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3,801,490

PYROCHLORE ELECTRODES

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9 Claims

ABSTRACT OF THE DISCLOSURE

Electrodes useful for electrochemical reactions are disclosed. Also disclosed are electrolytic cells using such electrodes and the use of such electrodes in the conduct of electrochemical reactions. The electrodes have a pyrochlore-containing surface on a suitable electroconductive base.

BACKGROUND

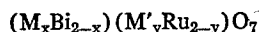
Numerous electrochemical reactions such as the electrolysis of brines, hydrochloric acid, and sulphates, electroplating, electrowinning, electrolytic production of metal powders, electrolytic cleaning, electrolytic pickling, and the electrochemical generation of electric power, involve the use of non-consumable anodes. Previously, graphite anodes have been used in many of these processes, especially in such processes as the electrolysis of brines and the electrolysis of hydrochloric acid. More recently, electrodes have been developed for such processes utilizing a suitable electroconductive base or substrate and an electrocatalytic coating thereon. Typically such electrocatalytic coatings have been the platinum group metals; e.g., platinum, osmium, iridium, ruthenium, palladium and rhodium, as well as their oxides.

SUMMARY OF INVENTION

It has now been found that a particularly satisfactory electrode for the conduct of electrochemical reactions may be provided by the use of a pyrochlore surface on a suitable electroconductive substrate or base member. Pyrochlores are oxides of a high electrical conductivity, low chlorine overvoltage, and high chemical resistance.

DETAILED DESCRIPTION OF THE INVENTION

According to this invention an electrode is provided having a pyrochlore surface on an electroconductive substrate. Pyrochlores are metal oxycompounds having the stoichiometric formula



where M is an ion of yttrium, thallium, indium, lead, scandium, silver, cadmium or the rare earth metals, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. M' is an ion of platinum, palladium, titanium, tin, chromium, rhodium, iridium, antimony, lead, germanium, tungsten, selenium and gold. x is a number in the range of 0 to 2, and y is a number in the range of 0 to 2.

In quaternary metal ion and tertiary metal ion pyrochlores, most commonly M will be lead and M' will be iridium. In pyrochlores containing the ions of only two metals x will be 0, y will be either 0 or 2, and the pyrochlore will contain bismuth and either ruthenium, rhodium or iridium.

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Pyrochlores provide a particularly satisfactory electrode material because they combine a high electrical conductivity comparable to that of the metals, with a high resistance to chemical attack comparable to that of the refractory metal oxides. Moreover, pyrochlores provide the high surface area normally associated with the oxides of the platinum group metals and the low chlorine overvoltages normally associated with the platinum group metals themselves.

The bulk electrical conductivity of compressed powders of $Bi_2Ru_2O_7$ is on the order of about 0.5×10^3 to about 2×10^3 (ohm centimeters)⁻¹. Moreover, the pyrochlores, such as bismuth-ruthenium oxide bismuth-rhodium oxide and bismuth-iridium oxide, are resistant to attack by aqua regia at 70° C. and by nascent chlorine. Furthermore, when applied as a thin coat on a titanium base, $Bi_2Ru_2O_7$ provides an electrode having a chlorine overvoltage of about 0.06 volt at a current density of 200 amperes per square foot.

Pyrochlores are a family of oxides having a cubic crystal structure with an Fd3m crystal habit, a 227 crystal number, and a Schoenflies number of O_h^7 . The crystallography of the pyrochlores is particularly described in J. Montmory and F. Dertaut, *Pyrochlore-Related Structures*, *Compt. Rend.*, 252, 4171 (1961); J. Longo and J. Goodenough, *Preparation and Properties of Oxygen-Deficient Pyrochlores*, *Mater. Res. Bulletin*, 4 (3) 191 (1969).

While an electrode that is a bulk pyrochlore body is within the contemplated scope of this invention, such electrodes will not normally be utilized for reasons of economy. Preferably, the pyrochlore electrodes of this invention will be in the form of an electrode having a pyrochlore surface on a suitable electroconductive substrate. The pyrochlore surface may be as thin as eight angstroms. But, as a practical matter, the surface will be at least 60 microinches thick and, preferably, in excess of 150 to 200 microinches thick. The pyrochlore surface need not, however, be greater than about 250 to 300 microinches in thickness. While a pyrochlore surface greater than 300 microinches in thickness (for example, as thick as 800 microinches or more) may be used without deleterious effect, no additional advantages are obtained thereby. Most frequently the pyrochlore surface will be from about 60 to about 300 microinches thick. According to one exemplification of this invention, the pyrochlore will be in direct contact with the base member and the electrolyte.

