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(54) Electrode with lead base and method of making same.

(57) An electrode with a base of lead or lead alloy provided with catalytic particles of an inert refractory oxide activated by means of a catalyst, which particles are partly embedded, anchored and electrically connected to the base. The underlying lead or lead alloy remains electrochemically inactive and the base thereby serves only as a stable conductive support. Preferably, the electrode is an anode for oxygen evolution with titanium particles at the surface of its base, which particles are catalytically activated by means of ruthenium-manganese oxide.

The anode may be used more particularly in cells for electrowinning metals with a higher degree of purity with respect to conventional cells equipped with anodes consisting of lead or a lead alloy.

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ELECTRODE WITH LEAD BASE AND METHOD OF MAKING SAME

Technical Field

The present invention relates to dimensionally stable electrodes, and more particularly to anodes for oxygen evolution in an acid electrolyte, such as are used e.g. in processes for electrowinning metals from acid electrolytes.

Background Art

Lead or lead alloy anodes have been widely used in processes for electrowinning metals from sulphate solutions. They nevertheless have important limitations, such as a high oxygen overvoltage and loss of the anode material leading to contamination of the electrolyte, as well as the metal product obtained on the cathode.

Anodes of lead-silver alloy provide a certain decrease of the oxygen overvoltage and improvement of the current efficiency, but they still have the said limitations as a whole.

It has been proposed to use dimensionally stable titanium anodes with a platinum metal oxide coating for anodic evolution of oxygen, but such anodes are generally subject to more or less rapid passivation and oxidation of the titanium base.

It has also been proposed to provide the titanium base with a protective undercoating comprising a platinum group metal beneath the outer coating, but such coatings do generally not provide sufficient protection of the titanium base to justify the high cost of using precious metals.

Metal electrowinning cells generally require a large anode surface and operate at a low current density in order to ensure an even electrodeposition of metal on the cathode, so that the cost of using a titanium base becomes relatively important and must also be taken into account.

Dimensionally stable anodes with mixed oxide coatings comprising platinum group metals and valve metals are described in U.S. Pat. 3 632 498. An example of this patent relates to the preparation of a fine Ti-Pd mixed oxide powder which is then applied by rolling or hammering into a rod of soft-quality titanium. However, the amount of precious metal incorporated in the mixed oxide powder and applied to the electrode in this manner could be prohibitive for various industrial applications. Thus, when the electrode surface is to be substantially covered with the mixed oxide powder, and more particularly when the electrode is intended for operation at a relatively low current density such as is used in metal electrowinning, the cost of precious metal thus applied in the form of a mixed oxide may be especially prohibitive.

Disclosure of the Invention

An object of the invention is to provide an improved anode for evolving oxygen in an acid electrolyte.

Another object of the invention is to provide an anode with a base of lead or lead alloy with improved electrochemical performance for anodically evolving oxygen in an acid electrolyte, so as to be able to substantially avoid loss of the anode material, whereby to avoid said limitations of conventional lead or lead alloy anodes.

A further object of the invention is to provide a simple method of making such an electrode with improved performance.

These objects are essentially met by the invention as set forth in the claims.

The electrochemical performance of the anode is improved in accordance with the invention by providing the anode with titanium particles which are catalytically activated by means of ruthenium in oxide form and are partly embedded at the surface of the anode base of lead or lead alloy, so that they are firmly anchored and electrically connected to the base. The remaining, non-embedded part of said catalytic particles thus projects from said surface of the anode base, and thereby can present a surface for oxygen evolution which can be considerably larger than the underlying surface of the anode base of lead or lead alloy.

Said partly embedded catalytic particles are preferably arranged according to the invention, so that they substantially cover the entire surface of the lead or lead alloy base, present a maximum surface for oxygen evolution, and thereby more especially provide a substantially uniform distribution of the anode current density.

The use of ruthenium to catalytically activate titanium particles in accordance with the invention is particularly advantageous since ruthenium can provide an excellent electro-catalyst for oxygen evolution at a relatively low cost with respect to other metals of the platinum group.

The catalytic particles applied according to the invention advantageously consist of titanium sponge and may have a size lying in the range between 150 and 1250 microns, and preferably in the range of about 300-1000 microns.

The amount or loading of said catalytic particles applied according to the invention per unit area of the anode base should generally be adequate to substantially cover the anode base.

It has now been found that relatively high particle loadings corresponding to more than 400 g/m^2 are generally necessary for the manufacture of electrodes with satisfactory performance. Higher loadings up to 1000 g/m^2 or more have likewise been found to be advantageous.

