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[54] **ELECTRODES FOR ELECTROCHEMICAL CELLS**
6 Claims, No Drawings

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ABSTRACT: An electrode for use in electrochemical processes comprising a film-forming metal support member carrying a semiconducting coating consisting of tin dioxide, oxides of antimony and optionally a chlorine-discharge catalyst selected from the difluorides of manganese, iron, cobalt, nickel and mixtures thereof.

ELECTRODES FOR ELECTROCHEMICAL CELLS

The present invention relates to electrodes for electrochemical cells. More particularly it relates to electrodes which are particularly useful as anodes in corrosive media.

In recent years much effort has been expended in developing electrodes which are substantially resistant to wear under corrosive electrochemical conditions, particularly under the anodic conditions in the electrolysis of aqueous solutions of alkali metal chlorides. Most of the effort has been directed to the use of thin films of the platinum group metals deposited in a variety of ways on supporting structures made of film-forming metals (sometimes called "valve metals"), notably on titanium, because the platinum metals have a very low-wear rate under corrosive electrochemical conditions and in most electrolytes any exposed areas of the film-forming metal supports very quickly develop a resistant oxide coating which prevents further attack, at least under anodic conditions, where attack on most other conducting support materials would be the most severe.

The present invention provides an electrode of the coated film-forming metal variety which avoids the use of the expensive platinum metals.

It is known, for example from the textbook Chemical Physics of Semiconductors by J. P. Suchet (D. Van Nostrand Company Ltd., 1965), that crystalline inorganic compounds which are electrically nonconducting, particularly the oxides and sulfides of the metals and metalloids, and crystalline compounds formed between two such oxides or sulfides can be converted into semiconductors by doping the parent material with other inorganic materials, usually elements, oxides, sulfides or halides or combinations of these. The semiconductor produced may be of the controlled valency type or of the type in which there is nonstoichiometry between the ions of opposite electrical charge in the crystal lattice or of a hybrid type in which there is the controlled valency type of semiconductivity together with the aforesaid nonstoichiometry.

To produce a semiconductor by the mechanism of controlled valency, the parent compound must contain an element of variable valency. By suitable doping, a solid solution is formed between the parent compound and the added material (dopant) in which a minor proportion of the cations in the parent crystal lattice are replaced by cations of the dopant which are one unit higher or lower in valency, whereby an equal number of the ions of the element of variable valency are induced to take up a valency state correspondingly one unit lower or higher than normal in the parent lattice so as to preserve electrical neutrality in the whole crystal lattice. A nonstoichiometric semiconductor essentially contains lattice defects and can be produced by partial removal of anions or cations from a crystal lattice or by adding excess positive or negative ions of the type already present or by adding foreign atoms of valency differing from the original atoms in the parent material under conditions where controlled valency changes are not permissible. Methods of producing semiconducting materials by controlled valency and nonstoichiometry are more fully discussed in the paper Controlled-Valency Semiconductors by E. J. W. Verwey et al., Philips Research Reports No. 5, 173–187, 1950.

We have now found that semiconducting mixtures of tin dioxide and oxides of antimony can be formed as adherent coatings on a film-forming metal support to produce an electrode which is particularly resistant to electrochemical attack when connected as an anode in an aqueous chloride electrolyte. We have furthermore found that the overpotential required for the liberation of chlorine gas in electrolysis at an electrode produced in this manner can be reduced by incorporating as chlorine-discharge catalyst in the semiconducting coating a small amount of one or more of the difluorides of manganese, iron, cobalt and nickel.

According to the present invention, therefore, we provide an electrode for use in electrochemical processes, which comprises a support of a film-forming metal as hereinafter defined carrying on at least a part of its surface a coating consisting of a semiconducting mixture of tin dioxide and oxides of antimony alone or in admixture with a chlorine-discharge catalyst, wherein the weight ratio of tin dioxide:oxides of antimony calculated as Sb_2O_3 is in the range 5:1 to 100:1 and the chlorine-discharge catalyst is present in an amount up to 3 percent by weight of the total coating and is selected from the difluorides of manganese, iron, cobalt, nickel and mixtures thereof.

The preferred electrode coatings contain 0.1–1 percent by weight of the chlorine-discharge catalyst. The preferred catalyst is manganese fluoride.

