Dec. 7, 1965 C. E. TIRRELL ETAL **3,222,267**

PROCESS AND APPARATUS FOR ELECTROLYZING SALT SOLUTIONS

Filed April 5, 1962 2 Sheets-Sheet 1

FIG. 1

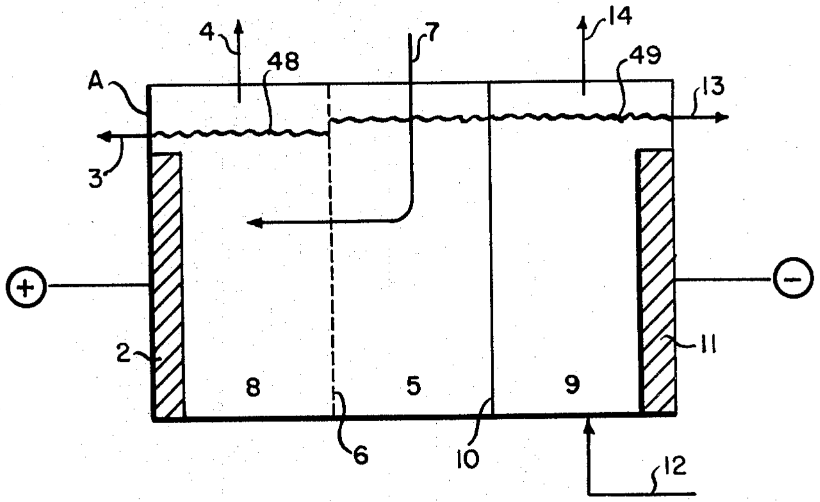
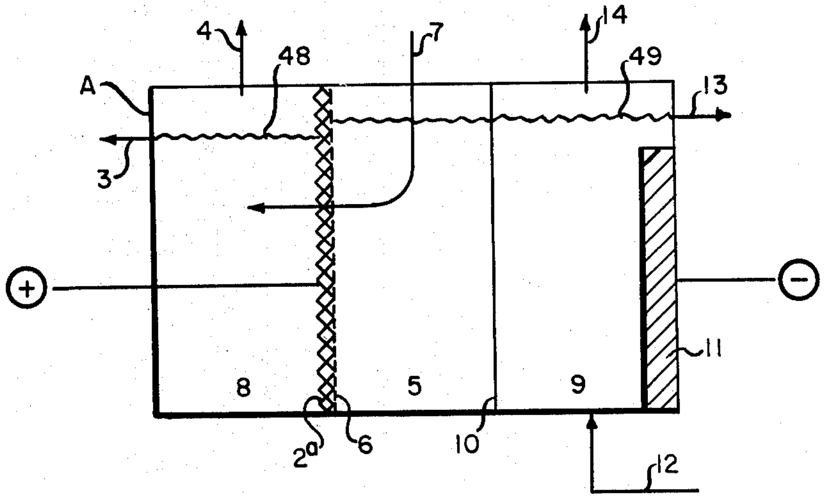


FIG. 2



INVENTORS:
Charles E. Tirrell
Edgardo J. Parsi

by:

ATTORNEY

Dec. 7, 1965 C. E. TIRRELL ETAL 3,222,267

PROCESS AND APPARATUS FOR ELECTROLYZING SALT SOLUTIONS

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FIG. 3

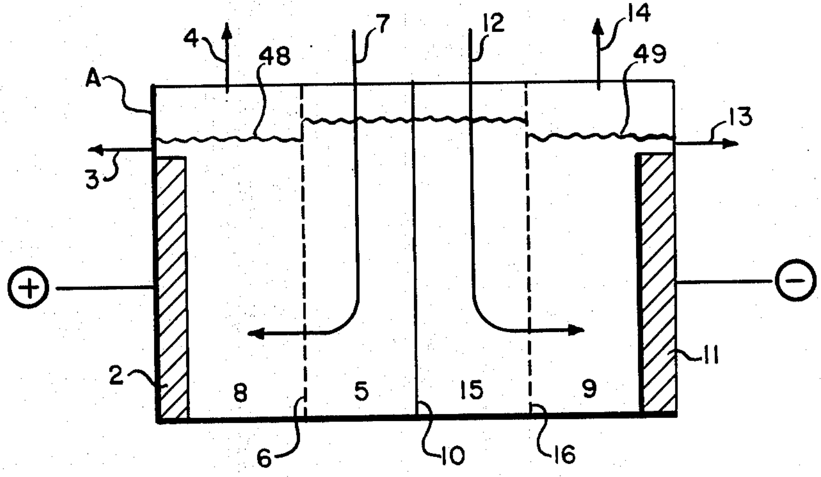


FIG. 4

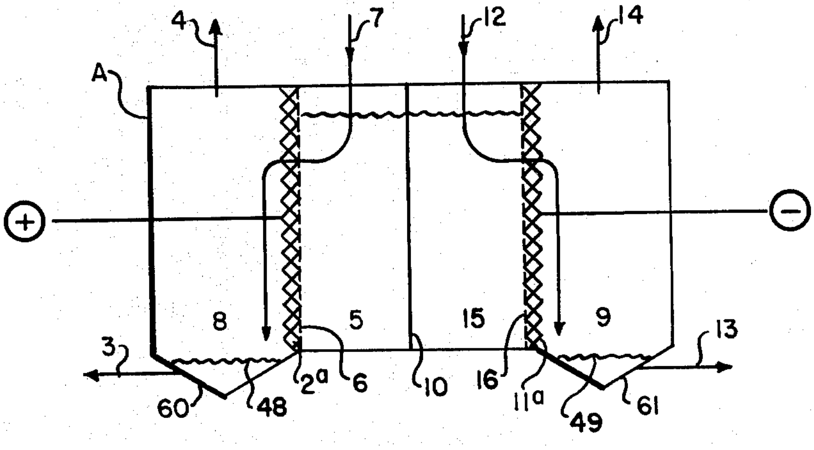
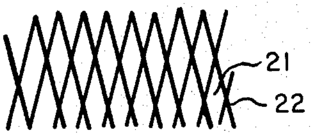


