

ANODE FOR ELECTROLYSIS

BACKGROUND OF THE INVENTION

5 The production of chlorine is essentially carried out by electrolysis of alkali chloride solutions, in particular sodium chloride solutions, by means of three alternative technologies based on diaphragm, mercury cathode or, in the most advanced case, ion-exchange membrane electrolyzers, equipped with anodes consisting of expanded or variously perforated titanium sheets provided with an electrocatalytic coating
10 comprising platinum group metals and/or oxides thereof, optionally in admixture; anodes of such kind are for instance commercialised by Industrie De Nora under the trade-mark DSA[®]. A common problem to the three technologies is the need of limiting the molar oxygen content in chlorine at levels below 2% and preferably not higher than 1%: oxygen is generated by the unavoidable secondary reaction of water
15 oxidation and hampers most processes making use of chlorine, in particular dichloroethane synthesis, which is the first step of PVC production. According to teachings of the prior art, in order to obtain low oxygen contents the anodes, whose coating is obtained by painting the titanium substrate with a noble metal precursor solution subsequently decomposed by a thermal treatment, are then subjected to a
20 final thermal treatment which nevertheless entails some energy consumption penalties, which can be estimated on average at about 50-100 kWh/ tonne of product depending on the duration and on the temperature applied.

The same anodes are moreover employed in hydrochloric acid electrolysis, which is
25 acquiring a growing interest since hydrochloric acid is the typical by-product of all major chlorine-using industrial processes: the increase in the productive capacity of present-day plants involves the generation of remarkable quantities of acid whose allocation on the market is significantly difficult. Hydrochloric acid electrolysis leads to formation of chlorine which can be recycled upstream giving rise to a substantially
30 closed cycle, free of significant environmental impact, which is nowadays a decisive factor to obtain the construction licenses from the competent authorities. The problem characterising the application of noble metal-coated titanium anodes in this context is directly associated with the strong aggressiveness of hydrochloric acid: the

latter, penetrating through the defects of the electrocatalytic coating, corrodes the titanium-coating interface and provokes the detachment thereof in a relatively short time, with consequent plant shut-down. A first countermeasure suggested by the prior art, consisting of employing substrates made of titanium-palladium alloy, which
5 is renowned for its peculiar corrosion resistance and used for the construction of critical equipment of chemical plants, has led to no sensible result. A second remedy, consisting of improving the protection of the titanium substrate by increasing the thickness of the catalytic coating, could not be applied beyond certain limits, as it has been observed that excessively thick coatings become extremely brittle and are
10 therefore subject to remarkable detachment phenomena of purely mechanical nature. The preferred solution so far provides the electrocatalytic coating to be obtained as a multiplicity of overlaid individual layers: the thus-obtained anode presents a reduced number of defects and is therefore characterised by a better operative lifetime. Nevertheless it has been observed that the advantages in terms of prolonged lifetime
15 are counterbalanced by penalties in terms of higher operative voltages, entailing an electrical energy consumption increase of about 50-150 kWh/tonne of chlorine.

Similar problems arise also in all those electrochemical processes, in particular electrometallurgical ones, wherein noble metal-coated titanium electrodes are used
20 as oxygen-evolving anodes: these processes often involve the use of highly concentrated acidic solutions, in particular by sulphuric acid, which turn out to be aggressive for the currently employed titanium substrates. Measures such as those recalled for the hydrochloric acid case are routinely applied with the purpose of obtaining acceptable lifetimes.

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It is one object of the present invention to provide an anode for industrial electrolytic processes overcoming the limitations of the prior art, especially in terms of energy consumption and chemical resistance to acidic solutions.

30 Under another aspect, it is one object of the present invention to provide an anode for industrial chlorine-evolving electrolytic processes overcoming the limitations of the prior art in terms of oxygen content in the product chlorine.

Under a further aspect it is one object of the present invention to provide an anode for industrial oxygen-evolving electrolytic processes, for instance electrometallurgical processes, overcoming the limitations of the prior art in terms of duration and operative cell voltage.