Additionally, the pyrochlores may be used to provide an electroconductive layer on the electroconductive base or substrate with the pyrochlore surface having a further exterior coating of a suitable catalytic or electrocatalytic material. For example, the exterior surface may be an electrocatalyst having a low chlorine overvoltage with the pyrochlore providing a corrosion-resistant electroconductive layer between the exterior surface and the substrate, protecting the substrate from corrosion. Alternatively, the exterior surface may be a surface catalyst having a high porosity to allow the flow of electrolyte and current through the surface catalyst containing layer to the pyrochlore surface and then back through the surface catalyst containing layer to the bulk of the electrolyte. The external surface, when present, should have a porosity of from about 0.50 to about 0.85.

Suitable surface catalytic materials include for example, bimetal spinels, such as cobalt aluminate (CoAl_2O_4), nickel aluminate (NiAl_2O_4), iron aluminate (FeAl_2O_4), or similar bimetal spinels. The catalytic exterior surface may also be provided by perovskites or perovskite bronzes, such as the tungsten bronzes, e.g., sodium tungstate, potassium tungstate, and the vanadium bronzes, e.g., sodium vanadate, potassium vanadate, and the like. Alternatively, the catalytic exterior surface may contain a delafossite, such as PtCoO_2 , PdCoO_2 , PdRhO_2 , PdCrO_2 , and the like.

Alternatively, other electrocatalytic materials, such as ruthenates, ruthenites, rhodates, rhodites, and the like may be used to provide a porous exterior surface on the pyrochlore coating.

According to the exemplification of this invention where a porous, exterior surface is provided atop the pyrochlore, an electrode is provided having a layer of from about 60 to about 300 microinches thick of $\text{Bi}_2\text{Ru}_2\text{O}_7$ on a titanium substrate, with a coating on the $\text{Bi}_2\text{Ru}_2\text{O}_7$ of CoAl_2O_4 , the coating having a thickness of from about 100 to about 800 microinches and a porosity of from about 0.50 to about 0.80.

According to still another exemplification of this invention, the pyrochlore surface may have interposed between it and the electrolyte a porous layer of a substantially non-reactive material, such as titanium dioxide, vanadium oxide, tantalum oxide, tungsten oxide, niobium oxide, hafnium oxide, zirconium oxide, and the like, or silicon dioxide. This additional exterior coating serves to provide further mechanical durability to the pyrochlore surface. Additionally, these porous exterior coatings provide added surface area for surface-catalyzed reactions of the electrode products, or of the electrode reagents. Preferably, the porous exterior coatings are formed in situ as will be described hereinafter. According to this exemplification an electrode is prepared having a 60 microinch to 300 microinch thick layer of $\text{Bi}_2\text{Rh}_2\text{O}_7$ on a titanium base, with a porous, external layer of TiO_2 from 100 microinches to 800 microinches thick.

According to still another exemplification of this invention, various materials may be admixed with the pyrochlore material. For example, conductive materials, such as delafossites, perovskites, perovskite bronzes, platinum group metals, oxides of platinum group metals, and mixed carbides, nitrides, and borides resistant to the electrolyte may be admixed with the pyrochlore.

These materials may be present to provide additional conductivity or reactivity. Alternatively, these materials may be present to provide additional catalytic surface area or reduced chlorine overvoltage. According to this exemplification, for example, an electrode may be prepared having a surface from 60 to 300 microinches thick containing $\text{Bi}_2\text{Ru}_2\text{O}_7$ particles admixed with RuO_2 particles.

Other materials, such as the oxides of titanium, tantalum, niobium, hafnium, tungsten, aluminum, vanadium and other film-forming metals, as well as silicon, may be admixed with the pyrochlore to provide additional durability to the surface. Any oxide which may be formed in situ during the preparation of the surface, is substantially non-reactive with the electrolyte and has a crystal structure compatible with the pyrochlore structure which may be used to bind the pyrochlore particles to the substrate. According to this exemplification an electrode may be prepared having from about twenty to about ninety weight percent TiO_2 admixed with $\text{Bi}_2\text{Rh}_2\text{O}_7$ in a surface from about 60 to about 300 microinches thick.

As described hereinabove, while the pyrochlore-coated electrodes of this invention may include an electrode that is a solid bulk pyrochlore mass, such electrodes will not normally be utilized for reasons of economy. Preferably, the pyrochlore electrodes of this invention will be in the form of an electrode having a pyrochlore surface on a suitable electroconductive substrate.

