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(54) Title: MEMBRANE-ELECTRODE STRUCTURE FOR ELECTROCHEMICAL CELLS (57) Abstract A membrane-electrode structure for use in an electrochemical cell comprising an ion exchange membrane with a cathode layer and an intermediate layer between the cathode and the membrane. The intermediate layer comprises 5 to 80 percent by weight of inorganic solid particles and 95 to 20 percent by weight of an ionic conductive polymeric binder.		

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MEMBRANE-ELECTRODE STRUCTURE FOR ELECTROCHEMICAL CELLS

The present invention relates to an improved membrane-electrode structure for use in an ion exchange membrane electrolytic cell. More particularly, the invention is concerned with the use of an intermediate layer for the membrane-electrode structure of chlor-
5 alkali electrolyzers to reduce the amount of hydrogen in chlorine.

It is known to attain an electrolysis by a so called solid polymer electrolyte (SPE) type electrolysis of an alkali metal chloride wherein a cation exchange membrane of a fluorinated polymer is bonded with a gas-liquid permeable catalytic anode on one surface
10 and/or a gas-liquid permeable catalytic cathode on the other surface of the membrane.

This prior art electrolytic method is remarkably advantageous as an electrolysis at a lower cell voltage because the electric resistance caused by the electrolyte and the electric resistance
15 caused by bubbles of hydrogen gas and chlorine gas generated in the electrolysis can effectively be decreased. This has been considered to be difficult to attain in the electrolysis with cells of other configurations.

A high percentage of hydrogen in chlorine poses problems in
20 chlorine liquefaction processes. Extra steps are required to prevent the formation of dangerous gas mixtures. The hydrogen problem is a severe drawback if a cost effective method to reduce hydrogen percentage cannot be identified.

The anode and/or the cathode in the prior art electrolytic cell
25 are bonded on the surface of the ion exchange membrane so as to be partially embedded. The gas and the electrolyte solution are readily

permeated so as to remove, from the electrode, the gas formed by the electrolysis at the electrode layer contacting the membrane. That is, there are few gas bubbles adhering to the membrane after they are formed. Such a porous electrode is usually made of a thin porous
5 layer which is formed by uniformly mixing particles which act as an anode or a cathode with a binder. It has been found that when an electrolytic cell having an ion exchange membrane bonded directly to the electrode is used, the anode in the electrolytic cell is brought into contact with hydroxyl ions which migrate back from the cathode
10 compartment, and accordingly, both chlorine resistance and alkaline resistance for anode material are required for this prior art method and an expensive material must be used. When the electrode layer is directly bonded to the ion exchange membrane, a gas is formed by the electrode reaction between an electrode and membrane and certain
15 deformation phenomenon of the ion exchange membrane causes the characteristics of the membrane to deteriorate. In such an electrolytic cell, the current collector for the electric supply to the electrode layer which is bonded to the ion exchange membrane, should closely contact the electrode layer. When a firm contact is not
20 obtained, the cell voltage may be increased. Therefore, the cell structure for securely contacting the current collector with the electrode layer according to the prior art is disadvantageously complicated.

Additionally, in chlor-alkali electrolyzers where the cathode is
25 directly bound to the membrane there is permeation of hydrogen through the membrane which enters the anolyte compartment and mixes with the chlorine. High percentages of hydrogen are then found in the chlorine so as to cause problems in the liquefaction process.

Prior means for reducing the hydrogen percentage includes 1) the use
30 of a platinum black layer on the anode side of the membrane, 2) the use of a layer (for example Ag) less electroactive than the electrode layer itself between the membrane and the electrode, 3) the use of thickened membranes, and 4) the use of a membrane with a lower permeation rate for hydrogen permeation. These methods have proved to
35 be expensive and ineffective.

Perfluoro membranes which are used as membranes for electrolysis

reactions usually have fairly low water contents. As compared with conventional ion exchangers with same amount of water contents, the conductivity of the perfluoro membranes are abnormally high. This is because of phase separation existing in the perfluoro ionic membranes.

5 The phase separation greatly reduces the tortuosity for sodium ion diffusion. The hydrogen diffusion path is the aqueous ionic region and the amorphous fluorocarbon region. Therefore, the tortuosity experienced by the hydrogen molecules is also low for the phase-segregated fluorocarbon membranes as compared with conventional

10 hydrocarbon ionic membranes.