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These and other objects will be made clear by the following description, which shall not be intended as limiting the invention whose extent is solely defined by the appended claims.

10 DESCRIPTION OF THE INVENTION

The anode according to the present invention comprises a titanium alloy substrate provided with an electrocatalytic coating based on noble metals and/or oxides thereof, said titanium alloy including elements suitable for being oxidised during the formation of said electrocatalytic coating, preferably at a concentration of 0.01 to 5% by weight.

In one preferred embodiment, the anode of the invention comprises a substrate consisting of a titanium alloy including one or more elements selected from the group consisting of aluminium, niobium, chromium, manganese, molybdenum, ruthenium, tin, tantalum, vanadium and zirconium; in another embodiment, such alloy further comprises one or more elements selected among nickel, cobalt, iron and copper.

In one particularly preferred embodiment of the present invention, the titanium alloy used as the anode substrate contains 0.02-0.04% by weight ruthenium, 0.01-0.02% by weight palladium, 0.1-0.2% by weight chromium and 0.35-0.55% by weight nickel.

Independently of their final utilisation, titanium anodes with a noble-metal based active coating are manufactured by a procedure comprising the pre-treatment of a titanium substrate by sandblasting and/or attack in acidic solution, and the application of an electrocatalytic coating based on platinum group metals or oxides thereof, optionally in admixture, by thermal decomposition at 450-550°C of paints containing suitable precursors of the final metals and/or oxides.

The coating may present defects in form of pores or cracks whose presence is believed to be an important cause of operative lifetime reduction in the specific case of operation in the presence of aggressive acidic solutions, as in the case of hydrochloric acid solutions used for hydrochloric acid reconversion to chlorine and of sulphuric acid solutions employed in many electrometallurgical processes: these solutions may creep into the defects until reaching the interface with the titanium substrate and start a corrosion process which in a short time can lead to coating detachment and consequent electrolyser shut-down.

It was demonstrated that the defect population is a function of the coating application procedure: in particular, the past experience indicates that the higher is the thickness (or specific loading), the lower is the presence of defects in the electrocatalytic coating; on the other hand, for a given thickness or specific loading, the more fractioned is the application - in other words, the higher is the number of individual layers applied - the lower is the presence of defects. In the latter case it is apparent that the overall thermal treatment, which is a function of the number of individual layers, may be protracted for quite a long time.

In the case of anodes for electrolysis of acidic solutions, similarly lengthy thermal treatments are also necessary to endow the coating with an adequate resistance to dissolution: it is presumable that this positive effect is associated with crystallisation processes of the coating material leading to elimination of the more vulnerable amorphous fraction.

A similar situation is also experienced when this kind of anodes is employed in chlor-alkali electrolysis, with the industrial users often requiring the oxygen content in chlorine to stay below certain limits, for example less than 2% and preferably less than 1%: such a result is in fact obtained by subjecting the anodes to a further final thermal treatment.

The industrial experience has shown that extending the duration of treatments at temperatures of 450 to 550°C, although allowing to achieve the above mentioned

advantages, entails a rather severe penalty in terms of electrochemical working potential decrease, with a corresponding increase in the electrical energy consumption of up to 100 kWh/ton in the case of chlorine production.

- 5 As an example of such penalties, in the following table 1 are reported the data relative to the electrochemical potential $E_{\text{Cl}_2, \text{SCE}}$ (SCE = saturated calomel reference electrode) and the oxygen content in chlorine as a function of the overall thermal treatment time (d, given in hours) obtained with anodes for chlorine evolution in chlor-alkali electrolysis, the other production parameters remaining constant (substrate of
10 pure titanium grade 1 according to ASTM B 265, electrocatalytic coating consisting of non-stoichiometric mixed oxide of ruthenium, iridium and titanium, RuIrTiO_x).

Table 1					
d (h)	1	2	3	4	5
$E_{\text{Cl}_2, \text{SCE}}$ (V)	1.08	1.10	1.14	1.18	1.25
% O_2	2.20	1.95	1.60	1.25	< 1

- Entirely similar results were obtained making use of titanium-palladium alloy as the
15 substrate (ASTM B 265, grade 7, palladium 0.12-0.25% by weight), whose higher cost would even have been acceptable, at least in some applications, in exchange for possible voltage and lifetime gains.