FIG. 5



INVENTORS:

Charles E. Tirrell

Edgardo J. Parsi

by:

ATTORNEY

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PROCESS AND APPARATUS FOR ELECTROLYZING SALT SOLUTIONS

Charles E. Tirrell, Wayne, Pa., and Edgardo J. Parsi, Wellesley Hills, Mass., assignors to Ionics, Incorporated, Cambridge, Mass., a corporation of Massachusetts

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The portion of the term of the patent subsequent to June 2, 1981, has been disclaimed

10 Claims. (Cl. 204—98)

This application is a continuation-in-part of our copending U.S. application Serial No. 108,061 filed May 5, 1961, now Patent No. 3,135,673 issued on June 2, 1964.

This invention relates to electrolytic processes and apparatus for the electrochemical conversion or oxidation and reduction of electrolytic solutions. More particularly it relates to processes and apparatus which employ three compartment or four compartment electrolytic cells.

Briefly, the three compartment cell contains an ion-exchange membrane which is hydraulically impermeable to solutions, but selectively permeable to cations, said membrane separating and defining the cathode compartment from the anode feed compartment and a spaced acid resistant hydraulically permeable diaphragm separating and defining the anode compartment from the anode feed compartment. The anode feed compartment therefore being defined by a cation-permeable membrane facing the cathode side and on the anode side by a hydraulically porous diaphragm. Thus, the three compartment cell employs the following chamber arrangement; anode chamber/anode feed chamber/cathode chamber. The electrolytic salt solution is passed into the anode feed chamber and tap water or other conducting solutions are passed into the cathode compartment or chamber. A direct electrical potential is impressed upon the cell causing migration of cationic ions of the electrolyte through the cation-permselective membrane into the cathode compartment where combination with hydroxyl ions produced by the electrolysis of water at the cathode produces the corresponding metal hydroxide; and passage of the electrolyte solution containing the anionic groups plus a small portion of the cationic ions of said electrolyte through the hydraulically permeable diaphragm into the anode compartment where combination of the anionic groups with hydrogen ions produced by the electrolysis of water at the anode produces the corresponding acid which, mixed with the original electrolyte forms an anolyte effluent product, for example, acid salt.

In the four compartment or chamber cell there is included a fourth chamber, a cathode feed chamber made by the addition of a second porous diaphragm. Said second diaphragm separates and defines the cathode chamber from the cathode feed chamber. Thus, the configuration of chambers in this type of cell is arranged as follows: anode chamber/anode feed chamber/cathode feed chamber/cathode chamber. Operation of this cell is similar to the above described three compartment cell with the exception that the tap water is not passed directly into the cathode chamber but instead into the cathode feed chamber where the tap water carries along in its flow into the cathode chamber via the porous diaphragm, those cations that have migrated through the cation-permeable membrane. The cations then combine with the hydroxyl ions produced at the cathode to form the metal hydroxide. The advantages, improvements, variations, and combinations that may be accomplished by use of the above described process and apparatus will be more fully described hereinafter.

The processes of this invention relating to the conversion of soluble salts into their corresponding metal hydroxides and acid salts may be directed in general toward those applications wherein it is desired to recover acid salt and base values from substantially waste salt solutions, in particular, the waste sodium sulfate liquor derived from the neutralization of caustic cellulose acetate in the spinning bath operation of the viscose rayon industry or from pickle liquor of the steel industry.

Electrolytic cells, for example caustic-chlorine cells, now commonly employed for salt conversion are of two general types: (1) diaphragm and (2) mercury, and are distinguished chiefly by the purity of the corresponding metal hydroxide produced and production per unit floor space. Mercury cells are of such design that the product hydroxide solution is of a high degree of purity, i.e., the hydroxide may have a contaminating foreign anion concentration of less than about 0.05% of the concentration of the hydroxide, this advantage being the mercury cell's principal inducement toward its employment in commercial installations. Mercury cells typically employed in the electrolysis of waste sodium sulfate spinning liquor consist of an electrolyzing chamber containing a sulfate-resistant alloyed anode and a cathode consisting of a flowing bed or rotating vortex of mercury which reacts with sodium ions to form a sodium amalgam film upon its surface; subsequently this sodium amalgam-mercury composition is withdrawn from the cell and passed through an amalgam decomposing chamber wherein a flow of water countercurrent to the flow of mercury effluent converts the amalgam to a substantially pure aqueous solution of sodium hydroxide. Disadvantages of this process are the high initial capital investment necessitated by the large inventory of mercury required, a relatively high energy consumption, an undesirably high ratio of floor space per unit of product and relatively low power efficiencies resulting from the wider spacing between the electrodes.

