

[54] **MERCURY DIAPHRAGM CHLOR-ALKALI CELL AND PROCESS FOR DECOMPOSING ALKALI METAL HALIDES**

2,967,807 1/1961 Osborne et al. 204/266
2,967,806 1/1961 Osborne et al. 204/266
3,438,879 4/1969 Kircher et al. 204/296

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[51] Int. Cl. C01d 1/06, C01b 7/06

[58] Field of Search 204/266, 128, 98, 204/296

[56] **References Cited**

UNITED STATES PATENTS

3,220,941 11/1965 Osborne 204/266

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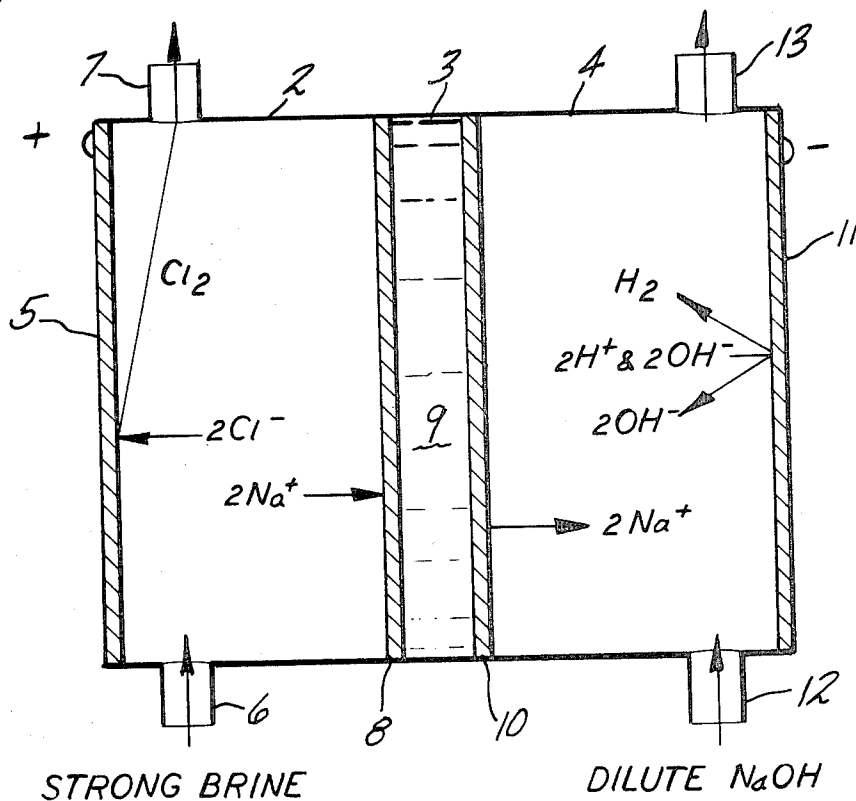
[57] **ABSTRACT**

An electrolytic cell for electrolysis of alkali metal halides having a diaphragm structure comprising cation permeable diaphragms enclosing an immobilized continuous phase of liquid alkali metal amalgam.