- The inventors have surprisingly observed that it is possible to manufacture anodes
20 with lengthy overall thermal treatment times without experiencing a sensible deterioration of the electrochemical working potentials when the substrate consists of suitable titanium alloys, in contrast with the teachings of the prior art: the invention therefore provides anodes of higher quality capable both of functioning with extended operative lifetimes in hydrochloric acid solution electrolysis or in sulphuric acid-
25 containing electrolytes currently employed in electrometallurgy, and of producing chlorine with low oxygen percentages in chlorine-caustic soda electrolysis.

- In particular, very interesting results were obtained with titanium alloys containing one or more elements of a first set consisting of aluminium, niobium, chromium,
30 manganese, molybdenum, ruthenium, tin, tantalum, vanadium and zirconium,

optionally added with elements of a second set comprising nickel, cobalt, iron, copper. It was also found that titanium alloys only containing one or more elements of the second set proved less efficient in preventing the electrochemical potential deterioration under the effect of a lengthy heating. Moreover, the presence of iridium, rhodium, palladium and platinum in the alloy turned out to be irrelevant, even though the addition of such elements may in any case result advantageous to prevent certain kinds of corrosive attacks which take place when anodes remain immersed in aggressive solutions during electrolyser shut-down procedures, as known to those skilled in the art.

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Without being bound to any particular theory, a possible explanation of the positive effects of the elements of the first set as hereinbefore defined might be given considering first of all the reasons for the electrochemical potential increase of titanium anodes subjected to lengthy thermal treatments: it is a widely held opinion that the potential decay is caused by the growth of a titanium oxide film at the interface between coating and substrate during the coating formation step: since the thermal treatment is carried out at 450-550°C in the presence of air, titanium metal is in fact prone to be oxidised by oxygen diffusing across the coating. Titanium oxide produced in this way is scarcely conductive, therefore becoming a site for an ohmic drop adding up to the real electrochemical potential during operation: such ohmic drop is of modest extent, so that its impact on the electrochemical potential remains negligible until the titanium oxide film is thin enough. The latter is true only if the overall thermal treatment duration does not exceed certain values, which is the contrast with the need of producing anodes characterised by satisfactory operative lifetime in aggressive environments (reduced number of individual layers with still significant residual defects) or by low oxygen percentages in chlor-alkali applications.

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The elements of the first set as hereinbefore defined are firstly characterised by being easily oxidised in the process conditions typical of electrocatalytic coating application, particularly as regards temperature and presence of air: it can be thus supposed that these elements act as dopants of titanium oxide, which acquires thereby a far higher electrical conductivity than the corresponding oxide which grows on unalloyed titanium. A second aspect might be given by the capability of forming

solid solutions, at least at the low concentrations of use, typically in the range 0.01-5% by weight: the solid solutions wherein the alloyed elements are uniformly dispersed would allow the same elements to disperse in a similarly uniform manner in the superficial titanium oxide phase, endowing it with the same above seen characteristics of electrical conductivity even at a modest content of alloyed elements. The elements of the second set, also oxidisable during coating formation, are nevertheless known to give rise in general to segregated phases in form of microparticles dispersed within the metal matrix and in particular localised in correspondence of the crystal grain borders: as a possible consequence of this discontinuous distribution on a microscopic scale, their presence inside the titanium oxide is also likely to be inhomogeneous, with a less pronounced effect on the electrical conductivity.

Some among the more significant results obtained by the inventors are presented in the following examples, which shall not be intended as limiting the scope of the invention.