The phase-segregation characteristics of the fluorocarbon membranes provides the high migration rates for sodium ions, thus relatively lower ionic resistivity is also the cause for the high hydrogen diffusion rates and the resulting high percentage of hydrogen

15 in chlorine. Moreover, the high permeation rate of hydrogen is even more enhanced by the high solubility of hydrogen in the fluorocarbon membranes because of the hydrophobic interaction between hydrogen molecules and the fluorocarbon chains. Therefore, reducing hydrogen permeation rates by increasing the thickness of the membranes or

20 modifying the structure of the membranes would not be very effective because the sodium migration rate would be reduced as one tries to reduce the hydrogen diffusion rate; and the tortuosity effect is difficult to introduce because of the phase separation.

A retardation layer is defined as a layer between the electrode

25 layer and the membrane to retard hydrogen permeation. Any kind of layer can have a certain effect to retard hydrogen permeation as long as it is (1) inactive for electrolytic hydrogen generation, and (2) flooded. The latter requirement is also important for low resistance (that is, lower voltage and good performance). With these

30 considerations a layer of a blend of inert solid particles (usually inorganic) and binders (usually organic) would serve the purpose best.

The need for a binder is obvious: the binder can (1) bind the components in the barrier layer together and also (2) provide the necessary adhesion between the retardation layer and the electrode

35 layer and that between the retardation layer and the membrane. The function of the solid particles is also two fold: (1) providing the

physical strength to the barrier layer so that there is very limited interpenetration between different layers during fabrication, and (2) forming an agglomerate with the binder.

The reason that the retardation layer is better than the
5 membrane itself in retarding hydrogen permeation is because (1) it allows hydroxide and sodium ions to migrate at a faster rate so relatively small voltage penalty has to be paid. On the other hand, in the membrane, sodium ion diffusion is slowed down by the coulombic interaction exerted by the sulfonate or carboxylate groups. The
10 situation is even worse when the membrane is immersed in strong caustic solution as in the chlor-alkali membrane. This is particularly severe for the carboxylic membranes. Ion pairing between sodium ions and carboxylate groups and hydroxide ions is believed to be the cause for the very slow diffusion rate when membrane dehydration occurs
15 under this condition. The solubility of hydrogen is much lower in caustic solution than in the membrane, so the permeation rate (the product of diffusion coefficient and solubility) of hydrogen can be reduced by a larger factor compared with that of the sodium and hydroxyl ions. By introducing the blend of inorganic particles and
20 binder and with the necessary morphology, the resistance of the caustic solution is increased. The ratio of the resistivity of the porous medium saturated with electrolyte, R_p , to the bulk resistivity of the same electrolyte solution, R_b is commonly called "formation resistivity factor",

25
$$F = R_p/R_b = X/O.$$

This equation describes the relationship between F and "electric tortuosity", X, and O, the porosity. X is different from hydraulic tortuosity which takes into account the fact the effective path length experienced the diffusing species is increased by the presence of
30 impermeable blocking materials. On the other hand, X also takes into account the special effects due to convergent-divergent nature of the capillaries, called constrictedness, besides the hydraulic tortuosity.

Since conductivity is proportional to diffusion rate of the ionic species, formation resistivity factor is also related to
35 diffusion rate in the porous medium, D_p , and the diffusion rate in the bulk electrolyte, D_b , by the following equation:

$$F = R_p/R_b = D_b/D_p$$

The present invention provides an improved membrane-electrode structure for use in electrochemical cells which comprises a retardation layer between an ion exchange membrane and the cathode.

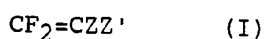
- 5 The retardation layer comprises a blend of 5 to 80 percent by weight of inorganic solid particles with 95 to 20 percent by weight of a thermoplastic polymers binder having a melting point of 230°F to 540°F (110 to 232°C).

- 10 As described above, the function of the retardation layer is to provide porosity and tortuosity so as to impede hydrogen diffusion. That is, when a retardation layer with a porosity in the range of 5 percent to 90 percent is prepared, it is preferable to have a porosity in the range of 20 percent to 60 percent, preferably, in the range of 30 percent to 50 percent. Advantageously, the tortuosity/porosity
15 ratio is in the range of 2-500, preferably in the range of 5-100, and more preferably in the range of 10-50.

