PRODUCTION OF SODIUM CHLORATE

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ABSTRACT

An electrolytic cell comprising a tank having a closed top and an open bottom. An anode closure plate extends over the bottom of the tank to form the bottom wall of the cell. A plurality of vertically positioned anodes are secured to the closure plate and are spaced to receive a cathode member between adjacent pairs of anodes. The electrodes are mounted in the cell in a manner such that they are completely submerged in electrolyte in the cell.

4 Claims, 5 Drawing Figures
FIG. 1

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PRODUCTION OF SODIUM CHLORATE

This application is a division of application Ser. No. 708,819 filed Feb. 28, 1968 now U.S. Pat. No. 3,598,715.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrolytic cell which is capable of operating at relatively high current efficiency over extended periods of time with little or no maintenance. The electrolytic cell of this invention is particularly adapted for the electrochemical conversion of aqueous sodium chloride to sodium chloride and, for convenience, the cell will be described in connection with that process. It will be understood, however, that the cell of this invention is not limited in use to the production of sodium chloride for it may be used in many other electrochemical operations, such as, for example, the manufacture of alkalai metal and alkaline earth metal hypochlorites, perchlorates, chlorine, caustic and the like.

2. Description of the Prior Art

In general, sodium chloride is produced commercially by electrolysis of an aqueous solution of sodium chloride in an electrolytic cell. One type of sodium chloride cell used today employs graphite anodes and steel cathodes which are partially submerged in an electrolyte in the cell. Generally, the anodes are in the form of plates or rods and the cathodes are in the form of vertical sheets or cooling coils disposed in substantially parallel relationship between adjacent pairs of graphite anodes. In operation, hydrogen gas is evolved at the cathode and elemental chlorine is generated at the anodes to form sodium hypochlorite in the electrolyte which is subsequently converted to the sodium chloride product.

It has been observed, however, that attrition of the graphite anodes occurs during the electrolysis operation leading to an ever increasing anode-cathode gap with a corresponding increase in cell voltage and a decreasing efficiency of operation. In addition, when the electrodes are only partially submerged in the electrolyte, corrosion of the electrodes occurs at the interface of the electrolyte and the gases present in the cell, thereby reducing the useful life of the electrodes. Furthermore, a portion of the elemental chlorine formed at the anode may escape with the cell gases making it necessary to add more acid to the electrolyte to maintain the pH of the electrolyte at a desired acid value.

SUMMARY OF THE INVENTION

The present invention provides a compact electrolytic cell which is capable of operating in a continuous manner, at a high current efficiency, over extended periods of time. This cell has a relatively low operating cost due, in part, to the prolonged life of the electrodes, which results in a substantial reduction in electrode material costs and cell rebuilding and maintenance costs.

Broadly, the electrolytic cell of this invention comprises a tank having a closed top and an open bottom. An anode closure plate extends over the bottom of said tank and forms the bottom wall of the cell. A plurality of vertically arranged, bottom entering anodes and a plurality of vertically disposed, substantially parallel cathode members are mounted within the cell. The anodes are secured to the closure plate and are suitably spaced to receive a cathode member between each adjacent pair of anodes. Preferably, the anodes are formed of platinized titanium and may be in the form of sheets, rods, strips or the like. The electrodes are mounted in the cell in a manner such that they are completely submerged in the electrolyte in the cell. This arrangement of the electrodes permits substantially all of the platinum surface to be effectively used as anode surface and prevents corrosion of the electrodes at the interface of the electrolyte and the cell gases, as frequently occurs in electrolytic cells used heretofore.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a view, partly in elevation and partly in section of an embodiment of the electrolytic cell of this invention.

FIG. 2 is a view, partly in elevation and partly in section of another embodiment of the cell.

FIG. 3 is a top plan view of a portion of the electrolytic cell shown in FIG. 2 with a portion broken away to show the novel anode-cathode arrangement of this embodiment.

FIG. 4 is a sectional view of a portion of the top of the cell illustrating an embodiment for introducing electrolyte into the cell.

