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3,788,968

LAYERED ELECTRODE

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4 Claims

ABSTRACT OF THE DISCLOSURE

An electrode, especially useful as an anode in the electrolysis of alkali metal chlorides, includes a graphite body, a first surface covering of a hard ceramic such as titanium carbide or titanium nitride and at least one metal and/or metal oxide of the platinum group and a second oxide coating which is electrically porous and resistant to the electrolysis conditions.

BACKGROUND

This invention relates to an electrode having a graphite body and to a process of manufacturing same. More particularly, this invention relates to an electrode and especially an anode useful for the electrolysis of alkali metal chlorides.

It is known that simple graphite anodes when used in the electrolysis of alkali metal chlorides have a high overvoltage, do not resist corrosion sufficiently and are not stable in shape, i.e., they are not wear resistant. Increasing corrosion and increasing wear result in a further increase of the voltage and current consumption so that the electrode must be frequently readjusted and must finally be replaced.

There have been numerous experiments to overcome the technical disadvantages of graphite electrodes. For this purpose, the graphite has been coated with various substances in an attempt to increase the chemical stability of the graphite, or catalytically effective substances have been applied with the intention of reducing the overvoltage of the chlorine at the graphite.

PRIOR ART

To improve the chemical stability of the graphite, it has been proposed to treat graphite with fluorine (French Pat. 1,506,442), or to impregnate graphite with certain ketones (U.S. Pat. 3,046,216) or with oils (U.S.S.R. Pat. 201,341; Czech Pat. 100,959), with drying oils, French Pat. 1,335,152), with pitch (French Pat. 1,541,750), or with synthetic resin (Belgian Pat. 634,242; Belgian Pat. 708,888; British Pat. 1,070,042) and to apply low-melting alloys, for instance, of lead and bismuth (British Pat. 1,136,808).

To reduce the chlorine overvoltage, it has been proposed to coat graphite with titanium (opened Dutch application 6605125) to coat it with titanium, zirconium or tantalum and to activate the metal layer with a platinum metal (printed German application 1,286,513; British Pat. 1,609,403; French Pat. 1,516,524).

Another route which has been adopted in the art resides in that graphite is replaced by suitable metals, particularly titanium. In British Pat. 941,177 and French Pat. 1,419,603, an electrode has been proposed which has a body of titanium, which is activated by a surface coating of a platinum metal or a platinum metal alloy.

A large number of publications relate to the formation of effective activating layers for the base metal, which consists of titanium or titanium, tantalum, zirconium or columbium (British Pat. 964,631; British Pat. 974,570;

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British Pat. 984,973; British Pat. 1,136,869; opened Dutch application 6402931; opened Dutch application 6606302; U.S. Pat. 3,055,811; printed German application 1,467,221).

Further proposals for coating the titanium base metal call for an application of oxide coatings of titanium dioxide or tantalum pentoxide, which coatings are rendered semiconducting (printed German application 1,814,576; South African Pat. 68/7,482), or for an application of alloys of molybdenum or tungsten with iron, cobalt or nickel (British Pat. 1,004,380) or for an application of ruthenium dioxide (British Pat. 1,168,558).

Considerable attention has also been directed to the provisions of a two-layer electrodes consisting mainly of titanium. Such layers consist of a noble metal and a protective porous coating of the base metal (French Pat. 1,502,587), of noble metal and titanium dioxide (Dutch Pat. 99,396), or of noble metal and silicon dioxide (opened Dutch application 6612095), or of layers which are applied from the electrolyte, to which water-glass, zirconium oxychloride, aluminum chloride, gallium chloride, and boric acid may be added for this purpose (opened Dutch application 6612096; printed German application 1,567,925), or of platinum or iron, which is subsequently oxidized (U.S. Pat. 3,103,484).

