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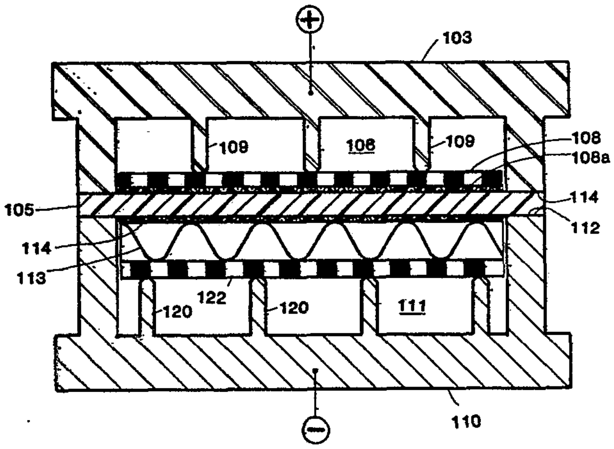
(54) **Method of generating halogen, an electrode-membrane assembly, an electrolytic cell and a semipermeable ion-exchange membrane for said method.**

(57) Aqueous alkali metal hydroxide is electrolyzed to generate elemental halogen in a cell having a sandblasted membrane (105) or other rough or abraded surfaced ion exchange membrane (105) with the rough surface exposed to electrolyte. While the surface may be on either the anodic or cathodic side lower voltage is attained when it is on the cathodic side. This is especially true when the cathode has an open structure and is in direct contact with the rough surface but unbonded thereto whereby liquid electrolyte is in ready contact both with the electrode and the membrane (105). The electrode is gas and electrolyte permeable and may be in the form of an electroconductive screen (108a, 114) or several electroconductive screens (108a, 114) in face to face contact. These screens (108a, 114) or opposed surfaces thereof may have different hydrogen or halogen overvoltages. Often in such a case the film or screen surface having the higher overvoltage is in contact with the rough membrane (105) surface and the surface or screen having the lower overvoltage is spaced from the membrane (105) with the higher overvoltage surface interposed between the membrane (105) and the lower overvoltage surface. The low overvoltage surface of course is in direct electrical contact with the higher overvoltage surface. Generally the surface having the low overvoltage is greater in area than the surface having the high overvoltage.



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Specification

The invention herein is directed to electrolysis of aqueous electrolytes and is particularly concerned with the electrolysis of aqueous halides such as hydrogen halide or alkali metal halide to generate halogen in elemental state.

State of the Art

It is known to electrolyze aqueous alkali metal chloride or like halide in a membrane cell having an ion exchange (normally cation exchange) membrane which separates anode from cathode. Since the membrane itself is generally impermeable or substantially so to gas and liquid flow, the electrolysis generates chlorine at the anode and alkali at the cathode the alkali being of high purity and containing only very low chloride concentration.

One type of cell which has been proposed for such electrolysis is the solid polymer electrolyte cell.

A solid polymer electrolyte cell is characterized by an ion exchange membrane, which separates electrode of the cell and by the fact that one or both electrodes are in intimate contact with the membrane. Frequently these electrodes are deposited in the form of a porous coating or layer of electrocatalytic and electroconductive material, resistant to the electrolysis conditions. The current distribution over the electrodes bonded onto the membrane is provided by current conducting grids pressed against the electrodes. The solid polymer electrolyte cells present (with respect to conventional membrane cells in which the cathode and frequently both anode and cathode are separated from the membrane) several advantages useful in different electrolysis processes. More precisely :

1) The overall voltage between electrodes is lower because the interelectrodic distance is reduced practically to the membrane thickness.

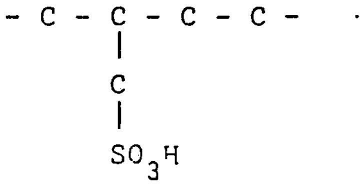
2) The so-called "bubble effect" is eliminated or at least minimized, i.e. the difficulty normally encountered in electrolytic processes where gas is evolved at the electrode accumulates in the zone between electrodes is avoided because evolved gas can be released behind the electrodes to the inside of the cell compartment.

3) The cells may be very compact and thus the ohmic drops at the current distribution structures can be reduced.

The ion permeable diaphragms are cation exchange polymers in the form of thin flexible sheets or membranes. Generally they are imperforate and do not permit a flow of anolyte into the cathode chamber but it has also been suggested that such membranes may be provided with some small perforations to permit a small flow of anolyte therethrough, although the bulk of the work appears to have been accomplished with imperforate membranes.

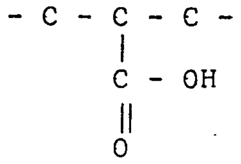
Typical polymers which may be used for this purpose include fluorocarbon polymers such as polymers of trifluoroethylene or tetrafluoroethylene or copolymers thereof which contain ion exchange groups are used for this purpose. The ion exchange groups normally are cationic groups including sulfonic acid, sulfonamide, carboxylic acid, phosphonic acid and the like, which are attached to the fluorocarbon polymer chain through carbon and which exchange cations. However, they may also contain anion exchange groups.

Typical such membranes have the general formula :



$$-\mathrm{C}-\underset{\underset{\mathrm{SO_3H}}{|}}{\underset{\mathrm{C}}{\underset{|}{\mathrm{C}}}}-\mathrm{C}-\mathrm{C}-$$

or



$$-\underset{\underset{\underset{O}{\|}}{C-OH}}{\overset{}{C}}-$$

Such membranes include those fluorocarbon ion exchange polymers manufactured by the Du Pont Company under the trade name of "Nafion" and by Asahi Glass Company of Japan under the trade name of "Flemion". Patents which decribe such membranes include British Patent No. 1,184,321 and U.S. Patent No. 3,282,875 and No. 4,075,405.

Since these diaphragms are ion permeable but do not permit anolyte flow therethrough, little or no halide ion migrates through the diaphragm of such a material in an alkali chloride cell and therefore the alkali thus produced contains little or no chloride ion. Furthermore, it is possible to produce a more concentrated alkali metal hydroxide in which the catholyte produced may contain from 15 to 45% NaOH by weight or even higher. Patents which describe such a process include U.S. Patents No. 4,111, 779 and No. 4,100,050 and may others. The application of an ion exchange membrane as an ion permeable diaphragm has been proposed for other uses such as in water electrolysis.

In cells of the type contemplated, the cathode is in close proximity to or in direct contact with the ion exchange membrane. They must be sufficiently permeable to permit rapid escape of evolved gas from the points of their evolution and to provide ready access of liquid electrolyte to these points as well as rapid removal of evolved alkali or other electrolysis produced from such points. Thus the electrodes are normally quite porous.

In an effort to simplify and reduce the cost of constructing such cells foraminous electrodes (screens or the like), which are not bonded to the membrane, have been tested. However, it has been noted that this may be accomplished by an increase in cell voltage and/or reduction in cathode efficiency. This is particularly true when more concentrated alkali containing for example 20 percent by weight or more of NaOH of equivalent alkali is produced.

The Invention

According to this invention it has been found that lower voltage in this process can be achieved with unbonded electrodes if the ion exchange membrane surface is rough, i.e. has a roughened or abraded or porous surface. Thus it is found, particularly in the case of carboxylic membranes, that the cell voltage may be reduced substantially by roughening the normally smooth surface of the ion exchange polymer, for example by sandblasting or by other convenient method of roughening the membrane surface, such as by sputter etching, embossing, pressing powdered ion exchange polymer into the membrane surface, sandpapering, sandblasting such surface or by other convenient method.

The visual effect of this treatment is to substantially reduce the transparency of the membrane which typically is made opaque or barely translucent by the roughening process. In use, however, transparency may slightly increase.

The surface, after roughening treatment, has an increased surface area. Where sandblasting is used as the roughening method and the treatment is intense enough, the surface is characterized by the presence of microcracks or pits of small diameter of width (usually less than 10 microns and often 1 to 5 microns or less, even being below one micron).

These surface imperfections are shallow rarely being greater in depth of 5 or 10 microns and generally less than one micron.