Diaphragm type electrolytic cells overcome these cited disadvantages to a satisfactory extent. However, they are characterized by the production of a product metal hydroxide solution which has a considerably low degree of purity. Cells of this category employ one or more diaphragm permeable to flow of electrolyte solution, but impervious to passage of gas bubbles, thus separating the cell into two or more compartments; for example, a three-compartment cell containing two porous diaphragms is described in U.S. Patent No. 1,126,627. The processes associated with this type of cell comprise the steps of transferring from either or both the anode and the center compartment to the cathode compartment by means of permeation through the diaphragm(s) a relatively concentrated aqueous salt solution which is passed into the anode or center compartment at a rate sufficient to repress the migration of hydroxyl ions toward the anode, thereby producing as a catholyte effluent the corresponding metal hydroxide and free hydrogen gas, while at the anode, free oxygen or chlorine gas is produced and, in the case of the original salt solution consisting of sodium sulfate, a mixture of the salt and the corresponding acid. Employment of diaphragm-type electrolytic cells achieves relatively high production of products per unit floor space, lower energy requirements and higher current efficiencies, but incurs the serious disadvantage of producing as the catholyte effluent product the hydroxide solution in a very dilute and impure form, i.e., the product may consist of about 12% hydroxide and about 12% of the original salt. In the use of a saturated NaCl feed solution, concentration and separation of the hydroxide by the use of three-stage evaporators is required wherein the salt crystallizes out, and a final NaOH concentration of about 50% is achieved. The hydroxide obtained using these supplementary and expense-incurring processes is still contaminated by about 1% of the original salt and therefore falls short of the purity achieved in a mercury cell which produces a caustic well within the specification limits of rayon grade caustic soda. It has been a consistent feature of every diaphragm-type electrolytic cell proposed heretofore, that the product hydroxide is characterized by a purity below that value signifying a "rayon grade" caustic, due to the permeation of the anion groups of the original salt through the non-permselective diaphragm separating the cathode from the feed electrolyte solution.

It has been proposed in U.S. Patent No. 2,681,320 that permselective membranes be interposed in an electrolytic cell in place of non-permselective diaphragms in order that such "rayon grade" caustic be achieved. However, no provision is made for a three- or a four-compartment electrolytic cell containing both a permselective membrane and non-permselective diaphragm. In the instance of employment of only one cation-permselective membrane, which separates the anode from the cathode compartment to form a two-compartment cell, the hydrogen cations formed by the electrolysis of water at the anode will migrate into the cathode chamber through the cation-permselective membrane in conjunction with the metallic cations and result in neutralizing the hydroxyl ions being formed at the cathode. In the instance of employment of both anion and cation membranes in a three-compartment cell, the center compartment, which is comparable to the anode feed compartment of the three-compartment cell of the present invention, is bounded on the anode side by an anion-permselective membrane, the same phenomenon of migration toward the cathode of hydrogen ions formed at the anode through the intervening anion-permeable membrane will occur due to the inherent inefficiency toward repression of hydrogen ion permeation of those anion-permselective membranes known in the art. For example, starting with a 1.0 normal sodium sulfate solution introduced into the center compartment, a comparatively high efficient anion membrane will function in such a manner that about 50% of the current passing through said membrane is conveyed by the passage of hydrogen ions through said membrane toward the cathode, the remaining current being carried by the anions migrating toward the anode. Consequently, the insertion of an anion-permselective membrane in place of a non-permselective diaphragm in this case, is of no value due to the membrane's low anion permselectivity.

In U.S. Patent No. 3,017,338, an electrolytic process and cell for making caustic soda and chlorine is disclosed employing a spaced porous diaphragm and cation-exchange membrane defining a three-chamber cell. The present invention employs a different novel arrangement of the porous diaphragm and cation-exchange membrane with the procedure for conversion of the feed solution such as to effect a much wider and more useful application of the principle of electrolytic conversion of feed electrolytes as will be more fully hereinafter disclosed.

Construction of a three-compartment electrolytic cell in accordance with the present invention, wherein the partition between the anode compartment and the anode feed compartment is a porous non-selective diaphragm and wherein the partition between the anode feed compartment and the cathode compartment is a cation-permselective membrane, allows management of the electrolysis in such a manner that passage of the feed electrolytic solution into the anode feed compartment may be controlled to such a rate that the resulting flow of electrolytic solution into the anode compartment via the diaphragm is sufficiently rapid to substantially prevent the undesired migration of hydrogen ions from the anode chamber to the cathode chamber. The minimizing of the migration of hydrogen ions toward the cathode by a countercurrent flow of electrolytic solutions is effected substantially by means of a porous non-permselective diaphragm inserted between the anode and the influent electrolytic solution.

It has been discovered in accordance with the present invention that such a three-compartment cell not only prevents substantially the flow of hydrogen ions toward the cathode, which would otherwise cause a loss of caustic production, but also furnishes as the catholyte effluent product a "rayon grade" caustic. The same corresponding purity of product is similarly obtained in the electrolytic conversion of other feed salt electrolytes such as pickle liquor, waste Na_2SO_4 liquor, etc.

Another object of this invention is the provision of a method for electrochemical conversion of aqueous electrolyte solutions of high purity products overcoming many of the disadvantages of the prior art.

Another object of the present invention is to provide an improved process for the regeneration of waste sodium sulfate liquor obtained from the spinning operations in the viscose rayon industry.

It is a further object to provide such a process wherein the resultant caustic soda product is of "rayon grade" purity and the product sodium acid sulfate is of a composition suitable for use in rayon spinning operations.

