

PATENT SPECIFICATION

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(54) BIPOLAR ELECTRODE

(71) We, CHLORINE ENGINEERS CORP., LTD., Kasumigaseki Bldg., No. 2-5 Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, Japan, a Japanese Company, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a bipolar electrode of the kind which comprises an anode member and a cathode member separated from each other by a partition wall and electrically and structurally connected to each other, and which is suitable for electrolyzing aqueous solutions of alkali metal chlorides for the production of alkali metal chlorates, or alkali metal hydroxides and chlorine.

A conventional bipolar electrode of the kind specified is disclosed in U.S. Patent 3,859,197 and has the structure shown in Figure 1. In Figure 1, reference numeral 1 represents a composite member obtained by explosion welding of a titanium plate 4 and a mild steel plate 5. The composite member 1 is fitted into an opening in a partition wall 16 formed from a titanium sheet 2 and a mild steel sheet 3 so that the composite member forms a part of the partition walls 16. The outer edge portion of the titanium plate 4 of the composite member 1 is welded to the wall of the opening in the titanium sheet 2, and the outer edge portion of the mild steel plate 5 is welded to the wall of the opening in the mild steel sheet 3.

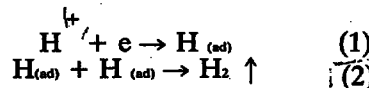
The titanium plate 4 of the composite member 1 is welded to a titanium spacer 6 which in turn is welded to a titanium anode member 7, whereas the mild steel plate 5 of the composite member 1 is welded to a mild steel cathode member 9. Thus, the anode member 7 and the cathode member 9 are connected electrically and structurally by the composite member 1 to form a bipolar electrode having an anode compartment 10

and a cathode compartment 11.

The anode member 7 is made of a mesh-like titanium substrate having formed thereon a coating of a platinum-group metal or a platinum-group metal oxide, and the cathode member 9 is in the form of a grid.

The conventional bipolar electrode described above has the defect that the metal employed on the cathode-side (hereinafter "cathode-side metal") of composite member has poor adhesion to the metal employed on the anode-side (hereinafter "anode-side metal") of the composite member so that they tend to separate from each other physically. Moreover, when the electrode is operated for long periods of time, titanium hydride forms at the joint portion of the composition member resulting in a separation of the metals of which the bipolar electrode is constructed. The reason is while metals suitable as the cathode member such as iron, or nickel, have a low hydrogen overvoltage at the cathode and easily permit permeation of hydrogen atoms, materials suitable as the anode substrate, such as titanium, readily form hydrides.

Hydrogen evolution in the electrolysis of an aqueous solution of an alkali metal chloride occurs according to the following two-stage reaction.



It is known that reaction (2) determines the rate of the entire reaction. For this reason, the surface of iron which is a cathode-side metal of the composite member is always filled with $\text{H}_{(ad)}$, a part of which permeates through the iron and finally reaches the portion of the composite member where the metals are joined. At this portion, the hydrogen reacts with the titanium used as the anode-side metal to form physical brittle titanium hydride and thus cause a

breakage of the portion where the metals are joined to occur. Consequently, the metals become electrically insulated from each other, and the voltage between both surfaces of the composite member increases until finally the electrode becomes useless. The time which elapses until this phenomenon occurs varies depending on the current density at the portion where the metals are joined and the thickness of the cathodeside metal. For example, it was found that a composite material composed of an iron plate having a thickness of 10 mm and explosion-welded to a titanium plate became useless in 1.5 to 3 years when used at a current density of 200 A/dm².

A bipolar electrode of the type shown in Figure 2 has been proposed in an attempt to remove the defects described above. The electrodes include a composite member 12 having an anode-side portion 13 made of a metal, such as titanium or a titanium alloy, which is also used as the substrate of an anode member 7 and a cathode-side portion 15 made of a metal, such as mild steel or an alloy of mild steel, which is also used as the base of a cathode member 9, the portions 13 and 15 being bonded to each other by way of an interlayer portion 14 made of copper or a copper alloy such as brass. The portions 13, 14 and 15 are in the form of plates, and are bonded by explosion or friction welding. The portion 14 may be composed of two or more laminated layers.

