

April 4, 1972

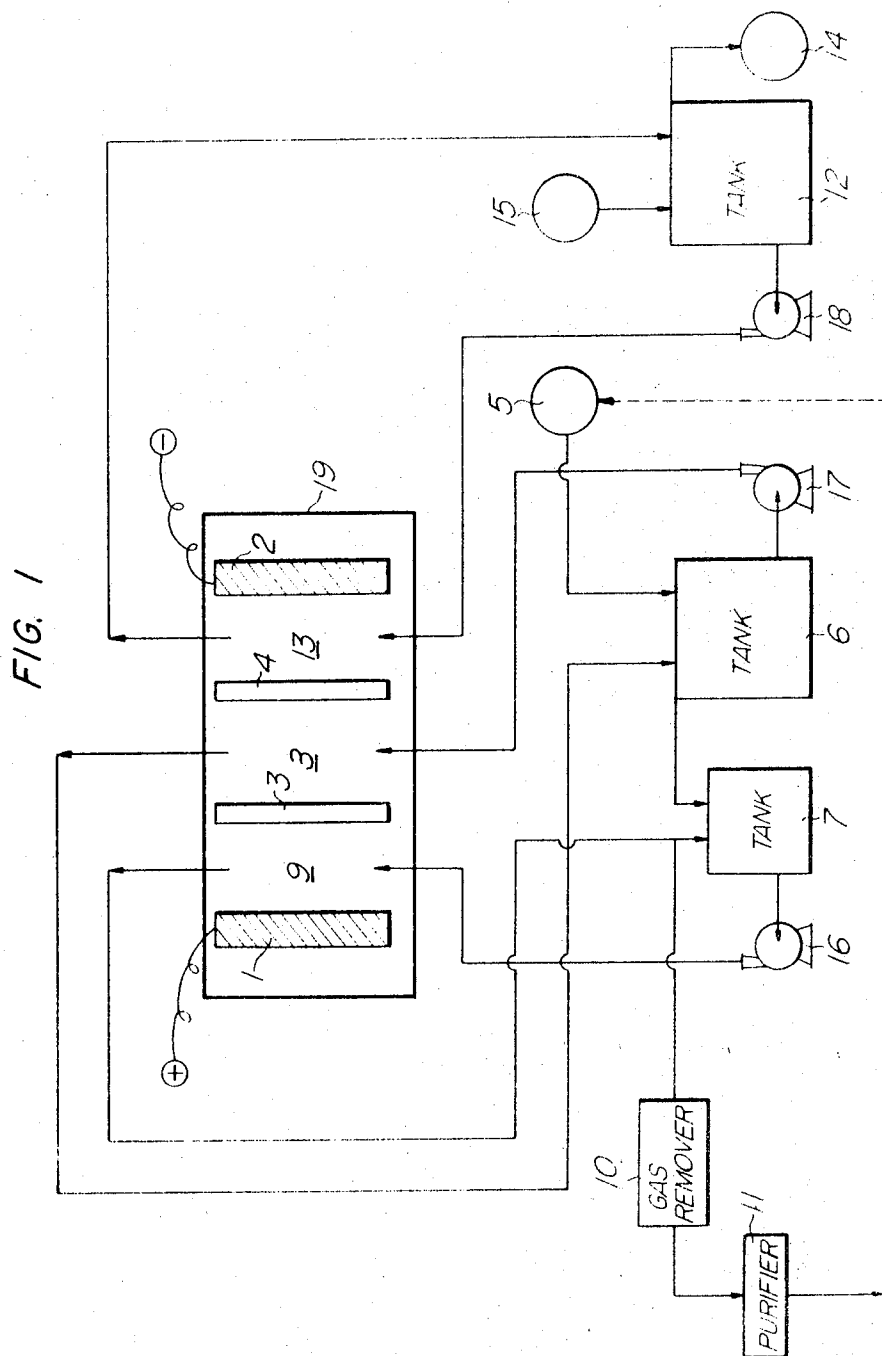
MITSUO YOSHIDA ET AL

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ELECTROLYSIS OF SALT SOLUTION