It is a further object to provide a method whereby electrolytic salt solutions can be electrolyzed in such manner as to produce salt-free product hydroxide and the corresponding acid salt.

It is a further object to provide an electrolytic method for the preparation of organic acids and inorganic acids of slight ionization from the corresponding soluble salts.

It is a further object to provide a method for the electrolysis of salt solutions wherein the migration to the cathode of hydrogen ions formed at the anode is effectively prevented.

It is a further object to provide a method wherein the migration to the anode of hydroxyl ions formed at the cathode is effectively prevented.

It is a further object to provide foraminous electrodes for support of the porous diaphragms.

Still further objects will appear from the following description and appended drawings and claims.

The foregoing and related objects of the present invention are accomplished by employment of a three-compartment or a four-compartment electrolytic cell containing one ion-exchange membrane selectively permeable to cations and acid-resistant hydraulically permeable diaphragm, such cells diagrammatically illustrated in vertical cross-section in the drawings do not in any way represent an attempt to construct the concept of the invention which is sufficiently broad to permit variations and modifications of such electrolytic cells.

FIGURE 1 is a diagrammatic representation in vertical cross section of a three-compartment electrolytic cell of the present invention containing a self-supporting diaphragm.

FIGURE 2 is a slight variation of the cell of FIGURE 1 wherein the anode is of foraminous or expanded metal and forms the support for the porous diaphragm.

FIGURE 3 is also a diagrammatic representation of a four-compartment cell in vertical cross section, employing self-supporting porous diaphragms.

FIGURE 4 is a variation of the cell of FIGURE 3 wherein both foraminous electrodes are used as porous diaphragm supports with said electrodes operating unsubmerged.

FIGURE 5 is an enlarged further representation of the configuration of expanded metal electrodes.

In FIGURE 1, the anode compartment **8** of cell A contains a chemically resistant anode **2** and is provided with outlet **3** for the anolyte effluent product and outlet **4** for gaseous anode products such as oxygen. The anode compartment is separated from the anode feed compartment **5** by means of an acid resistant hydraulically permeable non-permselective diaphragm **6**, said anode feed compartment **5** containing an inlet **7** through which the electrolytic feed solution is introduced. The cathode compartment **9** is separated from the anode feed compartment by a cation-exchange membrane **10** selectively permeable to cations and such cathode compartment is provided with a conventional cathode **11** and conduit **12** through which water is passed into the cathode compartment. Outlet **13** serves to withdraw the catholyte effluent product, and exit pipe **14** removes gaseous cathodic products such as hydrogen. Some modifications of this general assembly of apparatus will be described hereinafter.

In FIGURE 2, the cell configuration and method of operation is fairly similar to that described in FIGURE 1. However, the difference being that the cell of FIGURE 2 had an important added feature in that the porous diaphragm **6** is supported on a foraminous or porous anode **2***a*. The foraminous electrode is constructed in that its pore sizes are larger than the pore size of the supported diaphragm so that the resistance of electrode to hydraulic flow of electrolyte solution is negligible as compared to that of the microporous diaphragm. The use of a supporting porous electrode allows the electrode to be operated partially or completely unsubmerged in liquid, that is, the liquid level in the electrode compartment need not completely cover the electrode.

In the general aspect of operation of this invention, the electrolyte solution, for example, a nearly saturated solution of sodium sulfate, is introduced into the cell through conduit **7** at a rate and pressure sufficiently high so that the passage of said electrolyte through the porous diaphragm **6** is at a rate sufficiently rapid to curtail substantially the migration of hydrogen ions from the anode toward the cathode.

Simultaneously, water is passed into the cathode compartment at a rate corresponding to the concentration of hydroxide desired in the resultant catholyte effluent product, and a direct electric current is impressed upon the cell. Upon the influence of the impressed electric current, the cationic constituents of the electrolytic solution, for example, sodium ions, pass through the cation-permselective membrane into cathode compartment where combination with hydroxyl ions produced at the cathode by the electrolysis of water produces the corresponding hydroxide, sodium hydroxide, which is withdrawn through outlet **13** in a concentration dependent upon the rate of flow of water into the cathode compartment. The electrolytic solution of anode feed compartment **5** now having been partially depleted of its positive ions passes through the diaphragm into the anode compartment where combination of its free anionic groups with hydrogen ions produced by electrolysis of water at the anode produces the corresponding acid, for example, sulfuric acid, which is withdrawn together with unreacted electrolytic solution through outlet **3** as a mixture of the original salt and its corresponding acid salt, for example, sodium bisulfate. In the case, for example, wherein 50% of the sodium ions of a sodium sulfate solution are effectively transferred to the cathode compartment, the resultant anolyte effluent product will be a stoichiometric solution of sodium bisulfate, such solution being suitable for use in rayon spinning operations.

The processes may be more clearly understood with reference to the following series of equations wherein the electrolytic salt employed is sodium sulfate.