It is also known to replace activated titanium electrodes by electrodes of nickel or nickel alloys, rhodium or iridium, which may be platinized (British Pat. 1,026,115), or by electrodes of columbium, tantalum, tungsten, zirconium, which are activated with rhodium, iridium, palladium or platinum (French Pat. 1,393,835; French Pat. 1,208,618); or by an electrode which comprises a perforated metallic carrier electrode which comprises a porous layer of a metal, such as nickel, cobalt, iron, and contains in its pores a metal dispersion (French Pat. 1,410,157).

The printed German application 1,421,047 discloses an anode which is made from a titanium alloy and which has been coated with a thin layer of titanium nitride by being heated in a nitrogen or ammonia atmosphere so that the anode will resist aggressive fluids and its conductivity is improved.

While the particular developments based on activated electrodes of titanium or tantalum have resulted in considerable technical progress, the known electrolytic processes and electrodes still involve considerable disadvantages.

Those known electrodes made from titanium or tantalum which are made without a graphite body are expensive and often have a low dimensional stability and are not short circuit-proof. Besides, most electrodes made from titanium or tantalum have the disadvantage that the activating layer does not have sufficient bond strength under the electrolysis conditions. If a reduction in current consumption is to be accomplished, reactivation is indispensable within certain times, which in most cases are short.

SUMMARY

It is an object of the invention to avoid the known disadvantages of prior electrodes and to provide an electrode which is especially useful as an anode for the electrolysis of alkali metal chlorides and which is dimensionally stable and short circuit-proof and which has a high conductivity and minimizes the overvoltage such as is involved in the discharge of chlorine. The electrode of the invention comprises a graphite body having a first surface covering comprising a hard ceramic and of at least one metal and/or metal oxide of the platinum metals and a second oxide coating which is electrically porous and resists the chemical conditions of the electrolysis.

DESCRIPTION

The first surface covering on the graphite body may consist of a mixture of a hard ceramic and at least one metal and/or metal oxide of the platinum metals, or the first covering may consist of two layers, namely, a lower layer of a hard ceramic and an upper layer of a metal and/or metal oxide of the platinum metals.

The hard ceramic is preferably titanium carbide and more particularly titanium nitride.

A metal from the platinum group and/or any of the oxides thereof can be used in the first covering with the ceramic material. The platinum metals include Ru, Rh, Pd, Os, Ir and Pt. An oxide of a platinum metal is a particularly suitable constituent of the first covering.

An oxide coating of silicon dioxide, titanium dioxide, zirconium dioxide, columbium pentoxide or tantalum pentoxide is preferably used to protect the first surface covering.

The graphite body can have any shape suitable for use as an electrode. Thus, it can be a rod, bar, sheet, block, etc. The graphite body can also be referred to as a skeleton, or frame, or an inner core, etc.

To manufacture the electrode, body of graphite is provided with a first surface covering comprising a hard ceramic and at least one metal and/or metal oxide of the platinum metals, and the covering is subsequently protected with an oxide coating, which is electrically porous and resists the chemical conditions of the electrolysis.

The covering on the graphite body may be formed in any of three ways:

(1) A hard ceramic and at least one metal and/or metal oxide of the platinum group (Group VII) are jointly applied in a mixture by plasma spraying.

(2) The hard ceramic is first applied by plasma spraying and at least one metal and/or metal oxide of the platinum group is produced from a suspension or solution by impregnation and subsequent annealing at an elevated temperature, which is suitably in the range of 300–600° C.

(3) The hard ceramic is first applied by plasma spraying and at least one metal and/or metal oxide of the platinum group is deposited from the gaseous phase on the hard ceramic layer.

For the first covering, the hard ceramic is preferably titanium carbide and particularly titanium nitride, and the metal and/or metal oxide of the platinum group is preferably an oxide of a platinum metal.

In a suitable development of the process, the protective second coating is produced by a hydrolytic decomposition of the chlorides of silicon, titanium, zirconium, columbium or tantalum followed by volatilization of the solvent.

