Title: ASSEMBLIES FOR ELECTROCHEMICAL DEVICES

Abstract: 7-layer MEA assemblies with gasket, comprising: a film of ionomeric membrane (3) having size variations in the two orthogonal plane directions, x and y, lower than 4%, determined according to the formula: (A-B)×100/B, wherein: B is the membrane length in the x or y direction, after drying under vacuum for a time of 1 h at 105°C and at a residual pressure lower than 30 mBar; A is the membrane length in the same direction where B is measured after membrane treatment in distilled water at 100°C for 30 minutes; two GDL sheets (1 and 2) made of a porous material having on one surface an electrocatalytic layer coextensive with the membrane (3) surf- face; the two sheets (1 and 2) positioned so that the electrocatalytic layer comes into contact, respectively, with each of the two membrane faces; a gasket (4) positioned according to a frame shape along the assembly perimeter.
ASSEMBLIES FOR ELECTROCHEMICAL DEVICES

The present invention relates to 7-layer MEA (Membrane Electrode Assembly or electrode-membrane assemblies or simply assemblies), also called 7-layer MEA, having a gasket placed along the external perimeter of the assembly according to a frame shape having a high gas seal and the 7-layer assembly being obtainable also with a continuous process. The membrane-electrode assemblies are used in electrochemical devices, in particular in PEM (proton exchange membranes) fuel cells.

The present invention refers also to the preparation of membrane-electrode assemblies by a continuous process.

It is known in the prior art that in the fuel cell the MEA is placed among the bipolar plates of the cell. The membrane-electrode assembly in the simplest embodiment is formed of an ionomeric membrane acting, as an electrolyte, having an electrocatalytic layer (catalyzed area) applied on both sides. This assembly is called Catalyst Coated Membrane (CCM) or 3-layer MEA.

It is also known that in the fuel cells, 7-layer MEAs are used obtained by applying on each of the two surfaces of a 3-layer MEA, in sequence, the following layers:
- a gas microdiffusion layer having hydrophobic characteristics generally formed of a mixture of carbon powder and PTFE;
- a gas macrodiffusion layer, having hydrophobic characteristics, generally formed of carbon fibers or carbon tissues treated with PTFE.

Generally the gas microdiffusion layer is already joined to the gas macrodiffusion layer to form a composite called GDL (gas diffusion layer), or gas diffusor.

The single reaction cells (MEA+bipolar plates) are assembled in electrical series thus obtaining a device called fuel cell stack.

As known, the PEM fuel cells comprise a MEA, i.e. a core wherein there is an
ionomeric membrane having on each side an electrode layer containing the catalyst for the combustion reaction, on each of the two electrode layers there is at least one gas diffusion layer GDL, generally two, the MEA is in contact with the bipolar plates.

In each bipolar plate, facing the 7-layer MEA, there is at least one channel wherein the comburent is fed, generally air or pure oxygen and another channel for the fuel, for example pure hydrogen, or gaseous mixtures containing hydrogen, or methanol or ethanol aqueous solutions.

In the PEM fuel cell a gasket is generally used, interposed between the MEA and the two bipolar plates so that during the assembling of the MEA between the bipolar plates an insulating zone both from the electrical point of view and for the gas sealing is formed. The gasket indeed prevents the mixing of the reacting gases, thus avoiding an explosion risk and a cell performance decrease. Besides, the gasket also assures the sealing of optional cooling fluids used to cool the PEM fuel cell.

The 7-layer MEA assemblies are known in the prior art and are obtainable through the following processes: See for examples J. of Power Sources, "PEM Fuel Cell Electrodes" 130 (2004) pages 61-76.

One process applies by hot pressing on both sides of an ionomeric membrane one gas diffusion layer, in contact with the membrane, the diffusion layer being formed of a GDL having an electrocatalytic layer.

Another process prepares a CCM by applying an electrocatalytic layer on both sides of an ionomeric membrane, and then applying by hot pressing a GDL on each of the CCM sides.

7-layer MEAs with integral gasket are industrially produced and known in the prior art.

Patent application WO 99/04,446 describes 7-layer MEA assemblies with elastomeric gaskets obtained by a continuous process. The membrane, the electrocatalytic layers and the GDL of the 7-layer MEAs are coextensive and thus they have the same perimeter. The continuous process comprises a step wherein from a 7-layer MEA having suitable sizes, assemblies, having the sizes required for
the final use, are cut out. The obtained MEAs are placed in a mold and by injection molding a gasket is applied along the MEA frame or MEA external perimeter. In this step the gasket must be applied so to penetrate for some millimeters into the porous structure of each of the two GDLs and furthermore adhere to the ionomeric membrane along the cut perimeter. The disadvantages of this 7-layer MEA of this patent application is to have a low duration in the hydration/dehydration cycles during the fuel cell functioning.

Tests carried out by the Applicant by using a press for preparing the 7-layer MEA with gasket have shown that after 75 cycles, a decay of the PEM fuel cell performances takes place.

In patent application US 2005/0014056 a 7-layer MEA with gasket is described wherein the two GDL have different surfaces each other. The first GDL has surface size lower than that of the ionomeric membrane, the second GDL is coextensive with the membrane. The GDL having lower size is centered on the membrane so that a frame, of at least 1 mm, of membrane is not covered by said GDL. The drawback of this assembly is that it is not obtainable by a continuous process, since the GDL having surface sizes lower than the membrane must be positioned so as to result centered with respect to the membrane. This represents a remarkable drawback, from the industrial point of view, since it lowers the productivity. As a matter of fact, the process of this patent application results not continuous.

In patent application WO 2004/114,451 a 7-layer MEA with gaskets is described wherein the membrane edges extend beyond the edges of at least one of the two GDL. This assembly has the same drawback of the ones described in patent application US 2005/0014056: the MEA is not obtainable in a continuous way.

The need was felt to have available 7-layer MEA assemblies with gaskets, having the following combination of properties:
- improved duration in the PEM fuel cell, even after repeated hydration/dehydration cycles typical of electrochemical devices, even more than 200 cycles, by using the test described below;
- their obtainment also with a continuous process and thus with high productivity.

The Applicant has unexpectedly and surprisingly found 7-layer MEA assemblies with gasket solving the above mentioned technical problem.

An object of the present invention is represented by 7-layer MEA assemblies with gasket, comprising (see Fig. 2 and 3):

- an ionomeric membrane film (3) having size variations in the two orthogonal plane directions, x and y, lower than 4%, preferably lower than 3%, determined by the expression:

\[(A-B)x100/B\]

wherein:

- B is the membrane length in the x or y direction, after drying under vacuum for a time of 1 h at 105°C and at a residual pressure lower than 30 mBar;
- A is the membrane length in the same direction in which B is measured, after membrane treatment in distilled water at 100°C for 30 minutes;
- two GDL sheets (1) and (2) in porous material having on one surface an electrocatalytic layer, not shown in the Figures, coextensive with the membrane (3) surface;
- the two sheets (1) and (2) placed so that the electrocatalytic layer contacts, respectively, each of the two membrane surfaces;
- a gasket (4) placed according to a frame shape along the assembly perimeter.