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2 Sheets-Sheet 1



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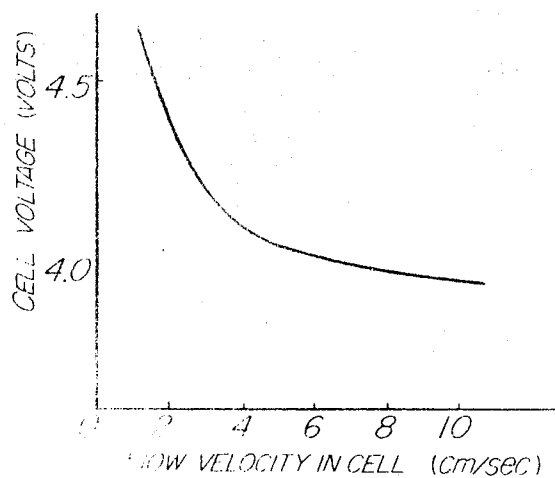
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2 Sheets-Sheet 2

FIG. 2



1

3,654,104

ELECTROLYSIS OF SALT SOLUTION

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3 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous solution of alkali metal halide or hydrochloric acid is electrolyzed in an electrolytic cell consisting of at least one unit cell which comprises a cathode, an anode, a cation exchange membrane, and a neutral diaphragm having a water permeability of not more than 5 cc./min. cm.² under a pressure difference of 1 kg./cm.², where the cation exchange membrane and the neutral diaphragm are juxtaposed at a distance between the cathode and the anode to form an anode compartment between the anode and the neutral diaphragm, an intermediate compartment between the neutral diaphragm and the cation exchange membrane, and a cathode compartment between the cation exchange membrane and the cathode, by passing each compartment solution at a flow velocity of at least 3 cm./sec., while keeping an inside pressure of the intermediate compartment higher than that of the anode compartment.

This invention relates to a process for electrolysis of an aqueous electrolyte solution, and more particularly, it relates to a process for electrolyzing an aqueous solution of alkali metal halide or hydrochloric acid in a three-compartment electrolytic cell containing a neutral diaphragm and a cation exchange membrane.

Several proposals have been made concerning processes for electrolysis of an aqueous electrolyte solution by utilizing an ion exchange membrane. It is, however, very difficult to employ them commercially, because they have some serious defects from an industrial point of view.

In U.S. Pat. Nos. 3,017,338 and 3,135,673, for example, there are disclosed methods for obtaining caustic soda by electrolyzing an aqueous sodium chloride solution in a three-compartment electrolytic cell containing a cation exchange membrane and a highly water-permeable neutral diaphragm. These prior methods have the inevitable drawbacks that caustic soda of low grade, i.e. containing impurities, is formed as a by-product; since the whole amount of feed electrolyte solution must be passed to the corresponding compartment through the neutral diaphragm, this is liable to cause clogging of the neutral diaphragm and so stationary, stable operation for a long period is hardly expected; and polarization of the cation exchange membrane is apt to occur, which results in an increase in the electric voltage required for the electrolysis.

It is an object of this invention to overcome the above-said drawbacks of the heretofore-proposed methods for electrolyzing the aqueous electrolyte solution by using an ion exchange membrane and a neutral diaphragm. That is, the object of the present invention is to provide a method by which the electrolysis of alkali metal halide or hydrochloric acid may be carried out while maintaining the conditions at high current density under low voltages with high stability for a long period.

It has now been found the above object is attained by carrying out the electrolysis in a three-compartment electrolytic cell which contains a neutral diaphragm having very low water-permeability and a cation exchange mem-

2

brane, while passing the electrolyte solution under restricted condition.

The electrolytic cell employed in this invention consists of at least one unit cell which comprises a cathode, an anode, a cation exchange membrane and a neutral diaphragm having a very low water permeability, where the cation exchange membrane and the neutral diaphragm are juxtaposed at a distance between the cathode and the anode so that the cation exchange membrane and the neutral diaphragm may be at the cathode side and at the anode side respectively, to form an anode compartment defined by the anode and the neutral diaphragm, an intermediate compartment defined by the neutral diaphragm and the cation exchange membrane and a cathode compartment defined by the cation exchange membrane and the cathode. According to this invention, an aqueous electrolyte solution is passed through the anode compartment and the intermediate compartment and a cathode solution through the cathode compartment at flow velocities of at least cm./sec. respectively, while keeping an inside pressure of the intermediate compartment higher than an inside pressure of the anode compartment.

The invention is further explained by referring to the accompanying drawings.