By "suitable electroconductive substrates or base members" is meant a substrate having an electrical resistivity within economic limits for its intended use, e.g., 10^2 (ohm-centimeters)⁻¹ or higher, and being substantially non-reactive with the electrolyte and the products of electrolysis. For example, in the electrolysis of brines, a suitable electroconductive substrate would be one that is substantially non-reactive with sodium hydroxide, sodium chloride, or hydrochloric acid solutions and not attacked by nascent chlorine.

The preferred electroconductive substrate or base materials are the valve metals. The valve metals are those metals which form an oxide film under anodic conditions. The valve metals include titanium, tantalum, niobium, hafnium, tungsten, aluminum, zirconium, vanadium, and alloys thereof. For reasons of cost and availability, titanium and titanium alloys are preferred as the substrate for the electrodes of this invention. Where the electrodes of this invention are intended for use in chlor-alkali cells, the valve metal substrates are substantially impervious to the electrolyte. That is, the valve metal base is characterized by the substantial absence of pores and interstices such that the interior of the valve metal base is not wet by the electrolyte. However, the electrodes of this invention may be in the form of arrays of rods and bars, or in the form of mesh or perforate or foraminous sheets, thereby allowing for passage of electrolyte and gases around the electrode structure. Such electrodes, while themselves macroscopically electrolyte permeable to the bulk flow of electrolyte have members that are microscopically impermeable to the flow of electrolyte.

Alternatively, other materials such as graphite or carbon may be used as the electroconductive substrate or base material without deleterious effects. A laminate of a valve metal and a less expensive metal such as iron or steel may be used with a pyrochlore coating on the valve metal. For example, an electrode may be provided having a $\frac{1}{32}$ inch thick titanium sheet bonded to a steel plate, with a 150 to 300 microinch thick pyrochlore surface on the titanium sheet.

Alternatively, titanium hydride or other electroconductive, anodically-resistant hydrides may be used as the electroconductive substrate or base member of the electrode of this invention. The hydride may be present as the sole base member, or it may be in the form of a plate of the hydride on another material. For example, the hydride may be present as a hydride surface of the metal used in providing the base, e.g., a titanium base with a titanium hydride layer between the titanium metal base and the pyrochlore surface.

A layer of an electroconductive material more conductive than the pyrochlore and also resistant to the electrolyte may be interposed between the pyrochlore and the substrate or base member. Such intermediate layer may be a platinum group metal such as metallic ruthenium, rhodium, palladium, osmium, iridium, or platinum, or alloys thereof. Particularly satisfactory alloys include platinum-palladium alloys, especially those having from 3 to about 15 percent platinum based on the total weight of the platinum and palladium; and platinum-iridium alloys, especially those having from about 2 to about 50 weight percent iridium based on the total weight of the platinum and iridium. Alternatively, the intermediate layer may be an oxide of a platinum group metal such as ruthenium oxide, rhodium oxide, palladium oxide, osmium oxide, iridium oxide, or platinum oxide, or mixtures thereof. Such mixtures may include mixtures of platinum oxide and palladium oxide having from about 3 to about 15 weight percent platinum oxide based on the total weight of the palladium oxide and platinum oxide, or platinum oxide and iridium oxide containing from about 2 to about 50 weight percent iridium oxide based on the total weight of the platinum oxide and the iridium oxide. Such an intermediate layer may also contain mixtures of one platinum group metal and the oxide thereof

or mixtures of one platinum group metal and the oxide of another platinum group metal. Additionally, oxides of other metals such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, tungsten, and aluminum may be present in the intermediate coating with the platinum group metals or the oxides thereof. The intermediate layer may also contain electrically conductive, corrosion resistant, oxygen containing compounds of the platinum group metals. Such compounds include the delafossites, such as PtCoO_2 , PdCoO_2 , PdCrO_2 , PdRhO_2 , PdRuO_2 , and PdPbO_2 .

The intermediate layer, when present, is normally from about 20 to about 120 microinches thick, and preferably from about 60 to about 120 microinches thick. It may be thinner, for example, as thin as 5 microinches, if applied uniformly so as to provide a pore-free coating. It may also be thicker, but without any significant effect. Thus, according to this exemplification, an electrode may be provided having a $\text{Bi}_2\text{Ru}_2\text{O}_7$ pyrochlore layer 60 to 300 microinches thick on a titanium base with an intermediate layer of PtCoO_2 delafossite, from 60 to 120 microinches thick, between and in electrical contact with the titanium and the pyrochlore.