The membranes used in this patent application have reduced size variations in both orthogonal directions x, y of the plane. Preferably, the used membranes do not have significant size variations in the directions x, y of the plane, i.e. said size variations are substantially absent. As a matter of fact it has been found by the Applicant that, by starting from membranes obtainable for example by extrusion, at temperatures for example in the range 230°C-300°C, by simultaneous biaxial stretching in the two orthogonal plane directions (biaxial stretching) or by other methods indicated
below, 7-layer MEA assemblies are obtainable having a longer duration in cell tests comprising hydration/dehydration cycles compared with the membranes obtained by extrusion by stretching them in only one direction, generally in the x direction, optionally followed by a stretching in the other direction.

Other processes for obtaining membranes with low size variations or even substantially with no size variations in the two orthogonal directions of the plane x, y, are for example the following.

The casting process comprises the following steps:

1) preparation of a liquid dispersion comprising a (per)fluorinated ionomer as above defined, in acid or salified form, wherein the ionomer concentration is comprised, as per cent by weight, between 0.5% and 40%, preferably between 0.5% and 25%;

2) placing the liquid dispersion prepared in step 1) as a layer or film on a support inert under the conditions used in the process of the present invention;

3) optional removal of the solvent from the dispersion applied in 2) for at least 80% by weight, preferably for at least 90%, still more preferably for at least 95% by weight with respect to the initial solvent of the used dispersion thus obtaining a raw membrane on the inert support layer or film;

4) first thermal treatment at temperatures from 130°C to 200°C, preferably from 140°C to 200°C; and

4a) second thermal treatment at temperatures from 160°C to 280°C, preferably from 180°C to 240°C, the difference between the temperature used in step 4a) and that used in step 4) being at least of 20%; thus obtaining a membrane on the inert support;

5) detachment of the membrane from the support.

By an inert support it is meant a support which substantially remains chemically and physically unchanged under the conditions used for preparing the membrane.

In step 1) the solvent used is selected from C₁-C₃ alcohols, preferably C₃,
n-propanol and/or iso-propanol; or from mixtures, preferably with water, of said C$_1$-C$_3$ alcohols. During the preparation also other organic solvents can be used, in addition to the above mentioned solvents, provided that they are miscible with water and/or with the above mentioned alcohols. An example of optional solvent is dimethyl sulphoxide (DMSO).

In step 2) the formation of the layer with the dispersion of step 1) on the inert support is carried out with the methods known in the prior art; for example it can be carried out by brush coating, dip coating, spray coating, casting with knife, kiss-coating, serigraphy, ink-jetting, curtain coating, etc. The inert support can be formed of one of the following materials: non porous PTFE, polyimide, in particular commercialized with the trademark Kapton®, MFA, PFA, polyesters, such as PET.

In step 3) solvent removal is generally carried out by operating at temperatures from 25°C to 95°C, preferably at atmospheric pressure, until obtaining a content of residual solvent in the film within the above indicated limits.

The thermal treatments in steps 4) and 4a) are carried out for a time generally higher than 15 minutes and preferably lower than 10 hours.

In step 5) the membrane detachment from the surface of the inert material layer or film is carried out with the known methods of the prior art, for example by dry processes, or by dipping in water, generally at room temperature (25°C).

Another process for obtaining the membranes of the invention with the above reduced size variations is the impregnation of an inert porous support with an ionomer solution, comprising the following steps:

1') preparation of a liquid dispersion comprising a (per)fluorinated ionomer, in acid or salified form, wherein the ionomer concentration is comprised, as per cent by weight, between 0.5% and 40%, preferably between 0.5% and 25%;

2') formation of a layer or film of the liquid dispersion prepared in step 1') on the surface of the porous inert material, the latter being under the form of a film or layer, removal of the excess dispersion, thus obtaining a film of impregnated porous inert material;
3') application on one side of the impregnated porous inert material film or layer obtained in step 2') of a support of a preferably non porous material and with smooth surfaces, inert under the conditions used in the subsequent thermal treatments step 4');
3a') optional removal of the solvent;
4') first thermal treatment at temperatures from 130°C to 200°C, preferably from 140°C to 200°C; and
4a') second thermal treatment at temperatures from 160°C to 280°C, preferably from 180°C to 240°C, obtaining a membrane on a support, the difference between the temperature used in step 4a') and that used in step 4') being at least of 20°C;
5') detachment of the membrane from the support.

In step 1') the same solvents used in step 1) of the above described process by casting are used.

In step 2') the porous film or layer can be formed of any inert support. Preferably a (per)-fluoropolymer porous support is used for its high chemical resistance. Still more preferably porous PTFE, preferably bistretched, is used. The film or layer of the inert porous support can also be available in the form of a porous tissue or a polymeric net. In step 2') the formation of the layer from the dispersion on the support is carried out as described in step 2) of the above described casting process.

In step 3') the inert support usable for the application to the film or layer of the impregnated porous inert support can be any continuous support, i.e. non porous, preferably with smooth surfaces. The same materials indicated in step 2) of the casting process can be used.

Steps 3a'), 4'), 4a') and 5') are carried out as described for steps 3), 4), 4a) and 5) of the casting process.

Preferably the gasket (4) is applied so to penetrate along the perimeter of the two GDL. Penetrations of about 1 mm (see (5) (6) of Fig. 2) are suitable.
For a better understanding of the invention in the Figures from 1 to 3 a preferred embodiment of the invention is represented.

Fig. 1 is a top view of a 7-layer MEA with gasket of the invention;
Fig. 2 is the AA' section of the 7-layer MEA with gasket of Fig. 1;
Fig. 3 shows a continuous process for obtaining the 7-layer MEA roll.

Fig. 1 shows a top view of 7-layer MEA with gasket according to the present invention from the part bearing the second sheet GDL (2). (4) indicates the gasket; (6) GDL (1) portion impregnated by the gasket (4) support.

Fig. 2 is the section AA' (see Fig. 1) of the 7-layer MEA with gasket according to the present invention, AA' being a section along the symmetry axis of the assembly parallel to the direction x of the membrane film (3). (2) and (4) have the same meaning as in Fig. 1. (5) indicates the part of the first sheet GDL (1) impregnated with the gasket (4); (6) indicates the part of the second sheet GDL (2) impregnated with the gasket (4); (7) indicates the contact zone between the membrane (3) and the gasket (4), corresponding to the membrane thickness.

The ionomeric membrane (3) generally contains as functional groups acid groups -SO₃H and/or -COOH.

The ionomeric membrane films usable in the 7-layer MEA of the present invention are obtainable with the above methods. Generally, when the extrusion and the simultaneous stretching in the two orthogonal directions x and y of the plane are used, the membrane containing the precursors of the acid functional groups -SO₃H and/or -COOH, i.e. the -SO₂F groups and/or -COOH precursors such as COOCH₃, is obtained. Then the hydrolysis of the acid precursors is carried out.

The stretching ratio in the simultaneous bistretching generally ranges from 15:1 to 100:1 and can be equal or different in the two directions. The membrane thickness is generally not lower than 5 µm. By stretching ratio it is meant the ratio between the membrane section before stretching and the membrane stretched section, said sections taken perpendicularly to the considered stretching direction.

