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GB 1495044
GB 1406395
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(54) Electrolytic Cell and Electrolytic Process of an Aqueous Alkali Metal Halide Solution

(57) A finger type electrolytic cell is provided positioning a cation exchange membrane 3 between cathodes and expandable dimensionally stable anodes 2 wherein spacers 4 are interposed between the opposite sides of the anodes so as to maintain the uniform anode-cathode spacing. Also disclosed is an electrolytic process of an aqueous alkali metal halide solution effecting the electrolysis while exerting the pressure on a cathode compartment using the electrolytic cell.

The invention enables the electrolysis at a low and stable cell voltage.

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

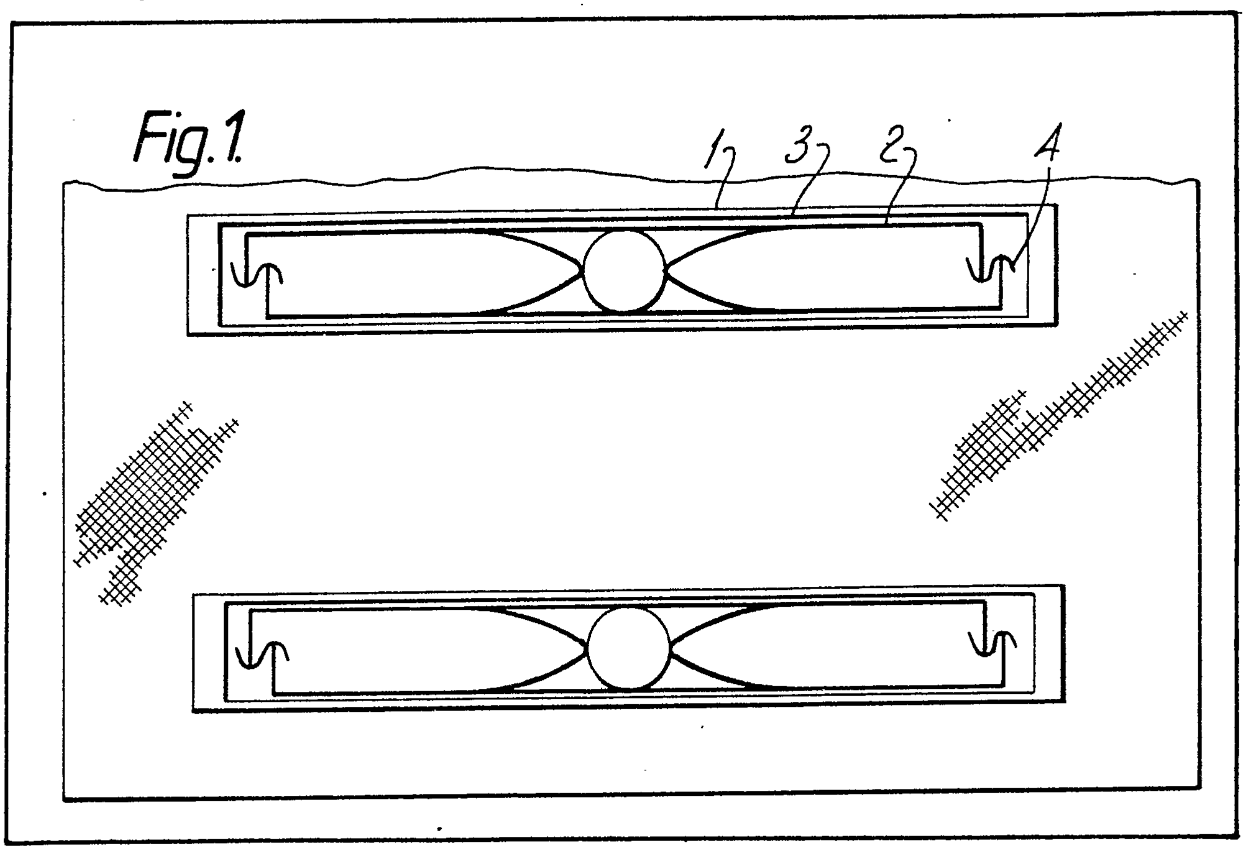

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Fig.1.