- The inorganic solid particles comprise one or more of the borides, carbides and nitrides of metals of Groups IIIB, IVA, IV B, VB and VI B of the Periodic Table. Typical examples of suitable
20 materials include SiC, YC, VC, TiC, BC, TiB, HfB, BV₂, NbB₂, MoB₂, W₂B, VN, Si₃N₄, ZrO₂, NbN, BN and TiB. Preferably, silicon carbide is used.

- The binder which is used in the invention comprises novel ion exchange polymers which can be used alone or blended with nonionic
25 thermoplastic binders. These polymers are copolymers of the following monomer I with monomer II.

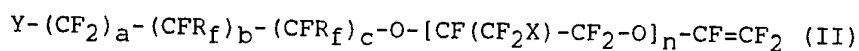
Monomer I is represented by the general formula:



where;

- 30 Z and Z' are independently selected from the group consisting of -H, -Cl, -F, or -CF₃.

Monomer II consists of one or more monomers selected from compounds represented by the general formula;



- 35 where;

Y is -SO₂Z

Z is -I, -Br, -Cl, -F, -OR, or -NR₁R₂;

R is a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

R₁ and R₂ are independently selected from the group consisting
5 of -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

a is 0-6;

b is 0-6;

c is 0 or 1;

10 provided a+b+c is not equal to 0;

X is -Cl, -Br, -F, or mixtures thereof when n>1;

n is 0 to 6; and

R_f and R_f are independently selected from the group consisting
of -F, -Cl, perfluoroalkyl radicals having from 1 to 10 carbon atoms
15 and fluorochloroalkyl radicals having from 1 to 10 carbon atoms.

The ionic binders can be mixed with a nonionic binder such as a fluorinated hydrocarbon, that is Teflon.

In accordance with the present invention, at least one of the electrodes, preferably, the cathode, is bonded to an ion exchange
20 membrane through a retardation layer for use in an electrolytic cell, particularly a chlor-alkali cell, so as to retard the diffusion of hydrogen.

The composition for preparing the retardation layer is preferably in the form of a suspension of agglomerate of particles
25 having a diameter of 0.1 to 10 microns, preferably 1 to 4 microns. The suspension can be formed with an organic solvent which can be easily removed by evaporation such as halogenated hydrocarbons, alkanols, ether, and the like. Preferable is Freon.

The inorganic particles are admixed with the particles of the
30 binder so as to comprise 5 to 80 percent by weight of total particles. A higher percentage of inorganic particles results in poor adhesion of the electrode layer to the retardation layer. The mixture of the inorganic particles and the binder are then suspended in an organic solvent and applied on an ion exchange membrane. The suspension can
35 be applied by spraying, brushing, screen-printing, and the likeso as to distribute the inorganic particles substantially throughout the

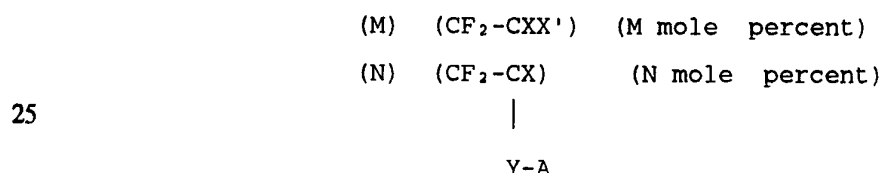
retardation.

After the organic solvent is evaporated, the composition is preferably heat pressed by a roller or press at 80 to 220°C under a pressure of 0.01 to 150 kg/cm² to bond the layer to the membrane. An electrode layer can then be heat pressed on the barrier layer under the same conditions.

The retardation layer is 0.3 to 3.0 mils (0.0076 to 0.0762 mm) in thickness, preferably 0.4 to 1.0 mils (0.0102 to 0.0254 mm).