The composite member 12 is fitted in an opening in a partition wall 16 so as to form part of the partition wall 16. More specifically, the outer edge portion of the portion 13 of the composite member 12 is welded to the wall of an opening in a sheet 2 of the partition wall 16, and the outer edge portion of the portion 15 is welded to the wall of an opening in a sheet 3 of the partition wall. When the composite member 12 is made part of the partition wall 16, the portion 14 made of copper or a copper alloy defining the interlayer of the composite member 12 must be arranged so that, in use, it is not exposed to the electrolyte solution.

With the structure shown in Figure 2, the copper or copper alloy portion used as the interlayer of the composite member does not permit permeation of hydrogen and, therefore, hydrogen which is generated on the cathode side during electrolysis does not reach the joint surface between the interlayer and the portion of titanium. Hence, the portion made of titanium does not separate from the portion made of copper or copper alloy. Moreover, the portion made of mild steel has very good adhesion to the portion made of copper or copper alloy and the portion made of copper or copper alloy does not easily form a hydride. Thus the portion made of mild steel does not tend to

separate from the portion made of copper or copper alloy.

However, since in the structure shown in Figure 2, the portions 13, 14 and 15 of the composite member are bonded together by only a surface-to-surface bond, the bond tends to be destroyed by mechanical factors or under severe electrolyzing conditions. Furthermore, since in the above structure the opening portion of the mild steel sheet 3 is welded to the outer edge portion of the mild steel portion 15, the mild steel portion 15 in the final electrode has no tolerance to heat deformation. Consequently, cracks occur in the welded part due to stress, or this structure tends to cause cracks to occur at the welded part due to temperature changes during electrolysis. Moreover, when cracks are present at the welded part of the portion 15 and sheet 3, the cracks increase during electrolysis, and the catholyte solution penetrates through the cracks. This causes a destruction of the joint part of the composite member 12, and the interlayer portion 14 made of copper or a copper alloy is corroded. Thus, an electrically insulated condition is generated within the composite member so inducing an increase in voltage between the opposite surfaces of the composite member.

An object of the present invention is therefore to provide a bipolar electrode in which the defects described above are minimized or alleviated.

Accordingly, the invention resides in a bipolar electrode comprising:-

(a) an anode member including a substrate made of an anticorrosive metal or metal alloy and an electrically conductive coating formed on the surface thereof;

(b) a cathode member comprising a metal or a metal alloy;

(c) a partition wall for separating the anode member from the cathode member, said partition wall comprising an anode-side sheet made of the same type of anticorrosive metal or metal alloy used as the substrate of said anode member and a cathode-side sheet made of the same type of metal or metal alloy used as the cathode member; and

(d) a composite member for electrically and structurally connecting the anode member and the cathode member to each other, said composite member comprising bonded together (i) an anode-side portion made of the same type of anticorrosive metal or metal alloy used as the substrate of the anode member, (ii) a cathode-side portion made of the same type of metal or metal alloy used as the cathode member, and (iii), as an interlayer, a portion made of an electrically conductive metal or metal alloy, which is resistant to the migration of hydrogen and is substantially impermeable to atomic hydro-

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rogen; wherein (1) pins made of an electrically conductive metal or metal alloy, which is resistant to the migration of hydrogen and is substantially impermeable to atomic hydrogen, are caulk-fitted in through-holes which are provided in said composite member (d) and which are outwardly diverging toward both surfaces of the composite member (d) so that the pins (1) adhere closely to the inside surfaces of the through-holes in the composite member (d), (2) the anode-side sheet and the cathode-side sheet of the partition wall (c) are sheets having no through-hole for inserting the pins in the composite member, (3) the cathode-side portion of the composite member (d) is welded to the surface of the inside of the cathode-side sheet of the partition wall (c) in a superimposed state, and (4) the surface of the inside of the anode-side sheet is resistance welded to the top surface of the anode-side portion of the composite member (d) in a superimposed state.

In the accompanying drawings,

Figures 1 and 2 are cross-section views of bipolar electrodes disclosed in the prior art,

Figure 3a is an enlarged cross-section view of a modification of said one example, and

Figure 4 illustrates one state during a method of forming the composite member used in the bipolar electrode of said one example.