FIG. 5 is an exploded view of the electrolytic cell of this invention showing the relationship of the components of the cell.

DESCRIPTION OF THE EMBODIMENTS

Referring to FIG. 1, there is illustrated the electrolytic cell 10 of this invention which comprises a tank 12 having a closed top 14 and an open bottom. The cell top 14 may be integral with the tank or may be removable secured in place by suitable means, such as bolts 15. Preferably, a removable top is provided in order to facilitate assembly of the cell and alignment of the electrodes. The upper portion of the tank walls may be flared outwardly to form flanges 16 which provide support and mounting means for the removable top.

The bottom edges of the tank wall may also be flared outwardly to form flanges 17 which provide support and mounting means for anode closure plate 20 and 22 which extends over the bottom of the tank and forms the bottom wall of the cell. Plate 20 is removably secured to the tank by suitable means such as bolts 19.

The tank 12 preferably is formed of an electrically conductive metal, with current being conducted to the walls of the tank. The entire tank is cathodically protected against corrosion, thereby enabling the tank to be constructed of iron or mild steel. However, the tank, if desired, may also be formed of an electrically non-conductive material such as ceramics, rubber, plastics and the like. When the tank is formed of a conductive metal, an electrically insulating gasket 28 is provided between flanges 17 and anode closure plate 20 to insulate the plate from the tank, and bolts 19 are insulated from flanges 17 or closure plate 20 by suitable means (not shown).

Insulating base members 23 are preferably provided to support the cell.

The cell top 14 is also formed of a corrosion resistant material which may be the same as, or different from, the material of which the tank 12 is formed. Preferably, the top is formed of an electrically non-conductive material such as polyvinyl chloride, polyvinyl dichloride, polyvinyl difluoride, natural or synthetic rubber, polyester resins, phenolic resins and the like.

The cell top is provided with an opening 24 through which gases are removed from the cell. The electrolyte may also be introduced into the cell through opening 24. Alternatively, a separate opening 25 may be provided in the cover to introduce electrolyte into the cell. Effluent cell liquor is removed through outlet 26.

The cell is provided with means which substantially prevents fresh electrolyte introduced into the cell from "short circuiting" to the outlet. According to one embodiment of the invention, distributing means may be provided within the cell for distributing the electrolyte uniformly therein. Thus, such means may comprise a perforated conduit (not shown) extending inside the cell from opening 25 along the bottom wall of the cell through which electrolyte is uniformly distributed across the bottom of the cell.

According to another embodiment, as shown in FIG. 4, packing material 30 is disposed within opening 24 in the cell top and is held in place by any suitable corrosion resistant supporting means 31 such as screening, mesh, perforated plates or the like. The packing material 30 may consist of saddles, beads, pellets, fibers, or the like of a material, such as tetrafluoroethylene fluorocarbon resins, which is inert to the electrolyte and the products of electrolysis. Electrolyte is conveyed to the cell by conduit means 32 and is introduced into...
the cell through packing 30. Gas formed in the cell during electrolysis passes upwardly through packing 30 and is removed through conduit means 33. Thus, fresh electrolyte passes through packing 30 countercurrent to the exiting cell gases which, in the production of sodium chloride, contain hydrogen and chlorine gases. The introduction of the electrolyte in this manner not only facilitates uniform distribution of the electrolyte in the cell but provides the additional advantage of scrubbing chlorine from the exiting cell gases. Thus, since the electrolyte introduced into the cell has a relatively low chlorine content, substantially all of the chlorine is scrubbed from the gaseous cell effluent when it is contacted with the electrolyte in this manner. Consequently, the gas stream recovered from the cell is substantially pure hydrogen and may be recovered. In addition, the return of the chloride to the cell in this manner tends to reduce the amount of acid required to be added to the electrolyte to maintain the pH of the cell liquor at a desired acid value.