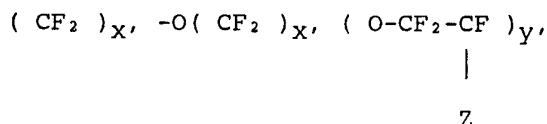
The cation exchange membrane on which the porous non-electrode layer is formed, can be made of a polymer having cation exchange groups such as carboxylic acid groups, sulfonic acid groups, phosphoric acid groups and phenolic hydroxy groups. Suitable polymers include copolymers of a vinyl monomer such as tetrafluoroethylene and chlorotrifluoroethylene, and a perfluorovinyl monomer having an ion-exchange group, such as a sulfonic acid group, carboxylic acid group and phosphoric acid group or a reactive group which can be converted into the ion-exchange group. It is also possible to use a membrane of a polymer of trifluoroethylene in which ion exchange groups, such as sulfonic acid groups, are introduced or a polymer of styrene-divinyl benzene in which sulfonic acid groups are introduced.

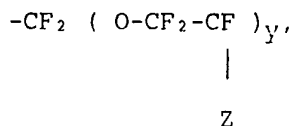
The cation exchange membrane is preferably made of a polymer having the following units:



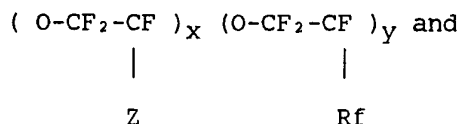
wherein X represents fluorine, chlorine or hydrogen atom or -CF₃; X' represents X or CF₃(CH₂)_m; m represents an integer of 1 to 5.

The typical examples of Y have the structures bonding A to fluorocarbon group such as

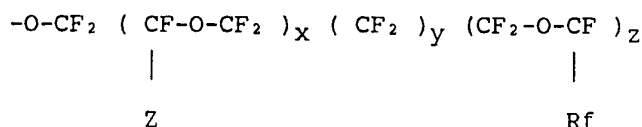




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x, y and z respectively represent an integer of 1 to 10; Z and Rf represent -F or a C₁-C₁₀ perfluoroalkyl group; and A represents -COOM or SO₃M, or a functional group which is convertible into -COOM or -SO₃M by, hydrolysis or neutralization, such as -CN, -COF, -COOR₁, -SO₂F and -CONR₂R₃ or -SO₂NR₂R₃, and M represents hydrogen or an alkali metal atom and R₁ represents a C₁-C₁₀ alkyl group.

It is preferable to use a cation exchange membrane having an ion exchange group content of 0.5 to 4.0 miliequivalence/gram dry polymer, especially 0.8 to 2.0 miliequivalence/gram dry polymer, which is made of said copolymer.

In the cation exchange membrane of a copolymer having the units (M) and (N), the ratio of the units (N) is preferably in a range of 1 to 40 mol percent preferably 3 to 25 mol percent.

The cation exchange membrane used in this invention is not limited to one made of only one kind of the polymer. It is possible to use a laminated membrane made of two kinds of the polymers having lower ion exchange capacity in the cathode side, for example, having a weak acidic ion exchange group such as carboxylic acid group in the cathode side and a strong acidic ion exchange group, such as sulfonic acid group, in the anode side.

The cation exchange membrane used in the present invention can be fabricated by blending a polyolefin, such as polyethylene, polypropylene, preferably a fluorinated polymer, such as polytetrafluoroethylene, and a copolymer of ethylene and

tetrafluoroethylene.

The electrode used in the present invention has a lower over-voltage than that of the material of the porous non-electrode layer bonded to the ion exchange membrane. Thus the anode has a lower
5 chlorine over-voltage than that of the porous layer at the anode side and the cathode has a lower hydrogen over-voltage than that of the barrier layer at the cathode side in the case of the electrolysis of alkali metal chloride. The material of the electrode used depends on the material of the retardation layer bonded to the membrane.

10 The anode is usually made of a platinum group metal or alloy, a conductive platinum group metal oxide or a conductive reduced oxide thereof.

The cathode is usually a platinum group metal or alloy, a conductive platinum group metal oxide or an iron group metal or alloy
15 or silver.

The platinum group metal are Pt, Rh, Ru, Pd, Ir. The cathode is iron, cobalt, nickel, Raney nickel, stabilized Raney nickel, stainless steel, a stainless steel treated by etching with a base.

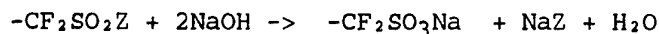
The preferred cathodic materials for use with the retardation
20 layer of the present invention are Ag and RuO₂.

