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METHOD OF MAKING AN ELECTROLYTIC ANODE

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ABSTRACT OF THE DISCLOSURE

An improved anode for the electrolysis of brines, comprised of a corrosion resistant valve metal substrate, a thin porous adherent exterior coating of silica, and between the substrate and exterior coating a thin layer of ruthenium oxide, is preferably prepared by applying a hydrophilic colloidal solution of silica on the ruthenium oxide and firing the coating.

CROSS-REFERENCES TO RELATED APPLICATIONS

The instant application is a division of application Ser. No. 880,932, filed Nov. 28, 1969, now Pat. No. 3,630,-766, which is in turn a continuation-in-part of application Ser. No. 786,438, filed Dec. 23, 1968.

BACKGROUND OF THE INVENTION

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 ove rthe 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 the metallic anodes. A factor which contributes to shortening the anode life is the so-called "undercutting" effect. For economic reasons the precious metal coatings are very thin films so that exposure of the substrate is imminent. This is particularly true in the use of low overvoltage coatings which are inherently porous. Although corrosion resistant, the valve metals are attacked through the press of these coatings 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 the thin coating 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 rate of flow and the excessive gassing is conducive to such mechanical wear. In mercury cells a contributing factor is amalgamation of the precious metals.

A further problem in mercury cells is "shorting" of the cell on contact of the precious metal with the mercury with consequent effects, such as amalgamation, change in the surface of the anodes with resultant harmful change in electrolytic properties, and cell stoppage.

A still further consideration which is of major importance in the highly competitive manufacturing processes involving the electrolysis of brines is the power consumption associated with the anodes. Power costs represent a substantial percentage of the total production costs and even a small reduction in power consumption produces a material economic advantage.

It was an object of this invention to provide metallic anodes with improved physical and electrical characteristics. It was a further object to provide a process for the electrolysis of brines which can be effected with materially lower production costs.

In accordance with this invention the electrolysis of brines can be effected with a materially lower power consumption. This is achieved by the use of an improved anode. The anode not only reduces the power consumption in the cell, but also it has been found to have long life and low metal losses due to mechanical wear and amalgamation. The resistance to amalgamation makes the anode particularly useful in mercury cells.

SUMMARY OF THE INVENTION

The anode of the present invention is comprised of a corrosion resistant metal substrate, a ruthenium oxide coating, and a thin porous adherent coating of silica over the ruthenium oxide. It is particularly important that the silica coating has a high surface area. To achieve this, the silica particles in the formulation from which the silica coating is developed have a surface area typically of at least about 30 square meters per gram ($m.^2/g.$).

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 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.

The silica coating not only minimizes the contact of the precious metal layer with the electrolyte, but also minimizes penetration of the electrolyte to the valve metal and thus limits the extent of "undercutting" effects. Another advantage is that it minimizes "shorting" and the concomitant problems. Surprisingly however, despite the dielectric characteristics of the exterior coating, these advantages are gained without sacrificing the desirable electrical properties of the precious metal anodes. Indeed, the exterior porous high surface area silica coating improves the electrolytic properties of the thin precious metal coatings. A still further advantage of the anodes of this invention is that the high surface area porous exterior coating is conducive to gas evolution. The silica coating is also useful in improving the mechanical coherence of the ruthenium oxide deposits applied in relatively great thicknesses.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The anodes of this invention are prepared by first forming a ruthenium oxide layer on the base metal substrate and then depositing a silica coating on the ruthenium oxide.

Many methods are known for forming adherent ruthenium oxide films on a metal substrate. For example, after etching and cleaning the surface of the base metal, ruthenium metal or a ruthenium salt is deposited on the substrate and then the coated substrate is subjected to elevated temperatures in an oxidizing atmosphere. The ruthenium metal or salt is deposited in a variety of well known ways, e.g. the ruthenium metal may be deposited as a finely divided dispersion in an organic vehicle or by plating, sputtering, vacuum deposition, the ruthenium salt may be deposited by applying such salt dispersed or dissolved in an organic or aqueous medium. The conversion to the oxide is then effected by firing the coating in an oxygen-containing atmosphere, e.g. air, at a temperature above about 400° C. The firing time depends on the temperature, oxidizing atmosphere used, and the thickness of the ruthenium metal coating applied. Typically a suitable ruthenium oxide is formed by firing the metal film in air at 500° C. for about five minutes, however temperatures in the range of 400° to 1000° C. and even higher may be used.