The anode closure plate 20 which forms the bottom wall of the cell has a plurality of anode members 35 secured thereto in spaced apart, substantially parallel relationship to each other. Anode members 35 are mounted perpendicularly on plate 20, see FIG 5, and are secured thereto by any suitable means such as by welding or the like. According to a preferred embodiment of the invention, the anode members consist of an electrolytically conductive base metal provided with a thin surface layer of a noble metal or noble metal alloy. Any of the "valve" metals, namely titanium, tantalum, zirconium, aluminum, niobium and alloys thereof may be used as the base metal. The noble metal may be selected from the group consisting of platinum, iridium, rhodium, palladium, ruthenium and alloys thereof. Generally, it is preferred to use anodes consisting of titanium metal or a titanium alloy as the base metal coated with platinum metal or platinum alloy. The noble metal may be applied to the base in any suitable manner such as by roll cladding, explosive cladding, thermal decomposition, electrolyte decomposition and the like. A layer of noble metal or noble metal alloy of between about 5 to 500 micro-inches, and preferably between about 20 to 100 micro-inches, in thickness is provided on the base metal. The thickness of the base metal portion of the anodes is such that the anodes are sufficiently rigid to require no additional support when secured to the closure plate, as described above. Commercially available sheets 0.1 to 0.15 inch in thickness are particularly suitable. However, sheets as thin as 0.05 or as thick as 0.5 inch may be used. Although the use of anodes formed of a conductive base metal surfaced with a noble metal is generally preferred in the cell of this invention, it is to be understood that graphite anodes may also be used in the cell if desired.

While the anode members 35 preferably are in the form of sheets, as illustrated in FIG. 3, other suitable configurations, such as strips, rods, metal mesh and the like, may also be used. The structure of the cell insures that the anode members are completely submerged in electrolyte during operation of the cell. Thus, the members extend vertically from the anode closure plate to a point below the level of the electrolyte in the tank.

As shown in FIG. 1, anode closure plate 20 consists of two metal layers integrally bonded together. The upper surface 21 of the plate, to which the anode members 35 are secured, is formed of a metal selected from the group consisting of titanium, tantalum and columbium or other metal which is resistant to the corrosive action of the electrolyte in the cell. Due to the relatively poor electrical conductivity of these metals a lower or backing layer 22 of a more conductive metal, such as copper, aluminum, tantalum, nickel or the like is secured to upper layer 21 to facilitate uniform distribution of current to the anodes. Anode bus bars 36 are affixed to the conductive backing layer.

A plurality of cathode members are provided in the cell, with a cathode member being provided between each adjacent pair of anode members. The cathode members are mounted in the cell so that they are completely submerged in electrolyte. The cathode members may be of any suitable structural design capable of being fitted between the parallel anode members. As shown in FIG. 1, the cathode members generally consist of vertically disposed conductive metal sheets 40. The sheets 40 may be supported in the cell by any suitable means such as by integrally attaching the sheets to the inside surface of opposing walls of the tank. The sheets 40 are suitably spaced to receive an anode member 35 between each adjacent pair of cathode sheets. Since the sheets 40 are covered by electrolyte they may be formed of iron or mild steel. The thickness of such sheets may vary from about 0.1 to 0.5 inch.

Preferably, the electrolytic cell of this invention utilizes as the cathode members, the cathode assembly disclosed and claimed in patent application Ser. No. 708,820, entitled "CATHODE ASSEMBLY," by Duane N. Goens and George G. Gale, filed Feb. 28, 1968, and assigned to the same assignee as the present application. As shown in FIGS. 2, 3 and 5 a plurality of such cathode assemblies 42 are secured, as by welding or the like, to the inside surface of opposing sidewalls of the tank with the cathode assemblies 42 being spaced to receive an anode member between each adjacent cathode assembly. In this manner, each anode surface opposes a cathode surface so that all of the anode surfaces are protected from hydrogen evolved by the gas evolved at the cathode surfaces. The cathode assemblies 42 and the anode members 35 are positioned in the cell as close together as possible without contacting one another, in order to minimize IR drop in the cell and thereby maintain high power efficiency. Particularly satisfactory results are obtained when the spacing between the anode and cathode surfaces is about 0.25 inch.