The catalytic particles advantageously comprise a minimum amount of ruthenium, corresponding to at most 6 % by weight of the titanium of said particles, evenly distributed on a very large surface.

The high loadings of catalytic particles indicated above e.g. 500-1000 g/m^2 may nevertheless necessitate quite high ruthenium costs. Consequently, it is particularly important to reduce the loss of ruthenium during anodic operation as far as possible.

It has now been established experimentally that activating the titanium particles with manganese as well as ruthenium in oxide form increases the stability of the catalyst with respect to ruthenium dioxide alone or in other combinations.

This improved electrocatalytic performance and stability of the Ru-Mn oxide system under the conditions of oxygen evolution in acid media constitutes a particularly advantageous feature of the catalytically activated titanium particles used on a lead base according to the present invention.

It has also been found that the formation of titanium oxide by thermal decomposition on the activated particles provides a further improvement of the stability of the particles.

It has moreover been established that a more efficient use of the ruthenium is achieved when larger activated particles are first pressed into the lead anode base and this is followed by pressing smaller particles, which may advantageously have a higher proportion of ruthenium than the larger particles. This 2-step pressing procedure has been found to improve the contact with the lead base as well as the long-term stability of the catalytically activated particles.

It has moreover been found that an additional pressing step to apply non-activated particles of a valve metal or a valve metal oxide, more particularly zirconium dioxide, can further increase the stability of the activated particles. This is especially important in processes for electrowinning metals from electrolytes containing Mn^{2+} ions, where the deposition of poorly conducting MnO_2 can be detrimental for anode performance.

The following examples serve to illustrate different modes of carrying out the present invention.

Example 1

An activating solution was prepared by dissolving 0.57 g $RuCl_3$.aq. and 1.33 g $Mn(NO_3)_2$.aq. in 4 ml 1-butyl-alcohol. The solution was then diluted with six times its weight of 1-butyl-alcohol.

3.25 g of Ti sponge (particle size greater than 630 microns) was degreased with trichlorethylene, dried and impregnated with the activating solution. After each impregnation, the titanium sponge was dried at 100°C for about 1 h. A heat treatment was then effected at 200°C for 10 minutes and finally at 400°C under an external air flow for about 10 minutes. This activation procedure was carried out 5 times. The Ru and Mn loadings thus obtained amounted to 28.4 mg Ru/g Ti and 36.0 mg Mn/g Ti.

The same activating solution was used also on 4.9 g Ti sponge (particle size 315-630 microns). The temperatures for drying and heating as well as the number of impregnations were identical to those applied to the larger particles. However, the duration of the heat treatment at 400°C was 12 minutes. The Ru and Mn loadings in this case amounted to 27 mg Ru/g Ti sponge and 34 mg Mn/g Ti sponge.

The activated titanium sponge particles were then pressed onto a lead sheet coupon. The larger particles size (greater than 630 microns) were pressed first at 290 kg/cm^2 to give Ti, Mn and Ru loadings per unit lead-sheet area of 322, 11.5 and 9.1 g/m^2 respectively. Subsequently, smaller activated titanium particles (315-630 microns) were then pressed at 360 kg/cm^2 to give Ti, Mn and Ru loadings of 400, 13.7 and 10.8 g/m^2 respectively.

An electrode sample (L 62) was thus obtained with a lead base uniformly covered with Ru-Mn oxide activated titanium sponge particles in an amount corresponding to 722 g/m^2 Ti sponge, 19.9 g/m^2 Ru and 25.2 g/m^2 Mn.

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrode potential (oxygen half-cell potential) at a current density of 500 A/m^2 amounted to 1.57 V vs. NHE after 68 days, 1.59 V after 194 days, and 1.75 V after 210 days of anodic operation.

For comparison, another anode sample (L 61), which was obtained by directly pressing smaller particles of activated Ti sponge on lead, with higher Ru and Mn loadings corresponding to 27.9 and 35.4 g/m^2 respectively, exhibited anode potential of 1.62 V after 69 days of operation under identical conditions, and a potential of 1.63 V when anode operation was stopped after 194 days.

A further anode sample (L 76) was prepared like L 62 but the larger particles were only activated 4 times instead of 5. The overall Ru and Mn loadings amounted in this case to 22.1 and 28.0 g/m^2 respectively. The anode was tested under identical conditions and showed a potential of 1.5 vs NHE after 22 days and 1.8 V after 140 days of operation.

Example 2

An anode sample (L 64) was prepared like L 62 of Example 1 but with higher Ru and Mn loadings of 23.1 and 29.3 g/m^2 respectively. The anode was tested in a Zn electrowinning solution containing Mn^{2+} as a major impurity.

