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[54] **ELECTRODES WITH MULTICOMPONENT COATINGS**

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[57] **ABSTRACT**

Electrodes useful in a wide variety of electrolytic processes comprise a conductive substrate bearing on at least a portion of the surface thereof a four-component coating, said components being the oxides of tin, antimony, at least one platinum group metal, and a valve metal selected from the group titanium and tantalum.

14 Claims, No Drawings

ELECTRODES WITH MULTICOMPONENT COATINGS

BACKGROUND OF THE INVENTION

Recent years have seen a proliferation of dimensionally stable electrodes, i.e., wear resistant conductive substrates bearing on the surface thereof an electrically conductive, electrocatalytically active coating. Among these have been electrodes coated with (1) an antimony oxide-doped tin oxide containing a platinum metal oxide as the electrocatalytic agent or (2) mixed crystals (solid solutions) of a valve metal oxide and a platinum metal oxide. While such electrodes are far superior to the previously employed graphite, particularly in the area of chlor-alkali electrolysis, understandable efforts have continued to extend the life of these electrodes (that is, reduce the platinum metal wear-rate per unit of product) and/or to reduce the tendency of the coatings to passivate (that is, increase in operating potential to a point at which further operation becomes impractical), especially under oxygen-evolving conditions. Further, owing to inherent limitations relating both to life and passivation tendencies, no single electrode coating system has been found applicable to use in a wide variety of electrochemical processes.

STATEMENT OF THE INVENTION

Therefore, it is an object of the present invention to provide a coated electrode having a long coating life.

It is a further object of the present invention to provide an electrode, the coating of which is extremely resistant to passivation.

It is a still further object of the present invention to provide an electrode, the properties of which may be adapted for use in a variety of electrochemical processes.

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

There has now been found an electrode comprising an electrically conductive supporting substrate bearing on at least a portion of the surface thereof a coating consisting essentially of from 1.0 to 10.0 percent antimony oxide, from 30 to 90 percent tin dioxide, from 1.0 to 50 percent of at least one platinum group metal oxide, and from 0.5 to 30 percent of a valve metal oxide selected from the group consisting of titanium and tantalum oxides, with the proviso that the mole ratio of tin to antimony oxides is between 95:5 and 85:15. Further, within the aforestated ranges, those coatings having high valve metal and platinum metal oxide concentrations are particularly useful as anodes at which oxygen is evolved. On the other hand, those coating compositions having low valve metal oxide concentrations and moderate concentrations of platinum metal oxides are particularly useful in chlor-alkali electrolysis.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As stated, the invention lies in a combined coating of oxides of tin, antimony, at least one platinum group metal, and a valve metal selected from the group titanium and tantalum on a conductive substrate, useful as an electrode, especially as an anode, in a variety of electrochemical processes including electrowinning of metals (e.g., copper, nickel, and zinc) from aqueous solution; chlor-alkali electrolysis including chlorine, chlorate, or hypochlorite production; electroplating; oxygen evolution from organic acidic solutions; ozone generation; cathodic protection; electrodialysis; and the like.

Suitable substrates include generally any metal of sufficient electrical conductivity and mechanical and chemical resistance to the cell environment in which it is to be employed. For example, these materials may include nickel, steel, stainless steel, titanium, niobium, zirconium, and tantalum. Especially preferred for most applications are titanium, niobium, or tantalum substrates. Of course, those substrates bearing an exterior coating, such as copper or aluminum-cored titanium or a platinum or other conductive metal layer over a titanium substrate, are contemplated. Generally, prior to deposition of the coating and in order to provide a base to which the coating may be satisfactorily anchored, an etching or other cleaning operation is employed.

The configuration of the electrode will vary considerably with the application intended but may generally be in the form of a rod or a sheet, either continuous or foraminous, of the appropriate material.

What may be considered the first of the components in the coating composition is tin dioxide, preferably present in the form of crystalline SnO_2 and employed within the range of from 30 to 90 percent by weight of the total coating composition on an oxide basis, especially 30 to 50 percent for oxygen applications and 60 to 90 percent for chlorine.

The antimony oxide component enters into the tin oxide crystal lattice, rendering same more electrically conductive. Although the antimony is present in an indeterminate oxide form owing to its entrance into the tin oxide crystal lattice, it may be expressed for convenience sake as Sb_2O_3. Thus, on this basis, the antimony oxide is present within the range of from 1.0 to 10, preferably 4.0 to 10, percent by weight.