The hydrolysis of the precursors of the acid functional groups of the membrane
(3) comprises two steps: the first is carried out in basic conditions and the second in acid conditions, obtaining the ionomers with functional groups in the acid form, -SO_3H and/or -COOH. For example, in case of sulphonyl -SO_2F precursor groups, they are transformed into sulphonic groups -SO_3H by the following steps:

- salification of the -SO_2F form into the -SO_3Me^+ form, wherein Me is an alkaline metal;
- acidification of the -SO_3Me^+ form into the -SO_3H form.

The activation can for example be carried out by dipping the ionomeric membrane in an alkaline aqueous solution, for example containing 10% by weight of KOH, at a temperature between 60°C and 80°C, for a time over 2 hours, until disappearance of the -SO_2F groups (determined by IR analysis) and formation of the -SO_3Me^+ group. At the end of the salification step the ionomeric membrane is washed with water at a temperature between 20°C and 80°C. The acidification step is carried out, for example, by dipping the ionomeric membrane in salified form in an acid aqueous solution, for example, containing 20% by weight of HNO_3, at room temperature for a time between 0.5 and 2 hours. At the end a washing is carried out by dipping in water, at a temperature in the range 20°C-80°C.

The GDL (1) and (2) sheets are generally formed of the following layers:

- a gas microdiffusion layer, having hydrophobic characteristics, generally formed of a mixture of carbon powder and PTFE;
- a gas macrodiffusion layer, with hydrophobic characteristics, generally formed of carbon fibers or carbon tissues treated with PTFE.

The electrocatalytic layer is applied on the side of each GDL wherein there is the microdiffusion layer. A spray process of an hydroalcoholic dispersion containing the catalyst, described hereinafter, in admixture with the ionomer can be used at this purpose. The obtained GDL is then dried in an oven at 80°C for 20 minutes.

GDL sheets having on one of the two surfaces an electrocatalytic layer are commercially available. See for example those called ELAT® LT250EW (E-TEK).

The membrane and the electrocatalytic layers of the MEA device according to
the present invention are obtainable by using preferably (per)fluorinated ionomers with sulphonic groups in -SO$_3$H acid form or salified, having equivalent weight from 380 g/eq to 1,600 g/eq, preferably from 500 to 1,200 g/eq, still more preferably 750-950 g/eq. The preferred ionomers comprise the following units:

(A) monomeric units deriving from one or more fluorinated monomers containing at least one ethylene unsaturation;

(B) fluorinated monomeric units containing -SO$_2$F sulphonyl groups in such amount that the ionomer has the equivalent weight in the above mentioned range.

Alternatively homopolymers formed of monomeric units (B) can be used as ionomers.

The ionomers containing sulphonic groups in acid form -SO$_3$H can be obtained by hydrolysis of the -SO$_2$F groups, and optionally salification of the -SO$_3$H groups, as described above in step 1b).

The (A) fluorinated monomers are selected from the following:

- vinilydene fluoride (VDF);
- C$_2$-C$_8$ perfluoroolefins, preferably tetrafluoroethylene (TFE);
- C$_2$-C$_8$ chloro- and/or bromo- and/or iodo-fluoroolefins such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene;
- CF$_2$=CFOR$_{R_1}$ (per)fluoroalkylvinylethers (PAVE), wherein R$_{R_1}$ is a C$_1$-C$_6$ (per)fluoroalkyl, for example trifluoromethyl, bromodifluoromethyl, pentfluoro-propyl;
- CF$_2$=CFOX perfluoro-oxyalkylvinylethers, wherein X is a C$_1$-C$_{12}$ perfluoroxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl;
- fluorovinylethers (MOVE) of general formula CF$_{X_1}$=CF$_{X_2}$OCF$_2$OR$_{Al}$, wherein R$_{Al}$ is a linear, branched C$_1$-C$_6$ (per)fluoroalkyl group or C$_5$-C$_6$ cyclic, or a linear or branched when possible C$_1$-C$_6$ (per)fluoroxyalkyl group containing from one to three oxygen atoms; when R$_{Al}$ is fluoroalkyl or fluoroxyalkyl as defined
above it can contain from 1 to 2 atoms, equal or different, selected from the following: H, Cl, Br, I; $X_{A}$ = F, H, preferably F; the preferred fluorovinylethers are:

(MOVE 1) $\text{CF}_2=\text{CFOCF}_2\text{OCCF}_2\text{CF}_3$, (MOVE 2) $\text{CF}_2=\text{CFOCF}_2\text{OCCF}_2\text{CF}_2\text{OCF}_3$, (MOVE 3) $\text{CF}_2=\text{CFOOCF}_2\text{OCCF}_3$.

The (B) fluorinated monomers are selected from one or more of the following:

- $\text{F}_2\text{C}=$CF-O-CF$_2$CF$_2$SO$_2$F;
- $\text{F}_2\text{C}=$CF-O-[CF$_2$CX$_A$F-O]$_{nA}$-(CF$_2$)$_{nB}$SO$_2$F
  wherein $X_A$ = Cl, F or CF$_3$; $nA = 1-10$, $nB = 2, 3$;
- $\text{F}_2\text{C}=$CF-O-(CF$_2$)$_{nC}$SO$_2$F; $nC=3-10$;
- $\text{F}_2\text{C}=$CF-Ar-SO$_2$F wherein Ar is an aromatic ring, the ring can be substituted in one or more free positions by aliphatic chains from 1 to 10 carbon atoms, optionally containing heteroatoms.

Other fluorinated monomers (B'), which can be used alternatively to (B) for preparing the ionomers, are those having equivalent weight as reported for sulphonic monomers; the monomers (B') containing precursor groups which are transformed by hydrolysis into -COOH acid groups, optionally with their subsequent salification. These monomers can be optionally used in admixture with those containing -SO$_2$F groups (monomers (B)).

Fluorinated monomers (B') used for preparing the ionomers containing -COOH acid groups have the following structures:

- $\text{F}_2\text{C}=$CF-O-CF$_2$CF$_2$-Y;
- $\text{F}_2\text{C}=$CF-O-[CF$_2$-CX$_A$F-O]$_{nA}$-(CF$_2$)$_{nB}$-Y
  wherein $X_A$ = Cl, F or CF$_3$; $nA = 1-10$, $nB = 2, 3$;
- $\text{F}_2\text{C}=$CF-O-(CF$_2$)$_{nC}$-Y; $nC = 3-10$;
- $\text{F}_2\text{C}=$CF-Ar-Y wherein Ar is an aryl group;

wherein Y is a precursor group of the carboxylic group, selected from the following: CN, COF,COOH, COOR$_B$, COO$^+$Me, CONR$_{2b}$R$_{3b}$, wherein $R_B$ is C$_1$-C$_{10}$, preferably C$_1$-C$_3$ alkyl and $R_{2b}$ and $R_{3b}$, equal or different, are H or have the $R_B$ meaning, Me is
an alkaline metal.

As said, the fluorinated monomers (B') having the above described formulas can be in admixture with the fluorinated monomers containing -SO₂F sulphonyl groups, the total amount of the monomers (B) and (B') being such that the ionomer equivalent weight is in the above indicated range.