The advantages which are afforded by the invention reside particularly in that the electrode has a high durability (wear resistance) and dimensional stability as well as desirable electrical properties. Because of the excellent conductivity of the hard ceramics and the activation by a metal and/or metal oxide of the platinum metals, the overvoltage of the chlorine is reduced to a value which is economically desirable. The electrode is highly short circuit-proof. An erosion of the layer of platinum metal or platinum metal oxide is prevented by the oxide with which the electrode is coated on the outside. The invention enables the use of graphite, which is economically desirable, as a base or core material in making the electrode.

The invention will be illustrated with reference to the following examples which are not intended to limit the invention in any way.

EXAMPLE 1

A graphite block having dimensions of 40 x 40 x 15 millimeters is covered on one side by plasma spraying with titanium nitride so that a layer is formed which has a thickness between 0.1 and 0.3 millimeter. The titanium nitride layer is washed with alcohol and subse-

quently dried and is then covered with a solution of 1 gram RuCl_3 in 5 milliliters butanol and 2 grams linseed oil in such a manner that about 15 grams ruthenium per square meter are applied. This covering is baked for 15 minutes at 400° C. in an atmosphere of hydrogen or town gas so that a mixture of ruthenium metal and ruthenium oxide is formed. This layer is coated with a solution of 5 grams TiCl_4 in 20 milliliters butanol and the resulting coating is also baked for 15 minutes in the stated atmosphere at 400° C.

EXAMPLE 2

A graphite block is coated with titanium nitride as described in Example 1. Thereafter, the titanium nitride layer is covered with a homogeneous layer of ruthenium metal deposited from the gaseous phase. For this purpose, the graphite block is heated under a vacuum or in a protective gas atmosphere to temperatures above 300° C. by induction heating. As a volatile ruthenium compound, the diatomic metal complex of ruthenium (II) or (O) with benzene or hexamethylbenzene is used. The complex is thermally decomposed on the heated surface of the titanium nitride so that metallic ruthenium is deposited. This layer is protected by an electrically porous SiO_2 layer, which is formed by the application of a mixture of 5 grams SiCl_4 in 20 milliliters butanol and subsequent baking at 400° C.

EXAMPLE 3

A graphite block is covered with titanium nitride as in Example 1 and is covered with a palladium-iridium resinate solution and baked at 400° C. The resulting covering of 15 grams per square meter is then protected by a porous tantalum pentoxide layer, which has been formed by brushing an alcoholic tantalum pentachloride solution onto the nitride layer, followed by annealing at 400° C. within 15 minutes.

EXAMPLE 4

A graphite block is covered with a mixture of titanium nitride and ruthenium oxide (3%) by plasma spraying. In this step, the resulting ruthenium metal-oxide mixture is concentrated at the surface of the titanium nitride layer and is subsequently protected by a porous zirconium oxide layer, which is formed by the application of an alcoholic ZrCl_4 solution and subsequent annealing at 400° C.

What is claimed is:

1. Electrode comprising a graphite body having a first surface covering comprising a hard ceramic selected from the group of titanium carbide and titanium nitride and of at least one metal and/or metal oxide of the platinum group and a second protective oxide coating from the group of the oxides of silicon, titanium, zirconium, columbium and tantalum over said first covering which is electrically porous and resistant to electrolysis conditions.

2. Electrode of claim 1, wherein said first surface covering comprises a mixture of said hard ceramic and at least one metal and/or metal oxide of the platinum metals.

3. Electrode of claim 1 wherein said first surface covering comprises said hard ceramic base layer and a layer of at least one metal and/or metal oxide of the platinum group over said ceramic layer.

4. Electrode of claim 1, wherein said first covering contains an oxide of a platinum metal.

References Cited

UNITED STATES PATENTS

3,649,485	3/1972	Chisholm	204—95
3,657,102	4/1972	Keith et al.	204—290 F
3,663,280	5/1972	Lee	204—290 F

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204—291, 294

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,788,968 Dated January 29, 1974

Inventor(s) Jürgen Müller et al

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

Col. 2, line 9, "68/7,482" should read

-- 6,807,482 --.

Col. 3, line 32, "VII" should read

-- VIII --.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
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