Where sputter-etching is used as the roughening method, the surface is typically of a papillar or needle-like nature. The papillas or needles have a height generally above 0.5 microns, preferably between 1 and 6 microns, and are uniformly distributed over the surface. The distance between crests rarely exceeds 50 microns and preferably is below 10 microns, usually being 0.1 to 5 microns.

Embossing, for example, by rolling the membrane through roughened rolls surfaces is also a convenient way to produce the desired roughening of the membrane surfaces.

The exact reason for the observed voltage reduction is not clearly understood. Quite possibly it may be due to an effective increase in overall surface area of the membrane which is exposed to and in contact with the electrolyte (either anolyte or catholyte or both).

For example, it is known that during operation, concentration gradients arise at the interfaces between the membrane surface and the anolyte and between the opposite surface of the membrane and the catholyte. Such concentrations gradients act as potential barriers opposing to the migration of the ions, which are carriers of the electrolysis current across the cell. One can visualize these concentration gradients as representing the interfacial ohmic drops due to the presence of the membrane with ion transport characteristics different to those of the liquid electrolytes along the passage of the electrolysis current across the cell. These ohmic drops can not be completely inhibited and their substantial contribution to the overall cell voltage is well accepted and understood.

It is believed, without being bound by these theories, that the modification of the morphology of the membrane surface, which consists of changing the essentially smooth surface of the membrane in a needlelike or pitted surface, substantially improves the electrochemical behaviour of the membrane through various mechanisms:

a) the modification of the surface morphology results in a substantial increase of the real exchange area of the interface between the membrane and the liquid electrolyte contacting the membrane itself. Consequently, the kinetics of the diffusive ion transfer through the boundary layer appears to be highly favoured. The increase exchange surface corresponds to a proportional decrease in the real ion current density.

b) The peculiar morphology of the membrane surface modified according to the process of the present invention improves the efficiency of the convective ion transfer due to the motion normally imposed to the electrolyte near the membrane surface, said motion being either induced by forced circulation or generated by gas evolution on the adjacent electrode surface.

c) The wettability of the membrane surface by the liquid electrolyte is also improved by the increased roughness.

Thus the cathodic side or the anodic side of the membrane or both sides thereof may be provided with the rough surface. The roughness herein contemplated is in addition to any irregularity in the surface which may be caused by the relatively coarse fabric reinforcement which is often present as an interlayer in such membranes. That is in the present invention the polymer between the meshes of the tetrafluoroethylene fabric is rough or roughened.

The electrode normally bears against the rough surface but remains unbonded to such surface although it may also be spaced from the roughened surface of the membrane. The electrolyte has free access to both the surface of the electrolyte permeable electrode and the rough surface of the membrane and evolved gas is free to escape. Of course the periphery or a portion thereof or one or more small centrally located local areas of the electrode may be bonded or spot bonded to the membrane to minimize separation of membrane from electrode. However, the major part and generally 75 to 90 percent or even all of the electrode surface remains unbonded to, but preferably pressed against the roughened surface of the membrane.

The active electrode surface where the halogen or hydrogen or other electrolytic reaction takes place may bear directly against or be pressed against the rough surface. Alternatively the electrode may be a composite which as an intermediate electroconductive surface which has a relatively high overvoltage (hydrogen or halogen) and which is in direct contact with the rough or abraded surface of the membrane and a further surface spaced from the membrane which has a lower overvoltage where the electrolytic reaction (cathodic or anodic) predominately takes place.

For example, the electrode may comprise a pair of electroconductive screens, the first or foremost of which is pressed against the rough membrane surface but has a relatively high overvoltage (hydrogen or halogen as the case may be) and a second screen or layer of several screens of lower overvoltage which is pressed against the rear surface of the first screen. According to a further embodiment, the electrode may comprise a single electroconductive screen or wire mat having a single surface or surface coating of relatively high overvoltage in contact with the rough membrane surface and a more remote portion which has a lower overvoltage surface or which is coated with a material such as platinum group metal or conductive oxide thereof of relatively lower overvoltage generally the area of the low overvoltage surface substantially exceeds often by 25-50% or more the area of the high overvoltage surface.

Where a cathode of a single composition (exposed surface) is used the cathode may comprise a nickel or iron or stainless steel or copper porous foil or screen open to gas and electrolyte flow. Such screen or foraminous foil may if desired be coated with a metal or metal oxide or other conductive and corrosion resistant material having an exceptionally low hydrogen overvoltage such as a platinum group metal or oxide; e.g. ruthenium oxide, palladium oxide, platinum metal, nickel sulfide or the like.

Where the cathode has two surfaces - one high, the other low hydrogen overvoltage, the high overvoltage cathode surface may comprise stainless steel, iron or nickel in the form of a screen of such metal or may comprise a silver or cadmium or like metal coating on a nickel or stainless steel or iron screen. Alternatively the nickel or silver or like metal may be in the form of a thin porous foil. The low overvoltage section may have a surface comprising a platinum group metal or oxide thereof or nickel sulfide or other such material of lower hydrogen overvoltage.

The membrane surface is abraded or roughened sufficient to effectively increase the surface area in direct contact with the electrolyte. Thus the surface area of the abraded surface of a membrane of given size generally is at least about 25 percent and often 50 to 100% or more greater than the surface area of a membrane of such size or dimension with a smooth surface. For example, a square membrane sheet one meter square has an overall or enclosed area of one square meter. However by adequate sandblasting or etching or embossing, the sheet may be roughened enough to increase its surface area to 1.25 - 1.5 square meters or even higher although the overall area enclosed by the periphery of the sheet remains the same.

Generally the depth of penetration of the pitted or roughened area is small, rarely exceeding about 25 microns and generally the depth of the roughened area is below 10 microns, generally being below 5 microns. Also the average distance between crests of the roughened area is small, rarely exceeding 50 microns and preferably being below 10 microns, usually being 0.1 to 5 microns.

The roughening of the membrane surface may be achieved by sandblasting the membrane one or more times with sand or quartz particles of 50 to 150 microns for a few seconds up to one or two minutes, rarely more than 20-30 seconds per treatment. Also it may be accomplished by cathode sputter etching or by embossing the sheet or by casting the sheet in contact with a roughened mold surface.

The treatment is advantageously accomplished by laying the membrane upon a solid surface which is usually horizontal but may be vertical or inclined to the vertical and the horizontal. The roughening may be accomplished by applying the roughening treatment to the exposed surface of the supported membrane.

Generally the abrading of the ion exchange polymer is achieved by sandblasting or otherwise abrading a dry polymer, i.e. a polymer sheet which is in equilibrium with the atmosphere under ordinary temperatures and humidity. For example, the sandblasting may be conducted in air at a temperature of 10 to 35°Centigrade. The dry sheet is one in equilibrium with the atmosphere at 10 - 35°C and normal relative humidity for example 40-60%. Often it contains some water. The amount of water present depends upon the concentration of ion exchange groups therein and for membranes having 1 to 1.6 milliequivalents of ion exchange capacity per gram of dry polymer the water content may be 0.04 to 0.15 grams of water per gram of dry membrane. When the temperature of the membrane to be subjected to sandblasting is higher the water content may be lower, unless the atmospheric humidity is higher.

The dry sheet is conveniently sandblasted by impinging an air stream of quartz particles having a particle size of 50 to 150 microns or even finer against the dry membrane at room temperature.

Large size membranes have been successfully sandblasted by laying the membrane vertically against a steel plate mounted on a carriage which is drawn horizontally at a constant speed of 220 mm/min.

A spray gun, operating with compressed air at 5 kg/cm^2 and equipped with a spray nozzle of 9.0 mm diameter spaced 70 mm from the surface of the membrane is moved up and down at a substantially constant speed of 325 mm/min.

Alternatively the membrane may be cooled to below 10°C for example 0 to minus 25°C or lower and the refrigerated membrane sandblasted.

According to a further embodiment of this invention the membrane may be swelled for example by boiling in water or heating at 50 to 120°C in aqueous alkali metal hydroxide containing for example 5 to 40% by weight of NaOH until the swelling of the membrane has stabilized. Such a membrane is swelled up to about 5-10 percent in each direction of its original dimensions and may contain up to about 25% by weight of water. A membrane so swelled may be abraded or sandblasted for use as herein contemplated.

