

Partially fluorinated electrospun proton exchange membranes

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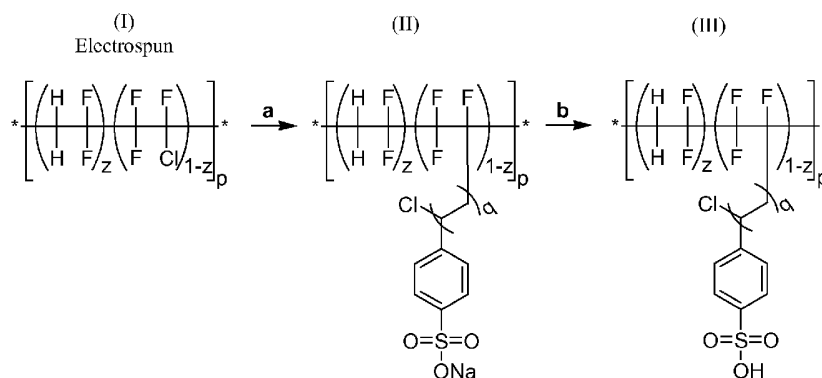


Fig. 2

(57) Abstract: The present invention relates to a novel porous membrane layer, to a novel method for producing a membrane, and the membranes produced by the novel method. The present invention further relates to a fuel cell comprising the porous layer, as well as any use of the porous layer in a fuel cell or in a filter. The porous membrane layer comprises a plurality of randomly oriented fibers manufactured by electrospinning, wherein the fibers comprise a graft copolymer, wherein the graft copolymer comprises a backbone and at least one side chain, wherein the backbone comprises a partially fluorinated copolymer, and wherein at least one side chain of the graft copolymer comprises a polymerization product of a polymerizable proton donor group or a precursor thereof.

Partially fluorinated electrospun proton exchange membranes

Field of invention

The present invention relates to a novel porous membrane layer, to a novel method for producing a membrane, and the membranes produced by the novel method. The present invention further relates to a fuel cell comprising the porous layer, as well as any use of the porous layer in a fuel cell or in a filter.

Background of invention

Electrolytes, which can conduct ions and which are impermeable to the chemical reactants, are an essential component of electrochemical devices such as fuel cells, electrolyzers, and batteries. Proton conducting materials are a type of electrolyte materials in which protons are the primary charge carriers. Proton conducting materials are typically in solid form, and may be a ceramic, a composite or a polymer.

Polymeric proton conductors in the form of thin membranes are, for example, used in fuel cells for mobile applications, such as fuel cell driven vehicles. The polymeric materials have the advantage of potentially cheaper material costs and fabrication costs, compared to ceramic materials, and are therefore of commercial interest. The membranes are called proton exchange membrane or polymer electrolyte membrane (abbreviated PEM), and fuel cells with PEM materials are called PEM fuel cells (PEMFC). PEM fuel cells, in which methanol is used as fuel, are also called DMFC (direct methanol fuel cells).

The most commonly used PEM material is the commercially available polymer Nafion in hydrated form. Nafion exhibits high proton conductivity, it is chemically stable, and it possesses mechanical properties suitable for a thin membrane. Nafion is a sulfonated tetrafluoroethylene based perfluorocopolymer. The chemical structure of Nafion is illustrated in Figure 1, where n and m are degrees of polymerization, which is the number of repeating units in the polymer chain, and z denotes the molar fraction. The favourable mechanical properties are ascribed to the flexible polymeric backbone of tetrafluoroethylene (i.e. similar to Teflon), and the high proton conductivity is ascribed to the ionic group of sulfonic acid ($-\text{SO}_3\text{H}$). Due to the presence of the ionic repeating units, Nafion is an ionomer (i.e. a polymer with ionic groups).

35

However, Nafion suffers from disadvantages such as high cost, high permeability of common fuels e.g. methanol, and low proton conductivity at high temperature/low humidity conditions. The current market price of Nafion is 1100-1600 USD/m², and it is estimated that Nafion constitutes ca. 20 % of the cost of a PEMFC unit. High fuel or
5 methanol permeability is critical for PEM fuel cells, and especially the DMFC operated on methanol. The permeability results in loss of fuel, which equalates to loss of the fuel cell energy efficiency, and thus costs.

In view of the disadvantages associated with the use of Nafion, alternative membrane
10 materials are of interest. Thus, membranes of other proton conducting polymers have been studied, e.g. by Y.W. Kim et al. (in Journal of Membrane Science (2008), 313, 315-322) [1], where a graft copolymer with a main chain, or backbone, of poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE), and side chains of poly(styrenesulfonic acid) (PSSA), i.e. abbreviated P(VDF-co-CTFE)-g-PSSA, was
15 suggested. The proton conducting copolymer was synthesized from P(VDF-co-CTFE), which was grafted with a sulfonated monomer (e.g. styrene sulfonic acid) using solution ATRP (atom transfer radical polymerization). Membranes with increasing content of PSSA showed increasing proton conductivity, and were described as promising membrane candidates with proton conductivity comparable to Nafion.

20 In the previous work, as e.g. the work by Y.W. Kim et al, the graft copolymer such as P(VDF-co-CTFe)-g-PSSA and similar graft copolymers, were manufactured by solution ATRP, i.e. the copolymers were grafted in a solution containing soluble precursors of the side chains and the backbone.

25 Materials comparable to P(VDF-co-CTFE), i.e. any partially fluorinated copolymer may be grafted, based on e.g. [4], and furthermore proton conduction similar to grafted PSSA may be obtained or expected for any material comprising polymerizable proton donor group or precursor thereof as indicated by e.g. [5].

