

Feb. 12, 1974

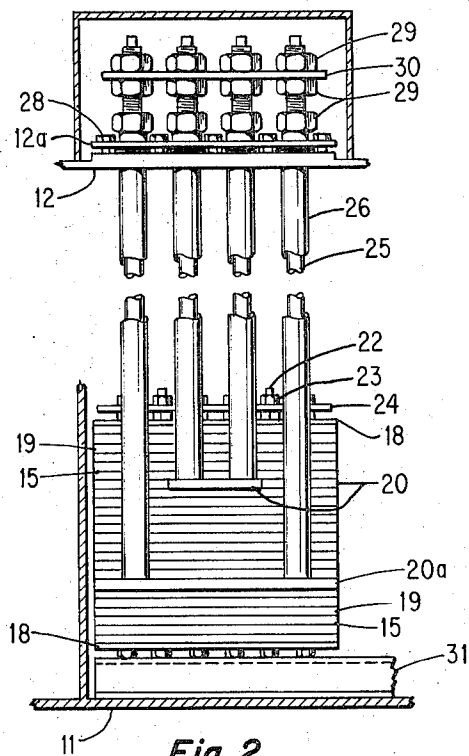
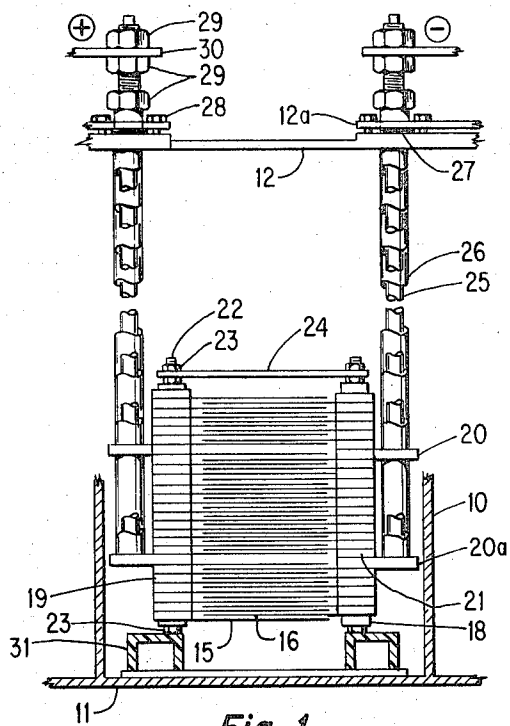
R. E. LOFTFIELD