Optionally the invention fluorinated ionomers can contain from 0.01% to 2% by moles of monomeric units deriving from a bis-olefin of formula:

\[ R_1R_2\, C = CH - (CF_2)_m - CH = CR_5R_6 \]  \hspace{1cm} (I)

wherein:
\( m = 2-10 \), preferably 4-8;
\( R_1, R_2, R_5, R_6 \), equal to or different from each other, are H or C₁-C₅ alkyl groups, preferably H.

Preferably the membranes and the electrocatalytic layers of the present invention device contain perfluorinated ionomers obtainable from ionomers comprising:
- monomeric units deriving from TFE;
- monomeric units deriving from CF₂=CF₂CF₂SO₂F.

The membranes generally have a thickness ranging from 5 micrometers to 200 micrometers, preferably from 10 to 80 micrometers, more preferably from 15 to 60 micrometers. The electrocatalytic layers generally have a thickness ranging from 3 micrometers to 50 micrometers, preferably from 5 to 30 micrometers.

The electrocatalytic layers comprise one ionomer and a catalyst. The latter is preferably Pt or a mixture of Pt with one or more metals, as for example Ru, Rh, Mo. The catalyst is finely dispersed and preferably supported on carbon powder. The powders known with the following commercial names: Vulcan XC-72, Ketjen Black, Black Pearls, Shawinigan Acetylene Black, etc. can for example be used. The ionomer used in an electrocatalytic layer has a composition and/or equivalent weight equal to or different from the ionomer used in the membrane and/or in the other electrocatalytic layer. The ratio by weight between catalyst and ionomer generally
ranges from 0.5 to 4, preferably between 0.5 and 2.5. The ratio by weight between the catalyst metal and the support in powder is preferably higher than or equal to 10%. When as fuel hydrogen is used, said ratio is comprised between 20% and 60%, when methanol is used, the ratio is between 60% and 100%.

The ratio \( \text{mg of catalyst metal/cm}^2 \) of electrocatalytic layer generally ranges from 0.01 to 2. When in the cell hydrogen is used as fuel, the ratio \( \left( \text{mg of catalyst metal}/\text{cm}^2 \right) \) of electrocatalytic layer preferably ranges from 0.01 to 0.7 \text{ mg/cm}^2, preferably using at the cathode side a ratio ranging from 0.1 to 0.7 \text{ mg/cm}^2. When methanol is used as fuel, said ratio preferably ranges from 0.3 to 1 \text{ mg/cm}^2 at the anode side and from 0.5 to 2 \text{ mg/cm}^2 at the cathode side.

As gaskets, polymers selected from silicones, fluorosilicones, fluoroelastomers, EPDM (rubbers), thermoplastic elastomers (for example styrene-butadiene block copolymers) are used.

As already said in the description of the Figures of the present invention, in the 7-layer MEA assemblies with gasket of the present invention, the contact between the membrane (3) and the gasket (4) (see Fig. 2) takes place along the whole perimeter of the membrane (3), for a thickness equal to that of the membrane.

It has been surprisingly and unexpectedly found that the 7-layer MEA with gaskets according to the present invention have a longer duration in the fuel cells, since they substantially maintain unaltered (+2% with respect to the value determined before the beginning of the test) the voltage of the open circuit, even after numerous hydration and dehydration cycles, determined according to the test reported hereinafter.

The 7-layer MEA with gasket is assembled in a test device Fuel Cell Technologies® and is subjected to continuous dehydration and hydration cycles characterized as follows:

A) dehydration:
- gas fed to the anode circuit: hydrogen hydrated with dew point 30°C;
- gas fed to the cathode circuit: air hydrated with dew point 30°C;
- cell temperature: 80°C;
- reacting gas pressure: 1,5 bar (hydrogen side), 1,3 bar (air side);
- drained current with electronic load: 20 ampere, corresponding to 800 mA/cm²;
- duration: 60 minutes;

B) hydration:
- gas fed to the anode circuit: hydrogen hydrated with dew point 85°C;
- gas fed to the cathode circuit: air hydrated with dew point 85°C;
- cell temperature: 80°C;
- reacting gas pressure: 1,5 bar (hydrogen side), 1,3 bar (air side);
- drained current with electronic load: 20 ampere, corresponding to 800 mA/cm²;
- duration: 60 minutes.

The dehydration/hydration cycles are repeated up to 200 times. At the beginning of the test and after every 25 cycle repetitions the integrity of the adhesion between membrane/gasket is checked through the measurement of the voltage at open circuit, i.e. with drained current equal to zero, after the hydration cycle.

A further object of the present invention is a process for producing 7-layer MEA assemblies with gasket, comprising the following steps (see Fig. 3):

1) obtainment of a roll of a 7-layer MEA assembly, see Fig. 3, by assembling of
- a film of membrane (3) having size variations in each of the two orthogonal plane directions, x and y, lower than 4%, preferably lower than 3%, determined as above described, with
- two GDL sheets, (1) and (2), each having on one surface an electrocatalytic layer (not shown in Fig. 3), having the same sizes as length and width of the membrane (3) film;

wherein the two sheets GDL (1) and (2) are placed so that the electrocatalytic layer contacts, respectively, each of the two faces of the membrane, the two GDL sheets are placed coextensive with the two
surfaces of the membrane (3);

2) the roll obtained in 1) is cut perpendicularly to the assembling direction in the requested formats;

3) application of one gasket to the formats obtained in 2).

The assembling of step 1) can be carried out for example by calendering or hot lamination between two rolls, or by hot molding of the films (1) and (2) on the film (3), etc. The hot calendering between two rolls is preferred.

Fig. 3 shows the application of the first sheet GDL (1) and of the second sheet GDL (2) on the two opposite surfaces of the membrane (3) film.

In step 1) the assembling process is preferably carried out at temperatures in the range 110°C-200°C, more preferably 120°C-180°C. The assembling speed is generally comprised between 0.1 and 50 meters/minute, preferably from 0.1 to 20 meters/minute. The pressure exerted by the lamination rolls on the assembly is generally comprised between 5 and 40 Kg/cm².

Alternatively, step 1) can be carried out in two steps, in the first the GDL (1) is applied to the membrane (3) and in the second step the GDL (2) is applied on the free membrane surface.

The gasket application in step 3) can be carried out by press molding of the gasket on the format, preferably the gasket is applied by injection molding. This step is preferably carried out at temperatures in the range 130°C-220°C and at pressures generally comprised between 100 and 250 bar and for a time between 60 and 600 seconds. During the gasket application it is preferable that the gasket penetrates the GDL sheet, preferably for at least 1 mm. These zones are represented in Fig. 2 with (5) and (6). The Applicant has surprisingly and unexpectedly found that the invention membrane use implies a long duration of the invention assembly.

According to another embodiment of the present invention, an electrocatalytic layer is applied to the membrane (3) film on each side, then the GDL sheets (1) and (2) are applied without the electrocatalytic layer. The electrocatalytic layers can be applied on the membrane for example by a continuous decal process, as described in
USP 6,933,003, by direct casting of the electrocatalytic layer on the membrane or by spraying the catalytic ink on the membrane, as for example described in US 2005/0163920.