At all events the roughened membrane is swelled by hydrolysis before being assembled in the cell. Usually this is done by immersion in hot diluted alkali metal hydroxide or diluted brine and generally this swelling or conditioning is effected after the sandblasting or equivalent roughening process. This may expand the size of the pits or imperfections in the membrane surface. However microcracks produced in the surface by the sandblasting tend to be sealed by the swelling so as to reduce likelihood of leakage or flow of anolyte or catholyte across the membrane through such cracks.

The electrode in contact with the rough surface should be permeable to liquid electrolyte and evolved gas. Thus it may be a permeable screen or wire mat or even a porous foil. Because it is unbonded to the rough surface free access of electrolyte and escape of evolved gas from between the membrane and the screen is ensured.

A cell particularly useful for this purpose is one diagrammatically illustrated in the accompanying drawing in which:

Fig. 1 is a diagrammatic horizontal sectional view of the cell having the membrane sandblasted as described above installed therein, and

Fig. 2 is a diagrammatic vertical sectional view of the cell of Fig. 1.

Fig. 3 is an electron microscope photograph showing the surface of an untreated membrane of the laminate type.

Fig. 4 is an electron microscope photograph showing the surface of the membrane of Fig. 3 after the roughening treatment.

Fig. 5 is an optical microscope photograph showing the surface of an untreated membrane of the homogeneous type.

Fig. 6 is an optical microscope photograph showing the surface of the membrane of Fig. 5 after the roughening treatment.

As shown in Figures 1 and 2, the cell comprises an anode end plate 103 and a cathode end plate 110, both mounted in a vertical plane with each end-plate in the form of a channel having side walls respectively enclosing an anode space 106 and a cathode space 111. Each end plate also has a peripheral seal surface on side-walls projecting on each side of the cell from the plane of the respective end plate 104 being the anode seal surface and 112 being the cathode seal surface. These surfaces bear against a membrane or diaphragm 105 which stretches across the enclosed space between the side walls separating anode from cathode. This membrane is provided at least on the cathode side with the roughened surface as described above.

The anode 108 may comprise a relatively rigid uncompressible sheet of expanded titanium metal or other perforate, anodically resistant substrate, preferably having a non-passivable coating thereon sucha as a metal or oxide or mixed oxide of a platinum group metal. This sheet is sized to fit within the side walls of the anode back plate and is supported rather rigidly by spaced electroconductive metal or graphite ribs 109 which are fastened to and project from the web or base of the anode end plate 103. The spaces between the ribs provide for ready flow of anolyte which is fed into the bottom and withdrawn from the top of such spaces. The entire end plate and ribs may be of graphite, alternatively, they may be of titanium clad steel or other suitable material. The rib ends bearing against the anode sheet 108 may or not be coated, e.g. with platinum or like metal to improve electrical contact and the anode sheet 108 may be also welded to the ribs 109. The anode rigid foraminous sheet 108 is held firmly in an upright position. This sheet may be of expanded metal having upwardly inclining openings 10 directed away from the membrane (see Fig. 2) to deflect rising gas bubbles towards the space 109 and away from the membrane.

More preferably, a fine mesh pliable electrolyte permeable screen 108a of titanium or other valve metal coated with a non-passivatable layer which is advantageously a noble metal or conductive oxides having a low chlorine overvoltage for the anodic reaction (e.g. chlorine evolution), is disposed between the rigid foraminous sheet 108 and the membrane 105. The screen 108a usually a fine mesh screen provides a density of contacts of extremely low area with the membrane in excess of at least 30 contacts per square centimeter. It may be spot welded to the coarse anode screen 108 or not as described.

On the cathode side, ribs 120 extend outward from the base of the cathode end plate 110 a distance which is a fraction of the entire depth of the cathode space 111. These ribs are spaced across the cell to provide parallel space for vertical electrolyte flow from bottom to top and engage the cathode which is in sheet or layer from i.e. it's thickness dimension is much less than its width and height. The cathode end plate and ribs may be made of steel or a nickel iron alloy or other cathodically resistant material. On the conductive ribs 120 is welded a relatively rigid pressure plate 122 which is perforate and readily allows circulation of electrolyte from one side thereof to the other. Generally, these openings or louvers are inclined upward and away from the membrane or compressible electrode toward the space 111 (see also Fig. 2). The pressure plate is electroconductive and serves to impart cathodic polarity to the electrode and to apply pressure thereto and it may be made of expanded metal or heavy screen of steel, nickel, copper or alloys thereof.

A relatively fine flexible screen 114 bears against the rough surface which is on the cathode side of the active area of diaphragm 105. This screen because of its flexibility and relative thinness, assumes the contours of the diaphragm and therefore that of anode 108. A metal screen mat 113 is disposed behind the screen and this compressible mat is cathodic and serves as part of the cathode surface or at least is cathodically polarized. The screen 114 is composed of nickel wire or other electroconductive cathodically resistant wire which has a surface of relatively low hydrogen overvoltage and may be coated with a lower hydrogen overvoltage coating such a coating of a platinum group metal or oxide thereof.

Preferably two or more electroconductive metal screens are interposed between the rough membrane surface and the compressible mat 113. In such a case it is often advantageous to provide a screen of relatively higher hydrogen overvoltage in direct contact with the membrane surface and a second screen or bank of screens which have a surface of relatively lower hydrogen overvoltage behind but in contact with the higher overvoltage screen. In that case the high overvoltage screen surface may be of iron or steel or nickel, whereas the surface of the more remote screen or screens may comprise a platinum group metal or conductive oxide thereof or nickel sulfide or other low overvoltage coating. Usually the differential in hydrogen overvoltage between the two types of surfaces ranges from 0.05 to 0.5 volts, rarely being above 0.6 volt. Of course the screen surfaces are in close electrical contact with each other since the screens are pressed tightly together and against the membrane by the compressible mat.

The screens advantageously are fine in mesh and provide many contact points of extremely low area with the membrane and with the nex adjacent screen usually being at least 30 contacts per square centimeter. A compressible electroconductive mat 113 is disposed between the cathode screen 114 and the cathode pressure plate 122.

As illustrated in Fig. 1, the mat 113 is a crimped or wrinkled compressible wire-mesh fabric which fabric is advantageously an open, mesh knitted-wire mesh of the type described in U.S. application for United States Letter Patent Serial No. 102629 filed December 11, 1979, wherein the wire strands are knitted into a relatively flat fabric with interlocking loops. This fabric is then crimped or wrinkled into a wave or undulating form with the waves being close together, for example, 0.3 to 2 centimeters apart, and the overall thickness of the compressible fabric is 2 to 10 millimeters. The crimps may be in zig-zag or herringbone pattern and the mesh of the fabric is coarser, i.e. has a larger pore size than that of screen 114.

As illustrated in Fig. 1, this undulating fabric 113 is disposed in the space between the finer mesh screen or screens 114 and the more rigid expanded metal pressure plate 122. The undulations extend across the space and the void ratio of the compressed fabric is, notwithstanding compression, preferably higher than 75%, preferably between 85 and 96%, of the apparent volume occupied by the fabric. The waves extend in a vertical or inclined direction so that channels for upward free flow of gas and electrolyte are provided which channels are not substantially obstructed by the wire of the fabric. This is true even when the waves extend across the cell from one side to the other because the mesh openings in the sides of the waves permit free flow of fluids.

The end-plates 110 and 103 are clamped together and bear against membrane 105 or a gasket shielding the membrane from the outside atmosphere disposed between the end walls. The clamping pressure compresses the undulating fabric 113 against the finer screen or screens 114 and the roughened membrane to a thickness substantially less than the fabric in its uncompressed state. This in turn presses the screen 114 against the membrane and thus the anode surface of the membrane presses against anode 108a.

In the operation of this embodiment, substantially saturated sodium chloride aqueous solution is fed into the bottom of the anolyte compartment of the cell and flows upward through channels or spaces 105 between ribs 109 and depleted brine and evolved chlorine escapes from the top of the cell.