30 Membrane materials with nano fibrous microstructure made by electrospinning have recently been described, e.g. by L. Wu et al. (in Physical Chemistry Chemical Physics (2013) 15, 4870-4887) [2]. For example, very high proton conductivities have been reported on single fibers of Nafion made by electrospinning. However, when
35 incorporating the fibers into membranes, the alignment of the fibers in a membrane resulted in poor through-plane proton conductivities.

Similarly, fibers made by electrospinning of any polymer or any partially fluorinated copolymer is obtainable as indicated by e.g. [3].

5 Proton conducting membranes of other ordered microstructures have also been investigated. Wu et al. described membrane materials of ordered meso porous scaffolds (of silicon-poly(sulfopropyl methacrylate)) with aligned through-plane pores, where the porous scaffold was further modified by surface initiated (SI) ATRP. However, the obtained membrane showed poor proton conductivity, and the fabrication
10 of a suitable ordered scaffold was indicated to be complex.

Nano fibrous microstructures made by electrospinning may also have other applications such as for use in filters, e.g. for filtration in the molecular range, micro particle range or macro particle range.

15

Summary of invention

The present invention provides a novel porous layer for a membrane that can be fabricated by a simpler and more flexible method, using cheaper materials, and which have comparable or superior properties compared to Nafion with regards to proton
20 conductivity, mechanical properties and methanol permeability.

The first aspect of the invention relates to a porous membrane layer comprising a plurality of randomly oriented fibers manufactured by electrospinning, wherein the fibers comprise a graft copolymer,
25 wherein the graft copolymer comprises a backbone and at least one side chain, wherein the backbone comprises a partially fluorinated copolymer, and wherein at least one side chain of the graft copolymer comprises a polymerization product of a polymerizable proton donor group or a precursor thereof.

30 The second aspect of the invention relates to a method for producing a membrane, comprising the steps of:

- (a) providing a micro-porous and fibrous layer manufactured by electrospinning and comprising a partially fluorinated copolymer comprising at least one halogen other than fluorine,
- 35 (b) applying surface initiated radical polymerization, preferably SI ATRP, to graft a

polymerization product of a polymerizable proton donor group, or a precursor thereof, such as a graft copolymer in salt form, and

(c) optionally acid treating the graft copolymer, whereby the precursor forms an acidic group, such as sulfonic acid or phosphonic acid, whereby the copolymer becomes proton conducting.

A third aspect of the invention relates to a membrane produced by the novel method, and a fourth aspect of the invention relates to a fuel cell comprising the novel porous layer.

A further aspect of the invention relates to any use of the novel porous layer in a fuel cell, a PEM fuel cell, DMFC, or in a filter.

Description of Drawings

The invention will in the following be described in greater detail with reference to the accompanying drawings.

Figure 1 shows the chemical structure of Nafion, where n and m are degrees of polymerization and z denotes the molar fraction.

Figure 2 illustrates the processing steps for forming P(VDF-co-CTFE)-*g*-PSSA when grafting by SI ATRP in an embodiment of the current invention. An electrospun P(VDF-co-CTFE) membrane with the chemical structure (I), is grafted by the SI ATRP step (a) involving 4SSNa, CuCl, 2,2'-bipyridine, methanol-water at 60 °C, to form P(VDF-co-CTFE)-*g*-P4SSNa with the chemical structure shown in (II). The grafted membrane is further treated in step (b), which is an acid treatment with HCl (1 M), whereby P(VDF-co-CTFE)-*g*-PSSA with the chemical structure (III) is formed. The number of repeating units in the backbone and grafted chain are designated by p and q , respectively, and z denotes the comonomer molar fraction.

Figure 3 shows a SEM micrograph (by ELMARCO s.r.o.) of an embodiment of the electrospun P(VDF-co-CTFE) membrane, or the platform membrane, as obtained by the method described in Example 2.

Figure 4 shows a SEM micrograph of the grafted P(VDF-co-CTFE)-g-P4SSNa membrane (the micrograph was acquired by Danish Technological Institute), denoted Membrane 1 and described in Example 3.

5 **Figure 5** shows an overlay of ATR FTIR spectra of the electrospun P(VDF-co-CTFE) membrane and the grafted P(VDF-co-CTFE)-g-P4SSNa membrane, denoted Membrane 1.

10 **Figure 6** shows an overlay of TGA thermograms of the electrospun P(VDF-co-CTFE) membrane and the grafted P(VDF-co-CTFE)-g-P4SSNa membrane, denoted Membrane 1.

15 Figure 7 shows a long-term durability test of a DMFC at an output of 8 mA using respectively a membrane 4 from Example 3 (square symbols), and a Nafion 117 membrane (circular symbols).

Detailed description of the invention

Method of manufacturing

20 The novel porous layer comprises of graft copolymer material, where the material has a novel fibrous microstructure. An embodiment of the process to manufacture the material and the graft copolymer is illustrated in Figure 2.

25 In the process, a backbone of a partially fluorinated copolymer backbone is first provided. In Figure 2, the provided backbone is poly(vinylidene fluoride-co-chlorotrifluoroethylene), which is abbreviated as P(VDF-co-CTFE), and the chemical structure is shown in structure (I). The copolymer comprises vinylidene fluoride and chlorotrifluoroethylene repeating units; the number of repeating units is designated as p , and z denotes the molar fraction of the comonomer. The backbone is furthermore provided as an electrospun material, which means that the copolymer material has a porous microstructure further comprising of a plurality of randomly oriented fibers.