11 Claims, 4 Drawing Figures

Cl_2 & SPENT BRINE

CONCENTRATED $NaOH + H_2$



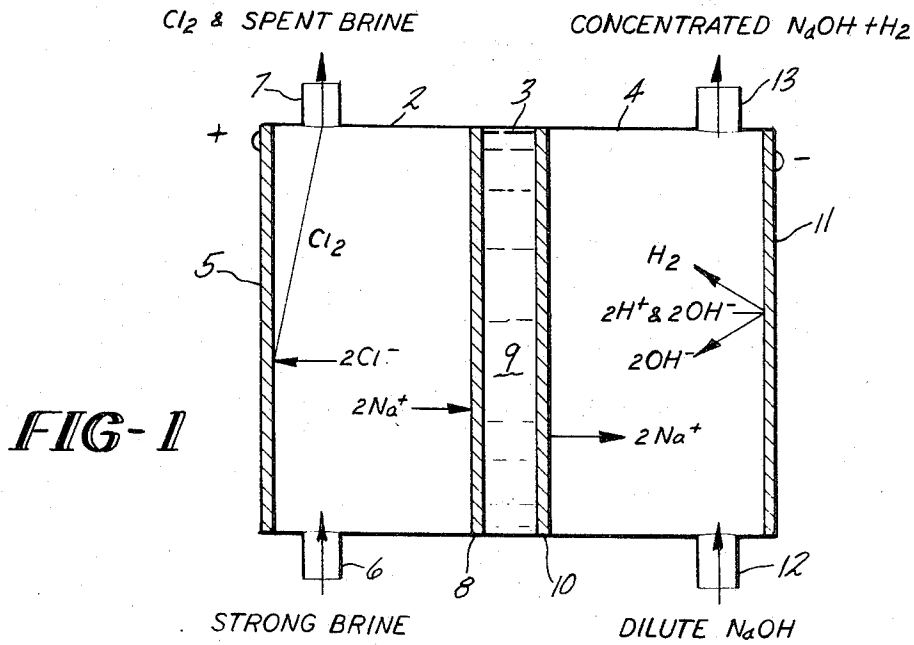
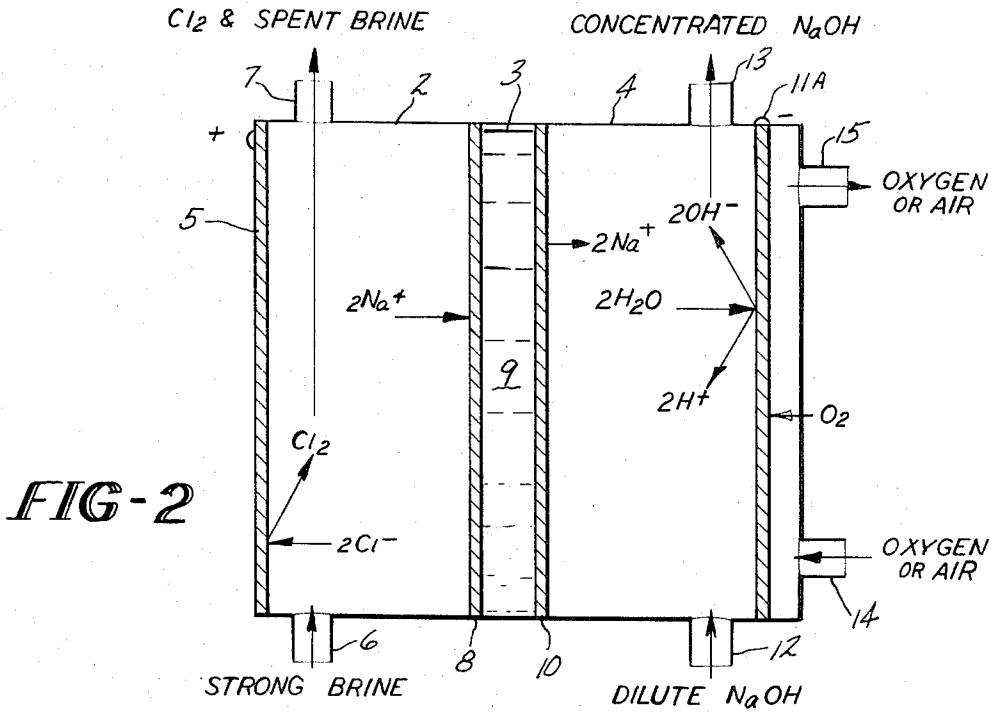