In this specification, by a "film-forming metal" we mean one of the metals titanium, zirconium, niobium, tantalum and tungsten or an alloy consisting mainly of these elements and having anodic polarization properties similar to the commercially pure elements as is known in the art. For the manufacture of electrodes that are to be used as anodes in the electrolysis of aqueous chloride solutions the preferred film-forming metals are titanium and alloys which are based on titanium and have anodic polarization properties comparable with those of titanium.

A semiconducting coating consisting of tin dioxide and oxides of antimony may suitably be bonded to the surface of a film-forming metal support by coating the chemically cleaned support with a solution of a thermally decomposable organo compound of tin e.g., a tin alkoxide, and an antimony halide, e.g., antimony trichloride, in an organic solvent, drying the coating by heating, e.g., at 100°–200° C., to evaporate the solvent and then heating the coating in an oxidizing atmosphere, e.g., air, at a higher temperature, suitably in the range 250°–800° C., to convert the tin and antimony compounds to oxides of these elements. A desired thickness of the semiconducting layer may be built up by repeating as many times as necessary these coating, drying and further heating steps. Alternatively when a desired thickness of the semiconducting layer is built up by applying a plurality of coatings the further heating step to convert the tin and antimony compounds to oxides may be carried out each time after applying and drying a number of coatings, for instance after each second or third coating has been applied.

A suitable modification of this coating technique for incorporation of a chlorine-discharge catalyst into the electrode coating when desired is to suspend in the aforesaid coating solution of tin and antimony compounds a fine particulate preformed sinter of tin dioxide, antimony trioxide and the catalyst, e.g., manganese fluoride, which has been obtained by mixing together these ingredients in particulate form, compacting the mixture, heating the compacts, suitably at about 1,000° C., and then reducing the sintered compacts to fine particulate form, e.g., less than 5 microns. The ratio of tin compounds:antimony compounds in both the solution and the sintered material are chosen so as to be approximately the same and to lie in the previously defined range of 5:1 to 100:1. The proportion of catalyst in the sintered material is chosen so as to provide up to 3 percent by weight, preferably 0.1–1 percent by weight, of catalyst calculated on the total tin and antimony compounds and catalyst in the coating composition when the tin and antimony compounds are calculated as equivalent SnO_2 and Sb_2O_3. A particularly suitable procedure for carrying out this coating technique will be apparent from the following examples, which further illustrate the manufacture of electrodes according to the invention and their testing as anodes in the electrolysis of sodium chloride brine.

EXAMPLE 1

A composition suitable for coating on to an electrode suppot was prepared by boiling under a reflux condenser for 12 hours a mixture of 15 g. of stannic chloride, 0.4 g. of water and 55 g. of n-amyl alcohol and then stirring into 5.8 g. of the resultant mixture 0.125 g. of antimony trichloride. Twelve coats of this composition were painted on to a strip of titanium which had been immesed overnight in hot oxalic acid solution to etch the surface, then washed and dried. Each coating was dried in an oven at 200° C. before the next coat was applied and after each third coat the structure was heated in air in a furnace at 450° C. to convert the coating substantially to the oxides of antimony and tin. The total weight of the finished coating was 11.0 g./m.^{2} of the titanium surface. The theoretical composition of the finished coating was SnO_2 90 percent, oxides of antimony (calculated as Sb_2O_3) 10 percent by weight.

The coated titanium was operated successfully as an anode in chlorinated brine containing 21.5 percent w/w NaCl at pH 3 and 65° C. with a current density of 8 kA/m.^{2}. The chlorine overpotential was initially 470 mv. and had risen to 480 mv. after 5 days.

EXAMPLE 2

The procedure of example 1 was repeated but with the amount of antimony trichloride in the coating composition reduced to provide a finished coating on the electrode of theoretical composition SnO_2 99 percent, oxides of antimony (calculated as Sb_2O_3) 1 percent by weight. Under the same conditions of test as an anode as in example 1 the initial chlorine overpotential was greater than 1,000 mv.

EXAMPLE 3

The procedure of example 1 was repeated but with the amount of antimony trichloride in the coating composition increased to provide a finished coating on the electrode of theoretical composition SnO_2 85.5 percent, oxides of antimony (calculated as Sb_2O_3) 14.5 percent by weight. The chlorine overpotential recorded in the test was the same as with the electrode of example 1, both initially and after 5 days.