The exterior high surface area porous silica coating is deposited from a dispersion or solution containing hydrophilic silica or a silica compound precursor in very fine particle size, and the silica coating is fired to develop an adherent coating. It has been found particularly suitable to form the silica coating from a silica having a very fine particle size, e.g. having a surface area of at least 30 square meters per gram ($m.^2/g.$). A preferred method is to deposit the silica from an aqueous hydrophilic colloidal silica solution. The coatings are fired at a temperature greater than about 400° C. to promote bonding. When fired at temperatures lower than about 400° C., the coatings are not sufficiently adherent. Preferred temperatures for forming an adherent porous coating are 600° to 1000° C. and higher, e.g. suitable coatings have been formed at 1200° C. Coatings formed in this manner are adherent and porous and have a high surface area.

More than one coating of silica may be applied. Generally, the silica coatings are effective at a thickness of up to about 200 microinches. Thicker coatings are often not sufficiently porous. Alternatively, multiple thin coatings may be formed by depositing alternate layers of ruthenium oxide and refractory oxide, thereby forming a hard durable multilayer coating on the substrate. The temperature range for firing the successive alternate layers is in the range of about 400° C. to 1000° C., and even higher temperatures may be used. It is not required that all layers be fired at the same temperature. Generally, however, the final layer is preferably fired at a temperature above 800° C. Coatings of improved adherence and uniformity can be formed, for example, at temperatures of 1200° C. without unduly sacrificing the electrical characteristics of the anode. The electrical properties vary with the crystalline structure of the Ti substrate; grades of Ti, e.g. having greater yield strength, are more resistant to oxidation during high temperature firing in air. They also vary with the degree of cold rolling given the Ti prior to coating and with the thickness of the RuO_2 coatings. Although the multilayer coatings are effectice at thicknesses of over 200 microinches, there is no advantage in forming thicker coatings because of their durability even when exceedingly thin.

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.

Examples 1, 2 and 3 show comparative tests in diaphragm and mercury electrolysis cells using various

anodes. For each anode a sheet of commercially pure titanium, ½" x 3" x 0.063", is prepared for coating by etching in concentrated hydrochloric acid for a period of 18 hours at room temperature and cleaning in fluoboric acid. In these examples the coatings are prepared as follows:

RuO_2 coatings are prepared as follows:

An aqueous solution of $RuCl_3$ (containing 10.35% by weight of Ru) is applied to one side of a titanium sheet using a brush. Successive coats are applied, each being fired at 500° C. in air for five minutes until a coating of the desired thickness is obtained. Alternatively a ruthenium resinate solution (containing 4% by weight Ru) is applied. In still another alternative method an alcohol based paint is used. This paint is composed of 1 g. of $RuCl_3$, 1 ml. of linalool and 30 ml. of 2-propanol. X-ray diffraction analysis of samples similarly prepared, by firing the deposited coating in air at the indicated conditions, showed that a major portion of the ruthenium was converted to ruthenium oxide.

Porous adherent silica coatings are prepared as follows:

After forming the RuO_2 layer, it is overcoated with SiO_2 by applying a formulation containing hydrophilic colloidal silica. Ludox HS, and aqueous colloidal silica solution, is used in the formulations. The formulations contain about 10% colloidal silica and 90% water. Film forming additives such as sodium titanate, silicate or borate may be incorporated in minor amounts in the colloidal silica solution. For example, suitable coatings are made from a formulation composed of 10% colloidal silica, 0.5% sodium titanate and 85.5% water. Successive coats of silica are applied and fired in air at 500° C. for 5 minutes until a coating of the desired thickness is obtained.

The thickness of the coatings is determined gravimetrically.

EXAMPLE 1

Two samples are prepared having a RuO_2 coating equivalent to 17 microinches of Ru metal on a titanium substrate.

Sample A is overcoated with 100 microinches of SiO_2 using the method described above. The silica has a surface area of about 70 $m.^2/g.$

Sample B is used as prepared.

Sample A and Sample B are used as anodes in a laboratory scale diaphragm cell for the electrolysis of 25% NaCl solution. The tests are run at a temperature of 35° C. and a current density of 1000 amperes per square foot (a.s.f.). The chlorine overvoltage is determined with a conventional Luggin capillary probe, and the results are set forth in Table I.

TABLE I

	Sample A	Sample B
Coating	RuO_2 and SiO_2 overcoating	RuO_2
Thickness of Ru in coating (microinches)	17	17
Initial overvoltage at 1,000 a.s.f. (millivolts)	70	69
Initial cell potential at 1,000 a.s.f. (volts)	3.50	3.85
Overvoltage after 210 hours at 1,000 a.s.f. (millivolts)	15	(*)
Cell potential after 210 hours at 1,000 a.s.f. (volts)	3.80	(*)

*After 210 hours, Sample B would not draw the specified current density at its initial cell potential. Upon raising the cell potential rapid disintegration of both the coating and the substrate resulted.

This example demonstrates the superior electrical and wear properties of the anode having the SiO_2 exterior coating of this invention over an anode having a RuO_2 layer and no overcoating of silica.

EXAMPLE 2

Samples similar to those described in Example 1 are prepared. Sample C is a titanium substrate with a RuO_2

coating having a thickness equivalent to 17 microinches of Ru. Sample D is a titanium substrate with a RuO_2 layer equivalent to 17 microinches of Ru and 100 microinches overcoating of silica. Each of the samples is masked with pressure tape so that an area of 0.049 in.^{2} of coating remains exposed. Samples C and D are then used as anodes in a small cell using a mercury pool as the cathode and a 25% NaCl solution as the electrolyte. The anodes are subjected to a mercury shorting test as follows:

The exposure area of the test coating is allowed to generate chlorine at 1000 a.s.f. in the brine and then it is submerged in the mercury pool and the change in current density is measured. The tests show that Sample D, having the RuO_2 layer and the SiO_2 exterior coating is very much less susceptible to shorting than the same coating without the protective exterior coating of SiO_2.

It will be appreciated that since the resistance to shorting is higher the anodes of this invention may be positioned in closer spacial relationship with a mercury cathode without danger of shorting and with concomitant lower power requirements.

EXAMPLE 3

Samples similar to those described in Example 1 are prepared, except that the RuO_2 layer is thinner. Two samples are prepared each having a RuO_2 coating equivalent to 2 microinches of Ru on a titanium substrate.

Sample E is used as prepared.

Sample F is overcoated with 170 microinches of SiO_2 using the method described above.

Samples E and F are used as anodes in a laboratory scale diaphragm cell and tested for chlorine overvoltage using the procedure described in Example 1. The cell using Sample F, the anode in accordance with this invention, has an initial chlorine overvoltage of 220 millivolts and a cell potential of 4.30 volts. The cell using Sample E as the anode shows erratic behavior. The coating of Sample E is poorly adherent and the erratic results are believed to be attributable to this poor adherence of the coating and also to the insufficient protection provided by the RuO_2 coating of this degree of thinness.

This test demonstrates the improved physical and electrical properties of anodes of this invention. Such improvements not only permit operation of a cell wtih lower power requirements but also demonstrates the improved life of the anodes since they are operable with thinner coatings of precious metal than anodes without such coatings.

EXAMPLE 4

Two sheets of commercially pure titanium, ½" x 3" x 0.063", are prepared for coating by sandblasting the surfaces with aluminum oxide grid followed by cleaning with an abrasive cleanser. Both sheets are then coated on both sides with a formulation composed of (by weight) 11.5% ruthenium chloride, 42.3% 2-propanol, and 46.2% linalool. The coated substrates are heated to 300° to 400° C. for 1 to 2 minutes and then fired at 500° C. for 5 minutes in an open air furnace to form a RuO_2 coating.

Sample G is prepared by repeating the application of the ruthenium formulation and heat treatment twice, so that a total of three coats of ruthenium oxide are applied.

Sample H is prepared by overcoating the first ruthenium oxide coating with a porous silica coating. The porous silica coating is formed by applying an aqueous colloidal silica solution composed of (by weight) 31.6% Ludox HS (containing 30% SiO_2), 0.5% sodium titanate powder, and 67.9% water. The silica-coated substrate is heated to 500° C. for 5 minutes. Thereafter the procedure of applying and firing alternate coatings of ruthenium oxide and silica is repeated twice.

