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(72) Inventor; and

(71) Applicant: DÜRR, Robin Nils [DE/SE]; Von Kraemers
Allé 29 lgh 1303, 752 37 Uppsala (SE).

(74) Agent: BRANN AB; Box 3690, Stockholm 103 59 (SE).

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(54) Title: PROCESS FOR PREPARING A MEMBRANE ELECTRODE ASSEMBLY

(57) Abstract: Processes for manufacturing membrane electrode assemblies for use in electrochemical cells are disclosed. The processes comprise the steps of: depositing a layer of a liquid composition capable of being solidified by freezing onto an electrode, cooling the electrode with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition thereby forming an electrode coated with a solidified layer of the liquid composition, arranging the electrode on a surface of a membrane, and heating the electrode and membrane arrangement for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid composition and preferably not higher than a glass transition temperature of the membrane.



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PROCESS FOR PREPARING A MEMBRANE ELECTRODE ASSEMBLY

FIELD OF INVENTION

The invention relates to a process for attaching an electrode to a membrane, and more particularly a process for manufacturing a membrane electrode assembly for use in an electrochemical cell.

BACKGROUND

Due to the global warming caused by greenhouse gases like carbon dioxide, a rising effort is made in the transition from fossil fuel-based energy carriers to alternative renewable energy carriers like hydrogen. Hydrogen can be generated by an electrochemical process, in which water is split into molecular hydrogen and oxygen, i.e. water electrolysis. The necessary energy can be provided by renewable energy sources like water, wind or solar energy making the hydrogen clean and green with no additional carbon dioxide evolving from the process itself. This water electrolysis cell, or electrolyzer, is an example for an electrochemical cell.

In the heart of most electrochemical cells there is a membrane electrode assembly (MEA). The membrane separates the cell into two halves: the anodic and the cathodic compartment.

Today most MEA are formed by hot pressing of the electrodes with a membrane in between. Such a process puts limitations, particularly on the membrane used in the process which need to have certain thermoplastic properties for the process to work.

US 9490488 B2 discloses Polybenzimidazole (PBI)-based MEAs for high temperature polymer electrolyte membrane fuel cell (PEMFC) prepared by direct hot pressing of catalyst layer on Teflon sheets on to both sides of phosphoric acid doped PBI membranes. The MEAs show two times higher performance compared to the MEAs prepared by normal brush coating at an operating temperature of 160°C.

There is still a need for a more efficient and more versatile process to produce a membrane electrode assembly which allows the use of a larger variety of membranes. Another need in the area is a process for assembling a membrane electrode assembly wherein both electrodes can be assembled with the membrane simultaneously.

SUMMARY OF THE INVENTION

The object of the invention is to overcome the drawbacks of the prior art. This is achieved by the process as defined in claim 1.

10 The invention is based on using a liquid composition, which is capable of being solidified by freezing, for accomplishing adhesion of an electrode to a membrane, and facilitating arranging a membrane and an electrode on to each other.

In its most generic form the present invention provides a process for attaching
15 an electrode to a membrane, i.e. a process of preparing a membrane electrode assembly comprising an electrode and a membrane.

Accordingly, in a first aspect the present invention relates to a process 10 for preparing a membrane electrode assembly (MEA) 100 comprising an electrode 101 and a membrane 102, which process comprises the following steps: 10:1
20 depositing a layer of a liquid composition onto a first electrode 101, which liquid composition is capable of being solidified by freezing; 10:2 cooling the first electrode with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode coated with a layer of solidified liquid composition; 10:3
25 arranging on a first surface of a membrane 102 the first electrode coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the first side of the membrane; and, 10:4 heating the arranged electrode 101 and membrane 102 for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid
30 composition thereby forming a membrane electrode assembly 100 comprising the first electrode and the membrane.

By means of the above process a membrane electrode assembly comprising an electrode attached to a membrane can be prepared. If desired, a second electrode 103 can be attached to a membrane electrode assembly obtained by means of the above process. Preferably, the second electrode 103 is attached
5 by means of the inventive process.

Accordingly, in another aspect present invention relates to a process 30 for preparing a membrane electrode assembly (MEA) 110 comprising two electrodes 101, 103 and one membrane 102, which process comprises the following steps: 30:1 depositing a layer of a liquid composition onto a first
10 electrode 101, which liquid composition is capable of being solidified by freezing; 30:2 cooling the first electrode 101 with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode 101 coated with a layer of solidified liquid composition; 30:3 arranging on a first surface of a membrane
15 102 the first electrode 101 coated with the layer of solidified liquid composition with the layer of the solidified liquid composition facing the first side of the membrane; 30:4 heating the arranged first electrode and membrane for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid composition, thereby forming a membrane electrode
20 assembly 100 comprising the first electrode and the membrane; 30: 5 depositing a layer of a liquid composition onto a second electrode 103, which liquid composition is capable of being solidified by freezing; 30:6 cooling the second electrode 103 with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition,
25 thereby forming a second electrode 103 coated with a layer of the solidified liquid composition; 30:7 arranging on a second opposite surface of the membrane 102 of the membrane electrode assembly 100 comprising the first electrode 101 and the membrane 102 obtained in step 30:4 the second electrode 103 coated with the layer of solidified liquid composition with the
30 layer of the solidified liquid composition facing said second opposite side of the membrane of the membrane electrode assembly 100 comprising the first electrode 101 and the membrane 102 obtained in step 30:4; 30:8 heating the arranged second electrode 103 and membrane of the membrane electrode

assembly 100 comprising the first electrode and the membrane obtained in step 30:4 for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid, thereby forming a membrane electrode assembly 110 comprising the first electrode 101, the membrane 102, and the second electrode 103.

Alternatively, instead of carrying out attachment of two electrodes sequentially to a membrane, the electrodes can be simultaneously attached to a membrane.

Accordingly, in yet an aspect the present invention relates to a process 20 for preparing a membrane electrode assembly (MEA) 110 comprising two electrodes 101, 103 and one membrane 102, which process comprises the following steps: 20: 1 depositing a layer of a liquid composition onto a first electrode 101, and onto a second electrode 103, which liquid composition is capable of being solidified by freezing; 20:2 cooling the first electrode 101 with the deposited layer of liquid composition and the second electrode 103 with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode 101 coated with a layer of solidified liquid composition, and a second electrode 103 coated with a layer of solidified liquid composition; 20:3 arranging on a first surface of a membrane 102 the first electrode 101 coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the first side of the membrane, and arranging on a second opposite surface of the membrane 102 the second electrode 103 coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the second opposite side of the membrane; 20:4 heating the arranged first electrode 101, membrane 102, and second electrode 103 for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid composition, thereby forming a membrane electrode assembly 110 comprising the first electrode 101, the membrane 102, and the second electrode 103.

In preferred embodiments of the inventive processes a washing step is included after the heating step (10:4, 30:4, 30:8, 20:4).

Preferably, pressure is applied during the heating step (10:4, 30:4, 30:8, 20:4).

