PARTIAL REPLACEMENT OF RUTHENIUM WITH TIN IN ELECTRODE COATINGS

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3 Claims

ABSTRACT OF THE DISCLOSURE

An electrode is disclosed which comprises an electrically conductive, particularly titanium, substrate at least partially covered with a solid solution-type coating consisting essentially of titanium, ruthenium and tin dioxides.

REFERENCE TO A COPENDING APPLICATION

This is a continuation-in-part of my copending Ser. No. 104,740, filed Jan. 7, 1971, now abandoned.

BACKGROUND OF THE INVENTION

Recent years have seen a rise in the popularity of dimensionally stable electrodes, particularly dimensionally stable anodes, especially in those areas where consumable electrodes, such as graphite anodes, had previously been almost exclusively employed. The technology most affected to date has been the chlor-alkali industry wherein these electrodes have made remarkable inroads into an area traditionally dominated by graphite anodes.

While differing significantly in their properties, the various dimensionally stable anodes proposed and in use generally employ some combination of a valve metal and a precious metal. In the initial stages of development, the electrodes proposed were valve metals provided with a precious metal coating, e.g., platinum-titanium. Despite extensive efforts throughout the chlor-alkali industry, however, such anodes found little practical application, primarily owing to the high rate of consumption of precious metal during production. Claims of the literature to the contrary notwithstanding, in fact it was found difficult to reduce the wear rate of these anodes to a value of less than 0.5 gram of precious metal per ton of chlorine produced. When one weighs the price of precious metals against the fact that in 1969 in the United States alone greater than 9,400,000 tons of chlorine were produced, it becomes apparent that such a wear rate is indeed prohibitive.

A significant advance in the art was the development of the mixed oxide, or "solid solution-type," electrode coating. Commonly, an electrode again comprises a valve metal base, generally titanium, however the coating is a solid solution of a valve metal oxide and a precious metal oxide, typically, titanium dioxide-ruthenium dioxide. In these solid solution coatings, atoms of valve metal in the characteristic rutile valve metal oxide lattice are randomly replaced with atoms of precious metal. The result is an electrode which, when employed as an anode in the electrolysis of an aqueous sodium chloride solution, for example, not only exhibits a low chlorine overvoltage but further exhibits wear rates within the range of from 0.10-0.15 gram of precious metal per ton of chlorine produced. Such electrodes are finding ready acceptance in a variety of electro-chemical industries.

It becomes apparent that as the demand for such electrodes increases, the supply of precious metals will be sorely tested. Hence no decrease in their already-high price can be anticipated.

STATEMENT OF THE INVENTION

Therefore it is an object of the present invention to provide a dimensionally stable electrode exhibiting at least the advantages of a titanium dioxide-ruthenium dioxide solid solution electrode, while allowing a reduction in the amount of ruthenium employed.

This and further objects of the present invention will become apparent to those skilled in the art from the specification and claims which follow.

A dimensionally stable electrode has now been found which comprises an electrically conductive substrate bearing on at least a portion of the surface thereof a solid solution-type coating consisting essentially of:

(a) titanium dioxide,
(b) ruthenium dioxide and
(c) tin dioxide,

the mole ratio of titanium dioxide: ruthenium dioxide plus tin dioxide being within the range of 1.5-2.5:1 and the tin dioxide representing from 35 to 50 mole percent of the combined tin and ruthenium dioxides.

In essence the discovery is that from 35 to 50 mole percent of the ruthenium dioxide present in the coating may be replaced with tin dioxide. Expressed in another manner, from about 16 to 24 weight percent of the total coating is SnO₂. For example, and according to the preferred embodiment, in place of a coating containing two moles of TiO₂ per mole of RuO₂, may be used a coating containing, for every two moles of TiO₂, 0.5 mole of RuO₂ and 0.5 mole of SnO₂. The potential of such anode, as measured for example by its chlorine overvoltage (that is, the potential at which chlorine is discharged when the electrode is employed as an anode in an aqueous sodium chloride solution), is at least equal to a tin-free anode, with the tin-substituted anode's overvoltage often, in fact, being somewhat lower. Further, the spread between the potentials at which chlorine and oxygen are discharged at an anode containing SnO₂ within the stated range, is further displaced than when employing a conventional TiO₂/RuO₂ anode. The result of this is less contamination of chlorine gas with oxygen and a higher Cl₂ efficiency.

In addition to the foregoing and its readily apparent implication of savings in raw materials based on the difference in price between tin and ruthenium, a further, significant and unexpected advantage accrues. When a titanium anode coated with a TiO₂-RuO₂ solid solution in which 50% of the RuO₂ has been replaced with SnO₂ (2TiO₂:0.5RuO₂+0.5SnO₂) is employed as an anode for chlorine production, a wear-rate of only 0.01 gram of ruthenium per ton of chlorine is evidenced. Compared with a non-tin substituted anode of the same nature (2TiO₂:RuO₂), this is a difference of one order of magnitude (0.01 vs. 0.10-0.15).

The implications of the foregoing findings will be readily apparent to one skilled in the art. To begin with, a reduced amount of ruthenium may be employed in fabricating the electrode coating. Further, the cost in ruthenium consumed per ton of chlorine produced is lowered. However, perhaps most significantly, the life expectancy of an anode in a commercial installation is extended. That is, for every one year of life of a conventional TiO₂-RuO₂ solid solution-coated titanium anode in a chlorine cell, an active life of 1.4 to 3 years will be obtained by substituting 50 percent of the RuO₂ with SnO₂.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

By use of the term "electrically conductive substrate" it is intended to refer to any material which exhibits suf-
icient mechanical strength and chemical resistivity to support the coating in the intended application. Generally valve metals, such as titanium, tantalum, zirconium and niobium are used owing to their relatively good conductivity and especially to their ability to form an inert oxide coating under anodic conditions. If desired, the substrate may have a core of a more conductive material, such as copper. Another variation is the provision of special "intermediate" layers on the substrate, such as oxygen barrier layer, e.g., manganese dioxide. 