Referring to Figure 3a, there is shown therein the composite member 12 and part of the partition wall 16 of the bipolar electrode. The composite member is a mutually bonded structure comprising an anode-side portion 13 made of a metal or a metal alloy, such as titanium or a titanium alloy, which is also used as a substrate of the anode member, a cathode-side portion 15 made of a metal, such as mild steel or a metal alloy, which is also used as the material of the cathode member, and an interlayer portion 14 made of copper or an alloy of copper disposed between the portions 13 and 15. The portions 13, 14 and 15 may be formed into plates of various shapes such as a circular shape, an elliptical shape or a rectangular shape, and are bonded by explosion or friction welding. The composite member 12 includes through-holes 19 which diverge towards each of the opposite major surfaces of the member. A pin 20 made of an electrically conductive metal or an alloy of an electrically conductive metal, such as copper or a copper alloy (e.g. brass), which is resistant to the migration of hydrogen and is substantially impermeable to atomic hydrogen is fitted by caulking in each of the through-holes 19.

The partition wall 16 is made by superimposing an anode-side sheet 2 made of a metal, such as titanium or a titanium alloy, used

as the substrate of the anode member on a cathode-side sheet 3 made of a metal such as mild steel or a mild steel alloy, used as the cathode member. The sheet 3 is in the form of a flat plate, whereas the sheet 2 includes a curved portion arranged so as to define a space with the sheet 3. The composite member 12 is located within said space with the cathode-side portion being engaged with the internal surface of the cathode-side sheet 3 of the partition wall 16, and being welded around its periphery to the sheet 3. Moreover the arrangement is such that the anode-side sheet 2 of the partition wall is superimposed on the top surface of the anode-side portion 13 of the composite member 12, the sheet 2 and the portion 13 being secured together by resistance welding. A spacer 6 used to connect the anode member (not shown) and a spacer 8 used to connect the cathode member (not shown) are welded respectively to the anode-side sheet 2 and the cathode-side.

In the modification of said one example shown in Figure 3b, the composite member 12 is bonded between an anode-side sheet 2 in the form of a flat plate and a cathode-side sheet 3 which is formed with a curved surface for receiving the member 12. This arrangement has the advantage that the cathode-side sheet is commonly made of mild steel which is more pliable and more easily deformed than the anode-side sheet 2.

Figure 4 shows a method of forming the composite member 12 described above. The pins 20 are longer than the through-holes 19, and each is like a countersunk rivet having a head 21 at one end which diverges toward the free end surface of the head. Each pin 20 is inserted in one of the through-holes 19 until the head 21 is located in one divergent end portion of the hole and the pin is then pressed from both ends using a suitable press device (not shown). The end of the pin 20 remote from the head 21 is thus caulk-fitted in the through-hole 19 in close adhesion. The projecting ends of the pin 20 are then finished with a grinder so that they become smooth and continuous with the top and bottom surfaces of the composite member 12.

The anode member employed in the above example and the modification thereof is conveniently formed of a valve metal or a valve metal-based alloy, suitable metals and alloys including electrically conductive passivable metals which are passivated by the formation of an inert, non-conductive layer of the oxide thereof on the surface thereof. A typical example of such a metal is titanium, but other examples include tantalum, niobium, hafnium and zirconium and alloys where one or more of these metals predominate.

In the above example and the modifica-

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tion thereof suitable cathode member materials are materials which have a high electrical conductivity, which are readily available and which have adequate resistance to chemical corrosion when used as a cathode. Examples of such metals are iron, aluminum, nickel, lead, tin and zinc and alloys such as mild steel, stainless steel, bronze, brass, monel and cast iron. A (low carbon) mild steel is commonly used as the material for the cathode member.

Suitable materials for the interlayer portion 14 include electrically conductive materials resistant to atomic hydrogen migration, such as copper, gold tin, lead, nickel, cobalt, chromium, tungsten, molybdenum and cadmium. Alloys of these metals can also be used.

Suitable materials for the pins 20 include the hydrogen migration resistant materials described herein as suitable for the interlayer portion 14. Preferred materials are those which are ductile and workable, for example, copper, gold, tin, lead, nickel, cadmium and alloys thereof.

Suitable materials for spacers 6, 8 are electrically conductive materials resistant to environmental corrosion (e.g., by electrolyte and gas) in the anode and cathode compartment.

