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NL-3508 AB Utrecht (NL)(54) **Anodes with extended service life and methods for their manufacturing.**

(57) Anodes for the generation of electrochemical processes, consisting of a support and an electrocatalytically active top-layer which contains iridium-oxide; a method for producing them and an electrochemical cell in which the anode is applied. The lifetime of such anodes may be prolonged substantially by choosing the oxygen/iridium-ratio between 2.1 and 2.9, the average particle size of the iridium-oxide being between 3 and 100 nm. The lifetime may be prolonged even further by the presence of an intermediate layer, between support and top-layer, consisting of an oxide of Ta, Nb, Co or of Pb or of a mixture thereof, if desired mixed with other metal-oxides. This intermediate layer affixes either directly to the support and the top-layer, or indirectly, via one or more additional intermediate layers.

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The invention concerns industrial electrodes with increased service life, methods for their manufacturing, an electrochemical cell, in which these electrodes are applied and electrochemical processes, in which oxygen gas is generated as main or side product. The invention in particular concerns the composition of and methods for the manufacturing of electrodes, which are used as anodes in industrial electrochemical processes, in which the anodic process consists fully or partly of the generation of oxygen. It also concerns processes, in which these anodes are used.

Such processes take place for example, when the electrolyte contains water and furthermore corrosive components, such as alkali or acid, in particular sulfuric acid, whether or not mixed with other inorganic or organic components.

It has been found that an anode according to the invention may also be used and even offers advantages over existing anodes, when oxygen generation is not the only anodic process or even not the principal anodic process or with other anodic processes. This is for instance the case, when the electrolyte contains sea water.

An anode according to the invention has advantages for oxygen generation in sulfuric acid medium, but also in the use or co-use of other inorganic or organic acids in the electrolyte or in electrolytes with a neutral or acid composition.

These anodes have the special property that they function for a longer period of time during the oxygen generation in sulfuric acid medium than the state-of-the-art Industrial anodes. Moreover, they function for a longer period of time in a number of cases in other electrochemical processes and with electrolytes of other compositions. Processes, in which this extended functioning has been established, include water electrolysis, electroplating of tin, zinc, chromium, nickel and copper, in batch or in continuous processes, sea water electrolysis and cathodic protection.

This invention is based on the demand for a longer service life of anodes than achieved in state-of-the-art anodes. This is necessary because of the heavier working conditions for anodes in advanced electrochemical cells and processes, like a very high current density. For each electrochemical processes, the principle holds that an optimum in service life of the anode is obtained by a certain chemical and morphological composition, layer design and method for manufacturing the anode.

In the literature, many compositions and methods for manufacturing industrial anodes have been described. However, in particular an oxygen-generating anode with an electrocatalytically active coating of an iridium oxide, whether or not mixed with tantalum oxide, has yielded a very stable anode for the use in sulfuric acid as an electrolyte.

Such known anodes are applied onto an electrically conductive support, existing of titanium or another valve metal, such as Ta, Nb, Zr, Hf, Mo and/or W, as such or in an alloy. They have been described in the literature, like by Comninellis et al. and by Busse et al. in the Proceedings of the Symposium on Performance of Electrodes for Industrial and Electrochemical Processes, The Electrochemical Society, Pennington (NJ), Volume 89-10, 1989, p. 229 and 245 respectively. Such anodes may be prepared by dissolving tantalum chloride and/or iridium chloride in an alcohol, in the desired proportions. This solution is applied onto the substrate layerwise followed by a heat-treatment at approximately 450 °C. The resulting anodes yield an extended service life, in sulfuric acid as a test electrolyte, with respect to previously used anode compositions. In several studies, a mixed iridium oxide/tantalum oxide coating (for example in 70/30 ratio) has been found to give the best results in service life under the applied conditions.

Anodes with this composition and by the mentioned method show a good service life with respect to previously used coating compositions and methods, also at the high current densities (for example at 30,000 A/m²), such as those which are applied in modern, rapid, electroplating techniques. Under these conditions, high demands are put on the anodes. Since the prolonged anode service life leads to greater reliability of operation and lower operating costs, achieving an extended service life is an important advantage for the electrochemical industry. The explication below shall reveal the invention and it compares the invention with existing knowledge and technology with respect to service life of such anodes.

Service life of anodes: the roles of crystallinity and adhesion

As described in the literature, various mechanisms exist for the de-activation of such anodes. In practice, this de-activation becomes notable by an increased applied voltage at constant current. Several types of problems are mostly pointed out as responsible for this deactivation, i.e. the growth of an oxygen skin on the substrate (underneath the coating), which acts insulating and detaching on the coating. Also, a loss of electrocatalytic activity of the coating by loss of noble metal and/or its activity have been mentioned. We shall give below insights on these practical problems for a better understanding of the solutions to them, without claiming the completeness or even correctness of the arguments.

It is observed experimentally that during anode manufacturing, by extreme heat treatment in an oxygen atmosphere of the conductive metal support, in particular titanium, or upon oxygen generation by a working anode, an insulating layer is formed of titanium oxide, which approaches the formula TiO_2 in its composition. However, otherwise this oxide may have any composition TiO_x , in which $0 < x < 2$. This titanium oxide
 5 may occur in various structures, among which are the crystal forms rutile and anatase or an amorphous form. We have observed experimentally with the aid of Raman spectroscopy that in our supports and the anodes, made from them according to the invention, the oxide of the Ti support has the rutile structure. This does not exclude however, that anatase and/or amorphous Ti oxides occur after some anode manufacturing methods and/or in some parts of the oxide skin, which occurs on the Ti metal.

10 Crystalline iridium dioxide IrO_2 occurs in the same crystal form (rutile) with crystal lattice distances, which are not too different from rutile TiO_2 . We believe therefore that this agreement in crystal structures may be a major reason for our observation that IrO_2 and TiO_2 layers show good adhesion. This may be one explanation, why iridium oxide coatings, according to the invention, have such a good service life. The layered structure of the coating and the heat treatment after each application of a layer promotes the good
 15 adhesion between the titanium support oxide and the deposited iridium oxide, also between the successive iridium oxide deposits.

However, the titanium oxide, which is formed during the anode action does not undergo such an adhering heat treatment. Moreover support oxide growth leads to a support volume increase. Therefore, this oxide growth may lead to detachment of the coating from the support and it may limit the service life of the
 20 anode.

Also, it is true that the electrical conduction of the anode is restricted by conversion of titanium oxide TiO_{2-x} , grown on the Ti support as oxygen deficient and therefore electrically conductive oxide (an n-type semi-conductor), into the stoichiometric, non-conductive TiO_2 . This conversion is effectuated by the highly oxidising environment, which is created by the anode during oxygen generation.

25 To prevent these two effects of formation of an insulating titanium oxide layer and detachment of the coating, the use of an intermediate layer (type A) has been proposed. This layer prevents the penetration of corrosive electrolyte to the underlying metal support. Thereby it is prevented that electrocatalytic processes are started at the support with the mentioned damaging effects, also by intermediates in these processes. An example is the German Patent Application DE 3219003, which describes an electrode for oxygen
 30 generation, consisting of a Ti support, an intermediate layer of a conductive oxide of tantalum and/or of niobium in quantities between 0.001 and 2 g/m², with an electrode coating of Ta_2O_5 and/or IrO_2 . This intermediate layer is found to be very effective for protection of the support and for extending the service life of the anode. However, that invention uses stoichiometric iridium dioxide and ditantalum pentoxide. In the present invention it is found that the composition IrO_2 has electrocatalytic properties, which are far
 35 inferior to a special form of so-called 'hydrous iridium oxide', iridium hydroxy-oxide, which contains many hydroxyl groups, especially at the electrocatalytically active surface, e.g. represented by the approximate structural formula $\text{IrO}(\text{OH})_2$. In this latter iridium hydroxy-oxide, hereafter called iridium oxide, the oxygen/iridium ratio is 3, whereas in IrO_2 this ratio is 2.