Its potential after 60 h and 120 h of operation as an oxygen evolving anode in this medium, amounted respectively to 1.68 V and 1.73 V vs. NHE. The current density was 400 A/m^2. No deposit of Mn-oxide occurred during this period.

For comparison, lead samples comprising either only large activated particles (size greater than 630 microns) or only smaller ones (size 315 - 630 microns), with overall Ru and Mn loadings corresponding to 19-20 and 24-25 g/m^2 respectively, showed a higher anode potential of about 1.72 - 1.75 V vs. NHE after 60 h of operation. A thick anodic deposit of Mn oxide was observed in both cases.

Example 3

Ti sponge (particle size 315 - 630 microns) was activated like in Example 1. It was then pressed onto lead at 270 kg/cm2 to give a loading of Ti, Mn and Ru corresponding to 427, 15.1 and 11.9 g/m2 respectively. Finally particulate ZrO_2 (particle size 150-500 microns) was pressed with a pressure of about 410 kg/cm^2 on top of the Ti sponge to give a ZrO2 loading corresponding to 248 g/m^2.

The electrode sample thus obtained (L 82) was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrode potential at a current density of 500 A/m^2, amounted to 1.50 V vs NHE after 150 h of anodic operation. It amounted to 1.59 V after 293 days, and is still operating. This corresponds to a voltage saving of 410 mV with respect to pure, untreated lead.

Example 4

Ti sponge (particle size 315 - 630 microns) was activated first with a Ru and Mn containing solution as described in Example 1.
The activation method was also identical to the one described in Example 1.

Following this activation, a top-coating was applied by impregnation with a solution containing Ti-butoxide which was prepared by diluting 1.78 g Ti-butoxide in 3.75 ml 1-butyl-alcohol and 0.25 ml HCl.

The impregnated sponge was dried at 100°C for about 1 h. A heat treatment was then effected at 250°C for 12 minutes and finally at 400°C under an external air flow for about 12 minutes.

The resulting activated titanium particles were then pressed on lead at about 250 kg/cm^2. The electrode sample (L 84) was thus obained with a lead base uniformly covered with Ru-Mn oxide activated titanium sponge particles "topcoated" with Ti-oxide in amounts corresponding to 13.3 g Ru/m^2, 16.9 g Mn/m^2, 5.8 g Ti/m^2 and 515 g Ti sponge/m^2.

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). Its potential at a current density of 500 A/m^2 amounted to

1.49 V vs NHE after 130 h of anodic operation. This corresponds to a 510 mV saving over untreated lead. The anode potential amounted to 1.64 V after 128 days, which corresponds to a 360 mV saving over untreated lead.

Example 5

Ti sponge (particle size 315-630 microns) was activated first with a Ru-containing solution prepared by dissolving 134 g of $RuCl3H_2O$ per liter of butyl-alcohol. The Ti sponge was impregnated with the Ru containing solution, heated at 120°C during 20 minutes in order to evaporate the solvent, heat treated at 250°C for 15 min. and finally at 450°C for another 15 min. This impregnation, drying and baking was repeated four times. The ruthenium loading thus obtained amounted to 30 mg/g of Ti sponge.

Following this activation, a top-coating of TiO_2 was applied on the activated particles by impregnation with a solution obtained by mixing 1.8 g of titanium butoxide with 3.75 ml of butyl-alcohol. The drying, heating and baking steps were the same as mentioned above for the Ru containing activating solution. These steps were repeated twice to give a loading of titanium, applied as TiO_2, amounting to 5 mg/g Ti sponge.

The activated titanium particles were then pressed on lead at 250 kg/cm^2 onto a lead sheet coupon, with a particle loading of 500 g/m^2 corresponding to 15 g/m^2 Ru and 2.5 g/m^2 of Ti applied to the particles uniformally distributed on the lead surface.

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrode potential at a current density of 500 A/m^2 amounted to 1.66 V vs NHE after 2000 hours of anodic operation.

Example 6

TiO_2 rutile particles having a size ranging from 315 to 630 microns are activated by impregnation with the following solution :0.54 g $RuCl_3.H_2O$; 1.8 g butyltitanate; 0.25 ml HCl; and 3.75 ml butyl-alcohol.

After impregnation, the particles are dried at 100°C in air and baked at 440°C for 10 minutes under air flow. This procedure is repeated 4 times. The resulting particles are activated with RuO_2-TiO_2.

The particles are then pressed onto a lead sheet coupon by applying a pressure of 250 kg/cm^2. The particle loading amounted to 400 g/m^2 corresponding to a Ru and Ti loading of 15 and 16 g/m^2 respectively(applied as RuO_2-TiO_2).