(1) Through the cation-exchange membrane **10**:

$$Na^+(\text{anode feed compartment}) \rightarrow Na^+(\text{cathode compartment})$$

(2) At cathode **11**:

$$H_2O \rightleftarrows OH^- + H^+, \quad Na^+ + OH^- \rightleftarrows NaOH$$

(3) Through the diaphragm **6**:

$$Na^+ + (\text{excess})SO_4^-(\text{anode feed compartment}) \rightarrow Na^+ + (\text{excess})SO_4^-(\text{anode compartment})$$

(4) At the anode **2**:

$$H_2O \rightleftarrows OH^- + H^+, \quad SO_4^- + Na^+ + H^+ \rightleftarrows NaHSO_4$$

Other embodiments of the invention using a four-compartment cell are described in FIGURES 3 and 4. In order to obtain high current efficiencies and thus a high production rate, it is necessary to prevent the electrode products, for example, the hydrogen ions at the anode and the hydroxyl ions at the cathode, from mixing together due to a back migration of these ions. A four-compartment cell minimizes this back migration of these ions by placing a porous acid resistant diaphragm **6** between the anode **2** and anode feed chamber **5**, and similarly inserting a caustic-resistant second diaphragm **16** between the cathode **11** and cathode feed chamber **15**. Both diaphragms are hydraulically permeable to the flow of a liquid solution. Thus, the ion-exchange membrane **10** divides the cell into two distinct sections, each section being a mirror image of the other.

In general, the respective solutions are directed to the feed chambers and are allowed to percolate through the diaphragm in a direction which is opposite to that of the migrating ions, at a velocity greater than that of the moving ions. By such a method, the ions are flushed back into their respective electrode chambers.

FIGURE 4, which is the preferred apparatus of carrying out the purposes of this invention, employs foraminous electrodes **2***a* and **11***a* on which a porous diaphragm **6** and **16** are deposited respectively thereon. The electrodes are operated unsubmerged; that is, the level of the anolyte solution **48** and catholyte solution **49** is below the lowest section of the electrodes, said solutions accumulating in their respective collection sections **60** and **61**.

The cell of FIGURE 4 is operated as follows:

During the electrolysis, the negatively-charged hydroxyl ions produced at the cathode **11***a* are attracted through the porous cathode diaphragm **16** in the direction of the anode **2***a*. Due to the cation-membrane barrier, the negative ions are substantially prevented from further migration into the anode feed chamber **5**. However, when the concentration of these hydroxyl ions accumulates sufficiently within the cathode feed chamber **15**, many will pass through the membrane **10** due to diffusion and also to the inherent inefficiency of the membrane to prevent 100% anion exclusion. The greater the concentration of negative ions in contact with the membrane, the greater the rate of loss through said membrane. To counteract these effects, water is directed by conduit **12** into cathode feed chamber **15** and allowed to flow through the diaphragm-cathode combination **16** and **11***a* and trickle down the unsubmerged side of the porous cathode grid **11***a*, rapidly flushing down cathodic products into the cathode collection chamber **61** where it is withdrawn through outlet **13**. The sweep of the water through the diaphragm will minimize back migration of hydroxyl ions and also pass to the cathode collection section any hydroxyl ions which may have migrated into the cathode feed chamber. Thus, the current that is wasted by being carried by the hydroxyl ions migrating in the direction of the anode is minimized, thus achieving higher efficiencies and production rates. Of course, the greater the concentration of hydroxyl ions being formed at the cathode surface, the greater the tendency for back migration and diffusion. By operating the cathode unsubmerged so that the level of the cathode solution **49** is below the cathode, whatever concentration of hydroxide formed at the cathode surface is quickly and efficiently removed down the cathode and into the collection chamber **61**. In accordance with the novel cell of this invention, it is possible to maintain a relatively small concentration of hydroxide in the cathode feed chamber **15** while still withdrawing a highly concentrated caustic product from the collection chamber **61**. Since the greater the concentration of hydroxyl ions in contact with the membrane **10**, the greater the loss therethrough, it is preferable that the concentration in the cathode feed chamber be kept down to a minimum. It has been found that by using a diaphragm of sufficiently small porosity in conjunction with a feed solution of sufficiently high pressure and velocity, the concentration of hydroxide in the cathode feed chamber can be maintained at less than ⅓ the concentration of caustic recovered from the cathode collection chamber. The use of an unsubmerged foraminous cathode has an added advantage in that gas disengagement from the cathode surface, for example, hydrogen, is more readily accomplished since there is no bulk liquid present to entrap or make difficult the release of cathodically formed gases.

The relationship at the anode is analogous to the cathode arrangement. The electrolytic solution, for example, a saturated brine, is introduced into the anode feed chamber **5** by inlet **7** at a rate and pressure sufficiently high so that in its passage through the diaphragm **6**, the positively-charged hydrogen ions formed at the anode **2** are repelled in their natural tendency to migrate toward the cathode and are simultaneously being washed down into the anode collection chamber **60**. The anolyte is then removed at outlet **3**. The sweep of the feed electrolyte through the porous diaphragm-anode combination **6** and **2*a*** carries anodic oxidation products, for example, chlorine, away from the anode metal where such products can be extremely destructive to the metal. Also, the sweep of the electrolyte assures a maximum concentration of fresh feed electrolyte at the anode surface, and also at the surface of the membrane **10**. The use of a diaphragm separating the anode from the membrane will also prevent attack and erosion of the membrane surface by oxidants of the anolyte solution, especially dissolved and gaseous chlorine. The oxidants formed at the anode are prevented from contacting the membrane surface since the sweep of electrolyte feed solution will essentially flush back these highly corrosive products. It is therefore readily apparent that the use of a four-compartment cell utilizing porous electrodes as a diaphragm support material, combined with unsubmerged operation of the electrodes in accordance with this invention, results in superior and unexpected advantages over prior art electrolytic apparatus.