FIG. 1 shows a sectioned schematic view of the electrolytic cell used in this invention and a flow diagram showing an embodiment of the present invention.

FIG. 2 is the graph showing a relation between a flow velocity within an electrolytic cell and voltage of the cell of Example 3.

In FIG. 1, an electrolytic cell 19 consists of an anode 1, a cathode 2, a neutral diaphragm 3, and a cation exchange membrane 4, where the neutral diaphragm 3 and the cation exchange membrane 4 are juxtaposed at a distance from about 1 to 10 mm. between the anode 1 and the cathode 2 so that the neutral diaphragm may be at the anode side and the cation exchange membrane at the cathode side, whereby there are formed an anode compartment 9 by the anode 1 and the neutral diaphragm 3, an intermediate compartment 8 by the neutral diaphragm 3 and the cation exchange membrane 4 and a cathode compartment 13 by the cation exchange membrane 4 and the cathode 2. The thickness of each compartment is usually several millimeters. In FIG. 1, an electrolytic cell consisting only of one unit cell is shown for simplicity of illustration, but a practical electrolytic cell consists of a stack of a plurality of such unit cells.

As the material for the anode 1, there may be used the anode materials usually used in the conventional electrolytic cell, for example, graphite, platinum, and titanium or tantalum plated with a noble metal such as platinum or rhodium.

As the material for the cathode 2, there may be employed the cathode materials usually used in the conventional electrolytic cell, for example, iron, stainless steel, and nickel.

In the present invention, it is necessary that the neutral diaphragm 3 have a water permeability as low as possible, and it is desirable that the water permeability under a pressure difference of 1 kg./cm.² be not more than 5 cc./min. cm.², preferably not more than 2 cc./min. cm.². The neutral diaphragm having such properties may be easily manufactured by known methods, from an acid-resistant and chlorine-resistant material, e.g. blue asbestos, polytetrafluoroethylene ("Teflon") and polyesters, and it can be reinforced, if necessary, by surface-treatment, incorporation of a reticular material of polyvinylidene chloride (Saran), polyester or polyethylene as a core or along the surface of the diaphragm. For example, a neutral diaphragm of blue asbestos is obtained by dispersing a binder such as a latex of polyvinylidene chloride (Saran), into

3

an aqueous slurry of blue asbestos, then subjecting the slurry to make a diaphragm and pressing the same, and if necessary, applying a suitable material such as divinylbenzene onto the surface of the resultant diaphragm; or the diaphragm of plastics may be obtained by mixing the plastics such as polytetrafluoroethylene, polyvinylidene chloride and polyethylene terephthalate with a plasticizer, then molding the mixture into film, and extracting the plasticizer out of the film.

As the cation exchange membrane 4, there may be employed any one which is prepared according to the well-known method, but among which there are preferably used those having the properties of a low alkali diffusion from the cathode compartment 13 to the intermediate compartment 8 and a good cation transport number.

In this invention the feed electrolyte solutions are alkali metal halides such as sodium chloride and potassium chloride, and hydrochloric acid. When the alkali metal halide is fed the products obtained are essentially a solution of the corresponding hydroxide, gaseous hydrogen and chlorine. When hydrochloric acid is fed the products are essentially gaseous hydrogen and chlorine.

Now, the present electrolytic method will be explained for the case when the feed solution is an alkali metal halide, referring also to FIG. 1 wherein each compartment solution is recycled between the tanks for recycle and the electrolytic cell.

An aqueous salt solution 5 to be electrolyzed is supplied to a tank 6 for recycle of an intermediate compartment solution. The intermediate compartment solution is supplied from the tank 6 to the intermediate compartment 8 by means of a pump 17. Although a very small portion of the intermediate compartment solution sometimes passes from the intermediate compartment 8 to the anode compartment 9 through the neutral diaphragm 3, almost all of the intermediate compartment solution leaves the intermediate compartment and returns to the tank 6. A portion of the thus returned solution is supplied to a tank 7 for recycle of the anode compartment solution. The anode compartment solution is supplied from the tank 7 to the anode compartment 9 by means of a pump 16, and returned again to the same tank 7, after the gas generated at the anode has been separated. A portion of the returned anode compartment solution leaving the electrolytic cell is, after the residual anode gas being removed therefrom at an anode gas-removing apparatus 10, then admixed with the raw material salt and water, and supplied to the tank 6 as a solution 5 through an apparatus 11 for purifying an aqueous salt solution.