The obtained activated lead electrode was tested as an anode in an aqueous solution containing 150 gpl H_2SO_4 at room temperature. The applied anode current density applied amounted to 500 A/m^2. An oxygen half cell potential of 1.75 V vs NHE was obtained after 300 hours of operation. After 1000 hours, the anode potential reached the same value as that of an anode of pure, untreated lead.

Example 7

An activating solution was prepared as described in Example 1, but instead of diluting it six times (example 1), it was diluted with only three times its amount of n-butyl-alcohol.

4.11 g of Ti sponge (particle size 400-630 microns), was impregnated with the activating solution. After each impregnation, the titanium sponge was dried at 100°C for about 1 hour. A heat treatment was then effected at 250°C for about 10 minutes and finally at 400°C under an external air flow for about 10 minutes. This activation procedure was carried out 3 times. The Ru and Mn loadings thus obtained amounted to 36.2 mg Ru/g Ti and 45.8 mg Mn/g Ti.

The activation procedure, described in Example 1 for the Ti sponge with a particle size larger thant 630 microns, was applied also in this case for the larger particles (greater than 630 microns). However, the activation was carried out only 4 times. The Ru and Mn loadings thus obtained amounted to 23.5 mg Ru/g Ti and 29.9 mg Mn/g Ti.

The activated titanium sponge particles were then pressed and partly embedded at the surface of a lead sheet coupon. The larger particles (size greater than 630 microns) were pressed first at 240 kg/cm^2 to give Ti, Mn and Ru loadings per unit lead sheet areea of 350, 10.5 and 8.3 g/m^2 respectively. An electrode sample (L95) was thus obtained with a lead base uniformly covered with Ru-Mn oxide activated titanium sponge particles in an amount corresponding to 760 g/m2 Ti sponge, 23.2 g/m2 Ru and 29.3 g/m2Mn. This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrode potential, at a current density of 500 A/m^2, amounted to 1.65 V vs NHE after 287 days of anodic operation.

For comparison, another anode sample (L93), which was obtained by directly pressing smaller particles of activated Ti sponge at 280 kg/cm^2 on lead, with Ru and Mn loadings corresponding to 15.4 and 19.5 g/m^2 respectively, was tested under identical conditions. The electrode potential, after 289 days, was 1.78 V vs NHE.

A further anode sample (L92) was prepared like L95 but the smaller particles (400-630 microns) were activated like in Example 1 (L62). The overall Ti, Mn and Ru loadings amounted in this case to 726, 22.5 and 17.7 g/m^2 respectively. Pressing of the larger particles and smaller particles was carried out at 290 kg/cm^2 and 410 kg/cm^2 respectively. The anode has been tested under identical conditions and showed a potential of 1.78 V vs NHE after 289 days of operation.

Example 8

An activating solution was prepared as described in Example 7.
4,22 g of larger particles (particle size above 630 microns) was activated twice under the conditions specified in Example 7 to give 21.5 mg Ru/g Ti and 27.4 mg Mn/g Ti.

Another activating solution was applied to Ti sponge with a smaller particle size ranging from 400-630 microns. This activation solution corresponds to the one described in Example 7 with the difference that it was diluted with only twice its amount of 1-butyl-alcohol. Two activations were carried out in accordance with Example 7. The Ru and Mn loadings per gram Ti amounted to 25.9 and 32.9 mg respectively.

An anode sample (L 120) was prepared by pressing the larger particles first at 210 kg/cm^2 to give Ti, Mn and Ru loadings of 360, 9.8 and 7.7 g/m^2 respectively. Smaller activated titanium particles (400-630 microns) were then pressed at 320 kg/cm^2 to give Ti, Mn and Ru loadings of 420, 13.9 and 10.9 g/m^2 respectively. The overall Ti, Mn and Ru loadings thus obtained amounted to 780, 23.7 and 18.6 g/m^2 respectively.

The electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrodes potential, at a current density of 500 A/m^2, amounted to 1.58 V vs NHE after 218 days of anodic operation.

Example 9

Titanium sponge (400-630 microns) was oxidized as follows, prior to activation with Ru-Mn oxide.

4.74 g of titanium sponge was activated once with the activation solution described in Example 1. The heat treatment was carried out at 400°C for 13 minutes under an external air flow, after subjecting the Ti sponge to drying at 100°C. The Ru and Mn loadings were 5.2 and 6.6 mg/g Ti sponge respectively. The sponge was then subjected to heat treatment for 45 h at 480°C under an external air flow to convert it into its respective oxide.