BRIEF DESCRIPTION OF ATTACHED DRAWINGS

Fig. 1a is a schematic illustration of a membrane electrode assembly 100
5 comprising an electrode and a membrane

Fig. 1b is a schematic illustration of a membrane electrode assembly 110
comprising two electrodes 101, 103 and a membrane 102.

Fig. 2 is a flow-chart of a process according to the invention.

Fig. 3 a) and b) are flow-charts of processes according to the invention.

10 Fig. 4 a) and b) show MEAs prepared according to one embodiment of the
invention.

Fig. 5 shows a schematic illustration of one embodiment of the invention.

Fig. 6 a), b), and c) show MEAs prepared according to one embodiment of the
invention.

15 Fig. 7 shows a MEA prepared according to one embodiment of the invention.

LIST OF ABBREVIATIONS USED

MEA – membrane electrode assembly

T_g – glass transition temperature

20 PEM – proton exchange membrane

PEMFC – proton exchange membrane fuel cell

AEM – anion exchange membrane

AEMFC – anion exchange membrane fuel cell

PEMEC – proton exchange membrane electrolyzer cell

25 AEMEC – anion exchange membrane electrolyzer cell

DMFC – direct methanol fuel cell

DMSO – dimethyl sulfoxide

GDL – gas diffusion layer

SPEAK – sulfonated polyaryletherketone

5 PTFE – polytetrafluoroethylene

As used herein, the term “membrane electrode assembly”, and the abbreviation “MEA”, are used to refer to an assembly comprising at least one electrode and one membrane, such as one electrode 101 and one membrane
10 102, or two electrodes 101, 103 and one membrane 102, wherein the electrodes are attached to opposite surfaces of the membrane.

Further embodiments and advantages of the invention will be apparent from the detailed description and appended claims.

15 DETAILED DESCRIPTION

As described above in an electrochemical cell like an electrolyzer, electrical energy can be stored in chemical bonds, as chemical energy, such as in hydrogen which is a renewable energy carrier. This hydrogen can be used for example in fuel cells to convert the stored energy back to electrical energy. A
20 fuel cell is another kind of electrochemical cell, which converts chemical energy into electricity, i.e. electrical energy. Hydrogen and/or hydrocarbons are often used as fuel in electrochemical cells. At the heart of most electrochemical cells is a membrane electrode assembly (MEA). The most common electrochemical cells with a MEA are proton exchange membrane
25 electrolyzer cell (PEMEC), anion exchange membrane electrolyzer cell (AEMEC), proton exchange membrane fuel cell (PEMFC), anion exchange membrane fuel cell (AEMFC), direct methanol fuel cell (DMFC), Artificial leaf (an electrochemical cell which performs artificial photosynthesis) and redox flow batteries.

An electrochemical cell comprises an anodic and a cathodic compartment, each comprising an electrode at which the reaction occurs. The compartment, and hence the electrodes, are separated by the membrane. The electrode in the anodic compartment, i.e. the anode, and the electrode in the cathodic compartment, i.e. the cathode, are connected by an external circuit. Figure 1b shows a schematic illustration of a membrane electrode assembly (MEA) 110, comprising a membrane 102, a first electrode 101 and a second electrode 103.

The membrane 102 could be a proton exchange membrane (PEM) or an anion exchange membrane (AEM). In a proton exchange membrane electrolyzer cell (PEMEC) water oxidizes at the anode which produces oxygen and protons. The protons travel through the membrane 102 to the cathode, at the cathode the protons are reduced to hydrogen. In an anion exchange membrane electrolyzer cell (AEMEC) water is reduced at the cathode forming hydrogen and hydroxide ions (OH⁻). The hydroxide ions are transported through the membrane 102 to the anode, where they are partly oxidized, forming oxygen and water.

During the oxidation, electrons are formed at the anode and are consumed in the reduction at the cathode. The electric energy required to drive the two reactions, is stored in the reaction products H₂ and O₂.

Examples of reaction at the respective electrode are:

Anodic reaction (oxidation): $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$

Cathodic reaction (reduction): $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

In addition to the electrodes 101; 103, the membrane 102 is an essential element of a MEA 110. The membrane 102 is normally an ion exchange membrane formed by a solid polymer. It functions as a separator between the anodic and cathodic compartment. In electrochemical cells e.g. fuel cells, electrolyzer cells, etc. the electrodes 101; 103 are preferably arranged close to each other, with the membrane 102 in between, in order to obtain high efficiency. Therefore, the electrodes 101; 103 and the membrane 102 are assembled to form a membrane electrode assembly 110 that is very thin, usually around 1 mm thick, i.e. with a close contact between the membrane

102 and both electrodes 101; 103. A large distance between the electrodes 101; 103 leads to an increased resistance, and hence a lower efficiency.

In embodiments where the MEA is used in a proton exchange membrane fuel cell (PEMFC) it is further important that any catalyst is in contact with the electrical circuit as well as in contact with a proton conductive polymer, which transports the protons from the anode to the cathode. The proton conductive polymer can be part of the membrane 102. The catalyst can be arranged either directly on the membrane, or in contact with a proton conductive polymer connecting the catalyst with the membrane. Furthermore, any catalyst has to be in electrical contact with the reagent (H₂ and/or O₂).

Today, the most common way to form a MEA 110 is to press hot electrodes 101, 103 against a proton exchange membrane at a temperature above T_g of the membrane 102. Such a process limits the type of membrane that can be used to a membrane having thermoplastic properties with a suitable glass transition temperature, T_g. Typically, the membrane in the prior art MEAs is a membrane made of a polymer of the registered brand NAFION® having a T_g value of ~100-130°C.

An embodiment of the inventive process 10 for preparing a membrane electrode assembly (MEA) 100 is schematically illustrated in Figure 2.

In one embodiment a membrane electrode assembly 110 comprising two electrodes 101; 103, one on each side of a membrane 102, is formed in the processes 20 and 30, respectively. Such a membrane electrode assembly 110 can be formed in a process 20 by assembling both electrodes 101; 103 simultaneously with the membrane 102, or in a process 30 by first assembling the first electrode 101 with the membrane 102 followed by similar steps (30:5-30:8) for assembling the second electrode 103 with the membrane 102. An embodiment of the inventive process 20 is schematically illustrated in Figure 3a.

In the inventive process 20 described above and illustrated in Figure 3a both electrodes 101; 103 are arranged with the membrane 102 at the same time in step 20:3. This is advantageous since it decreases the number of steps needed

which makes the process both time and energy saving. Such a process 20 additionally requires only one step of heating instead of two, as required in the inventive sequential process 30.

5 An embodiment of the inventive process 30 is schematically illustrated in Figure 3b.

The processes 10; 20; 30 according to the invention utilizes the freezing temperature of the liquid composition, therefore it is advantageous that the liquid composition has a freezing temperature that is not too low. An overly low freezing point of the composition could render the electrode(s) brittle, and therefore fragile and amenable to be damaged when handled in the process at the required low temperature. Also, a freezing temperature below that obtainable by a conventional freezer is not very practical, since it severely limits the available useful means for freezing. On the other hand, an overly high freezing point may require heating to a temperature at which the membrane risks being damaged.