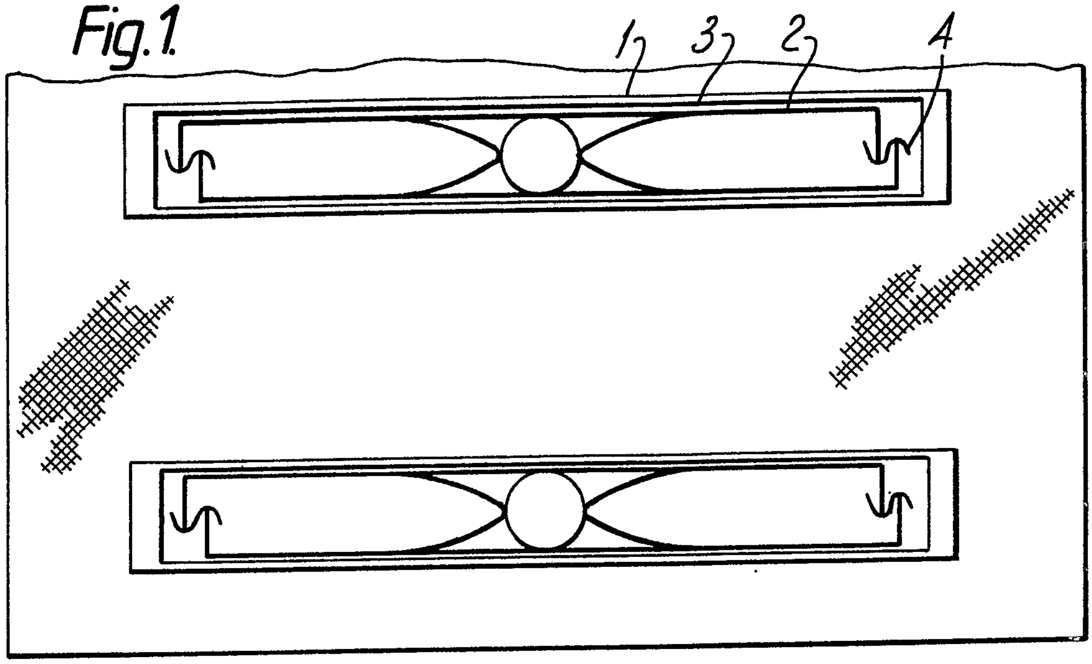


Fig. 2.

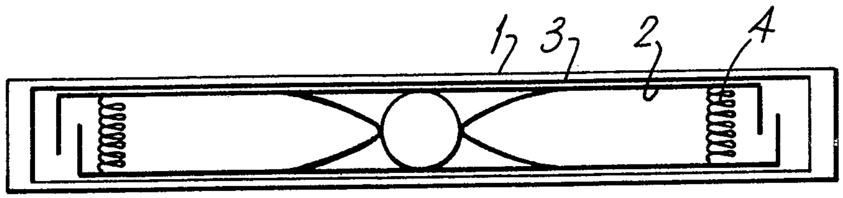


Fig. 3.