FIG-3

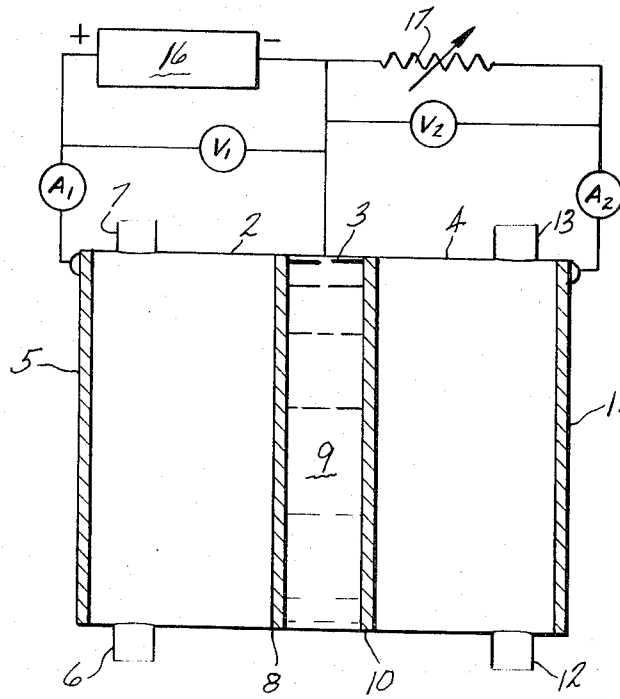
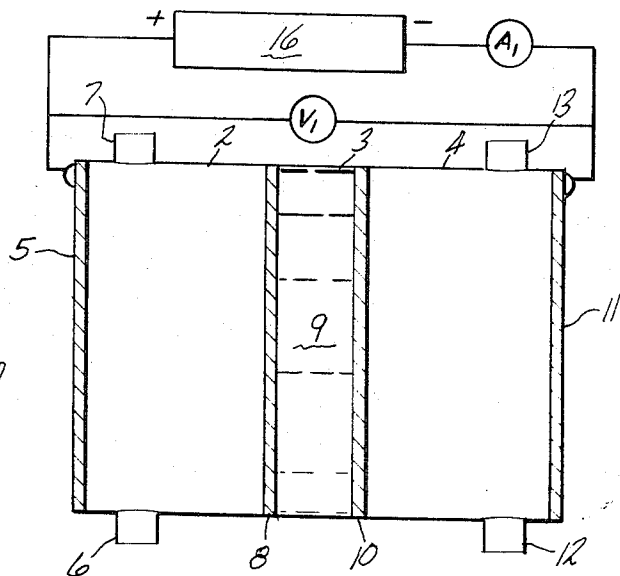


FIG-4



MERCURY DIAPHRAGM CHLOR-ALKALI CELL AND PROCESS FOR DECOMPOSING ALKALI METAL HALIDES

This invention relates to an electrolyzing process for cheaply and efficiently producing a halogen gas, hydrogen and an alkali metal hydroxide solution of high concentration containing substantially no alkali metal halide by electrolysis of an alkali metal chloride or bromide solution. More particularly, a concentrated alkali metal hydroxide solution is produced by electrolyzing an alkali metal chloride solution using an improved diaphragm cell in which cation permeable diaphragms enclose an immobilized continuous phase of liquid alkali metal amalgam between an anode compartment and a cathode compartment.

The mercury cathode cell process is well known in the electrolysis of an alkali metal halide. However, the high theoretical electrolysis voltage of the mercury cathode cell effects a high cost of electric power per unit weight of the products.

Known diaphragm cell processes operate at lower cell voltages but have the disadvantage that the alkali metal hydroxide produced contains considerable amounts of alkali metal chloride. The cost of equipment and processing required to concentrate the dilute alkali metal hydroxide solution and separate the alkali metal chloride increases the cost of production and offsets the economic advantage of the lower cell voltage of the diaphragm cells.

Operation of the mercury cathode cell process in conjunction with the diaphragm cell process, has been disclosed, for example, in U.S. Pat. Nos. 3,321,388 and 3,051,637. This combination results in the necessity for large capital investments and extensive space requirements, but does not completely eliminate the disadvantages mentioned above.

