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3,689,383

METHOD OF COATING AN ELECTRODE

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U.S. Cl. 204—95 2 Claims

ABSTRACT OF THE DISCLOSURE

The novel anode may be used in the electrolysis of an aqueous solution such as of alkali metal chloride. The anode includes a base member having a conductive coating or surface comprising an oxy-compound of a platinum group metal such as ruthenium and an alkaline earth metal, typically calcium, or a rare earth metal such as lanthanum.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of my copending U.S. application Ser. No. 811,615, filed Mar. 28, 1969, now U.S. Pat. 3,616,446.

BACKGROUND OF THE INVENTION

This invention relates to electrodes for electrolytic cells and, more particularly, to a corrosion-resistant, dimensionally-stable anode such as for electrolysis of aqueous alkali metal chloride in the production of elemental chlorine or alkali metal chlorate.

The electrolysis of aqueous alkali metal chloride solutions such as solutions of sodium chloride or potassium chloride is conducted on a vast commercial scale. In the production of alkali metal chlorate, anodes and cathodes, or bipolar electrodes which when arranged in a spaced electrical series in an electrolytic cell may serve as both anode and cathode, are immersed in an aqueous solution of the sodium chloride or the like and an electrical potential is established between the electrodes. In the past, graphite or carbon electrodes have been used as anodes or as the bipolar electrodes in series. In consequence of the electrochemical reactions which occur, alkali metal chlorate is produced either directly in the cell or outside the cell after the solution is allowed to stand.

The electrolysis of alkali metal chloride to produce elemental chlorine and alkali metal hydroxide is conducted in two general types of cells—the diaphragm and the mercury cathode cell. In the diaphragm cell, the cell is divided into two compartments—the anode compartment and the cathode compartment—which are separated by a porous diaphragm usually of asbestos. The cathode is of perforate metal and the asbestos diaphragm is in contact with the cathode. The anode, usually of carbon or graphite, is disposed centrally in the anode compartment.

In the mercury cathode cell, the cathode is a flowing stream of mercury which flows along a solid metal base connected to the negative pole of a power source. The anode, again of carbon or graphite, is spaced from the mercury cathode and, as electric current flows, the sodium or like alkali metal is evolved and collected in the mercury as an amalgam which is removed from the cell. Outside the cell the mercury amalgam is contacted with water in a "denuder" to remove the sodium as sodium hydroxide solution and the mercury is then recycled.

In operating each of the above-described cells one is confronted with a common problem; namely, that during the course of the electrolysis, the carbon or graphite electrode erodes and/or decomposes. Consequently, as the electrodes wear away or erode, the spacing between the

electrodes increases with resulting increase in voltage between electrodes. This, together with the reactions which cause degradation of the anode, results in a loss of current efficiency for the production of the desired product. The graphite anodes ultimately must be replaced. In all these cells this erosion increases as the anode current density is increased. At the same time, the trend of operation is toward high current density to increase the amount of product produced per unit cell. Thus it has become necessary to resort to anodes or bipolar electrodes which remain dimensionally stable and do not erode appreciably over long periods of cell operation.

The present invention is directed to the provision of an improved stable electrode and to electrolytic cells, particularly to cells of the type described above which contain such electrodes as the anode or anodic surface thereof.

Electrodes herein contemplated normally should possess a certain degree of rigidity and, in any event, they must have surfaces which exhibit good electrolytic characteristics. These characteristics, particularly in the case of anodes, include low oxygen and chlorine overvoltage, resistance to corrosion and decomposition in the course of use as anodes in the electrolytic cell, and minimum loss of coating during such use. It is well known that certain metals, metallic oxides, and alloys are stable during electrolysis and have other superior properties when used as anodes. Such metals typically include the members of the platinum group; namely, ruthenium, rhodium, palladium, osmium, iridium, and platinum. These metals are not satisfactory for construction of the entire electrode since, for example, their cost is prohibitive. Therefore, these metals, metallic oxides, and alloys are commonly applied as a thin layer over a strength or support member such as a base member comprising titanium, tantalum, zirconium, niobium, and alloys thereof. These support members have good chemical and electrochemical resistance to the alkali metal chloride electrolyte and the products of electrolysis, e.g., chlorine, hypochlorite and/or chlorate, but may be lacking in good surface electroconductivity because of their tendency to form on their surface an oxide having poor electroconductivity.