Of course, the cell of FIGURE 4 can be modified so that only one electrode whether cathode or anode is used as a porous support medium for the diaphragm with the remaining electrode being of the conventional type. Also, both electrodes can be operated completely or partially submerged or varied so that only one electrode remains submerged in liquid.

The electrolyte employed may be any water soluble electrolytic material such as inorganic salts, acids and bases and organic salts. In the case that the electrolyte is of a basic or acid nature, the processes disclosed herein are applicable toward its purification of ionic impurities; such as cationic impurities, in the instance of the electrolyte being of acidic nature, and anionic impurities in the instance of the electrolyte being of basic character. The employment of an electrolytic salt whose corresponding acid is weakly ionized, for example, sodium acetate or potassium fluoride, permits, as a result of such anodic formation of the slightly ionized acid a relatively small quantity of free hydrogen ions available for migration toward the cathode, with a corresponding reduction in the flow rate of the feed electrolytic solution to conform to the degree of ionization of the corresponding acid, whereby said reduction in flow rate permits a comparatively high degree of transference of the alkali metal cation into the cathode compartment, and correspondingly, less of the original electrolyte solution passing through the diaphragm into the anolyte compartment. Employment of such salts in the process of this invention thereby produces a catholyte effluent product, of the corresponding caustic at a comparatively high rate and a production of anolyte effluent of the corresponding acid, associated with a comparatively small amount of the original electrolytic salt. It is apparent that the processes of this invention thus afford efficacious methods for the preparation of organic acids and inorganic acids of slight ionization from their corresponding soluble salts.

Application of these processes toward the electrolysis of inorganic salts whose corresponding acids are strongly acidic, for example, sodium sulfate or potassium chloride, results in the production, as the anolyte effluent product, of a mixture of such acid with the original inorganic salt, the ratio between the two constituents being determined by the rate at which the electrolytic solution is introduced into the anode feed compartment. In the case of the electrolyte being a salt of a dibasic or tribasic acid, the anolyte product will be the corresponding acid salt and accompanied to a small degree by some of the original salt. The flow rate of the eletrolytic solution may be regulated so that the salt content of the anolyte product is of a desired value, for example, in the case of sodium sulfate, the flow of an aqueous solution of the same into the anode feed compartment may be regulated so that the anolyte effluent product is solely a solution of sodium bisulfate, i.e., the rate will be controlled so that the equivalents of the original salt entering the anode compartment are equal to the equivalents of sulfuric acid being formed therein.

The temperature of the electrolytic feed solution and the catholyte influent water may vary from above its freezing point to below its boiling point. However, in general, it is preferred that relatively high temperatures be employed, i.e., above about 60° C., since the impressed voltage required to pass a specific current through an electrolytic cell tends to vary inversely with the temperature of the electrolytic medium.

The anode employed is a chemically-resistant conductive material and may be, for example, of platinum, rhodium, or noble metal coated tantalum or titanium. The cathode of FIGURES 1 and 2 is of conventional construction, being conveniently of steel or nickle. The electrodes may properly be positioned in either of two methods. An electrode may be fixed to a side of its compartment as shown in FIGURES 1 and 2 or suspended in it by conventional means. It may, depending upon the nature of the diaphragm or permselective membrane employed, be necessary or desirable to utilize the electrode as a support for such diaphragm or membrane in which case a foraminous electrode is constructed, preferably in the form of a screen mesh or expanded metal and positioned contiguous to the partition being supported.

Such a cell incorporating expanded metal electrodes is diagrammed in FIGURES 2 and 4 and a section of the expanded metal itself in FIGURE 5.

Expanded metal is the preferred material for use as foraminous supporting electrodes and is readily available commercially. The expanded mesh is made by cutting in alternately placed rows a series of fine slits in a sheet of the desired metal and pulling the sheet perpendicular to the direction of the slits, resulting in the expansion of the slits to form essentially diamond- or other shaped holes. As seen in FIGURE 5, the diamond-shaped holes **21** can be made in various dimensions so that the total available surface area of the metal **22** will vary correspondingly. For use as an anode, the expanded material is fabricated from an electrolytic valve metal preferably tantalum, titanium, or niobium, which is coated with a noble metal such as platinum or rhodium. For purposes of this invention, the dimension of the diamond-shaped holes should be small enough to allow proper support of a microporous diaphragm, but also sufficiently large so as to not offer any appreciable resistance to hydraulic flow therethrough. The holes are of a size larger than the pore size of the porous diaphragm.

Although the use of noble metal coatings of electric valve metals as electrodes is well known in the art, the combination of such expanded metals as both an electrode and a support media for a porous diaphragm makes it unique. Such support makes it possible to employ diaphragms (less than .010″ thick) in electrolytic cells without adding appreciably to the total electrical resistance of the electrolytic cell. Without such support, it is not possible to use extremely thin and fragile diaphragms by themselves. Expanded metal electrodes have an advantage over microporous metal or carbonaceous electrodes in that disengagement of those gases produced at the electrode surface during electrolysis is more readily accomplished.

The non-permselective diaphragm is of such design and porosity that it will allow passage of electrolyte solution under a hydraulic head or other pressure means therethrough, and is preferably of such suitable microporous material such as rubber, ceramic, polyethylene, canvas, polyvinylchloride, asbestos, polytetrafluoroethylene, or other synthetic fabrics.