Alkali metal halide brines have been electrolyzed in diaphragm cells having cation permeable diaphragms enclosing a compartment containing a solution of an alkali metal salt or water containing a gas such as CO₂. See U.S. Pat. Nos. 2,967,807; 3,220,941 and 3,438,879. Unwanted leakage or transfer of solutions from the cathode compartment back to the center compartment and from the center compartment back to the anode compartment occurs in these cells. This results in the loss of alkali metal ions in the formation of undesirable reaction products.

British Patent 16,048 of Oct. 23, 1913 discloses a porous diaphragm composed of, for example, pumice, charcoal or manganese dioxide containing a mercuric salt which is chemically reduced to metallic mercury and retained in the diaphragm along with an oxidizing agent to absorb or react with hydrogen formed. Sodium chloride brine is electrolyzed in both the anode and cathode compartments.

Alkali metal hydroxide is not formed in this cell which employs diaphragm materials of limited conductivity and contaminates the mercury with oxidizing agents.

The novel cell and process of the present invention is characterized by an improved amalgam diaphragm cell for the electrolytic decomposition of aqueous alkali metal halides having an anode compartment with an anode, anolyte inlet means and outlet means for anolyte and chlorine gas, and a cathode compartment having a cathode, catholyte inlet means and outlet means for aqueous alkali metal hydroxide and hydro-

gen gas, and a diaphragm structure separating said anode compartment from said cathode compartment. The improved diaphragm structure has cation permeable diaphragms enclosing an immobilized, continuous phase of liquid alkali metal amalgam.

The cell of the present invention eliminates the defects of the conventional diaphragm and mercury cathode cells while retaining their advantages. These advantages are: the alkali metal hydroxide contains no alkali metal chloride, concentrated alkali metal hydroxide is obtained directly from the cell, the decomposition voltage is low, small amounts of mercury are required and mercury losses are greatly reduced.

The cell of the present invention employs cation permeable diaphragms enclosing an immobilized continuous phase of liquid alkali metal amalgam uncontaminated by oxidizing or absorption agents. Dilute alkali metal hydroxide or water is used in the cathode compartment so that hydrogen is discharged at the cathode and not within or at the diaphragm. Therefore, hydrogen does not build up in the amalgam or at the cation permeable diaphragms. In addition, concentrated alkali metal hydroxide is formed in the cathode compartment.

The cation permeable diaphragms enclosing an immobilized continuous liquid phase of alkali metal amalgam of the cell of this invention prevent solutions leaking from the anode or cathode compartments and prevent the back migration of ions. Alkali metal ions are effectively transferred to the cathode compartment for use in the desired end product.

The cation permeable diaphragms employed in the electrolytic cells of the present invention are suitably constructed using ion exchange resins which have been formed into continuous thin sheets. When a cation active ion exchange resin is employed a cation permeable membrane is produced, i.e., one which selectively permits passage of cations through its structure from one compartment of the cell to the next adjacent compartment in the direction toward the cathode under the influence of an impressed voltage and when wet with electrolyte. Suitable diaphragms for use in the cells of this invention are constructed using cation exchange resins of the "Amberlite" type formed into continuous sheets as described in U.S. Pat. Nos. 2,681,319 and 2,681,320. Such sheets are continuous, nonporous, self-supporting, pliable, permselective membranes or pellicles which comprise a matrix of any suitable material which is chemically resistant to chlorine and caustic soda and which is not wettable by mercury. Suitable matrix materials include asbestos, glass fibers, polymeric resins, for example, polystyrene sulfonic acid, polyfluoroalkylene sulfonic acid, vulcanized natural or synthetic rubber, polyethylene, polypropylene, polyisobutylene, polytetrafluoroethylene, polyvinyl chloride and copolymers of vinyl chloride with vinyl esters of lower aliphatic acids. Distributed intimately and uniformly in the matrix are particles of an insoluble, infusible ion exchange resin. Cation-exchange resin particles are of such size as to pass through a United States Standard sieve No. 50 and are present in the diaphragm in an amount equal to 25 percent to 75 percent of the total weight of said diaphragm. The efficiency attainable in using such diaphragms in electrolysis is in part a function of its porosity, or the number of macropores or leakage points occurring between the resin particles in the sheet or fiber.