By determining the O/Ir ratio in an iridium oxide, one characterises this oxide. Hydroxy-oxides $\text{IrO}_2 + x\text{H}_y$
 40 are characterised by a molar excess x of oxygen and a molar amount y of hydrogen.

Also, the iridium oxide must be stable and conduct the electrical current well during the entire anode service life. For that purpose, the composition IrO_2 is well-sintered. Also, one needs well-developed and well-sintered particles of the iridium oxide electrocatalyst.

Thus, the two demands on the electrocatalytically active top layer, containing iridium oxide, are
 45 contradictory in nature and a well-balanced compromise has been reached in anodes according to the invention.

The invention

50 Anodes, according to the invention contain iridium oxides, in which the O/Ir ratio is larger than 2, e.g. 2.5. They are prepared according to specific procedures and they show variations to larger and smaller x in $\text{IrO}_2 + x$, depending on the chosen manufacturing conditions.

Thus, improved anode top layers have been obtained with an O/Ir ratio between 2.1 and 2.9. It is probable that in this material are combined the properties of electrically well-conducting IrO_2 and of an
 55 electrocatalytically very active material, like for instance a composition $\text{IrO}(\text{OH})_2$. This is not meant to exclude other compositional possibilities.

This mixed oxide/hydroxide of iridium shows both a long-lived good electrical conduction and a high electrocatalytic activity, resulting in material with a surprisingly long-lived electrocatalytic stability. It differs

considerably in chemical composition from stoichiometric IrO_2 , but also, according to crystallographic/morphological analysis with X-ray powder diffractometry (XRPD) and high-resolution transmission electron microscopy (HR-TEM) it has a crystal structure, which may best be described as 'rutile-like', a modified IrO_2 structure.

Furthermore, this material consists of sintered crystallites with an individual particle size mainly between 5 and 15 nm for a number of very durable anode samples. However, also for anodes with smaller and larger iridium oxide particles (3-100 nm), a very high electrocatalytic activity and stability of the anodes has been found with respect to anodes, prepared by previously described procedures. Surprisingly, this iridium oxide, whether or not mixed with tantalum oxide, is both very active and stable for a long time in anodes, according to the invention.

It seems essential for obtaining these properties to choose a right combination of starting compounds, concentrations, the solvent (e.g. n-butanol) and the applied heating procedures, in particular heating temperatures, heating times and temperature gradients. Thus, an anode is obtained, according to the invention, of which the electrocatalytically active top layer signifies an improvement with respect to known top layers, like the ones described in the German patent DE 3219003.

Hereafter, differences are indicated between the iridium oxide, as applied in anodes according to the invention and the iridium oxide, as described in the literature, in particular during the presence of tantalum oxide in the electrocatalytically active top layer, with Ir/Ta metal mole ratios, which are identical or almost identical. These differences are brought about by the differences between the known methods for the manufacturing of iridium oxide, whether or not mixed with tantalum oxide, and the methods according to the invention.

In British Patent GB 1399576 a mixed crystal material is used of tantalum oxide and iridium oxide. The definition of a mixed crystal material has been given in British Patent GB 1195871, among other references, as: 'By mixed-crystal material is generally understood that the molecular lattices of the oxide of the film-forming metal ... (in casu tantalum oxide) ... 'are intertwined with the molecular lattices of the other material constituting the coating.' (in casu iridium oxide), and further: 'The importance of the restriction that the coating must behave as a mixed-crystal material rather than as a mere mixture of the two oxides can be shown by means of several examples.' From this it follows that a mixed-crystal material has a different structure than a real mixture of the two oxides at the same gross chemical composition. A mixed-crystal material of iridium oxide and tantalum oxide has other anode properties, among which stability and service life, than a real mixture of these oxides.

In an anode, according to the invention, iridium oxide is present as such, or in mixtures with other metal oxides, in a very finely divided crystalline form, as established by XRPD and HR-TEM. Where present, tantalum oxide is present in a non-crystalline, amorphous phase. Therefore, no mixed-crystal material of iridium oxide and tantalum oxide has been obtained.

Comninellis and Vercesi, Journal of Applied Electrochemistry 21 (1991) 335-345, have described the morphology of their anodes with $\text{IrO}_2/\text{Ta}_2\text{O}_5$ coatings on Ti basis. They found with scanning electron microscopy (SEM) that IrO_2 occurs, partly in the form of crystal needles, having dimensions at least larger than 100 nm, typically up to several micrometers. Furthermore, they find that the remainder of IrO_2 is dispersed in the amorphous phase. Also, they suggest a correlation between electrocatalytic activity and the density of the needles on the coating surface.

In the electrocatalytically active top layer of iridium oxide, whether or not mixed with tantalum oxide, according to the invention, such needles have not been found. The iridium oxide occurs in a so-called nanocrystalline form with an usual particle size distribution far below 100 nm. Also the dimensions of the crystalline unit cell (measured according to the rutile structure) deviate significantly from those of pure rutile IrO_2 , as known from the ASTM-Powder Data File and as found by Comninellis and Vercesi. Iridium oxide as used in the invention, whether or not in a mixture with tantalum oxide (preferably less than 20 mole percent, calculated as Ta_2O_5), may be converted by heating at 800 °C or above into well-crystallised and well-characterised rutile- IrO_2 . However, it loses its excellent properties as long-lived, electrocatalytically very active top layer by this treatment.

In another composition of the anode, according to the invention, an electrocatalytic top layer is used, consisting of mixed oxides of iridium oxide and cobalt oxide, or iridium oxide and lead oxide, or iridium oxide with a mixture of these two oxides. Such a top layer is manufactured by a similar method as described in the invention for mixed iridium/tantalum oxides. Also, an anode, according to the invention, with a top layer of iridium/tantalum/cobalt oxide, containing preferably at least 50 mole percent of iridium oxide, gives an improved service life with respect to known anodes.

An anode, according to the invention, contains therefore in the electrocatalytic top layer a special form of iridium oxide, having the formula $\text{IrO}_2 + x\text{H}_2\text{Y}$, characterised by a O/Ir ratio $(2+x)$ higher than 2, viz.

between 2.1 and 2.9 and preferably with an O/Ir ratio around 2.5. The special composition and morphology of the iridium oxide, present in anodes, according to the invention, may be obtained by one of the methods, according to the invention and possibly by other methods, which are not described in the invention.

5 Application of intermediate layers

An anode, according to the invention, has an electrocatalytic coating (top layer), consisting of iridium oxide and cobalt, lead and/or tantalum oxide, preferably with at least 50 mole percent iridium oxide and no more than 20 mole percent tantalum oxide, which top layer is directly deposited onto the support or through
 10 one or more intermediate layers. The intermediate layers serve to protect the support from the corrosive action of the electrolyte and the (intermediate) products of the electrochemical process or the process itself. They also serve for adhesion between support and either an intermediate layer or a top layer, or between an intermediate layer and top layer, or a combination of these layers. The definition of support also includes for this purpose the oxide skin, which is present on it before it undergoes a method according to the
 15 invention or the oxide skin, which is formed on the substrate as a consequence of a method for manufacturing an anode according to the invention, in an electrochemical cell according to the invention or as a consequence of an electrochemical process, using an electrochemical cell, according to the invention.