The foregoing ranges of tin and antimony oxides are further qualified by the proviso that they be present, respectively, in the range, on a mole ratio basis as the oxides, of 95:5 to 85:15, especially 90:10. In this fashion there is obtained the desired doping effect of the antimony on the tin oxide without the presence of an excess separate phase of antimony oxides.

The third component of the coating is at least one "platinum group metal oxide", by which term it is intended to include the oxides of platinum, palladium, ruthenium, iridium, rhodium, and osmium, preferably ruthenium, iridium, rhodium, and palladium, and especially mixtures of ruthenium with iridium, rhodium, or palladium oxides. These platinum group metal oxides are present in their most highly oxidized form and within the range of from 1.0 to 50 percent by weight. When the electrode is being fabricated for use as an anode at which oxygen is evolved, primarily or as a coproduct, amounts within the range of from 20 to 40 percent platinum metal oxide are preferred. On the other hand, when a chlor-alkali anode is intended, amounts within the range of 1.0 to 25 percent are preferred.

The final component is a valve metal oxide selected from the group consisting of titanium and tantalum oxides. While the titanium is present in the form of TiO_2 and is generally crystalline (rutile) in nature, when tantalum is employed, an essentially amorphous tantalum oxide results. Therefore, although it is expressed as

Ta_2O_5, it is understood that mixtures of tantalum oxides may in fact be present. The amounts of valve metal oxides employed are generally within the range of from 0.5 to 30 percent by weight, especially 15 to 25, for oxygen-evolving applications and 0.5 to 3.0 for chlor-alkali electrolysis. Further, for a chlor-alkali application, titanium is preferred as the valve metal whereas in oxygen-evolving applications the preferred valve metal is tantalum, although they are interchangeable in many instances. Generally speaking, the use of small amounts of the valve metal oxide acts to extend the life of the electrode coating while the incorporation of larger amounts adds resistance to passivation.

In summary, an example of a preferred anode for oxygen-evolving applications is a coating of from 30 to 50 percent SnO_2, 4.0 to 8.0 percent Sb_2O_3, 20 to 40 percent platinum metal oxide, and 15 to 25 percent valve metal oxide on a titanium, tantalum, or niobium substrate.

On the other hand, an example of a preferred chlorine anode is a coating of 60 to 90 percent SnO_2, 4 to 10 percent Sb_2O_3, 1.0 to 25 percent platinum metal dioxide, and 0.5 to 3.0 percent titanium or tantalum oxide on a titanium substrate.

While many of the variety of methods known for producing mixed metal oxide coatings may be employed, the preferred method of preparing the multicomponent coating composition of the substrate is by deposition from a solution of the appropriate thermochemically decomposable salts. For example, it is desirable to paint or brush an acidified alcoholic solution of said salts onto the substrate followed by drying at 100°–140° C for from 3 to 10, especially 5, minutes and finally by baking in an oxidizing atmosphere, e.g., air, at 450° to 520° C, espically 500° C, for from 5 to 10, especially about 7, minutes. This procedure may then be repeated any number of times until the desired coating thickness is obtained, for example, 6 to 10 coats. The preferred solvents for the thermally decomposable salts are the lower alkanols, such as ethanol, propanol, amyl alcohol, and especially n-butyl alcohol, although other solvents including water, may be employed, to which there is generally added from 0 to 50 percent by volume of an acid, such as concentrated hydrochloric acid (36%). The concentration of the salts from which the coating composition is derived is such as to give a metal content in solution within the range of 50 to 200 grams per liter. The salts employed are generally any thermally decomposable inorganic or organic salt or organic ester of the metals in question such as the chlorides, nitrates, alkoxides, alkoxy halides, resinates, amines, and the like. Specific and illustrative examples include potassium hexachlororuthenate, hexachloroiridic acid, ruthenium trichloride or tribromide, orthobutyl titanate, tantalum pentachloride, antimony trichloride or pentachloride, and stannic chloride or dibutyl tin dichloride.

It will be understood by those skilled in the art that it is possible to use a number of combinations of preformed oxides of the various component metals and salts of the remaining materials, although it is generally believed that preformed valve metal oxides should not be employed nor should separately preformed tin and antimony oxides be used. Further, if thermal decomposition is incomplete, small amounts of salts may remain without detrimental effect in the coating, for example, small amounts of chloride in the primarily oxide coating.