The cation permeable diaphragms of this invention may be made in a number of different ways, depending on the geometric design of the cell itself. One method is to use two sheets of membrane made in accordance with U.S. Pat. No. 2,681,319 or U.S. Pat. No. 2,681,320, separated by a gasket-type spacer having the inlets and outlets to the resulting compartment positioned either in the spacer or through the membranes. In another method a continuous envelope is formed from the said Amberlite type cation permeable diaphragm, allowing a space between the folded sheets to form the amalgam-containing structure. When the cell design is such as to require large sheet-like cation permeable diaphragms to be spaced from each other by a gasket-type spacer, it is desirable to reinforce at least one of the diaphragms by placing a grid against the face of the diaphragm in order to prevent buckling. The grid may consist of a rigid screen or similar type structure of suitable material of construction disposed across the entire surface of the diaphragm.

Cation permeable diaphragms also suitable for use in this invention include those microporous metals which are wettable by mercury. Microporous diaphragms of iron, nickel and copper and their alloys are suitably used. Particularly suitable are those of nickel and iron. Porous metal diaphragms are available with a wide range of pore sizes, for example, from 22 to 1,220 microns. A preferred pore size range for microporous metal diaphragms used in this invention is 50 to 200 microns.

Alkali metal amalgams enclosed by the cation permeable diaphragms employed in the cells of this invention consist of mercury containing from about 0.005 to 0.5 weight percent of the alkali metal employed. Preferably the amalgam should contain from about 0.1 to about 0.3 weight percent of alkali metal. While the use of sodium amalgam is preferred in the cell of this invention, amalgams of potassium and lithium, for example, are also suitable.

Suitable electrodes for use in this invention are composed of graphite or metal, for example, nickel, zirconium, tungsten or titanium electrodes having a thin coating over at least part of their surface of a platinum group metal or oxide thereof. The term "platinum group metal" as used in this specification means an element of the group consisting of ruthenium, rhodium, palladium, osmium, iridium and platinum and alloys thereof. The term "titanium" includes alloys consisting essentially of titanium. These coated electrodes have the advantage of substantially complete resistance to corrosion. The electrodes are suitable made in various forms, for example, a plate, screen or perforated plate.

Use of oxygen or oxygen-containing gases as depolarizing agents for the cathode in electrolytic cells for producing halogens has been described, for example, in U.S. Pat. Nos. 3,481,487 and 3,291,708. This known method of depolarization is also useful in the cell of the present invention.

An oxygen-depolarized cathode, a microporous catalyzed body formed of suitable materials such as microporous graphite having distributed therein a catalytic metal or porous form of corrosion-resistant metal can be employed. Suitable metals include, for example, silver, gold or other noble metals including platinum and mixtures thereof, or a sintered microporous mat or grid of silver, gold, platinum, iridium among others, alone, or coated upon a metal such as titanium, colum-

bium, tantalum, and the like. These porous metal cathodes are suitable formed by pressing or sintering the powdered metals or by other known means.

The alkali metal halide brines electrolyzed in the cell of the present invention include especially those of sodium, potassium and lithium. However, the present invention is equally applicable to other alkali metal chlorides and bromides.

While dilute alkali metal hydroxides are preferred for introduction into the cathode compartment to form concentrated alkali metal hydroxide, water is also suitably used. Inorganic compounds, for example, carbon dioxide or sulfur dioxide which are capable of reacting with the migrating alkali metal ions are suitably introduced into the aqueous catholyte.