3,791,947

ELECTROLYTIC CELL ASSEMBLIES AND METHODS OF CHEMICAL PRODUCTION

Filed Jan. 26, 1972

3 Sheets-Sheet 1



Feb. 12, 1974

R. E. LOFTFIELD

3,791,947

ELECTROLYTIC CELL ASSEMBLIES AND METHODS OF CHEMICAL PRODUCTION

Filed Jan. 26, 1972

3 Sheets-Sheet 2

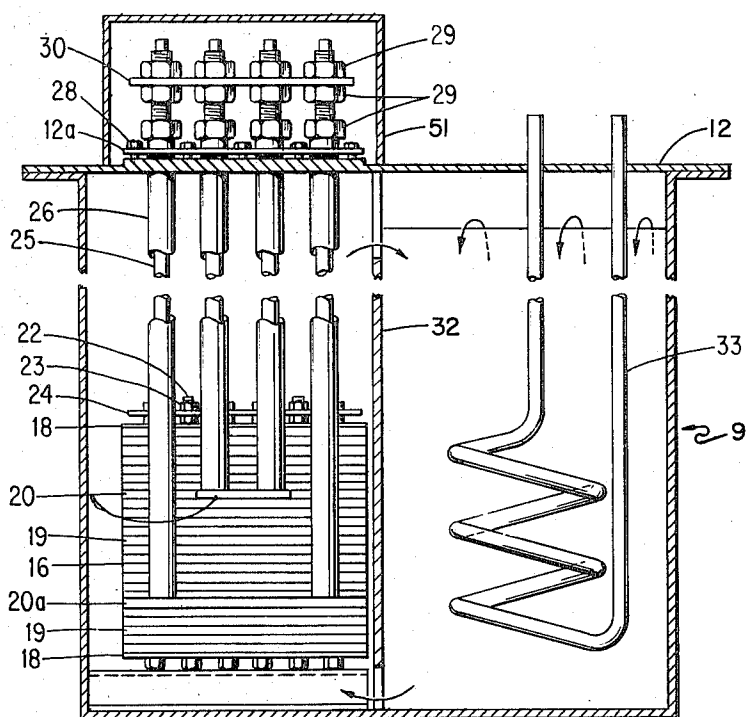


Fig. 3

Feb. 12, 1974

R. E. LOFTFIELD

3,791,947

ELECTROLYTIC CELL ASSEMBLIES AND METHODS OF CHEMICAL PRODUCTION

Filed Jan. 26, 1972

3 Sheets-Sheet 3

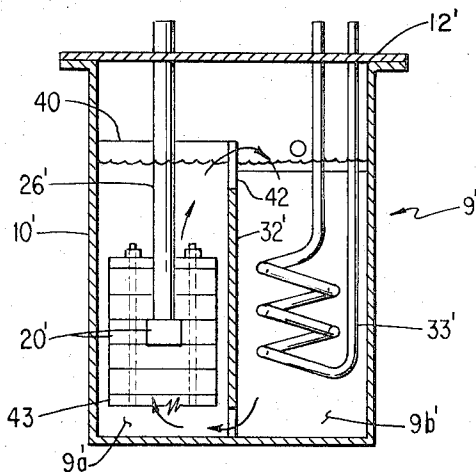


Fig. 4

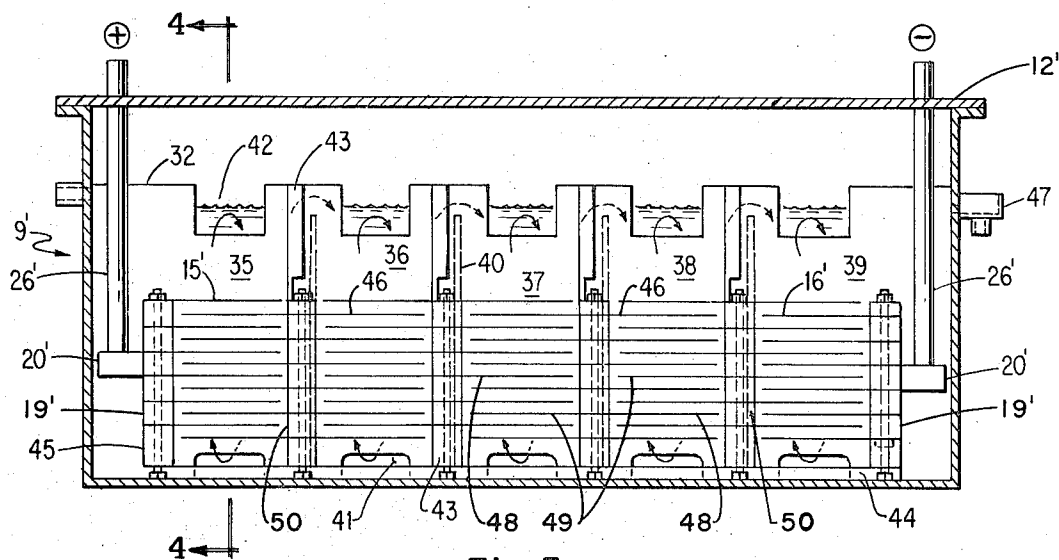


Fig. 5

1

2

3,791,947
**ELECTROLYTIC CELL ASSEMBLIES AND
METHODS OF CHEMICAL PRODUCTION**
Richard E. Loftfield, Chardon, Ohio, assignor to
Diamond Shamrock Corporation, Cleveland, Ohio
Filed Jan. 26, 1972, Ser. No. 220,902
Int. Cl. C01b 11/26

U.S. Cl. 204—95

5 Claims

ABSTRACT OF THE DISCLOSURE

Electrode assemblies and cells for electrolytic processes, including the production of alkali metal hypochlorite, alkali metal chlorate, and other inorganic and organic chemical products, comprise a diaphragm-less electrolytic cell having at least one assembly of a plurality of planar, parallel, closely spaced foraminous dimensionally stable substantially horizontally disposed anodes and a plurality of parallel foraminous cathodes substantially horizontally disposed, the cathodes interleaved with the anodes in substantially face-to-face closely spaced parallel alignment. Organic chemical products, alkali metal hypochlorite and alkali metal chlorate are produced by placing the assembly of electrodes provided with means for supplying current to the individual anodes and current from the individual cathodes, in alkali metal halide solutions, solutions of organic electrolytes and electrolyzing the solutions while maintaining operating parameters suitable for the production of alkali metal hypochlorite and alkali metal chlorate and organic chemical products.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates generally to novel electrode assemblies and electrolytic cells for the electrolysis of solutions of electrolytes. More specifically, the present invention relates to novel diaphragm-less type electrolytic cells for the electrolysis of organic chemical and aqueous metal halide solutions and the production of organic chemical products and both alkali metal hypochlorite and alkali metal chlorate in which cells improved electrical power efficiency and overall economy in operation are provided. Electrical power efficiency as used herein, encompasses both current efficiency and cell voltage.

(2) Description of the prior art

In the prior art manufacture of products such as alkali metal hypochlorite and alkali metal chlorate, a typical electrolytic cell was so constructed that the electrodes were closely spaced in vertical position in the absence of a diaphragm. To obtain maximum power efficiency, the tendency was to space the electrodes as closely as possible so that the electrolyte flowing therebetween offered as little resistance to the passage of current as possible. However, the formation of a gaseous product at the electrodes produced an insulating effect which lowered the power efficiency unless the gas was caused to be removed rapidly from the anode. The problem of gas bubble removal was thus the limiting factor in the determination of the space setting between the electrodes. If the space was adjusted for minimum electrical resistance, the gas bubbles were impeded in rising and a loss of power efficiency and increased voltage resulted from the insulating effect of the bubbles on the anode. If the space gap was larger than necessary to permit gas bubbles to escape, a greater amount of voltage was required to overcome the increased resistance which resulted in a reduction in electric power efficiency.

In one prior cell, a minimum space is provided between the electrodes for electrolyte passage while permitting

escape of the gases formed, by vertical channels provided in the anodes whereby the gas tends to rise in the said channeled portion of the anode. This type of cell has provided some improvement, but, since the channel space cannot exceed a fixed size without loss of power efficiency only a limited improvement in gas bubble removal is available by this construction.

In another typical known process for making alkali metal hypochlorite and alkali metal chlorate, chlorine gas and alkali metal hydroxide were produced in anode and cathode compartments, respectively, of an electrolytic cell provided with a porous diaphragm wherein alkali metal halide is electrolyzed. The chlorine gas and alkali metal hydroxide individually produced and separated from each other are then subsequently reacted. Various cell designs have been used for including the mixing and reaction chambers in either enclosed or isolated association with the cell. However, such cells and methods are not entirely satisfactory since additional equipment and space requirements and frequent maintenance and replacement of diaphragms prohibitively increase production costs.

Since such problems are prevalent in the production of alkali metal hypochlorite and alkali metal chlorate and other chemical compounds in electrolytic cells, a definite need exists for electrolytic cells capable of economical operation and requiring minimum maintenance.

SUMMARY OF THE INVENTION

It is an object of this invention to provide diaphragm-less electrolytic cells and economical processes for the production of alkali metal hypochlorite and alkali metal chlorate and other inorganic chemical products.

It is a further object of this invention to provide a diaphragm-less electrolytic cell having parallel, planar, closely spaced foraminous substantially horizontally disposed electrodes and good power efficiency.

Another object of this invention is to provide multi-unit diaphragm-less electrolytic cells having closely-spaced parallel planar foraminous substantially horizontally disposed electrodes and improved power efficiency for electrolysis of aqueous alkali metal halide solutions and other inorganic and organic electrolytes.

These and other objects and advantages of the invention herein disclosed will be apparent to those skilled in the art from the following specification, the appended claims and by reference to the drawings wherein like numerals represents the same or similar parts and in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevation of a unit assembly of a plurality of electrodes in a single electrolytic cell chamber with the chamber wall partially broken away and the cover removed.