Water or dilute sodium hydroxide is fed into the bottom of the cathode chamber and rises through channels 111 as well as through the voids of the compressed mesh sheet 113 and evolved hydrogen and alkali is withdrawn from the top of the cell. Electrolysis is caused by imparting a direct current electric potential between the anode and cathode end plates.

As shown in Fig. 2 at least the upper openings in pressure plate 122 are louvered to provide an inclined outlet directed upwardly away from the compressed fabric 113, whereby some portion of evolved hydrogen and/or electrolyte escapes to the rear electrolyte chamber 111. Therefore, the vertical spaces at the back of the pressure plate 122 and the space occupied by compressed mat 113 are provided for upward catholyte and gas flow.

By recourse to two such chambers, it is possible to reduce the gap between pressure plate 122 and the membrane and to increase the compression of sheet 113 while still leaving the sheet open to fluid flow and this serves to increase the overall effective surface area of the active positions of the cathode.

According to the improved method of this invention for the electrolysis of sodium chloride, aqueous brine containing from 140 to 300 grams per liter of sodium chloride is circulated within the anode compartment of the cell. Chlorine is evolved at the anode while the solvated ions tend to migrate through the cation membrane and reach the cathode where caustic soda of substantial concentration above 15-20% by weight and hydrogen is evolved. Solutions containing 25 to 40 percent by weight of alkali metal hudroxide may be produced with anode and cathode efficiencies above 90% frequently above 95%.

It will be seen that the cathodically polarized section includes the end plate 110 and pressure plate 122 mat 113 and the screen or assembly of screens 114 which bear against the membrane.

The rear screen and/or the mat 113 is coated with a coating or surface which has a low or substantially negligible hydrogen overvoltage. Typical coatings include a mixture of nickel and conductive ruthenium oxide, platinum black or platinum metal or other such coating of a low hydrogen overvoltage material. The depth of this active area may be expanded by coating the compressible wire fabric 113 with the same material.

Since electrolyte flow is rapid through the compressed fabric 113 and the mesh of the screen 114 a large portion of the sodium hydroxide produced may be evolved a distance away from the membrane surface and in any event evolved sodium hydroxide or other alkali is removed by the flowing electrolyte flowing through the mat and sweeping the screens.

The advantage of the roughened membrane surface is particularly noticeable when the cathode side of the membrane comprises a carboxylic cation exchange polymer (usually fluorocarbon polymer). Such membranes are especially advantageou since they can be used to produce cathode efficiencies above 90 to 95 percent or even higher. By roughening the cathode surface in contact with the cathodically polarized electrode surface it is found that substantially lower voltages may be achieved at current densities of 1000 amperes per square meter or above. Voltage reductions ranging from 10 to several hundred millivolts have been observed by sandblasting the cathode surface of the membrane the amount of the reduction increase with increasing current density.

Somewhat smaller differences may occur with other membranes. Often these membranes are multilayer in structure. One typical example is a membrane comprising a layer of polyfluoroethylene polymer containing sulfonic ion exchange groups an interlayer of a relatively coarse screen or fabric of polyfluoroethylene polymer usually having openings about 0.2 - 0.5 centimeters square and a second ion exchange fluorocarbon polymer having carboxylic ion exchange groups. The several layers are bonded together for example by heat and pressure. Such a laminate has a more strongly acid i.e. the sulfonic side and a more weak acid, i.e. the carboxylic side. The carboxylic layer is generally thinner than the sulfonic layer.

Other laminated membranes may comprise two sulfonic or phosphoric layers of different acidity or concentration of acid groups. For example, two layers of sulfonic ion exchange polymer of different equivalent weights, i.e. different concentration of groups may be bonded together. Also a sulfonic polymer may be treated on one side to reduce the acidity, for example by treating with an amine.

The weaker acid side is generally the cathode side of the membrane.

The figures 3, 4, 5 and 6 are microphotograph of the cathodic side of membranes showing the morphological modification of the membrane surface after the roughening treatment.

The roughening was obtained in both instances by sandblasting with quartz particles ranging in size from a diameter of 50 to 150 microns sprayed by a compressed air gun operating with air at 5 atmospheres pressure through a nozzle of 70 mm diameter maintained at a distance of 25 mm from the membrane surface for a period of about 20 seconds.

Figures 3 and 4 are electron microscope photographs at 320 magnification of the untreated sample (Fig. 3) and of the sample after sandblasting (Fig. 4).

The membrane is a fluorocarbon polymer cation exchange membrane which is a laminate of two layers bonded together with an interlayer of polytetrafluoroethylene mesh for mechanical support. One of these layers is a copolymer of tetrafluoroethylene and perfluorovinylether sulphonyl acid having an equivalent weight of about 1100. The other layer is a film of a copolymer of tetrafluoroethylene and a perfluoroethylene ether which contains carboxylic groups. This carboxylic sheet also has an equivalent weight of about 1100. The surface shown in Figures 3 and 4 is that of the carboxylic side of the laminated membrane.

Figures 5 and 6 are optical microscope photographs at 200 magnification of the untreated sample (Fig. 5) and of the same sample after sandblasting (Fig. 6).

The membrane is an unsupported homogeneous sheet of a copolymer of tetrafluoroethylene and of a sulphonyl fluorinated perfluorovinylether as produced by Du Pont de Nemours under the designation of Nafion(R) 120.

The following examples are illustrative:

EXAMPLE I

The membrane treated is a fluorocarbon polymer cation exchange membrane which is a laminate of two layers bonded together. One of these layers is a copolymer of a polyfluoroethylene (tetrafluoroethylene) and a perfluorovinyl ether sulfonyl fluoride (or acid) having an equivalent weight of about 1100. The other layer is a sheet of a copolymer of the polyfluoroethylene (tetrafluoroethylene) and a perfluoroethylene ether which contains carboxylic groups. This carboxylic sheet has also an equivalent weight of about 1100.

The two layers are laminated and bonded together with an interlayer of polytetrafluoroethylene screen to provide mechanical support. The membrane is dry, i.e. it is in equilibrium with the normal humidity of the surrounding atmosphere and the sandblasting is conducted at 20 to 25 degrees centigrade. The thickness of the membrane is 0.3 millimeters with the carboxylic layer being about 0.1 millimeters.

Square sheets of this type of membrane 10 centimeters by 10 centimeters are laid vertically on a smooth solid base and sandblasted on the carboxylic surface with quartz particles ranging in diameter from 50 to 150 microns, sprayed by compressed air at 5 atmospheres pressure through a nozzle maintained at a distance of 25 millimeters from the membrane surface over a period of about 30 seconds. The carboxylic surface of such sheets is thus roughened.

Several treated sheets are assembled in different cells of the type described above after conditioning by heating at about 80°C in an aqueous solution containing 2-3 percent by weight of sodium chloride until the dimensions of the sheet (swelling) has stabilized.

The cells have anodes as described above comprising expanded titanium metal with an electroconductive ruthenium oxide coating thereon. A fine flexible ruthenium oxide coated titanium screen is interposed between the expanded metal and the anode (sulfonic) side of the membrane.

The sheets are installed with the sandblasted carboxylic surface on the cathode side. As illustrated in the drawing and described above the cathode comprises a cathode backplate and pressure plate engaging a knitted metal crimped compressible mat 113 which compresses against the screen or screens which in turn are pressed against the membrane surface.

In one test the membrane is unsandblasted and has only such surface irregularity as is imparted by the reinforcing polyfluoroethylene screen. In other tests the sandblasted membrane is in contact with a single screen (runs no. 2 and 3). In others several screens are assembled and pressed by the mat against the screens. In these cases (Runs 3 to 6) the screen surface bearing against the membrane has a higher hydrogen overvoltage than does the more remote screen. The order of arrangement of cathode parts is : pressure-plate - mat - first screen - second screen - membrane.

The cell is operated circulating aqueous brine containing 215 to 225 grams per liter of sodium chloride through the anolyte compartment and aqueous sodium hydroxide through the catholyte compartment with enough alkali hydroxide withdrawn and water added to the catholyte to maintain the hydroxide concentration at 30% by weight NaOH. Voltage imposed is enough to achieve the specified current density.