The liquid composition can be composed differently, so as to adapt the characteristics of the composition as desired with regard to freezing point, solubility, vapor pressure, wetting of the electrode(s) and/or membrane, for example so as to exhibit a desired suitable freezing point, for a suitable solubility of a desired additive, such as a catalyst or a binder, for a suitable limited solubility of the membrane therein, for a desired vapor pressure.

The liquid composition comprises at least one liquid solvent capable of being solidified by freezing. In a preferred embodiment the liquid composition comprises a first liquid solvent and an additional second solvent. The first and additional second solvents should be miscible with each other. The liquid composition suitably has a freezing point of -30°C or higher, typically of 0°C or higher, preferably 10°C or higher, more preferably 15°C or higher, and preferably not higher than 100°C , more preferably not higher than 50°C .

In a preferred embodiment the first and/or the additional second solvent is a polar solvent. In one embodiment each one of the at least one first solvent and

the additional second solvent has a dipole moment of at least 1.5, preferably at least 2.0, more preferably at least 2.5.

In one embodiment the first solvent in the liquid composition is selected from dimethyl sulfoxide (DMSO), water, C₄-C₇ alcohol preferably tert-butanol, 5 cyclohexanol, cyclohexane, terpineol or a mixture of two or more thereof. In a preferred embodiment the liquid composition comprises a first solvent and at least one additional second solvent. The additional second solvent is preferably selected from water, alcohols, preferably C₁-C₃ alcohols, for example methanol and ethanol, acetone, more preferably 2-propanol or 10 ethanol. The additional second solvent could be used to decrease the concentration of the first solvent, especially if the first solvent is harmful to the membrane if in contact at high concentrations for an extended period of time. An additional advantage of using also an additional second solvent is the ability to adjust the viscosity of the liquid composition, the freezing point, 15 spreadability and vapor pressure. The viscosity could additionally be altered by the use of other additives. The additional second solvent could additionally be used to improve the dispersion of the liquid composition on the electrode(s).

In one embodiment, after the deposition of the liquid composition on the electrode in the deposition step 10:1; 20:1; 30:1; 30:5, and prior to the cooling 20 of the liquid composition in the subsequent step 10:2; 20:2; 30:2; 30:6, an additional solvent-evaporation step is included, wherein a desired amount of the content of one or more solvents contained in the layer of the liquid composition is reduced by evaporation. Such evaporation step may be desired in order to increase the freezing point of the layer of liquid composition 25 deposited on the electrode. Typically, in such additional evaporation step, a lower boiling point solvent may be evaporated. Evaporation of solvent prior to cooling could for example be performed at room temperature, or at 25-75°C, or at 25-50°C, or 25-35°C.

In one embodiment the liquid composition in the depositing step 10:1; 20:1; 30 30:1; 30:5 comprises at least one first solvent and at least one additional second solvent. In one embodiment the liquid composition comprises 1-20 vol % of the first solvent and 80-99 vol% of the additional second solvent(s),

preferably 2-15 vol% of the first solvent and 85-98 vol% of the additional second solvent(s). The liquid composition can further comprise a catalyst, and, optionally, also additives, preferably a binder. In one embodiment the binder is a polymer that is soluble in at least one of the solvents in the liquid composition. Preferably the polymer is an ion conductive polymer, and more preferably the binder is a polymer that is polyaryl-ether ketone-based, or polystyrene-based, or polysulfone-based, or polybenzimidazole-, or polyacrylic acid-based, or polyaromatic-based, or partly or fully fluorinated-based. The binder can also be a mixture of different polymers.

10 The liquid composition should preferably be homogenously deposited on the electrode(s) 101, 103 in the depositing step 10:1; 20:1; 30:1; 30:5. A non-homogenous distribution of the liquid composition may risk damaging the membrane 102. The liquid composition is believed to stay on the surface of the electrode(s) due to non-covalent bonds between at least one of the solvent(s) and the surface of the electrode(s) 101; 103. The electrode(s) 101; 15 103 can be hydrophobic or hydrophilic.

In the cooling step 10:2; 20:2; 30:2; 30:6, the deposited layer of liquid composition is frozen by cooling at or below the freezing point of the liquid composition to obtain a frozen layer of the liquid composition. The frozen liquid composition provides for a solid surface to be arranged on the membrane in the arranging step 10:3; 20:3; 30:3; 30:7. This allows for an easy assembling of the electrode(s) 101, 103 with the membrane. The membrane usually swells, deforms, rolls, and/or wrinkles when in contact with a liquid. The frozen liquid layer of the invention does not cause such problems, which 25 is the reason for the easier assembling.

Additionally, if needed, the process 10; 20; 30 according to the invention allows for correction of the position during assembling of the electrode 101; 103 with the membrane 102, that is at a time after freezing and prior to heating. Accordingly, the present invention allows for simplified aligning of the membrane and electrode in relation to each other at a time after freezing (10:2; 30 20:2; 30:2; 30:6) and prior to heating (10:4; 20:4; 30:4; 30:8).

The first electrode 101 is assembled with the membrane 102 in the arranging steps 10:3; 20:3; 30:3, and the second electrode 103 is assembled with the membrane 102 in the arranging steps 20:3 and 30:7, respectively. The heating in step 10:4; 20:4; 30:4; 30:8 should be selected so as to result in a sufficient
5 adhesion of the membrane to the electrode(s) allowing for the resulting membrane electrode assembly 100, 110 obtained from the heating step to be handled without separating. The solvent(s), the first solvent and the optional additional second solvent in the liquid composition can preferably be selected so as to interact with the membrane 102 which may facilitate a “gluing” effect
10 between the membrane 102 and the electrode(s) 101; 103. Without being bound by theory, a sufficient adhesion between the membrane 120 and the electrode(s) 101; 103 could be accomplished due to swelling of the membrane 102 into the at least one electrode 101; 103. The sufficient adhesion could also be due to that the liquid composition slightly dissolves or solvates the
15 surface of the membrane 102 during the heating.

Heating is applied in the heating step 10:4; 20:4; 30:4 and 30:8 for a pre-determined period of time. The heating is carried out at a temperature above the freezing temperature of the liquid composition and preferably below a glass transition temperature, T_g , of the dry membrane 102. In one embodiment
20 pressure is applied during the heating in the heating step 10:4; 20:4; 30:4; 30:8. The pressure is only a light pressure so that the adhesion between the membrane 102 and the electrode(s) 101; 103 is enhanced. In one embodiment the pressure is 0.01-1.5 bar. It could for example be achieved by the pressure being applied by a hot press made from two steel blocks with a heating element
25 inside. During the heating the first solvent and optionally additional second solvent in the liquid composition at least partly evaporates.