It has been unexpectedly and surprisingly found by the Applicant that the assemblies according to the present invention show, during the use in electrochemical devices, for example fuel cells, a duration longer than that of the known assemblies of the prior art, even after repeated hydration/dehydration cycles typical of electrochemical devices, even more than 200 cycles, by using the above test.

As said, the process of the present invention allows to obtain a 7-layer MEA assembly from a 7-layer MEA roll also by a continuous process. A gasket is then applied to the 7-layer MEA as described in step 3).

A further object of the present invention is represented by electrochemical devices, in particular fuel cells, comprising the invention assemblies.

The preparation of the ionomers used for preparing the membranes can be carried out with a radical polymerization process in mass, solution, suspension, emulsion. See USP 3,282,875, USP 6,639,011, USP 6,555,639.

The polymerization in aqueous emulsion or in microemulsion can for example be mentioned. The surfactants which can be used in these polymerizations are (per)fluorinated surfactants, for example salts (as defined below) of the perfluorooctanoic, perfluorononanoic, perfluorodecanoic acid, or their mixtures, etc., (per)fluoropolyethers with an acid end group (example COOH, SO\textsubscript{3}H), salified with NH\textsubscript{4}\textsuperscript{+} or with alkaline metal cations, the other end group being (per)fluorinated, optionally containing one H or Cl atom. The number average molecular weights of the perfluoropolyether surfactants generally range between 300 and 1,800, preferably between 350 and 750.

The microemulsion polymerization is well known in the art. See USP 6,555,639.

In particular the ionomer preparation is carried out by using an aqueous
emulsion wherein in the reaction medium, as surfactants, those of formula:

\[ R_t\cdot X_1 \cdot M^+ \]

are used, wherein:
X\(_1\) is equal to -COO, -SO\(_3\);  
M is selected from H, NH\(_4\) or an alkaline metal;  
R\(_t\) represents a (per)fluoropolyether chain, preferably having average number molecular weight comprised between about 300 and about 1,800, preferably from 300 to 750, said (per)fluoropolyether chain comprising repeating units selected from one or more of the following:

a) \(-\left(\text{C}_{3}\text{F}_{6}\text{O}\right)\cdot\)  
b) \(-\left(\text{CF}_{2}\text{CF}_{2}\text{O}\right)\cdot\)  
c) \(-\left(\text{CFL}_{0}\text{O}\right)\cdot\) wherein L\(_0\) = -F, -CF\(_3\);  
d) \(-\text{CF}_{2}\left(\text{CF}_{2}\right)_{z'}\text{CF}_{2}\text{O}\cdot\) wherein z' is an integer 1 or 2;  
e) \(-\text{CH}_{2}\text{CF}_{2}\text{CF}_{2}\text{O}\cdot\).

R\(_t\) is monofunctional and has a (per)fluoroxyalkyl end group T, for example CF\(_3\)O-, C\(_2\)F\(_5\)O-, C\(_3\)F\(_7\)O-; optionally in perfluoroalkyl end groups one fluorine atom can be substituted by one chlorine or hydrogen atom. Examples of these end groups are Cl(C\(_3\)F\(_5\)O)-, H(C\(_3\)F\(_5\)O)-. The unit a) C\(_3\)F\(_6\)O can be CF\(_2\)-CF(C\(_3\)F\(_3\))O- or -CF(C\(_3\)F\(_3\))CF\(_2\)O-.  

The polymerization in aqueous emulsion is well known in the prior art. See USP 6,639,011.

In the above mentioned formula R\(_t\) preferably has one of the following structures:

1) \[ T\cdot\left(\text{CF}_{2}\text{O}\right)_{x'}\left(\text{CF}_{2}\text{CF}_{2}\text{O}\right)_{b'}\cdot\text{CF}_{2}\cdot \]
   with b/a comprised between 0.3 and 10, extremes included, a being an integer different from 0;  
2) \[ T\cdot\left(\text{CF}_{2}\right)_{z'}\left(\text{CF}_{2}\text{O}\right)_{b'}\cdot\text{CF}_{2}\cdot \]
   wherein z' is an integer equal to 1 or 2;  
3) \[ T\cdot\left(\text{C}_{3}\text{F}_{6}\text{O}\right)_{r'}\left(\text{C}_{2}\text{F}_{4}\text{O}\right)_{b'}\left(\text{CFL}_{0}\text{O}\right)\cdot\text{CF}_{2}\cdot \]
   with r/b = 0.5-2.0, b being different from zero; (r+b)/t = 10-30;
a, b, b', r, t, are integers, the sum of which is such that R is has the above mentioned number average molecular weight values; T = -OCF₃ or -OCF₂Cl.

The compounds wherein R₁ has the formula 3) wherein b = 0, are still more preferred.

The (per)fluoropolyethers R₁ are obtainable with well known processes of the prior art, see for example the following patents herein incorporated by reference: USP 3,665,041, USP 2,242,218, USP 3,715,378 and EP 239,123. The fluoropolyethers functionalized with hydroxyl termination are for example obtained according to the patents EP 148,482, USP 3,810,874, from which the functional end groups are obtained with the processes indicated in these patents.

It is possible to use in polymerization chain transfer agents. For example iodide and/or bromides of alkaline or alkaline-earth metals, according to what described in USP 5,173,553. Preferably chain transfer agents containing hydrogen, such as hydrocarbons, alcohols, in particular ethyl acetate and ethane are used.

The polymerization initiators used in the present invention process are preferably radical inorganic initiators, such as for example ammonium and/or potassium and/or sodium persulphate, optionally in combination with ferrous, cuprous or silver salts. The method of the initiator feeding in the polymerization reactor can be in a continuous way or with an only addition at the beginning of the polymerization.

The polymerization reaction is generally carried out at temperatures in the range 25°C-70°C, preferably 50-60°C, under pressure up to 30 bar (3 MPa), preferably higher than 8 bar (0.8 MPa).

Monomer (B) and optionally (B') is fed into the polymerization reactor in a continuous way or by steps.

When the polymerization is completed, the ionomer is isolated by conventional methods, such as coagulation by addition of electrolytes or by freezing.

If desired, the membrane can be crosslinked. When the membranes are obtained by extrusion then the crosslinking is not carried out.

In order to carry out the crosslinking, the crosslinkable ionomer of which the
membrane is formed, is mixed with crosslinking agents. The sulphonlic fluorinated ionomers are crosslinked for example by peroxidic way. In this case they must contain radical attack sites in the chain and/or in end position to the macromolecules, for example iodine and/or bromine atoms.

Preferably the crosslinkable fluorinated sulphonlic ionomers comprise:
- monomeric units deriving from TFE;
- monomeric units deriving from CF₂=CF-O-CF₂CF₂SO₂F;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

The introduction in the chain of said iodine and/or bromine atoms can be carried out by addition, in the reaction mixture, of brominated and/or iodinated "cure-site" comonomers, such as bromo- and/or iodo-olefins having from 2 to 10 carbon atoms, as described for example in USP 4,035,565 and USP 4,694,045, or iodo- and/or bromo- fluoro-alkylvinylethers, as described in USP 4,745,165, USP 4,564,662 and EP 199,138, in amounts such that the "cure-site" comonomer content in the final product is generally comprised between 0.05 and 2 moles per 100 moles of the other basic monomeric units.