In a preferred embodiment of an anode according to the invention, a longer service life is realised by combining a top layer of iridium oxide or iridium oxide, mixed with tantalum oxide, with an intermediate
 20 layer of type A, consisting preferably of tantalum oxide with 0-49 mole percent of iridium oxide, cobalt oxide or lead oxide, or a mixture of two or more of these three metal oxides. In another preferred composition, the tantalum oxide in the intermediate layer is fully or partly replaced by iridium oxide with similar service life. In a further preferred embodiment, the intermediate layer has a different composition, type B, containing electrically conductive titanium oxide or tin oxide.

25 This embodiment may be realised as described hereafter, for example by manufacturing tin oxide with the approximate chemical formula SnO_2 , mixed with indium oxide to give a solid solution of indium tin oxide (ITO) or other mixture, or by manufacturing titanium oxide with approximate chemical formula TiO_2 , mixed with tantalum oxide, in particular with ditantalum pentoxide Ta_2O_5 , whether or not in a solid solution.

The layer thickness of an intermediate layer (measured as the quantity of metal coverage in g/m^2) may
 30 be as large as that of the top layer, but in many investigated anodes it is smaller. For practical reasons, in many anodes according to the invention the coverage by iridium oxide in the top layer is approximately 10 g/m^2 , calculated as the noble metal. However, the extension of service life by compositions and methods according to the invention has been found also for anodes with a lighter or heavier coverage with iridium oxide.

35 An anode according to the invention is schematically built up as follows, in its most simple form (type 1).

Type 1:
 Support | top layer.

40 The schematic built-up of an anode with one intermediate layer of type A (called anode type 2) is as follows:

Type 2:
 45 Support | intermediate layer type A | top layer.

Furthermore it has been found that the service life of an anode may be prolonged by using two intermediate layers, viz. one of type A and one of type B, which are described below. These layers may be applied with either different composition or with different methods or with both. A possible explanation is
 50 that one of these intermediate layers, further called type A, is so chosen that it provides an optimum protection of the underlying support and the native oxide layer on it against penetration of the electrolyte and of the products or intermediates of the electrochemical process of oxygen generation and/or of the other electrochemical processes, occurring in the electrolyte. This layer A serves to prevent the further growth of an oxide skin on the underlying support. This oxide growth is a main cause for de-activation of an
 55 anode upon prolonged use, in particular during oxygen generation and even more in particular with an electrolyte, containing sulfuric acid.

The other intermediate layer, type B, may serve in this explanation in particular for promoting the adhesion between the layers above and under it. Also it will retard the de-activation of the anode by

detachment of adjacent layers.

In the following the correctness of this explanation is assumed for better describing the improved action of intermediate layers on the service life of anodes in the invention.

The two-in-one function (protection and adhesion) of one intermediate layer is now split up in two intermediate layers with different functions and different possibilities for composition and manufacturing. This splitting of the two functions is schematic and possibly oversimplified. However, it has led to a realisation of an increased service life with respect to corresponding anodes with one intermediate layer, which is ascribed to a separate optimisation of the specific functions of each intermediate layer.

It shall be clear that in the layered structure of an anode according to the invention the second intermediate layer may be built-in in two ways, types 3 and 4, which are illustrated in the following scheme.

Schematic structure of anodes according to the invention, with a support, two intermediate layers and a top layer.

Type 3:

Support | intermediate layer type A | intermediate layer type B | top layer.

Type 4:

Support | intermediate layer type B | intermediate layer type A | top layer.

Also it shall be clear that this structure may be extended as desired to three intermediate layers, in which the intermediate layer type A is provided on both sides by an intermediate layer type B, both layers being applied with equal or different compositions and/or methods. This leads schematically to an anode structure, type 5.

Type 5:

Support | intermediate layer type B | intermediate layer type A | intermediate layer type B | top layer.

The description, given here, of the action of the intermediate layers is only meant to explain the service life-extending action of intermediate layers. It does not in any way restrict the scope of application of the anodes in question.

In Figure 1 through 5, the anode structure according to types 1 through 5, respectively, are illustrated, for the sake of simplicity on a flat support. It shall be clear that anodes with these layer structures, according to the invention, may exist also with other support forms, like cylinders or in gauze.

The choice of materials and manufacturing methods for the anode structure with two types of intermediate layers, according to the invention, leads to the following description.

MATERIALS CHOICE

Intermediate layer type B

Upon use of the preferred support, titanium or an alloy of titanium with one or more valve metals, like Ta, Nb, Hf or Zr, an oxide skin may be formed on the titanium upon application of a method according to the invention, the oxide having a rutile or rutile-like structure. Also the iridium oxide in the top layer has a rutile-like structure. The intermediate layer B shall therefore be preferably composed of one or more metal oxides with a rutile (-like) structure, schematically represented by the chemical formula MO_2 . This formula also includes those oxides, which are often described as MO_2 , but which are actually characterised by small deviations of stoichiometry, e.g. with deviations in the oxygen stoichiometry of no more than 0.1, or by lattice defects.

Metal oxides with rutile structure have been described, e.g. by Rogers et al. in Inorganic Chemistry 8 (1969) 841. They occur among other metals in single or composite oxides for Ti, Sn, Si, Ge, Mn, Cr, V, Rh, Ru, Ir, Pt, Re, Os, Mo, W, Ta, Nb or Pb. The dioxides MO_2 of these metals may therefore in principle be used for improvement of the adhesion of two layers of an anode, e.g. on a Ti basis, thus extending the service life.

In the intermediate layer or layers B, those metal oxides MO_2 with a rutile structure are applied in the invention, which effectively conduct electrical current. This is in particular the case for those rutile-metal oxides MO_2 , which show metallic conduction themselves, such as IrO_2 , RuO_2 or PtO_2 , and for those metal oxides MO_2 , which may become n- or p-type semi-conducting oxides by a small modification. For a non-stoichiometric iridium oxide $\text{IrO}_2 + x$ we expect p-type conduction. This p-type behaviour is well known to be

supported by doping with small amounts of lower-valent metals, which may be present in amounts, varying from parts per hundred-thousand to over one percent. The presence of such amounts of these metals may improve the service life of anodes.

N-type behaviour is found for example in modified TiO_2 and SnO_2 . A well-known example of conductive SnO_2 is iridium-tin oxide, which has been successfully applied in the invention.

For titanium oxide the modification may be carried out in two ways.

The first is the one, in which titanium oxide has the formula TiO_{2-x} , with x any value between 0.001 and 0.6. For small x -values up to approximately 0.008, the original rutile structure of TiO_2 is kept. For larger values of x , so-called Magneli phases are formed with modified rutile structures, like those described by Millot and others in Progress in Solid State Chemistry 17 (1987) 263-293. Both forms of oxygen-deficient TiO_{2-x} are useful for application in adhering intermediate layers. However, these oxides TiO_{2-x} have a tendency to oxidise in the oxidising environment during anode operation, thereby reducing the oxygen deficiency x . Such an oxidation may lead upon prolonged continuation to the formation of non-conductive TiO_2 , therefore to anode de-activation. For this reason, the application of this way to make the titanium oxide conductive is preferably done by using at least one Magneli-phase material, represented by the molecular formula $\text{Ti}_n\text{O}_{2n-1}$, with $n = 3-8$, i.e. with O/Ti ratios between 1.66 and 1.875, therefore with x -values between 0.125 and 0.34. These oxides may both be obtained separately (ex-situ) as well as on the substrate (in-situ). For that purpose the literature gives various methods, for example in the references of the cited article by Millot et al. In the invention, the manufacturing of titanium suboxides TiO_{2-x} is preferably carried out in situ, by heating of a suitable, commercially available titanium-containing precursor, such as TiCl_4 or tetrabutyl titanate, in a suitable atmosphere (vacuum or another inert atmosphere, low in oxygen gas pressure). Also and in particular, plasma spraying of titanium oxide particles, will yield a good result, in vacuum or in air atmosphere. These stable titanium oxide intermediate layers prolong the anode service life according to the invention.