DESCRIPTION OF THE INVENTION

The present invention provides an electrode having excellent electrolytic characteristics. The electrode has a coating or exposed surface comprising an oxy-compound including a platinum group metal and an alkaline earth metal, particularly calcium or a rare earth metal such as lanthanum. According to one method of producing the anode of the present invention, a thermally-decomposable organic mixture containing a thermally-decomposable ruthenium organic compound and a thermally-decomposable calcium organic compound is applied to a conductive, chemically-resistant base member. The electrode is heated to decompose and/or to volatilize the organic matter and other components, leaving a deposit of an electroconductive oxy-compound of ruthenium and calcium, probably in the form of preferably calcium ruthenium trioxide, hereinafter called calcium ruthenite ($CaRuO_3$), or calcium ruthenium tetra oxide, hereinafter called calcium ruthenate ($CaRuO_4$), or mixtures thereof. The electrode of the present invention has a low chlorine and oxygen overvoltage. Whereas calcium oxide reacts or is rapidly eroded when used as an anode in the contemplated electrolysis, the oxy-compound of ruthenium and calcium herein contemplated is stable over a long period of time when used as an anode with little or no loss of calcium or ruthenium.

The electrode base is preferably of titanium, and one or a plurality of layers of a mixture of certain thermally-decomposable metal compounds such as organic and inorganic salts of both calcium and ruthenium are applied

to the base and decomposed by heating the coated base. Especially useful for this purpose are mixtures of ruthenium resinate and calcium resinate, as well as ruthenium chloride ($RuCl_3$) and calcium formate [$Ca(HCO_2)_2$]. The resulting coating following heating comprises an oxy-compound including ruthenium and calcium and is believed to be in the form of calcium ruthenite ($CaRuO_3$) although some calcium ruthenate ($CaRuO_4$) may also be present. Resinates of the type used herein are manufactured by the Hanovia Division of Englehart Industries. The metallic resinates may be mixed with an organic solvent or diluent, such as terpenes and aromatics, typically oil of turpentine, xylene, and toluene, before being applied to the base member for further increasing adhesion.

As a general rule, the coating is applied as a series of thin layers in order to promote maximum adhesion of the coating to the base. The layers, which are an intimate mixture of the calcium and ruthenium salts, are then heated between coating operations to volatilize or drive off the organic matter, solvent, decomposition products, etc., and form the oxy-compound of the metals as a thin film on the base member.

The exact temperature to which the electrode coating should be heated depends upon the time of heating and temperature at which the calcium compounds and ruthenium compounds decompose. It should be high enough to cause formation of the oxy-compound of the alkaline earth metal and ruthenium, such as the alkaline earth metal ruthenate or ruthenite. Care should be taken to select temperatures and duration of heating that will provide the oxy-compound rather than calcium oxide and the elemental platinum group metal. Typically, the temperature may be in the range of 300° C. to 800° C. for between 10 minutes and 2 hours. The heating step is most advantageously conducted in an atmosphere containing elemental oxygen such as air or other oxygen-inert gas mixtures although an atmosphere of pure oxygen can be used. The oxy-compound thus formed is crystalline or amorphous depending upon the temperature of heating; the higher the temperature and the longer the heating, the greater the crystallinity of the product. Both crystalline, particularly if such crystals are very small in size, and non-crystalline coatings have good electroconductivity. However, products of improved adhesion and conductivity are obtained when care is exerted to maintain the coatings in a state where crystallinity is low. As used herein, low crystallinity will mean an X-ray diffraction pattern of less than 700% above background when measured on a Philips Diffractometer under the following conditions: The detector is a sealed proportional counter operated at 35 kv., 15 milliamperes on the X-ray tube and at 1000 counts per second full scale. Copper radiation is used and the Philips Diffractometer is adjusted as follows: 1° divergence slit, 0.006 inch receiving slit, and 1° scatter slit. The detector is rotated at 2° two theta per minute with a time constant of 2 seconds and the specimen is rotated at 1° per minute.

The organic and inorganic compounds may, if desired, be applied by brushing a coating on the titanium base member or, alternatively, by any other method of application such as spraying or dipping. The electrode must then be heated to a temperature sufficient to drive off the organic and inorganic products and to form the oxy-compound described above.