30

35 The electrospun partially fluorinated copolymer is used as backbone, or main chain, for grafting a polymerization product of a polymerizable proton donor group, or a precursor thereof. The polymerizable proton donor group or precursor thereof comprises at least one double bond, which can engage in radical polymerization, and at least one proton

donor group, which enables proton transfer through the material. The precursor of the polymerizable proton donor group comprises inorganic or organic salt of the latter. In the embodiment shown in Figure 2, the grafted chain is poly(4-styrenesulfonic acid sodium salt), also denoted poly(sodium 4-styrenesulfonate) and abbreviated P4SSNa, and q is the number of repeating units in P4SSNa. P4SSNa is also a precursor of a polymerization product of a polymerizable proton donor group, where the corresponding polymerizable proton donor group would be styrenesulfonic acid (SSA) and the polymerization product of the polymerizable proton donor group would be poly(styrenesulfonic acid), abbreviated PSSA. The grafting results in the formation of P(VDF-co-CTFE)-g-P4SSNa with the chemical structure shown in (II).

The grafting may be carried out as a SI ATRP step indicated as step (a) in Figure 2. The SI ATRP process may involve 4SSNa, CuCl, 2,2'-bipyridine, and methanol-water at temperatures above room temperature, such as ca. 60 °C.

In the embodiment shown in Figure 2, the SI ATRP process results in the formation of P(VDF-co-CTFE)-g-P4SSNa. Thus, the term "grafting" as used herein is used synonymously with the terms functionalization of the main chain, and the polymerization to form the side chain (such as P4SSNa).

Known polymerization products of polymerizable proton donor groups include polymers with sulfonic acid groups (such as poly(styrenesulfonic acid), PSSA) and polymers with phosphonic acid groups. In Figure 2, the grafted P4SSNa chain is a precursor to the PSSA comprising the proton donor groups. The precursor is converted to the corresponding proton donor group by an acidic treatment, indicated as step (b) in Figure 2, resulting in the graft copolymer P(VDF-co-CTFE)-g-PSSA with the chemical structure (III). The acidic treatment may for example be carried out using HCl (1 M).

The described method may be used for producing a membrane of the novel porous layer. In an embodiment of the invention, the polymerizable proton donor group or precursor thereof is selected from the group consisting of sulfonated monomers, phosphonated monomers, monomers containing acidic NH, CH, CH₂ groups linked to an electron-withdrawing group, and the salts of the mentioned monomers, and combinations thereof. In an embodiment of the invention, the graft copolymer comprises multiple polymerization products of polymerizable proton donor groups or

precursors thereof, wherein the multiple polymerizable proton donor groups or precursors thereof are from a combination of the monomers selected from the group consisting of sulfonated monomers, phosphonated monomers, monomers containing acidic NH, CH, CH₂ groups linked to an electron-withdrawing group, and the salts of the mentioned monomers. In a further embodiment, the grafted polymerization product is a precursor, comprising poly(sodium 4-styrenesulfonate) (P4SSNa). In a further embodiment, the acid treated graft copolymer is P(VDF-co-CTFE)-g-PSSA.

The described method of manufacturing results in a proton conducting material (due to the grafted side chain comprising proton donor groups), which displays high proton conductivity and low methanol permeability (due to the hydrophobic electrospun microstructure).

Furthermore, the described method provides a flexible method for the manufacturing of electrospun materials of graft copolymers, as an electrospun material comprising the backbone, can be used as a platform for variable types and degrees of grafting. In addition, the combination of electrospinning and SI ATRP provides a method using cheap starting materials.

20 Electrospinning

As described previously, the polymer backbone is provided as an electrospun material, which means a material with a porous and fibrous microstructure, where the fibers are randomly oriented.

25 The use of electrospinning provides the fibrous microstructure. Electrospinning is a manufacturing technology known to fabricate fibers and fibrous microstructures. By the term "fiber" as used herein is meant objects with a physical appearance similar to a thread. By the term "fibrous structure" as used herein is meant a structure consisting of or comprising of fibers.

30 Fibers and fibrous structures have several applications due to the special properties related to the fiber structure, such as enhanced mechanical and conducting properties.

35 Fibers consisting of polymer material such as nylon (i.e. polymer fibers) are traditionally fabricated by extrusion. Electrospinning is a relatively new and alternative fabrication

route, where fibers with diameters in the nanometer range can be produced. The polymer fiber is in this case produced by discharging a polymer solution in air from a nozzle under high voltage.

- 5 The electrospun fibers may be deposited directly on a substrate, and thereby forming a layer, and the layer may be used as a membrane.

The deposition parameters will determine the dimensions or size of the fibers (such as the fiber diameter and fiber length), as well as the packing density of the fibers, which
10 will determine the porosity of the layer, the type of porosity (e.g. closed, or open and percolated), and the pore size range (e.g. pores in the micron-sized range, and/or nano-sized range). By the term "percolated" porosity as used herein is meant open porosity, or effective porosity, which is pores that are connected and open to the surroundings, such that a fluid or gas can percolate through the material.

15

In addition to the porosity characteristics, the microstructure may be characterised by the packing density of the fibers. The packing density may be stated as the basis weight, which has the unit weight per area (e.g. g/m^2). The basis weight may therefore be an indication of the robustness of the membrane.

20

When the electrospun material of the copolymer backbone is further grafted (as embodied in Figure 2), the electrospun microstructure will change, as the grafting will result in altered dimensions of the fibers. Thus, the fibers will expand in dimension, and decrease the porosity of the microstructure due to the expanding fibers.

25

When the porous layer of the invention is used in e.g. a fuel cell, it is advantageous that the layer thickness is low, such that the resistance of the layer will be low, but some thickness is also required for sufficient mechanical support. In an embodiment of the invention, the porous layer thickness is below 200 μm , more preferably below 100 μm ,
30 and most preferably below 50 μm or below 25 μm .

Furthermore, when the porous layer of the invention is used in a fuel cell or a filter, it is advantageous that the microstructure comprises fibers of nano sized dimensions, and that the porosity of the microstructure is sufficient, fine and interconnected, such that

the pores of the porous layer can contain fluid (e.g. water or steam), which is known to facilitate the proton conduction through the layer.