FIG. 2 is an end elevation of the anode arrangement of the electrodes of FIG. 1 with the cover included, the end wall of the chamber removed and with the center wall and circulation area deleted.

FIG. 3 is an end elevation of the cathode arrangement of FIG. 1 with the end wall of the chamber removed and the chamber cover, center wall and circulation area included.

FIG. 4 is a cross-sectional view of the electrode assembly of FIG. 5 taken along the line 4—4 showing the assembly arranged in a chamber also having a cooling coil and a baffle plate disposed in a chamber with arrows indicating the direction of solution flow.

FIG. 5 is a side elevational view of the embodiment of this invention comprising a multi-unit assembly of a plurality of electrodes in an electrolytic cell with a side wall deleted and with arrows showing the directional flow of the solution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to one embodiment of this invention there is provided a single assembly of a number of parallel, substantially horizontally disposed, closely spaced foraminous dimensionally stable anodes and a like number of horizontally disposed parallel foraminous cathodes interleaved with said anodes in substantially parallel face-to-face relation and the assembly being spaced from the bottom of a cell chamber having side, bottom and end walls, the peripheral edges of the assembly being preferably partially or substantially completely enclosed. A single assembly may be used for electrolytic processes either as an individual assembly positioned in a single chamber or as a plurality of single assemblies positioned in a corresponding number of single chamber, or in a single chamber with each assembly being separated by a partition, the assemblies being connected to each other in conventional series fashion by connecting the cathodes and anodes of adjacent assemblies.

In a second embodiment of this invention, there is provided a multiplicity of bipolar electrode assemblies having parallel, substantially horizontally disposed, closely spaced foraminous electrodes, each electrode including a dimensionally stable anode portion and a cathode portion, said cathode portions interleaved with said anode portions in substantially parallel face-to-face relation, each assembly in spaced relation from the bottom wall of a chamber having side, end and bottom walls, the peripheral edges of each assembly being preferably partially or substantially completely enclosed.

The multiplicity of bipolar electrode assemblies are horizontally interposed between a terminal assembly of spaced horizontally disposed substantially parallel dimensionally stable foraminous anodes and a terminal assembly of spaced horizontally disposed substantially parallel foraminous cathodes. An electrically insulating and substantially liquid sealing partition separates each bipolar electrode assembly from horizontally adjacent bipolar electrode assemblies and from the terminal anode and terminal cathode assemblies. The bipolar electrodes are common to adjacent electrode assemblies, extend through the separating partitions and have anode and cathode portions on opposite sides of said partitions. The cathode portions of the bipolar electrode assembly adjacent the terminal anode assembly are interleaved with the anodes of the terminal anode assembly and the anode portions of the bipolar electrode assembly adjacent the terminal cathode assembly are interleaved with the cathodes of the terminal cathode assembly. All other anode and cathode portions of the bipolar electrode assemblies are interleaved with horizontally adjacent portions of the bipolar electrodes in alternating polarity arrangement. The embodiment includes additional electrolyte inlet and outlet means associated with the chamber means for sequential passage of electrolyte from each partitioned assembly to each horizontally adjacent assembly and from the terminal cathode partitioned assembly and means for supplying electric current to the anodes of the terminal anode assembly and means for withdrawing current from the cathodes of the terminal cathode assembly.

The common interleaved electrode portions comprise electrical connection means between adjacent electrode assemblies by functioning as bipolar electrodes between adjacent assemblies, one end portion of the electrode having the opposite polarity of the other end portion of the electrode. The electrical current thus passes from one portion of one polarity of a common electrode in one cell to the other portion of the same common electrode of opposite polarity in an adjacent cell. The current also is transferred from the surface of each portion of the common electrode to adjacent electrode surfaces of opposite polarity within the individual cell where the bipolar electrode portion is positioned.

Wherever a number of cathodes or cathode portions of an electrode are described as interleaved with a plurality of anodes in an electrode assembly in this specification and claims, such description includes an individual cathode or cathode portion of an electrode positioned between a pair of anodes or juxtaposed a single anode, the cathode or cathode portion in such juxtaposed position being a terminal cathode of the electrode assembly.

In each of the above embodiments the electrolyte passes rapidly from a point below the lower terminal electrode through the entire electrode assembly by virtue of the openings in all of the foraminous electrodes, the preferably partially or substantially completely enclosed peripheral edges of the assembly and the lift effect of the gases produced at the electrodes. Considerably increased circulation rates of the electrolyte upwardly from a point below the assembly through all the electrodes in a direction approximately perpendicular to the surfaces of the electrodes is effected by partially or completely substantially enclosing the peripheral edges of the electrode assembly. In the case of the single assembly, the electrodes are enclosed on the end or longitudinal peripheral edges by the various spacers, holding bars, conducting bars and shims or washers which maintain the electrodes in assembled position. The side or transverse peripheral edges of each electrode assembly are substantially enclosed in one modification by positioning the assembly in closely spaced relationship to each cell chamber or partition side wall. For example, the assembly is positioned so that approximately one-eighth of an inch space or gap is established between the edges of the electrodes and the sides of the cell chamber walls. In another modification, the peripheral edge of the electrode assembly are not positioned as closely adjacent the side walls and electrically non-conducting spacers, inert to the cell environment, are inserted between the side walls of the cell chamber and the side or transverse peripheral edges of the electrodes of the assembly so that a small space of approximately one-eighth of an inch is provided between the electrode edges and the spacer surface facing the electrode edges. In another modification, either all or some of the peripheral edges may be substantially enclosed by attaching impervious sheets of electrically non-conducting material such as plastic and the like to the supporting frame by any suitable means which provides the desired enclosure and does not interfere with the efficient operation of the assembly. For some purposes, temperature control means are required to be positioned in the cell chamber and, in one modification, the electrode assembly is positioned close to a side wall and cooling coils are arranged adjacent the opposite side wall. In this modification, a center wall having an open portion at its lower end adjacent with the bottom wall of the cell and a cutout portion at its upper end is positioned between the electrode assembly and the cooling coil to regulate the circulatory flow of the electrolyte over the top of the center wall downwardly past the cooling coils underneath the open portion of the plate spaced from the bottom of the cell and upwardly through the entire assembly of electrodes in a direction approximately perpendicular to the electrode surfaces. In both the first and second embodiments of this invention, the electrodes are maintained in closely spaced face-to-face relation by the spacers, shims, conductor bars and end bars utilized to maintain the electrodes in assembled position. The closely spaced electrodes are maintained free from electrical contact by electrically non-conductive separators interwoven through or positioned within the openings of the foraminous electrodes. When flat or cylindrical elements are used as separators they are generally interwoven through alternate openings on the outer edges of the electrodes but may also be interwoven through other portions of the electrodes. The electrically non-conductive separators should be constructed of materials inert to the cell environment and