Results are obtained as stated in the following table with cathode and anode current efficiencies of 96% or above.

TABLE 1

Run	Surface Composition				Membrane	Observed Voltage (Volts)	
	Pressure Plate	Mat Surface	First Screen	Second Screen		2000 Amperes per Square Meter	3000 Amperes per Square Meter
1	Nickel	Nickel	Nickel	-	Unsandblasted	3.76	4.28
2	"	"	"	-	Sandblasted Cathode Side	3.26	3.58
3	"	"	Nickel Ruthenium Coating	-	"	3.23	3.48
4	"	"	"	Nickel	"	3.11	3.41
5	"	"		Conductive Nickel Oxide Coating	"	3.14	3.38

TABLE I (Follows)

Run	Surface Composition				Membrane	Observed Voltage (Volts	
	Pressure Plate	Mat Surface	First Screen	Second Screen		2000 Amperes per Square Meter	3000 Ampere per Square Meter
6	Nickel	Nickel	Iron Sulfide	Nickel	Sandblasted Cathode Side	3.18	3.47
7	"	"	Iron	Nickel	" "	3.22	3.48
8	"	"	Nickel Ruthenium Oxide	Nickel	" "	2.97	3.20

In these tests water circulation is controlled to produce 30% by weight of NaOH. Temperature of the cell was maintained at 65-70°C.

EXAMPLE 2

In a further series of tests membrane sheets 14 by 14 centimeters are sandblasted and assembled in similar cells with results as obtained in the following table.

TABLE II

Run	Surface Composition				Membrane	Observed Voltage (Volts)	
	Pressure Plate	Mat Surface	First Screen	Second Screen		2000 Amperes per Square Meter	3000 Amperes per Square Meter
7	Nickel	Nickel	Nickel-Ruthenium Oxide	Nickel	Sandblasted Cathode Side	3.20	3.29
8	Iron	"	"	Nickel-Silver	" "	3.10	3.19
9	Nickel	"	"	Nickel	" "	3.16	3.24

In the above tests 30% by weight sodium hydroxide is obtained.

EXAMPLE 3

The following table reports results of further tests with membranes of the type used in examples 1 and 2, 10 x 10 centimeters in size. The anode used comprised a coarse titanium screen pressed against a finer titanium screen pressed against the anode side of the membrane. Both screens were coated with conductive ruthenium oxide. Sodium chloride solution combining 230 grams per liter of NaCl and having a pH of 3 is circulated through the anolyte chamber. 30% NaOH by weight is produced.

TABLE III

Run	Surface Composition				Membrane	Observed Voltage (V) 3000 Amperes per Square Meter
	Pressure Plate	Mat Surface	Third Layer	Fourth Layer		
1	Nickel	Nickel Wire	Nickel Screen	-	Unroughened	4.28
2	"	"	Screen Coated with Iron Sulfide	Nickel Screen	"	4.28
3	"	"	"	"	Cathode Side Sandblasted	3.25
4	"	"	"	Graphite Cloth 1 mm Thick	"	3.68
5	"	"	"	Cadmium Coated Nickel Screen	"	3.32

EXAMPLE 4

The membrane tested here is a multilayer membrane designated Nafion 315, manufactured by E.I. Du Pont Company, composed of a laminate of one layer of fluorocarbon polymer with sulfonic acid groups and an equivalent weight of 1500 and a second similar sulfonic polymer with an equivalent weight of 1100 with an interlayer of tetrafluoroethylene polymer cloth with a percent of open area of 25%.

The weaker acid side of these sheets are sandblasted as described in Example 1.

TABLE IV

Run	Surface Composition				Membrane	Observed Voltage (Volts)	
	Pressure Plate	Mat Surface	First Screen	Second Screen		2000 Amperes per Square Meter	3000 Amperet per Square Meter
1	Nickel	Nickel	Nickel	-	Unsandblasted	3.30	3.65
2	"	"	"	-	Sandblasted	3.07	3.35
3	"	"	Nickel-Ruthenium Oxide		"	2.96	3.22
4	"	"	"	Nickel	"	2.94	3.17
5	"	"	Iron	"	"	3.00	3 26

Sodium hydroxide solution containing 15 percent by weight of NaOH was obtained in these runs.

While the above examples are primarily directed to roughening the cathode side of the membrane, the anode side or both sides may be roughened. Greater improvement in voltage has accrued with a membrane roughened on the cathode side.

According to a further embodiment the membrane may be roughened or etched by methods other than sandblasting. For example, a membrane having a roughened surface may be obtained by pressing the membrane against a rough roll or plate to impart the rough surface to the membrane.

A membrane surface having an especially high surface area may be obtained by etching the surface to produce a membrane surface or surfaces which exhibit a papillon or needle-like strata. Such needles have a height generally above 0.5 microns preferably between 1 to 6 microns.

The preferred treatment consists in subjecting the film of ion-exchange resin to sputter etching by ion bombardment in a pressure reduction vacuum chamber at an absolute pressure ranging from 10^{-4} Torr and 5.10^{-1} Torr, at a temperature between -10°C and 40°C, by holding the membrane in the cathode dark space within the discharge zone, between two electrodes and applying an high frequency voltage between these electrodes, while keeping the discharge power in the range from 0.1 to 2.0 W/cm^2. A particularly efficacious method is described in the U.S. patent no. 4.155.826, which description is incorporated herein by express reference.

Other different method may be also used, such as, for example, treating the membrane with a solution of an alkali metal, e.g. sodium, in a mixture of naphthalene and tetrahydrofuran in liquid ammonia.

The following is a typical example of this embodiment.

EXAMPLE 5

A series of sheets of permeselective cation membrane, consisting of a copolymer of tetrafluoroethylene and sulphonyl-fluorinated perfluorovinylether, constituted by a laminate having a thickness of 0.4 mm, comprising two layers of NAFION$^{(R)}$ equivalent weight 1500 and NAFION$^{(R)}$ equivalent weight 1100 on a Teflon support cloth with a percent of open area of 25%, produced by E.I. Du Pont under the trade mark Nafion[(R)] and designated Nafion 315, were subjected to sputter etching.

Each membrane sample (5 x 5 cm) is individually placed in an apparatus, consisting in a vacuum chamber containing two plane and parallel aluminium electrodes spaced 110 mm apart. The membrane is adequately put in contact with the cathode, with the surface to be treated facing the anode. The inside of the chamber is previously brought to an absolute pressure between 10^{-4} and 10^{-5} Torr and then filled with Argon at a fixed pressure ranging from 5.10^{-3} to 5×10^{-1} Torr. An alternate voltage of 13.56 MHz is applied to the electrodes and the discharge power is maintained by varying the discharge voltage applied to the electrodes.

During the treating time, the pressure inside the chamber is kept constant at the prefixed value by providing a steady flux of Argon through the chamber and releasing gas.

In this case, the gaseous products resulting from the decomposition of a membrane are continuously diluted by the Argon flux. Discharging was effected every half period of the alternating voltage. As a matter of fact, whenever the voltage of the electrode contacting the membrane is negative, the positive ion resulting from the discharge are accelerated and impinge against the membrane surface, thus etching the surface. The positive charges tend to build up at the membrane surface, resulting in an increased potential. The potential difference between the membrane surface and the electrode opposed thereto decrease until discharging break down. During the next half period, the potential of the electrode contacting the membrane becomes positive with respect to the other electrode and consequently electrons enter into the

the membrane surface from the ionized space and neutralize the positive ions. As a result, in the next half period the potential difference between the electrodes becomes large enough to cause discharging and the positive ions are accelerated again and inpinge against the membrane surface, thus etching the surface.

Therefore, the sputter etching of the membrane occurs mainly in the cathode dark space of the discharging, wherein the kinetc energy of the ion is 10 to 100 times as great as that obtained by glow discharge occurring in plasma. The membrane sheets, subjected to variable treating time, are treated in the same way on both surfaces by turning the membrane on the cathode plate.