In some embodiments a catalyst is comprised in the MEA 100, 110. The catalyst increases the reaction rate of one or more of the different chemical reactions at the MEA during use and hence, increases the efficiency of the
30 electrochemical cell. As described above, in one embodiment the catalyst is added to the liquid composition in the depositing step 10:1; 20:1; 30:1; 30:5. The catalyst should not be destroyed by the solvent(s), and hence the type of

catalyst should be determined depending on the type of solvent, or mixture of solvents, used in the liquid composition. In one embodiment the catalyst comprised in the liquid composition is selected from platinum, iridium oxide, ruthenium oxide, nickel oxide, iron oxide, cobalt oxide, copper oxide, and molybdenum sulfide or from other transition metal chalcogenides (e.g. transition metal oxides, transition metal sulfides, transition metal selenides), and from transition metal pnictides (e.g. transition metal nitrides, transition metal phosphides), more typically from platinum, iridium oxide and ruthenium oxide. In other embodiments the catalyst is immobilized on at least one of the electrodes 101, 103 prior to starting the inventive process 10, 20, 30, of forming a MEA 100, 110. Examples of such an immobilized catalyst include metal complexes or catalysts, which are directly synthesized on the electrodes, comprising the above-mentioned catalysts.

Another advantage of the inventive processes 10; 20; 30 is that said processes enable use of many membranes commercially available today and also enable use of otherwise suitable materials that up to now has not been available for MEA preparation due to the limitation of T_g . The membrane 102 in a MEA 100, 110 is an ion exchange membrane, i.e. a proton exchange membrane or an anion exchange membrane, where ions can move through. As described above, the function of the membrane 102 is to separate the two compartments, i.e. the anodic and the cathodic compartment as well as to allow transportation of ions and/or protons. The membrane 102 generally comprises a polymer having a stable backbone. It can further comprise cationic and/or anionic groups, as for example sulfonic groups, phosphonic groups, ammonium groups either as a side-group or incorporated in the backbone. In a preferred embodiment the membrane 102 is selected from a polymeric membrane, preferably a proton exchange membrane or an anion exchange membrane, more preferably a polymeric membrane with a glass transition temperature above 150°C, preferably above 180°C, more preferably above 200°C. In preferred embodiments the membrane 102 has a glass transition temperature below 700°C, preferably below 500°C, more preferably below 400°C.

A MEA 100 manufactured by a process 10 according to the invention comprises at least one electrode 101. A MEA 110 manufactured by a process 20; 30 according to the invention comprises two electrodes 101; 103. The two electrodes 101; 103 are arranged on each side of the membrane 102, i.e. on a first surface and second opposite surface of a membrane 102, respectively. The first electrode 101 may function as anode and the second electrode 103 may function as cathode. In preferred embodiments the electrode(s) 101; 103 comprise(s) an open porous and electrically conductive material, preferably a gas diffusion layer, metal foams or metal meshes, more preferably carbon cloth, carbon paper, nickel, titanium, copper, iron or its combinations in a foam or mesh structure. A preferred electrode is a carbon gas diffusion electrode. Specific examples of electrodes which have been successfully used are e.g. the following: H23I2, H23, H23C4 from Freudenberg, Sigracet® 39BC from SGL Carbon.

Specific examples of useful membranes are membranes made e.g. from any one of the following polymers: SPAEK, PDD59+20% PBIOO®, and Nafion®. Accordingly, a membrane made from the polymer Nafion®, which is a proprietary name of Dupont/Chemours, can be used according the invention.

A washing step may preferably be included after the heating step 10:4; 20:4; 30:4; 30:8 to remove excess liquid composition from the formed MEA 100, 110. Excess liquid composition could be damaging to the membrane 102 over time.

In the processes according to the invention 10; 20; 30 the at least one first solvent and the optional additional second solvent(s) in the liquid composition is at least partly removed by heating in the heating step 10:4; 20:4; 30:4; 30:8. Depending on the temperature during the heating the frozen solvent(s) is evaporated. The heating is performed at or above the freezing temperature of the liquid composition, but preferably not higher than a glass transition temperature of the dry membrane 102, and more preferably at a temperature below a glass transition temperature of the dry membrane 102. At temperatures higher than a glass transition temperature of the dry membrane 102 there is a risk for the membrane to get brittle, and/or degrade, and/or

damage the catalyst and/or membrane 102. In one embodiment the heating is performed at a temperature of up to 80°C-200°C above the freezing temperature of the liquid composition, preferably at a temperature of up to 50°C-150°C above the freezing temperature of the liquid composition, more preferably at a temperature of up to 15-70°C, most preferably 30°C-70°C above the freezing temperature of the liquid composition, such as 34°C-70°C above the freezing temperature of the liquid composition. The heating is performed during a pre-determined period of time. In one embodiment the pre-determined period of time is in the range of 30 seconds to 15 minutes.

10

EXAMPLES

Example 1

A liquid composition was formed from SFS (a sulfonated polymer) as binder, dimethyl sulfoxide as a first solvent and water and 2-propanol as additional second solvents using the following amounts 11 mg/mL SFS in a mixture of 11.9 vol.% DMSO, 53.3 vol.% H₂O and 36.8 vol.% 2-propanol. After the formation of a homogeneous mixture in an ultrasonic bath, 485 µL of this mixture was drop casted on a 16 cm² gas diffusion layer, GDL, (H23I2, Freudenberg). After the additional solvents were expected to be evaporated, the GDL was put in the freezer to solidify the DMSO. After the DMSO was solidified as observed by visual inspection, it was assembled with a dry sulfonated polyaryletherketone (SPAEK) membrane and put covered in thin polytetrafluoroethylene (PTFE) sheets in a press at room temperature for 40 minutes. Then the temperature of the press was increased to 100°C for 1.5 hours. The membrane electrode assembly (only one electrode) was washed and swelled in water, to remove remaining DMSO and investigate the connection of the membrane to the electrode. Even after swelling the membrane stayed very well attached with no delamination at all. During the combining of the electrode with the solidified composition with the membrane, the membrane wrinkled a little, which implied that the mixture was not fully solidified, which could be due to water decreasing the freezing point of the DMSO too much, or

30

an insufficiently long freezing time. Figure 4 shows the membrane electrode assembly with H23I2 electrode on one side of the SPAEK membrane, a) after assembling, and b) after washing and swelling in water.

5 Example 2 – comparative example

A test with an uncoated GDL and SPAEK confirmed that use of the inventive solidified composition is necessary. The assembly was pressed at 70°C for 50 minutes with an additional weight of 6.34 kg on 16 cm², which equals approximately an additional pressure of 0.4 bar. The electrode and membrane
10 did not adhere to each other.

Example 3 – comparative example

Another test was done, using same constituents of the liquid composition as in Example 1, except for the first solvent DMSO, which was omitted. A new
15 composition was produced with 11 mg/mL SFS in a mixture of 50 vol.% H₂O and 50 vol.% 2-propanol. 485 µL of this mixture was drop-casted on a 16 cm² GDL (H23I2, Freudenberg). This electrode was dried completely and the SPAEK membrane was positioned on top. The electrode and membrane assembly was again covered with PTFE sheets, to prevent the material to
20 possibly stick to the hot press and heated up to 70°C for 50 minutes. This experiment did not result in adhering the membrane to the electrode. Dry SPAEK and dry SFS are therefore not the reason for the good adhesion between electrode and membrane.