In the process employing the cell of the present invention, an aqueous solution of an alkali metal chloride is electrolyzed in an anode compartment containing an anode, an anolyte inlet and an outlet for anolyte and chlorine gas produced at the anode. In the cathode compartment, containing a cathode, a catholyte inlet and an outlet for catholyte and hydrogen, water is electrolyzed to produce hydrogen gas. Alkali metal cations are transferred from the anode compartment to the cathode through the cation permeable diaphragms, and through the alkali metal amalgam under the influence of the decomposition voltage across the electrodes of the cell.

Accompanying FIGS. 1-4 illustrate the invention. Corresponding parts bear the same numbers in all FIGURES.

FIG. 1 represents an electrolytic cell of this invention which comprises an anode compartment 2, a diaphragm structure 3, and a cathode compartment 4. Anode compartment 2 contains an anode 5 and is filled with a concentrated solution of alkali metal chloride brine. Also contained in the anode compartment are a brine inlet 6 and outlet 7 for depleted brine and chlorine gas. Diaphragm structure 3 comprises cation permeable diaphragms 8 and 10 enclosing an immobilized continuous phase of liquid sodium amalgam 9. Cathode compartment 4 contains cathode 11 and is filled with dilute alkali metal hydroxide which enters the compartment thru inlet 12. Also included in cathode compartment 4 is outlet 13 for concentrated alkali metal hydroxide and hydrogen gas.

In accordance with this invention, a saturated solution of alkali metal chloride brine is fed into the anode compartment 2 through brine inlet 6. Anode 5 and cathode 11 are supplied with electric current at a suitable potential. Brine is electrolyzed in anode compartment 2 forming chlorine gas which is removed with the depleted brine through outlet 7. Alkali metal ions pass through cation permeable diaphragm 8 into an immobilized continuous phase of liquid sodium amalgam 9. Sodium ions pass thru cation permeable diaphragms 10 into cathode compartment 4. Alkali metal ion transfer is caused by the voltage gradient and the rate is influenced by their concentration. At cathode 11, water forms hydroxyl ions and hydrogen gas. Concentrated alkali metal hydroxide and hydrogen gas are removed thru outlet 13.

FIG. 2 represents an oxygen depolarized cell of the invention. Cathode compartment 4 contains porous cathode 11A and an inlet 14 and an outlet 15 for oxygen or air which converts the discharged hydrogen to water. This reduces the overall cell voltage of the oper-

ating cell and results in lower power requirements per ton of product.

FIGS. 3 and 4 represent electrical circuits for operating the cell of the present invention, wherein 16 is a source of direct current, 17 is a variable resistance, A_1 and A_2 are a first and second ammeter and V_1 and V_2 are a first and second voltmeter.

EXAMPLE I

A cell was constructed as shown in FIG. 3. A saturated sodium chloride brine was fed into anode compartment 2 thru inlet 6. Anode 5 and cathode 11 were supplied with a suitable potential to electrolyze the brine, forming chlorine gas and sodium ions in the anode compartment. Chlorine gas and depleted brine were removed thru outlet 7. Sodium ions were transferred via cation permeable diaphragm 8, the immobilized continuous phase of liquid sodium amalgam 9 and the cation permeable diaphragm 10 into cathode compartment 4.

Nickel fiber metal membranes were employed as cation permeable diaphragms 8 and 10. A circuit containing rectifier 16, voltmeter V_1 and ammeter A_1 was connected between graphite anode 5 and sodium amalgam 9 to establish a mercury cell containing an immobilized continuous phase of liquid sodium amalgam. Sodium amalgam 9 and graphite cathode 11 were connected in a circuit containing resistor 17, voltmeter V_2 and ammeter A_2 . As the resistance was reduced, current flowed in this circuit indicating a potential between the immobilized continuous phase of liquid sodium amalgam and cathode 11. The following data were obtained.

