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[54] **ELECTROLYTIC ANODE**

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[63] Continuation-in-part of Ser. No. 786,407, Dec. 23, 1968, Pat. No. 3,616,329.

[52] **U.S. Cl.**..... **204/98,** 117/221, 117/230, 204/99, 204/181, 204/219, 204/252, 204/266

[51] **Int. Cl.**..... **C01d 1/06**

[58] **Field of Search**..... 204/98, 99, 219, 204/220, 252, 258, 290 F, 266

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[57] **ABSTRACT**

An improved anode for the electrolysis of brine is comprised of a corrosion resistant valve metal substrate and a thin adherent exterior coating consisting esentially of ruthenium oxide and a carbide, the carbide being inert to the electrolysis environment. An especially effective anode has a coating of ruthenium oxide and boron carbide.

5 Claims, No Drawings

ELECTROLYTIC ANODE

This application is a continuation-in-part of application Ser. No. 786,407, filed Dec. 23, 1968 and now U.S. Pat. No. 3,616,329.

This invention relates to novel anodes for cells used for the electrolysis of brines, and more particularly to improved anodes comprised of platinum group metal coated electrolytic valve metals and a method for obtaining such anodes.

The anodes of the present invention are particularly useful in cells used for the production of chlorine and caustic soda by the electrolysis of an aqueous solution of sodium chloride. In such cells graphite anodes are usually used commercially. Although the graphite anodes are not entirely satisfactory because their wear rates are high and impurities such as CO_2 are introduced in the products, no satisfactory substitutes have yet been found.

Platinum group metal coated electrolytic valve metals have been proposed as substitutes for graphite anodes. These metallic anodes offer several potential advantages over the conventional graphite anodes, for example, lower overvoltage, lower erosion rates, and higher purity products. The economic advantages gained from such anodes, however, must be sufficiently high to overcome the high cost of these metallic anodes. Anodes proposed heretofore have not satisfied this condition. Therefore commercialization of the platinum group metal anodes has been limited.

One problem is the life of the metallic anodes. A factor which contributes to shortening the anode life is the so-called "undercutting" effect. For economic reasons the low overvoltage precious metal coatings are very thin films which are inherently porous. Although the electrolytic valve metals are substantially corrosion resistant, the valve metals are slowly attacked through the pores of these coatings causing "undercutting" with subsequent loss of the precious metal film, thereby shortening the life of the anodes.

Another problem is the loss of precious metal during operation of the cell. Although the loss is gradual, it is costly because the precious metals are expensive and because the erosion of thin coatings shortens the anode life. The loss of precious metal may be from mechanical wear. At the high current densities desirable in commercial installations, the increased flow rate of brine and excessive gassing are conducive to such mechanical wear. In mercury cells a contributing factor is amalgamation of the precious metals.

Still another problem is providing such coated anodes by an economically feasible method.

It is the object of this invention to provide, by an economically feasible method, metal electrolytic anodes with improved life and lower metal losses without sacrificing the low overvoltage characteristics of the precious metal coating.

In accordance with the present invention a precious metal anode is provided which has long life and lower precious metal losses due to mechanical wear and amalgamation. The resistance to amalgamation makes the anode particularly useful in mercury cells. It was a further advantage of the anodes of this invention that the electrical properties were equal and even superior to conventional anodes using a greater equivalent weight of platinum group metals.

The anode of the present invention is comprised of a corrosion resistant metal substrate and a coating consisting essentially of ruthenium oxide and a carbide. Generally any carbide may be used that is inert to the environment of the cell. Preferably the carbide should also have relatively good electrical conductivity. By way of example, the carbides that may be used are compounds of the elements selected from the group B, Si, Ti, Hf, V, Nb, Ta, Cr, Mo, and W, and combinations thereof.

The carbides that are particularly useful are those of the so-called giant molecule covalent type and the interstitial type. The term "giant molecule covalent carbide" refers to carbides characterized by complete covalent bonding, which results in high degrees of hardness and inertness. These carbides have a perceptible electrical conductivity. Boron carbide (B_4C) and silicon carbide (SiC) belong to this class of carbides. Chromium carbide (Cr_3C_2) is also believed to possess some of these characteristics. The interstitial carbides most useful for the anodes of the present invention are those having relatively large metal atoms (radius equal to about 1.3A. or greater) so that the carbon atoms in the interstices do not appreciably distort the metallic lattice. Typical interstitial carbides are TiC, VC, NbC, TaC, MoC, and WC. All of these carbides, both the covalent and interstitial type, are essentially insoluble in hydrochloric acid. It has been found, however, that coatings prepared with boron carbide have exceptionally good adherence as well as superior electrical properties.

