An electrolytic cell comprising a plurality of alternating, vertically disposed cathodes and anode plates, current lead-in metal bars connected to the lower ends of the anode plates, the metal bars and the lower ends of the anodes being embedded in and supported by a mass of electrically and thermally non-conducting rigid material such as concrete containing a chlorine resistant polyester resin. The anode plates may be comprised of a titanium type metal or alloy covered with an active layer containing a platinum group metal, alloy or compound. Included is means for feeding electrolyte to the cell while preventing unwanted flow of electricity through the feed ducts comprising a horizontal grooved disc for dividing the electrolyte into a plurality of radial droplet streams.

15 Claims, 8 Drawing Figures
ELECTROLYTIC CELL AND METHOD OF ASSEMBLING SAME

BACKGROUND OF THE INVENTION

The present invention relates to improvements in electrolytic cells with vertical electrodes, for example, cells for the manufacture of chlorate or hypochlorite and diaphragm cells for the manufacture of chlorine.

In the electrolysis of alkali metal halide, cells with graphite anodes are being replaced by cells in which the anodes are thin plates of a film forming material covered by an active layer.

In the present specification, by "film forming material" is meant a material of high electrical conductivity which, in the presence of the electrolyte, spontaneously forms on itself an impermeable film which has a very high electrical resistance. In practice, the film forming materials used in electrolysis are metals of the titanium type, for example titanium, tantalum and niobium, or alloys of metals of this type.

The film forming material may constitute the whole of the anode plate or it may form an impermeable surface layer deposited on a support made of a cheaper material such as copper.

The aforesaid active layer may contain a metal of the platinum group, i.e., platinum, palladium, ruthenium, rhodium, osmium or iridium, in the form of a free metal, an alloy of these metals, or a compound (for example an oxide) of at least one of these metals.

The advantages of metal anodes over graphite anodes are numerous and well known: better electrical conductivity, higher mechanical strength, less cumbersome, no contamination of the electrolyte nor overloading of the diaphragm.

An important problem to be resolved in the construction of cells with vertical metal anodes lies in keeping the anodes in alignment in the interior of the cell and in connecting them to a current lead. One solution which has been proposed is that customarily used for graphite anodes, which consists in immersing the lower part of the anodes in a mass of molten metal (normally lead or a lead alloy) which, after freezing, is covered by a protective layer against the corrosive action of the electrolyte, for example, by a layer of bitumen. This method is nevertheless difficult to apply in the case of metal anodes, because during solidification and cooling of the mass of metal large internal strains develop which can cause deformation of the anode plates. The deformation of the anode plates interferes with the internal geometry of the cell by destroying the uniformity of the anode-cathode distances.

In order to resolve this difficulty it has been proposed in British Pat. Specification No. 1181659 to employ metal anodes in the form of a box, reinforced by cross braces and optionally provided with channels forming expansion joints.

The manufacture of metal anodes of this type is more expensive. Furthermore the use of metal anodes in the form of a box cancels the aforementioned advantage of thin anodes as being less cumbersome in the cell.

The solution proposed in British Pat. Specification No. 1125493 avoids these disadvantages. In the electrolytic cell described in that patent, the anodes are single metal plates or rows of single metal plates which are bolted, riveted or welded to a horizontal metal plate forming the base of the cell. This plate is made of a metal of the titanium type to form a current lead to the anodes and to resist the corrosive action of the electrolyte by spontaneous formation of an impermeable protective film.

The use of a film forming metal plate as the base of the cell is a costly solution. Furthermore, it necessitates firm anchorage of this plate on a sub-foundation of concrete to avoid deformation of the plate during use of the cell. This deformation of the plate aided by the internal stresses of thermal origin which arise during operation of the cell, causes lateral displacements of the anodes between the cathodes. Such deformation of the metal plate supporting the anodes is also encouraged by the temperature variations to which it is submitted during shutdown periods.

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide a novel electrolysis cell which overcomes the above-mentioned disadvantages of prior art cells. Another principal object of the invention is to provide a novel method for constructing an electrolysis cell.