may have any suitable geometric configuration. Generally, the separators are polyvinylidene chloride, polyvinyl chloride, chlorinated polyvinyl chloride, polyvinyl fluoride, tetrafluoroethylene and the like and may be of solid or hollow cylindrical flat or other suitable configuration. Other types of spacers capable of satisfactory use are electrically non-conductive strips provided with projections adapted to be tightly positioned within the electrode openings and button type members such as semispherical elements arranged on opposite sides of the electrode openings and joined by an engaging member, such as, a stem, extending through the electrode openings. The separators are positioned to prevent electrical contact or shorting between the electrodes and, at the same time, provide maximum flow of the electrolyte through the openings in the electrodes.

Referring to the drawings and particularly FIGS. 1 to 3, a cell chamber shown generally at 9, has side walls 10, a bottom 11 and cover 12. An assembly of electrodes comprises a plurality of dimensionally stable anodes 15, and a plurality of cathodes 16. The cell chamber and cover may be constructed of any material which is not adversely affected by the environment of use and is usually made from a plastic material such as polyethylene, polyvinyl chloride, chlorinated polyvinyl chloride, tetrafluoroethylene and the like. A preferred material of construction of the cell chamber and cover of the invention is polyvinyl chloride with a fiber glass overlay.

The dimensionally stable anodes 15 comprise an electrically conductive substrate with a surface coating thereon of a solid solution of at least one precious metal oxide and at least one valve metal oxide. The electrically conductive substrate may be any metal which is not adversely affected by the cell environment during use and also has the capability, if a breakdown in the surface coating develops of preventing detrimental reaction of the electrolyte with the substrate. The geometrical configuration of the anodes may vary provided foraminous anodes of suitable shape for forming the structural assembly are used. Generally, the substrate is selected from the valve metals including titanium, tantalum, niobium and zirconium. Expanded mesh titanium sheet is preferred at the present time.

In the solid solutions an interstitial atom of a valve metal oxide crystal lattice host structure is replaced with an atom of precious metal. This solid solution structure distinguishes the coating from physical mixtures of the oxides since pure valve metal oxides are, in fact, insulators. Such substitutional solid solutions are electrically conductive, catalytic and electrocatalytic.

In the above-mentioned solid solution host structure the valve metals include titanium, tantalum, niobium and zirconium while the implanted precious metals encompass platinum, ruthenium, palladium, iridium, rhodium and osmium. Titanium dioxide-ruthenium dioxide solid solutions are preferred at this time. The molar ratio of valve metal to precious metal varies between 0.2-5:1, approximately 2:1 being presently preferred.

If desired, the solid solutions may be modified by the addition of other components which may either enter into the solid solution itself or admix with same to attain a desired result. For instance, it is known that a portion of the precious metal oxide, up to 50%, may be replaced with tin dioxide without substantial detrimental effect on the overvoltage. Likewise, the defect solid solution may be modified by the addition of cobalt compounds particularly cobalt titanate. Solid solutions modified by the addition of cobalt titanate, which serves to stabilize and extend the life of the solid solution, are described more completely in co-pending application Ser. No. 104,703 filed Jan. 7, 1971. Other partial substitutions and additions are encompassed. Another type of dimensionally stable anode which may be used with good results in the practice of this invention consists of mixtures of chemically

and mechanically inert organic polymers and solid solutions of valve metal and precious metal oxides as at least a partial coating on an electrically conductive substrate. Particularly useful materials in such anodes are the above-described solid solutions in admixture with fluorocarbon polymers such as polyvinyl fluoride, polyvinylidene fluoride and the like coated on at least part of the surface of an electrically conductive substrate consisting of the above-described valve metals and other suitable metals. Such anodes and preparation thereof are disclosed and more completely described in co-pending application Ser. No. 111,752 filed Feb. 1, 1971.

One other type of dimensionally stable anode capable of satisfactory use in this invention consists of a valve metal substrate bearing a coating of precious metals or precious metal alloys, particularly platinum alloys on at least part of its surface.

The above-mentioned preferred solid solution coatings are described in more detail in British Pat. No. 1,195,871.

The cathode may be any suitable material or metal capable of sustaining the corrosive cell conditions and a useful metal is generally selected from the group consisting of stainless steel, nickel, titanium, steel, lead and platinum. Alternately, any sintered or otherwise porous catalytic surface with low hydrogen overvoltage may be used. In some cases the cathodes may be coated with the solid solutions above described for coating the dimensionally stable anodes. Support posts 22 are terminally threaded bolts or studs of metal capable of sustaining the corrosive cell conditions, preferably titanium, and extend through apertures in one end of each cathode and of each anode. Support frame bars 18 are positioned adjacent the upper and lower terminal electrodes. Spacing bars 19, arranged between each electrode, shims 21 and conductor bars 20, are each provided with apertures through which support posts 22 extend. The combination of the support posts, support frame spacing and conductor bars, and shims comprise the support means for the plurality of electrodes. The support posts 22 holding the electrodes, various spacers, conductors, and shims have externally threaded ends which are held in position by internally threaded nuts 23. The anodes, maintained in such supported position at their apertured ends terminate at their other ends at a point just short of the cathode supporting means. The cathodes are mounted in the same manner and terminate short of the anode supporting means. Such arrangement avoids short circuiting of the cell electrode assembly by preventing contact of the electrodes with cell elements having an opposite electrical charge. In the drawing the cathode supporting arrangement includes more spacers or shims than the anode arrangement since less cathodes are included in the assembly and in order to maintain level electrode surfaces additional spacers are necessary for the cathode arrangement. Stabilizing fixture 24 consisting of strips of electrically non-conducting plastic material such as polyethylene, polyvinyl chloride, chlorinated polyvinyl chloride, tetrafluoroethylene and the like is attached to the upper terminal ends of support posts 22 by threaded nuts 23 and washers (not shown) to prevent shifting, particularly horizontal movement of the electrodes.