Alternatively, or also in combination with "cure-site" comonomers, the introduction of iodine and/or bromine end atoms can be carried out by addition to the reaction mixture of iodinated and/or brominated chain transfer agents, such as for example the compounds of formula R₁(n)(I)x(Br)y, where R₁ is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x and y are integers comprised between 0 and 2, with 1 ≤ x+y ≤ 2 (see for example USP 4,243,770 and USP 4,943,622). It is also possible to use as chain transfer agents iodides and/or bromides of alkaline or alkaline-earth metals, according to what described in USP 5,173,553.

Preferably crosslinking of radical type uses ionomers containing units of the bis-olefin of formula (I) and iodine in end position.

The sulphonlic ionomer is crosslinked by radical way at a temperature in the
range 100°C-200°C, in connection with the type of peroxide used, by adding a peroxide capable to generate radicals by heating. Generally, the peroxide amount is between 0.1% and 5% by weight with respect to the polymer. Among the peroxides which can be used, the following ones can be mentioned: dialkylperoxides, such as for example di-terbutyl-peroxide and 2,5-dimethyl-2,5-di(terbutylperoxy)-hexane; dicumyl peroxide; dibenzoyl peroxide; diterbutyl perbenzoate; di-1,3-dimethyl-3-(terbutylperoxy)butylcarbonate. Other peroxidic systems are described, for example, in the patent applications EP 136,596 and EP 410,351.

Furthermore the following components can optionally be added to the ionomer mixture with the crosslinking agents:

- a crosslinking co-agent, in amount comprised between 0.5 and 10%, preferably between 1 and 7% by weight with respect to the polymer; among crosslinking co-agents it can be mentioned: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphate; N,N-diallyl-acrylamide; N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinil-methyltrisiloxane; N,N'bisallylbicyclo-oct-7-ene-disuccinimide (BOSA); bis olefin of formula (I), triazines;

- a metal compound, in amounts comprised between 1% and 15%, preferably between 2% and 10% by weight with respect to the polymer, said metal compound selected from divalent metal oxides or hydroxides, such as for example Mg, Zn, Ca or Pb, optionally associated to a weak acid salt, such as for example stearates, benzoates, carbonates, oxalates or phosphites of Ba, Na, K, Pb, Ca;

- conventional additives such as thickeners, pigments, antioxidants, stabilizers and the like;

- inorganic or polymeric reinforcing fillers, preferably optionally fibrillatable PTFE. Preferably the fillers have particle size from 10 to 100 nm, preferably 10-60 nm.

As said, the ionomeric membrane film (3) which is a flat film is characterized in
having size variations in the two orthogonal plane directions, x and y, lower than 4%, preferably lower than 3%, determined according to the following formula:

\[(A-B)\times100/B,\]

wherein:
- B is the membrane length in the x or y direction, after drying under vacuum for a time of 1 h at 105°C and at a residual pressure lower than 30 mBar;
- A is the membrane length in the same direction where B is measured, after membrane treatment in distilled water at 100°C for 30 minutes.

Preferably the ionomeric membrane films have the size variations in the two orthogonal plane directions x and y, substantially absent, i.e. the membrane does not show significant size variations.

These membranes are obtained with the processes indicated in the text, in particular with the above described process by casting and by impregnation.

The following Examples illustrate with non limitative purposes the present invention.

EXAMPLES

Methods

Determination of the membrane size variations in the x and y direction

The size variation in the x and y direction is determined according to the following formula:

\[(A-B)\times100/B\]

wherein:
- B is the length of the membrane film in the considered direction, after drying under vacuum for a time of 1 h at 105°C and at a residual pressure lower than 30 mBar;
- A is the membrane length in the considered direction after treatment in distilled water at 100°C for 30 minutes.
Test of duration in fuel cell of 7-layer MEA with gasket

The 7-layer MEA with gasket is assembled in a test device Fuel Cell Technologies® and is subjected to continuous hydration and dehydration cycles characterized as follows:

A) dehydration:
- gas fed to the anode circuit: hydrogen hydrated with dew point 30°C;
- gas fed to the cathode circuit: air hydrated with dew point 30°C;
- cell temperature: 80°C;
- reacting gas pressure: 1.5 bar (hydrogen side), 1.3 bar (air side);
- drained current with electronic load: 20 ampere, corresponding to 800 mA/cm²;
- duration: 60 minutes;

B) hydration:
- gas fed to the anode circuit: hydrogen hydrated with dew point 85°C;
- gas fed to the cathode circuit: air hydrated with dew point 85°C;
- cell temperature: 80°C;
- reacting gas pressure: 1.5 bar (hydrogen side), 1.3 bar (air side);
- drained current with electronic load: 20 ampere, corresponding to 800 mA/cm²;
- duration: 60 minutes.

The dehydration/hydration cycle is repeated up to 200 times. At the beginning of the test and after every 25 cycle repetitions the integrity of the adhesion between membrane/gasket is checked through the measurement of the voltage at open circuit, i.e. with drained current equal to zero, after the hydration cycle.

A damaging of the MEA with gasket is indicated by a significant decrease, higher than 2% with respect to the starting value, of the voltage determined at open circuit.

Pull off test ISO 4624

The test has been carried out under the following conditions:
- specimen area: 615.4 mm²;
- pull off rate: 0.5 mm/min;
- type of adhesive used: VHB (3M).

EXAMPLE A

Polymerization and obtainment of an ionomer having equivalent weight 870 g/eq in SO₃H form

In a 22 litre autoclave the following reactants are introduced:
- 11.5 litres of demineralized water;
- 980 g of sulphonic monomer of formula CF₂=CF-O-CF₂CF₂-SO₂F;
- 3,100 g of an aqueous solution at 5% by weight of a fluoropolyoxyalkylene with acid end group having number average molecular weight 521, potassium salified, of formula:

\[ CF₂ClO(CF₂CF(CF₃)O)ₙ(CF₂O)ₘCF₂COOK \]

wherein \( n/m = 10 \).

The autoclave, kept under stirring at 540 rpm, is heated to 60°C. 225 ml of an aqueous solution having a 6 g/l concentration of potassium persulphate (KPS) are then fed into the autoclave. The pressure is brought to 1.3 absolute MPa by introducing TFE. The reaction starts after 4 min. The pressure is maintained at 1.3 absolute MPa by introducing TFE. When 1,000 g of TFE have been fed into the reactor, 175 g of the sulphonic monomer of formula CF₂=CF-O-CF₂CF₂-SO₂F are added. Then 175 g of the same sulphonic monomer are introduced in the reactor every 200 g of TFE fed to the reactor is 4,000 g.

The reaction is stopped after 233 minutes by interrupting the TFE feeding, cooling and venting the reactor under vacuum. The produced latex has a solid content of 28.5% by weight. The latex is coagulated by freezing and defrosting, the polymer separated from the mother waters, washed with water up to a constant pH of the washing waters.

The equivalent weight of the copolymer results to be of 870 g/eq, corresponding to a composition 85.5% molar of TFE and 14.5% molar of sulphonic
monomer.