25 Example 4

Another test was done using a cobalt doped and carbonized metal organic framework (MOF) as catalyst. 50 mg of this catalyst was dispersed in an ultrasonic bath for 1 hour and 15 minutes in a mixture of 2.4 vol.% DMSO as first solvent, 30.2 vol% H₂O and 67.5 vol.% 2-propanol as additional second
30 solvents and 11 mg/mL SFS as a binder. 480 µL of this solution was drop-

casted on different GDLs (H23C4, H23, H23I2), the excessive additional solvent was allowed to evaporate for 10 minutes, then the electrode with a layer of the liquid composition was put in the freezer for 30 minutes. After solidification of the composition, the GDL was placed with the side with the solidified composition face down on the membrane. The resulting arrangement, schematically illustrated in Figure 5, was placed between two thin PTFE sheets in the pre heated hot press and heated up to temperatures from 100°C to 200°C for 10 minutes. Figure 6 shows MEAs with different GDL on one side of the SPEAK membrane and different hot press temperatures: Fig 6a) H23C4 GDL assembled at a temperature of 100°C, Fig 6b) H23 GDL assembled at a temperature of 120°C, and Fig 6c) H23I2 GDL assembled at a temperature of 200°C.

A MEA was obtained for all electrode types tested in example 4. However, a too high temperature during the assembling was damaging to the SPAEK as can be seen in Figure 6c).

Example 5

A liquid composition is prepared using 55.6 mg/mL SFS (a sulfonated polymer) as a binder in DMSO as first solvent (12 vol.%) and 2-propanol as additional solvent (88 vol.%). The mixture was stirred for 1 hour and 40 minutes to obtain a homogenous composition. 287 μ L of this composition was drop-casted homogeneously on a 16 cm² H23 GDL (provided by Freudenberg Performance Materials SE & Co. KG). The coated GDL was left at room temperature for 20 minutes, at which temperature 2-propanol evaporates. The electrode with the still wet liquid composition was then put in the freezer to solidify the liquid composition for 1 hour and 10 minutes. The side with the solidified composition was afterwards placed face down on a sulfonated polyaryl ether ketone (SPAEEK) membrane. Both the SPAEK membrane and the electrode were covered with a thin PTFE sheet, to prevent them from sticking to the hot press. The PTFE sheet - membrane - GDL - PTFE sheet arrangement was now placed in the preheated hot press (100°C). The press was closed without any additional pressure applied and the arrangement was heated for

10 minutes. After that the resulting MEA was removed from the hot press and cooled down, the result can be seen in Figure 7.

Successful results were also obtained using the following materials and conditions as set forth in examples 6-10 below.

5

Example 6

In this example a SPAEK membrane, an H23 electrode, water as liquid composition, a heating temperature of 90°C during a period of time of 10 min, with an applied pressure of 1182 g to a surface of 2.55 cm² were used.

10 H23, is a carbon gas diffusion electrode from Freudenberg.

Example 7

In this example a SPAEK membrane, a 39BC electrode, tert-BuOH:Acetone as liquid composition, a heating temperature of 60°C during a period of time 15
15 min, with an applied pressure of 1182 g to a surface of 1.2 cm² were used.

39 BC is a carbon gas diffusion electrode from SGL Carbon.

Example 8

In this example a MEA 110 was formed with a SPAEK membrane and two
20 H23C4 electrodes, using DMSO:IPA as liquid composition, a heating temperature 80°C during a period of time of 15 min, with an applied pressure of 600 g to a surface of 3.75 cm².

H23C4 is a carbon gas diffusion electrode from Freudenberg.

25 Example 9

In this example a Nafion membrane was attached to an H23I2 electrode, using tert-BuOH as liquid composition, a heating temperature 60°C during a period of time of 16 min, with an applied pressure of 500 g to a surface of 1 cm².

The membrane used is a proton exchange membrane made from the polymer
5 Nafion® which is a proprietary name of Dupont/Chemours.

Example 10

In this example a Nafion membrane was attached to an H23I2 electrode, using
10 terpineol as liquid composition, a heating temperature 90°C, during a period
of time of 15 min, with an applied pressure of 500 g to a surface of 1 cm².

The membrane used is a proton exchange membrane made from the polymer
Nafion® which is a proprietary name of Dupont/Chemours.

CLAIMS

1. A process (10) for preparing a membrane electrode assembly (MEA) (100), which process comprises the steps:

5 10:1 depositing a layer of a liquid composition onto a first electrode (101), which liquid composition is capable of being solidified by freezing;

10:2 cooling the first electrode (101) with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode (101) coated with a layer of solidified liquid composition;

10 10:3 arranging on a first surface of a membrane (102) the first electrode (101) coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the first side of the membrane (102); and,

10:4 heating the arranged electrode (101) and membrane (102) for a pre-determined period of time wherein the heating is done above the freezing
15 temperature of the liquid composition thereby forming a membrane electrode assembly (100) comprising the first electrode (101) and the membrane (102).

2. A process (30) for preparing a membrane electrode assembly (MEA) (110), which process comprises the following steps:

20 30: 1 depositing a layer of a liquid composition onto a first electrode (101), which liquid composition is capable of being solidified by freezing;

30:2 cooling the first electrode (101) with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode (101) coated with a layer of
25 solidified liquid composition;

30:3 arranging on a first surface of a membrane (102) the first electrode (101) coated with the layer of solidified liquid composition with the layer of the solidified liquid composition facing the first side of the membrane (102);

30:4 heating the arranged first electrode (101) and membrane (102) for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid composition, thereby forming a membrane electrode assembly (100) comprising the first electrode (101) and the membrane (102);

5 30:5 depositing a layer of a liquid composition onto a second electrode (103), which liquid composition is capable of being solidified by freezing;

30:6 cooling the second electrode (103) with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a second electrode (103) coated with a layer of the solidified liquid composition;

10

30:7 arranging on a second opposite surface of the membrane (102) of the membrane electrode assembly (100) comprising the first electrode (101) and the membrane (102) obtained in step 30:4 the second electrode (103) coated with the layer of solidified liquid composition with the layer of the solidified liquid composition facing said second opposite side of the membrane (102) of the membrane electrode assembly (100) comprising the first electrode and the membrane obtained in step 30:4;

15

30:8 heating the arranged second electrode (103) and membrane (102) of the membrane electrode assembly (100) comprising the first electrode and the membrane obtained in step 30:4 for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid, thereby forming a membrane electrode assembly (110) comprising the first electrode (101), the membrane (102), and the second electrode (103).