The constituent elements of the composite member 12 are bonded to one another by a surface-to-surface adhesion, and a pin 20 made of an electrically conductive metal such as copper or an alloy or copper is inserted in each through-hole with funnel-shaped ends in intimate adhesion to the inside surface of the through-hole. Consequently, the mechanical strength of the composite member is increased, and the composite member does not separate even under severe conditions. Furthermore, the anode-side sheet of the partition wall is welded by resistance welding onto the top surface of the anode-side portion of the composite member. Thus, even if the surface of the pin 20 is exposed on the surface of the anode-side sheet of the partition wall, resistance welding can be easily performed without being affected by the pin because the pin has good electric conductivity.

In addition, in the bipolar electrode described above, the composite member 12 is not connected in the through-hole of the partition wall by mere insertion, but the cathode-side portion of the composite member is welded to the cathode-side sheet 3 which has no through-hole for insertion. Thus, tolerance exists at the partition wall. Hence, cracks do not easily form due to stress during welding. Even if cracks should occur, there is no likelihood of the permeation of the catholyte solution since the welded portion between the cathode-side portion of the composite member and the

cathode-side sheet of the partition wall is not exposed to the catholyte solution. For this reason, the interlayer of the composite member is not corroded, and the bonded portions of the composite member are not destroyed. The electrode can, therefore, be operated in a stable manner for long periods of time.

WHAT WE CLAIM IS:-

1. A bipolar electrode comprising:-

(a) an anode member including a substrate made of an anticorrosive metal or metal alloy and an electrically conductive coating formed on the surface thereof;

(b) a cathode member comprising a metal or a metal alloy;

(c) a partition wall for separating the anode member from the cathode member, said partition wall comprising an anode-side sheet made of the same type of anticorrosive metal or metal alloy used as the substrate of said anode member and a cathode-side sheet made of the same type of metal or metal alloy used as the cathode member; and

(d) a composite member for electrically and structurally connecting the anode member and the cathode member to each other, said composite member comprising bonded together (i) an anode-side portion made of the same type of anticorrosive metal or metal alloy used as the substrate of the anode member, (ii) a cathode-side portion made of the same type of metal or metal alloy used as the cathode member, and (iii), as an interlayer, a portion made of an electrically conductive metal or metal alloy, which is resistant to the hydrogen; wherein (1) pins made of an electrically conductive metal or metal alloy, which is resistant to the migration of hydrogen and is substantially impermeable to atomic hydrogen, are caulk-fitted in through-holes which are provided in said composite member (d) and which are outwardly diverging toward both surfaces of the composite member (d) so that the pins (1) adhere closely to the inside surfaces of the through-holes in the composite member (d), (2) the anode-side sheet and the cathode-side sheet of the partition wall (c) are sheets having no through-hole for inserting the pins in the composite member, (3) the cathode-side portion of the composite member (d) is welded to the surface of the inside of the cathode-side sheet of the partition wall (c) in a superimposed state, and (4) the surface of the inside of the anode-side sheet is resistance welded to the top surface of the anode-side portion of the composite member (d) in a superimposed state.

2. A bipolar electrode as claimed in Claim 1, wherein the substrate of said anode member is made of titanium, tantalum, niobium, hafnium or zirconium or an alloy of at least one of these metals, wherein said

tion thereof suitable cathode member materials are materials which have a high electrical conductivity, which are readily available and which have adequate resistance to chemical corrosion when used as a cathode. Examples of such metals are iron, aluminum, nickel, lead, tin and zinc and alloys such as mild steel, stainless steel, bronze, brass, monel and cast iron. A (low carbon) mild steel is commonly used as the material for the cathode member.

Suitable materials for the interlayer portion 14 include electrically conductive materials resistant to atomic hydrogen migration, such as copper, gold tin, lead, nickel, cobalt, chromium, tungsten, molybdenum and cadmium. Alloys of these metals can also be used.

Suitable materials for the pins 20 include the hydrogen migration resistant materials described herein as suitable for the interlayer portion 14. Preferred materials are those which are ductile and workable, for example, copper, gold, tin, lead, nickel, cadmium and alloys thereof.

Suitable materials for spacers 6, 8 are electrically conductive materials resistant to environmental corrosion (e.g., by electrolyte and gas) in the anode and cathode compartment.