EXAMPLE 4

Eighteen grams of antimony trioxide were boiled in concentrated nitric acid until evolution of oxides of nitrogen ceased. Eighty-four grams of metallic tin were dissolved in concentrated nitric acid with heating, and the precipitated tin dioxide formed was thoroughly mixed with the precipitate of antimony oxide and heated for a further period in concentrated nitric acid. The precipitated mixture was washed free from acid and dried in air at 200° C. To the dried mixed oxides was added 3 percent by weight of manganese difluoride. The resultant mixture was pressed into pellets (1,000 lb./in.^{2}) and fired in air in a furnace at 800° C. for 24 hours. After firing, the mixture was crushed and the particle size reduced to $<60\mu$. It was subsequently recompacted into pellets and fired as before at 1,000° C. for 24 hours. The resultant material was crushed and the particle size reduced to $<5\mu$ by ball milling.

A solution of an alkoxy-tin compound was prepared by boiling under reflux for 24 hours a mixture of 15 g. of stannic chloride and 55 g. of n-amyl alcohol. Into the resultant solution were dissolved 2.13 g. of antimony trichloride.

A composition suitable for coating on to an electrode support was prepared by suspending 0.17 g. of the above-mixed fluoride/oxide material in 3.6 g. of the antimony-trichloride-alkoxy-tin solution. This coating composition was painted on to a strip of titanium which had been immersed overnight in hot oxalic acid solution to etch the surface, washed and dried. The coating of paint was dried in an oven at 150° C. and then two further coats of the same composition were applied and dried in the same manner, after which the coated strip was heated in a furnace in air at 450° C. for 15 minutes to convert the coating substantially to oxides of antimony and tin with manganese fluoride. The whole coating operation and final heating in air at 450° C. was then repeated three times to increase the thickness of the coating. The total weight of the finished coating was 21.2 g./m.^{2} and the theoretical composition of the coating was SnO_2 85.6 percent, oxides of antimony (calculated as Sb_2O_3) 13.7 percent, MnF_2 0.7 percent by weight.

The coated titanium was operated successfully as an anode in chlorinated brine under the same conditions as in the test of example 1. The chlorine overpotential was 275 mv. initially and this had risen to 330 mv. after 5 days.

Another titanium strip was coated in the same manner. When operated under the same conditions as an anode, except that the current density was raised to 10 kA/m.^{2}, the initial chlorine overpotential was again 275 mv. and after 30 days' operation the overpotential was still stable at 330 mv.

EXAMPLE 5

A coated titanium electrode was prepared by the method of example 4 but with 5 percent by weight of cobalt difluoride added to the mixture of tin and antimony oxides before pressing and firing instead of 3 percent of manganese difluoride. The total weight of the finished coating on the titanium strip was 12.3 g./m.^{2} and the theoretical composition of the coating was SnO_2 85.2 percent, antimony oxides (calculated as Sb_2O_3) 13.6 percent, CoF_2 1.2 percent by weight.

The coated titanium electrode was operated successfully as an anode under the same conditions as in the test of example 1. The chlorine overpotential was 330 mv. initially and this had risen to 400 mv. after 3 days on load.

What we claim is:

1. An electrode for use in electrochemical processes, which comprises a support selected from titanium, zirconium, niobium, tantalum, tungsten and alloys thereof, and a coating on at least a part of the surface of said support, said coating consisting essentially of a semiconducting mixture of tin dioxide and oxides of antimony, wherein the weight ratio of tin dioxide to oxides of antimony is in the range 5:1 to 100:1, calculated as Sb_2O_3.

2. An electrode according to claim 1 wherein the support consists of titanium or an alloy based on titanium and having anodic polarization properties comparable with those of titanium.

3. An electrode according to claim 1, wherein the said coating contains additionally a chlorine discharge catalyst in amount up to 3 percent of the total weight of the coating and the said catalyst is selected from the group consisting of manganese difluoride, iron difluoride, cobalt difluoride, nickel difluoride and mixtures thereof.

4. An electrode according to claim 3, wherein the coating contains 0.1–1 percent by weight of the chlorine-discharge catalyst.

5. An electrode according to claim 3 wherein the chlorine-discharge catalyst is manganese difluoride.

6. An electrode according to claim 3, wherein the support consists of titanium or an alloy based on titanium and having anodic polarization properties comparable with those of titanium.

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