20

25 3 A process (20) for preparing a membrane electrode assembly (MEA) (110) which process comprises the following steps:

20:1 depositing a layer of a liquid composition onto a first electrode (101), and onto a second electrode (103), which liquid composition is capable of being solidified by freezing;

20:2 cooling the first electrode (101) with the deposited layer of liquid composition and the second electrode (103) with the deposited layer of liquid composition to a temperature at or below the freezing temperature of the liquid composition, thereby forming a first electrode (101) coated with a layer of solidified liquid composition, and a second electrode (103) coated with a layer of solidified liquid composition;

20:3 arranging on a first surface of a membrane (102) the first electrode (101) coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the first side of the membrane, and
10 arranging on a second opposite surface of the membrane (102) the second electrode (103) coated with the layer of solidified liquid composition with the layer of solidified liquid composition facing the second opposite side of the membrane;

20:4 heating the arranged first electrode (101), membrane (102), and
15 second electrode (103) for a pre-determined period of time wherein the heating is done above the freezing temperature of the liquid composition, thereby forming a membrane electrode assembly (110) comprising the first electrode (101), the membrane (102), and the second electrode (103).

20 4. The process according to any one of the previous claims, wherein the liquid composition comprises a first solvent, preferably selected from dimethyl sulfoxide, water, tert-butanol, cyclohexanol, cyclohexane, terpineol, or a mixture of two or more thereof.

25 5. The process according to any one of the previous claims, wherein the liquid composition comprises a catalyst, preferably selected from platinum, iridium oxide, ruthenium oxide, or other transition metal oxides, transition metal chalcogenides and transition metal pnictides.

6. The process according to any one of the previous claims, wherein the liquid composition comprises a binder, which binder preferably is polyaryl-ether ketone-based, polystyrene-based, polysulfone-based, or polybenzimidazole-, or polyacrylic acid-based, or polyaromatic-based, or partly or fully fluorinated-based.
7. The process according to any one of the preceding claims, wherein the liquid composition has a freezing point of 0 °C or higher, preferably 10 °C or higher, more preferably 15 °C or higher.
8. The process according to claim 4, wherein the liquid composition additionally comprises at least one additional second solvent, preferably the liquid composition comprises 1-20 vol % of the first solvent and 80-99 vol% of the additional solvent(s), more preferably 2-15 vol% of the first solvent and 85-98 vol% of the additional solvent(s).
9. The process according to claim 8, wherein said at least one additional second solvent is selected from water, alcohols, and acetone, preferably selected from water, C₁-C₃ alcohols, and acetone, more preferably selected from 2-propanol and ethanol.
10. The process according to any one of the preceding claims wherein the membrane (102) is selected from a proton exchange membrane and an anion exchange membrane, more preferably a polymeric membrane with a glass transition temperature above 150°C, preferably above 180°C, more preferably above 200°C.
11. The process according to any one of the preceding claims, wherein the electrode(s) (101; 103) comprise(s) an open porous and electric

conductive material, preferably gas diffusion layer, metal foams or metal meshes, more preferably carbon cloth, carbon paper, nickel, titanium, copper, iron or its combinations in a foam or mesh structure.

- 5 12. The process according to any one of the preceding claims wherein the heating is done at a temperature of up to 80°C above the freezing temperature of the liquid composition, preferably up to 50°C above the freezing temperature of the liquid composition.
- 10 13. The process according to any one of the preceding claims, wherein the pre-determined period of time is in the range of 30 seconds to 15 minutes.
- 15 14. The process according to any one of the preceding claims, wherein, in addition, a washing step is included after the heating step (10:4, 30:4, 30:8, 20:4).
- 15 15. The process according to claim 14, wherein pressure is applied during the heating step (10:4, 30:4, 30:8, 20:4).
- 20 16. The process according to any one of the preceding claims, wherein, in addition, an evaporation step is included after the deposition step (10:1; 20:1; 30:1; 30:5) and prior to the cooling step (10:2; 20:2; 30:2).