EXAMPLE 1

Some anodes directed to chlorine evolution by hydrochloric acid electrolysis were prepared by adopting the following procedure:

- a. acquisition of the following titanium alloys as 1 mm thick sheets (content of additional elements as weight percentage):
- Alloy 1: titanium - ruthenium (0.08/0.14%)
 - Alloy 2: titanium - aluminium (1.0/2.0%)
 - Alloy 3: titanium - tantalum (5%)
 - Alloy 4: titanium - aluminium (2.5/3.5%) - vanadium (2.0/3.0%)
 - Alloy 5: titanium - molybdenum (0.2/0.4%) - nickel (0.6/0.9%)
 - Alloy 6: titanium - chromium (0.1/0.2%) - nickel (0.35/0.55%) - ruthenium (0.02/0.04%) - palladium (0.01/0.02%)
 - Alloy 7: titanium - palladium (0.12/0.25%) (reference prior art)
 - Alloy 8: titanium - iron (0.5%)

- Alloy 9: pure titanium grade 1 according to ASTM B 265 (reference prior art)
- b. cold cutting of the previous sheets in square plates of 5 cm side
- 5 c. pre-treatment of one side of each plate by sandblasting followed by degreasing and hydrochloric acid etching
- d. application on the pre-treated side of a coating consisting of ruthenium and titanium mixed oxide comprised of a multiplicity of individual layers, each layer
- 10 being obtained by thermal decomposition of an aqueous paint containing the chlorides of the two metals at 480-490°C during 10 minutes, for a total of 25 layers corresponding to an overall ruthenium loading of 50 mg.
- 15 The thus-activated plates, with the addition of a further plate identified as alloy 9B and provided with a coating with the same composition and loading, but obtained by application of only 13 individual layers followed by a final thermal treatment of 4 hour overall duration on a 9 type alloy, were operated at a current density of 0.5 A/m² in electrolysis cells fed with 14% by weight hydrochloric acid at 60°C. A perfluorinated
- 20 Nafion 324 ion-exchange membrane commercialised by DuPont/USA subdivided the cells into two compartments, anodic and cathodic, respectively containing the plates under test and zirconium cathodes of the same size. During electrolysis the electrochemical potentials $E_{Cl_2, SCE}$ (V, reference: saturated calomel) of the plates working as chlorine-evolving anodes were measured, and periodic tests of coating
- 25 adhesion were carried out: the relevant data are collected in Tables 2a and 2b.

Table 2a						
	alloy 1	alloy 2	alloy 3	alloy 4	alloy 5	alloy 6
$E_{Cl_2, SCE}$ (init.)	1.060	1.062	1.064	1.055	1.060	1.060
$E_{Cl_2, SCE}$ (1000 hours)	1.070	1.065	1.070	1.070	1.065	1.065
$E_{Cl_2, SCE}$ (2000 hours)	1.070	1.070	1.090	1.085	1.075	1.065
adhesion test	positive	positive	positive	local detachments	positive	positive

Table 2b			
	alloys 7 and 9	alloy 8	alloy 9B
$E_{Cl_2, SCE}$ (init.)	1.200-1.210	1.15	1.190
$E_{Cl_2, SCE}$ (1000 hours)	1.220-1.225	1.17	1.180
$E_{Cl_2, SCE}$ (2000 hours)	1.240-1.250	1.16	1.235
adhesion test	positive	local detachments	negative

- 5 The data of Tables 2a and 2b show that the use of titanium alloys containing, according to the invention, elements of the first set, first of all allows meeting the target of operating at low electrochemical potentials with an electrical energy saving around 50-100 kWh/tonne of chlorine, even though a manufacturing procedure comprising the deposition of a high number of individual layers is followed in order to
- 10 obtain coatings virtually free of through defects. Such a result of high industrial relevance furthermore goes along with a remarkable stability of the coating, which is not affected by significant detachments from the substrate.

The data in Tables 2a and 2b demonstrate that the elements of the second set as hereinbefore defined, provided they are present in significant amounts, are per se capable of guaranteeing improved electrochemical potentials over the prior art, albeit
5 of lesser extent than those obtainable with alloying elements of the first set (see alloy 8).