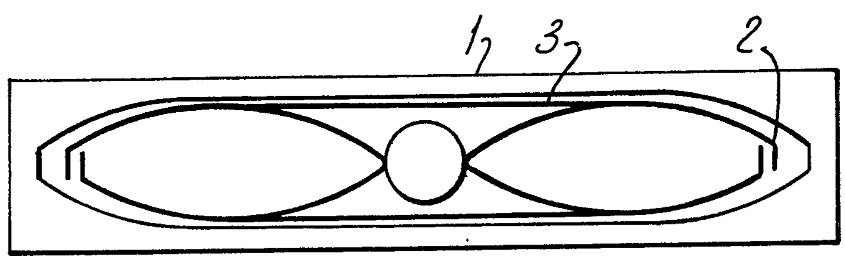
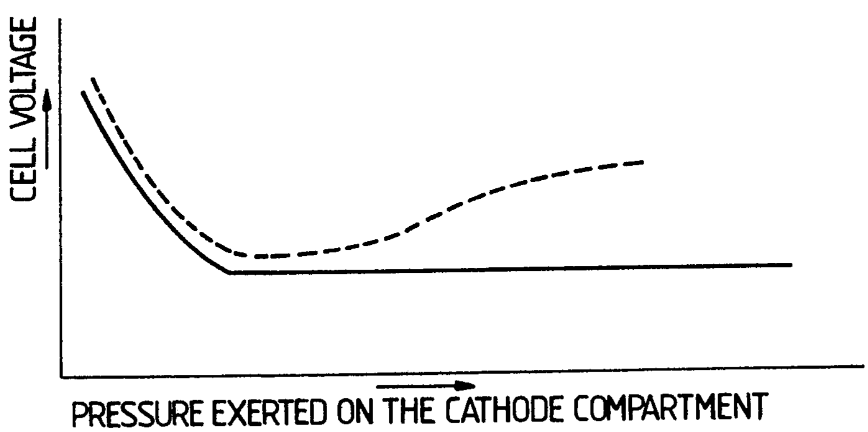


Fig. 4.



SPECIFICATION

Electrolytic Cell and Electrolytic Process of an Aqueous Alkali Metal Halide Solution

The present invention relates to an electrolytic cell and electrolytic process of an aqueous alkali metal halide solution using a cation exchange membrane. More specifically, it relates to a finger type electrolytic cell providing a cation exchange membrane between cathodes and expandable dimensionally stable anodes in which the spacers are placed between the opposite sides of the anodes so as to hold the uniform anode-cathode spacing, and an electrolytic process of an aqueous alkali metal halide solution carrying out the electrolysis while exerting the pressure on a cathode compartment using said cell.

Halogen, hydrogen and an alkali metal hydroxide have been commercially produced by a mercury process and diaphragm process. The mercury process, however, has a risk of environmental contamination due to loss of mercury and thus the operational efficiency is decreasing year by year.

A diaphragm process, on the other hand, normally employes a liquid transferable diaphragm usually comprising asbestos by which an electrolytic cell is partitioned into an anode compartment and a cathode compartment. The anode compartment and the cathode compartment have a plurality of anodes and cathodes, respectively.

In operating the diaphragm process, brine is introduced into the anode compartment where halogen gas is generated, then brine is passed through the diaphragm into the cathode compartment where an alkali metal hydroxide is produced. The alkali metal hydroxide so obtained contains a large amount of an alkali metal halide and thus its utilization is limited.

Recently, a selective permeable cation exchange membrane has been proposed in place of a diaphragm which has normally been employed. Such a membrane permits passage of ion but hardly permits passage of a hydraulic flow.

In operation of the ion exchange membrane process, brine is charged into an anode compartment in which halogen is generated. An alkali metallic ion is then passed through the membrane and transported selectively into a cathode compartment. The alkali metallic ion reacts with hydroxyl ion generated by electrolysis of water to produce an alkali metal hydroxide.

Ion exchange membrane electrolytic processes have an advantage capable of producing an alkali metal hydroxide with a relatively high purity and high concentration as compared with conventional diaphragm processes. As an electrolytic cell for effecting ion exchange membrane electrolysis, a filter-press type electrolytic cell is well-known to the arts.

Ion exchange membrane electrolytic processes are normally carried out maintaining a certain distance between electrodes and a cation exchange membrane. Various devices have been focused on the distance between the electrodes and the cation exchange membrane or the uniform spacing between electrodes, since the absence of such uniform spacing increases cell voltage. Efforts have also been made to improve finishing of the surface of the electrodes, thus resulting in high cost of an electrolytic cell. The processes for eliminating the drawbacks of high cell voltage and high content of an alkali metal halide in an alkali metal hydroxide attendant on the conventional ion exchange membrane electrolytic process have been studied and proposed by some of the present inventors in for example, Japanese Patent Publication (non-examined) No. 47,877/1979 which is capable of holding low cell voltage by bringing an anode and a cathode into contact with a cation exchange membrane. This process is applied to a variety of electrolytic cells, but, in particular, suitable for electrolytic cells which are known as finger type electrolytic cells. In the process, an expandable dimensionally stable anode may also be used. This anode possesses a function of expanding by force of a spring and enables moderate contact of the anode and the cathode with the cation exchange membrane by the adjustment of expanding force of the spring.