5 In an embodiment of the invention, the porous layer comprises fibers, wherein the diameter of the fibers is below 500 nm, more preferably below 250 nm, and most preferably below 150 nm.

10 In a further embodiment, the porosity of the porous microstructure is between 10-80 vol%.

In a further embodiment, the porosity of the porous microstructure is interconnected and percolated.

15 In a further embodiment of the invention, the porosity comprises micron-sized pores and/or nano-sized pores.

Backbone

20 A graft copolymer is broadly defined as a branched copolymer in which the side chains may be structurally distinct from the main chain, also called the backbone. Thus, graft copolymers may be regarded as a special type of branched polymers, where a branched polymer in general consists of a single main chain with one or more polymeric side chains. Further, in a graft copolymer, the main chain may be a copolymer, i.e. it is a polymer formed from two or more different monomers.

25 Processes, such as the SI ATRP process described in Figure 2, where the main chain is functionalized with a side chain may also be described as grafting. Furthermore, by SI ATRP the side chain may be a polymerization product formed by polymerization from the main chain. Thus, the term "graft copolymer" may also be defined as a graft copolymer manufactured by grafting.

30 By the term "graft copolymer" as used herein is meant a graft copolymer manufactured using a process of grafting. An example of a graft copolymer is P(VDF-co-CTFE)-g-PSSA, where the grafted side chain of PSSA, or a precursor thereof, is structurally different from the main chain (backbone) of the copolymer P(VDF-co-CTFE).

35

The backbone of the current invention is a partially fluorinated copolymer. By the term “partially fluorinated copolymer” as used herein is meant a fluoropolymer or a fluorocarbon-based polymer, wherein at least one repeating unit in the main chain, comprises at least one C-F (carbon-fluorine) bond, and preferably in addition there is at least one C-H bond in at least one repeating unit in the main chain that has not been replaced by a C-F bond.

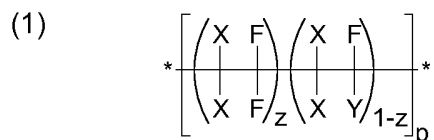
In contrast to a partially fluorinated copolymer is a fully fluorinated copolymer, also known as a perfluorinated copolymer, in which all the C-H bonds in the main chain have been replaced by C-F bonds. An example of a fully fluorinated copolymer is tetrafluoroethylene-based copolymers, such as the main chain for Nafion as shown in Figure 1. A partially fluorinated copolymer may comprise a random copolymer, and/or block copolymer, different ratios between the monomers of the copolymer, and is not restricted to linear but may comprise graft or star copolymer or any combination thereof.

Grafting of the backbone of a partially fluorinated copolymer may be facilitated by a carbon-halogen bond in the main chain, where the halogen is not fluorine. In an embodiment of the invention, the partially fluorinated copolymer comprises a further halogen other than fluorine, which serves as grafting site for the polymerizable proton donor group or precursor thereof, such as the inorganic or organic salt thereof.

In a further embodiment of the invention, the grafting site halogen is selected from the group consisting of chlorine (Cl), bromine (Br), and iodine (I).

25

In a further embodiment of the invention, the partially fluorinated copolymer has the chemical structure shown in (1):



Wherein:

X = H and/or F

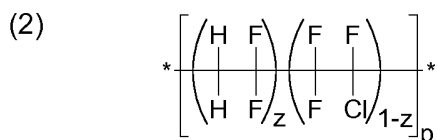
Y = Cl and/or Br and/or I

p is the number of repeating units (also known as degree of

polymerization)

z is molar fraction, wherein $z = 0.02-0.98$

In a further embodiment, the partially fluorinated copolymer is poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE)), with the chemical structure shown in (2):



5

Side chain

The grafted side chains may be grafted by surface initiated radical polymerization, such as SI ATRP, and in an embodiment of the invention, the initiating site for the grafting is the non-fluorine halogen.

10

The grafted side chain comprises a polymerization product of a polymerizable proton donor group or precursor thereof, whereby the graft copolymer becomes or can become proton conducting. The grafted side chains may include side chains of variable length, as well as chains comprising different proton donors.

15

The grafted side chain may also be a precursor for a polymerization product of a polymerizable proton donor group, such as a chain comprising the corresponding inorganic or organic salt of the polymerizable proton donor group, and where the precursor can be converted to a proton donor, e.g. by an acidic treatment.

20

Known polymerization products of polymerizable proton donor groups include polymers with an ionic acid group, such as polymers comprising a sulfonic acid group or a phosphonic acid group, and where the polymer may comprise styrenes, acrylates, methacrylates, ethacrylates, and vinyl acids.

25

Another type of polymerizable proton donor groups includes compounds comprising NH-, CH-, and CH₂-acid groups, where the acid group may be linked to an electron-withdrawing group (EWG). By the term "EWG" as used herein is meant a group that draws electron density from neighboring atoms towards itself. Examples of EWG are carbonyl, ester, amine, nitrile, sulfonyl, and nitro groups.

30

In an embodiment of the invention, the polymerizable proton donor group comprises at least one double bond, which can engage in radical polymerization, and at least one ionic acid group, or at least one acidic group which may be linked to an electron-withdrawing group (EWG).

In a further embodiment of the invention, the polymerizable proton donor group or precursor thereof is selected from the group consisting of sulfonated monomer, phosphonated monomer, and monomers containing acidic NH, CH, and CH₂ groups linked to an electron-withdrawing group (EWG), and combinations thereof.

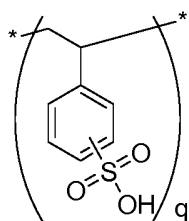
In a further embodiment of the invention, the polymerizable proton donor group or precursor thereof is selected from the group consisting of styrenes, acrylates, methacrylates, ethacrylates and vinyl acids, and combinations thereof, which further comprise a sulfonic or phosphonic acid group, or wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of NH-, CH-, and CH₂- acids, and combinations thereof.