On the other hand, the cathode compartment solution is likewise recycled between a tank 12 for recycle of the cathode compartment solution and the cathode compartment 13 by means of a pump 18, and after the gas generated at the cathode has been separated, a portion of the returned cathode compartment solution leaving the electrolytic cell is taken out of the electrolytic system as the product. To the tank 12 water 15 is supplied separately.

In the present invention, it is necessary that the pressure of the intermediate compartment 8 be higher than that of the anode compartment 9 within the electrolytic cell at said solution recycle. Furthermore, it is important for the operation of low voltage, as shown in the examples which follow, that the flow velocity of each compartment solution be at least 3 cm./sec. By doing so, the transference of some amount of solution from the intermediate compartment 8 to the anode compartment 9 through the neutral diaphragm 3 may occur.

If a neutral diaphragm having a high water permeability is used, a large amount of the intermediate compartment solution is passed to the anode compartment 9 at the lower part of the electrolytic cell, but it is hardly passed at the upper part of the electrolytic cell. Therefore, a portion of the anode compartment solution flows back to the intermediate compartment 8 at the upper part of

4

the electrolytic cell, and it becomes impossible to effect operation worth the provision of the neutral diaphragm 3. That is, it is impossible to effect the operation of supplying an aqueous salt solution free of chlorine gas to the surface of the cation exchange membrane 4. Furthermore, there is almost no flow of the intermediate compartment solution at the surface of the cation exchange membrane 4, resulting in increase in voltage.

On the other hand, when a neutral diaphragm 3 having a very low water permeability is used according to this invention, substantially no transference of the solution from the intermediate compartment 8 to the anode compartment 9 through the neutral diaphragm 3 occurs; furthermore, substantially no flow velocity is changed at both upper and lower parts of the intermediate compartment 8; and a very small amount of the intermediate compartment solution is only transferred to the anode compartment equally on the entire surface of the neutral diaphragm 3. Thus, according to this invention, clogging of the neutral diaphragm 3 and contamination of the anode compartment solution into the intermediate compartment never occur; the properties of the neutral diaphragm 3 and the cation exchange membrane 4 are not deteriorated even when they are used for a prolonged period of time.

In the present invention, the flow velocity of each compartment solution within the electrolytic cell is adjusted to at least 3 cm./sec., whereby the distribution of solution flow may be improved, a fear of polarization of the cation exchange membrane 4 may be completely eliminated, and disengagement of the gases at the anode 1 and cathode 2 from the electrode surfaces may be accelerated to keep a stable operation under a low voltage.

In the foregoing, the explanation has been made as to the case that each compartment solution is recycled between the electrolytic cell and the tanks, but it is possible to eliminate the tanks in the embodiment of the present invention.

The process of this invention relating to the conversion of alkali metal halide and hydrochloric acid into their corresponding halogen, metal hydroxide and hydrogen are illustrated by the following examples which are not to be construed as limiting.

EXAMPLE 1

Electrolysis of sodium chloride by using a neutral diaphragm having a high water permeability which is not included in the scope of this invention.

There was used an electrolytic cell consisting of: as an anode a platinum-plated titanium electrode; as a cathode a stainless steel electrode; as a neutral diaphragm a polyester fabric having a water permeability as high as 20 cc./min. cm.² under a pressure difference of 1 kg./cm.²; and as a cation exchange membrane a homogeneous membrane prepared by copolymerizing the phenyl ester of vinyl sulfonic acid, styrene and divinylbenzene as its principal constituents and hydrolyzing the thus obtained copolymer; an available area for current passage of the electrodes, the membranes and the diaphragm being 500 cm.² (5 cm. x 100 cm.); an interelectrode distance being 8 mm.; the thicknesses of the anode compartment, the intermediate compartment and the cathode compartment being 2.5 mm., 2.0 mm. and 2.8 mm. respectively; and the thicknesses of the neutral diaphragm and the cation exchange membrane being 0.5 mm. and 0.2 mm. respectively. An aqueous 5 N NaCl solution was recycled as both anode compartment solution and intermediate solution, and an aqueous 5 N NaOH solution was recycled as the cathode compartment solution. The solution temperature and the D.C. electric current were 60° C. and 75 a. (15 a./dm.²), respectively. The flow velocity of each compartment solution was 4 cm./sec. at the inlet of the electrolytic cell and the pressure in the intermediate compartment was made higher by approx. 0.10 kg./cm.², than the pressure in the anode compartment. By passing an electric current, most portions of the intermediate compart-

ment solution were transferred to the anode compartment through the neutral diaphragm at the lower part of the electrolytic cell, and on the contrary, the anode compartment solution was transferred to the intermediate compartment at the upper part of the electrolytic cell. The returned intermediate compartment solution only corresponded to a flow velocity of 0.5 cm./sec. Through the cell voltage was 4.58 v., the alkali current efficiency was 92%.