A finger type electrolytic cell used in the present invention includes not only a finger type construction cell such as that described at page 93, *Chlorine — Its Manufacture, Properties and Uses,* edited by J. S. Scone, issued by Reinhold Publishing Corporation, New York, 1962, incorporated herein by reference, but also a flattened tube type construction. Nowadays, a flattened tube type construction cell is also generally referred to as a finger type electrolytic cell.

In the electrolytic process using a cation exchange membrane, it is disclosed in, for example, Japanese Patent Publication (non-examined) No. 109,899/1975 that pressure is exerted on a cathode compartment to contact the membrane with an anode under which condition the electrolysis is operated.

However, when electrolysis is effected by a finger type electrolytic cell providing a cation exchange membrane between a cathode fixed and an expandable dimensionally stable anode, in which a cathode compartment is under an increased pressure, there arises a disadvantage that the anode-cathode spacing is variable according to pressure exerted, thus to result in changes in cell voltage. In Fig. 4 a broken line shows the change in cell voltage to the pressure exerted on the cathode compartment. This is because the anode-cathode spacing expands as it goes near both end portions of the expandable dimensionally stable anode, thus to change an average anode-cathode spacing, as illustrated in Fig. 3 showing the anode-cathode spacing and the position of the cation exchange membrane, since the cation exchange membrane is pushed against the anode with an increase in the pressure exerted on the cathode compartment.

An object of the present invention is to provide an electrolytic cell and electrolytic process for the production of halogen, hydrogen and an aqueous alkali metal hydroxide liquor by electrolysis of an aqueous alkali metal halide solution at low cell voltage.

Another object of the present invention is to provide an electrolytic cell and electrolytic process which comprises maintaining the uniform spacing so as to position the anode and the cathode immediately adjacent to the membrane.

The present inventors have found after a series of studies that the foregoing objects are achieved by the present invention.

That is, the present invention is to provide a finger type electrolytic-cell for the production of halogen, hydrogen and an aqueous alkali metal hydroxide liquor by electrolysis of an aqueous alkali metal halide solution which cell comprises a plurality of expandable dimensionally stable anodes and a cathode box providing a cathode between adjacent anodes, and a cation exchange membrane between adjacent anodes and cathodes, wherein spacers are interposed between the opposite sides of the anodes so as to maintain the uniform anode-cathode spacing.

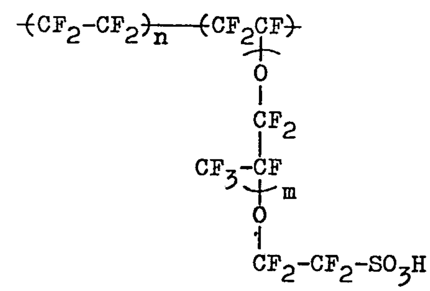
Fig. 1 or Fig. 2 is a horizontal sectional view of an embodiment illustrating the present invention.

That is, on or along the vertical surface of a cathode 1 a cation exchange membrane 3 is positioned, then an expandable dimensionally stable anode 2 is located in the inside of the membrane 3. Between the opposite sides of the expandable dimensionally stable anode 2 spacers 4 are interposed to fix and maintain the uniform anode-cathode spacing. The positioning of the cation exchange membrane on the finger type electrolytic cell is readily effected in such a manner as disclosed in, for example, Japanese Utility model publication (non-examined) Nos. 100,952/1979 and 26,015/1980 that a cation exchange membrane cylindrically formed in secured using a membrane installation frame to a finger type electrolytic cell by bolts or clips.