The second approach for obtaining conductive titanium oxide consists of introducing higher-valent metal ions for substitution of the tetravalent titanium ion in the oxide. A doped titanium oxide $\text{Ti}_{1-h}(\text{M}_h)\text{O}_{2+k}$ is applied, in which a small part h of the Ti is replaced by pentavalent ions, like Ta or Nb, or hexavalent ions as Mo or W, with a possible simultaneous increase of the oxygen stoichiometry by an amount k . These doped titanium oxides have been found not to be subject to oxidation to the same extent as TiO_{2-x} . Therefore, they are more stable in anodes as intermediate layer B than the corresponding anodes with oxygen-deficient oxides. Therefore, an anode according to the invention preferably contains titanium oxide, homogeneously doped with niobium oxide and/or tantalum oxide, the iridium and/or tantalum contents of the titanium oxide being minimally 0.0010 mole percent, but preferably over 0.0025 mole percent with an upper limit not exceeding 10 mole percent. At equal doping levels, the anode with titanium oxide, containing tantalum oxide as intermediate layer B, is more stable than the one with titanium and niobium oxide. Therefore the titanium oxide/tantalum oxide intermediate layer B is preferred. The solubility of tantalum oxide in solid titanium oxide is some weight percents with the materials and methods of the invention. Additional non-dissolved tantalum oxide is present as a second phase. It does not disturb the good action of the mixed oxide in the intermediate layer up to 70 mole percent of tantalum.

An intermediate layer of type B in an anode according to the invention in this embodiment contains preferably a mixture of titanium oxide and tantalum oxide, with minimally 0.0010 and preferably minimally 0.0025 mole percent of tantalum and maximally 70 mole percent. This intermediate layer is preferably obtained by dissolving titanium and tantalum compounds, preferably titanium tetrachloride or tetrabutyl titanate and tantalum pentachloride or tantalum penta-chloride or -butoxide, in an alcohol, for example n -butanol, and by applying the solution by the same method as the other layers, which are applied before or after this intermediate layer, whether or not with addition of hydrochloric acid.

Furthermore, service life-extending action has been obtained by admixture in the intermediate layer type B of the following rutile-type metal oxides, which have not been mentioned before: SiO_2 , CeO_2 , MnO_2 , CrO_2 , VO_2 (tetragonal or monoclinic), RhO_2 , $\alpha\text{-ReO}_2$, OsO_2 , MoO_2 , WO_2 , TaO_2 , NbO_2 and PbO_2 . This includes also those metal oxides $\text{MO}_2 + x$ with a rutile or rutile-like structure, in which the stoichiometry deviates from the ideal value 2 by an amount x ($0 < x < 0.5$).

The materials choices and/or the layer sequences in the anodes according to the invention differ from those of known anodes.

In British Patent GB 2239260, an electrode is described with long service life for oxygen generation, in which two types of layers are applied interchangeably. This electrode may be manufactured with one lower layer and one upper layer, so that it shows agreement with an electrode (anode) according to the invention. However, that electrode possesses a lower layer, which is composed of 40-79.9 metal mole percent of iridium oxide and 60-20.1 metal mole percent of tantalum oxide, plus an upper layer, which is composed of

80-99.9 metal mole percent of iridium oxide and 20-0.1 metal mole percent of tantalum oxide. In that electrode, a large amount of the expensive noble metal iridium is used in the lower layer. In an electrode (anode) according to the invention, having one intermediate layer of tantalum oxide with iridium oxide and a top layer of iridium oxide with tantalum oxide, the lower layer contains less iridium oxide, namely 0-39 metal mole percent, yielding a surprisingly good service life.

In Japanese Patent JP 2-190491 a top layer is described, containing 5-95 mole percent of iridium oxide and additional tantalum oxide, with an intermediate layer of a platinum dispersion in tantalum oxide, whether or not mixed with iridium oxide, up to 20 mole percent. This platinum dispersion is not used for anodes according to the invention, because it may lead to dissolution of the noble metal upon prolonged contact with the electrolyte, therefore to distabilisation of the intermediate layer and also because it increases the costs of the intermediate layer.

In publication JP 2-61083 a top layer of 30-80 mole percent of iridium oxide is described, containing 70-20 mole percent of tantalum oxide, with an intermediate layer of 85-95 mole percent of tantalum oxide and furthermore iridium oxide. The formula of the iridium oxide is given as IrO_2 and of the tantalum oxide as Ta_2O_5 . In a preferred composition according to the invention another composition of iridium oxide is used in the top layer, namely $\text{IrO}_2 + x\text{H}_y$, calculated as IrO_2 , with less than 20 mole percent of tantalum oxide, calculated as Ta_2O_5 .

In publication JP-63-235493 the top layer consists of iridium oxide. The intermediate layer contains maximally 50 mole percent Ta in the form of tantalum oxide, furthermore iridium oxide. In the preferred composition of the intermediate layer according to the invention, it contains 60-100 mole percent tantalum as tantalum oxide, plus iridium oxide or another oxide in 39-0 mole percent.

In publication JP-60-22074 a top layer of iridium oxide or iridium oxide with tantalum oxide is mentioned, together with an intermediate layer of tantalum oxide with titanium oxide and/or tin oxide.

In the published German Patent Application DE 3401952 an intermediate layer is used of tantalum oxide, titanium oxide and/or tin oxide, moreover containing a platinum dispersion, in combination with a top layer of iridium oxide or iridium oxide with tantalum oxide.

Anodes, which are manufactured according to these published methods and with the mentioned compositions, deviate in essential points from anodes according to the invention. For the latter anodes, a longer service life is found at the same or even lower costs, or the extended service life more than compensates for higher costs.

Manufacturing methods

A method for manufacturing anodes according to the invention consists of cleaning a support and preferably by etching it, to remove undesired surface oxides and other surface components, among which surface contaminants. The support may be subsequently kept clean in a non-oxidising environment or it may form a natural oxide skin in an oxidising environment, for example air.

Subsequently, solutions of the desired metal compounds and compositions are applied to the support, layerwise, with suitable application methods, like those which are usual in the paint industry, like by painting with a brush or roller. These solutions onto the support are subsequently dried at ambient or higher temperature. These solutions, which are called 'paint' in the production, are preferably prepared from metal compounds, which are soluble in alcohols with the chemical formula $\text{C}_n\text{H}_{2n} + 1\text{OH}$, preferably with n-values ranging from 1 to 5, more in particular with $n = 4$ and especially with normal butanol. In these solutions water may be present by accident or on purpose as a minor or major component. The metal compounds must be soluble in the alcohol or the aqueous alcohol or in water. In the latter case they will remain in solution by dispersing well or by addition of the alcohol.