Briefly, an electrolytic cell of the invention comprising cathodes alternating with anodes, wherein each anode consists of a single metal plate or a row of metal plates in prolongation of one another. Each plate has its two faces made of a film-forming material and coated at least partly with a layer comprising a metal or a compound of a metal of the platinum group. The faces of the anode plates are substantially vertical and substantially parallel, and the lower portion of each plate is fixed to a pedestal forming the base of the cell and is connected to a current lead. The current lead comprises an array of horizontal metal bars, each bar extending between a neighboring pair of anodes and being clamped between these anodes by a clamping means. The lower portions of the anode plates, the metal bars and the clamping means are embedded in and sealed in a mass of electrically and thermally non-conducting rigid material which constitutes the pedestal and retains the plates vertically and laterally. The metal bars also serve as spacers between the plates or the rows of plates which constitute the anodes.

One advantage of a cell according to the invention resides in the possibility of using for the metal bars constituting the current lead a metal of better electrical conductivity and lower cost than the film forming metals, for example copper or aluminum. These bars are in effect isolated from the electrolyte by the aforesaid mass of non-conducting rigid material.

Another advantage of the invention results from embedding the anode plates in a mass of thermally non-conducting material. This mass, which serves to retain the anode plates vertically and laterally, undergoes only moderate heating during operation of the cell, so that there is no risk of it deforming or cracking in service, nor of causing deformation of the anode plates. A cell according to the invention is therefore adapted for using, as the anodes, unit metal plates or rows of unit metal plates that are thin, and the cell may have a narrow anode-cathode gap.

In comparison to known cells, cells according to the invention have the appreciable advantages of reduced size and higher energy yield.

In the cell according to the invention, it is advantageous to make the mass of embedding material leak-proof and resistant to corrosion by the electrolyte.
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In a preferred form of the invention, conceived so as to still further reduce the internal stresses in the body of the sealing mass, the anodes consisting of single plates or rows of plates are divided into several successive groups. The plates of each of these groups are clamped to the corresponding metal bars lying between them, independently of the plates of the other groups, which lie themselves clamped to their corresponding metal bars.

By reducing the internal stresses in the mass of embedding material the aforesaid preferred embodiment of the cell allows the use of a large number of anodes and, consequently, the construction of monopolar cells of large capacity and power. This embodiment of the cell also restricts damage to the current lead-in bars caused by occasional infiltration of electrolyte into the mass of embedding material.

In another advantageous embodiment of the invention, also conceived with a view to reducing the effect of internal stresses in the mass of material surrounding the metal bars, the assembly formed by these bars, the lower portion of the anode plates, and the clamping means which hold the bars and the plates together is enclosed in a resilient membrane. By virtue of its elastic properties this membrane absorbs an appreciable proportion of the expansion stresses of the metal bars. Preferably, the membrane is leak proof and made of a material which is resistant to corrosion by the electrolyte to protect the metal current lead-in bars against occasional infiltration of electrolyte into the mass of embedding material.

In carrying out the present method of assembling a cell, before making the pedestal in which the anode plates and the current lead-in bars are fixed, at least two horizontal joints are placed on a foundation, suitably of reinforced concrete, and the anode assemblies are made separately by clamping the vertically disposed anode plates at their lower edges to interposed horizontal current lead-in bars. The anode assemblies are then placed across the horizontal joints, and the pedestal is formed by pouring an electrically and thermally non-conducting embedding material around the joints, the current lead-in bars, and the lower parts of the anode plates so that the embedding material forms the pedestal after setting and hardening and then retains the anode plates vertically and laterally.

The invention will be further understood with reference to the accompanying drawings, which represent by way of example several embodiments of cells according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows in transverse elevation, partially cut away, one embodiment of a cell according to the invention.

FIG. 2 is a longitudinal elevation, partially cut away, of the cell shown in FIG. 1.

FIG. 3 shows on a larger scale a detail of FIG. 2.

FIGS. 4 and 5 show respectively in plan and in elevation an anode assembly of the cell of FIGS. 1 and 2.

FIG. 6 is on a larger scale a partial section in the plane VI—VI of FIG. 4

FIG. 7 shows on a larger scale a detail of FIG. 2 in elevation, partially cut away.

FIG. 8 is a partial transverse section of the foundation and the anode assemblies of the cell of FIGS. 1 and 2 before pouring the mass which forms the pedestal.

DETAILED DESCRIPTION OF THE INVENTION

In the Figures, like parts have been numbered alike. The embodiments shown in the Figures relate to diaphragm cells for the manufacture of chlorine.

Referring to the drawings and more particularly to FIGS. 1 and 2, the cell comprises, on a foundation 1 of reinforced concrete supported by insulators 2, a pedestal 3 forming the base 4 of the cell. The anodes are fixed vertically to the pedestal 3 by their lower end portions. They each comprise a row of flat plates 5 made of titanium, coated over at least part of their two faces by a layer of a platinum group metal, alloy or compound. The coating material may advantageously comprise mixed crystals of ruthenium dioxide and titanium dioxide.