In order that those skilled in the art may more readily understand the present invention and certain preferred embodiments by which it may be carried into effect, the following specific examples are afforded.

EXAMPLE 1

A series of electrodes is prepared and evaluated as anodes as follows. In each instance, the quantity of thermally decomposable salt set forth in Table 1 is dissolved in 45 ml of ethanol with stirring. The resultant solution is brushed onto an expanded titanium mesh substrate, previously cleaned by etching for 30 minutes in boiling (18%) aqueous hydrochloric acid. The solution is applied to the mesh by brushing, followed by drying the anode for 3 minutes at 110° C and firing in air at 500° C and 7 minutes. This brushing, drying, and baking procedure is repeated until a coating containing 1.7 grams of ruthenium per square foot of anode surface is obtained (usually 6–10 coats). Following the final baking, the electrodes are evaluated as anodes in a 150 g/l sulfuric acid solution at 3 amperes per square inch opposite a titanium mesh cathode and at an electrode gap of 2 inches. The test is continued until the anodes have passivated, i.e., a voltage of 8.0 volts or greater is obtained. The lifetime of the anode, that is, the number of hours of successful operation until passivation occurs, is reported in the following Table 1.

TABLE 1

Anode	$SnCl_4.5H_2O$ g	SnO_2 %	$SbCl_3$ g	Sb_2O_3 %	$RuCl_3.xH_2O$ (38%) g	RuO_2 %	$TaCl_5$ g	Ta_2O_5 %	Lifetime hrs.
1	—	—	—	—	12	70.9	4.5	29.1	106
2	20.2	59.3	1.5	6.6	10.2	34.1	—	—	165
3	5.3	16.4	0.4	1.8	17.2	61.9	4.5	19.9	189
4	10.6	34.0	0.8	3.7	11.4	41.8	4.5	20.5	408
5	15.1	47.2	1.1	5.1	7.6	27.6	4.5	20.1	650

From this it is apparent that Anodes 4 and 5, according to the present invention, are greatly superior to either an anode combining the valve metal and platinum group metal (anode 1) or the platinum metal-antimony-tin system (Anode 2). Further, Anode 3 illustrates that the range of components of the present invention is critical to obtaining an anode having a long lifetime.

EXAMPLE 2

Four electrodes were prepared from the following solutions:

Anode 6 — 50 ml n-butanol, 12.5 g $SnCl_4 \cdot 5H_2O$, 0.9 g $SbCl_3$, and 1.1 g $RuCl_3 xH_2O$ (38% Ru).

Anode 7 — 45 ml ethanol, 5.0 g orthobutyl titanate,

1.1 g $SbCl_3$, 15.1 g $SnCl_4 \cdot 5H_2O$, and 7.6 g $RuCl_3 \cdot xH_2O$ (38% Ru).

Anode 8 — 50 ml n-butanol, 12.5 g $SnCl_4 \cdot 5H_2O$, 0.91 g $SbCl_3$, 7.0 g orthobutyl titanate, and 1.1 g $RuCl_3 \cdot xH_2O$ (38% Ru).

Anode 9 — 45 ml ethanol, 4.5 g $TaCl_5$, 1.1 g $SbCl_3$, 15.1 g $SnCl_4 \cdot 5H_2O$, and 7.6 g $RuCl_3 \cdot xH_2O$ (38% Ru).

Each anode is prepared by applying six coats of the solution by brush, with heating in air between each coat first at 110° C for 3 minutes followed by 7 minutes at 500° C.

These electrodes are evaluated as anodes in a horizontal mercury cell spaced 0.14 inch above and parallel to a mercury cathode flowing at a rate of 450 ml/minute. The electrolyte is a 310 g/l brine solution having a pH within the range of 3–6 and a temperature of about 70° C. To establish the wear-rate of the anodes, electrolysis is conducted at 6 amperes per square inch for 500 hours, the loss being determined by weight differential. Results, together with the composition of each anode coating calculated on an oxide basis, appear in Table 2.

TABLE 2

Anode	SnO_2 %	Sb_2O_3 %	RuO_2 %	TiO_2 %	Ta_2O_5 %	Wear-Rate g/ton Cl_2
6	83.8	8.1	8.1	—	—	0.29
7	55.4	6.4	30.6	7.6	—	0.25
8	81.9	8.9	7.9	1.3	—	0.14
9	47.4	5.2	27.2	—	20.2	0.11

From the table, it is evident that Anode 6, without the added valve metal oxide, exhibits the highest wear-rate. When tantalum is employed (Anode 9) or using relatively small amounts of titanium (Anode 8), the best results are obtained.