A part of the polymer is separated from the washing waters and is treated with a 20% by weight KOH solution at 80°C for 6 hours, by keeping under stirring. For a part by weight of polymer 10 parts by weight of KOH solution are fed. At the end washings with demineralized water are performed until the washing waters have a constant pH. 10 parts by volume are added for a part by weight of polymer of a 20% HCl solution, maintaining under stirring at room temperature for 2 h. At the end washings with demineralized water are effected until the washing waters show a constant pH. The steps of the HCl solution addition and of the successive washing with water are repeated for two further times. The polymer under the SO₃H form is recovered and dried for 40 h at 80°C.

EXAMPLE B
Preparation of a ionomer dispersion in SO₃H form obtained in the Example A

A 8.6% by weight dispersion of the sulphonic ionomer obtained in the Example 1 is prepared by dissolving 18.8 g of ionomer in 200 g of a quaternary mixture formed of 39 g of H₂O, 80 g of isopropanol, 80 g of n-propanol and 1 g of a fluorophosphateoxyalkylene having formula:

\[ CF₂H-O(CF₂CF₂O)ₘ(CF₂O)ₙ-CF₂H \]

having a boiling range comprised between 80°C and 120°C and number average molecular weight of 350. Solubilization is carried out at room temperature for 24 hours in a glass vessel equipped with a mechanical stirrer. At the end the dispersion shows a Brookfield viscosity, determined with a Synchro Electric® model LVT viscosimeter, measured at 25°C with runner No. 4 at 60 rpm, of 1,000 cP.

EXAMPLE C
Obtainment of an ionomeric membrane by casting of the dispersion obtained in the Example B

The ionomeric membrane is prepared by depositing on a Kapton support having a 50 μm thickness a liquid strip made of the dispersion prepared in Example 2, having a length of about 30 cm. By a stratifying Braine® knife, set at a knife heigh
700 μm, the dispersion is dragged on a Kapton® support so as to form a continuous layer of liquid. The drag direction is the x direction of the membrane. Then the liquid strip is dried in stove at 65°C for 30 minutes by evaporating most of the solvent. It is thus formed a raw ionomeric membrane on the Kapton support.

The annealing step is carried out by transferring in stove at 150°C for 1.5 hours the membrane on the Kapton support, followed by a step of 0.5 h at 210°C having the membrane on the support. At the end of the step the Kapton support is removed from the ionomeric membrane by immersion in water.

The size variations, measured according to the above described method, are equal to 3% in both the membrane directions x and y.

**EXAMPLE 1**

Obtainment of a 7-layer MEA with gasket according to the present invention and duration test in cell

A 7-layer MEA having 5.4 x 5.4 cm sizes is assembled with the membrane obtained in the Example C and two GDL of the LT250E-W type having a catalytic layer applied on the side coming into contact with the ionomeric membrane, by using a hot pressing process under the following conditions:

- temperature: 150°C;
- pressure: 15 Kg/cm²;
- time: 5 minutes.

The membrane sizes are 5.4 x 5.4 cm.
The sizes of the first GDL are 5.4 x 5.4 cm.
The sizes of the second GDL are 5.4 x 5.4 cm.
The assembly is carried out so that the GDLs result coextensive to the membrane.

As gasket, the fluorinated elastomer Tecnoflon® FOR 435 is used.

The 7-layer MEA is inserted in a Terenzio® Presse model molding press by using suitable sealing frames so as to obtain a frame gasket having 7 x 7 cm external sizes. The penetration of the gasket material in the porous matrix of the 7-layer MEA
GDL is 2 mm on each of the 4 perimeter sides. In this way a central surface remains on each of the two faces of the 7-layer MEA, not covered by the gasket material, having 5 x 5 cm sizes on the side of the first GDL and 4.8 x 5 cm sizes on the side of the second GDL.

The molding conditions for applying the gasket are the following:

- temperature: 170°C;
- pressure: 180 bar;
- time: 90 seconds.

The so obtained 7-layer MEA with gasket is transferred into a test device Fuel Cell Technologies® and subjected to the test conditions hereinabove set forth.

The open circuit voltage value determined at the beginning of the test is 948 mV, after 200 cycles the registered value is 950 mV, i.e. it substantially remains unaltered as it is within the experimental error.
CLAIMS

1. 7-layer MEA assemblies with gasket, comprising:
   - a film of ionomic membrane (3) having size variations in the two orthogonal plane directions, x and y, lower than 4%, preferably lower than 3%, determined by the following expression:
     \[(A-B) \times 100/B,\]
   wherein:
   - B is the membrane length in the x or y direction, after drying under vacuum for a time of 1 h at 105°C and at a residual pressure lower than 30 mBar;
   - A is the membrane length in the same direction where B is measured, after treatment of the membrane in distilled water at 100°C for 30 minutes;
   - two GDL sheets (1) and (2) in porous material having on one surface an electrocatalytic layer, coextensive with the membrane (3) surface;
   - the two sheets (1) and (2) placed so that the electrocatalytic layer contacts, respectively, each of the two membrane surfaces;
   - a gasket (4) disposed according to a frame shape along the assembly perimeter.

2. Assemblies according to claim 1, wherein the ionomic membrane (3) contains acid functional groups -SO_3H and/or -COOH.

3. Assemblies according to claims 1-2, wherein the ionomic membrane films (3) are obtainable by extrusion and simultaneous bistretching in the two orthogonal plane directions and subsequent hydrolysis of the acid precursors -SO_3H and/or -COOH.

4. Assemblies according to claim 3, wherein the stretching ratio in the simultaneous bistretching is generally comprised between 15:1 and 100:1.

5. Assemblies according to claims 1-4, wherein the GDL (1) and (2) sheets are
formed of the following layers:
- a gas microdiffusion layer, having hydrophobic characteristics, preferably formed of a mixture of carbon powder and PTFE;
- a gas macrodiffusion layer, with hydrophobic characteristics, preferably formed of carbon fibers or carbon tissues treated with PTFE.

6. Assemblies according to claims 1-5, wherein the membrane and the electrocatalytic layers are obtainable by using (per)fluorinated ionomers with sulphonic groups in -SO₃H acid or salified form, having equivalent weight from 380 g/eq to 1,600 g/eq, preferably from 500 to 1,200 g/eq, still more preferably 750-950 g/eq.

7. Assemblies according to claim 6, wherein the ionomers comprise the following units:
   (A) monomeric units deriving from one or more fluorinated monomers containing at least one ethylene unsaturation;
   (B) fluorinated monomeric units containing -SO₂F sulphonyl groups in such amount that the ionomer has the equivalent weight in the above mentioned range.

8. Assemblies according to claims 6-7, wherein the ionomers are homopolymers formed of monomeric units (B).

9. Assemblies according to claims 6-8, wherein the ionomers containing the sulphonic groups in acid form -SO₃H are obtainable by hydrolysis of the -SO₂F groups, and optionally, salification of the -SO₃H groups.