By this method, Nafion$^{(R)}$ 315 sheets treated on both surfaces are obtained, which exhibit on both surfaces microscopic needlelike structures, whose dimensions were more or less marked according to the different treating conditions.

The membrane exhibits, at a first investigation, a strong opacity, with respect to the translucency of the material before treatment.

The opacity was more evident in those samples wherein the surface treating conditions results in a more marked etching.

A further morphological analysis allowed to estimate qualitatively and quantitatively, the needlelike structure originated on the treated surfaces.

In the following Table I the results obtained by the microscopic investigation are shown, as well as the treating conditions at which the different samples have been subjected. Particular emphasis has posed to the qualitative description of the etching degree of the different samples, the peak to peak height of the needles and the papillar density expressed as mean value of the papillar number over a length of about 5 microns.

As it can be easily seen, the etching degree, i.e. the peak to peak dimensions of the needlelike hollows, varies as a function of different parameters, more precisely, being fixed the distance between the electrodes, gas pressure, discharge power and treating time. Under the same conditions, the parameters which play the major role in effecting the etching degree are the treating time and the power discharge, the pressure being not so affective. Moreover, the proper appearance of the surface changes passing from a papillar structure, showing less marked hollows and pyramidal needles, corresponding to short treating times and high discharge powers, to needlelike structures characterized by sharp hollows and thin needles, which tend to assume a filamentary character, corresponding to long treating times and low discharge powers.

TABLE V

Sample No.	Atmosph.	Pressure Torr	Distance between electrodes 10^{-3} m	Treating time sec.	Discharge Power Watt/cm^2	Etching Depth	Papillas Density No. counted Every $5x10^{-6}$m
1	Argon	$5x10^{-3}$	110	60	4	5	2
2	"	"	110	30	4	2.5	3
3	"	"	"	125	2	3.5	4
4	"	"	"	60	2	3	3
5	"	"	"	30	2	1.5	2
6	"	$5x10^{-2}$	"	30	4	2.5	3
7	"	"	"	60	4	3.5	3
8	"	"	"	60	2	2	2
9	"	"	"	125	2	3.5	4
10	"	"	"	60	1	0.5	2
11	"	"	"	125	1	1	3
12	"	$5x10^{-1}$	"	60	4	3.5	3
13	"	"	"	60	2	3	3
14	"	"	"	125	2	3.5	4

EXAMPLE 6

NAFION(R) 315 membrane sheets, morphologically modified on both the surfaces according to the example 5, are successively conditioned. The sheets have been hydrolyzed and salified in NaCl brine, 2-3% diluted, at a temperature of about 80°C to change the SO_3H groups into SO_3Na. Then the sheets are tested in cells comprising an anode made of titanium coated with an electrocatalytic layer of mixed oxides of Ti and Ru and a mild steel cathode, under the following operating conditions:

Anolyte	NaCl at 240 g/l
Anolyte pH	3 - 4
Cathode concentration	NaOH at 18%
Current density	3.000 A/m^2
Temperature	80 °C
Distance between anode and membrane	1 mm
Distance between cathode and membrane	1 mm

Under the same conditions two comparative Nafion(R) 315 sheets have been also tested. Sample indicated by A was not subjected to any surface treatment, while sample indicated by B was previously treated by sandblasting on both the surfaces with substantially spherical quartz particles, having a diameter comprised between 50 and 150 microns, sprayed by means of compressed air at 5 atm through a nozzle maintained at a distance of 25 mm from the membrane surface for about 10 seconds.

In table VI are listed the operating conditions of the different membrane sheets.

TABLE VI

Sample No.	Cell Voltage Volts	Faradic Yield Calculated on Caustic Soda Production - %
1	3.65	82
2	3.64	83
3	3.65	82
4	3.66	82
5	3.67	82
6	3.65	82
7	3.66	83
8	3.66	83
9	3.66	82
10	3.72	82
11	3.69	83
12	3.66	82
13	3.64	82
14	3.63	82
A	3.75	82
B	3.74	82

The resulting data clearly show that an appreciable reduction in the cell voltage is achieved whenever the membrane sheets morphologically modified according to the invention are used, with respect to cell voltages obained when using both the un-treated sample A and the sandblasted sample B.

The particularly small size of the test cells used in the experiments of this example and the spaced position of the electrodes with respect to the membrane surface does not make possible a direct comparison of the cell voltages of this example with those of examples 1 to 4, however, the relative differences of cell voltages between the various samples should hold true when tested in larger sizes and with the same cell configuration of the other example.

Particularly meaningful is the fact that all the samples treated according to the method of this example provide a decrease in the cell voltage and this decrease substantially is in the order of about 100 millivolts for almost all samples, except for the samples no. 10 and 11, whose morphological modification seems quite unsufficient, that is under the optimum degree.

EXAMPLE 7

A series of square sheets 10 x 10 cm, consisting of single, unsupported sheet of a copolymer of tetrafluoroethylene and a sulphonylfluorinated perfluorovinylether, having a thickness of about 0.4 mm, produced by E. I. Du Pont and designated Nafion(R) 120, have been subjected to various surface roughening processes according to the instant invention.

Some samples were sandblasted according to the method of example 1, for varying periods of time, as indicated in Table VII, over both surfaces.

Some samples were scraped over both surfaces with a needle comb producing an array of parallel "cuts" spaced 1 mm apart. The "cuts" had a depth of about 10 microns and a width of about 3 microns. A single or multiple pass was used to produce an increased density of cuts. Vertical, horizontal, and criss-crossing passes of the membrane under the needle comb were used to modify the pattern of the incision on the surface of the membrane, as indicated in table VII.

Other samples were pressed in a vice between two sheets of abrasive paper no. 60 to impress the roughness pattern of the abrasive paper onto the membrane surfaces.

The membrane samples, after hydrolysis in hot diluted brine were assembled in similar test cells as described in Example 1, with the following results :

TABLE VII

Run	Surface Composition				Membrane Treatment	Observed Voltage (Volts)	
	Pressure Plate	Mat Surface	First Screen	Second Screen		2000 A/m^2	3000 A/m^2
1	Ni	Ni	Ni	Ni	None	3.09	3.35
2	"	"	"	"	Sandblasted 40"	2.96	3.18
3	"	"	"	"	Sandblasted 2'	2.95	3.13
4	"	"	"	"	Combed 1 pass vertical	3.98	3.18
5	"	"	"	"	Combed 1 pass horizontal	2.95	3.20
6	"	"	"	"	Combed 2 inclined passes at ± 30° from vertical	2.92	3.13
7	"	"	"	"	Combed 3 passes vertical	2.94	3.14
8	"	"	"	"	Pressed between abrasive paper No. 60	2.80	3.00

Sodium hydroxide solution containing 15 percent by weight of NaOH was obtained in these runs.

Again the test confirmed that a large reduction of the cell voltage is obtained by roughening of the membrane surface.

Particularly meaningful is the fact that the voltage reduction is consistently found to be in the same order of magnitude whichever method of roughening is used as far as a sufficient degree of roughening, or of surface area increase is provided. Moreover, a reduction in cell voltage is observed with all kinds of membrane tested, both of the laminated type, as well as of the homogeneous type.

All the tests, which have been carried out on membranes morphologically modified on the cathode side surface ontly or on the anode side surface, according to the method of the present invention, have shown that in the electrolysis of NaCl brine, under the anove cited conditions, this reduction is lower than the reduction obtained in the cell voltage with membrane treated on both surfaces and such partial reduction seems to be substantially additional.

Particularly, it has been observed that the main contribute to the decrease in the cell voltage is due to the modification of the cathode surface (reduction of the cell voltage of about 50-500 millivolts) while the modification of the anode side of the membrane results in a decrease in the cell voltage of about 40-30 millivolts.

The above process may be conducted in the electrolysis of aqueous alkali metal chloride containing 150 to 325 grams per liter of alkali metal chloride and the amount of water fed to the catholyte chamber being controlled to produce a convenient concentration of NaOH ranging from 5 to 40 or more, preferably 25 to 40 percent NaOH by weight. Other alkali metal halides or other aqueous halides including hydrochloric acid and other metal halides may be electrolyzed to produce the corresponding halogens (chlorine, bromide, iodide etc.)