The cation permselective membrane is commonly of the type consisting of cation-exchange resin prepared in the form of thin sheets; said membranes being substantially impervious to water and to ions carrying a negative charge but permeable to ions carrying a positive charge. Permselectivity toward cations is defined as the membrane's possession of a higher transport number for cations than that of the solution in which it performs. It is essential that the membrane employed in the processes of the present invention have as high a cation transport number as possible and be substantially nonpermeable to anions.

The art contains many examples of cation-exchange materials which can be formed into cation-permselective membranes. The mechanism underlying the operation of an ion-exchange membrane is determined from its construction which consists of a polymeric structure containing dissoluble ionizable radicals, one ionic compound being fixed into the polymeric matrix, the other a mobile and replaceable ion electrostatically associated with the fixed compound. The replacement of the mobile ions by ions of like sign in the solution in which the membrane is immersed is the particular property of such membranes which characterizes it as an ion exchange material. The type of cation exchange membrane ordinarily affording the highest permselectivity toward cations is that in which carboxylic acid groups are fixed into a polymeric matrix, the preparation of one such preferred type of membrane being described in U.S. Patent 2,731,408, wherein is disclosed a method for preparing membranes consisting of a matrix of copolymers of divinyl benzene and an olefinic carboxylic compound. For example, divinyl benzene and an olefinic carboxylic compound such as an anhydride, ester, or chloride derivative of acrylic acid are copolymerized in a suitable solvent. The solid polymeric material recovered is then saturated with water or an aqueous solution of an acid or base to convert the anhydride, ester, or acid radicals in the polymeric matrix to their acidic or alkali metal salt form. Alternative cation exchange materials may be prepared by the condensation of resorcylic acid with formaldehyde, by the use of sulfonated or carboxylated humic materials, etc.

The resinous material is incorporated into a sheet-like reinforcing matrix in order to increase the mechanical strength and heat resistance of the membranes. Suitable reinforcing materials include, for example, woven or felted materials, such as glass filter cloth, polyvinylidene chloride screen, cellulose paper, asbestos, polytetrofluoroethylene or Saran cloth and similar porous materials of adequate strength.

The process of this invention relating to the conversion of soluble salts into their corresponding metal hydroxide and acid salts with the recovery of such products are illustrated by the following examples which are not to be construed as limiting.

Example 1

An electrolytic cell as shown in FIGURE 2 was operated to convert an electrolyte of sodium sulfate into sodium hydroxide and its acid salt of sodium bisulfate. It employed a platinized expanded titanium anode **2** on which was supported a .010″ thick microporous polyethylene diaphragm **6**. This diaphragm thus defines and separates the anode compartment **8** from the anode feed compartment **5**. The cathode compartment **9** contained a nickel sheet cathode **11** and was separated from the anode feed cell **5** by a self-supporting carboxylic type cation-exchange membrane **10** made as a copolymer of acrylic acid and divinyl benzene. The spacing between electrodes was about ¼″. A 10% solution of sodium sulfate was introduced into the anode feed compartment through conduit **7** at such a rate and pressure that the percolation of this electrolyte through the porous diaphragm **6** and expanded anode **2** was sufficient so as to appreciably prevent the back migration or diffusion of anodic products into the anode feed compartment. Since the positively charged hydrogen ions formed at the anode surface tend to travel in the direction of the negatively charged cathode, the sodium sulfate electrolyte is allowed to percolate through the microporous diaphragm at a velocity greater than that of the opposing migrating hydrogen ions. The result being that the hydrogen ions are effectively washed back into the anode compartment. Water is introduced into the cathode compartment through a conduit **12** at a rate depending upon the caustic concentration desired as the catholyte product. The catholyte product and anode product effluents were recovered respectively from overflow outlets **13** and **3**. The electrolysis was conducted at a current density of 100 amps per square foot of membrane area. The total cell voltage was 4.3 at a solution temperature of 80° C. At steady state conditions, the catholyte effluent from outlet **13** analyzed to be 2 normal NaOH and the anode effluent from outlet **3** analyzed to 0.75 normal acid concentration, representing a current efficiency of 90%. The electrodes were operated substantially submerged in solution as shown by the liquid levels **48** and **49**.

Example 2

The cell configuration indicated by FIGURE 4 was employed to electrolyze a solution of sodium chloride using unsubmerged operation of both porous electrodes as shown by the liquid levels at **48** and **49**. The same type cation-exchange membrane **10** was used in this example as that of Example 1. The cathode **11***a* was made of 8 mesh nickel screen which supported a .010″ thick microporous polyvinyl chloride diaphragm containing average pore sizes in the order of 10–16 microns. The anode **2***a* consisted of platinized expanded tantalum having diamond-shaped holes measuring ¼″ in its longest dimension and ⅛″ across. Because of the highly corrosive nature of the anolyte solution, a chemically inert microporous Teflon diaphragm **6** (porosity size 15–20 microns) was used as the partition between the anode chamber **8** and anode feed chamber **5** and was supported by the expanded anode. Since both electrodes were the porous type, it was possible to lessen the electrode spacing distance to less than ¼″.

Saturated brine and water were used as the feed solutions to the anode feed chamber **5** and cathode feed chamber **15**, respectively, by means of their respective inlet conduits **7** and **12**. During operation the feed solutions were allowed to percolate through their respective porous diaphragms at a rate and pressure sufficient to minimize back migration of the products formed at the electrode surfaces. The passed solution would then trickle down the full length of their respective electrode surfaces carrying therewith the products formed at the electrodes into the lower placed collection chambers **60** and **61** from which they were withdrawn through effluent conduits **3** and **13**. The electrolysis produced a catholyte effluent of sodium hydroxide and hydrogen gas and an anolyte effluent of hydrochloric acid, chlorine gas and unreacted excess sodium chloride.