Suitable precursors are metal chlorides, like tantalum pentachloride TaCl_5 and titanium tetrachloride TiCl_4 , also the chloroiridic acid H_2IrCl_6 is taken in this category, in all occurring forms, including hydrates and aqueous solutions; metal alkoxides, among which are mentioned tetra-alkoxy-titanium and penta-alkoxy-tantalum compounds, like tetra-ethoxy and tetra-butoxy-titanium and penta-ethoxy- and penta-butoxy-tantalum; metal b-diketonates, like the acetylacetonates, dipivaloylmethanates (also called tetramethyloc-tanedionates) and tri- or hexafluoroacetyl-acetonates of iridium, tantalum, cobalt or titanium. The concentrations of the metal compounds may vary per applied layer. Per 'paint' layer a heat treatment may be given or per complete functional layer according to anode types 1 through 5. By repeated 'painting', the layer will obtain the desired layer thickness. For each subsequent layer another method may be applied. Upon heat treatment of a layer, the support and all previously applied layers will undergo this heat treatment. The temperature may be increased to the desired end temperature, preferably between 400°C and 650°C , very rapidly, more slowly, or stepwise.

All factors mentioned above have an influence on quality and service life of the anode.

For application of intermediate layers, other methods are also very suitable. For instance, during anode manufacturing, one or more adhering and/or protecting intermediate layers have been made in a vacuum oven or in ovens with an inert (= non-oxygen-containing or oxidising) gas atmosphere, at temperatures
 5 between 400 °C and 1000 °C, resulting in an anode with long service life.

Upon application of an intermediate layer, consisting of tantalum oxide and/or niobium oxide, whether or not mixed with titanium oxide, by plasma spraying, the resulting anode has a long service life.

An anode according to the invention, therefore with extended service life, especially distinguishes itself physically from known anodes by an electrocatalyst, which is based on iridium oxide, including mixtures of
 10 iridium oxide with other metal oxides, having a composition and morphology, which deviate from those of known anodes for oxygen generation, based on iridium oxide. Both the materials choice and the manufacturing method are of importance for this result. Extended service life of anodes has been achieved also by application of one or more protecting and/or adhering intermediate layers of different compositions and by various methods.

Also, it has been found that an electrochemical cell, in which oxygen is generated, besides possibly other anodic products, has a longer service life, when it contains an anode according to the invention. In particular this is the case when the electrolyte has an acid composition, like when it contains sulfuric acid besides other components, like water. However, when the electrolyte has a basic composition or when it contains sea water or other sodium chloride or other metal chloride-containing components, the cell with an
 15 anode according to the invention demonstrates an extended service life with respect to corresponding cells with a known anode. Therefore it can be said that an oxygen-generating electrochemical process is preferably carried out in an electrochemical cell, containing an anode according to the invention.

EXAMPLES

The invention shall be demonstrated with some examples. In these examples the indicated compositions of oxide mixtures have been calculated with the number of moles of the stoichiometric compounds, for instance iridium oxide as IrO₂ and tantalum oxide as Ta₂O₅. Furthermore, it is noted that only within one
 25 Example anodes have been compared, as they have been prepared and tested in the same way, unless the Example teaches otherwise.

Example 1

Anodes 1-3 were prepared according to the invention by dissolving a mixture of chloroiridic acid H₂IrCl₆ and tantalum pentachloride TaCl₅ or tantalum penta-ethoxide Ta(OEt)₅ in n-butanol in the desired proportions, until a total concentration of the metals was reached of 7 weight percent. This 'paint' was layerwise applied with a brush onto a cleaned and etched titanium cylinder with a diameter of 3 mm and a surface area for submersion into the electrolyte of 1 cm². After application of each layer, the anode was placed in an oven, which was heated to 450 °C and kept there for 20 minutes in an air atmosphere. In total, appr. 10
 35 g/m² noble metal was applied on every anode. These anodes were connected by a titanium holder to a measuring equipment.

The service life test in this Example and all following Examples was carried out by submersing the anodes in 37 percent sulfuric acid as electrolyte. The cell further consisted of two counter electrodes, made of graphite plate. The current density was 50,000 A/m². This current density was kept constant during the
 40 service life test by regulating the voltage. The cell temperature was 40 °C. As the end of the service life the time was chosen, where the applied voltage was twice the value of the initial voltage. Measured service lifes are given in Table 1.

Service lifes of anodes, which were obtained on a 99/1 Ti/Ta alloy were not significantly different from those with the Ti support.

Table 1

Service life of anodes with various precursors				
Anode nr.	Top layer composition (mole%)	Tantalum compound	Noble metal coverage (g/m ²)	Service life (days)
1	IrO _x /TaO _x (85/15)	Ta(OEt) ₅	10.4	2.5
2	IrO _x /TaO _x (85/15)	Ta(OEt) ₅	11.5	2.5
3	IrO _x /TaO _x (85/15)	TaCl ₅	10.4	3

From this it is concluded that tantalum pentachloride and tantalum penta-ethoxide are both suitable precursors for the manufacturing of top layers of mixed iridium oxide/tantalum oxide. See also Claims 2, 32-35, 41, 42 and 45.

Example 2

Anodes 4-6 were manufactured according to the invention, with an electrocatalytic top layer of iridium oxide or of mixed iridium oxide/tantalum oxide, according to the method of Example 1. For comparison, also anodes 7-9 were manufactured with iridium oxide and with iridium oxide, mixed with tantalum oxide, by a method which differs from that of Example 1 and also anode 10 was manufactured, again by a different method. Anodes 4-10 were investigated with X-ray diffractometry XRD, HR-TEM and the IrO_x top layer in elemental analysis. The analyses demonstrate that anodes 4-6 contain the iridium oxide in a very finely divided nanocrystalline form with individual particle size around 10 nm. The O/Ir ratio in anodes 4 and 5 is around 2.5. In the tantalum oxide-containing anode 6, the tantalum oxide is present as an amorphous phase, next to rutile-like iridium oxide particles. Anodes 7-9 show crystalline IrO₂ in the rutile structure with particle sizes greater than 100 nm and O/Ir ratios in anodes 7 and 8, which are close to 2.

The tantalum oxide in anode 9 is present in separate crystalline phases of Ta₂O₅. The analyses of anode 10 show that no visible crystallinity is present (individual particle size smaller than 3 nm) and that the O/Ir ratio is high, around 3.0.

The results of the elemental analyses and of service life tests, according to Example 1, however at a current density of 30,000 A/m², are given in Table 2.

Table 2

Analyses and service lifes of anodes on the basis of various types of iridium oxide or of mixed iridium oxide/tantalum oxide				
Anode nr.	Composition top layer (mole%)	O/Ir ratio	Particle size (nm)*	Service life (days)
4	IrO _x	2.4	11	13
5	IrO _x	2.6	10	12
6	IrO _x /TaO _x (85/15)		8	32
7	IrO _x	2.0	> 100	5
8	IrO _x	2.05	> 100	6
9	IrO _x /TaO _x (85/15)		> 100	9
10	IrO _x	3.1	< 3	6

* Average value.