Also, the polymers comprising the binders of the present invention desirably have an equivalent weight within a certain desired range namely, 550 to 1200. It is possible to tailor the polymer preparation steps in a way to produce a polymer having an equivalent
25 weight within the desired range. Equivalent weight is a function of the relative concentration of the reactants in the polymerization reaction.

The polymers comprising the binders of the present invention desirably have a melt viscosity within a certain desired range. It is
30 possible to tailor the polymer preparation steps in a way to produce a polymer having a melt viscosity within the desired range. The melt viscosity is based upon the concentration of the initiator and by the temperature of the reaction.

The polymer obtained by one of the above process is then
35 hydrolyzed in an appropriate basic solution to convert the nonionic thermoplastic form of the polymer to the ionic functional form which

will have ion transport properties. The hydrolysis step is particularly important in the process because during the hydrolysis step the nonfunctional polymer film is heated and reacted as shown below during which process, the polymer is softened and swollen with moisture in a controlled manner. Incomplete hydrolysis leaves covalently bonded functional groups whose lack of mobile ions lead to insulating regions within the binder. The density of the hydrolysis solution is preferably between 1.26 and 1.28 grams per ml at ambient temperature. The hydrolysis process requires two moles of NaOH for each mole of the functional group in the polymer, as shown in the following equation:



where Z is -I, -Br, -Cl, -F, -OR, or -NR₁R₂;

R is a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

R₁ and R₂ are independently selected from the group consisting of -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical, preferably phenyl or a lower alkyl substituted phenyl.

For hydrolysis, the copolymers are placed in the hydrolysis bath at room temperature, with inert, mesh materials holding the copolymers in the liquid, making sure that there are no trapped bubbles around the films. The bath is then heated to 60°C to 90°C and then held at that temperature for a minimum of four hours to insure complete hydrolysis and expansion to the correct level.

After the hydrolysis heating step, the bath is allowed to cool to room temperature and the polymers are then removed from the bath and rinsed with high purity deionized water, then placed in a deionized water bath to leach out residual ionic substances.

A pore former which can be leached out after fabrication may be used in forming the retardation layer. It is advantageous that the pores formed by the pore former are interconnected and extended from the membrane-electrode interface to the electrode-catholyte interface.

The present invention will be further illustrated by certain examples and references which are provided for purposes of illustration only and are not intended to limit the present invention.

Example IPreparation of Binder

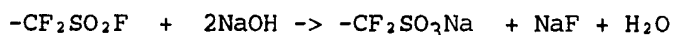
This example shows the preparation of a sulfonic fluoropolymer having an equivalent weight of 794 and a low shear melt viscosity of 50,000 poise (dyne sec-cm⁻²) at 250°C and 4.25 sec⁻¹ and a 100°C water absorption of 50 percent.

A 132 liter glass-lined reactor equipped; with an anchor agitator, H-baffle, a platinum resistance temperature device, and a temperature control jacket was charged with 527 grams of ammonium perfluorooctanoate, 398.4 grams of Na₂HPO₄·7H₂O, 328.8 grams NaH₂PO₄·H₂O and 210.8 grams of (NH₄)₂S₂O₈. The reactor was then evacuated down to 0.0 atmosphere, as measured on the electronic pressure readout, and then an inert gas (nitrogen) was added to pressure up the reactor to a pressure of 448 kPa. This was done a total of 4 times, then the reactor was evacuated one more time. 99 liters of deoxygenated, deionized water was added, the agitator was started and heat was applied to the jacket. An agitator was set to 250 revolutions per minute (rpm) and then 15 ml of a terminating agent such as isopropyl alcohol was added, followed by 16.65 kg of 2-fluorosulfonyl perfluoroethyl vinyl ether was added. When the temperature reached 50°C, tetrafluoroethylene (TFE) gas was fed to the reactor at a rate of from 0.5 to 0.567 kg per minute, until a pressure of 1060 kPa is reached over a period of 17 minutes. The feed was continued until a total of 18.18 kg. of TFE had been added to the reactor. At that time, the feed was stopped and then nitrogen was blown through the gas phase portion of the system and ambient temperature water was added to the reactor jacket. The materials react to form a latex. The latex was transferred to a larger vessel for separation and stripping of residual monomer. After the contents were allowed to settle, a bottom dump valve was opened to allow separate phase monomer to be drained away. The vessel was then heated and a vacuum was applied to remove any further monomer components. After this, a brine system circulates 20°C brine through cooling coils in the vessel to freeze the latex, causing coagulation into large polymer agglomerates. After freezing was completed, the latex was allowed to thaw with slight warming (room temperature water) and the latex was transferred into a centrifuge