A close spacing of the electrodes of about 0.03 inch is maintained by hollow or solid cylindrical or flat lengths of electrically insulating plastic such as polypropylene, polyvinylidene chloride, polyethylene, interwoven in the openings of the foraminous cathodes at spaced intervals.

The current conducting means comprises internally threaded upper and lower conductor bars 20 and 20a, respectively, which are positioned between the electrodes at spaced intervals and are held in position by the supporting posts 22 extending through apertures in said conductor bars. The conductor bars are positioned at two different levels for current distribution purposes and current is supplied to the said conductor bars by externally threaded

rods 25 which are threadably secured to the conductor bars at the internally threaded portions of said bars which extend beyond the side edges of the electrode assembly. Hollow tubes 26 are mounted to encase the rods 25. Contact of said rods with cell fluids is prevented by back-up rings and rubber gaskets positioned adjacent the conductor bars and by lower cover assembly section 12, upper cover section 12a, rubber gaskets 27 and threaded bolts 28. The upper terminal ends of the copper rods are also externally threaded and have positioned thereon adjacent the threaded portion a tank cover assembly which comprises a first cover member 12 and a second separate section of the tank cover 12a. Both cover sections have corresponding apertures adapted to enclose each tube in tight-fitting relationship. The cover sections are secured to each other and to the rubber gaskets 27 encasing the tubes at the surface junctions of the cover sections by threaded bolts 28 extending through corresponding apertures in each section. Internally threaded nuts secured to the lower externally threaded portion of each upper rod exert sufficient pressure on the upper terminal surfaces of each tube to maintain a tight seal of the space between the rod and tube at the point where the rod extends above said tube. A pair of nuts 29 threadably engage the upper ends of the externally threaded portion of each rod to hold an apertured portion of an elongated busbar 30 rigidly between the mating surfaces of said nuts when secured. The busbar is provided with a plurality of apertures corresponding approximately to the diameter of each rod and is adapted to be mounted in electrical contact with said cylinders and a power source (not shown). A protective hood 51 constructed to electrically insulating material such as the previously described plastics may be positioned over the busbar connections to minimize chemical and atmospheric corrosion of said connections.

The means for spacing the electrode assembly from the bottom wall of the cell chamber may be at least one pair of pallets mounted on the bottom wall of the cell chamber and said pallets are designated in the accompanying drawings as numeral 31. The pallets may be of any material inert to the cell environment and of varying configuration provided they are so constructed that they support the electrode assembly to permit the electrolyte flow at an angle of substantially 90° to the surfaces of the electrodes. By such arrangement the electrolyte entering the cell chamber at any given position is drawn through all the electrodes of each assembly from a locus below the lower terminal electrode upwardly at an angle of approximately 90° by the upward flow of the gases formed by the decomposition of the alkali metal halide.

The metals used in the construction of the electrical conducting means may be any type of metal which efficiently conducts a current such as copper or aluminum and the like and copper is preferred. Some of the electrical fittings such as the nuts 29 used for connecting the terminals of the electrically conducting rod may be constructed of brass and the like material. When the electrically conducting rods are constructed of copper it is desirable to protect this material from the cell environment and in this invention tubes are provided to protect the copper rods from the cell environment. The tubes may be constructed of various materials resistant to the cell conditions such as plastics, ceramics and valve metals including tantalum, niobium, titanium and zirconium. Titanium is preferred. The conductor bars 20 may be constructed of any electrically conducting valve metal as defined above. Titanium is preferred. The various other materials used in construction of the electrode assembly other than the electrodes and non-metallic separators such as the shims, spacers, supporting posts, nuts and washers should be made of any material resistant to the cell environment such as metals, plastics and ceramic materials. A valve metal, as defined above, is suitable for the construction of such parts which are to be immersed in the

cell electrolyte and of the valve metals, titanium is preferred.

The conductor bars may be arranged in various positions and the position selected should be one that provides proper current distribution to the cell assembly. As noted, a plurality of electrodes are used and the number will vary in accordance with the size of the cell and the configuration thereof.

The number of electrodes for the cells of this invention should be not more than the plurality which provides sufficient flow of solution through the assembly and also sufficient release of gases formed during electrolysis. It is preferable to use more than one cell unit connected in series rather than increase the number of electrodes and corresponding height beyond the point at which a decrease in power efficiency occurs. Any number of unit cells assemblies of electrodes may be connected in series within a single cell chamber or individual cell assemblies within single compartments may be connected in series.

As noted above adjacent electrodes must be closely-spaced to provide minimum electrical resistance and at the same time permit rapid flow of electrolyte through their open portions in conjunction with the rapid upward flow of gases formed during electrolysis. The space between adjacent electrode surfaces may range from about 0.01 inch to about 0.25 inch for satisfactory operation of the cell. However, for obtaining maximum power efficiency a space of from about .02 inch to about .04 inch should be maintained between adjacent electrodes. The space may be maintained by any material such as ceramics and which will not corrode in the environment and will not conduct an electrical current. Various plastics such as polyethylene, polyvinyl chloride, polypropylene and the like may be used and such materials may be spherical, hemi-spherical, flat, cylindrical, or of any other suitable configuration which will prevent contact of the electrodes and short circuiting.

The electrode alternating arrangement may vary such that one terminal electrode is an anode and the other terminal electrode is a cathode.