Finally, the data in Tables 2a and 2b indicate that the performances of the anodes in accordance with the invention prove largely superior with respect to both those of the
10 anodes comprising coatings made of few but highly defective individual layers (see alloy 9B, prior art) and those of anodes with coatings consisting of many individual layers applied to pure titanium or to titanium alloys containing non-oxidisable elements such as palladium (see alloy 9 and alloy 7, prior art).

15 EXAMPLE 2

Some anodes for electrolysis of sodium chloride solutions were prepared by adopting the following procedures:

- 20 a. acquisition of the following titanium alloys as 1 mm thick sheets (content of additional elements as weight percentage):
 - Alloy 2: titanium - aluminium (1.0/2.0%)
 - Alloy 5: titanium - molybdenum (0.2/0.4%) - nickel (0.6/0.9%)
 - Alloy 6: titanium - chromium (0.1/0.2%) - nickel (0.35/0.55%) - ruthenium
25 (0.02/0.04%) - palladium (0.01/0.02%)
 - Alloy 9: pure titanium grade 1 according to ASTM B 265 (reference prior art)
- b. cold cutting of the previous sheets in square plates of 5 cm side
- c. pre-treatment of one side of each plate by sandblasting followed by degreasing and hydrochloric acid etching
- 30 d. application on the pre-treated side of a coating consisting of ruthenium, iridium and titanium mixed oxide comprised of a multiplicity of individual layers, each layer being obtained by thermal decomposition of an aqueous paint containing the chlorides of the three metals at 490-500°C during 10 minutes, for a total of 11

layers corresponding to an overall ruthenium + iridium loading of 55 mg. The plates were further subjected to final thermal treatments for a duration (d) of 1 to 4 hours.

- 5 The thus-activated plates were operated at a current density of 0.4 A/m² in electrolysis cells at 90°C. A perfluorinated Nafion 982 ion-exchange membrane commercialised by DuPont/USA subdivided the cells into two compartments, anodic and cathodic, with the plates under test and nickel cathodes of the same dimensions installed therein. The two compartments respectively contained a sodium chloride
10 solution at a concentration of 220 g/l and pH 3 and a 32% by weight sodium hydroxide solution.

During electrolysis the electrochemical potentials $E_{Cl_2, SCE}$ (V, reference: saturated calomel) of the plates working as chlorine-evolving anodes and the oxygen content in
15 product chlorine were measured: the relevant data are collected in Table 3.

Table 3		
	oxygen in chlorine (mol %)	$E_{Cl_2, SCE}$
alloy 2, d = 0 hours	2.4	1.08
alloy 2, d = 2 hours	1.6	1.10
alloy 2, d = 4 hours	1.1	1.10
alloy 5, d = 0 hours	2.3	1.09
alloy 5, d = 2 hours	1.7	1.08
alloy 5, d = 4 hours	1.0	1.09
alloy 6, d = 0 hours	2.3	1.07
alloy 6, d = 2 hours	1.6	1.08
alloy 6, d = 4 hours	0.9	1.08
alloy 9, d = 0 hours	2.4	1.08
alloy 9, d = 2 hours	1.5	1.16
alloy 9, d = 4 hours	0.8	1.25

The data in Table 3 show that in the case of anodes according to the invention comprising a suitable titanium alloy as the substrate it is possible to carry out a final

thermal treatment in order to diminish the oxygen content in chlorine to levels of complete industrial satisfaction without any significant potential penalty taking place. Such a result is not pursuable with the anodes according to the prior art wherein the titanium substrate, free of the alloying elements in accordance with the invention, forms a non-conductive oxide, which grows thicker with the protraction of the thermal treatment to which the anode is subjected (see alloy 9): the growth of the non-conductive oxide entails an obvious worsening of the anodic working potential, which can be quantified as about 100 kWh/tonne of chlorine.

10 EXAMPLE 3

Two pairs of 1 mm thick square plates of 2 cm side, obtained by cold cutting of alloy 6 and alloy 9 (prior art) sheets were treated as follows:

- 15 a. pre-treatment of one side of each plate by heavy sandblasting in order to produce a high surface-roughness degree, followed by degreasing and hydrochloric acid etching
- b. application to the pre-treated side of each plate of a coating consisting of iridium and titanium mixed oxide comprised of a multiplicity of individual layers, each layer being obtained by thermal decomposition of an aqueous paint
20 containing the chlorides of the two metals at 490-500°C during 10 minutes, for a total of 16 layers corresponding to an overall iridium loading of 32 mg.