The present invention is principally directed to a coating of an oxy-compound of calcium and ruthenium such as calcium ruthenate [$Ca(RuO_4)$] and calcium ruthenite [$Ca(RuO_3)$]. The oxy-compound, preferably, has a ratio by weight of 1 calcium to between x and y of ruthenium, whereby x may be as low as 1 but rarely less than 0.25 and wherein y may be as high as 4 but rarely higher than 10. Usually, the ratio is about 1 calcium to 2.5 ruthenium. However, it should be recognized that a platinum group metal or the oxide of a platinum group metal, as well as a limited amount of other impurities, could be present in the oxy-compound. For example, some amorphous titanium dioxide could be present. Also, some calcium oxide could be present when the electrode is initially made; however, such calcium oxide would quickly dissolve once the electrode is placed in operation. Some calcium could also be present as other compounds of calcium such as calcium sulfate.

Other electroconductive oxy-compounds of other alkaline earth metals and ruthenium such as strontium ruthenate [$Sr(CuO_4)$], strontium ruthenite [$Sr(RuO_3)$], barium ruthenate [$Ba(RuO_4)$], barium ruthenite [$Ba(RuO_3)$], and [$Ba_{5/6}Sr_{1/6}(RuO_3)$] may be applied to the titanium or other conductive base in lieu of the calcium-ruthenium compound and the thus-coated anode used to electrolyze alkali metal chloride solution.

Although it is preferable to form the oxy-compound in situ from organic compounds of the alkaline earth metal and the platinum metal, the pre-formed electroconductive oxy-compound may be applied to the base member, for example, by suspending the oxy-compound in a fluid carrier such as titanium resinate, applying the suspension of the oxy-compound of the alkaline earth metal and ruthenium to the base member, and removing the fluid carrier such as by evaporation. Alternatively, the resinates of barium, strontium or magnesium may be applied to the titanium or like base, together with ruthenium resinate, as described in connection with calcium resinate and ruthenium resinate in Example I. Moreover, the oxy-compound can be formed in situ from inorganic compounds of the alkaline earth metal or rare earth metal and the platinum group metal as shown in Example III. The inorganic compounds must be decomposable to form the oxy-compound, for example, by heating. The term alkaline earth metals as used herein includes barium, calcium, strontium, and magnesium. The term rare earth metals as used herein includes lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

In each of the following examples, the titanium base plate was cleaned or etched prior to application of the coating. The etching process comprised submerging the plate for about 30 seconds in a solution containing 1% HF, said solution being concentrated with respect to HCl. The plate was then washed in water and submerged in concentrated HCl at about 40 to 50° C. for 1½ hours.

EXAMPLE I

Electrode I-A was prepared by forming in situ an oxy-compound coating including ruthenium and calcium on a 2 inch by 2¾ inch titanium plate. The oxy-compound was formed from organic compounds of ruthenium and calcium. The titanium base plate had a thickness of 1/16 inch and was thoroughly cleaned by etching. The titanium plate was then coated with a mixture comprising 4 grams of a ruthenium resinate solution and 4.53 grams of a calcium resinate solution. The ruthenium resinate solution contained 4% by weight ruthenium. The calcium resinate solution contained 1.4% by weight calcium. In preparing electrode I-A, sufficient toluene was added to the mixture to make the concentration of calcium and ruthenium 0.05 molar. Ten layers of such mixture were applied to electrode I-A. Following application of each of the layers 1-4 and 6-8, the electrode was heated for 10 minutes at 400° C. Following coatings 5 and 9, the electrode was heated at 500° C. for 10 minutes. After applying the tenth layer, the electrode was heated to 550° C. for 10 minutes. The electrode I-A was analyzed by X-ray diffraction [1]

[1] X-ray diffraction analysis was conducted on a Philips Diffractometer operating as described in X-Ray Diffraction Procedures by Clug and Alexander. The detector was a sealed proportional counter which was operated at 35 kv., 15 milliamperes on the X-ray tube and at 1000 counts per second full scale. Copper radiation was used and the Philips Diffractometer was adjusted as follows: 1° divergence slit, 0.006 inch receiving slit, and 1° scatter slit. The detector was rotated at 2° two theta per minute with a time constant of 2 seconds. The specimen was rotated at 1° per minute.

and no pattern was found. The coating on the titanium was about 6.0 microinches in thickness as ruthenium. The coating thickness determination was conducted on a Philips X-Ray Spectrograph operating substantially as described in Handbook of X-Ray by Kaelble, McGraw-Hill (1967). The electrode I–A was paired with a cathode and operated in a laboratory chlorate cell. The cell contained about 1½ liters of a brine solution. The brine solution was maintained at a concentration of 100 to 125 grams NaCl per liter, 500 to 600 grams $NaClO_3$ per liter, and a pH of 6.8. The following tables show the results obtained:

Elapsed hours of operation	Cell temperature (° C.)	Current (amperes)	Current density (amperes per square foot)	Initial cell voltage (volts)	Final [1] cell voltage (volts)
0–50	32–33	3.7	100	2.72	2.75
50–149	42–44	7.4	200	3.03	3.05

[1] The increase in voltage may be due to polarization of the electrodes and a change in the concentrations of the cell solutions as a result of electrolysis.