Styrenes

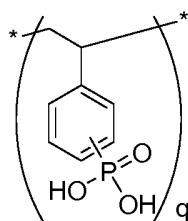
Examples of the polymerization products of a polymerizable proton donor group or precursor thereof are poly(styrenesulfonic acid) and poly(styrene phosphonic acid). In an embodiment of the invention, the polymerization product of the polymerizable proton donor group or precursor thereof is a polystyrene comprising sulfonic acid groups, or phosphonic acid groups.

In a further embodiment of the invention, the polymerization product of polymerizable proton donor group is poly(styrenesulfonic acid), or poly(styrene phosphonic acid), with the respective chemical structures (3) and (4) shown below:

(3)

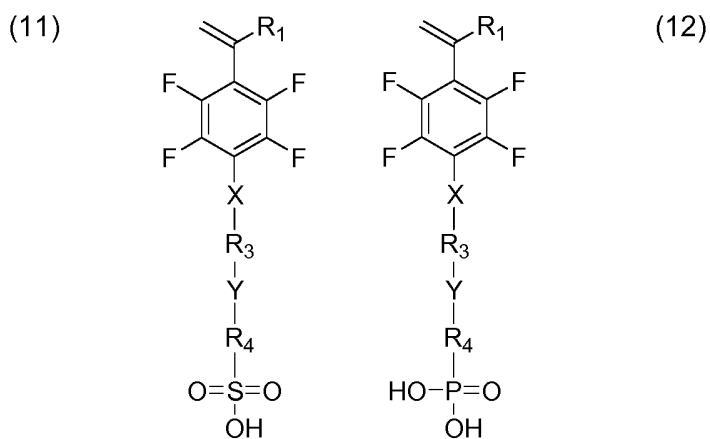
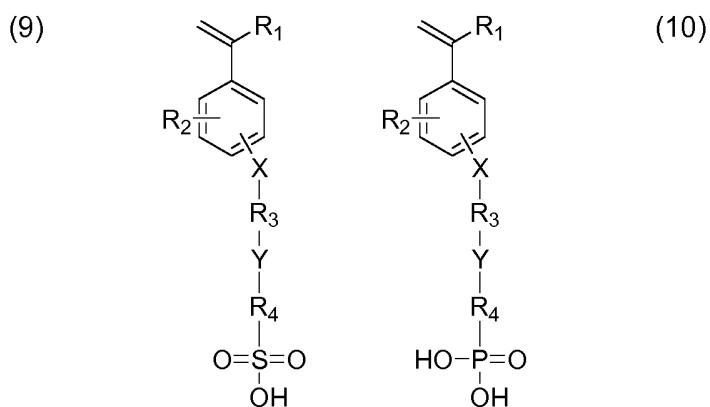
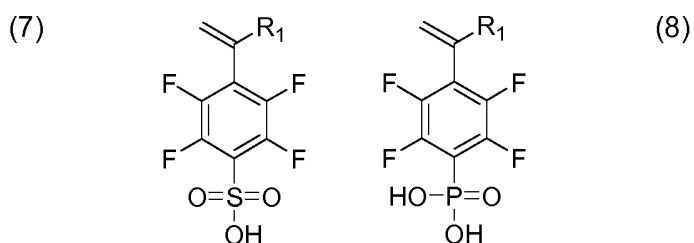
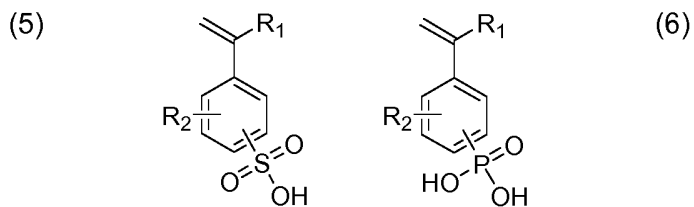


(4)



The polymerizable proton donor group may be other types of styrenes comprising a sulfonic acid group or a phosphonic acid group. General chemical structures of such are shown below in (5) - (12).

5



In the chemical structures **R₁**, **R₂**, **R₃**, **R₄**, **X** and **Y** denote:

R₁ = H, CH₃, CH₃CH₂

R₂ = H or halogen or hydrocarbon fragment (linked to the aromatic ring directly or
5 through heteroatom such as O, N, S) or partially or fully halogenated hydrocarbon
fragment (linked to the aromatic ring directly or through heteroatom such as O, N, S)

X = absent, or O or N or S

R₃ = absent, or hydrocarbon (such as alkanediyl, cycloalkanediyl, alkenediyl,
10 alkynediyl, arenediyl, etc.) or halogenated hydrocarbon (such as halogenated
alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) fragment(s) or
poly(ethylene glycol) chain

Y = absent, or O or N or S

R₄ = absent, or hydrocarbon (such as alkanediyl, cycloalkanediyl, alkenediyl,
15 alkynediyl, arenediyl, etc.) or halogenated hydrocarbon (such as halogenated
alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) fragment(s) or
poly(ethylene glycol) chain.