The plates were installed in undivided cells containing a 10% by weight sulphuric acid solution at 60° and zirconium cathodes of the same size. The plates were operated as anodes for oxygen evolution at a current density of 2 A/cm² in order to simulate substantially more severe operating conditions than those typical of electrometallurgical processes such as fast zinc electroplating of steel sheets or copper-foil deposition of controlled thickness.

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During operation the electrochemical potentials of the plates were detected: the measured values were 1.35 V/SCE and 1.55 V/SCE respectively for the anodes according to the invention consisting of the catalytic coating applied to alloy 6 and for

the anodes in accordance with the prior art wherein the electrocatalytic coating was applied to titanium free of alloying elements (alloy 9). Thus, similarly to what seen in example 1 for hydrochloric acid solution electrolysis, also in the case of anodes suitable to be operated in electrometallurgical processes in contact with aggressive sulphuric solutions, electrocatalytic coatings comprised of a multiplicity of individual layers can be advantageously applied, allowing to eliminate or at least reduce to marginal levels the presence of defects which might hamper the lifetime without simultaneously incurring an electrochemical potential penalty.

- 10 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.

CLAIMS

1. Anode for electrochemical processes comprising a metallic substrate and an electrocatalytic coating with a titanium oxide layer in between containing platinum group metals and/or oxides thereof formed by a multiplicity of individual layers obtained by thermal decomposition of soluble precursors, the metallic substrate being made of a titanium alloy containing at least one element oxidisable in the conditions of said thermal decomposition, said at least one oxidisable element being selected from a first set consisting of aluminium, niobium, chromium, manganese, molybdenum, ruthenium, tin, tantalum, vanadium and zirconium, said anode further comprising a titanium oxide layer interposed between the metallic substrate and the electrocatalytic coating, wherein an oxide of said at least one oxidisable element, obtained during said thermal decomposition, is partially dispersed inside a titanium oxide layer, and wherein said titanium alloy of said metallic substrate further comprises at least one element selected from a second set consisting of nickel, cobalt, iron and copper.
2. The anode of one of claim 1 wherein said at least one oxidisable element is present at a concentration of 0.01 to 5% by weight.
3. The anode of one of the claims 1 to 2 wherein said titanium alloy includes 0.02-0.04% by weight ruthenium, 0.01-0.02% by weight palladium, 0.1-0.2% by weight chromium and 0.35-0.55% by weight nickel.
4. Anode for electrochemical processes comprising a metallic substrate provided with an electrocatalytic coating containing platinum group metals and/or oxides thereof formed by a multiplicity of individual layers obtained by thermal decomposition of soluble precursors, the metallic substrate being made of a titanium alloy including 0.02-0.04% by weight ruthenium, 0.01-0.02% by weight palladium, 0.1-0.2% by weight chromium and 0.35-0.55% by weight nickel.
5. The anode of any one of the previous claims wherein said individual layers making up said catalytic coating are obtained by successive thermal decomposition steps of overall duration higher than 1 hour.
6. The anode of claim 5 wherein said electrocatalytic coating is further subjected to a final thermal treatment.
7. Electrolytic cell characterised by being equipped with an anode of any one of the previous claims.
8. Use of the cell of claim 7 for the electrolysis of a hydrochloric acid solution.
9. Use of the cell of claim 7 in a chlorine-caustic soda electrolysis process.
10. Use of the cell of claim 7 for an electrometallurgical process with oxygen anodic evolution in an acidic electrolyte.
11. Anode of claims 1 or 4 substantially as hereinbefore described with reference

to any one of the Examples.

12. Electrolytic cell of claim 7 substantially as hereinbefore described with reference to any one of the Examples.
13. Use according to any one of claims 8 to 10 substantially as hereinbefore described with reference to any one of the Examples.