The corrosion resistant metal substrates, the so-called valve metals, used for electrolytic anodes are well known in the field. They are much less expensive than platinum group metals and they have properties which render them substantially corrosion resistant to the anodic environments in electrolysis cells. Examples of suitable corrosion resistant valve metals are Ti, Ta, Nb, Hf, Zr, W, Al, and alloys thereof. It is also well known to have the valve metal as a layer on a base metal such as copper which is a good conductor but corrosive to the environment, and such modifications are within the scope of this invention.

Anodes of this invention are suitably prepared by depositing a slurry of a carbide in the form of a fine powder in a liquid medium containing ruthenium on a corrosion resistant substrate and then firing the coating in an oxidizing atmosphere such as air to drive off the liquid and form an adherent coherent coating of ruthenium oxide and the carbide. The coating may be deposited using the usual techniques such as by brushing, spraying or dipping. The coating may also be applied by electrophoresis. Suitably the carbide is present as a powder having a particle size of no greater than 250 microns. Preferably at least some of the carbide particles have a diameter no greater than about 10 microns. The ruthenium is present as a salt, oxide or the metal per se; it is present dispersed as a fine powder or dissolved in the aqueous or organic medium. When the slurry contains ruthenium as a salt or metal, the coated substrate is heated at a temperature in the range of about 400° to 800° C. to convert such ruthenium to ruthenium oxide and to form an adherent coherent coating. The time required to convert the ruthenium metal or salt to the oxide depends on the temperature used. Typically the coated substrates are fired in air at 500° C. for 5 minutes; but longer firing times are also used. When the slurry contains ruthenium as ruthenium oxide, the coating is heated to higher temperatures, e.g., about 1,000°

C. and higher, for a period of time necessary to sinter the particles and form an adherent coherent coating.

Alternatively the ruthenium salt, oxide or metal is applied on the substrate followed by an application of the finely divided boron carbide and the coated substrate is fired as indicated above.

It should be understood that conversion of the ruthenium metal and salts may not be complete under the firing conditions given. Normally an equilibrium will be reached under which conversion is to predominantly ruthenium oxide and the balance ruthenium. Such materials are within the contemplation of this invention. It will be noted that the presence of the carbide in the ruthenium salt mixture makes it possible to use the ruthenium salt in the formulation in a higher concentration than previously possible and still obtain a coating of principally ruthenium oxide. This is one of the main advantages of using the mixed carbide coating.

It should be further understood that the precursor composition may contain an additive for improving the adherence, continuity and abrasion resistance of the coating. The use of such additives is well known in the ceramic art for forming thin adherent precious metal coatings, and they are commonly referred to as fluxes. The choice of ingredients for the flux is dictated in part by the composition of the substrate. It is well known, for example, to use salts and resinates of bismuth, chromium, lead, cadmium, tin, copper, boron, antimony, titanium, tantalum, silicon, and uranium. The use of such ingredients is well understood by those skilled in the art of compounding precious metal decorating compositions.

The concentration of ruthenium oxide in the coating ranges from about 5 to 90% by weight and the carbide content ratio ranges from about 10 to 95% by weight. With respect to boron carbide, for example, it has been found that higher percentages of boron carbide increase the adherence of the coating without excessive sacrifice of the electrical characteristics. One preferred embodiment contains about 50% ruthenium oxide and 50% boron carbide.

Several applications of the dispersion may be deposited, preferably firing at the indicated temperature is performed after each application.

The following examples are given by way of illustration and not as a limitation of the invention. It will be appreciated that modifications within the scope and spirit of the invention will occur to those skilled in the art.

The examples show comparative tests in an electrolytic diaphragm cell using various anodes.

In each anode the substrate is a sheet of commercially pure titanium 1/2 inch × 3 inches × 0.063 inch. The titanium sheets are prepared for coating by etching in concentrated hydrochloric acid for 18 hours at a room temperature and cleaning in fluoboric acid.