The electrolysis was conducted at 125 amps per square foot of membrane area, at a total cell voltage of 4.1 and at a temperature of 95° C. The steady state cathode product was 4.4 normal rayon grade caustic, representing a current efficiency of 95%. The caustic in the cathode feed chamber analyzed to less than 1.2 normal.

The above examples represent a few typical methods of operation that can be performed with electrolytic cells of this configuration and as such are not intended to limit the area of this invention to only such operations.

Another novel application of the processes of the present invention is directed toward the removal of carbon dioxide from air or other gases, said application being of particular significance with respect to purification of air in closed systems wherein it is either inconvenient or impossible to introduce a continuing supply of materials such as carbon dioxide absorbing fluids; an example of such a closed system being a submarine. This application comprises the following steps and installations:

(1) An electrolytic cell equivalent in design and function to those described herein is constructed and operated with an electrolytic influent feed solution of sodium sulfate, for example, 3 N. The catholyte effluent product is aqueous sodium hydroxide and the anolyte effluent product is sodium bisulfate. The anode compartment is also the site for the production of oxygen which is passed into the atmosphere of the particular system being purified.

(2) The product sodium hydroxide solution is conducted to a "scrubbing" apparatus wherein the atmosphere or particular gas whose purification is desired is passed and its content of carbon dioxide absorbed by the caustic, forming sodium carbonate. The carbonate-containing solution is then (3) combined with an equivalent amount of the anolyte effluent product sodium bisulfate to regenerate the original sodium sulfate feed solution. This sodium sulfate solution is recycled (4) to the electrolytic cell. Since the sodium sulfate is thus substantially regenerated, the production of oxygen is dependent wholly upon the electrolysis of water, whose source is ordinarily readily available.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom conforms to the spirit of the invention and is intended within the scope of the claims.

Thus, having described the invention, what is claimed is:

1. A four-compartment electrolytic cell comprising a terminal anode compartment, an adjacent anode feed compartment, a next adjacent cathode feed compartment and a terminal cathode compartment, said terminal compartments containing therein an anode and cathode repectively, the terminal anode compartment separated from its adjacent anode feed compartment by a first liquid-permable porous diaphragm, the terminal cathode compartment separated from its adjacent cathode feed compartment by a second liquid-permeable porous diaphragm, said feed compartments of anode and cathode being separated and defined from each other by a cation-selective ion-exchange membrane, inlet means only for passing an electrolyte solution into said anode feed compartment with means for maintaining pressure in said feed compartment greater than the pressure in the adjacent anode compartment to cause said electrolyte solution to pass through said first liquid-permeable diaphragm into said anode compartment, inlet means only for passing an electrolyte solution into said cathode feed compartment with means for maintaining a pressure in said feed compartment greater than the pressure in the adjacent cathode compartment to cause said electrolyte solution to pass through said second liquid-permeable diaphragm into said cathode compartment, means for impressing a direct current transversely through said compartments, membrane and porous diaphragms, and separate outlet means only for withdrawing from the anode and cathode compartments solutions and gaseous electrode products from each of said compartments.

2. The cell of claim 1 wherein at least one electrode is comprised of a foraminous material on the surface of which is deposited a porous diaphragm, said porosity of the electrode being greater than that of said porous diaphragm.

3. The cell of claim 2 wherein the foraminous electrode consists of expanded metal material.

4. The cell of claim 1 wherein the fluid-permeable porous diaphragms consist of microporous polyvinyl chloride.

5. The cell of claim 1 wherein the fluid-permeable porous diaphragm consists of polytetrafluoroethylene material.

6. The method of converting electrolytic salt solutions into their corresponding acid and base solutions in a four-compartment electrolytic cell having a terminal anode compartment separated from its adjacent anode feed compartment by a first fluid-permeable porous diaphragm, a terminal cathode compartment separated from its adjacent cathode feed compartment by a second fluid-permeable porous diaphrgam, said feed compartments being separated and defined from each other by a cation-selective ion-exchange membrane, the method comprising introducing said salt solution into the anode feed compartment while maintaining a pressure in said feed compartment to cause said salt solution to pass through said first liquid permeable diaphragm into said anode compartment, introducing an electrolytic solution into the cathode feed compartment while maintaining a pressure in said feed compartment to cause said electrolyte solution to pass through said second liquid-permeable diaphragm into said cathode compartment, passing a direct current transversely through said compartments, membranes and porous diaphragms, to cause migration of cations from the anode feed compartment into the cathode compartment, and removing the corresponding acid and base solutions and gaseous electrode products from the anode and cathode compartments respectively.

7. The method of claim 6 wherein at least one electrode is operated unsubmerged.

8. The method of claim 6 wherein the solution introduced into the cathode feed compartment is water.

9. The method of claim 6 wherein the feed salt solution to the anode feed compartment is sodium sulfate and the products obtained are essentially solutions of sodium hydroxide and sodium bisulfate, and gases of hydrogen and oxygen.

10. The method of claim 6 wherein the feed salt solution to the anode feed compartment is sodium chloride and the products obtained are essentially solutions of sodium chloride and hydrochloric acid, and gases of hydrogen and chlorine.

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JOHN H. MACK, *Primary Examiner.*

JOSEPH REBOLD, MURRAY TILLMAN, *Examiners.*