A spacer used in the present invention may be of any shape, if only fixing and maintaining the anode-cathode spacing not so as to expand beyond the desired spacing, i.e., not so as to shrink the distance between the opposite sides of the expandable dimensionally stable anode. A spacer possessing elasticity, for example, a spring may also be used. As exhibited in Fig. 1, a S-shaped spacer having elasticity may be also used which supports both ends of the opposite sides of the anode. Two or more springs having a suitable length may be also used, as illustrated in Fig. 2, between the opposite sides of the anode. A plate type spacer may also be interposed between the opposite sides of the anode.

The spacer material used suitably in the present invention is one whose surface or entirety is resistant to halogen, including, for example, an erosion-resistant plastic such as heat-resistant vinyl chloride resin, a fluorinated polymer such as tetrafluoroethylene polymer, an erosion-resistant metal such as titanium, and the like.

The cation exchange membrane used in the present invention includes a fluorinated polymer membrane having cation exchange groups, an example of which is a perfluorosulfonic acid perfluorohydrocarbon polymer membrane, sold by E. I. Du Pont de Nemours & Company under the trademark "Nafion". The perfluorosulfonic acid perfluorohydrocarbon used in the examples that follow has the following structure:



in which the concentraion of exchange groups is described as about 1,100 to 1,500 g of dry membrane per an equivalent of SO_3^- exchange groups. Moreover, such cation exchange membranes may also be employed as having weak acid groups of carboxylic acid, phosophoric acid and the like, singly or in combination of sulfonic acid group.

The cathode material used suitably in the present invention is an electroconductive material resistant to catholyte such as ion, steel, nickel or an alloy thereof. The shape of the cathode is, for example, an expanded metal mesh, a metal plate having perforations or slits, rods or the like.

The anode material used suitably in the present invention is an anolyte-resistant valve metal such as titanium, tantalum, zirconium, tungsten or the like. A valve metal serving as the anode includes platinum group metals, mixed oxides of valve metals and platinum group metals or the like. The anode may be in various shapes such as an expanded metal mesh, a metal plate having perforations or slits, rods or the like.

When the aqueous alkali metal chloride solution is electrolysed using the finger type electrolytic cell of the present invention, brine is supplied continuously into an anode compartment providing expandable dimensionally stable anodes, between the opposite sides of which spacers are interposed, where chlorine gas and sodium ion (Na^+) are generated. Chlorine gas so prepared is discharged with suction from the cell under the negative pressure of 10 to 100 mm H_2O to atmosphere pressure. The depleted brine is discharged by overflowing from the cell.

Sodium ion passes through the membrane into a cathode compartment where it reacts with the hydroxyl ion generated in the cathode compartment to produce sodium hydroxide. The obtained sodium hydroxide is diluted with water added into the cathode compartment to give an aqueous sodium hydroxide liquor having 10 to

40% concentration, then discharged from the cell. Hydrogen gas generated in the cathode compartment is discharged from the cell while the pressure being exerted in the range of 20 to 200 mm H_2O, preferably 50 to 150 mm H_2O to atmospheric pressure controlled by the increased pressure by a water seal pot or suction by a blower compressor.

On the cathode compartment the pressure is exerted by hydrogen gas and the exerted pressure is transported through the membrane to the expandable dimensionally stable anode. The expandable dimensionally stable anode, nevertheless, is not shrinked by spacers positioned between the opposite sides of the anode and hence the uniform anode-cathode spacing is maintained. Accordingly, the electrolysis is effected in a state that the respective surfaces of both the anode and the cathode are in intimate contact with the cation exchange membrane.

In Fig. 4 a solid line shows the relationship between the pressure exerted on the cathode compartment and cell voltage in the electrolytic process of the present invention. It is understood that substantially constant cell voltage is maintained, even where the cathode compartment in under an increased pressure.

According to the present invention, cell voltage is maintained low and stable because the anode-cathode spacing is not expanded more than desired even when the increasing pressure is imposed on the cathode compartment.