Then, further operation was carried out by adjusting the flow velocities of the anode compartment solution and the intermediate compartment solution to 1 cm./sec. and 7 cm./sec. at the inlet of the electrolytic cell respectively, and could be effected without any transference of the anode compartment solution to the intermediate compartment in the electrolytic cell, but the returned intermediate compartment solution only corresponded to a flow velocity of 1.0 cm./sec. The cell voltage was 4.40 v. and the alkali current efficiency was still 92%. However, in that case, the purified salt solution could not be supplied in time to the tank 6 for recycle of the intermediate compartment solution, and a portion of the returned anode compartment solution had to be supplied to the tank 6 for recycle of the intermediate compartment solution, resulting in contamination of chlorine gas into the intermediate compartment solution.

The contamination of the chlorine gas into the intermediate compartment solution caused the cation exchange membrane to deteriorate, and the voltage was increased by about 0.2 v. after a continuous operation of 100 hours, and the alkali current efficiency was reduced by 4%, that is, to 88%.

EXAMPLE 2

Electrolysis of sodium chloride by using a neutral diaphragm having a low water permeability.

Electric current was passed through the same electrolytic cell under the same conditions as in Example 1, except that there was used a neutral diaphragm of blue asbestos sheet whose surface had been treated with divinylbenzene for reducing its porosity and reinforced with a Saran net along the surface, having a water permeability as high as 5 cc./min. cm.² under a pressure difference of 1 kg./cm.², and a flow velocity of each compartment solution was adjusted to 4 cm./sec. at the inlet of the electrolytic cell. As a result, the intermediate compartment solution transferred to the anode compartment through the neutral diaphragm amounted to about 50 cc./min., and the returned intermediate compartment solution corresponded to a flow velocity of about 3.1 cm./sec. No contamination of chlorine gas was brought about at all. By passing continuously an electric current for 100 hours, the cell voltage was 4.20 volt and stable. No deterioration of the cation exchange membrane was brought about, and the alkali current efficiency was 93%.

EXAMPLE 3

The relation between the flow velocity in each compartment at the outlet and the voltage was determined in the same electrolytic cell under the same conditions as in Example 2, and one of the results is shown in FIG. 2. The electrolytic conditions are given below:

Anode and intermediate compartment solutions: 5 N NaCl,
Cathode compartment solution: 5 N NaOH, solution,
Temperature: 60° C., and
Electric current: 75 a. 15 a./dm.²).

EXAMPLE 4

An electrolytic cell consisting of 7 unit cells, each unit cell having an available area of 70 dm.² (70 cm. x 100 cm.) for current passage and all the unit cells being stacked in a filter press was used, where there was used as an anode a platinum-plated titanium electrode, as a cathode an iron electrode, as a neutral diaphragm a blue

asbestos sheet incorporated with a polyester fabric as a core material and surface-treated with divinylbenzene for reducing its porosity, and as a cation exchange membrane a membrane of the vinyl sulfonic acid-divinylbenzene type. The interelectrode distance was 8 mm. There were used an aqueous ca. 5 N NaCl solution as both anode and intermediate compartment solutions, an aqueous 5 N NaOH solution as a cathode compartment solution, and a saturated NaCl solution as a purified aqueous salt solution to be supplied to the tank 6 for recycle of the intermediate compartment solution. Operation was carried out at a solution temperature of 70° C. with a current of 7350 a. (15 a./dm.²) at a flow rate of each compartment solution of about 40 lit./min. and a flow velocity of about 7 cm./sec. within the electrolytic cell, while keeping the pressure within the intermediate compartment higher by about 0.1 kg./cm.² than that within the anode compartment. No contamination of chlorine gas into the intermediate compartment solution was brought about, and the amount of the intermediate compartment solution transferred to the anode compartment through the neutral diaphragm was about 5 lit./min. and was not changed almost at all. The cell voltage was 3.80 v. and the alkali current efficiency was 94.5%. No deterioration of the cation exchange membrane was brought about, and no change was observed in the water permeability and electric resistance of the neutral diaphragm. Stable operation could be continued for 93 days.