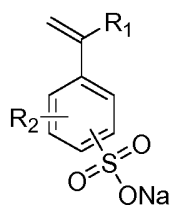
The grafted side chain may also be a corresponding inorganic- or organic salt of the
20 side chain, or monomer. For example, the corresponding sodium salt of the sulfonic
acid containing monomer in (5) is shown in (13), and the corresponding organic salt is
shown in (14), wherein:

R₁ = H, CH₃, CH₃CH₂

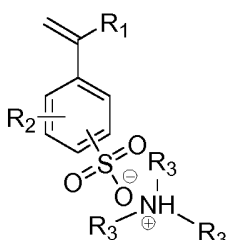
R₂ = H or halogen or hydrocarbon fragment (linked to the aromatic ring directly or
25 through heteroatom such as O, N, S) or partially or fully halogenated hydrocarbon
fragment (linked to the aromatic ring directly or through heteroatom such as O, N, S)

R₃ = hydrocarbon fragment

(13)



(14)



30 If a grafted side chain is an ionic salt, the corresponding proton donor group (i.e. the
sulfonic acid group or phosphonic acid group) may be formed by acidification. The

acidification may be carried out by exposure to an acid, whereby the salt cation (e.g. Na) is replaced by a proton. In an embodiment of the invention, the grafted chain with proton donor group is poly(styrenesulfonic acid) obtained from acidic treatment of poly(sodium 4-styrenesulfonate).

5

In an embodiment of the invention, the grafted side chain is poly(styrenesulfonic acid) obtained from acidic treatment of a grafted side chain of poly(sodium 4-styrenesulfonate). In a further embodiment of the invention, the grafted copolymer is P(VDF-co-CTFE)-*g*-PSSA, or P(VDF-co-CTFE)-*g*-P4SSNa.

10

Acrylates, methacrylates, ethacrylates

The grafted side chains may also be acrylates, methacrylates, and ethacrylates, comprising sulfonic or phosphonic acid groups, and corresponding inorganic- or organic salts thereof, and combinations thereof. Below are illustrated examples of sulfonic acid group (15) or phosphonic acid group (16) containing monomers, wherein:

15

$R_1 = \text{H, CH}_3, \text{CH}_3\text{CH}_2$

$X = \text{absent, or O or N or S}$

$R_2 = \text{absent, or hydrocarbon (such as alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) or halogenated hydrocarbon (such as halogenated$

20

alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) fragment(s) or poly(ethylene glycol) chain

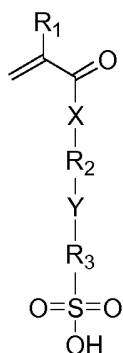
$Y = \text{absent, or O or N or S}$

$R_3 = \text{absent, or hydrocarbon (such as alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) or halogenated hydrocarbon (such as halogenated$

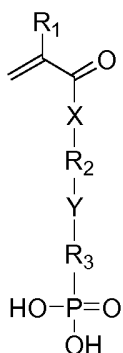
25

alkanediyl, cycloalkanediyl, alkenediyl, alkynediyl, arenediyl, etc.) fragment(s) or poly(ethylene glycol) chain.

(15)



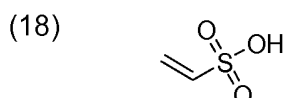
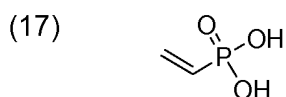
(16)



Vinyl acids

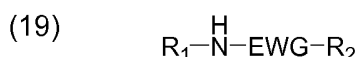
The grafted side chains may also be vinyl acids, comprising sulfonic or phosphonic acid groups, and corresponding inorganic- or organic salts thereof, and combinations thereof. Below are illustrated examples of phosphonic acid group (17) or sulfonic acid group (18).

5

NH, CH, CH₂ acids

The grafted side chains may also be NH-, CH-, and CH₂-acids, as illustrated in structural Formula (19), wherein: **R**₁ comprises radically polymerizable group(s) such as ethenyl, 1-methylethenyl, 1-ethylethenyl, EWG is electron-withdrawing group such as carbonyl, ester, amine, nitrile, sulfonyl, nitro, **R**₂ is absent, or comprises EWG such as fluoroalkyl or chloroalkyl or fluoroalkanedyl and alkyl, cycloalkyl, alkenyl, alkynyl, aryl group(s) or chloroalkanedyl and alkyl, cycloalkyl, alkenyl, alkynyl, aryl group(s)

15

**Examples**Example 1: Nafion

The conductivity and methanol permeability of a Nafion sample was measured. Nafion N117 was purchased from Ion Power, Inc. The conductivity was measured using a 2-probe setup. The sample was acidified by treating with 1M H₂SO₄ before the measurements. The methanol permeability was measured in a two-chamber setup; methanol concentration was estimated using quartz crystal microbalance with dissipation. The results are summarised in Table 1 below.

25

Table 1. Conductivity and methanol permeability for PEM membranes.

Membrane	Conductivity [mS/cm]	Methanol permeability relative to Nafion
Nafion	80	1.00

Membrane 1	39	0.85
Membrane 2	76	0.90
Membrane 3	100	2.00

Example 2: Membranes of P(VDF-co-CTFE) - Platform structure

Poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE)) was obtained from Solvay. The P(VDF-co-CTFE) was electrospun by ELMARCO s.r.o. (Czech Republic) employing Nanospider™ technology. The electrospinning resulted in a porous, and mechanically stable membrane of approximately 50 µm thickness, and 32.60 g/m² basis weight was obtained. A scanning electron microscopy (SEM) (by ELMARCO s.r.o.) image of the membrane is shown in Figure 3. The electrospun membranes were used as a platform structure for functionalization or grafting by SI ATRP.

Before functionalization, the electrospun P(VDF-co-CTFE) membranes were immersed in methanol overnight. Methanol was replaced twice in the first two hours.

Example 3: SI ATRP - Functionalization

The membranes described in Example 2 were functionalized or grafted using SI ATRP. The grafting was carried out as a polymerization, where the process parameters include amounts of precursor and fluids, amount of platform membrane, deoxygenation procedures, and polymerization time.