The periphery of the pedestal 3 carries a cathode casing 6 made of steel, with an interposed sealing joint 7. The casing 6 supports foraminous steel structure shaped to form cathode pockets 8 which extend between the adjacent rows of anode plates 5, and the foraminous steel structure is covered with a diaphragm (not shown in the Figures).

A cover 9 of polyester is placed on the cathode casing 6 with an interposed sealing joint 10 and is firmly held on the casing by clamps 11 (FIG. 3).

A brine inlet conduit 12 extends downwardly through the top of cover 9 to a brine distributor 13 which will be described later. At the top of the cover there is also an outlet pipe 14 for escape of chlorine produced at the anodes. A liquid level indicator 15 is positioned at one side of the cover as seen in FIG. 2.

The upper end of cathode casing 6 is connected to a pipe 16 for removal of hydrogen produced in the cathode pockets and to a hydraulic safety valve 17 or a similar safety device for avoiding excessive hydrogen pressure in the cell.

At its lower end the cathode casing 6 communicates with a pipe 18 for removal of caustic liquor formed in the cathode pockets. An inverted U tube 19 is connected to pipe 18 by a joint 50 which allows the inclination of the U tube round the axis of pipe 18 to be varied at will.

According to the invention the rows of anode plates 5 are supported in the pedestal 3, which is constituted by a mass of a thermally and electrically non-conducting rigid material. This mass making up the pedestal 3 may advantageously be made of concrete containing as a binder a polyester resin which is resistant to chlorine, for example Atlac resin (trademark). It may alternatively be made of another electrically and thermally non-conducting material which is capable of sealing the anode plates 5 and retaining them vertically and laterally. If there is any risk of the material employed suffering from corrosion by the electrolyte it may be covered by a layer of leak proof material which is inert towards the electrolyte, such as a layer of bitumen.

The rows of anode plates 5 are also connected to a current lead. According to the invention, this current lead comprises metal bars 20, which are interposed between the rows of anode plates 5 and are imbedded in the mass of the pedestal 3.

In the direction perpendicular to the anode plates 5 the rows of plates are preferably divided into several groups of rows each group being separately connected to the respective current lead-in bars 20 independently.
of the other groups to form within the electrolytic cell—several distinct anode assemblies, for example, five anode assemblies in the embodiment of FIG. 2.

FIGS. 3, 4 and 5 show one of these anode assemblies. This assembly comprises, by way of example, five rows of three anode plates 5. Between these five rows of plates 5 are interposed respectively four metal bars 20 of rectangular cross-section, which extend horizontally throughout the length of the lower portion of the plates 5. The bars 20 and the plates 5 are firmly clamped to each other by means of nuts 21 screwed onto the threaded rods 22 (FIG. 6) which pass through the bars and the plates. Small horizontal bars 23, made of metal, are advantageously placed between the nuts 21 and the plates 5 in each end row of the anode assembly, so as to improve the contact of the anode plates with the bars 20 and to avoid a deformation of these plates.

Since the bars 20 serve as the current lead to the anode plates 5 they should be made of a metal of good electrical conductivity. They may be made of electrolytic copper, because they are effectively kept apart from the electrolyte by the large mass of the pedestal 3 which surrounds them.

In order to strengthen the anchorage of the anode assembly in the pedestal 3, the metal bars 20 may optionally be perforated with orifices 24 which are filled with the material of the pedestal 3.

During operation of the electrolytic cell, each anode assembly is supplied with current by means of the bars 20, of which one extremity extends outside the pedestal 3 and is connected to a current source (not shown).

With the aim of reducing the electrical resistances of the contact between the bars 20 and the anode plates 5, it is preferable that the threaded rods 22 be made of a metal which has a linear coefficient of thermal expansion less than that of the metal of the bars 20, for example the rods 22 may be made of steel when the bars 20 are copper. With this arrangement, when the cell is operating, the differential thermal expansion of the bars 20 and the threaded rods 22 increases the clamping force of the plates 5 between the bars 20.