Furthermore, water may be electrolyzed with the cell herein described to produce oxygen and hydrogen.

Although the present invention has been described with reference to details of certain embodiments thereof, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofaras included in the accompanying claims.

WHAT IS CLAIMED :

1. A method of generating halogen which comprises electrolyzing an aqueous halide between a pair of electrodes separated by an ion exchange membrane, characterized in that said membrane has a rough surface exposed to the electrolyte.

2. The method according to Claim 1, characterized in that the membrane has a surface roughness characteristic of a sandblasted surface.

3. A method according to Claims 1 or 2, characterized in that the cathode side of the membrane has a roughened surface.

4. A method according to Claims 1 or 2, characterized in that the cathode side of the membrane has the roughened surface and a gas and liquid permeable cathode bears against the rough surface and is in unbonded contact therewith.

5. The method according to Claims 1 or 2, characterized in that the cathode side of the membrane has a sandblasted surface.

6. The method according to Claims 1 or 2, characterized in that the cathode side of the membrane has a sputter etched surface.

7. A method according to any of the preceding claims, characterized in that both electrodes are in contact with the membrane.

8. A method according to any of the preceding claims characterized in that the membrane is rough enough to provide a surface at least 25 percent greater than the overall area of the membrane.

9. A method of generating halogen which comprises electrolyzing an aqueous halide in a cell having a pair of opposed electrodes separated by an ion exchange membrane, characterized in that said membrane has a roughened surface exposed to electrolyte and an electrolyte permeable electrode in unbonded contact with said roughened surface.

10. The method of Claim 9, characterized in that the rough surface is on the cathode side and in contact with a cathodically charged electrode.

11. The method of Claim 9 or 10 characterized in that the electrode comprises a foraminous electroconductive sheet in contact with the rough surface and a second foraminous electroconductive sheet in contact with said first sheet, said second sheet having a lower hydrogen overvoltage than said first sheet.

12. The method of any of Claims 9 or 10, characterized in that the electrode has an electroconductive surface of relatively high hydrogen overvoltage in contact with the rough surface and a second surface having a relatively lower hydrogen overvoltage spaced from said rough surface.

13. A method according to any of the preceding claims characterized in that the cathode side of the membrane comprises a carboxylic ion exchange resin.

14. A method according to any of the preceding claims characterized in that the average distance between the crests of the roughened surface is not in excess of 50 microns.

15. A method according to any of the preceding claims characterized in that the average depth of the valleys of the roughened surface is not in excess of 25 microns.

16. An electrode-membrane assembly characterized in that it comprises an ion exchange membrane sheet having a roughened surface and a gas and liquid permeable electroconductive electrode in sheet form and in unbonded contact with the rough surface.

17. The electrode-membrane assembly of claim 16, characterized in that the average depth of the valleys of the rough surface of the membrane abutting against the gas and liquid permeable electrode is less than 5 microns.

18. An electrolytic cell characterized in that it comprises an electrode-membrane assembly of Claim 16, extending across and dividing the cell into an anode compartment and a cathode compartment and a further electrode in contact with and extending along the side of the membrane opposite to said rough surface.

19. An electrolytic cell comprising an ion exchange membrane which is substantially impermeable to electrolyte flow, characterized in that said membrane has a surface roughness characteristic of a sandblasted surface directly exposed to electrolyte and a pair of opposed electrodes on opposite sides of the membrane, and disposed so as to permit access of electrolyte to said rough surface.

20. The cell of claim 16, characterized in that the membrane comprises a fluorocarbon polycarboxylic polymer having said rough surfaces.

21. The cell of Claim 19, characterized in that the rough surface is on the cathode side of the membrane and the cathode is gas and electrolyte permeable and in unbonded contact with said rough surface.

22. The cell of any of Claims 19 to 21, characterized in that the surface is rough enough to provide a surface area at least 25 percent greater than the overall surface area of the membrane.

23. The cell of any of Claims 19 to 21, characterized in that the average distance between crests of the roughened surface is not above 50 microns.

24. The cell of any of Claims 19 to 21, characterized in that the average depth of the valleys of the roughened surface is less than 25 microns.

25. A semipermeable ion-exchange membrane, suitable for electrolysis processes, essentially comprising a thin film of fluorinated polymer containing fixed polar groups, with an ion exchange capacity between 0.5 and 4.0 m.e. per gram of anhydrous resin, characterized in that at least one of the surfaces has a rough or porous morphology, wherein the distance between crests is comprised between 0.5 and 50 microns and the depth of the surface irregularities is comprised between 0.5 and 25 microns.

26. The membrane of claim 25, characterized in that the rough or porous morphology of the surface is obtained by subjecting the membrane to sputter-etching by ion-bombardment of the membrane surface in the cathode dark space of a high frequency discharge at an absolute pressure comprised between 10^{-4} and 5.10^{-1}Torr.