EXAMPLE 5

In the same apparatus as employed in Example 1, there were assembled the cation exchange membrane, which was prepared by polymerizing acrylic acid, divinylbenzene and styrene into a film shape and then saponifying the polymerizate with caustic soda, and the neutral membrane which was prepared by a paper-making process from an aqueous slurry of unravelled blue asbestos containing Saran latex as a binder material and then followed by being pressed under a pressure of 80 kg./cm.², which had a water permeability of 2 cc./min. cm.² under a pressure difference of 1 kg./cm.². A saturated aqueous solution of potassium chloride was supplied into the intermediate and anode compartments, and an aqueous solution of 5 N-KOH was supplied into the cathode compartment, at the linear flow velocity of 4 cm./sec. at the inlet part of each compartment. Electrolysis was carried out under the condition that the solution temperature and the D.C. electric current were 60° C. and 75 a. (15 a./dm.²), respectively.

The pressure within the intermediate compartment was made higher by approx. 0.1 kg./cm.² than that within the anode compartment.

As a result, the intermediate compartment solution transferred to the anode compartment through the neutral diaphragm amounted to approx. 18 cc./min., the returned intermediate compartment solution corresponded to a flow velocity of approx. 3.7 cm./sec., and no contamination of chlorine gas into the intermediate compartment solution was observed. By effecting a continuous electrolysis for 25 days the cell voltage showed 3.8 volts and stable, no deterioration of the cation exchange membrane and neutral diaphragm was found, and the alkali efficiency was 94%.

EXAMPLE 6

Electrolysis of an aqueous hydrochloric acid solution was carried out by use of the same electrolytic cell, ion exchange membrane and neutral diaphragm. Aqueous 10 N HCl solutions were fed into both the anode compartment and the intermediate compartment, and an aqueous 5 N HCl solution was fed into the cathode compartment, at the linear flow velocity of 4 cm./sec. at the inlet part of each compartment, at the temperature of 60° C. with a electric current density of 15 amp./dm.². The pressure

within the intermediate compartment was made higher by approx. 0.05 kg./cm.² than that within the anode compartment. As the result, a intermediate compartment solution transferred to the anode compartment through the neutral diaphragm amounted to approx. 22 cc./min., the returned intermediate compartment solution corresponded to a flow velocity of approx. 3.6 cm./sec. and no contamination of chlorine gas into the intermediate solution was observed. By effecting the continuous electrolysis for 100 hours a cell voltage showed 3.20 volts and stable, and substantially no deterioration of the cation exchange membrane and the neutral diaphragm was observed.

What we claim is:

1. In a method for electrolyzing an aqueous solution of alkali metal halide or hydrochloric acid by using an electrolytic cell consisting of at least one unit cell which comprises a cathode, an anode, a cation exchange membrane and a neutral diaphragm, where the cation exchange membrane and the neutral diaphragm are juxtaposed at a distance between the cathode and the anode so that the cation exchange membrane and the neutral diaphragm may be at the cathode side and at the anode side respectively, to form an anode compartment defined by the anode and the neutral diaphragm, an intermediate compartment defined by the neutral diaphragm and the cation exchange membrane, and a cathode compartment defined by the cation exchange membrane and the cathode, the improvement which comprises passing the aqueous solution to be electrolyzed through the anode compartment and the intermediate compartment and a cathode solution

through the cathode compartment at flow velocities of at least 3 cm./sec., respectively, while using a neutral diaphragm having a water permeability of not more than 5 cc./min. cm.² under a pressure difference of 1 kg./cm.² and keeping an inside pressure of the intermediate compartment higher than that of the anode compartment whereby a part of the intermediate solution is introduced into the anode compartment through said neutral diaphragm.

2. The improvement according to claim 1, wherein the aqueous solution to be electrolyzed is an aqueous alkali metal halide solution.

3. The improvement according to claim 1, wherein the aqueous solution to be electrolyzed is an aqueous hydrochloric acid solution.

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