The constituent elements of the composite member 12 are bonded to one another by a surface-to-surface adhesion, and a pin 20 made of an electrically conductive metal such as copper or an alloy or copper is inserted in each through-hole with funnel-shaped ends in intimate adhesion to the inside surface of the through-hole. Consequently, the mechanical strength of the composite member is increased, and the composite member does not separate even under severe conditions. Furthermore, the anode-side sheet of the partition wall is welded by resistance welding onto the top surface of the anode-side portion of the composite member. Thus, even if the surface of the pin 20 is exposed on the surface of the anode-side sheet of the partition wall, resistance welding can be easily performed without being affected by the pin because the pin has good electric conductivity.

In addition, in the bipolar electrode described above, the composite member 12 is not connected in the through-hole of the partition wall by mere insertion, but the cathode-side portion of the composite member is welded to the cathode-side sheet 3 which has no through-hole for insertion. Thus, tolerance exists at the partition wall. Hence, cracks do not easily form due to stress during welding. Even if cracks should occur, there is no likelihood of the permeation of the catholyte solution since the welded portion between the cathode-side portion of the composite member and the

cathode-side sheet of the partition wall is not exposed to the catholyte solution. For this reason, the interlayer of the composite member is not corroded, and the bonded portions of the composite member are not destroyed. The electrode can, therefore, be operated in a stable manner for long periods of time.

WHAT WE CLAIM IS:-

1. A bipolar electrode comprising:-

(a) an anode member including a substrate made of an anticorrosive metal or metal alloy and an electrically conductive coating formed on the surface thereof;

(b) a cathode member comprising a metal or a metal alloy;

(c) a partition wall for separating the anode member from the cathode member, said partition wall comprising an anode-side sheet made of the same type of anticorrosive metal or metal alloy used as the substrate of said anode member and a cathode-side sheet made of the same type of metal or metal alloy used as the cathode member; and

(d) a composite member for electrically and structurally connecting the anode member and the cathode member to each other, said composite member comprising bonded together (i) an anode-side portion made of the same type of anticorrosive metal or metal alloy used as the substrate of the anode member, (ii) a cathode-side portion made of the same type of metal or metal alloy used as the cathode member, and (iii), as an interlayer, a portion made of an electrically conductive metal or metal alloy, which is resistant to the hydrogen; wherein (1) pins made of an electrically conductive metal or metal alloy, which is resistant to the migration of hydrogen and is substantially impermeable to atomic hydrogen, are caulk-fitted in through-holes which are provided in said composite member (d) and which are outwardly diverging toward both surfaces of the composite member (d) so that the pins (1) adhere closely to the inside surfaces of the through-holes in the composite member (d), (2) the anode-side sheet and the cathode-side sheet of the partition wall (c) are sheets having no through-hole for inserting the pins in the composite member, (3) the cathode-side portion of the composite member (d) is welded to the surface of the inside of the cathode-side sheet of the partition wall (c) in a superimposed state, and (4) the surface of the inside of the anode-side sheet is resistance welded to the top surface of the anode-side portion of the composite member (d) in a superimposed state.

2. A bipolar electrode as claimed in Claim 1, wherein the substrate of said anode member is made of titanium, tantalum, niobium, hafnium or zirconium or an alloy of at least one of these metals, wherein said

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5 cathode metal is made of iron, aluminium,
nickel, lead, tin or zinc or an alloy of at least
one of these metals, wherein said interlayer
is made of copper, gold, tin, lead, nickel,
cobalt, chromium, tungsten, molybdenum
or cadmium or an alloy of at least one of
these metals and wherein said pins are made
of copper, gold, tin, lead, nickel, or cad-
mium or an alloy of at least one of these
metals.

10 3. A bipolar electrode as claimed Claim
1, wherein the substrate of said anode mem-
ber is a valve metal or a valve metal alloy,
wherein said cathode member is made of
15 mild steel or nickel, wherein said interlayer
is made of copper or a copper alloy and
wherein said pins are made of copper or a
copper alloy.

20 4. A bipolar electrode as claimed in
Claim 1, wherein the anode member (a), the

cathode member (b), the anode-side sheet
of the partition wall (c), the cathode-side
sheet of the partition wall (c); the anode-
side portion of the composite member (d),
the cathode-side portion of the composite
member (d), and the interlayer of the com-
posite member (d, are made of titanium,
mild steel, titanium, mild steel, titanium,
mild steel, and copper, respectively.

5. A bipolar electrode comprising the
combination and arrangement of parts sub-
stantially as hereinbefore described with re-
ference to, and as shown in, Figures 3a, 3b,
and 4 of the accompanying drawings.

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