Alternatively, where an electrode is provided having a pyrochlore surface on a substrate, where the substrate material reacts with the pyrochlore to form an electrically insulating barrier after extended periods of electrolysis at high current density, there may be interposed between the substrate and the pyrochlore a layer of less-reactive material that is more resistant to the electrolyte than is the substrate or base member. By less-reactive material is meant a material that does not form an electrically-insulated barrier or aid in the formation of such a barrier when interposed between the pyrochlore and substrate. This less-reactive material may be a precious metal or oxide thereof as described hereinabove. The intermediate layer, when present, is normally from about 20 to about 120 microinches thick, and preferably from about 60 to about 120 microinches thick. It may be thinner, for example, as thin as 5 microinches, if applied uniformly so as to provide a pore-free layer. It may also be thicker, but without any significant effect.

The pyrochlore surface electrodes of this invention are useful in any electrochemical process where a non-consumable electrode is used. By "non-consumable" is meant an electrode that is not dissolved by the electrolyte and redeposited on the opposite electrode. For example, the electrodes of this invention may be used in the electrolysis of brines, sulphates, hydrochloric acid, phosphates, and the like. Alternatively, the electrodes of this invention are useful in those electrolytic processes where cations are deposited on a cathode; for example, an electrowinning, electrorefining, electroplating, electrophoresis, electrolytic cleaning, electrolytic pickling. Copper, nickel, iron, manganese, brass, bronze, cadmium, gold, indium, silver, tin, zinc, cobalt, chromium, and the like may be electroplated in suitable solutions onto cathodes. Alternatively, metal powders may be prepared by depositing cations out of solution onto a suitable cathode using the electrodes of this invention. The electrodes of this invention may be used for electrolytic cleaning using aqueous solutions of sodium phosphate, sodium carbonate, and the like. Additionally, electrolytic pickling of suitable materials rendered cathodic with respect to the anode of this invention may be carried out using the anode of this invention. The anode of this invention may also be used for electrolytic oxidation of organic compounds. For example, the electrolytic oxidation of propylene to propylene oxide or propylene glycol may be carried out using the electrodes of this invention. Metal structures such as ships' hulls may be cathodically protected using the anodes of this invention.

In each use of the electrodes of this invention enumerated above, the cell comprises an electrode pair having

an anode and a cathode, at least one member of the electrode pair being the pyrochlore-surfaced electrode herein contemplated, and means to establish an external voltage or electromotive force between the anode and the cathode whereby the anode is positively charged with respect to the cathode and an electrical current is caused to pass from one member of said electrode pair to the other member.

Additionally, the electrodes of this invention may be used in fuel cells. When used in fuel cells the pyrochlore surface of the electrodes may be permeable to the flow of electrolyte. Such electrolyte permeability may be provided by an electroconductive substrate having pyrochlore deposited therein, or by a dispersion of pyrochlore particles in a suitable inert media, or by other methods known in the art. Fuel cells using the electrode of this invention include a pyrochlore-containing electrode, an electrode of opposite polarity spaced from the pyrochlore-containing electrode, apparatus for feeding electrolyte into the space between the electrodes in order to internally generate electromotive force between said electrodes, and apparatus for recovering the electrical energy generated within the fuel cell.

The pyrochlores useful in providing the electrode surface of the present invention may be synthesized and include those synthesized by the methods described in U.S. Pat. 3,583,931 to Bouchard; and "Solid State Research," Lincoln Laboratory Report No. ESD-PR-66-403, pp. 21-22 (1966) by Longo et al.

A preferred method of synthesizing the pyrochlore useful in providing the electrode of this invention involves heating a finely divided source of an oxide of a platinum group metal with a source of bismuth oxide (Bi_2O_3) at a temperature of approximately 600°C . or higher. This reaction may be carried out either in the presence of oxygen or in the absence of oxygen. Most commonly the oxide of the platinum group metal is ruthenium oxide, rhodium oxide, or iridium oxide. The oxides of bismuth and ruthenium, rhodium, or iridium are typically present in an atomic ratio of one atom of bismuth as Bi_2O_3 to the one atom of the platinum group oxide. The oxides are ground together and the mixed powders are fired in an evacuated, sealed tube. The reaction is carried out at a temperature from about 600°C . to about 1100°C . and preferably from about 750°C . to about 1000°C . and most commonly from about 750°C . to about 850°C . Time of reaction is from about 1 hour to about 72 hours and most commonly from about 16 hours to about 48 hours.

The particular times and temperatures necessary for the synthesis of the pyrochlores useful in providing the electrode coatings contemplated herein depend upon the particle size of the precursors. For example, a satisfactory pyrochlore is obtained if minus 325 mesh powders of Bi_2O_3 and Rh_2O_3 , mixed and compressed into one-quarter inch pellets, are heated to 800°C . for from about 36 to about 42 hours. The preformed pyrochlore may then be applied to the substrate.