In FIGS. 3 and 4 the circulation of the solution within individual cells or compartments of a single cell chamber is indicated by the direction of the arrows. A center wall 32, positioned intermediate side walls 10, of chamber 9, is spaced from the bottom wall 11 of the chamber to induce flow of the solution within the chamber in a circulatory manner between the side walls 10. The center wall 32 divides the cell chamber into two sections 9a in which the electrode assembly is arranged and 9b a circulation section in which temperature control means are optionally disposed with the exception of the apertures in the lower end of said baffle. The electrode assembly is positioned on one side of the baffle with the peripheral edges of three sides of the assembly substantially enclosed by a side wall and the electrode support means at two end walls. The entire fourth lateral peripheral edge of the assembly is substantially enclosed by the side of the center wall adjacent said edge. The edges of the assembly may also be substantially enclosed by electrically non-conducting spacers inserted between adjacent walls. The assembly lateral edges may, if desired, be substantially enclosed in any other suitable manner. For example sheets or plates of electrically non-conducting materials such as plastics and ceramics may be mounted on or connected to the electrode support means to substantially enclose the entire peripheral edges of any or all sides of the electrode assembly. By substantially enclosing the entire lateral peripheral edges of the electrode assembly, the electrolyte introduced into the cell chamber in circulation section 9b is caused to flow through the opening where the baffle is spaced from the bottom wall of the tank into the electrode assembly section 9a to a point below the lower terminal or the lowermost electrode of the assembly. At this point the electrolyte is caused to rise and pass through all the electrodes of the assembly

by the lift effect of the ascending gas bubbles formed at the electrodes during electrolysis. The partially electrolyzed solution after passing upwardly through the entire electrode assembly flows over the baffle where it is spaced from top of the chamber or the upper level of the solution contained in the chamber. In this manner the solution flows around the baffle and through the electrode assembly in a number of circulatory passes. If a multiplicity of unit assemblies are connected in electrical series in individual cell chambers or compartments the solution after circulating around the baffle flows from each cell assembly chamber or compartment to the adjacent assembly in succession until reaching a solution outlet in the terminal assembly chamber. The successional flow of the solution may be effected by a suitable weir or overflow arrangement positioned in the appropriate end or compartment wall. The weir arrangement is designed to permit a predetermined rate of solution overflow and substantially prevent electric current leakage from one chamber to the next. The electrolyte may be indirectly supplied to individual electrode assemblies by introduction into the cell area located between a side wall of the chamber and the side of the baffle opposite from the electrode assembly whereby it flows under the lower open section of the baffle and upwardly through the entire electrode assembly. Alternatively, the electrolyte may be directly supplied to a point beneath the lower terminal electrode by introducing the solution through an inlet positioned below the terminal electrode of the assembly. A coil 33, for temperature control may optionally be arranged in the cell area between the side wall of the baffle opposite the electrode assembly and the side wall of the chamber opposed to the baffle.

FIGS. 4 and 5 illustrate a multi-unit electrolytic cell including a number of electrode assemblies wherein one terminal cell assembly of dimensionally stable anodes in compartment 35 is similar to the anode arrangement of FIG. 2, and the terminal cathode assembly in compartment 39 is similar to the cathode arrangement in FIG. 3. In compartments 36, 37 and 38 the electrodes 46 are bipolar electrodes, each electrode having one portion of one polarity positioned in one compartment and the other portion of opposite polarity extending into an adjacent compartment. All the electrodes of the multi-unit cell are interleaved foraminous bipolar electrodes common to two adjacent cells with the exception of the dimensionally stable anodes 15' in terminal assembly compartment 35 supplied with electric current by conductor bar 20', and cathodes 16' in terminal assembly compartment 39 from which current is withdrawn through conductor bar 20'. The dimensionally stable anodes 15' and cathodes 16' are the same type as anodes 15 and 16 above-described in connection with the unit assembly of FIGS. 1 to 3. The foraminous bipolar electrodes are constructed and positioned so that the assembly of bipolar electrodes 46 in each cell compartment horizontally interposed between the terminal electrode-assembly compartments comprises a plurality of foraminous planar parallel substantially horizontal dimensionally stable anode portions 48 adapted to receive a plurality of foraminous planar parallel substantially horizontal cathode portions 49 positioned in closely spaced substantially face-to-face relation to each anode. The electrodes of the assembly are in this manner alternately arranged in polarity both in vertical and end-to-end or longitudinal position with the interleaved bipolar electrodes being of opposite electrical charge in adjacent horizontally interposed cells. In the terminal anode assembly of compartment 35 the cathode portion of each bipolar electrode included in the compartment is positioned in closely spaced substantially face-to-face relation to each dimensionally stable anode. The dimensionally stable anode portion of each bipolar electrode included in the terminal cathode assembly compartment 39 is arranged in substantially face-to-face closely spaced rela-

tion to each cathode. The cell chamber 9' has a center wall 32' positioned intermediate the side walls 10' which divides the cell chamber and each compartment into an electrode section 9a' and a solution circulation section 9b'. Each compartment is separated from the adjacent compartment by a partition 43 positioned in the electrode section 9a' in electrically insulating and fluid-sealing engagement between the center wall 32' and chamber wall 10' and a partition wall 40 arranged in solution circulation chamber 9b' in liquid-sealing engagement between center wall 32' and chamber wall 10'. When electrolyte solution enters terminal anode assembly compartment 35 it flows from the circulation section 9b' through the lower open area 41 of baffle plate 32' into the electrode section 9a' to the space below the lowermost electrode of the electrode assembly. The lift effect of the rapidly ascending gas bubbles formed at the electrodes during electrolysis then causes the solution to rapidly flow from the space beneath the lower terminal electrode through the entire assembly of electrodes and over the upper open portion 42 in center wall 32' into circulation chamber 9b. Any unreacted gases remaining in the solution are disengaged therefrom at this point and removed from the cell chamber by suitable conventional means. The solution continues to circulate within compartment 35 a number of times dependent upon the flow of the electrolyte solution introduced into compartment 35. As the level rises in compartment 35 the solution flows over partition wall 40 in the circulation section into adjacent compartment 36. The flow occurs in such fashion as wall 40 is of less height than partition 43 in the electrode section but of greater height than open portion 42 of baffle plate 32'. The solution circulates within each compartment and flows successively to adjacent compartments in the same manner until it reaches terminal cathode assembly compartment where, after circulating as in the preceding compartments, it exits from the cell chamber through overflow weir 47. The electrolyte may also be supplied to the space beneath the lowermost electrode by inlet means positioned in the lower ends of the chamber side walls or the bottom wall of the chamber. The materials of construction of the multi-unit cell correspond to those of the single unit cell of FIGS. 1 to 3. The partitions 40 and 43 not included in the single unit cell may be the same as those of the cell wall. The peripheral edges of the electrode assembly are enclosed in the same manner as those of the unit cell assembly. The terminal individual or monopolar electrodes are provided with apertures at one end thereof, the bipolar electrodes of the interposed cells are provided with apertures at their midpoints and all the electrodes supported in assembled form by support means in a similar fashion to the unit cell by threaded bolts and apertured spacers, shims, conductor bars and nuts threadably connected to the ends of the threaded bolts to hold the electrodes in closely spaced assembled form. In both terminal electrode assemblies the support means may be the same materials as in FIGS. 1 to 3. The support means for the bipolar electrode assemblies of the interposed cell units differs from the support means of the terminal assemblies in that spacers 50 are electrically non-conductive material. Supports 45 maintain the electrode assembly in each compartment in spaced position from the bottom wall to permit proper solution flow through the electrode assembly. A base plate 44 is optionally connected to the assembly supports 45 for facilitating positioning of the entire group of electrode assemblies in the cell chamber 9'. The electrodes of the multi-unit cell assembly are prevented from contacting each other and resultant short circuit formation by electrically non-conductive separators of the same type and configuration as those of the unit cell electrode assembly above described.