The electrode surface area of electrode I–B was reduced to 1.5 x 1.5 inches to afford higher current density from the power supply and the electrolysis was resumed.

Elapsed hours of operation	Cell temperature (° C.)	Current (amperes)	Current density (amperes per square foot)	Initial cell voltage (volts)	Final [1] cell voltage (volts)
149–229	35–37	4.7	300	3.0	3.02
229–374	47–49	7.8	500	3.35	45
374–400	47–49	7.8	500	3.45	3.55

[1] See footnote [1] at bottom of table above.

An electrode I–B was prepared using a titanium plate 1 inch x ⅜ inch x 1/16 inch. Ten coats of the ruthenium resinate-calcium resinate mixture were applied together with heating as described with respect to electrode I–A. Electrode I–B was operated in the chlorate cell for 140 hours at a temperature of 90° C. The overvoltage ranged between 0.05 and 0.06 of a volt during such operation.

EXAMPLE II

The electrodes II–A and II–B were prepared in a manner similar to electrodes I–A and I–B except that the coating was an oxy-compound of ruthenium and strontium. The electrodes were prepared from 2 inch x 2¾ inch etched titanium plates. A mixture was prepared comprising 4 grams ruthenium resinate and 5.87 grams of strontium resinate. The strontium resinate solution contained 7.1% by weight strontium and the ruthenium resinate solution contained 4% by weight ruthenium. The molar ratio was 3 strontium to 1 ruthenium. In preparing electrodes II–A and II–B, the mixture was diluted with toluene to provide a strontium concentration of 0.1 molar. Ten layers of the respective mixtures were applied to the titanium plates. The electrodes II–A and II–B were heated to 400° C. for 10 minutes following the application of layers 1 through 4 and 6 through 8. The electrode was heated to 500° C. for 10 minutes following application of layers 5 and 9 and to 550° C. for 10 minutes following layer 10. The electrode II–A was analyzed by X-ray diffraction [2] and no definite pattern was found for either strontium oxide or ruthenium oxide. Electrode II–A had an oxy-compound coating thickness determined as mentioned in Example I of 14 microinches as ruthenium. The electrode II–A was operated as an anode in a laboratory chlorate cell substantially as described with respect to electrode I–A in Example I for a period of 235 hours at a current density of 500 amperes per square foot. The initial cell voltage was 3.6 volts and the final cell voltage was 3.95 volts. Electrode II–B was operated in an overvoltage cell substantially as described with respect to electrode I–B in Example I at 500 amperes per square foot and at 90° C. for 145 hours. The initial overvoltage was 0.04 volt and the final overvoltage was about 0.06 volt.

[2] See Example I for description of X-ray diffraction method.

EXAMPLE III

Electrode III was prepared by forming an oxy-compound coating of rhodium and magnesium on an etched titanium plate whose dimensions were 2 inches x 2¾ inches x 1/16 inch. The coating was formed by applying 6 coats of a mixture containing 2 grams rhodium resinate, 0.49 gram magnesium resinate, and 2.4 grams toluene. The mixture was 0.2 molar in rhodium and 0.1 molar in magnesium. The electrode was heat treated in the same manner described in Example II. The coating had a thickness as measured by X-ray of 18.2 microinches of ruthenium. Electrode III was operated as an anode in a laboratory chlorate cell similar to the one described in Example I for 20 hours at 500 amperes per square foot of anode surface. The cell voltage was 3.45 volts. Electrode III was removed from the cell and heated at 600° C. for 15 minutes. Electrode III was operated in the laboratory chlorate cell for 168 hours at 500 amperes per square foot. The initial cell voltage was 3.6 volts and the final cell voltage was 3.8 volts.