According to this embodiment, each cathode assembly comprises a pair of opposing cathodes having passage means therebetween. Each cathode of the assembly includes means for directing gas evolved at such cathode during electrolysis into the passage means between the opposing cathodes whereby the gas is directed from its natural upward path between the electrodes into the passage means between the opposing cathodes and is maintained within the cathode assembly as it bubbles to the surface of the electrolyte. Preferably, as illustrated in FIGS. 2, 3 and 5, each cathode assembly 42 is formed of a pair of substantially parallel sheets of expanded metal 43, with each sheet 43 forming a cathode of the assembly. The cathodes are maintained in spaced apart relationship to provide a continuous passage means 46 between the cathodes. The sheets may be maintained in this position by any suitable means, such as for example, spacing bars 45 vertically positioned between the sheets. Generally, the expanded metal is a continuous fabric of an open mesh network of interconnected, outwardly extending webs 44 which enclose openings of diamond, oval or other configuration. The webs 44 are, in general, flat in cross-section and are positioned at an angle of about between 20° and 70°, preferably between about 35° and 55° to the plane of the original sheet. If desired, only a single sheet of expanded metal may be disposed between each endwall of the tank and the anode member adjacent said endwall.

The electrolytic cell of this invention is well adapted for use in a continuous electrochemical process wherein an electrolyte is introduced into the cell to contact with the electrodes until the reaction has proceeded to a desired degree, whereupon the electrolyte is removed from the cell, passed to an external holding tank and recovered or recirculated to the same cell or an adjacent cell for further electrochemical treatment, if desired. The present cell may also be used in a batch process operation in which the electrolyte is circulated in the cell until the desired electrochemical reaction is completed.

One of the uses for which the electrolytic cell of this invention is particularly well suited is a continuous process for the production of chlorine dioxide. In such a process, an aqueous solution containing sodium chloride is electrolyzed in the cell of the present invention to provide a cell liquor rich in sodium chlorate. That liquor is removed from the cell and passed to a reactor where it is contacted with HCl to form a gaseous mix-
ture of chlorine dioxide and chlorine gas, which is recovered, and a solution which is depleted of chlorate values. This solution is then recycled to the electrolytic cell where it is again subjected to electrolysis to increase the concentration of sodium chlorate. This cycle may be continuously repeated. In this manner, substantially all of the sodium chlorate produced in the cell is converted into ClO₂ and Cl₂ with a high degree of efficiency.

The temperature of the electrolyte in the cell of this invention preferably is controlled by the introduction and circulation of cooled electrolyte into the cell.

The electrolytic cell of the present invention may be operated at high current densities with low voltage and with high current efficiency. Thus, the cell may be operated at a current density of between 25 to 1,000 amperes or more per square foot, so that a small compact cell is capable of a high production rate. The cell, when used in the electrolysis of aqueous sodium chloride solution to sodium chlorate, may be operated at a cell voltage of from about 3.0 to 4.0 volts with a current efficiency of 95 to 100 percent.

The present cell, when containing noble metal surfaced anodes, is capable of being operated at a substantially higher current density in the electrolysis of sodium chloride to sodium chlorate than conventional graphite-anode chloride cells and may be operated at temperatures higher than generally used in chlorate production. The noble metal surfaced anodes are resistant to oxidation and corrosion even at temperatures of 100°C. or above. Whereas graphite anodes tend to wear away in use, leading to an ever increasing anode-cathode gap with a corresponding increase in cell voltage, the noble metal surfaced anodes are relatively permanent in nature so that the original spacing between the electrodes may be maintained for long periods of time. Thus, high conductivity is maintained and the cell retains its original high efficiency.

The noble cathode assembly configuration shown in FIGS. 2, 3 and 5 is used in the present cell, its use insures that cathode gases are directed away from the anode surfaces thereby preventing the gas from eroding away the noble metal surface and minimizing the amount of gas present between the electrodes. In this manner, a low IR drop in the cell is maintained. Because of the high, constant current density, the relatively small compact cell of this invention has a relatively low operating cost due to the prolonged life of the electrodes which results in a substantial reduction in cell rebuilding and maintenance costs.