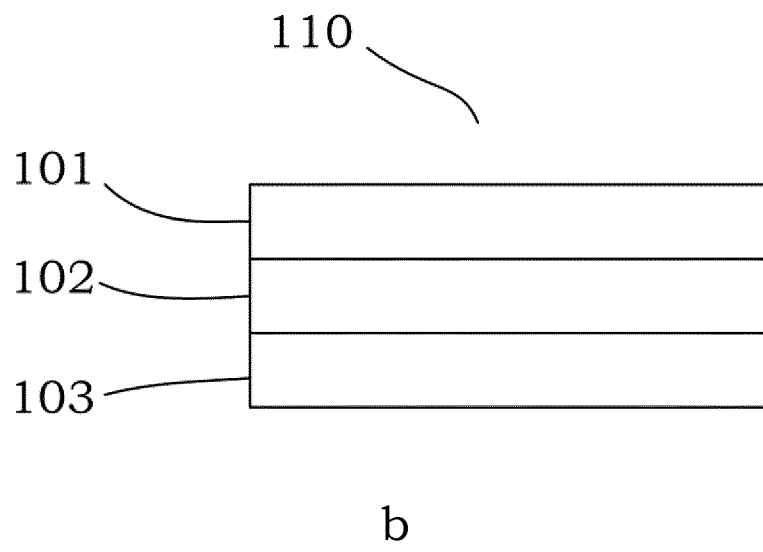
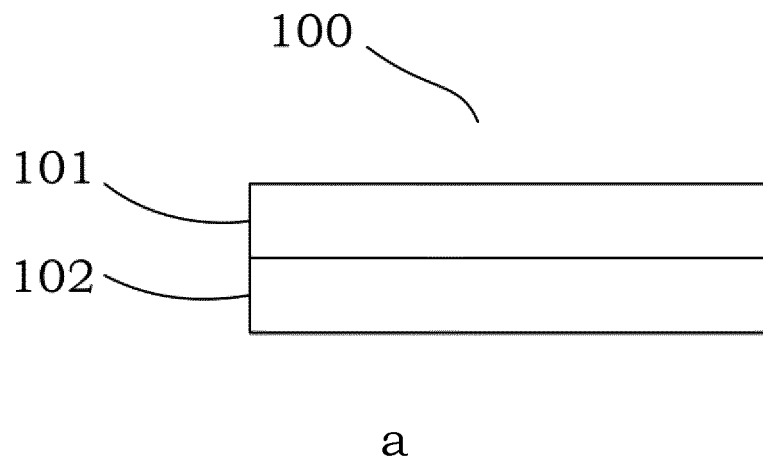
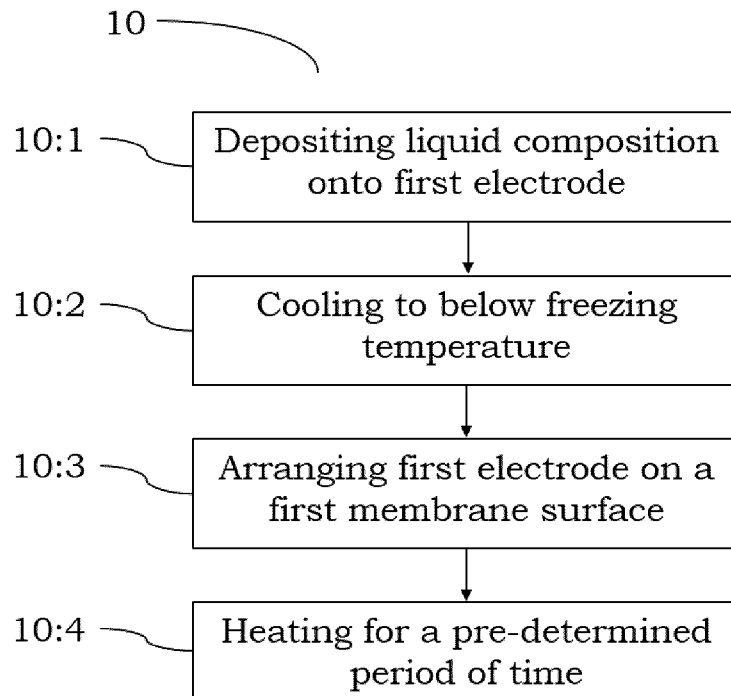
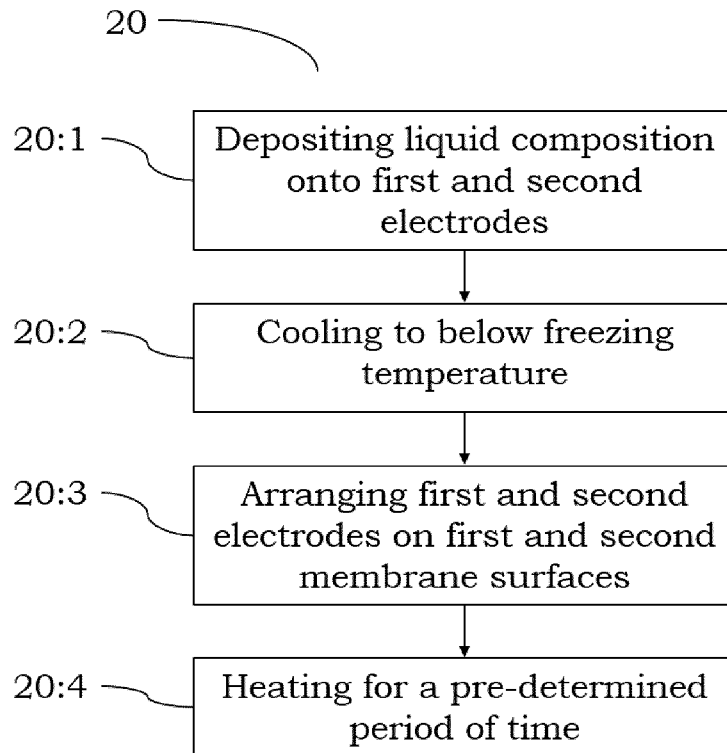
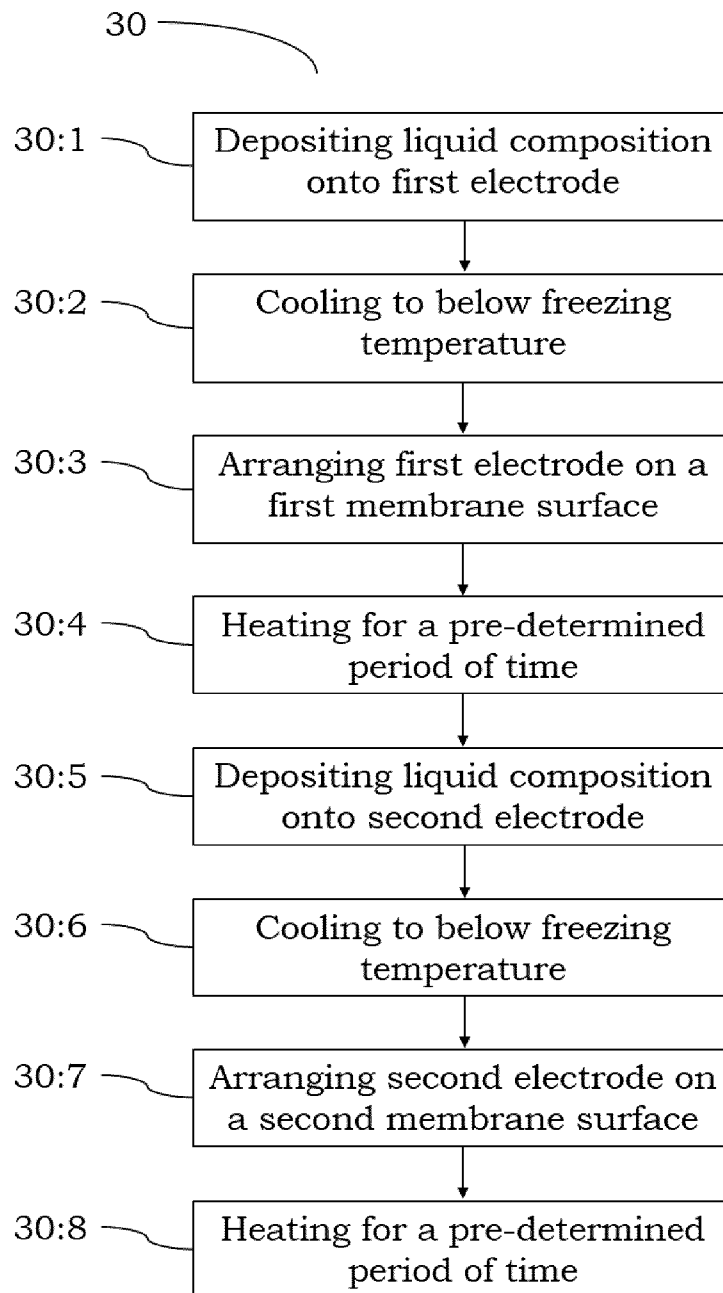


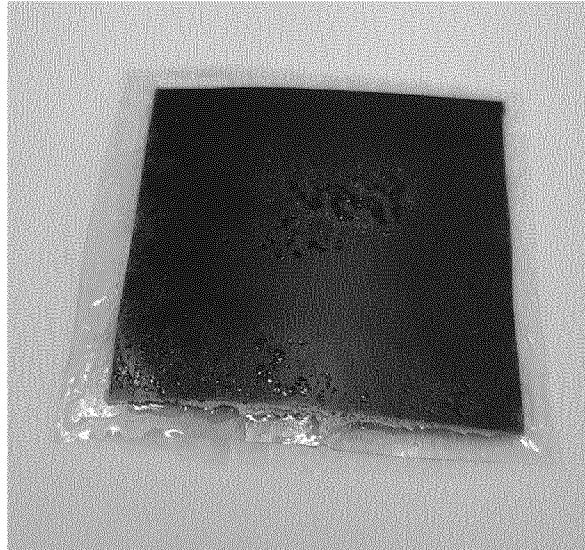
Fig. 1

**Fig. 2**

**Fig. 3a**

**Fig. 3b**

a)



b)