Alternatively, pyrochlore may be formed in situ on the substrate itself. This is carried out by firing bismuth (III) oxide powders and ruthenium, rhodium, or iridium powders in the proper proportions on the substrate itself. According to this exemplification bismuth oxide (Bi_2O_3), which is water-soluble, may be put into solution with a nitrate or chloride of the platinum group metal. This solution may then be applied directly to the substrate. The substrate, with the solution of Bi_2O_3 and the salt of the platinum group metal, is then heated to from about 300°C . to about 500°C . to drive off the volatiles and convert the salt to the oxide. Then the substrate is heated to from about 500°C . to about 600°C . to convert the oxides to the pyrochlore.

When a titanium member is utilized as the base or substrate member, the titanium member is prepared for use

as an electrode substrate or base member by degreasing an etching prior to deposition of the pyrochlore surface. Degreasing may be carried out by any of the methods well known in the art such as by the use of detergent, abrasives, or organic degreasing agents. Thereafter, the greased titanium base or substrate member is etched in hydrochloric acid or the like. The etching serves to remove the naturally occurring oxide film and substitutes therefore a hydride film.

The pyrochlore surface may be applied to the etched titanium substrate in a number of ways. For example, when the pyrochlore surface is prepared in situ, a liquid composition containing bismuth oxide and ruthenium chloride in a volatile solvent or a thermally-decomposable organic solvent is applied to the titanium base. The titanium base containing the liquid composition is then heated to a temperature of from about 300° C. to about 500° C. for from about 10 minutes to about 1 hour after the application of each coat, and then to from about 500° C. to about 500° C. to drive off the volatiles and convert

Alternatively, when the pyrochlore is preformed, a slurry of the pyrochlore may be prepared in a solvent such as ethanol, butanol, benzyl alcohol, phenol, benzene, cumene, or the like. The slurry may be brushed onto the surface of the titanium followed by heating to decompose or volatilize the solvent after each coat. The slurry may, additionally, contain a compound of silicon, titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, or other material capable of forming an oxide in situ during the process of volatilizing or decomposing the solvent. Most frequently such compounds will be a chloride such as titanium trichloride, $TiCl_3$, or a nitrate such as zirconium oxynitrate $ZrO(NO_3)_2$.

Alternatively, a slurry of the pyrochlore, an organic solvent such as phenol, butanol, or benzyl alcohol, ethanol, benzene, cumene, polyene, or the like, and either a silica compound or a metal compound that is soluble or dispersible in the organic solvent, e.g., a resinate, may be prepared. This slurry may be brushed onto the titanium providing, for example, from about 4 to about 8 coats of the slurry, with heating after each coat to decompose or volatilize the organic constituent. A final heating to about 500° C. or 600° C. for from about 10 minutes to one hour or longer may follow the heating after each coat. Alternatively, methods such as compression bonding or cathodic electrophoresis may be used to apply the coating of pyrochlore.

While the above-described methods of coating the titanium substrate with pyrochlore have described the use of a titanium, zirconium, or silicon compound to provide TiO_2 , ZrO_2 , or SiO_2 in the surface, this is not necessary for the function of the electrode. However, the titanium dioxide, silicon dioxide, or zirconium dioxide does provide additional strength and durability to the pyrochlore surface. Alternatively, oxides of hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, or the like may be formed in situ during the formation of the surface to provide a durable electrode surface.

The resulting electrode, prepared as described above, may be utilized as an electrode for the conduct of electrochemical reactions as hereinbefore described. The following examples are illustrative.

EXAMPLE I

An electrode was prepared having a $Bi_2Ru_2O_7$ pyrochlore surface on a titanium substrate. A titanium coupon $5\frac{1}{8}$ by $\frac{3}{8}$ by $\frac{1}{16}$ inch was washed with Comet (TM), a household cleanser containing abrasives and cleansers, rinsed in distilled water, and dipped in a 1 weight percent hydrofluoric acid solution for 1 minute. Thereafter, the coupon was inserted in 12 normal hydrochloric acid at 27° C. for 23 hours.

A solution was prepared containing 0.1860 gram of Bi_2O_3 , 0.2108 gram of $RuCl_3 \cdot 3H_2O$, 0.090 gram of $ZrO(NO_3)_2 \cdot nH_2O$, 2.0 grams of 4 normal HNO_3 containing 1 weight percent of GAF "IGEPAL 887" nonyl phenoxy polyethyleneoxy ethanol. Six coats of this solution were applied to the titanium coupon. After each of the first and second coats the coupon was heated to 300° C. for 10 minutes. After both the third and fourth coats the coupon was heated to 350° C. for 10 minutes. After both the fifth and sixth coats the coupon was heated at 400° C. for 15 minutes.