Solid solutions of the general type improved upon by the present invention are disclosed for example in U.S. Pat. 3,632,498 to H. Beer. The particular solid solution disclosed in Beer's patent with which the invention is concerned is the titanium dioxide: ruthenium dioxide coating. Methods disclosed in the aforementioned patent which result in a solid solution of this type are useful according to the practice of the present invention. Especially useful are the thermo-chemical techniques whereby successive layers of solid solution are deposited with intermediate heating in air as is described more fully in the specific example hereinbelow.

The mole ratio of titanium dioxide:ruthenium plus tin dioxide is within the range of 1.5-2.5:1. Within this range then, from 35 to 50 mole percent of the RuO₂ may be replaced with SnO₂. With amounts greater than 50 percent of SnO₂, the potential of the resultant electrode will be generally prohibitively high. Conversely, with amounts less than 35 mole percent of SnO₂, the only significant advantage is the elimination of a minor portion of more costly ruthenium, advantages such as the oxygen-chlorine potential displacement not being realized to a significant extent. Preferably, as the ratio of TiO₂:RuO₂:SnO₂ increases, the amount of tin substitution will decrease similarly.

As with other dimensionally stable electrodes, only a portion of the electrically conductive substrate need bear the electrically conductive coating, although the coating may of course be continuous. While the amount of coating applied per square foot of anode surface will vary according to considerations known to those skilled in the art, amounts within the range of from 3-6 grams per square foot (total oxides) may be conveniently applied for most commercial purposes. Porous protective coatings, e.g., ceramics, may be applied over the tin-substituted coating if desired.

It will be understood that the invention is independent of the mechanical configuration of the substrate and hence may take any shape which will allow the application of the coating. Thus, the electrodes may take the form of a wire, rod, cylinder, sheet or the like. Further, if the electrode is present in a sheet or plate form, it may be either solid or foraminous. Other configurations most useful in a particular application will be apparent.

In order that those skilled in the art may more readily understand the present invention, the following specific examples are afforded.

**EXAMPLE**

A master coating solution is as follows:

<table>
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<tr>
<th>RuCl₃ · 2.5H₂O (38.6% Ru)</th>
<th>SnCl₂ (anhydrous)</th>
<th>Butyl titanate (14.3% Ti)</th>
<th>HCl (36%)</th>
<th>Butanol</th>
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<tbody>
<tr>
<td>1,192 g</td>
<td>574 g</td>
<td>5,580 ml</td>
<td>760 ml</td>
<td>11,200 ml</td>
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The solution is prepared by partially dissolving the tin and ruthenium salts in the HCl and adding the butanol. After stirring until the salts dissolve, the butyl titanate is added and the solution is again stirred to ensure complete intermixing. Analysis of the solution gives the following composition in grams per liter: Ru 25.5, Ti 44.3 and Sn 20. This represents a TiO₂(RuO₂+SnO₂) mole ratio of 2.2:1 and 40.0 mole percent SnO₂ in (RuO₂+SnO₂).

A portion of this master solution is applied to an expanded titanium mesh substrate and the thus-coated titanium is heated in air to a temperature of 450°C for seven minutes. This procedure is repeated ten more times to result in a final coating weight of 1.5 grams per square foot of anode surface on a (RuO₂+SnO₂) basis.

Anodes prepared according to the foregoing are installed in a conventional mercury cell for the production of chlorine and caustic. After approximately eight months operation, during which time the cell in question produces 19.4 tons of chlorine, the anodes are removed and analyzed to determine the amount of ruthenium remaining. The average weight per cent of the anodes is determined to be 0.01 gram of ruthenium per ton of chlorine produced. Anodes operating in the same cell room, differing only in that no tin is present in the coating (a mole ratio of 2.0:1 still being used), show an average weight per cent of 0.10 gram per ton of chlorine. In addition, the cells employing the tin-substituted anodes exhibit average potentials 0.04 volt lower than the potential of cells employing the "conventional" DSA.

In another test of an electrode prepared as above, it is employed as the anode opposite an asbestos-coated steel mesh cathode in a diaphragm cell. Analysis of the cell gases indicates that between 22 and 25% less oxygen is produced than when employing the usual TiO₂:RuO₂ on Ti anode.

While the invention has been described with reference to certain preferred embodiments thereof, it is not to be so limited as is clear from the specification and appended claims.

I claim:

1. An electrode which comprises an electrically conductive substrate bearing on at least a portion of the surface thereof a solid solution-type coating consisting essentially of:
   (a) titanium dioxide,
   (b) ruthenium dioxide and
   (c) tin dioxide,
   the mole ratio of TiO₂:RuO₂:SnO₂ being within the range of 1.5 to 2.5:1 and the tin dioxide representing from 35 to 50 mole percent of the combined ruthenium and tin dioxides.

2. An electrode as in claim 1 wherein the substrate is titanium.

3. An electrode which comprises a titanium substrate bearing on at least a portion of the surface thereof a solid solution-type coating consisting essentially of titanium dioxide, ruthenium dioxide and tin dioxide, two moles of titanium dioxide being present for every mole of combined ruthenium and tin dioxides and the amount of tin dioxide being about 45 mole percent of the combined ruthenium and tin dioxides.

References Cited

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<table>
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<th>Inventor(s)</th>
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