EXAMPLE I

Sample A is prepared as follows:

An aqueous paint composed (by weight) of 3.13% boron carbide (milled to a fine particle size, 90% less than 8.2 microns and 50% less than 5.2 microns), 6.87% ruthenium chloride, and 90% water is applied to both sides of a previously prepared titanium sheet. The coated substrate is fired in air at 500° C. for 5 minutes. This procedure is repeated an additional six times to give a coating composed of 52.9% RuO_2 and 47.1% boron carbide (by weight). The total weight gain of the sample is 0.0263 grams. This deposit contains an amount of Ru equivalent in weight to a 17 microinch Ru coating. The deposit showed exceptionally good adherence and coherence. Sample B is prepared as follows:

A low overvoltage 70% Pt-30% Ir coating having a thickness of 27 microinches is applied to one side of a titanium sheet. The coating is applied from a paint using a known technique of application and firing. Sample C is prepared as follows:

A low overvoltage RuO_2 layer having a thickness equivalent to 17 microinches of Ru, determined gravimetrically, is prepared from an alcohol based paint containing $RuCl_3$, linalool and 2-propanol. The coating is converted to RuO_2 by heating in air at 500° C. for 10 minutes.

Samples A, B, and C are used as anodes in a laboratory scale diaphragm cell for the electrolysis of 25% NaCl solution. The tests are run at 35° C. and at a current density of 1,000 amperes per square foot (ASF). The chlorine overvoltage is determined with a conventional Luggin capillary probe, and the results are shown in TABLE I.

TABLE I

Sample	Thickness of Precious Metal in Coating (microinches)	Chlorine Overvoltage (millivolts)	Cell Potential (volts)
A	17	25	3.80
B	27	40	3.80
C	17	59	3.85

The results in TABLE I show that Anode A, the anode of this invention, has excellent overvoltage properties; the performance of anode A surpassed that of anode C, which has a comparable and equivalent thickness of precious metal but does not contain the carbide, and even surpassed anode B, which has more than one and one half the thickness of precious metal but does not contain the carbide.

An additional advantage of anode A is that for an equivalent weight of precious metal anode A is less expensive than anode B since Ru is less expensive than the Pt-Ir.

A still further advantage of anode A is that the presence of a carbide compound provides an effectively thicker coating for an equivalent weight of precious metal without the boron carbide and the presence of the carbide does not adversely affect the electrical characteristics and in fact shows improvement. In view of the greater thickness it could be expected that the coating would have longer life in commercial operation as illustrated in the next example.

EXAMPLE II

Sample A and C are used as anodes in a diaphragm cell such as described above. The cells are run at a current density of 1,000 ASF for 210 hours. The results are shown in TABLE II.

TABLE II

Sample	A	C
Coating	RuO_2+B_4C	RuO_2
Thickness of Ru in Coating (microinches)	17	17
Overvoltage after 210 hours at 1000 ASF	40	*
Cell Potential after 210 hours at 1000 ASF	3.80	*

*After 210 hours, Sample C would not draw the specified density at its initial cell potential. Upon raising the cell potential rapid disintegration of both the coating and substrate resulted. This demonstrates the superior life of the anode of this invention.

Sample A, an anode of this invention, was tested for an additional 200 hours at 3,000 ASF without failure, indicating that the anode will last at least twice as long as Sample C, which did not contain the carbide.

EXAMPLE III

Sample D is prepared as follows:

An aqueous paint composed (by weight) of 15% ruthenium chloride, 6.25% boron carbide (−325 mesh powder), 8.54% titanium chloride solution (containing 20% $TiCl_3$) and 70.11% water is applied to one side of a previously prepared titanium sheet. The coated substrate is fired at 725° C. for 10 minutes in air. This procedure is repeated to make a total application of five coats. This coating contains an amount of ruthenium oxide equivalent to 15 microinches of ruthenium coating. This coating has excellent adherence.

A reference anode similar to Sample B, described in EXAMPLE 1, is prepared, except that it had a 40 microinch Pt-Ir coating.

Using the laboratory scale diaphragm cell and procedure described in EXAMPLE 1 with Sample D and the reference sample as the anodes, Sample D is found to have a cell potential of 4.90 volts and an anode potential of 1.230 volts, and the reference anode a cell potential of 4.85 volts and an anode potential of 1.215 volts.

EXAMPLE IV

Sample E is prepared using the same procedure as described in EXAMPLE III, except that tungsten carbide in the form of a fine powder is used instead of boron carbide in the formulation.