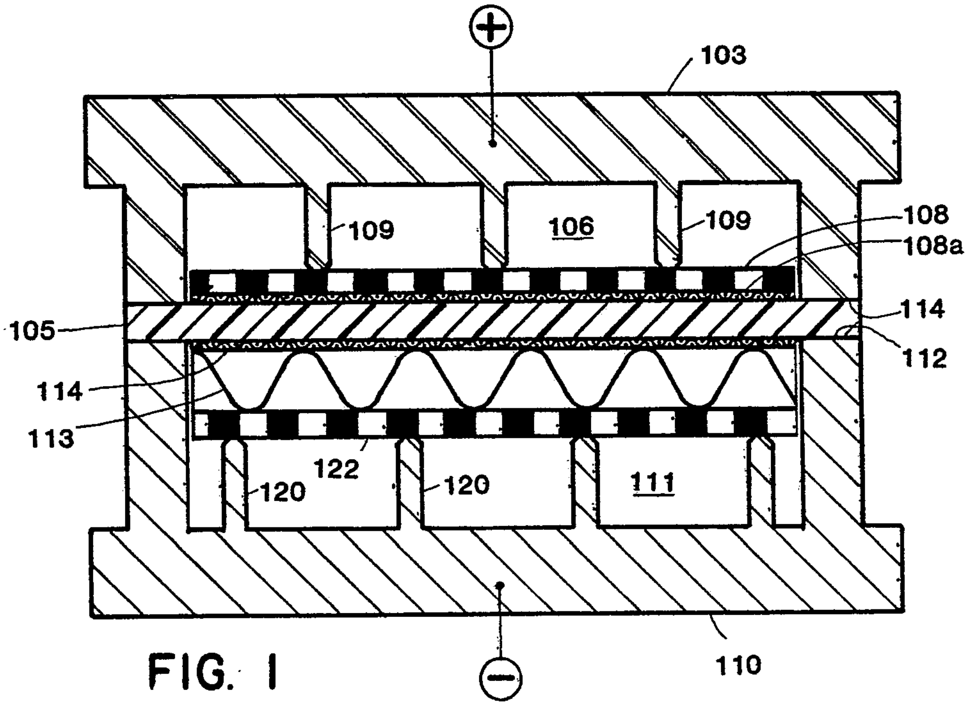

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FIG. 1

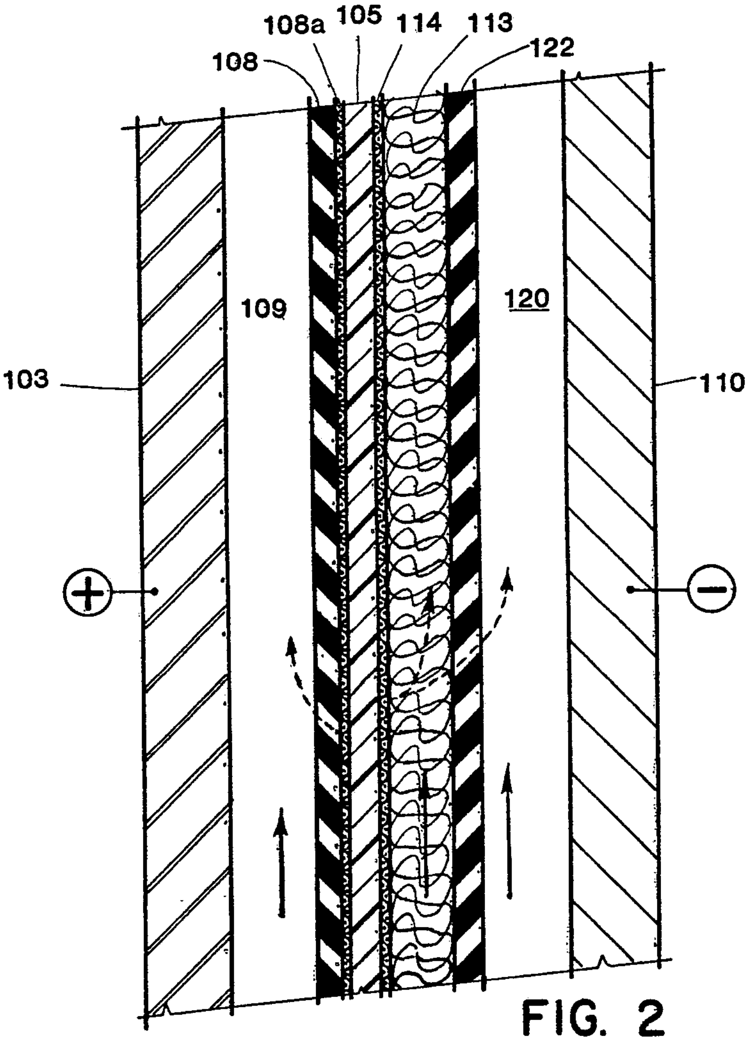
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FIG. 2

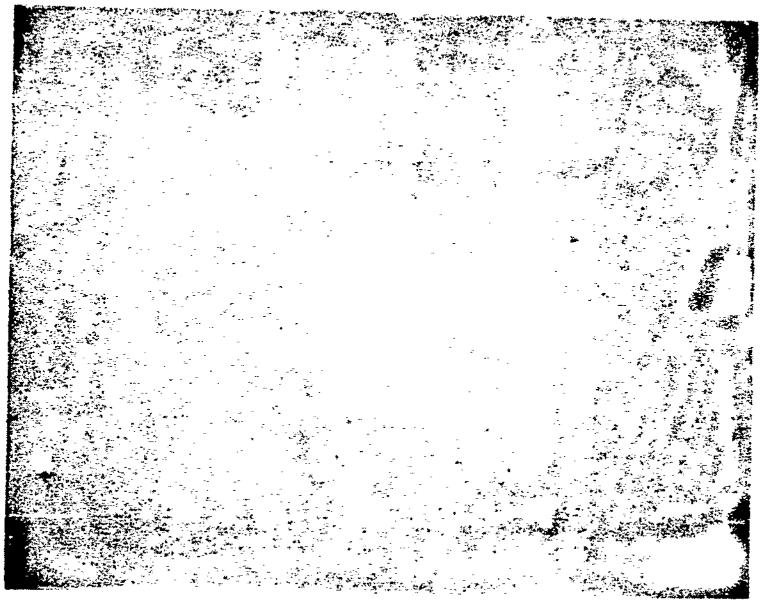

FIG. 3

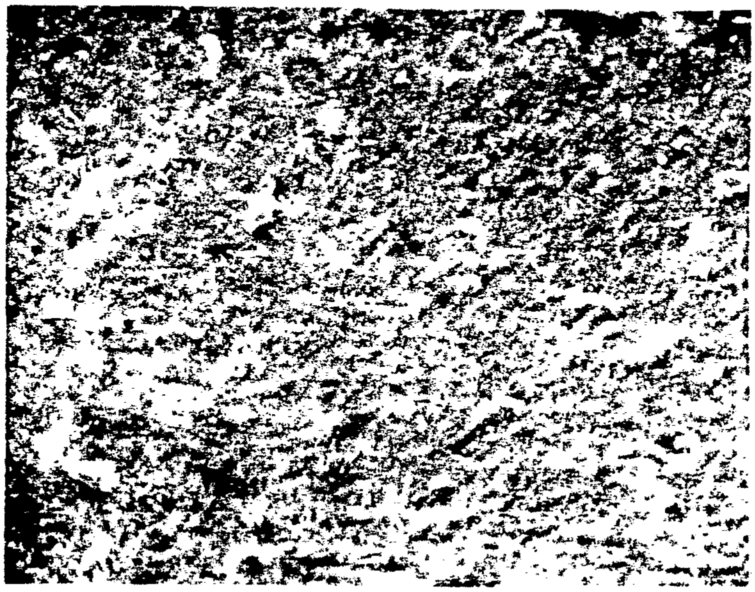

FIG. 4

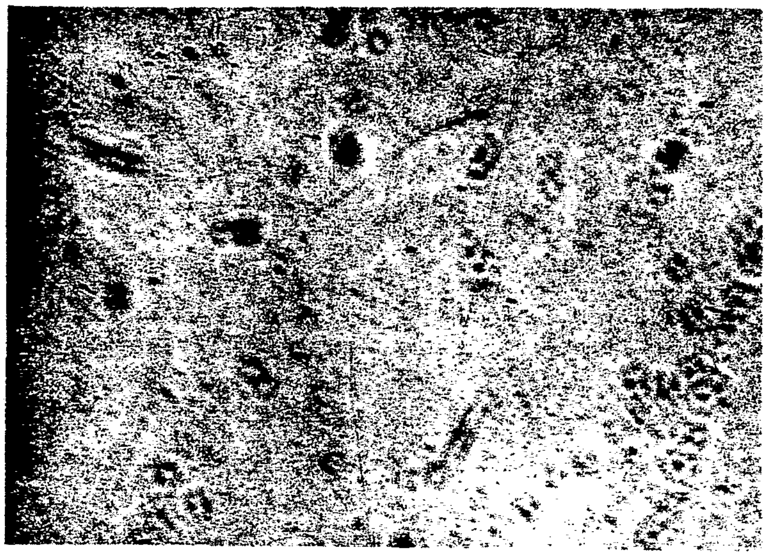

FIG. 5

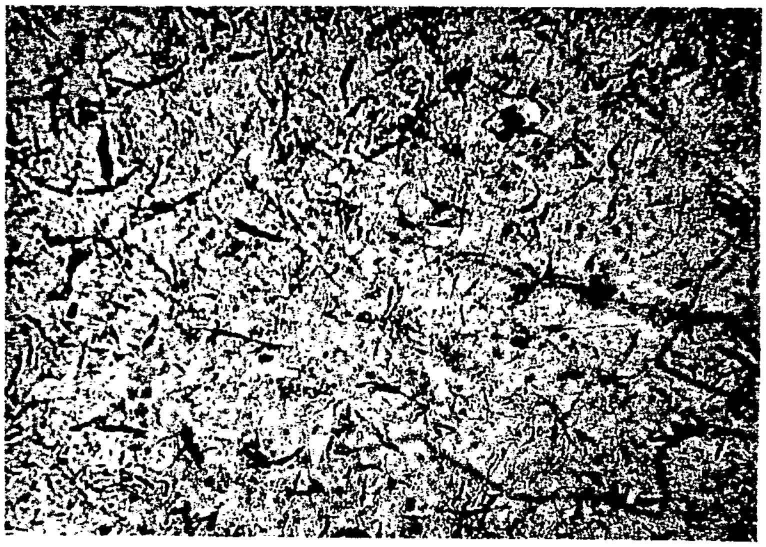

FIG. 6

0050188

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 81105076.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 2 043 108 (ASAHI KASEI KOGYO KABUSHIKI KAISHA) (01-10-1980) * Claims 1,7; pages 1-3 * ----	1,3,9, 10,13, 15,17, 18,20, 24	C 25 B 13/02 C 25 B 1/46 C 25 B 11/02
			TECHNICAL FIELDS SEARCHED (Int. Cl.³)
			C 25 B
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document

Place of search	Date of completion of the search	Examiner
VIENNA	27-11-1981	HEIN

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