EXAMPLE

The following example illustrates the use of the electrolytic cell of this invention in the electrochemical conversion of an aqueous solution of sodium chloride to sodium chlorate. An electrolytic cell was designed and constructed as shown in FIG. 5 and contained the cathode assemblies shown in FIGS. 2, 3 and 5. The cell contained 20 anodes welded to a closure plate formed of a thin titanium sheet bonded to a mild steel plate. The anodes were formed of titanium sheets, each about 0.1 inch in thickness and having from 25 to 50 micro-inches of platinum coated on each side of the titanium sheet. Twenty-one cathode assemblies, each constructed of two sheets of expanded mild steel separated by ¼ inch steel vertical spacing bars were welded to the inside walls of a mild steel tank. The electrodes were mounted in the cell to provide a ¼ inch spacing between adjacent cathode and anode surfaces.

An aqueous electrolyte containing about 265 grams per liter sodium chlorate, about 170 grams per liter sodium chloride and about 3 grams per liter sodium dichromate was introduced into the cell through an opening 25 in the cell cover. Sufficient electrolyte was introduced into the cell to completely cover the electrodes. Another portion of the electrolyte was introduced into an external holding tank from which the electrolyte was circulated through the cell during electrolysis. The cell was operated under the following conditions:

- **Current density**: 150 amps/sq. ft.
- **Cell voltage**: 3.0 to 3.2 volts
- **Temperature**: 60°C.
- **pH**: 6.9 to 7.2

During operation of the cell, electrolyte was continuously circulated between the cell and the external holding tank, with the electrolyte being removed from the cell through outlet 26 and being reintroduced through opening 25. Cell operating temperature was controlled by cooling the electrolyte passing from the holding tank to the cell and by adjusting the electrolyte feed rate.

Substantially all of the hydrogen gas evolved at the cathodes during electrolysis was directed into the space between the cathode surfaces and was retained between the cathode surfaces as it bubbled to the surface of the electrolyte and was removed from the cell through opening 24.

The cell was operated continuously for 10 days. At the end of the electrolysis operation the sodium chloride concentration in the electrolyte had been reduced to about 110 grams per liter while the sodium chlorate concentration had increased to about 350 grams per liter. Current efficiency of the cell during electrolysis was about 96 – 97 percent, based on the formation of sodium chlorate. Platinum loss rate from the anodes was very low, 0.012 Troy ounces per ton of chloride formed.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification and this application is intended to cover any variations, uses or adaptations of the invention. It will therefore be recognized that the invention is not to be considered as limited to the precise embodiments shown and described but is to be interpreted as broadly as permitted by the appended claims.

What is claimed is:

1. A process for the electrochemical conversion of sodium chloride in an aqueous solution to sodium chlorate which comprises

   introducing said aqueous solution into an electrolytic cell which contains a plurality of anode members and a plurality of cathode assemblies, each of said cathode assemblies comprising a pair of opposed, inclined surfaces having a passage therebetween, passing an electrical current through said anode members and said cathode assemblies to evolve hydrogen gas at said cathodes and generate chlorine at said anodes, a major portion of said chlorine reacting to form sodium chlorate in the electrolyte and a minor portion of said chlorine being evolved as chlorine gas, directing said hydrogen gas inwardly and upwardly between said pair of inclined surfaces and away from said anodes and removing said hydrogen gas said chlorine gas and said electrolyte from the cell.

2. The process defined in claim 1 in which said aqueous solution is introduced into said cell countercurrent to and in contact with said gases being removed from the cell whereby at least a portion of the chlorine gas is absorbed in said aqueous solution.

3. The process as defined in claim 1 in which each of said anode members comprise a sheet of a base metal having a noble metal surface.

4. The process as defined in claim 1 in which said cell is operated at a current density of about 100 to 300 amperes per square foot and a voltage of between 3 to 4 volts until a substantial amount of said sodium chlorate is converted to sodium chlorate.

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