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BIPOLAR ELECTRODE

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ABSTRACT OF THE DISCLOSURE

An improved dimensionally-stable bipolar electrode for use in electrochemical processes comprising a central valve metal layer, suitable anodic material on the anode side of the support and a barrier layer of silicon on the cathodic side of the valve metal. Such bipolar anodes function at reduced hydrogen permeability rates during use in electrolytic processes.

This invention relates to electrodes for use in electrolytic cells. More particularly, this invention relates to improved, corrosion-resistant, dimensionally-stable bipolar electrodes for the electrolysis of aqueous solutions of alkali metal chlorides in the production of alkali metal chlorates.

The electrolysis of aqueous solutions of alkali metal chlorides such as sodium chloride and potassium chloride has been conducted commercially for years on a wide scale.

Graphite electrodes have been employed in the past in various alkaline chloride electrolysis operations; however, there have been certain disadvantages which have arisen as a result of the use of graphite. One of the most serious of the disadvantages is the constant attrition of the graphite during the electrolysis operation. Attrition results in the increase of the clearance or spacing between the cathode and the anode which in turn causes an increase in the cell voltage drop and a resulting decreasing efficiency in cell operation.

Graphite anodes have a limited life, generally being on the order of about 1.0 inches in thickness on installation but at the end of 10–12 months of continuous use may be reduced in thickness to about 0.25 inches, with the attendant loss in power and efficiency. Such losses, including economic losses, have resulted in the proposed use of metallic electrodes and the use of bipolar cells.

Generally in the production of alkali metal chlorate, bipolar electrodes are now preferentially used which, when arranged suitably in an electrolytic cell, in a spaced electrical series, serve to function both as the anode and cathode in the cell. The electrodes are subjected to an electrical potential while immersed in the alkali metal chloride solution and, electrochemically, alkali metal chlorate is produced either in the cell itself, or outside the cell upon the standing of the solution.

The advantages of the use of bipolar cells and bipolar electrodes include:

(a) bipolar cells are relatively simpler and more economical to produce than are monopolar cells;
(b) the electrical contact for supplying current to the electrodes in bipolar cells is applied only through the first and last plates while the current supply to the anodes of monopolar cells must be supplied by electrical contact established with each individual anode;
(c) bipolar cells allow for the use of minimal distances between the electrodes which reduces voltage and allows for a reduction of the volume of electrolyte used.

Platinum group metal-coated electrolyte valve metals such as titanium have been proposed as substitutes for graphite anodes. The metallic electrodes have offered

several potential advantages over conventional graphite electrodes, as for example, lower overvoltage, lower erosion rates and the resulting electrolytic production of higher purity products. The economic advantages gained by the use of such electrodes, however, must be sufficiently high to overcome the high cost of these metallic electrodes.

One problem existant with bipolar electrodes based on anodic precious metal is that the titanium or valve metal support is attacked by hydrogen during the electrolysis on the cathode side, forming hydrides and causing disintegration of the electrode.

The present invention provides a bipolar electrode having excellent electrolytic use characteristics and excellent durability. The electrodes of the present invention are composite bipolar electrodes having a base layer of valve metal, an anodic coating, preferably platinum, on the side of the valve metal, and a barrier layer of silicon on the cathodic side of the valve metal.

The silicon layer exhibits a low hydrogen diffusion rate and effectively prevents the migration of cathodically produced hydrogen from reaching the valve metal surface.

The electrode comprises a central or inner layer of a valve metal of which the oxide is chemically resistant under anodic conditions to the electrolyte employed. The expression "valve metal" as employed herein is definitive of a metal which can function generally as a cathode in an electrolytic cell, but not generally as an anode, due to the formation, under anodic conditions, of the oxide of the metal, which oxide once developed is highly resistant to the passage therethrough of electrons.

The preferred valve metal is titanium, although tantalum or colombium may also be advantageously employed.

The expression "chemically resistant under anodic conditions" hereinbefore employed, as applied to the valve metal, indicates that the oxide is resistant to the corrosive surrounding electrolyte and is not, to an appreciable extent, subject to erosion, deterioration or to electrolyte attack.

A thin layer of the valve metal is adhered to the silicon layer by any suitable method known to the art, such as by sputtering the silicon onto the valve metal.

The thickness of the layers is not critical, it only being necessary that the thickness of the titanium or other valve metal central or inner layer furnish a self-supporting layer, and that the layer of silicon be of such thickness and characteristics as to provide and essentially hydrogen impermeable barrier layer. Generally, the valve metal layer is on the order of from about 0.10 inch to about 0.70 or 8.0 inches in thickness, with the layer of the silicon being on the order of from about 0.01 inch in thickness up to about 0.1 inch in thickness, if desired.

At least an operable portion of the opposing face of the central or inner layer has bonded thereto a layer of suitable anodic material chemically resistant under anodic conditions to the electrolyte used. The term "suitable anodic material" as employed herein refers to a material which is electrically conductive, resistant to oxidation and substantially insoluble in the electrolyte. Platinum is the preferred anodic material; however, it is also possible to utilize ruthenium, palladium, osmium, iridium, oxides of these materials, alloys of two or more of the metals, or suitable mixtures thereof.