Thereafter a slurry was prepared containing 0.50 gram of palladium-cobalt delafossite prepared as described in commonly-assigned, copending application Ser. No. 222,501, filed Feb. 1, 1972, 0.50 gram of a 4.5 weight percent titanium (calculated as the metal) solution of titanium tetrachloride in butanol, 0.375 gram of butanol containing 1 weight percent IGEPAL "CO-887," and 0.30 gram of phenol. Two coats of this slurry were applied on the pyrochlore surface of the coupon. The coupon was heated at 400° C. for 10 minutes. A coat of 2.25 weight percent titanium as titanium tetrachloride in butanol was then applied and heated to 400° C. for 10 minutes. Two additional coats of the palladium-cobalt delafossite solution described above were applied to the titanium coupon heating to 400° C. for 10 minutes. A second coat of 2.25 weight percent titanium as titanium tetrachloride in butanol was applied to the coupon and heated to 400° C. for 10 minutes.

An additional coat of the palladium-cobalt delafossite slurry prepared as described above was applied to the coupon and heated to 400° C. for 10 minutes. A final coat of 2.25 weight percent titanium as titanium tetrachloride in butanol solution was then applied to the coupon and heated to 400° C. for 10 minutes. The coupon was then further heated to 600° C. for 60 minutes.

The electrode having a palladium-cobalt delafossite surface with an intermediate pyrochlore layer of titanium substrate was tested as the anode in a beaker chlorate cell. The electrolyte was a solution of sodium chloride containing 310 grams per liter of sodium chloride. Electrolysis was commenced and chlorine was seen to be evolved. The chlorine overvoltage was 0.04 volt at 200 amperes per square foot and 0.07 volt at 500 amperes per square foot.

The electrode was then vigorously brushed with a wire brush until the X-ray diffraction pattern showed the presence of both the delafossite and a micro-crystalline pyrochlore on the surface of the electrode. The electrode was then tested as an anode. Chlorine was seen to be evolved from the anode, which had a chlorine overvoltage of 0.04 volt at 200 amperes per square foot and 0.05 volt at 500 amperes per square foot.

EXAMPLE II

An electrode was prepared having a $Bi_2Ru_2O_7$ intermediate surface on a titanium base with a palladium-cobalt delafossite exterior surface thereon.

A solution was prepared containing 0.1860 gram of Bi_2O_3 , 0.2108 gram of $RuCl_3 \cdot 3H_2O$, 2.0 grams of 4 N HNO_3 , and 1 weight percent IGEPAL "CO-887." A second solution was prepared containing 2.25 weight percent titanium as titanium tetrachloride in butanol.

One coat of the bismuth oxide-ruthenium trichloride solution was applied to a titanium coupon that had been etched and cleaned as described in Example I hereinabove. The coupon, with the one coat solution thereon, was heated to 300° C. for 10 minutes. A second coat of the bismuth oxide-ruthenium trichloride solution was brushed on the coupon and thereafter, without subsequent heating, a coat of the titanium tetrachloride solution was applied. The coupon was then heated to 300° C. for 10

minutes. Thereafter two coats of the bismuth oxide-ruthenium trichloride solution were applied to the titanium coupon. The coupon was heated to 350° C. for 15 minutes after each of the coats. A subsequent coat of the titanium tetrachloride solution was applied atop the bismuth oxide-ruthenium tetrachloride coat. Thereafter the coupon was again heated to 350° C. for 15 minutes.

Two additional coats of bismuth oxide-ruthenium trichloride solution were applied to the coupon. After each of the coats the coupon was heated to 400° C. for 15 minutes. Thereafter an additional coat of the titanium tetrachloride solution was applied and the coupon was heated to 400° C. for 15 minutes.

A palladium-cobalt delafossite slurry was prepared and applied atop the bismuth-ruthenium pyrochlore surface as described in Example I hereinabove, was heated to 575° C. for 60 minutes. Thereafter the electrode having an exterior palladium-cobalt delafossite surface and intermediate bismuth-ruthenium pyrochlore surface layer on a titanium substrate was tested as the anode in a beaker chlorate cell as described in Example I hereinabove. Chlorine was observed to be evolved. The chlorine overvoltage of the anode was found to be 0.05 volt at 200 amperes per square foot and 0.08 volt at 500 amperes per square foot.