3.5 g of the oxidized Ti sponge thus obtained was then activated as described in Example 1 with the only difference that an intermediate heat treatment was carried out at 250°C instead of 200°C after each activation. The Mn and Ru loadings per g sponge amounted to 32.8 and 25.8 mg respectively.

The preoxidized and activated Ti sponge was then pressed in two steps, first at 230 kg/cm^2 and then at 290 kg/cm^2 to give Mn and Ru loadings of 21.1 and 16.6 g/m^2 respectively. The loading of the oxidized Ti sponge amounted to 643 g/m^2. Considering the Mn and Ru loadings in the Ti-oxide, prior to final activation, the overall Mn and Ru loadings amount to 25.3 and 19.9 g/m^2 respectively.

The electrode has been tested in 150 gpl H_2SO_4 at 500 A/m^2 and its potential after 275 days of operation amounted to 1.65 V vs NHE.

Example 10

Two activating solutions were prepared with a larger Mn/Ru ratio than described in Example 1.

Solution A : 0.537 g $RuCl_3$.aq and 2.0819 g Mn $(NO_3)_2$.aq in 3.75 ml n-butyl-alcohol

Solution B : 0.537 g $RuCl_3$.aq and 4.6844 g $Mn(NO_3)_2$. aq in 3.75 ml n-butyl-alcohol

Both solutions A and B were diluted with 3 times their amount of n-butyl-alcohol prior to application. Solution A corresponds to a molar ratio of MnO_2/RuO_2 = 4 and solution B corresponds to a molar ratio of MnO_2/RuO_2 = 9.

4.27 g of Ti sponge (particle size 315-630 microns) was impregnated with diluted activation solution A. After each impregnation, the titanium sponge was dried at 100°C for about 1 h. A heat treatment was then effected at 250°C for 14 minutes and finally at 400°C under an external air flow for about 14 minutes. This activation procedure was carried out 3 times. The Ru and Mn loadings thus obtained amounted to 29.3 mg Ru/g Ti and 63.8 mg Mn/g Ti.

4.16 g of Ti sponge (particle size 315-630 microns) was impregnated with diluted activation solution B. The activation was carried out in the same manner as with activating solution A. The Ru and Mn loadings thus obtained amounted to 19.9 mg Ru/g Ti and 97.4 mg Mn/g Ti.

The activated Ti sponge particles were then pressed onto a lead sheet coupon. The larger particles (greater than 630 microns), activated as in Example 8, were pressed first at 230 kg/cm^2 to give Ti, Mn and Ru loadings per unit lead-sheet area of 449, 12.0 and 9.4 g/m^2 respectively. Subsequently smaller activated (with diluted solution A) Ti particles (315-630 microns) were pressed at 350 kg/cm^2 to give Ti, Mn and Ru loadings of 399, 25.5 and 11.7 g/m^2 respectively.

An electrode sample (L 164) was thus obtained with a lead base uniformly covered with Ru-Mn oxide activated titanium sponge particles in an amount corresponding to 848 g/m^2 Ti sponge, 20.8 g/m^2 Ru and 37.5 g/m^2 Mn.

This electrode sample was tested as an oxygen evolving anode in 150 gpl H_2SO_4. Its potential,at a current density of 500 A/m^2, amounted to 1.50 V vs NHE after 36 days of anodic operation.

For comparison, another anode sample (L 161), was obtained by directly pressing smaller particles of activated Ti sponge (with diluted solution A) at 320 kg/cm^2 on lead, with Ti, Ru and Mn loadings corresponding to 531, 15.6 and 34.0 g/m^2 respectively.

This electrode L 161 has been tested under identical conditions and showed a potential of 1.60 V vs NHE after 70 days of operation.

In another set of experiments, Ti sponge particles larger than 630 microns, activated as in Example 8, were pressed first at 230 kg/cm^2 to give Ti, Mn and Ru loadings per unit lead-sheet area of 428, 11.5 and 9.0 g/m^2 respectively. Smaller activated titanium sponge particles (size 315-630 microns), obtained with activating solution B, were then pressed at 350 kg/cm^2 to give Ti, Mn and Ru loadings of 493, 48.0 and 9.8 g/m^2 respectively. An electrode sample (L 163) was thus obtained with a lead base uniformly covered with Ru-Mn oxide activated titanium sponge particles in an amount corresponding to 921 g/m^2 Ti, 59.5 g/m^2 Mn and 18.8 g/m^2 Ru.

This electrode has been tested as an oxygen evolving anode in 150 gpl H_2SO_4 at 500 A/m^2. Its potential after 33 days of operation amounted to 1.57 V vs NHE.