The general procedure for of the functionalization included reagents of sodium 4-styrenesulfonate (4SSNa), CuCl, 2,2'-bipyridine, and methanol, purchased from Sigma-Aldrich and used without purification. A Schlenk tube equipped with a magnetic stirring bar and a rubber septum, was charged with 4SSNa, CuCl, 2,2'-bipyridine, methanol, and ultrapure water. The reaction mixture was stirred and deoxygenated by bubbling nitrogen through it.

Subsequently, a P(VDF-co-CTFE) membrane from Example 2, soaked in methanol, was introduced in the Schlenk tube. A fresh portion of methanol-ultrapure water mixture was added if necessary. The reaction mixture was deoxygenated further by bubbling nitrogen through it.

Polymerization was then conducted under nitrogen flow at 60 °C for a certain period of time. Afterwards, the membrane was washed with methanol-deionized water mixture (1:1) and then with deionized water overnight.

- 5 The membrane was acidified by stirring it for 1 h in approximately 1 M HCl heated to boiling.

Example 4: Membrane 1

10 For the manufacturing of Membrane 1, the general functionalization procedure as described in Example 3 was applied.

The amounts of reagents and process parameters were: 4SSNa (4.87 g), CuCl (0.038 g), 2,2'-bipyridine (0.124 g), methanol (15 mL), and ultrapure water (15 mL). The reaction mixture was deoxygenated for 45 min, and P(VDF-co-CTFE) membrane (0.23 g), methanol (5 mL), and ultrapure water (5 mL) were introduced. The reaction mixture was deoxygenated for 45 min. The polymerization was conducted for 24 h. The resulting membrane was denoted Membrane 1.

20 A SEM micrograph of the grafted Membrane 1 is shown in Figure 4. In comparison to the non-grafted platform membrane shown in Figure 3, most of the porosity has disappeared. This supports that the SI ATRP process has resulted in successful polymerization, as the pores have been filled by the grafted chains.

To verify the functionalization and surface modification, the obtained grafted Membrane 1 was investigated by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR). A Nicolet iS50 ATR spectrometer with a diamond crystal from Thermo Scientific was applied and used in the range of 4000-350 cm⁻¹. The obtained spectra are shown in Figure 5, where the lower spectrum is for the platform P(VDF-co-CTFE), and the upper spectrum is for the functionalized P(VDF-co-CTFE)-g-P4SSNa. The functionalized membrane's spectrum showed new bands at 1560-1700 cm⁻¹, 1130 cm⁻¹, and 1040 cm⁻¹ corresponding to the aromatic C=C, S=O asymmetric, and S=O symmetric stretching vibrations, respectively.

35 The thermal stability of the grafted membrane was also investigated. Figure 6 shows the thermogravimetric analyses (TGA) of the non-functionalized membrane (P(VDF-co-

CTFE), solid line), and the functionalized membrane (P(VDF-co-CTFE)-g-P4SSNa, dotted line). The TGA were carried out on a TGA Q500 apparatus from TA Instruments. Samples were heated from 20 °C to 800 °C with the heating rate of 20 °C/min under nitrogen flow. The weight loss up to 200 °C was attributed to the loss of water. On the other hand the weight loss in the temperature range of 235-360 °C was attributed to desulfonation. Thus, TGA can be a convenient means to quantify the ionic group content in the graft copolymer.

After the membrane was acidified (as described in Example 2), the conductivity and methanol permeability were measured using similar methods as described in Example 1, and the results are shown in Table 1. Compared to Nation, Membrane 1 showed ca. half the conductivity, but also reduced methanol permeability.

Example 5: Membrane 2

For the manufacturing of Membrane 2, the general functionalization procedure as described in Example 3 was applied.

The amounts of reagents and process parameters were: 4SSNa (5.48 g), CuCl (0.039 g), 2,2'-bipyridine (0.124 g), methanol (20 mL), and ultrapure water (20 mL) were taken. The reaction mixture was deoxygenated for 60 min, and P(VDF-co-CTFE) membrane (0.11 g) was introduced. The reaction mixture was deoxygenated for 90 min. The polymerization was conducted for 72 h. The resulting membrane was denoted Membrane 2.

After the membrane was acidified (as described in Example 2), the conductivity and methanol permeability were measured using similar methods as described in Example 1, and the results are shown in Table 1. Comparable conductivity to Nafion was observed, as well as slightly reduced methanol permeability compared to Nafion.

Example 6: Membrane 3

For the manufacturing of Membrane 3, the general functionalization procedure as described in Example 3 was applied.

The amounts of reagents and process parameters were: 4SSNa (6.53 g), CuCl (0.046 g), 2,2'-bipyridine (0.148 g), methanol (23.5 mL), and ultrapure water (23.5 mL) were

taken. The reaction mixture was deoxygenated for 60 min, and P(VDF-co-CTFE) membrane (0.13 g) was introduced. The reaction mixture was deoxygenated for 90 min. The polymerization was conducted for 46 h. The resulting membrane was denoted Membrane 3.

5

After the membrane was acidified (as described in Example 2), the conductivity and methanol permeability were measured using similar methods as described in Example 1, and the results are shown in Table 1. Conductivity superior to Nafion was observed, however the methanol permeability was also increased compared to Nafion.

10

Example 7: Membrane 4 and long-term durability test

For the manufacturing of Membrane 4, the general functionalization procedure as described in Example 3 was applied.

15

The amounts of reagents and process parameters were: 4SSNa (9.30 g), CuCl (0.075 g), 2,2'-bipyridine (0.236 g), methanol (40 mL), and ultrapure water (40 mL). The reaction mixture was deoxygenated for 45 min, and P(VDF-co-CTFE) membrane (0.44 g) was introduced. The reaction mixture was deoxygenated for 60 min. The polymerization was conducted for 44.5 h. The resulting membrane was denoted

20

Membrane 4.