EXAMPLE IV

Electrodes IV–A and IV–B were prepared by forming an oxy-compound coating on etched titanium plates whose dimensions were 2 inches x 2¾ inches x 1/16 inch. The oxy-compounds were formed from inorganic compounds of the platinum group metal and of the alkaline earth metal. The coating on electrode IV–A was formed by applying 6 coats of a mixture comprising on aqueous solution which was 0.2 molar in ruthenium chloride ($RuCl_3$) and 0.2 molar in calcium formate [$Ca(HCO_2)_2$]. Electrode IV–A was heated to 400° C. for 10 minutes following coats 1 through 3, to 450° C. for 10 minutes following coat 4, to 500° C. for 10 minutes after coat 5, and to 550° C. for 10 minutes following the final coat. The electrode IV–A had a coating of an oxy-compound of ruthenium and calcium. The thickness of the coating was 5.7 microinches as ruthenium. The electrode was operated as an anode in a chlorate cell substantially as described in Example I. The current density was 500 amperes per square foot. The cell voltage was 3.4 volts when electrolysis was begun and 3.6 volts after 77 hours of operation. The coating on electrode IV–B was formed by applying 6 coats of a mixture comprising an aqueous solution 0.2 molar in ruthenium chloride ($RuCl_3$) and 0.2 molar in strontium formate [$Sr(HCO_2)_2$]. The electrode was heated following each coat as described with respect to electrode IV–A. The electrode IV–B had a coating thickness of 6.9 microinches as ruthenium. The electrode IV–B was operated in a chlorate cell for 22 hours at a current density of 500 amperes per square foot. The cell voltage increased from 3.6 to 3.8 volts.

Other inorganic alkaline earth metal compounds and rare earth metal compounds from which the oxy-compound could be formed would include oxalates, acetates, and nitrates. Other inorganic platinum group metal compounds which may be used include the oxalates, nitrates, acetates, formates, carbonyls, tricarbonyl chlorides, chlorides, nitroso chlorides, and nitrohydroxides.

The broader aspects of the present invention would further include the electroconductive oxy-compounds of alkaline earth metals and other platinum group metals, such other platinum group metals including rhodium, palladium, osmium, iridium, and platinum. Thus, the oxy-compounds would include the rhodonates, palladates, osminates, iridinates, and platinates of calcium, strontium, barium, and magnesium. Oxy-compounds of alkaline earth metals and platinum group metals would specifically include such salts as calcium iridate [$Ca(IrO_3)$], strontium

iridite [$Sr_4(IrO_6)$], calcium rhodate [$Ca(RhO_4)$], strontium rhodite [$Sr_4(RhO_6)$], and strontium platinite

[$Sr_4(PtO_6)$]

The oxy-compound could include mixed alkaline earth metals and a platinum group metal, for example, salts in the form $A_2B(O_5O_6)$ wherein A is either strontium or calcium and B is magnesium, calcium, or strontium. The oxy-compound could include an alkaline earth metal and mixed platinum group metals. The oxy-compound could include an alkaline earth metal, a platinum group metal, and another metal such as $Ba_4Ti_2PtO_{10}$. In certain instances, particularly when platinum is present in the oxy-compound, care must be taken to avoid reducing the platinum group metal to the elemental metal.

The coating is principally comprised of the oxy-compound of an alkaline earth metal and a platinum group metal. However, it may further include some mixed oxides as well as some elemental platinum group metal.

Electrodes made according to the present invention are highly suitable for use as anodes in cells used for the electrolysis of aqueous alkali metal chloride solutions, typically diaphragm cells, mercury cathode cells, and chlorate cells such as those shown in U.S. Pats. Nos. 3,400,055; 3,337,443; 3,312,614; 3,287,250; 3,203,882; 3,119,664; 3,116,228; 2,897,463; and 2,719,117.

In its broader aspects, the present invention would include use of the electrode for electrolysis of a nonaqueous material such as a fused salt. A typical example of such use would be in the electrolysis of lithium chloride to produce lithium metal and chlorine gas.

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

What is claimed is:

1. In a process of electrolyzing an aqueous solution of alkali metal chloride, the improvement wherein such electrolysis is conducted with an anode having an electroconductive surface comprising an electroconductive oxy-compound of an alkaline earth metal and a platinum group metal.

2. The process as defined in claim **1** wherein said alkaline earth metal is calcium and said platinum group metal is ruthenium.

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FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—94, 128

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,689,383 Dated September 5, 1972

Inventor(s) Bernard J. DeWitt

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

In Column 8, line 26, "3,428,544 2/1969 Bianchi et al.----- 204---290F" should be replaced with --6,606,302 11/1966 Netherlands ----- 204---290F--.

Signed and sealed this 13th day of March 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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