Example 11

For comparison (with L 163 in Example 10), another anode sample (L 162) was obtained by directly pressing smaller particles (315-630 microns) of activated Ti sponge (with diluted solution B) at 290 kg/cm^2 on lead with Ti, Ru and Mn loadings corresponding to 652, 13.0 and 63.6 g/m^2 respectively.

The electrode has been tested at 500 A/m2 in 150 gpl H_2SO_4 and shows a potential of 1.74 V vs NHE after 18 days (430 h) of operation under these conditions.

Example 12

An activating solution was prepared by dissolving 0.54 g $RuCl_3 \cdot aq$ (38 % Ru) and 0.12 g $PdCl_2$ in 15 ml of butyl-alcohol. The solution was stirred until all the salts were dissolved and 1.84 g of butyltitanate was added.

3.5 g of titanium sponge having a particle size ranging from 315 to 630 microns was impregnated with this activated solution, dried at 140°C for 20 minutes, fired at 250°C for 15 minutes and finally fired for another period of 15 minutes at 450°C. All these heating steps were carried out in air. After cooling, the impregnating, drying and firing operations were repeated six times. The Ru and Pd loadings thus obtained on the particles amounted to 30 mg Ru/g Ti and 11 mg Pd/g Ti. The activated titanium sponge particles were pressed onto a lead sheet coupon with a pressure of 250 kg/cm^2 in order to get the respective loadings : 500 g/m^2 Ti sponge, 15 g/m^2 Ru, 5.5 g/m^2 Pd.

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl) at 500 A/m^2. The electrode potential (oxygen half-cell potential) amounted to 1.78 V vs NHE after 208 days of anodic operation.

Example 13

7 g of titanium sponge (particle size 315-630 microns) was impregnated with 1.4 ml of a solution containing 7 mg/ml of Ir in the form of $IrCl_3$ aq, dissolved in isopropyl-alcohol. After impregnation, the titanium sponge was dried at 140°C for 15 min., fired at 250°C during 10 min. and fired again at 450°C for 10 min., all of these steps being carried out in air.

The activated titanium sponge particles were pressed onto a lead sheet coupon by applying a pressure of 250 kg/cm^2. The amount of particles was chosen so as to obtain a titanium and iridium loading of 700 g/m^2 and 1 g/m^{2}respectively.

A second activating solution was the applied to the electrode sample in the following manner. A solution is prepared by dissolving 5.0 g of Mn $(NO_3)_2$. 4 H20 and 0.32 g Co (N03)2 6 H20 and 0.5 ml ethanol. This solution is applied to the electrode surface, dried for 15 minutes at 140°C and baked at 250°C (10 min.) in air. After cooling, the painting, drying and baking steps were repeated five times so as to get a final loading of 240 g/m^2 MnO_2 and 12 g/m^2 cobalt oxide (calculated as Co_3O_4).

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl). The electrode potential (oxygen half-cell potential) at a current density of 500 A/m^2 amounted to 1.78 Volts (vs NHE) after seven months of anodic operation.

Example 14

The electrode sample was prepared as in Example 13, except that $IrCl_3$ aq was replaced by $RuCl_3$ aq (14 mg/ml of Ru) and that the impregnation step was repeated twice so as to get a ruthenium loading of 4 g/m^2 for a titanium sponge loading of 700 g/m^2.

When tested under the same conditions as in example 13, the oxygen half cell potential amounted to 1.80 V (vs NHE) after 6 1/2 months of operation.

Example 15

An activating solution was prepared by dissolving 0.44 g $RuCl_3$ aq (38 weight % Ru), 0.090 g $SnCl_2.2H_2O$ + 0.52 g Mn $(NO_3)_2.4H_2O$ in four ml of butyl-alcohol.

2.5 g of titanium sponge (particle size 315-630 microns) was impregnated with this activating solution in the following manner : 0.77 ml of solution was uniformly applied to the titanium sponge, dried at 140°C during 15 min., baked at 250°C for 10 min. and at 420°C for 10 min., all drying and baking steps in air. After cooling, the titanium sponge was activated twice again, each time with 0.5 ml of activating solution, dried and baked as mentioned above.

The activated titanium particles were pressed onto the surface of a lead-calcium alloy (0.06 % Ca) coupon at 250 kg/cm^2 so as to get the following respective loadings : Ti 700 g/m^2, Ru 20 g/m^2, Sn 5.8 g/m^2 and Mn 13.7 g/m2.