In one embodiment of the cell according to the invention, the ends of the bars 20 which are downstream with respect to the direction of flow of electric current in these bars terminate short of the corresponding end of the row of plates 5 of the anode assembly. In order to maintain the spacing between the remaining ends of these plates and to ensure the rigidity of the anode assembly, spacer sleeves 25 (FIGS. 4 and 6) are interposed between these plates 5 and clamped between them by means of nuts 21 screwed onto the threaded rods 22 which pass through plates 5 and sleeves 25. This particular embodiment of the cell according to the invention economizes in metal for the bars 20 by taking account of the fact that the current density in the downstream zone of the bars is much lower than that in the upstream zone.

According to another feature of the invention, the lower portion of the anode plates 5, the bars 20, the rods 22, the nuts 21 and the sleeves 25 are enclosed in a resilient membrane 26 (FIG. 3) which is preferably leak proof and made of a material resistant to corrosion by the electrolyte. This membrane 26, which may for example be made of plasticized polyvinyl chloride, reduces the internal stresses in the mass of the pedestal 3 during operation of the cell. Furthermore, when it is leak proof and resistant to corrosion, it protects the metal bars 20 against the eventuality of the electrolyte infiltrating through the pedestal 3.

The adjacent anode plates 5 of each anode assembly may be fastened at their upper edge to projections 27 fixed to cross members 28 (FIGS. 1 and 2) so as to maintain a constant spacing between the plates 5 and the cathodes 8 and to prevent lateral bending of the plates.

The cell shown in FIGS. 1 and 2 is equipped with a brine distributor 13 at the discharge end of the electrolyte inlet pipe 12. This distributor 13 is shown in detail in FIG. 7. Its purpose is to create a very high resistance in the path of any current shunted by way of the common electrolyte feed vessel of a cell room.

According to the invention, the distributor 13 comprises an overflow vessel 30 into which the feed conduit 12 extends and which is supported on a substantially horizontal disc 29. The upper edge of the vessel 30 is advantageously serrated so as to split up the flow of electrolyte spilling over from the vessel 30. For the same purpose the upper face of the disc 29 preferably has radial grooves 31 to ensure a more uniform distribution of the electrolyte flowing over from this disc into the cell. The overflow vessel 30 is held axially on the disc 29 by means of several radial struts 32 fixed to the vessel 30 and to the disc 29, for example, by welding.

The distributor assembly 13 is held in the cell by a cylinder 33 fixed to the radial struts 32 and to the cell cover 9, for example, by welding.

The distributor 13 and the inlet pipe 12 may be made of chlorinated polyvinyl chloride or another material which is inert to the electrolyte and the products of electrolysis.

The distributor shown in FIG. 7 has the dual advantages of rendering negligible the loss of current shunted by way of the common electrolyte feed vessel and of forming a hydraulic seal against accidental escape of chlorine out of the cell by way of inlet pipe 12.

Table I lists the results of two tests involving electrolysis of a brine in a diaphragm cell according to this invention. The cell used was similar to the embodiment illustrated in the attached drawings and described hereabove. It comprised five anode assemblies as defined hereabove. In each anode assembly, each anode was constituted of a row of flat titanium plates having a thickness of about 2 mm and coated, on both faces, with a layer of ruthenium dioxide and titanium dioxide. The plates were clamped vertically between horizontal current lead-in bars. These bars and the lower portion of the anode plates were enclosed in a membrane made of plasticized polyvinyl chloride. The pedestal 3 of the cell was made of concrete containing a polyester resin able to resist corrosion by chlorine.

The total active anodic surface of the cell was approximately 26 m². The anode-cathode distance was about 13 mm.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>1st test</th>
<th>2nd test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (kA/m²)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>3.43</td>
<td>4.00</td>
</tr>
<tr>
<td>Amount of NaCl in the feeding brine (g/l)</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Amount of NaOH in the caustic liquor (g/l)</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Current efficiency (%)</td>
<td>96.2</td>
<td>97.5</td>
</tr>
</tbody>
</table>
It has been ascertained that the electrical resistance of the contact assembly of the anodic plates 5 clamped between the bars 20 did not increase during a working time of about 9 months, which confirms that this anode assembly has not been damaged during electrolysis. The electrolytic cell shown in FIGS. 1 and 2 may be constructed in the following manner.

A foundation 1 for the cell is first constructed and it is optionally supported on insulators 2. The foundation 1 is usually made of reinforced concrete. At least two horizontal joists 47 (FIG. 8) are then placed on the foundation 1 for supporting the anode assemblies of the cell. These joists are placed parallel to each other in the longitudinal direction of the cell (across the drawing of FIG. 2).