The bipolar electrodes are generally of unitary electrically conductive base construction, each dimensionally

stable anode portion of the base bearing a solid solution coating which may be one of the above-described solid solution coatings, and the cathode portion being the uncoated electrically conductive metal of the base. The cathode portion in some cases may also be coated in the same manner as the dimensionally stable anode portion.

It will be observed from the above description of the multi-unit cell that hydraulic flow of the solution between the electrode sections of the compartments is prevented by the partitions 43 and the electrode spacers 50 and that only the desired hydraulic solution flow from compartment to compartment is provided in the circulation sections of the compartments by the arrangement of the baffle plate and partition walls 40. Electrical current flow between the circulation sections is substantially prevented by the electrically non-conductive spacers 50 in the interposed bipolar electrode compartments.

In the production of alkali metal hypochlorite aqueous alkali metal halide solution is electrolyzed by a process comprising:

introducing an aqueous alkali metal halide solution into an electrolytic cell chamber having disposed therein at least one assembly of a plurality of substantially parallel flat foraminous dimensionally stable anodes and foraminous cathodes closely spaced, horizontally disposed, alternately arranged in substantially face-to-face relationship, the peripheral edges of the assembly being substantially enclosed, passing a direct current between the electrodes to electrolyze the alkali metal halide solution, whereby the gases evolved cause the solution to flow at an angle of about 90° to the horizontal surfaces of the electrodes, the temperature of the alkali metal halide solution ranging from about 15° C. to about 40° C. and the pH ranging from 6.0 to about 10.0 and recovering alkali metal hypochlorite from the cell chamber.

In another embodiment of the process for making alkali metal hypochlorite an aqueous solution having a concentration of about 25 to about 30 grams per liter of saline solution which may be aqueous sodium chloride or sea water is introduced into the electrolytic chamber, an electrical potential is imposed across the electrodes to electrolyze the saline solution whereby the gases released cause the electrolyte solution to flow upwardly through all the electrodes of the assembly at an angle of about 90° to the horizontal surfaces of the electrodes, the pH ranges from 8.5 to about 9.2 and the temperature ranges from about 20° C. to about 25° C. during electrolysis and sodium hypochlorite is recovered from the cell chamber. In this preferred embodiment the horizontally disposed dimensionally stable anode consists essentially of an expanded mesh titanium metal substrate having a surface coating of a solid solution of mixed crystals of titanium dioxide and ruthenium dioxide and the horizontally disposed foraminous cathode consists essentially of open mesh titanium. The process may be operated either batchwise or continuously by introducing a predetermined quantity of electrolyte into the cell chamber and terminating the cell operation when the decomposition of the electrolyte to the desired quantity hypochlorite product has been completed for batchwise operation, or by continuously introducing electrolyte into the cell chamber and removing the hypochlorite product therefrom continuously for continuous operation.

It has been surprisingly and unexpectedly found that the addition of small amounts of chromium and vanadium to the alkali metal halide electrolyte improves the current efficiency during electrolysis. The addition of chromium and vanadium may be made either by the use of sacrificial anodes appropriately disposed or arranged in the cell or by the addition of chemical agents containing these metals such as sodium chromate and sodium vanadate. It is especially unexpected and surprising that the current effi-

ciency is improved by the addition of very small amounts of chromium and vanadium on the order of from about 100 parts per billion to about 600 parts per billion, preferably about 300 parts per billion, to the alkali metal halide. While the exact function of chromium and vanadium in improving the current efficiency are not completely understood it is believed that the presence of such materials prevents the cathodic decomposition of the hypochlorite. However, it should be realized that the invention is not intended to be restricted by any theory, particularly where such extremely small additions of these chemical agents produce such unexpected and extensive improvements in current efficiency.

The cell is also useful in a process for making alkali metal chlorate which process comprises introducing an aqueous alkali metal halide solution containing 300 g.p.l. NaCl into an electrolytic cell chamber having disposed therein at least one stack of a plurality of flat foraminous dimensionally stable anodes and foraminous cathodes closely spaced, horizontally disposed, alternately arranged in substantially face-to-face relationship, the lateral peripheral edges of the assembly being substantially enclosed imposing an electrical potential across the electrodes to electrolyze the alkali metal halide solution whereby said solution is caused to flow in a direction of about 90° to the horizontal surfaces of said electrodes, while maintaining a temperature of about 60° C. to about 80° C. and a pH of about 6.0 to about 7.5 during the electrolysis, and recovering alkali metal chlorate from the cell chamber. In another preferred embodiment of this process an aqueous solution containing about 315 grams per liter of sodium chloride and about 2.0 grams per liter of sodium dichromate is introduced into the cell chamber for electrolysis and sodium chlorate is the recovered product. The electrodes employed in the preferred embodiment are a horizontally disposed expanded mesh titanium metal substrate having a surface coating of a solid solution of titanium dioxide and ruthenium dioxide, and the cathode is expanded mesh titanium metal. The temperature is maintained at about 60° C. to 70° C. and the pH at about 6.8 to about 7.2.

In order that those skilled in the art may more completely understand the present invention and the manner in which it may be carried into effect, the following specific examples are presented.

The table below illustrates the parameters and resultant products obtained in operating a unit assembly of the type shown in FIGS. 1 to 4 for the production of sodium hypochlorite. The data was obtained from a typical batch run with an initial salt concentration of 30 g.p.l. The temperature ranged between 23° C. to 27° C. with water flowing through cooling coils immersed in the solution.