This electrode sample was tested as an oxygen evolving anode in H_2SO_4 (150 gpl) at 500 A/m^2. The electrode potential amounted to 1.67 V vs NHE after 7 months of operation.

As may be seen from the above examples, an anode according to the invention can be fabricated in a simple manner and be used for prolonged evolution of oxygen at a potential which is significantly lower than the anode potential corresponding to oxygen evolution on lead or lead alloy under otherwise similar operating conditions.

It may be noted, that no loss of lead from the base could be observed when testing anode samples according to the invention, as described in the above examples, whereas a notable lead loss could be observed in the electrolyte when testing lead or lead alloy reference samples under the same conditions.

It has moreover been found that simultaneously applying heat and pressure, when partly embedding the valve metal particles in the lead or lead alloy at the surface of the anode base, can facilitate their fixation, while preventing the particles from being completely embedded in and/or flattened on the base.

It may also be noted that further improvements may well be expected with respect to the above examples by determining the best conditions for providing anodes according to the invention with optimum, stable electrochemical performance with maximum economy of precious metals.

It is understood that the catalytic particles may be applied and anchored to the lead or lead alloy base of the anode, not only by means of a press as in the examples described above, but also by any other means such as pressure rollers for example, which may be suitable for providing the essential advantages of the invention.

It has also been found that the application of heat (e.g. at about 250°C) during the pressing step can promote partial embedment of the catalytic particles into the lead or lead alloy surface.

The invention provides various advantages of which the following may be mentioned for example :

(a) The anode according to the invention can be operated at a significantly reduced potential, well below that of conventional anodes of lead or lead alloy currently used in industrial cells for electrowinning metals from acid solutions. The cell voltage and hence the energy costs for electrowinning metals may thus be decreased accordingly.

(b) Contamination of the electrolyte and the cathodic deposit by materials coming from the anode can be substantially avoided, since it has been experimentally established that oxygen is evolved on the catalytic particles at a reduced potential, at which the lead or lead alloy of the anode base is effectively protected from corrosion.

(c) Dendrite formation on the cathode which may lead to short circuits with the anode and can thereby burn holes into the anode, will nevertheless lead to no serious deterioration of the performance of the anode according to the invention, since it operates with oxygen evolution on the catalytic particles at a reduced potential, at which any part of the lead or lead base which is exposed does not undergo notable corrosion.

(d) Conventional lead or lead alloy anodes may be readily converted into improved anodes according to the invention and it thus becomes possible to retrofit industrial cells for electrowinning metals in a particularly simple and inexpensive manner to provide improved performance.

(e) The reduced cell voltage obtained with anodes according to the invention can be readily monitored so as to be able to rapidly detect any notable rise which may occur in the anode potential. The catalytic particles on the lead or lead alloy base may thus be readily reactivated or replaced whenever this should become necessary.

(f) Ruthenium can be used as catalyst in an extremely economical manner, by combining it in a very small proportion with titanium sponge particles applied in a many times larger amount to the anode base of lead or lead alloy. The cost of ruthenium can thus be justified by the resulting improvement in anode performance.

(g) Ruthenium can thus be used in very restricted amounts and combined with less expensive stable materials.

(h) Decreased short-circuits could be observed in copper electrowinning plants equipped with anodes according to the invention. This resulted in an improved cathodic current efficiency, thereby further increasing the energy savings already achieved by the reduced cell voltage due to operation of the anode for the invention at a reduced oxygen half-cell potential.

INDUSTRIAL APPLICABILITY

Anodes according to the invention may be advantageously applied instead of currently used anodes of lead or lead alloy, in order to reduce the energy costs required for industrially electrowinning metals such as zinc, copper, cobalt, and nickel and to improve the purity of the metal produced on the cathode.

Such anodes may be usefully applied to various processes where oxygen evolution at a reduced overvoltage is required.

CLAIMS

1. An anode for evolving oxygen in an acid electrolyte, comprising an anode base of lead or a lead alloy, characterized in that :

(a) catalytically activated titanium particles are uniformly distributed and partly embedded at the surface of the base so that they are firmly anchored and electrically connected to the base,

(b) the catalytically activated titanium particles comprise a minor amount of ruthenium in oxide form, so as to allow oxygen to be anodically evolved at a reduced potential at which the underlying lead or lead alloy remains electrochemically inactive and thereby essentially serves as a stable inert current conducting support for the catalytically activated particles.

2. The anode of Claim 1, characterized in that said particles consist of titanium sponge.

3. The anode of Claim 1 or 2, characterized in that said particles further comprise manganese in oxide form.

4. The anode of Claim 2 or 3, characterized in that catalytically activated titanium sponge particles in different size ranges are arranged on the base.