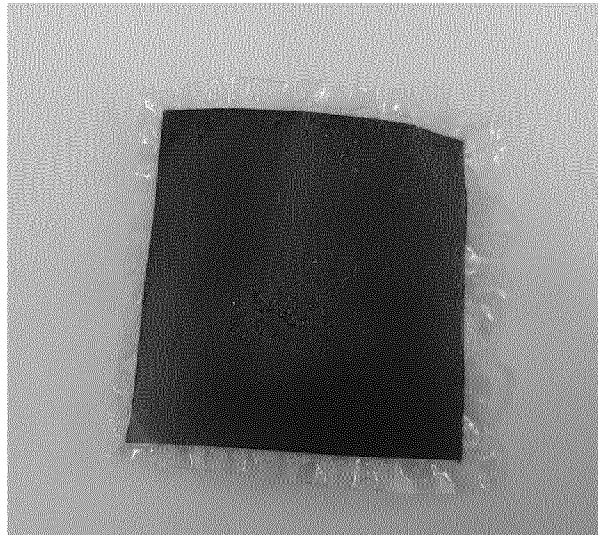


Fig. 4 a) and b)

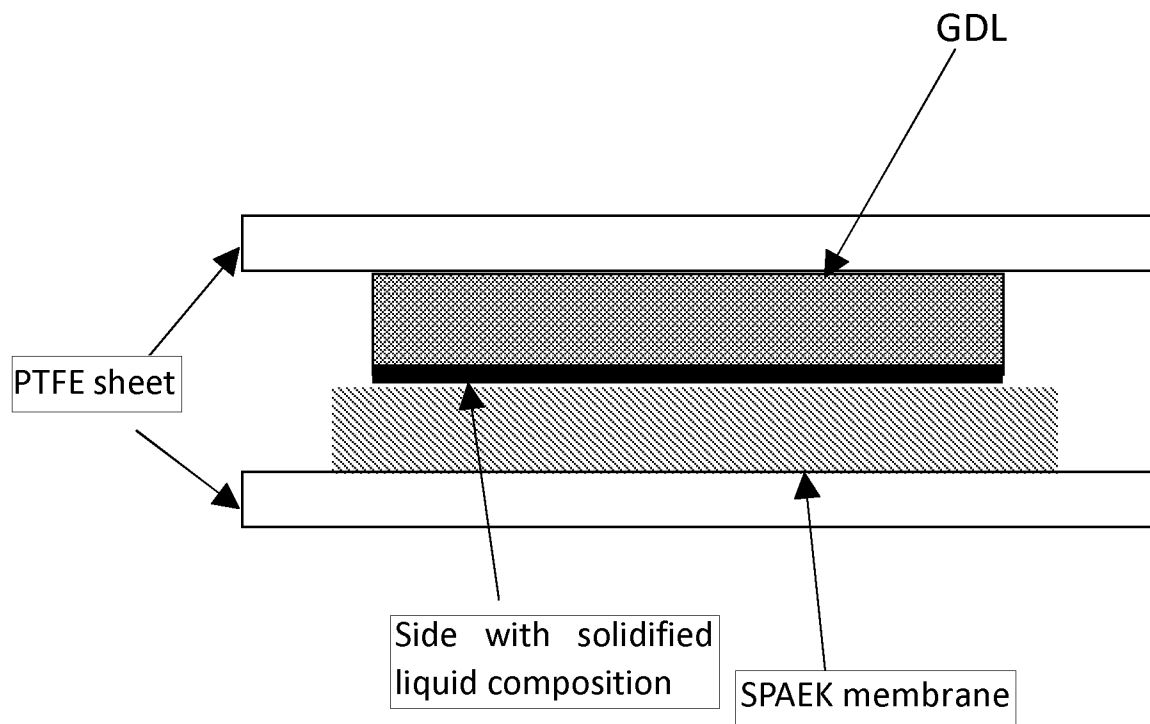
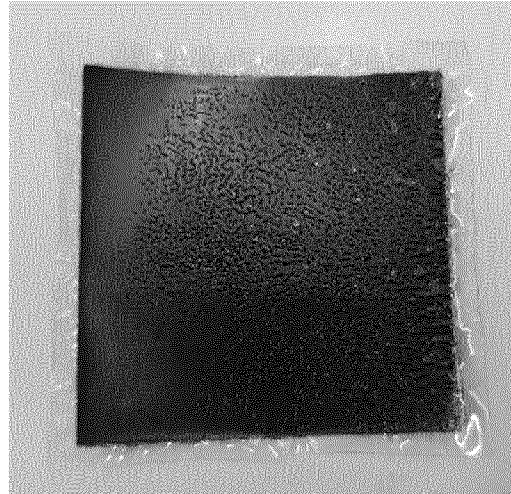
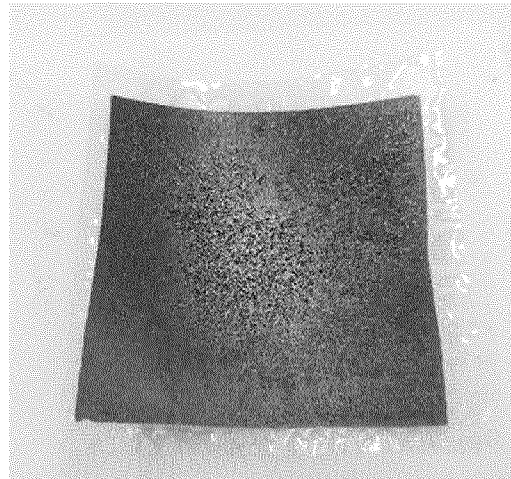


Fig. 5

a)



b)



c)



Fig. 6 a), b) and c)

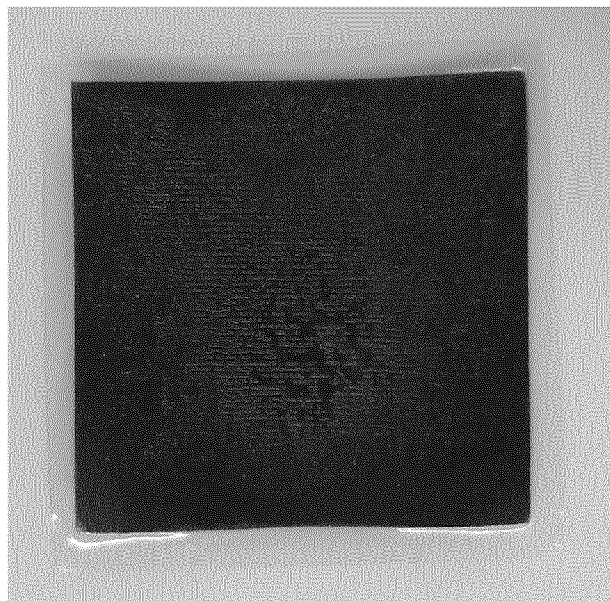


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2021/086252
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A. CLASSIFICATION OF SUBJECT MATTER
INV. **H01M4/86** **H01M4/88** **H01M4/90** **H01M4/92** **H01M8/1004**
ADD.

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 data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/199070 A1 (MIN MYOUNG-KI [KR] ET AL) 7 September 2006 (2006-09-07) abstract claims 1-21 <div style="text-align: center;">-----</div>	1-16

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"X" document of particular relevance;: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 18 March 2022	Date of mailing of the international search report 30/03/2022
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/086252

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