From these results it is concluded that, in iridium oxide or mixed iridium oxide tantalum oxide top layers, a form of iridium oxide is present which is very suitable for application in oxygen-generating anodes with a long service life, when these top layers are deposited by a method according to Example 1. This iridium oxide consists of very small crystalline particles of about 10 nm with a rutile-like structure. The O/Ir ratio in these particles is around 2.5, which is significantly higher than has been found for well-crystallised

IrO₂ with a rutile structure and particle size above 100 nm. No indications have been found for the formation of a so-called mixed-crystal material of iridium oxide and tantalum oxide under these conditions. In the iridium oxide/tantalum oxide anode, after heating by a method according to Example 1, an amorphous tantalum oxide phase is present and in the well-crystallised IrO₂ also crystalline Ta₂O₅. These crystalline compounds with big IrO₂ particles do not give mixed-crystal material here. They also show a short service life as a top layer in an anode. The service life of an anode may also be increased by addition of tantalum oxide to the top layer of iridium oxide. See also Claims 1, 26 and 30.

Example 3

Flat plate anodes 11-17 were manufactured, according to Example 1, having dimensions of 2.5 x 2.5 cm², at a different heating temperature of 420 °C, however and at various ratios between the amounts of iridium oxide and tantalum oxide, at a noble metal coverage of 10 g/m². Service lives were measured as recorded in Table 3, at a current density of 10,000 A/m² and an equal cell temperature for all cells, amounting to 30-35 °C during testing.

Table 3

Service life of anodes with various compositions of the top layer		
Anode nr.	Top layer composition (mole%)	Service life (days)
11	IrO _x /TaO _x (60/40)	14.5
12	IrO _x /TaO _x (70/30)	21.5
13	IrO _x /TaO _x (75/25)	89
14	IrO _x /TaO _x (80/20)	124
15	IrO _x /TaO _x (85/15)	283
16	IrO _x /TaO _x (90/10)	186
17	IrO _x	112

From this Table it follows that addition of tantalum oxide to iridium oxide in the top layer yields an improvement of the anode service life up to a certain composition, which is in this case at a mole ratio of appr. 85/15 of iridium oxide/tantalum oxide. See in this connection Claim 26.

Example 4

Anodes 18-24 were manufactured and tested with an iridium oxide/lead oxide top layer, according to Example 2, however with a cell temperature of 50 °C. The lead precursor was dibutyllead diacetate. The measured service lives are given in Table 4.

Table 4

Service lives of anodes with a top layer of iridium oxide/lead oxide		
Anode nr.	Top layer composition (mole%)	Service life (days)
18	IrO _x	5.0
19	IrO _x /PbO _x (95/5)	8.4
20	IrO _x /PbO _x (90/10)	14.1
21	IrO _x /PbO _x (85/15)	13.1
22	IrO _x /PbO _x (80/20)	13.3
23	IrO _x /PbO _x (75/25)	14.3
24	IrO _x /PbO _x (70/30)	8.5

From this Table it is concluded that addition of lead oxide to iridium oxide in the top layer gives an improvement of the service life of anodes up to a certain composition, which corresponds with less than 30 mole % lead oxide. See in this connection Claim 28.

Example 5

Anodes 25-27 were manufactured according to Example 1, with a top layer and no or one intermediate layer. The intermediate layer was manufactured from the metal chlorides, following a method as described in Example 1 for the top layer. The testing, however, differed from Example 1 by the current density, 30,000 A/m², and a cell temperature of 33 °C. The noble metal coverage for the top layer was 10 g/m², as was the total metal coverage for the intermediate layer. Service lives are given in Table 5.

Table 5

Service lives of IrO _x /TaO _x anodes with or without intermediate layer			
Anode nr.	Top layer composition (mole%)	Intermediate layer composition (mole%)	Service life (days)
25	IrO _x /TaO _x (85/15)	no intermed. layer	18.5
26	IrO _x /TaO _x (85/15)	CoO _x /IrO _x (60/40)	23
27	IrO _x /TaO _x (85/15)	TaO _x /IrO _x (61/39)	25

From this Table it follows that an intermediate layer of cobalt oxide/iridium oxide or of tantalum oxide/iridium oxide increases the service life of anodes with an identical top layer. See in this connection Claims 3-5 and 7.

Example 6

Anodes 28-30 were manufactured according to Example 1, with an iridium oxide/cobalt oxide top layer and a noble metal coverage of 10 g/m², having an intermediate layer of tantalum oxide/iridium oxide with a total metal coverage of 10 g/m². They were tested for service lives at a current density of 30,000 A/m². The results are given in Table 6.

Table 6

Service lives of iridium oxide/cobalt oxide anodes			
Anode nr.	Top layer composition (mole%)	Intermediate layer composition (mole%)	Service life (days)
28	IrO _x	TaO _x /IrO _x (61/39)	10
29	IrO _x /CoO _x (74/26)	TaO _x /IrO _x (61/39)	14
30	IrO _x /CoO _x (60/40)	TaO _x /IrO _x (61/39)	8

From this table it follows that addition of cobalt oxide to a top layer of iridium oxide by a method according to the invention increases the anode service life in the presence of an identical intermediate layer of tantalum oxide/iridium oxide, up to a certain composition, which corresponds to less than 40 mole percent of cobalt oxide. See Claim 27 in this connection.

Example 7

An anode (nr. 31) according to the invention was manufactured on a flat Ti plate. First an electrically well-conducting intermediate layer was deposited by plasma spraying of titanium dioxide (rutile) in vacuum, resulting in a layer thickness of 30 μm. Next, a second intermediate layer of tantalum oxide (3 g/m² of tantalum) was applied and on top of that a top layer was deposited, consisting of iridium oxide/tantalum oxide (mole ratio 85/15) to give a noble metal coverage of 10 g/m², using a method, according to Example 1, however at a heating temperature of 550 °C. The service life of this anode was 36 days at a current density of 30,000 A/m² and a cell temperature of 40 °C, which compares favourably with the service life of a comparable anode (nr. 32) without the titanium oxide intermediate layer, 19 days.

The composition of the titanium oxide intermediate layer was verified after plasma spraying with the aid of XRD. It mainly consisted of so-called Magneli phases with chemical composition Ti_nO_{2n-1}. See Claims 10-14 and 22.

Example 8

Anodes 33-39 were manufactured and tested for service life, according to Example 5, with no, one, two or three intermediate layer(s). The top layer was a mixture of iridium oxide and tantalum oxide in a 85/15 mole percent ratio and a noble metal coverage of 10 g/m². The intermediate layers were applied with a total metal coverage per layer of 5 g/m², according to the method for the top layer of Example 1, using metal chlorides, metal alkoxides or metal-b-dikatonates with similar results. The results are given in Table 7.

Table 7

Service lifes of anodes with various numbers and kinds of intermediate layers				
Anode nr.	Top layer composition (mole%)	Intermediate layer number*	Intermediate layer composition (mole%)	Service life (days)
33	IrO _x /TaO _x (85/15)	no interm. layer	no interm. layer	18.5
34	IrO _x /TaO _x (85/15)	1	TaO _x /IrO _x (61/39)	25
35	IrO _x /TaO _x (85/15)	1	TaO _x	29
36	IrO _x /TaO _x (85/15)	1 2	TiO _x ** TaO _x	34
37	IrO _x /TaO _x (85/15)	1 2	TiO _x /TaO _x (95/5) TaO _x	35
38	IrO _x /TaO _x (85/15)	1 2 3	TiO _x ** TaO _x TiO _x **	37
39	IrO _x /TaO _x (85/15)	1 2 3	TiO _x ** TaO _x TiO _x /TaO _x (95/5)	42

* Layer sequence from substrate

** By vacuum plasma spray

From this Table it follows that, at identical top layer, the service life of anodes increases with the number of intermediate layers, one of these in this Example consistently is tantalum oxide. Application of a titanium oxide layer on one side and even better on both sides of this protecting layer increases the service life of the anode. It is favourable for the service life when the TiO_x-layer/-layers is/are deposited by vacuum plasma spraying VPS, or if the TiO_x is deposited together with some TaO_x, according to a method of Example 1. See in this connection Claims 3, 10-14, 17-20, 22-26, 34-38 and 40.