5. The anode of Claim 4, characterized in that smaller particles comprise a greater amount of ruthenium than the larger particles in said size ranges.

6. The anode of Claim 1 , characterized in that said activated titanium particles further comprise titanium in oxide form.

7. The anode of any one of Claim 1, characterized in that said activated particles comprise titanium in an amount corresponding to more than 400 grams per square meter of the surface of the anode base.

8. The anode of Claim 1 , characterized in that it further comprises particles of valve metal and/or valve metal oxide, preferably ZrO_2, in addition to said activated particles.

9. A method of making the anode of Claim 1, characterized by the steps of :

(a) uniformly distributing on the surface of the anode base of lead or lead alloy catalytically activated titanium sponge particles comprising a minor amount of ruthenium and manganese in oxide form obtained by thermal decomposition of ruthenium and manganese compounds applied to said titanium sponge particles, and

(b) partly embedding said catalytically activated particles in the lead or lead alloy of said anode base.

10. The method of Claim 9, characterized in that large activated particles are first pressed into the surface of the anode base and smaller activated particles are then pressed into said anode base surface.

11. The method of Claim 10, characterized in that said smaller particles are provided with a greater amount of ruthenium than said large particles.

12. The method of Claim 10 or 11, characterized in that said large particles have a size greater than 600 microns and said smaller particles have a size from 300 to 600 microns.

13. The method of Claim 9, characterized in that said activated particles comprise titanium in an amount corresponding to more than 400 grams per square meter of the surface of the anode base.

14. The method of Claim 9, characterized in that titanium oxide is further formed on said catalytically activated particles by thermal decomposition of a titanium compound applied after forming the ruthenium and manganese in oxide form on said particles.

15. The method of Claim 9, characterized in that particles of valve metal and/or valve metal oxide are further pressed into the anode base after partly embedding said activated particles.

16. The method of Claim 15, characterized in that particles of zirconium dioxide are pressed and likewise fixed to the anode base after said catalytically activated titanium particles have been partly embedded.

17. An electrode comprising a base of lead or lead alloy and a catalyst for carrying out an electrochemical reaction, characterized in that catalytic particles consisting of an inert refractory oxide activated by means of a catalyst for the desired reaction are uniformly distributed and partly embedded at the surface of said base, so that they are firmly anchored and electrically connected to the base, so that the desired electrochemical reaction can be effected on said catalytic aprticles at a potential at which the underlying lead or lead alloy of the base remains electrochemically inactive and thereby essentially serves as a stable inert current conducting support for said catalytic particles.

18. The electrode of Claim 17, characterized in that said inert refractory oxide particles are activated by means of a catalyst comprising a noble metal.

19. The electrode of Claim 17 or 18, characterized in that said refractory oxide is titanium oxide in rutile form.

20. Use of an electrode according to Claim 17 as an anode for evolving oxygen in an acid electrolyte.

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EUROPEAN SEARCH REPORT

0087186
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EP 83 20 0195

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. 3)
P,X	EP-A-0 046 447 (DIAMOND SHAMROCK) * Page 17, line 20 - page 18, line 3; example 12; claims 1,8,9,12,20,21 * ---	1,6,17-20	C 25 C 7/02 C 25 B 11/04
P,X	EP-A-0 046 727 (DIAMOND SHAMROCK) * Examples 1-4,6,7,10-13; claims * ---	1-4,6-9,17-20	
X,Y	DE-A-2 948 565 (GOULD) * Page 18, line 13 - page 19, line 12; claims * ---	1-3,17	
X,Y	US-A-3 933 616 (BEER) * Column 2, lines 4-36; claims * ---	1,3,6,17-20	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
X,Y	US-A-3 840 443 (BEER) * Column 2, line 8 - column 3, line 9 * ---	1,3,6,17-20	C 25 C C 25 B
Y	US-A-4 003 817 (BIANCHI et al.) * Column 4, line 47 - column 5, line 28 * --- -/-	17-20	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-05-1983	GRUNDKE H.H.

CATEGORY OF CITED DOCUMENTS

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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. ³)
Y	DE-A-2 652 152 (DIAMOND SHAMROCK) * Page 8 - page 9, line 1; page 12, lines 4-9; page 14, lines 4-9 * ---	17-20	
Y	DE-A-2 035 212 (CONRADTY) * Page 3, line 19 - page 6 * ---	1,6,8,9,17-20	
Y	FR-A-2 346 468 (DIAMOND SHAMROCK) * Claims * -----	17-20	
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

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X : particularly relevant if taken alone
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