 55°C for 10 minutes. Each topcoating layer was then thermally decomposed at a temperature of

500°C for 10 minutes and allowed to cool down to room temperature before proceeding with the next layer.

The electrode thus obtained was labelled CS2.

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COUNTEREXAMPLE 3

A clean electrode substrate sample was coated with an electrochemically active coating as described in Example 1.

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The activated electrode was then coated with a topcoating solution of Ta precursor as described in COUNTEREXAMPLE 2 with the exception that the topcoating solution was applied in 18 layers, with a total loading of Ta of 18 g/m².

15 The electrode thus obtained was labelled CS3.

Samples S1, CS1, CS3 showed an average topcoating thickness of 4 micrometers, as measured with SEM cross section imaging. Sample CS2 showed an average thickness of 2 micrometers.

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COMPARISON TEST 1

All samples were measured for brightener consumption by running a dummy copper plating in Haring cell for 190 minutes at 25 ASF (Ampère per Square Foot).

25 For the anode, samples S1, CS1, CS2, CS3 were alternatively used inside a polypropylene bag.

The cathode was a brass plate.

30 The electrolyte contained water, sulphuric acid, formaldehyde, organic salt and copper sulphate. The organic salt, i.e. the brightener, was 3,3'-dithiobis[propansulfonate] of disodium.

The brightener consumption was measured by cyclic voltammetry stripping by determining the charge required to consume 1 l of brightener. The results are reported in Ah/l in Table 1.

5 COMPARISON TEST 2

All samples underwent a lifetime test in a beaker in H₂SO₄ 150 g/l at 1 kA/m², and were monitored every 1000 hours.

- 10 The deactivation times of each sample, corresponding to the time (in hours) required to measure a sudden increase of cell voltage above 6V, are listed in TABLE 1.

COMPARISON TEST 3

- 15 The barrier effect of samples S1, CS1, CS2, CS3 was measured by means of cyclic voltammetry in the presence of the redox probe Fe(II)|Fe(III).

A solution of 50 ml of Fe(II) was prepared with 20 g/l of Fe(II) from ferrous sulphate in H₂SO₄ 150 g/l.

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The experiment was carried out in a three-electrode cell at room temperature (25°C) at a scan rate of 20 mV/s.

- 25 The counterelectrode was a dimensionally stable titanium anode of 3 cm² active area and coated with the 65% iridium and 35% tantalum electrochemically active coating prepared as described in Example 1 and with no topcoating.

The reference electrode was a saturated calomel electrode.

- 30 For each tested sample S1, CS1, CS2, CS3, a baseline electrode referenced as BL was prepared according to the procedure set out in EXAMPLE 1, with the exception that no topcoating layer was applied over the electrochemically active coating.

Samples S1, CS1, CS2, CS3, and the baseline BL were cut to a 10 mm x 30 mm size and covered with Teflon tape so as to leave an active area of 10 x 10 mm².

The experiment consisted of five tests, where the working electrode was alternatively
5 selected from samples S1, CS1, CS2, CS3 and the baseline BL.

The peak height of the cyclic voltammogram was measured for all samples and BL.
The improvement in the topcoating barrier effect (TC BE) of each sample S1, CS1,
CS2, CS3, was calculated as the ratio between the peak height of the corresponding
10 baseline BL electrode and the peak height measured for the sample, i.e.:

$$\text{TC BE (sample)} = \text{peak height (BL)} / \text{peak height (sample)}.$$

The improvement in the topcoating barrier effect of each sample was then adjusted for
the total metal loading of the topcoating, as obtained by dividing the TC BE (sample) by
15 the amount of metal in the topcoating, measured in g/m², and expressing the number in
percentage (per g/m²).

The results of the measurements are listed in TABLE 1.

Sample	Brightener consumption (Ah/l)	Deactivation time (h)	TC BE	Adjusted TC BE (per g/m ²)
S1	26700	3761	9.47	105.2%
CS1	14100	3420	4.50	50.0%
CS2	24190	3548	7.52	83.6%
CS3	26000	3003	8.20	45.6%

20 TABLE 1

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 exclude the presence of other elements, components or additional process steps.

The discussion of documents, acts, materials, devices, articles and the like is included
5 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. An electrode suitable for the electroplating or electrodeposition of a metal from an electrolyte solution in an electrolytic cell comprising a conductive substrate, at
5 least one topcoating layer of a first composition and at least one electrochemically active coating layer of a second composition different from the first one, the electrochemically active coating layer being positioned between the conductive substrate and the topcoating layer, the first composition containing 90-100% niobium or oxides thereof, characterized in that said topcoating layer is
10 obtained via thermal decomposition of a precursor solution comprising an aqueous solution of niobium oxalate in acetic acid.
2. The electrode according to claim 1 wherein the first composition contains substantially 100% niobium or oxides thereof.
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3. The electrode according to claim 1 wherein the first composition contains at least one doping agent chosen from the group consisting of antimony, indium, molybdenum, tungsten, bismuth, tantalum or their oxides in an amount of 0.01-10% by weight.
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4. The electrode according to any one of claims 1-3 wherein the total amount of niobium in the topcoating layer is between 2-18 g/m².
5. The electrode according to any one of claims 1-4 wherein the second
25 composition consists of 50-80% iridium and 20-50% tantalum, expressed in weight percentage.
6. The electrode according to any one of claims 1-5 further comprising at least one underlayer containing a third composition different from the second composition, said underlayer being positioned between the conductive substrate and the
30 electrochemically active coating layer, the third composition preferably comprising a mixture of tantalum and titanium oxides.

7. The electrode according to any one of claims 1-6 wherein the conductive substrate is made of a valve metal selected from the group consisting of titanium, tantalum, zirconium, niobium, tungsten, aluminum, silicon, their alloys and intermetallic mixtures.
- 5
8. Method for manufacturing the electrode according to claim 1 comprising the formation of a topcoating over a conductive substrate, the conductive substrate being coated with an electrochemically active coating comprising at least one electrochemically active coating layer, the topcoating comprising at least one topcoating layer containing 90-100% niobium or oxides thereof, wherein the formation of said at least one topcoating layer comprises the sequential steps of:
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- (i) applying a precursor solution over the conductive substrate coated with the at least one electrochemically active coating layer;
- (ii) drying the precursor solution at a temperature of 50-100°C for 5-20 minutes, preferably at a temperature of 50-70°C for 7-15 minutes;
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- (iii) thermally decomposing the dried precursor solution at a temperature of 350-600°C for 5-20 minutes, preferably at a temperature of 470-550°C for 7-15 minutes;
- the precursor solution comprising a Nb precursor solution obtained by diluting an aqueous solution of niobium oxalate in acetic acid.
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9. An unseparated electrolytic cell for the electroplating or electrodeposition of a metal from an electrolyte solution comprising at least one anode and at least one cathode at least partially immersed in the electrolyte solution, the electrolyte solution containing an organic substituent and said metal in solution;
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- characterized in that said at least one anode is the electrode according to any one of claims 1-7.
10. A process for the electroplating or electrodeposition of a metal from an electrolyte solution, wherein the process is carried out in the electrolytic cell according to claim 11 and the at least one anode in said cell is operated so that the consumption of said organic substituent is reduced while maintaining anode potential in said cell.
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