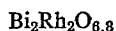
EXAMPLE III

An electrode was prepared having a bismuth-rhodium oxide pyrochlore surface on a titanium substrate. Rhodium oxide was prepared by heating Engelhard "Rh-110" rhodium oxide hydrate in air at 800° C. for 18 hours. The dehydrated Rh_2O_3 was mixed with B and A Reagent Grade Bi_2O_3 to yield a mixture of 0.9030 gram of Rh_2O_3 and 1.6580 grams of Bi_2O_3 . This mixed powder was ground and packed into an Alundum boat. The boat containing the Rh_2O_3 and the Bi_2O_3 was heated to 775° C. per 20 hours. Thereafter the resulting product was reground and repacked into an Alundum boat and heated for 36 hours at a temperature between 796° C. and 805° C. The resulting crystalline product was determined by X-ray diffraction to have the pyrochlore structure and to contain no observable amount of either Rh_2O_3 or Bi_2O_3 . The X-ray diffraction pattern of the powder sample is shown in Table 1.

TABLE 1

"d" value:	(I/I ₀) × 100
5.886	15
3.076	10
2.948	100
2.547	90
2.342	15
1.966	5
1.806	90
1.726	4
1.541	80
1.476	15

A slurry was prepared containing 0.20 gram of



0.30 gram of titanium (calculated as the weight of the metal) in a 4.2 weight solution of Engelhard Titanium Resinate, 0.15 gram of toluene, and 0.05 gram of phenol. Five coats of this slurry were brushed onto a titanium coupon that had been cleaned and etched as described in Example I hereinabove. After each coat the coupon was heated at the rate of 50° C. per 5 minutes to 400° C. and maintained thereat for 10 minutes.

Thereafter a solution containing 2.25 weight percent of titanium (calculated as the metal) in a solution of titanium tetrachloride in butanol was prepared. One coat electrode, having a bismuth-rhodium pyrochlore surface and the coupon was heated to 120° C. for 20 minutes. Thereafter the coupon was heated to 500° C.

and maintained thereat for 20 minutes. The resulting electrode, having a bismuth-rhodium pyrochlore surface on a titanium substrate, was tested as the anode in a beaker chlorate cell as described in Example I hereinabove. At a current density of 200 amperes per square foot the electrode had a chlorine overvoltage of 0.10 volt and chlorine was seen to be evolved.

EXAMPLE IV

An electrode was prepared having a bismuth-ruthenium pyrochlore surface on a titanium substrate. Bismuth-ruthenium oxide pyrochlore was prepared by mixing 1.8718 grams of ruthenium dioxide and 3.262 grams of bismuth oxide powders together. These were ground thoroughly and placed in an Alundum boat. The Alundum boat containing the mixed powders was heated to 790° C. for 16 hours. The resulting product was removed from the Alundum boat, reground, repacked into the Alundum boat, and heated at 780° C. for 19 hours. The resulting powder had an X-ray diffraction pattern showing sharp peaks identified with the pyrochlore structure and also small amount of ruthenium dioxide.

To the above product was added 0.16 gram of bismuth oxide. The powder was placed in an Alundum crucible and heated at 800° C. for 27 hours. The bismuth-ruthenium pyrochlore obtained thereby was then leached with 100 milliliters of two normal HCl and 100 milliliters of one normal HCl, washed with water and with acetone.

A slurry was prepared containing 0.20 gram of bismuth-ruthenium pyrochlore, 0.30 gram of Engelhard "Titanium Resinate" (containing 4.2 percent titanium calculated as the metal), 0.15 gram of toluene, and 0.05 gram of phenol. Five coats of this solution were applied to a titanium coupon that had been cleaned and etched as described in Example I hereinabove. After each of the five coats of slurry were applied, the coupon was heated at the rate of 50° C. per 5 minutes to 400° C. and maintained thereat for 10 minutes. Thereafter, one coat of a solution of titanium tetrachloride in butanol containing 2.25 percent titanium calculated as the metal was applied and heated first to 120° C. for 20 minutes and thereafter to 500° C. for 20 minutes.

The resulting electrode having a bismuth-ruthenium oxide pyrochlore surface on a titanium substrate was tested as the anode in a beaker chlorate cell. Chlorine was observed to be evolved from the anode. The resulting electrode had a chlorine overvoltage of 0.06 volt at 200 amperes per square foot and 0.12 volt at 500 amperes per square foot.

EXAMPLE V

The balance of the pyrochlore obtained in Example IV above was then reground, 0.25 gram of bismuth oxide was added to it, and it was placed in an Alundum boat and heated to 790° C. for 20 hours. The resulting product was removed from the Alundum boat, leached five times in two normal hydrochloric acid, washed with water and then with acetone.