where it was filtered and washed repeatedly with deionized water. The latex polymer cake was then dried overnight in a rotary cone dryer under vacuum (969 Pa) at 110°C. The water content of the polymer was tested by Karl Fischer reagent and found to be 140 ppm. The isolated
5 polymer was weighed and found to be 23,18 kg. The equivalent weight of the above polymer was determined to be 794.

The binder can be prepared in either thermoplastic form or ionic form. To prepare it in the thermoplastic form, the dried polymer was dispersed in a suitable solvent and attrited to a fine dispersion.

10 To prepare it in ionic form the polymer was then hydrolyzed in an approximately 25 weight percent NaOH solution. The density of the hydrolysis solution was between 1.26 and 1.28 grams per ml at ambient temperature. The hydrolysis process consumed two moles of NaOH for each mole of the functional group in the polymer, as shown in the
15 following equation:



The polymers were placed in the hydrolysis bath at room temperature, with inert, mesh materials holding the polymers the liquid-making sure that there were no trapped bubbles. The bath was
20 then heated to 60°C to 90°C and then held at that temperature for a minimum of four hours to insure complete hydrolysis and expansion to the correct level.

After the hydrolysis heating step, the bath was allowed to cool to room temperature and the polymers were then removed from the bath
25 and rinsed with high purity deionized water, then placed in a deionized water bath to leach out residual ionic substances.

Example 2

A suspension of particles SiC and the copolymer of Example 1 was formed in Freon at a ratio of 70:30. The resultant layer had a
30 tortuosity/porosity ratio in the range of 5-50. The composition was sprayed onto a high performance sulfonic carboxylic bilayer ion exchange membrane of Dow. After the solvent was evaporated the composition was hot pressed at 475°F (246°C) and 0.5-100 PSI to form a layer 0.4 mil (0.0102 mm) in thickness. An electrode layer of
35 Ag/RuO₂/ binder (76 percent:10 percent:8 percent) of 1 mil (0.0254 mm) in thickness was then sprayed on top of the barrier layer. The entire

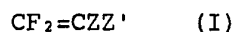
unit was then heated at 400°F (204°C) and pressed together at 0.5-100 Psi.

The electrode/retardation layer/membrane was then treated to get the final form for electrolysis. This could involve electrolysis in
5 an appropriate solution to hydrolyze the membrane and/or the binder if either of them is in the thermoplastic form.

The resulting structure can be used as the membrane for a chlor-alkali electrolyzer.

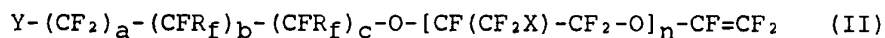
CLAIMS

1. A membrane-electrode structure for use in an electrochemical cell which has an ion exchange membrane with a cathode layer, characterized in the membrane-electrode structure also having a retardation layer between said membrane and said cathode layer, said retardation layer being a blend of 5 to 80 percent by weight of inorganic solid particles with 20 to 95 percent by weight of a thermoplastic ionic conductive polymer binder having a melting point of 230°F to 540°F (110 to 232°C), said inorganic solid particles having at least one of the borides, carbides, and nitrides of metals of Groups IIIB, IVA, IVB, VB, and VIB of the Periodic Table, said binder consisting of a copolymer of a monomer of the general formula:



wherein Z and Z' are independently selected from the group consisting of -H, -Cl, -F, or -CF₃, and

- at least one monomer selected from compounds represented by the general formula:



wherein Y is -SO₂Z

Z is -I, -Br, -Cl, -F, -OR or -NR₁R₂;

- wherein R is a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

R₁ and R₂ are independently selected from the group consisting of -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

- wherein:

a is 0-6;

b is 0-7;

c is 0 or 1;

provided $a+b+c$ is not equal to 0;

X is -Cl, -Br, -F, or mixtures thereof when $n > 1$; n is 0 to 6; and

- 5 R_f and R_f are independently selected from the group consisting of --F, -Cl, perfluoroalkyl radicals having from 1 to 10 carbon atoms and fluorochloroalkyl radicals having from 1 to 10 carbon atoms.