TABLE I

Example No.	Voltage	Current in amps.	Power in kilowatts hrs/pound of available chlorine	Product in grams/liter available chlorine	Current efficiency
1-----	3.73	1,280	1.470	1.9	86
2-----	3.73	1,280	1.59	3.7	80
3-----	3.73	1,280	1.76	7.1	70
4-----	3.73	1,280	2.27	9.9	56

In the examples of Table II below, which are illustrative of the practice of this invention for production of sodium hypochlorite, three assemblies of the type shown in FIG. 1 were connected in series in a single chamber provided with nonconductive partitions separating each assembly of an electrolytic cell. Aqueous sodium chloride solution containing about 30 g./l. of sodium chloride was continuously introduced into the chamber by charging a predetermined amount of tap water and saturated brine solution into the chamber in separate streams. The aqueous sodium chloride solution was continuously electrolyzed to form sodium hypochlorite by passing a direct current from the anodes to the cathodes. The temperature

of the chloride electrolyte ranged between about 15° C. to about 28° C. with water flowing through a set of electrically insulated cooling coils immersed in the chloride solution. The significant parameters of the process are presented below in tabular form.

TABLE II

Example No.	Voltage	Current in amperes	Power in kilowatt hrs./lb. of available chlorine	Saturated brine flow gals./minute	Tap water flow gals./min.	Product in grams/liter available chlorine	Current efficiency, percent
5-----	11.71	2,500	2.3	0.255	2.4	9.34	57
6-----	11.93	3,000	2.2	0.41	3.1	9.56	63
7-----	11.53	2,000	2.0	0.34	3.25	6.6	66

The examples included in Table III below show the results obtained by use of the process of this invention for the preparation of sodium chlorate. About 175 liters of saturated brine solution containing about 300 g./l. of sodium chloride and about 2.0 g./l. sodium dichromate were placed in a cell chamber containing a single assembly of electrodes shown in the attached drawings FIGS. 1 to 4. A potential was imposed between the electrodes and the cell operated batchwise in electrolyzing the brine solution for the time and at the parameters shown in the table.

TABLE III

Example No.	Current density, SAI	Duration of run, hours	Final sodium chlorate concentration, g./l.	Voltage, buss to buss	Temp., °C.	Current efficiency, percent	kWh./ton of chlorate direct current
8-----	2	2	40	3.77	58	92.6	5,580
9-----	2	2.5	203	3.88	47	88	6,050
10-----	1	1.5	185	3.33	47	94.0	4,860

Some of the advantages provided by the practice of the present invention are:

- (1) products such as sodium hypochlorite and sodium chlorate are quickly and efficiently produced by rapid reaction of the products formed at the anodes and cathodes due to the close proximity of the electrodes and rapid mixing of said intermediate products,
- (2) the attainable close-spacing of the electrodes provides a minimum anode-cathode electrical current path which results in low cell voltage, high current and high power requirement efficiencies, and
- (3) the foraminous electrodes permit rapid flow of solution through the electrode assembly which reduces gas blanket formation and product concentration polarization of the electrodes.

I claim:

1. A process for the electrolysis of a solution that releases at least one gaseous product at an electrode surface on the application of an electrolyzing current, which process consists essentially of:

- (a) providing an electrolytic cell including side, end, and bottom walls and having disposed therein at least one assembly consisting essentially of a plurality of parallel, horizontally disposed, foraminous, dimensionally stable anodes and a like number of parallel, horizontally disposed, foraminous, dimensionally stable cathodes, said anodes and cathodes being interleaved in an alternate, face-to-face, spaced apart arrangement, said assembly being substantially enclosed on four sides;
- (b) providing a solution that releases at least one gaseous product at an electrode surface upon electrolysis to said assembly from a point immediately subjacent the lower most electrode;
- (c) passing a direct, electrolyzing current between said anodes and cathodes;
- (d) causing said solution to flow upwardly through and at about a 90° angle to said foraminous electrodes by the lift effect of the gas generated on electrolysis.

2. A process for the electrolysis of an alkali metal chloride, which process comprises:

- (a) providing an electrolytic cell including side, end, and bottom walls and having disposed therein at least one assembly consisting essentially of a plu-

rality of parallel, horizontally disposed, foraminous, dimensionally stable anodes and a like number of parallel, horizontally disposed, foraminous, dimensionally stable cathodes, said anodes and cathodes being interleaved in an alternate, face-to-face, spaced apart arrangement, said assembly being substantially enclosed on four sides;

- (b) providing an aqueous alkali metal chloride solution to said assembly from a point immediately subjacent the lower most electrode;
- (c) passing a direct, electrolyzing current between said anodes and cathodes;

(d) causing said solution to flow upwardly through and at about a 90° angle to said foraminous electrodes by the lift effect of the gases generated on electrolysis.

3. A process as in claim 2 wherein the solution is maintained at a temperature within the range of 15° to 40° C. and a pH of from 6.0 to 10 and the product is alkali metal hypochlorite.

4. A process as in claim 3 wherein the solution contains from about 25 to 30 grams per liter alkali metal chloride.

5. A process as in claim 2 wherein the temperature is maintained within the range of 40° to 80° C., the pH within the range of 6.0 to 7.5, the alkali metal chloride concentration between about 300 and 315 grams per liter and the product is alkali metal chlorate.

References Cited

UNITED STATES PATENTS

827,721	8/1906	Gibbs	204—95
2,873,236	2/1959	Ferris	204—95
3,219,563	11/1965	Collins et al.	204—95
3,390,065	6/1968	Cooper	204—95
3,516,918	6/1970	Grotheer et al.	204—95
3,535,216	10/1970	Grotheer et al.	204—95
3,562,008	2/1971	Martinsons	204—290 F X
3,657,099	4/1972	Seko et al.	204—253
3,668,005	6/1972	Rixensart et al.	204—290 F X
3,539,486	11/1970	Fleck	204—95
3,598,715	8/1971	Goens et al.	204—95 X
3,640,804	2/1972	Westerlund	204—95

FOREIGN PATENTS

509,666	11/1920	France	204—95
754,132	3/1967	Canada	204—95

FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.