A reference anode having a low overvoltage 40 microinch coating of Pt-Ir is prepared for comparative electrical performance in a chlorine cell, as previously described.

The anode of the present invention, Sample E, has a cell potential and overvoltage performance comparable to the typical conventional low overvoltage Pt-Ir reference electrode. Sample E is found to have a cell potential of 5.90 volts and an anode potential of 1.210 volts, and the reference electrode a cell potential of 6.00 volts and an anode potential of 1.250 volts.

EXAMPLE V

Sample F is prepared as follows:

A paint formulation composed (by weight) of 8.0% silicon carbide (as a fine powder) 5.0% ruthenium chloride (40% Ru), and 87.0% 2-propanol is applied to one side of a previously prepared titanium sheet. The coated substrate is fired in air at 500° C. for 5 minutes. This procedure is followed a total of five times to give a coating composed of ruthenium oxide and silicon carbide containing an amount of Ru equivalent to a 7 microinch Ru coating.

Sample F is used as an anode in a laboratory scale chlorine cell test, previously described, and compared with a low overvoltage Pt-Ir reference anode similar to Sample B. Sample F is found to have a cell potential of 4.2 volts and an anode potential of 1.20 volts and the reference anode a cell potential of 4.1 volts and an anode potential of 1.17 volts.

EXAMPLE VI

Sample G is prepared as follows:

An aqueous paint composed (by weight) of 2.00% silicon carbide (having a particle size of less than 250 microns), 7.75% ruthenium chloride (38.6% Ru), 6.67% Ludox HS (an aqueous colloidal hydrophilic solution containing 30% SiO_2), and 83.58% water is applied to one side of a previously prepared titanium sheet. The coated substrate is fired at 500° C. for 5 minutes. This procedure is repeated an additional four times to give a coating compound of 50.0% RuO_2, 25.0% SiC, and 25.0% SiO_2. The total weight of the coating applied is 0.0111 grams. This deposit contains an amount of Ru equivalent to a 7.2 microinch Ru coating. The coating has excellent coherence and adherence.

Sample H is prepared as follows:

An aqueous paint, similar to that used for Sample G except that no SiC is present, is applied to a titanium sheet. The paint is composed of (by weight) 17.5% ruthenium chloride, 10.0% Ludox HS (an aqueous. colloidal, hydrophilic silica solution containing 30% SiO_2), and 72.5% water. As in the case of Sample G, five coats are applied. Each coat is fired at 550° C. for 10 minutes. The total weight gain is 0.0096 grams. This coating was not as adherent or coherent as the coating of Sample G.

Sample G and H are used as anodes a laboratory scale chlorine cell test, described in Example I and the results are shown in TABLE III with those using a reference anode, prepared similarly to Sample B.

TABLE III

Sample	Thickness of Precious Metal in Coating (microinches)	Chlorine Overvoltage (millivolts)	Cell Potential (volts)
G	7.2	40	4.23
H	12.5	144	4.85
Ref.	27	40	3.85

The examples demonstrate that the anodes of this invention, having a ruthenium oxide-carbide coating, have excellent electrical characteristics, comparable to conventional low overvoltage platinum coated anodes, and they have long life. In addition the anodes of the present invention are lower in cost than the conventional anodes.

We claim:

1. An anode for the electrolysis of brines comprised of a corrosion resistant valve metal substrate and a thin adherent coating consisting essentially of ruthenium oxide and silicon carbide, said carbide being inert to the electrolysis environment.

2. An anode of claim 1 wherein the thin coating is composed of 5 to 90% ruthenium oxide and 10 to 95% of the silicon carbide.

3. An electrolytic cell comprised of a mercury cathode and an anode comprised of a corrosion resistant valve metal substrate and a thin adherent coating consisting essentially of ruthenium oxide and silicon carbide, said carbide being inert to the cell environment.

4. In the electrolysis of an aqueous alkali metal chloride solution in a cell having a platinum group metal anode by a process comprising contacting said solution with the anode and electrolyzing said alkali metal chloride solution by passing a current through said solution, the improvement wherein said anode is comprised of a corrosion resistant valve metal substrate and a thin adherent coating consisting essentially of ruthenium oxide and silicon carbide, said carbide being inert to the cell environment.

5. A process of claim 4 wherein the cathode is comprised of mercury.

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