The X-ray diffraction pattern showed the sharp peaks characteristic of bismuth-ruthenium pyrochlore and a second material having the $Bi_2Ru_2O_7$ stoichiometry. The X-ray diffraction pattern of the powder sample is shown in Table 2.

A slurry was prepared containing 0.20 gram of the $Bi_2Ru_2O_7$ so prepared, 0.30 gram of a solution of titanium tetrachloride in butanol (containing 4.5 weight percent titanium calculated as the metal), 0.10 gram of butanol, and 0.15 gram of phenol. Five coats of this slurry were applied to a titanium coupon that had been degreased and etched as described in Example I hereinabove. After each of the first four coats the coupon was heated to 120° C. for 20 minutes, and then to 350° C. for 15 minutes.

TABLE 2

"d" value:	(I/I ₀) × 100
6.55 -----	5
6.37 -----	10
3.28 -----	20
3.09 -----	40
2.97 -----	100
2.94 -----	50
2.80 -----	30
2.68 -----	10
2.57 -----	55
2.49 -----	10
2.36 -----	10
2.25 -----	5
2.19 -----	10
2.13 -----	5
2.07 -----	5
1.98 -----	5
1.82 -----	65
1.79 -----	15
1.70 -----	5
1.64 -----	10
1.62 -----	5
1.55 -----	60
1.49 -----	10
1.47 -----	5
1.45 -----	5
1.44 -----	5
1.42 -----	3

After the last coat the coupon was heated to 500° C. for 20 minutes.

The resulting electrode, having a Bi₂Ru₂O₇ surface on a titanium base, was tested as the anode in a laboratory chlorine cell. Chlorine was seen to be evolved, and the chlorine overvoltage was 0.09 volt at 200 amperes per square foot and 0.19 volt at 500 amperes per square foot.

It is to be understood that although the invention has been described with specific reference to specific details of particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. An electrode having a valve metal substrate and an electroconductive surface thereon comprising:

a pyrochlore chosen from the group consisting of Bi₂Ru₂O₇ and Bi₂Rh₂O₇; and

an oxygen-containing compound chosen from the group consisting of perovskites, delafossites, and oxides of titanium, tantalum, zirconium, columbium, hafnium, tungsten, aluminum, vanadium, silicon, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

2. The electrode of claim 1 wherein the electroconductive surface contains from about ten to about eighty weight percent pyrochlore.

3. The electrode of claim 2 wherein the oxygen-containing compound is titanium dioxide and the electrocon-

ductive surface contains from about twenty to about ninety weight percent titanium dioxide.

4. In an electrolytic cell having an anode, a cathode, and external means for establishing an electromotive force between said anode and said cathode whereby to cause an electrical current to pass from said anode to said cathode, the improvement wherein said anode comprises a valve metal substrate having an electroconductive surface thereon comprising:

a pyrochlore chosen from the group consisting of Bi₂Ru₂O₇ and Bi₂Rh₂O₇; and

an oxygen-containing compound chosen from the group consisting of perovskites, delafossites, and oxides of titanium, tantalum, zirconium, columbium, hafnium, tungsten, aluminum, vanadium, silicon, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

5. The electrolytic cell of claim 4 wherein the electroconductive surface of the anode contains from about ten to about eighty weight percent pyrochlore.

6. The electrolytic cell of claim 5 wherein the oxygen-containing compound is titanium dioxide and the electroconductive surface contains from about twenty to about ninety percent titanium dioxide.

7. In a method of electrolysis wherein brine is fed to an electrolytic cell, an electrical current is caused to pass from an anode to a cathode, and chlorine is generated at the anode, the improvement wherein said anode comprises a valve metal substrate having an electroconductive surface thereon comprising:

a pyrochlore chosen from the group consisting of Bi₂Ru₂O₇ and Bi₂Rh₂O₇; and

an oxygen-containing compound chosen from the group consisting of perovskites, delafossites, and oxides of titanium, tantalum, zirconium, columbium, hafnium, tungsten, aluminum, vanadium, silicon, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

8. The method of electrolysis of claim 7 wherein the electroconductive surface of the anode contains from about ten to about eighty weight percent pyrochlore.

9. The method of electrolysis of claim 8 wherein the oxygen-containing compound in said electroconductive surface of the anode is titanium dioxide and the electroconductive surface contains from about twenty to about ninety weight percent titanium dioxide.

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FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—290 F

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,801,490 Dated April 2, 1974

Inventor(s) Cletus N. Welch

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

In Column 1, line 4, it should state --assignor to Nora International Company, Panama City, Panama-- .

In Column 11, line 47, "he" should be --the--.

Signed and sealed this 10th day of September 1974

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents