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ELECTRODE COATINGS

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U.S. Cl. 204—99 7 Claims

ABSTRACT OF THE DISCLOSURE

Electrocatalytic surfaces suitable for use as anodes in the electrolysis of aqueous alkali metal chlorides are prepared by coating a substrate with a palladium oxide surface containing a film-forming metal oxide, small quantities of an oxide of a second platinum group metal, and an oxide of an iron group metal. The resulting electrodes have a low overvoltage and are long lived in the electrolytic cell environment.

BACKGROUND

Chlorine and alkali metal hydroxides, such as lithium hydroxide, sodium hydroxide, and potassium hydroxide, are produced commercially by the electrolysis of brines in either of two electrolytic processes—electrolysis in a diaphragm cell or electrolysis in a mercury cell. Alkali metal chlorates are produced in a cell similar in structure to a diaphragm cell but not having a diaphragm.

The design and operation of mercury cells, diaphragm cells, and chlorate cells are more fully treated in Mantell, Electrochemical Engineering, McGraw-Hill, New York, N.Y. (1960), and Sconce, Chlorine, Reinhold, New York, N.Y. (1962).

Common to all three processes is the use of carbon anodes. These carbon anodes are a constant source of difficulty. They are short lived and subject to uneven wear and erosion. In mercury cells, frequent adjustment is required in order to maintain a constant voltage drop across the electrolyte. In diaphragm cells and chlorate cells, no provision is made for varying the anode-cathode space, and the voltage increases with time. Additionally, organic solvents present in the graphite electrodes may plug the diaphragm, resulting in a further increase in voltage. Reaction of the anode products with the graphite anode result in halogenated hydrocarbons being present in the anode product.

Many attempts have been made to remedy these problems. It has long been recognized that a superior anode would be one made of a solid precious metal. However, this is neither economical nor practical. The art shows many attempts to obtain a lower cost electrode having the long life and low voltage of a solid precious metal electrode as well as the low cost of a graphite electrode. These attempts have sought to provide a durable coating, usually of a platinum group metal or a platinum group metal oxide, on an electroconductive base.

However, such platinum group metal and platinum group metal oxide coatings have not proved to be particularly durable. They are subject to erosion from the anolyte and chlorine gas. By these and other mechanisms, more than 1.0 gram of coating may be lost per ton of chlorine produced. Additionally, under vigorous conditions of electrolysis, for extended periods of time, for example at anode current densities above about 125 amperes per square foot, for periods of time in excess of about twelve months, they appear to become corroded and lose their electrocatalytic activity. This is evidenced by a sudden increase in voltage in a short time. Typically, an increase of more than 1 volt is observed within one day.

Additionally, while platinum itself exhibits fairly satisfactory properties as an electrocatalytic surface, it is an expensive material.

SUMMARY OF INVENTION

It has been found that an electrocatalytic surface suitable for use as an anode in the electrolysis of brines may be provided by a palladium oxide coating containing a film-forming metal, small quantities of an oxide of a second platinum group metal, and an oxide of an iron group metal therein. Such an anode may be utilized in diaphragm cells and mercury cells for the production of chlorine, as well as in chlorate cells.

By oxide of an iron group is meant oxides of iron, cobalt, nickel, mixtures thereof, and mixed oxides thereof (as spinels).

By "film-forming metal" is meant aluminum, bismuth, niobium, tantalum, titanium, tungsten, vanadium, and zirconium, and mixtures and alloys thereof. Oxides of film-forming metals are oxides of the above metals and of alloys and mixtures thereof.

The coating is applied to a suitable electroconductive substrate. A suitable electroconductive substrate is one that is rendered resistant to oxidation at the substrate-electrocatalytic surface interface during the formation of the electrocatalytic surface and subsequent electrolysis. Such a substrate will not be oxidized at the interface between the substrate and the electrocatalytic surface during either fabrication or electrolysis. Nor will it be subject to corrosive attack by the gases liberated during electrolysis.

The film-forming metals, especially titanium, tantalum, and tungsten, provide suitable substrates.

The resulting electrode is long lived in the electrolytic cell environment and has satisfactory overvoltage characteristics. The resulting electrode is particularly useful for the electrolysis of brines to yield chlorine, as in mercury cells and diaphragm cells. The resulting electrode is also useful for the electrolysis of brines to yield chlorates.

DESCRIPTION OF THE INVENTION

An anode suitable for the electrolysis of aqueous solutions of alkali metal halides, or brines, is provided by an electrocatalytic surface comprising palladium oxide, an oxide of a film-forming metal, small quantities of an oxide of a second platinum group metal, and an oxide of an iron group metal.

Any suitable electroconductive metal rendered resistant to attack by the chlorine cell environment may be used as the substrate or support member of the electrode. Most commonly used are the "film-forming" or "valve" metals; that is, those metals which form a passivating oxide film, conductive only in the cathodic direction. Such metals include aluminum, bismuth, niobium, tantalum, titanium, tungsten, vanadium, zirconium, and alloys thereof. Titanium, tantalum, and tungsten are preferred. Titanium typically is used. Carbon and graphite may also be used. Such substrates may be in the form of a solid structural member or of a thin plate, up to about ¼-inch thick. Or the substrate may be perforate or foraminous in form, as provided, for example, by expanded mesh. When anodes having a perforate or foraminous substrate are used in mercury cells, they may be totally or only partially immersed in the electrolyte. When totally immersed in the electrolyte, only the surface of the anode facing the flowing cathode may be coated with the electrocatalytic anodic surface, or all of the surfaces of the anode may be coated with the electrocatalytic anodic surface. Likewise, when such anodes having perforate or foraminous substrate are used in diaphragm

cells, only one surface or both surfaces of the substrate may be coated with the electrocatalytic anodic surface.

When the electrocatalytic coating is applied directly to an untreated metallic substrate, as commercial grade titanium metal, in the presence of oxygen, the voltage drop across the cell soon becomes very high—on the order of about 10 volts. This increased voltage appears to be caused by the formation of oxides of the metal used in fabricating the substrate at the interface between the substrate and palladium oxide surface. While not wishing to be bound by this explanation, it is believed that either some actual oxidation of the unprotected bulk metal takes place at the interface or that there is some migration or intermetallic diffusion of oxygen atoms into the bulk metal, or possibly one of the oxides present in the surface may oxidize the substrate. This oxidation or migration does not have to proceed to a great extent in order to have deleterious effects.

In one exemplification of this invention utilizing a platinum group metal treatment of the substrate, the application of a platinum group metal directly to the surface of the substrate inhibits this oxidation, thereby reducing the anode voltage drop. Such substrates will be referred to as platinized substrates although all of the platinum group metals, as ruthenium, rhodium, palladium, osmium, iridium, and platinum, produce this effect. Platinum and ruthenium give better results. Platinum gives the best results.

In preparing electrodes according to this exemplification, the substrate is first etched to remove the naturally-occurring oxide coating, typically with hydrofluoric and hydrochloric acids. The substrate is then treated with a metal of the platinum group. In this treatment the metallic substrate member is coated with a solution of a compound of a platinum group metal. The compound should be readily thermally decomposable and yield, as products of decomposition, the metal, and volatiles. Typically used are organometallics as carbonates, formates, oxalates, and resinates. Inorganic salts such as nitrates and halides (as chlorides, bromides, and iodides) may also be used, as may oxides. Alternatively, the coating of the platinum group metal may be electrodeposited onto the structural member. While in still another embodiment of this invention the platinum group metal may be clad to the structural member.

The effect of the platinum group metal does not appear to be an actual physical protection of the member but rather a chemical or inhibiting effect. That is, it makes the substrate less receptive to either actual oxidation or to migration of oxygen. Very thin layers of the platinum group metal are effective. Satisfactory results have been achieved with the application of only three coats of a platinum resinate prior to applying the palladium oxide. X-ray data indicates that platinum group metal coatings of thicknesses from about 2 to 10 microinches are sufficient to give the desired result. By way of comparison, 10 microinches of platinum do not produce a satisfactory platinized titanium electrode where the platinum itself is the electrolyzing surface; a fairly thick, uniform platinum layer of greater than about 20 microinches is required in that case. After the electrode has received a platinum group metal coating, it is ready to receive the palladium oxide coating.

The electrocatalytic palladium oxide coating is then applied to the electroconductive substrate. While a palladium oxide coating is referred to, it should be understood that the coating is essentially palladium oxide and the oxide of a film-forming metal with small amounts of an oxide of a second platinum group metal, and small amounts of an oxide of an iron group metal (all of these terms having been defined previously), all in substantially uniform concentrations throughout the electrocatalytic surface.

The ratio of the oxide of the second platinum group metal to palladium oxide is expressed as the weight ratio of the two metals in the metallic state. For good results this ratio is typically from about .02 to about .15. When the weight ratio exceeds about .15, the excess amount of the second platinum group metal may be present in the metallic state.

When the weight ratio of the second platinum group metal to the palladium is below about .02, the corrosion resistance of the resulting coating is substantially the same as palladium oxide.

Additional durability and erosion resistance is imparted to the electrocatalytic surface by the addition of small amounts of iron group metals, such as iron, nickel, and cobalt. The iron group metals may be present as oxides, such as FeO, Fe_2O_3, CoO, and NiO and mixtures thereof. They may also be present as mixed oxides and spinels having the stoichiometric formulae Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$, and mixtures thereof. Additionally, they may be present as aluminum, chromium, and manganese spinels, such as $FeAl_2O_4$, $Fe^{II}Fe^{III}AlO_4$, $FeCr_2O_4$, $FeMn_2O_4$, $CoAl_2O_4$, $CoCr_2O_4$, $CoMn_2O_4$, $NiAl_2O_4$, $NiCr_2O_4$, $NiMn_2O_4$, and mixtures thereof.

The concentration of the iron group metal (expressed as

$$\left(\frac{\text{weight of iron group metals as metals}}{\text{weight of palladium, second platinum group metal, film-forming metal, and iron group metals, all as metals}} \times 100\right)$$

is typically from about 3 percent to about 25 percent, with better results being obtained at iron group metal concentrations from about 6 percent to about 22 percent. At iron group metal concentrations below about 3 percent, the durability of the electrocatalytic surface is substantially the same as a similar electrocatalytic surface having essentially no iron group metal therein. At concentrations above about 25 percent there is no apparent additional increase in durability of the electrocatalytic surface; and if no spinel is formed, the coating may deteriorate under vigorous conditions of electrolysis.

The surface coating also includes an oxide of a film-forming metal (as defined previously). Alternatively, silicon dioxide may be substituted for the oxide of the film-forming metal. The oxide of the film-forming metal constitutes from about 45 weight percent to about 75 weight percent (expressed as:

$$\left(\frac{\text{weight of film-forming metals, as metals}}{\text{weight of palladium, second platinum group metal, film-forming metal, and iron group metals, all as metals}} \times 100\right)$$

of the surface coating.

The precise concentration of the film-forming metal oxide may be determined either by experimentation or by the methods of optimization. The higher the concentration of film-forming metal, and more resistant the electrode is to corrosion. However, above a concentration of about 75 weight percent, the anode voltage increases significantly.

The electrocatalytic surface, comprising palladium oxide, an oxide of a second platinum group metal, an oxide of an iron group metal, and an oxide of a film-forming metal may be applied to the platinized substrate by a number of expedients.

In one exemplification the coating may be applied by brushing an intimate mixture of thermally decomposable compounds of the metals to be applied onto the substrate. The thermally decomposable compounds should yield the metals, or oxides of the metals, and volatiles upon decomposition. Suitable compounds include organic salts such as formates, oxalates, carbonates, and resinates. Inorganic salts such as nitrates and halides (as chlorides, bromides, and iodides) may also be used as may oxides. The mixture is applied to the substrate and heated in order to thermally decompose the compounds. The electrode may then be heated in an oxidizing atmosphere to oxidize those metals present in the metallic state to the oxide. Alterna-

tively, the coating may be applied by electrodeposition or by electroless deposition.

In order that those skilled in the art may more completely understand the present invention and the preferred methods by which the same may be carried into effect, the following specific examples are offered:

ELECTRODES

Electrodes were cut from 1/16 inch thick titanium in a size of 6 inches by 3/8 inch. Prior to coating, the titanium plate was washed with a household cleanser such as Comet (T.M.) and rinsed in distilled water. The cleaned electrode was immersed for 1 minute in 1 percent hydrofluoric acid to activate the surface for subsequent etching, rinsed in distilled water, and placed in an etching solution which consisted of concentrated (37%) hydrochloric acid at a temperature ranging from room to about 55° C. After the etching the electrodes were rinsed with distilled water and acetone and dried.

APPLICATION OF UNDERCOAT

A platinum resinate solution was used to obtain an undercoating. The solution was prepared by mixing 30 grams of Engelhard 05–X (T.M.) platinum resinate with 27 grams of toluene to yield a solution 4 percent platinum by weight. Each coat was brushed on and heated according to the following schedule:

Coat 1 and all subsequent coats except the last one coat were heated at a rate of 50° C. per 5 minutes to a temperature of 400° C. and maintained at 400° C. for 10 minutes.

The final coat was heated at a rate of 50° C. per 5 minutes to a temperature of 500° C. and held at 500° C. for 10 minutes.

ELECTROCATALYTIC SURFACE

The materials used to prepare the electrocatalytic surfaces were: Toluene; Palladium Resinate Solution, 9% palladium; Titanium Resinate Solution, 4.2% titanium; Platinum Resinate Solution, 12% platinum; Cobalt Resinate Solution, 3.1% cobalt; Iron Resinate Solution, 4.2% iron; and Nickel Resinate Solution, 9.4% nickel. All of the resinate solutions were prepared by the Hanovia Liquid Gold Division of the Engelhard Corporation. The coatings were applied with a brush as uniformly as possible. Each coating was heated in furnace to the desired temperature. The heating was started at room temperature and the temperature increased by 50° C. every 5 minutes until it reached the final level at which it was kept for 10–15 minutes. Before testing, the coating was filed to give a uniform size. For the 6 inches by 3/8 inch electrodes, the coating was filed to give a coating surface of 5 inches by 3/8 inch starting at one end of the electrode. Each electrode had a 1/8 inch hold at the filed end for electrical connection.

CATHODES

Titanium strips 5 inches by 0.4 inch, platinized on one side were used as cathodes.

CHLORATE CELL

The chlorate cell comprised a 1.5 liter jar with Plexiglas top. The Plexiglas top had holes for electrode connections, thermometer, and gas escape. An electrolyte of a 300 grams per liter solution of reagent grade sodium chloride was used. The pH of the electrolyte adjusted itself to a value of 10 to 11. The cell temperature adjusted itself to a value between 30° C. and 55° C., depending on the current density used.

DIAPHRAGM CELL

The second type of cell utilized was a laboratory diaphragm chlorine cell. In this cell the cathode was iron screen with a diaphragm wrapped onto the cathode. The diaphragm was a wrapped asbestos diaphragm. The electrolyte, a saturated solution of sodium chloride having a concentration of 310 grams per liter, was added at a constant rate; and hydrogen, chlorine, and caustic soda were recovered at a constant rate. Electrolysis was conducted at a current density of 250 to 500 amps per square foot. In this diaphragm cell, the anode under test could be connected in parallel with a platinized titanium anode utilized as a standard. This served as a correction for diaphragm effects.

CHLORATE CELL PROCEDURE

To start the test, the electrode which was fastened opposite and 0.5 inch from the cathode was placed in the cell filled with electrolyte, current turned on, and the cell voltage and temperature recorded periodically.

The examples are shown in Table I.

TABLE I

Example	I	II	III	IV	V	VI	VII
Weight percent:							
Platinum	4.6	4.6	4.6	3.9	3.6	3.6	3.6
Palladium	22.9	23	23	24.4	24.2	24.2	24.2
Titanium	66	66.6	66.2	55.6	49.5	49.8	49.8
First iron group metal	[1] 6.4	[2] 5.7	[3] 6.3	[1] 5.2	[1] 7.6	[1] 7.6	[1] 7.6
Second iron group metal				[2] 9.5	[2] 14.8	[2] 14.8	[2] 14.8
Coats of platinum undercoating	5	5	5	5	5	5	7
Surface coating:							
Coats	[4] 11	[4] 11	[4] 11	[4] 11	[5] 5	[6] 8	[7] 5
Platinum resinate	.014	.014	.014	.014	.022	.022	.022
Palladium resinate	.094	.094	.094	.117	.197	.197	.197
Titanium resinate	.580	.580	.580	.580	.870	.870	.870
First iron group metal resinate	[1] .025	[2] .050	[3] .075	[1] .024	[1] .059	[1] .059	[1] .059
Second iron group metal resinate				[2] .101	[2] .257	[2] .257	[2] .257
Toluene	3.15	3.65	3.65	.410	.600	.600	1.300
Cell	ClO_3	ClO_3	ClO_3	ClO_3	ClO_3	ClO_3	ClO_3
Current density (amps/sq. ft.)	500	500	500	500	500	500	500
Initial voltage	3.48	3.55	3.52	3.50	3.27	3.30	3.35
Final voltage				3.52	3.30	3.28	3.50
Time (hours)				17	315	266	814

[1] Nickel.
[2] Iron.
[3] Cobalt.
[4] Coats 1, 2, 3, 5, 7, 8 to 400° C.; coat 6 to 600° C.; coat 9 to 650° C.; coats 10, 11 to 600° C.
[5] Coats 1, 2, 3 to 400° C.; coat 4 to 450° C.; coat 5 to 600° C.
[6] Coats 1, 2, 3, 6, 7 to 400° C.; coat 4 to 450° C.; coat 5 to 500° C.; coat 8 to 600° C.
[7] Coats 1 to 4 to 400° C.; coat 5 to 600° C.

Although the invention has been described with reference to particular specific details and certain preferred details, it is not intended to thereby limit the scope of this invention except insofar as the details are recited in the appended claims.

What is claimed is:

1. An anode for the electrolysis of brines comprising:
a valve metal substrate, and
an electroconductive surface thereon comprising palladium oxide, platinum oxide, an oxide of an iron group metal, and an oxide of a film-forming metal where:
the weight ratio of the platinum oxide, calculated as the metal, to the total oxides of the platinum

group metals, calculated as the metals, is from about 0.02 to about 0.15; and

the weight ratio of the oxides of the iron group metals, calculated as the metals, to the total metal oxides, calculated as the metals, is from about 0.03 to about 0.25.

2. An anode of claim 1 wherein an intermediate layer comprising a platinum group metal is between the substrate and the surface.

3. The anode of claim 2 wherein the platinum group metal coating on the substrate is chosen from the group consisting of platinum, palladium, ruthenium, and osmium and mixtures thereof.

4. The anode of claim 1 wherein the oxide of the iron group metal is chosen from the group consisting of FeO, Fe_2O_3, CoO, NiO, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $FeAl_2O_4$, $Fe^{II}Fe^{III}Al_2O_4$, $FeCr_2O_4$, $FeMn_2O_4$, $CoAl_2O_4$, $CoCr_2O_4$, $CoMn_2O_4$, $NiAl_2O_4$, $NiCr_2O_4$, $NiMn_2O_4$, and mixtures thereof.

5. The anode of claim 1 wherein the oxide of the film-forming metal is chosen from the group consisting of oxides of aluminum, bismuth, niobium, tantalum, titanium, tungsten, vanadium, and zirconium.

6. A process for the electrolysis of aqueous alkali metal chlorides comprising:

causing said aqueous alkali metal chloride to pass between a flowable mercury amalgam cathode and an anode comprising:

a valve metal substrate, and

an electroconductive surface thereon comprising palladium oxide, platinum oxide, an oxide of an iron group metal, and an oxide of a film-forming metal where:

the weight ratio of platinum oxide, calculated as the metal, to the total oxides of the platinum group metals, calculated as the metals, is from about 0.02 to about 0.15; and

the weight ratio of the oxides of the iron group metals, calculated as the metals, to the total metal oxides, calculated as the metals, is from about 0.03 to about 0.25; and

causing an electrical current flow from said anode through said aqueous alkali metal chloride to said flowable mercury amalgam cathode.

7. A process for the electrolysis of aqueous alkali metal chlorides comprising:

causing said aqueous alkali metal chloride to pass between a cathode and an anode comprising:

a valve metal substrate, and

an electroconductive surface thereon comprising palladium oxide, platinum oxide, an oxide of an iron group metal, and an oxide of a film-forming metal where:

the weight ratio of platinum oxide, calculated as the metal, to the total oxides of the platinum group metals, calculated as the metals, is from about 0.02 to about 0.15; and

the weight ratio of the oxides of the iron group metals, calculated as the metals, to the total metal oxides, calculated as the metals, is from about 0.03 to about 0.25; and

causing an electrical current to pass from said anode through said alkali metal chloride to said cathodes.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,677,917 Dated July 18, 1972

Inventor(s) Aleksandrs Martinsons

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The Inventor's name is misspelled - The patent listed it as "Martinson instead of "Martinsons" - This is located in Column 1, Line 3.

In Column 8, line 4, Claim 6 - After the word "current,"the word --to-- is omitted before the word "flow"

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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