Hereinbelow, the present invention will be mentioned in more detail by way of examples that follow, which examples are not construed the limit the scope of the invention.

Example

To a monopolar finger type electrolytic cell comprising an FRP top cover, a plurality of expandable dimensionally stable anodes and a cathode box providing a cathode between adjacent anodes, between both ends of opposite sides of which anode S-shaped spacers are interposed as depicted in Fig. 1, "Nafion #315" membranes, produced and sold by E. I. Du Pont de Nemours & Company, which were cylindrically formed were positioned between the anodes and the cathodes to bring both electrodes into contact with the surface of the membrane. Into the anode compartment was continuously introduced an aqueous sodium chloride solution acidified by hydrochloric acid, and deionized water was continuously supplied into the cathode compartment. The cell was energized with a 2,000 A current while exerting pressure on the cathode side. The pressure exerted was 130 mm H_2O, current density was 23.5 A per dm^2 and temperature was controlled at 90°C. Operation was continued at a constant cell voltage of 3.2 V for a period of six months.

Comparative Example

A comparative experiment was carried out using the same finger type electrolytic cell providing cylindrically formed "Nafion #315" membranes as used in Example, except that spacers were not interposed between the opposite sides of the expandable dimensionally stable anode. Current of 2,000 A was supplied to the cell. The pressure of 130 mm H_2O was imposed on the cathode side, current density was 23.5 A per dm^2 and temperature was 80°C. Cell voltage was 3.6 V, which value was higher by 0.4 V than the case where the spacer was employed.

It was ascertained from the above comparison that the present invention enables the electrolysis at a low and stable cell voltage.

Claims

1. A finger type electrolytic cell for the production of halogen, hydrogen and an aqueous alkali metal hydroxide liquor by electrolysis of an aqueous alkali metal halide solution which cell comprises a plurality of expandable dimensionally stable anodes and a cathode box providing a cathode between adjacent anodes, and a cation exchange membrane between adjacent anodes and cathodes, wherein spacers are interposed between the opposite sides of the anodes so as to maintain the uniform anode-cathode spacing.

2. The finger type electrolytic cell of Claim 1, wherein the spacer possesses an expandable function.

3. The finger type electrolytic cell of Claim 2, wherein the spacer is a S-shaped spacer possessing elasticity.

4. The finger type electrolytic cell of Claim 2, wherein the spacer is spring type spacer.

5. The finger type electrolytic cell of Claim 1 wherein the spacer is a plate type spacer.

6. A process for the production of halogen, hydrogen and an aqueous alkali metal hydroxide liquor which comprises supplying an aqueous alkali metal halide solution to an anode compartment of a finger type electrolytic cell which cell comprises a plurality of expandable dimensionally stable anodes and a cathode box providing a cathode between adjacent anodes, and a cation exchange membrane between adjacent anodes and cathodes wherein spacers are interposed between the opposite sides of the anodes so as to maintain the uniform anode-cathode spacing, electrolyzing said aqueous alkali metal halide solution while exerting the pressure on a cathode compartment in such a manner that the respective surfaces of both the anode and the cathode are in intimate contact with the cation exchange membrane, and removing the aqueous alkali metal hydroxide liquor and hydrogen from the cathode compartment, and the aqueous alkali metal halide solution and chlorine from the anode compartment.

7. The process of Claim 6, wherein the spacer possesses an expandable function.

8. The process of Claim 7, wherein the spacer is a S-shaped spacer possessing elasticity.

9. The process of Claim 7, wherein the spacer is a spring type spacer.

10. The process of Claim 6, wherein the spacer is a plate type spacer.

11. The process of Claim 6, wherein the pressure is exerted on the cathode compartment in the range of 20 to 200 mm H_2O to atmospheric pressure.

12. The process of Claim 11, wherein the pressure is exerted on the cathode compartment in the range of 50 to 150 mm H_2O.

13. A finger type electrolytic cell as claimed in claim 1 substantially as described herein with reference to the accompanying drawings.

14. A process as claimed in claim 6 substantially as described in the Example herein.

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