Example 9

Anodes 40-46 were manufactured according to Example 1, with a Ti support, on which a tantalum oxide layer (1) was deposited and then an electrocatalytic top layer, consisting of iridium oxide or iridium oxide/tantalum oxide. When another intermediate layer (2) was applied between these two layers, consisting of tantalum oxide, mixed with iridium oxide, the service life of the anode was increased, see Table 8. With some lower layers (2) of type B (rutile oxides TiO₂, SnO₂ and a mixture of the two oxides), there is also additional advantage in service life, see anodes 43-46.

Service lifes were measured at a current density of 30,000 A/m², at 50 °C.

Table 8

Service lifes of anodes with a tantalum oxide intermediate layer (1), whether or not with an extra intermediate layer (2) and a top layer of iridium oxide, whether or not mixed with tantalum oxide, on a titanium support				
Anode nr.	Composition top layer (mole%)	Composition intermediate layers 1 and 2 (mole%)*	Metal coverage (layer) (g/m ²)	Service life (days)
40	IrO _x	TaO _x	(top): 10 (1): 3	10
41	IrO _x /TaO _x (85/15)	TaO _x	top: 10 (1): 3	25
42	IrO _x /TaO _x (85/15)	TaO _x /IrO _x (1) (75/25)	(top): 10 (1): 3	34
		TaO _x (2)	(2): 3	
43	IrO _x /TaO _x (85/15)	TaO _x (1)	(top): 10	31
		TaO _x /IrO _x (2) (75/25)	(1): 3 (2): 3	
44	IrO _x /TaO _x (85/15)	TaO _x (1) TiO _x (2)	(top): 10 (1): 3 (2): 3	30
45	IrO _x /TaO _x (85/15)	TaO _x (1)	(top): 10	48
		SnO _x (2)	(1): 3 (2): 3	
46	IrO _x /TaO _x (85/15)	TaO _x (1)	(top): 10	41
		TiO _x /SnO _x (2) (50/50)	(1): 3 (2): 3	

* Intermediate layers counted from the top layer.

From this Table, it is concluded that the service life of an anode increases at identical top layer and tantalum oxide intermediate layer by inserting a second layer between either the support and the first intermediate layer or between that layer and the top layer. This second intermediate layer may be either a tantalum oxide layer, containing iridium oxide, or a layer, consisting of titanium oxide, tin oxide or a mixture of the two oxides. Also the result shows that with identical intermediate layer (tantalum oxide), the service life of the anode increases by adding tantalum oxide to the iridium oxide top layer. See Claims 10, 12, 21, 22 and 26.

Figure 1 = Type 1

5

TOP LAYER
SUPPORT

Figure 2 = Type 2

10

TOP LAYER
INTERMEDIATE LAYER TYPE A
SUPPORT

15

Figure 3 = Type 3

20

TOP LAYER
INTERMEDIATE LAYER TYPE B
INTERMEDIATE LAYER TYPE A
SUPPORT

25

Figure 4 = Type 4

30

TOP LAYER
INTERMEDIATE LAYER TYPE A
INTERMEDIATE LAYER TYPE B
SUPPORT

35

Figure 5 = Type 5

40

TOP LAYER
INTERMEDIATE LAYER TYPE B
INTERMEDIATE LAYER TYPE A
INTERMEDIATE LAYER TYPE B
SUPPORT

45 Claims

1. Anode with increased service life, which is suitable for the generation of oxygen in electrochemical processes, in which the electrolyte contains water and furthermore corrosive components, said anode being composed of (i) a support with an oxide skin at its surface, said support being at least electrically conductive at its outside, pointing towards the electrolyte and consisting of titanium or a titanium alloy with another metal, (ii) an electrocatalytically active, porous top layer, which contains an iridium oxide, characterised in that the oxygen/iridium ratio is between 2.1 and 2.9; that the average individual particle size of the iridium oxide in the top layer is between 3 and 100 nm; that between (i) and (ii) an intermediate layer (iii) may be present, consisting of at least one oxide of tantalum, niobium, cobalt or lead, whether or not in a mixture with other metal oxides, which intermediate layer is called type A and which is either directly attached to (i) and (ii), or attached to (i) and/or (ii) by means of at least one extra intermediate layer (iv), called type B, while all mentioned layers are electrically conductive, separately and in connection with each other and the support.

2. Anode according to Claim 1,
characterised by the other metal in the titanium alloy being a valve metal and consisting of one or more
of the metals Ta, Nb, Zr, Hf, Mo or W.
- 5 3. Anode according to one of Claims 1 or 2,
characterised by having only one intermediate layer, which is of type A, consisting of tantalum oxide or
niobium oxide or a mixture of the two oxides, whether or not with one other metal oxide, tantalum oxide
and/or niobium oxide being present for at least 51 mole percent, calculated as metal.
- 10 4. Anode according to Claim 3,
characterised by the other metal oxide being an iridium oxide, which is present in less than 40 mole
percent.
- 15 5. Anode according to one of the Claims 1 or 2,
characterised by having one intermediate layer, which is of type A, consisting of cobalt oxide or a
mixture of cobalt oxide with at least one other metal oxide.
- 20 6. Anode according to Claims 1 or 2,
characterised by having one intermediate layer, which is of type A, consisting of cobalt oxide and
tantalum oxide and/or niobium oxide or of a mixture of cobalt oxide and tantalum oxide and/or niobium
oxide, with at least one other metal oxide.
- 25 7. Anode according to Claims 5 or 6,
characterised by the other metal oxide being an iridium oxide.
8. Anode according to Claims 3, 5 or 6,
characterised by the other metal oxide being a lead oxide.
- 30 9. Anode according to Claims 3, 5 or 6,
characterised by the other metal oxide being a mixture, containing at least iridium oxide and lead oxide.
- 35 10. Anode according to Claims 1 or 2,
characterised by two intermediate layers, one of these being of type A, containing at least 51 mole
percent of oxides of tantalum, niobium, cobalt and/or lead, whether or not mixed with at least one other
metal oxide, and the second of type B, containing at least 51 mole percent of one or more of the
dioxides of the metals M = Ti, Sn, Si, Ce, Mn, Cr, V, Rh, Ru, Ir, Pt, Re, Os, Mo, W, Ta, Nb or Pb.
- 40 11. Anode according to Claim 10,
characterised by the dioxides of said metals M not having the stoichiometric composition MO_2 , but a
deviating composition $MO_{2\pm x}$, in which x is between 0 and 0.5.
12. Anode according to Claim 11,
characterised by said metal dioxide being tin dioxide and/or titanium dioxide.
- 45 13. Anode according to Claim 12,
characterised by the tin dioxide and/or titanium dioxide having a lowered oxygen stoichiometry, in
which x is between 0 and 0.5.
- 50 14. Anode according to Claim 13,
characterised by the metal dioxide containing titanium dioxide with a lowered oxygen stoichiometry, in
which the non-stoichiometry x is between 0.125 and 0.34 and the titanium oxide having the structure of
one or more so-called Magneli phases.
- 55 15. Anode according to Claim 10,
characterised by the metal dioxide containing tin dioxide, which is mixed with indium oxide.
16. Anode according to Claim 15,
characterised by the metal dioxide containing tin dioxide, which is mixed with indium oxide in a solid

solution.