The composition of the samples is as follows:

Coating	Sample G, percent	Sample H, percent
RuO_2	100	43.3
SiO_2	0	56.7

The gravimetric weight gain in both samples is equivalent to 6.1 microinches of Ru metal. The weight of SiO_2 in Sample H is equivalent to 58 microinches of SiO_2.

Samples G and H are used as anodes in a laboratory scale diaphragm cell and tested for chlorine overvoltage using the procedure described in Example 1. Sample G having 3 coatings of ruthenium oxide has an initial chlorine overvoltage of 155 millivolts and a cell potential of 4.20 volts. Sample H, a multilayer RuO_2–SiO_2 coating prepared in accordance with the present invention, has an initial chlorine overvoltage of 10 millivolts and a cell potential of 4.30 volts. In addition the multilayer RuO_2–SiO_2 coating, applied in alternate layers, is more adherent than the RuO_2 coating of Sample G.

This example not only illustrates a method of preparing the RuO_2 and SiO_2 coating by depositing alternate layers of RuO_2 and SiO_2, but also further demonstrates the improved physical and electrical properties of anodes of this invention.

EXAMPLE 5

Sample I and J are prepared as follows:

Two sheets of commercially pure titanium 1" x 3" x 0.040" are prepared for coating in a manner similar to that described in Example 4. Approximately 5 microinches of ruthenium oxide are formed on both sides of these substrates from five applications of a formulation composed of 6% ruthenium chloride, 44% 2-propanol and 50% linalool, with firing after each application to form a ruthenium oxide coating. The firing conditions for both samples is 500° C. for 10 minutes in air but Sample J is thereafter fired at 1200° C. for 30 seconds in air. Observation of the color showed both samples to be mainly ruthenium oxide.

Both samples were then coated with approximately 100 microinches of SiO_2, deposited as described in Example 4, except that Sample J is subjected finally to a temperature of 1200° C. in air for 30 seconds.

In order to test the adherence of the coatings the following simple tape test is performed: Each sample is weighed to an accuracy of about 0.1 mg. White-gummed electrical tape is firmly pressed to both sides of the samples and then removed. This operation is repeated an additional two times, with clean tape used each time. The samples are then rinsed in acetone, scoured, rinsed in hot water and dried in a stream of hot air. Thereafter the samples are reweighed and the amount of coating removed determined by difference. The weight record of Samples I and J are shown below:

Samples	I	J
Weight of RuO_2 on 1" x 3"	.0074	.0078
Weight of SiO_2	.0250	.0257
Weight of composite coating	.0324	.0335
Weight of coating removed in tape test	.0045	.0013
Percent weight of coating remining after tape test	89.2	96.7

The results of this test show that the coatings formed by firing at the higher temperatures, e.g. 1200° C., have improved adherence.

The overvoltage characteristics of these coated anodes depends, in part on the thickness of the intermediate ruthenium oxide layer. Anodes having a ruthenium oxide coating of, for example, 40 microinches and a porous exterior silica coating fired at high temperatures, e.g. 1200° C., as described above, have not only excellent adherence but also excellent electrical properties.

What is claimed is:

1. A method of preparing an electrolytic anode comprised of a corrosion resistant valve metal substrate, a thin adherent porous exterior coating of silica, and between the substrate and exterior coating a thin layer of ruthenium oxide comprising:

(a) forming a thin film of ruthenium oxide on said substrate,

(b) applying a coating of hydrophilic colloidal solution of silica on said ruthenium oxide,

(c) firing the silica coating at a temperature of at least about 400° C. to form a thin adherent porous high surface area exterior coating of silica.

2. A method of preparing an anode according to claim 1 wherein the silica coating is fired at a temperature of about 600° to 1200° C.

3. A method of preparing an anode according to claim 1 wherein the rutheium oxide layer is formed by depositing on the substrate a coating selected from the group consisting of rutheium metal, ruthenium chloride, or a ruthenium resinate, and heating the coated substrate in air at a temperature of at least about 400° C.

4. A method of preparing an anode according to claim 1 wherein said anode has a multilayer coating of ruthenium oxide and silica comprising, depositing a second layer of ruthenium oxide on said silica coating and thereafter depositing a second silica layer on the second ruthenium oxide layer according to steps b and c of claim 1.

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