2. The structure of claim 1 wherein said retardation layer is 0.3 to 3 mils (0.0076 to 0.0762 mm) in thickness.

- 10 3. The structure of claim 1 wherein said retardation layer has a porosity of 5 percent to 90 percent and tortuosity/porosity ratio in the range of 2-500.

4. The structure of claim 1 wherein said inorganic particles are silicon carbide.

- 15 5. The structure of claim 1 wherein the binder includes nonionic thermoplastic polymeric material.

6. The structure of claim 1 wherein said cathode comprises a platinum group metal oxide and silver.

- 20 7. In an electrochemical cell having an electrode-membrane structure, characterized in that the said membrane-electrode structure comprises the structure of claim 1.

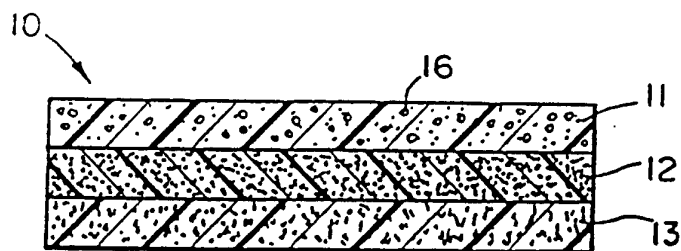


FIG. 1
PRIOR ART

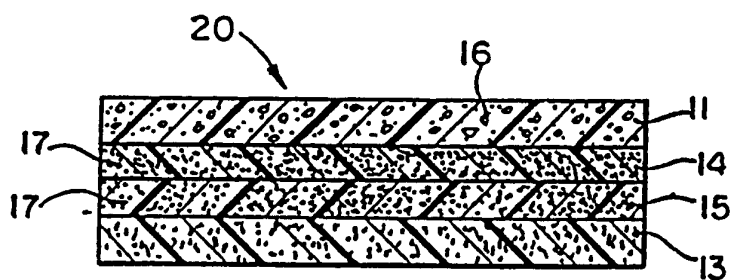


FIG. 2

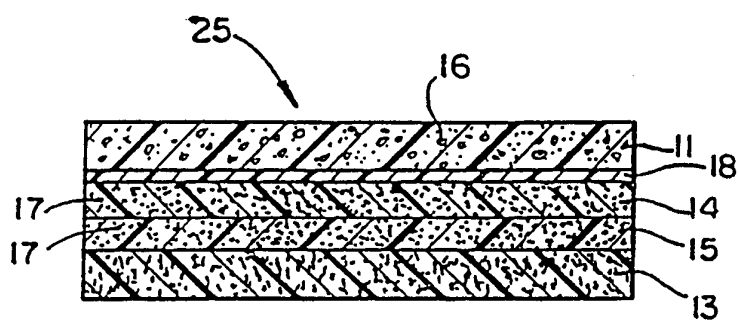


FIG. 3

INTERNATIONAL SEARCH REPORT

PCT/US 93/00547

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C25B9/00; C25B11/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C25B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	PATENT ABSTRACTS OF JAPAN vol. 006, no. 011 (C-088) & JP,A,56 133 481 (ASAHI GLASS CO LTD) 19 October 1981 see abstract ---	1,7
Y	US,A,4 992 126 (R.D. DOOR) 12 February 1991 see column 2, line 68 - column 3, line 43 see column 6 - column 8; claims 1-15 ---	1,7
A	EP,A,0 061 080 (ASAHI GLASS COMPANY LTD) 29 September 1982 see page 22 - page 26; claims 1-27 --- -/-	1,2,3,4
¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 SEPTEMBER 1993	16. 09. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	GROSEILLER P.A.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 006, no. 174 (C-123) & JP,A,57 089 490 (ASAHI GLASS CO LTD) 3 June 1982 see abstract ---	1,3,5
A	FR,A,2 519 030 (GENERAL ELECTRIC COMPANX) 1 July 1983 see page 27 - page 29; claims 1-16 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9300547
SA 69815

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for those particulars which are merely given for the purpose of information.

03/09/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-C- 1553107	04-04-90
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