17. Anode according to Claim 10,
characterised by the metal dioxide containing titanium dioxide, which is mixed with one or more oxides
5 of tantalum, niobium, antimony, bismuth, tungsten or molybdenum.
18. Anode according to Claim 10,
characterised by the metal oxide containing titanium dioxide, which is mixed with one or more oxides of
tantalum, niobium, antimony, bismuth, tungsten or molybdenum in a solid solution.
19. Anode according to Claim 17,
characterised by the titanium dioxide TiO_2 being mixed with ditantalum pentoxide Ta_2O_5 .
20. Anode according to Claim 17,
15 characterised by the titanium dioxide TiO_2 being mixed with ditantalum pentoxide Ta_2O_5 in a solid
solution.
21. Anode according to one of the Claims 10-20,
characterised by the layer structure of the anode being as follows: support, including support
oxide/intermediate layer type A/intermediate layer type B/top layer.
22. Anode according to one of the Claims 10-20,
characterised by the layer structure of the anode being as follows: support, including support
oxide/intermediate layer type B/intermediate layer type A/top layer.
23. Anode according to one of the Claims 1 or 2,
characterised by having three intermediate layers, having the layer structure as follows: support,
including support oxide/intermediate layer type B/intermediate layer type A/intermediate layer type
B/top layer, the intermediate layers type B being composed of one or more of the dioxides of Ti, Sn,
30 Si, Ce, Mn, Cr, V, Th, Ru, Ir, Pt, Re, Os, Mo, W, Ta, Nb or Pb and the intermediate layer type A
containing at least one oxide of tantalum, niobium, cobalt or lead.
24. Anode according to Claim 23,
characterised by the intermediate layers B having an identical composition.
25. Anode according to Claim 23,
characterised by the intermediate layers B having a different composition and/or being manufactured
by different methods.
26. Anode according to one of the Claims 1-25,
40 characterised by the electrocatalytically active top layer consisting of more than 80 mole percent
iridium oxide, calculated as IrO_2 and less than 20 mole percent tantalum oxide, calculated as Ta_2O_5 .
27. Anode according to one of the Claims 1-25,
45 characterised by the electrocatalytically active top layer consisting between 50-100 mole percent of
iridium oxide and between 50-0 mole percent of cobalt oxide.
28. Anode according to one of the Claims 1-25,
characterised by the electrocatalytically active top layer consisting between 50-100 mole percent of
50 iridium oxide and between 50-0 mole percent of lead oxide.
29. Anode according to one of the Claims 1-25,
characterised by the electrocatalytically active top layer consisting between 50-100 mole percent of
iridium oxide and further of a combination of at least two of the oxides of tantalum, cobalt and/or lead.
30. Anode according to one of the Claims 26-29,
55 characterised by the average size of the individual particles of iridium oxide in the top layer being 5-15
nm.

31. Anode to one of the Claims 1-30,
characterised by said anode containing tantalum oxide, consisting of Ta_2O_{5-x} , with x being between 0 and 1.

32. Method for manufacturing an anode according to one of the Claims 1-31,
characterized by the support, after cleaning and etching, being provided with a first layer by applying,
from an alcoholic solution of suitably chosen precursors, metal compounds in the correctly chosen
molar ratios and in the desired concentration in said solution, yielding the desired metal oxides in the
desired form and composition after a suitably chosen heat treatment by thermal dissociation and
oxidation, which actions of application and heat treatment per layer to be applied are repeated as often
as is necessary for achieving a desired layer thickness, after which, if desired, the second layer is
applied from an aqueous or alcoholic solution of the concerned metal compounds and in the desired
concentrations thereof with a free choice as to the method for applying it, followed by a heat treatment
and possibly under repetition of actions until a certain layer thickness is achieved, which may be the
same as in the first applied layer, or different in one or more of the aspects mentioned hereafter: the
choice of precursors, their concentration in solution, the choice of the solvent, the heat treatment and
the number of times for repetition of these actions until the desired layer thickness is achieved, after
which, if so desired, every next layer, intermediate layer or top layer, is applied in the same way as
described for the second layer, always per applied layer with the free choice of the aspects mentioned
before, until the number of desired layers (1-4) is reached.

33. Method according to Claim 32,
characterised by the use of chloroiridic acid H_2IrCl_6 as precursor for iridium, whether or not containing
crystal water, and furthermore for all mentioned metals the metal chloride, metal b-diketonate or metal
alkoxide.

34. Method according to Claim 33,
characterised by using as metal b-diketonate a metal acetylacetonate, a metal dipivaloylmethanate, a
metal hexafluoro- or trifluoroacetylacetonate and as metal alkoxide a metal methoxide, ethoxide,
propoxide, isopropylaldehyde, butoxide, secondary butylaldehyde, isobutylaldehyde or tertiary butylaldehyde.

35. Method according to Claim 34,
characterised by using as titanium compound titanium tetra-alkoxide and as tantalum compound
tantalum penta-alkoxide.

36. Method according to Claim 35,
characterised by using as alkoxide ethoxide or butoxide.

37. Method according to Claim 32,
characterised by using as alcohol n-butanol.

38. Method according to Claim 32,
characterised by heat treatments, occurring in air and at maximum temperatures between 400 °C and
650 °C.

39. Method according to Claim 32,
characterised by heat treatments during application of the intermediate layer or of the intermediate
layers, occurring in a vacuum oven or in another oven with inert, i.e. non-oxidising atmosphere, at
temperatures between 400 °C and 1000 °C.

40. Method according to one of the Claims 32-39,
characterised by an intermediate layer of tantalum oxide or niobium oxide or of a mixture of tantalum
oxide and niobium oxide separately or jointly with titanium oxide, applied onto the support by plasma
spraying of these oxides in powder form.

41. Electrochemical cell with an acid electrolyte,
characterised by an anode, according to one of the Claims 1-31, manufactured by a method, according
to one of the Claims 32-40.

42. Electrochemical cell according to Claim 41,
characterised by the acid being sulfuric acid.

5 43. Electrochemical cell,
characterised by having an anode according to one of the Claims 1-31, manufactured by a method
according to one of the Claims 32-40 and the electrolyte having an alkaline composition.

10 44. Electrochemical cell,
characterised by having an anode according to one of the Claims 1-31, manufactured by a method
according to one of the Claims 32-40 and the electrolyte being sea water.

15 45. Electrochemical process for anodic generation of oxygen and possibly other products,
characterised by this process occurring in an electrochemical cell according to one of the Claims 41-
44.

20 46. Electrochemical process for anodic generation of oxygen and possibly other products, for cathodic
protection,
characterised by this process occurring with an anode according to one of the Claims 1-31, manufac-
tured by a method according to one of the Claims 32-40.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3226

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-3 731 285 (CONRADTY GMBH) * column 5, line 35 - line 59 * * column 6; example 1 * ---	1,32,33, 37,38, 41,42,45	C25B11/10 C25C7/02 C23F13/12
D,X	GB-A-2 239 260 (TDK CORPORATION) * page 10; example 1 * Experiment No 1-5 * page 12; table 1 * ---	1,26,32, 33,34, 37,38, 41,42,45	
A	FR-A-2 599 050 (PERMELEC ELECTRODE LTD) * page 10 - page 15; tables 2,3,4 * -----	1-3,10, 27	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C25B C25C C23F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02 FEBRUARY 1993	Examiner GROSEILLER P.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			