V_1 (volts)	A_1 (milli-amps)	Resistance (17) (ohms)	V_2 (volts)	A_2 (milli-amps)
3	1500	500	0.94	1.8
3	1500	250	0.90	3.2
3	1500	100	0.87	7.2

Chlorine was produced at the anode and hydrogen at the cathode.

EXAMPLE II

Example I was repeated using the cell illustrated in FIG. 3 and employing polystyrene sulfonic acid cation permeable diaphragms 8 and 10. Application of a current of 1,000 milliamps (A_1) with a voltage of 4.6 (V_1) produced a current of 180 milliamps (A_2) and a voltage of 0.4 (V_2). Chlorine was produced at the anode and hydrogen at the cathode.

EXAMPLE III

A cell was constructed as shown in FIG. 4 employing polystyrene sulfonic acid cation permeable diaphragms 8 and 10. Current flow was 5.0 amps at 12.5 volts. Chlorine and hydrogen were generated at the anode and cathode respectively. A current density of 1.44 kiloamps per sq. meter, based on the area of cation permeable diaphragms, was sustained.

EXAMPLE IV

Example III was repeated using polypropylene mesh cation permeable diaphragms 8 and 10. Results for cell amperage and cell voltage measurements were as follows:

Amps.

Volts

1.0
2.0
3.0

7.4
10.4
13.8

Chlorine and hydrogen were generated at the anode and cathode respectively.

What is claimed is:

1. In a cell for the electrolytic decomposition of an alkali metal chloride or bromide, said cell having an anode compartment with an anode, anolyte inlet means and outlet means for anolyte and halogen gas and a cathode compartment having a cathode, catholyte inlet means and outlet means for aqueous alkali metal hydroxide and hydrogen gas and a diaphragm structure separating said anode compartment and said cathode compartment, the improved diaphragm structure having cation permeable diaphragms enclosing an immobilized continuous phase of liquid alkali metal amalgam.

2. The cell as claimed in claim 1 in which said diaphragms are polymeric resins.

3. The cell as claimed in claim 2 in which said polymeric resin is selected from the group consisting of polyethylene, polytetrafluoroethylene, polypropylene, polyisobutylene, vulcanized natural and synthetic rubber, polystyrene sulfonic acid, polyfluoroalkylene sulfonic acid, polyvinyl chloride and copolymers of vinyl chloride and vinyl esters of lower fatty acids.

4. The cell as claimed in claim 3 in which said polymeric resin contains particles of an ion-exchange resin dispersed throughout said resin, said particles being of such size as to pass through a U.S. Standard sieve size No. 50 and being present in said diaphragm in an amount equal to 25 percent to 75 percent of the total weight of said diaphragm.

5. The cell as claimed in claim 1 in which said diaphragm structure has two spaced-apart cation permeable polymeric resin diaphragms enclosing said immobilized continuous phase of liquid alkali metal amalgam.

6. The cell as claimed in claim 1 in which said diaphragm structure is a microporous metal selected from the group consisting of iron, nickel, titanium and copper.

7. The cell as claimed in claim 6 in which said microporous metal has pore sizes between 50 and 200 microns.

8. The cell as claimed in claim 1 having in combination means for contacting said cathode with an oxygen-bearing gas.

9. In a process for electrolytic decomposition of an aqueous alkali metal halide selected from the group consisting of chloride and bromide to form alkali metal hydroxide, hydrogen and halogen gas, wherein an electric current is passed between an anode immersed in an anolyte of said halide and a cathode immersed in a catholyte of said hydroxide, said anolyte and said catholyte being separately maintained, the improvement of electrically connecting said anolyte and said catholyte through an immobilized continuous phase of liquid alkali metal amalgam enclosed between cation permeable diaphragms.

10. The process as claimed in claim 9 in which said alkali metal is sodium.

11. The process as claimed in claim 9 in which said alkali metal halide is chloride.

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