EXAMPLE 3

An anode coating solution if prepared from 45 ml ethanol, 4.5 g $TaCl_5$, 1.1 g $SbCl_3$, 15.1 g $SnCl_4 \cdot 5H_2O$, and 7.6 g $RuCl_3 \cdot xH_2O$ (38% Ru). An etched titanium mesh substrate is coated by brushing, drying at 110° C for 3 minutes, and baking in air at 500° C for 7 minutes. The coating procedure is repeated until a coating having a platinum group metal content of 1 gram per square foot is obtained. This is labeled Anode 10.

Anode 11 is prepared in an identical fashion but substituting 0.92 g of $IrCl_3$ and 6.54 g $RuCl_3 \cdot xH_2O$ for the ruthenium content of Anode 10. Anode 12 is likewise similar with the exception that 1.28 g of $RhCl_3 \cdot 3H_2O$ and 6.65 g $RuCl_3 \cdot xH_2O$ comprise the platinum group metal content.

When evaluated according to the lifetime test described in Example 1 above, Anodes 10, 11, and 12 have lifetimes, respectively, of 185, 250, and 350 hours. This indicates the substantial improvement possible employing a mixture of platinum metal oxides in the coating.

We claim:

1. An electrode comprising an electrically conductive supporting substrate bearing on at least a portion of the surface thereof a coating consisting essentially of from 1.0 to 10 percent antimony oxide, as Sb_2O_3, on a weight basis, from 30 to 90 percent SnO_2, from 1.0 to 50 percent of at least one platinum group metal oxide, and from 0.5 to 30 percent of a valve metal oxide selected from the group consisting of titanium and tantalum oxides, with the proviso that the mole ratio of tin to antimony oxides is between 95:5 and 85:15.

2. An electrode as in claim **1** wherein the supporting substrate is selected from the group consisting of nickel, steel, stainless steel, titanium, niobium, zirconium, and tantalum.

3. An electrode as in claim **1** wherein the platinum metal oxide is RuO_2.

4. An electrode as in claim **1** wherein the valve metal oxide is TiO_2.

5. An electrode as in claim **1** wherein the valve metal oxide is amorphous tantalum oxide.

6. An electrode as in claim **1** wherein the ratio of tin to antimony oxides is about 90:10.

7. An anode for use in oxygen-evolving applications, which anode comprises an electrically conductive supporting substrate bearing on at least a portion of the surface thereof a coating consisting essentially of from 4.0 to 8.0 percent antimony oxide, calculated as Sb_2O_3, on a weight basis, from 30 to 50 percent SnO_2, from 20 to 40 percent of at least one platinum metal oxide, and from 15 to 25 percent of a valve metal oxide selected from the group consisting of titanium and tantalum oxides, with the proviso that the mole ratio of tin to antimony oxides is between 95:5 and 85:15.

8. An anode as in claim **7** wherein the substrate is selected from the group consisting of nickel, steel, stainless steel, titanium, niobium, zirconium, and tantalum.

9. An anode as in claim **7** wherein the platinum metal oxide is a combination of RuO_2 and IrO_2.

10. An anode as in claim **7** wherein the platinum metal oxide is a combination of ruthenium and rhodium oxides.

11. An anode as in claim **7** wherein the valve metal oxide is amorphous tantalum oxide.

12. An anode for use in chlor-alkali electrolysis, which anode comprises a valve metal substrate selected from the group consisting of titanium, niobium, zirconium, and tantalum bearing on at least a portion of the surface thereof a coating consisting essentially of from 4.0 to 10 percent antimony oxide, calculated as Sb_2O_3, on a weight basis, from 60 to 90 percent SnO_2, from 1.0 to 25 percent of at least one platinum group metal oxide, and from 0.5 to 3.0 percent of a valve metal oxide selected from the group consisting of titanium and tantalum oxides, with the proviso that the mole ratio of tin to antimony oxides is between 95:5 and 85:15.

13. An anode as in claim **12** wherein the substrate is titanium.

14. An anode as in claim **12** wherein the valve metal oxide is TiO_2.

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