The joists 47 are suitably made of the same material as that constituting the pedestal 3, for example, concrete with a polyester binder. They may however be made of another material, for example metal. The joists 47 are provided with transverse projections 48 on their upper surface, separated from each other by a distance substantially equal to the total width of each anode assembly without the nuts 21.

The anode assemblies are separately constructed beforehand in the cells by putting together the anode plates 5, the current lead-in bars 20, the small bars 23 and, if required, the spacer sleeve 25, by means of the threaded rods 22 and nuts 21 (FIGS. 4 and 5).

The rigid anode assemblies are then placed on the joists 47 between the projections 48. A form is placed on the foundation 1 around the joists 47 and the lower part of the anode assemblies that is supported by these joists. The material for embedding the joists 47 and the lower part of the anode assemblies is then poured into the form. When the mass has set and hardened the form is removed.

A thermally and electrically non-conducting material is employed for the aforesaid mass of embedding material which, after setting and hardening, constitutes the pedestal 3 of the cell, in which the anode assemblies are sealed.

When the material of pedestal 3 has set and hardened and the form has been removed, a cathode casing 6 is placed on the pedestal 3 with an interposed sealing joint 7 which is resistant to the electrolyte. A cover 9 is then placed on the cathode casing 6 with another interposed sealing joint 10.

I claim:

1. An electrolytic cell comprising a plurality of cathodes alternating with a plurality of generally vertical metal anode plates over a pedestal, said anode plates having each coated thereon an active layer containing a platinum group metal or metal compound, current supply means to said anode plates, comprising an array of generally horizontal metal bars, each bar extending between the lower ends of a neighboring pair of anode plates, and clamping means to clamp said anode plates and metal bars together to form an anode assembly, said metal bars, lower ends of the anode plates and clamping means being embedded and sealed in a monolithic mass of electrically and thermally non-conducting rigid material, whereby said mass forms at least part of the aforesaid pedestal and retains the anode plates vertically and laterally.

2. An electrolytic cell according to claim 1, wherein said rigid material is concrete containing a chlorine resistant polyester resin.

3. An electrolytic cell according to claim 1, wherein said anode plates each comprise an array of metal plates disposed in prolongation of one another.

4. An electrolytic cell according to claim 1, wherein said clamping means comprise metal rods passing through said bars and said neighboring anode plates, said rods having a linear coefficient of thermal expansion lower than that of said metal bars, and fastening means at the ends of said rods.

5. An electrolytic cell according to claim 1, wherein each metal bar terminates short of the ends of the neighboring anode plates clamped thereto.

6. An electrolytic cell according to claim 5, further comprising a spacer extending between the portions of said neighboring anode plates extending beyond the end of each metal bar.

7. An electrolytic cell according to claim 1, wherein at least some of said metal bars are provided with transverse openings extending therethrough, said openings being filled by portions of said mass of electrically and thermally non-conducting rigid material.

8. An electrolytic cell according to claim 1, wherein said anode plates and metal bars, clamped together, are distributed into a plurality of independent anode assemblies, which are retained remote from one another by a portion of said mass.

9. An electrolytic cell according to claim 8, wherein the metal bars, the lower portions of the anode plates, and the clamping means of each unit assembly are enclosed in a resilient membrane.

10. An electrolytic cell according to claim 9, wherein said membrane is leak proof and resistant to corrosion by electrolyte in the cell.

11. An electrolytic cell according to claim 10, wherein said membrane is made of plasticized polyvinyl chloride.

12. An electrolytic cell according to claim 1, further comprising a cell cover, an inlet pipe for admission of electrolyte passing through said cover, and a horizontal disc provided with radial channels for distributing electrolyte positioned vertically below the discharge end of said inlet pipe.

13. An electrolytic cell according to claim 12, further comprising an overflow vessel disposed around the discharge end of said inlet pipe and supported upon said horizontal disc.

14. In a process for assembling an electrolytic cell having a plurality of vertically disposed, alternating cathodes and anodes, wherein the improvement comprises initially preparing at least one anode assembly by clamping a plurality of metal plates at their lower edges to interposed current lead-in bars, placing at least two horizontal joists on a foundation, positioning each anode assembly on and across the joists, and embedding the current lead-in bars and the lower ends of the anode plates in a monolithic mass of electrically and thermally non-conductive material, and hardening said material to support and retain the anode plates in a substantially vertical position.

15. In a process according to claim 14, further comprising positioning at least two anode assemblies on and across the horizontal joists, and providing said joists with at least one transverse projection having a thickness substantially equal to the distance between two neighboring anodes.

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