The anodic material, preferably platinum, can be deposited upon the anodic side of the valve metal from any suitable source, such as from solutions of chloroplatinic acid, or from a thermally-decomposable organo-metallic, such as platinum resinate. For example, the metallic resinate may be mixed with an organic solvent or diluent, such as terpenes or aromatics, typically oil of turpentine, xylene or toluene, before being applied to the base mem-

ber. The electrode is heated to decompose and/or to volatilize the organic matter and other non-metallic components, leaving on the base member a layer of adherent electroconductive platinum. In producing a metallic anodic coating by such method, care should be taken to avoid oxide formation, for example, by limiting the temperatures of heating or by effecting heating in an oxygen-free atmosphere such as in a vacuum or under a nitrogen or argon blanket.

Heating may be effected in an air atmosphere; however, temperatures above about 600–650° C. are not recommended due to the possibility of oxidizing the valve metal.

In the production of an anodic oxide coating, the temperatures and times of heating are selected that will result in the formation of an oxide, preferably an oxide of a metal of the platinum group of metals, such as ruthenium. The temperature may vary depending upon the particular platinum metal used. Typically, the temperature may be in the range of from about 300 to about 600° C., preferably from about 350 to about 550° C., with such temperatures applied for periods on the order of from about 10 minutes to about 2 hours. The heating of the metal is most advantageously conducted in an atmosphere containing elemental oxygen such as air or other oxygen-inert gas mixtures although and atmosphere of pure oxygen could be used. The platinum group metal oxide is either crystalline or amorphous depending upon the temperatures of heating, with the degree of crystallinity increasing as temperatures and duration of heating are increased. Both crystalline, particularly if the crystals are small, and non-crystalline coatings have good electroconductivity. Where the coatings have a low degree of crystallinity, improved adhesion and conductivity are noted.

It is not necessary that the anodic material be applied in such a manner as to completely cover the entire surface of the valve metal central or inner plate. However, the total anodic side of the central or inner plate should be coated with the anodic material to the extent that the massed portion of the anodic material function effectively as an anode. It is preferred that the anodic material essentially cover the anodic side of the valve metal plate.

The anodic layer, preferably a platinum group metal or metal oxide, can be deposited to the extent of 0.0001 inch, although the use of lesser or greater thicknesses may be achieved, depending on the methods of deposition, it only being necessary that the anodic material be present on the anodic side of the central or inner plate in an amount sufficient to function effectively as the anode.

The anodic material, as hereinbefore stated, can be deposited on the central or inner layer of valve metal by any suitable method known to the art. The deposition can be effected, for example, by using a bath consisting of 4.5 grams platinic chloride and 22 m.; 37 percent hydrochloric acid dissolved in 2800 ml. water. The temperature is generally maintained between 70 and 85° C. and the current intensity is such that essentially no hydrogen is evolved at the valve metal panel. A graphite anode is used in the bath and the valve metal is made cathodic. The panel is agitated or moved during the plating operation, and the current is regulated as to preclude hydrogen involvement at the valve metal, with the anodic platinum metal being deposited at a thickness less than about 0.0001 inch. Minor variations may be effected in the deposition of the precious metal and varying thicknesses may be obtained by suitable modifications in the time consumed in the electroplating operation. Also, simultaneous deposition may be made of more than one component, as for example, by effecting a coating from a solution containing, in addition to platinum, another platinum group metal compound such as ruthenium, such other component being added to the electroplating bath whereby a desired resulting composite coating is obtained by the electrodeposition.

The electrodes of the present invention, as stated, find particular application in the electrolytic production of alkali metal chlorates. In producing chlorates using the electrodes of the present invention, the process may be carried out continuously by passing a solution containing alkali metal chloride through the cells at temperatures generally on the order of up to the boiling point of the electrolyte with the effluent liquor cooled or concentrated to promote crystallization of the chlorate produced in the cell. Advantageously, a small amount of chromate may be added to the liquor fed to the cell in order to promote chlorate formation, in accordance with methods known in the art.

A typical bipolar electrolytic unit which can be used with the novel electrodes of the present invention consists of a housing having spaced-apart end electrodes with the enclosed space defined by the walls and end electrodes divided intermediate at intervals by the bipolar electrodes into substantially isolated unit cells. For each individual electrolysis cell, there is an individual electrolysis zone substantially isolated from the reaction zones of the adjoining cells, the term "unit cell" referring to one of the chambers or sections into which the apparatus is divided by the bipolar electrodes. Such cell makeup permits of good circulation of the electrolyte between the zones.

A bipolar electrolytic cell utilizing the bipolar electrodes described has essentially minimal or no current leakage and voltages on the order of 3.8 to 4.0 can be employed, with a current density of about 4 amp/in.^{2}.

What is claimed is:

1. A bipolar electrode consisting of a core of valve metal, at least a portion of the anodic surface of which is conductively covered by a material selected from the group consisting of platinum, palladium, ruthenium, osmium, iridium, mixtures thereof and oxides thereof and a barrier layer of silicon on the cathodic side of the valve metal layer.

2. A bipolar electrode as defined by Claim **1** wherein the valve metal is titanium.

3. A bipolar electrode as defined by Claim **1** wherein the anode side covering material is platinum metal.

4. A bipolar electrode as defined by Claim **1** wherein the anode side covering material is ruthenium oxide.

5. A bipolar electrode as defined by Claim **2** wherein the anode side covering material is platinum metal.

6. A bipolar electrode as defined by Claim **2** wherein the anode side covering material is ruthenium oxide.

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