10. Assemblies according to claims 6-9, wherein the type (A) fluorinated monomers are selected from the following:
    - vinilydene fluoride (VDF);
    - C₂₋₈ perfluoroolefins, preferably tetrafluoroethylene (TFE);
    - C₂₋₈ chloro- and/or bromo- and/or iodo-fluoroolefins such as chlorotri-fluoroethylene (CTFE) and bromotrifluoroethylene;
    - CF₂=CFOR₁ (per)fluoroalkylvinylethers (PAVE), wherein R₁ is a C₁₋₈
(per)fluoroalkyl, for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl;

- \( \text{CF}_2=\text{CFOX} \) perfluoro-oxyalkylvinylethers, wherein \( X \) is a \( C_{1-12} \) perfluoroxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl;

- fluorovinylethers (MOVE) of general formula \( \text{CFX}_\text{A} = \text{CX}_\text{A} \text{OCF}_2 \text{OR}_\text{A} \), wherein \( \text{R}_\text{A} \) is a linear, branched \( C_{1-6} \) (per)fluoroalkyl group or \( C_6-C_6 \) cyclic, or a linear or branched when possible \( C_{1-6} \) (per)fluoroxyalkyl group containing from one to three oxygen atoms; when \( \text{R}_\text{A} \) is fluoroalkyl or fluoroxyalkyl as defined above it can contain from 1 to 2 atoms, equal or different, selected from the following: \( \text{H}, \text{Cl}, \text{Br}, \text{I} \); \( X\text{A} = \text{F, H, preferably F} \); the preferred fluorovinylethers are: (MOVE 1) \( \text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}_3 \), (MOVE 2) \( \text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3 \), (MOVE 3) \( \text{CF}_2=\text{CFOCF}_2\text{OCF}_3 \).

11. Assemblies according to claims 6-10, wherein the type (B) fluorinated monomers are selected from one or more of the following:

- \( \text{F}_2\text{C}=\text{CF-O-SF}_2\text{-CF}_2\text{-SO}_2\text{F} \);
- \( \text{F}_2\text{C}=\text{CF-O-[CF}_2\text{-CX}_\text{A}\text{F-O]_{nA}-(CF}_2\text{)_{nB}-SO}_2\text{F} }\)
  wherein \( X \text{A} = \text{Cl, F or CF}_3 \); \( nA = 1-10, nB = 2, 3 \);
- \( \text{F}_2\text{C}=\text{CF-O-(CF}_2\text{)_{nC}-SO}_2\text{F} \); \( nC=3-10 \);
- \( \text{F}_2\text{C}=\text{CF-Ar-SO}_2\text{F} \) wherein Ar is an aromatic ring, the ring can be substituted in one or more free positions by aliphatic chains from 1 to 10 carbon atoms, optionally containing heteroatoms.

12. Assemblies according to claims 6-11, wherein alternatively to the monomers (B), fluorinated monomers (B') containing precursor groups can be used, which are transformed by hydrolysis into -COOH acid groups, optionally with their subsequent salification, the monomers (B') optionally being used in admixture with those containing -SO_2F groups.

13. Assemblies according to claims 6-12, wherein the ionomers contain from
0.01% to 2% by moles of monomeric units deriving from a bis-olefin of formula:

$$\text{R}_1\text{R}_2\text{C} = \text{CH}-(\text{CF}_2)_m\text{CH} = \text{CR}_3\text{R}_6$$  \hspace{1cm} (I)

wherein:

- \( m = 2-10 \), preferably 4-8;
- \( \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_6 \), equal to or different from each other, are \( H \) or \( \text{C}_1-\text{C}_5 \) alkyl groups, preferably \( H \).

14. Assemblies according to claims 6-13, wherein the membranes and the electrocatalytic layers contain perfluorinated ionomers obtainable from ionomers comprising:

- monomeric units deriving from TFE;
- monomeric units deriving from \( \text{CF}_2=\text{CF-O-CF}_2\text{CF}_2\text{SO}_2\text{F} \).

15. Assemblies according to claims 1-14, wherein the electrocatalytic layers comprise one ionomer and a catalyst, preferably Pt or a mixture of Pt with one or more metals, preferably for example Ru, Rh, Mo, said catalyst being finely dispersed and preferably supported on carbon powder.

16. Assemblies according to claim 15, wherein the ratio by weight between catalyst and ionomer in each of the two electrocatalytic layers ranges from 0.5 to 4, preferably between 0.5 and 2.5.

17. Assemblies according to claims 15-16, wherein the ratio mg of catalyst metal/cm\(^2\) of electrocatalytic layer ranges from 0.01 to 2.

18. Assemblies according to claims 1-17, wherein the gasket is formed of polymers selected from silicones, fluorosilicones, fluoroelastomers, EPDM, thermoplastic elastomers.

19. A process for producing 7-layer MEA with gasket according to claims 1-18, comprising the following steps:

1) obtainment of a roll of a 7-layer MEA assembly by assembling of

- a film of membrane (3) having size variations in the two orthogonal plane directions, \( x \) and \( y \), lower than 4%, preferably lower than 3%, determined as above described, with
two GDL sheets, (1) and (2), each having on one surface an
electrocatalytic layer having the same length and width of the
membrane (3) film;
wherein the two sheets GDL (1) and (2) are placed so that the
electrocatalytic layer contacts, respectively, each of the two
faces of the membrane, the two GDL sheets are coextensive
with the two membrane (3) surfaces;
2) the roll obtained in 1) is cut perpendicularly to the assembling direction
in the requested formats;
3) application of a gasket to the formats obtained in 2).

20. A process according to claim 19, wherein the assembling in step 1) is carried
out by calendering or hot lamination between two rolls, or by hot molding of the
films (1) and (2) on the film (3).

21. A process according to claim 20, wherein calendering is used.

22. A process according to claims 19-21, wherein in step 1) the assembling is
carried out at temperatures in the range 110°C-200°C, preferably
120°C-180°C; the assembling rate being comprised between 0.1 and 50 me-
ters/minute, preferably from 0.1 to 20 meters/minute; the pressure exerted by
the lamination rolls on the assembly being comprised between 5 and 40
Kg/cm².

23. A process according to claims 19-22, wherein the step 1) is carried out in two
steps, wherein in the first step GDL (1) is applied to the membrane (3) and in
the second step the GDL (2) is applied on the free membrane surface.

24. A process according to claims 19-23, wherein the gasket application in step 3)
is carried out by injection molding.

25. A process according to claim 24, wherein the gasket application is carried out
at temperatures in the range 130°C-220°C and at pressures comprised
between 100 and 250 bar.

26. A process according to claims 19-25, wherein to the membrane film an
electrocatalytic layer is applied on each side and the sheets GDL (1) and (2) are successively applied without the electrocatalytic layer.

27. Electrochemical devices, in particular fuel cells, comprising the assemblies according to claims 1-18.

28. Use of the assemblies according to claims 1-18 in electrochemical devices, in particular in fuel cells.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INVI. H01M8/24 H01M8/02 H01M8/10 H01M2/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 99/04446 A (BALLARD POWER SYSTEMS [CA]; BARTON RUSSELL H [CA]; GIBB PETER R [CA];) 28 January 1999 (1999-01-28) cited in the application * see p.6, 1.1 - 25, p.7, 1.12 - p.8, 1.11, claims * the whole document</td>
<td>1-28</td>
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X Further documents are listed in the continuation of Box C. X See patent family annex.

Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance
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Authorized officer: Stellmach, Joachim
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