After the membrane was acidified (as described in Example 3), the conductivity was measured on the bench manufactured by IRD Fuel Cell A/S. The conductivity was obtained from a 4-point measurement, in which a current was applied at an outer set of electrodes and the voltage was measured across an inner set of electrodes under fully immersed conditions. The conductivity of 72 mS/cm was attained.

25

Long-term Durability Test

Long-term durability test was carried out in passive vapour feed DMFCs developed by Danish Technological Institute. The size was 5.5x9x9 mm³ for the entire fuel cell including fuel reservoir. The pervaporation membrane was an aquivion 15S membrane from Solvay. In the membrane electrode assembly 20.4 mg/cm² PtRu/C catalyst was employed for the anode side and 3.6 mg/cm² Pt/C was used on the cathode side. During the experiments, the cell was filled with 100 µL 20 M methanol solution on weekdays. The temperature was around 25 °C.

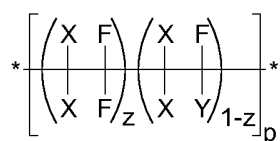
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Membrane 4 was compared to Nafion 117. The results are presented in Fig. 7. It is evident that Membrane 4 displays performance similar to Nafion 117 in the initial 2 week period. Although the cell performance degrades later on, the cell manages to stabilize maintaining over 80 % of its performance over the period of 5 weeks.

5 Items

The invention can be further described by the items listed below.

1. A porous layer for a membrane comprising a plurality of randomly oriented fibers manufactured by electrospinning,
 wherein the fibers comprise a graft copolymer,
 wherein the graft copolymer comprises a backbone and at least one side chain,
 wherein the backbone comprises a partially fluorinated copolymer, and
 wherein at least one side chain of the graft copolymer comprises a polymerization product of a polymerizable proton donor group or a precursor thereof.
2. The layer according to item 1, wherein the partially fluorinated copolymer comprises a further halogen other than fluorine, which serves as grafting site for the polymerizable proton donor group or precursor thereof, such as the inorganic or organic salt thereof.
3. The layer according to item 2, wherein the grafting site halogen is selected from the group consisting of chlorine (Cl), bromine (Br), and iodine (I).
4. The layer according to any of the preceding items, wherein the partially fluorinated copolymer has the chemical structure:



Wherein:

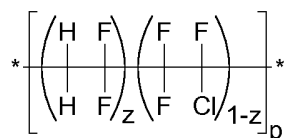
X = H and/or F

Y = Cl and/or Br and/or I

p is the number of repeating units (also known as degree of polymerization)

z is molar fraction and **z** = 0.02-0.98

5. The layer according to any of the preceding items, wherein the partially fluorinated copolymer is poly(vinylidene fluoride-co-chlorotrifluoroethylene) with the chemical structure:



5

6. The layer according to any of the preceding items, wherein the polymerizable proton donor group or precursor thereof comprises at least one double bond, which can engage in radical polymerization, and at least one ionic acid group, or at least one acidic group which may be linked to an electron-withdrawing group.

10

7. The layer according to any of the preceding items, wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of sulfonated monomer, phosphonated monomer, and monomers containing acidic NH, CH, and CH₂ groups linked to an electron-withdrawing group, and combinations thereof.

15

8. The layer according to any of the preceding items, wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of styrenes, acrylates, methacrylates, ethacrylates and vinyl acids, and combinations thereof, which further comprise a sulfonic or phosphonic acid group, or wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of NH-, CH-, and CH₂- acids, and combinations thereof.

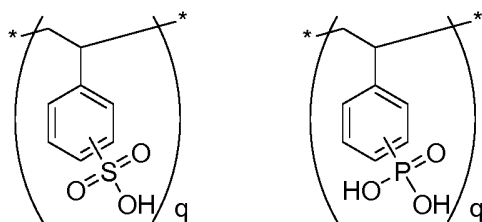
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25

9. The layer according to any of the preceding items, wherein the polymerization product of the polymerizable proton donor group or precursor thereof is a polystyrene comprising sulfonic acid groups, or phosphonic acid groups, or combinations thereof.

30

10. The layer according to any of the preceding items, wherein the polymerization product of the polymerizable proton donor group or precursor thereof is a poly(styrenesulfonic acid) or a poly(styrene phosphonic acid) with the chemical structures:



11. The layer according to any of the preceding items, wherein the grafted side chain is poly(styrenesulfonic acid) obtained from acidic treatment of a grafted side chain of poly(sodium 4-styrenesulfonate).
- 5 12. The layer according to any of the preceding items, wherein the graft copolymer is P(VDF-co-CTFE)-g-PSSA, or P(VDF-co-CTFE)-g-P4SSNa.
13. The layer according to any of the preceding items, wherein the layer thickness is below 200 μm , more preferably below 100 μm , and most preferably below 50 μm or below 25 μm .
- 10
14. The layer according to any of the preceding items, wherein the diameter of the fibers is below 500 nm, more preferably below 250 nm, and most preferably below 150 nm.
- 15
15. The layer according to any of the preceding items, wherein the porosity of the porous microstructure is between 10-80 vol%.
16. The layer according to any of the preceding items, wherein the porosity of the porous microstructure is interconnected and percolated.
- 20
17. The layer according to any of the preceding items, wherein the porosity comprises micron-sized pores and/or nano-sized pores.
- 25
18. A method for producing a membrane, comprising the steps of:
- (a) providing a porous, fibrous layer manufactured by electrospinning and comprising a partially fluorinated copolymer comprising at least one halogen other than fluorine,
- (b) applying surface initiated radical polymerization, preferably SI ATRP, to graft a polymerization product of a polymerizable proton donor group, or a precursor
- 30

thereof such as a graft copolymer in salt form, and

(c) optionally acid treating the graft copolymer, whereby the precursor forms an acidic group, such as sulfonic acid or phosphonic acid, whereby the copolymer becomes proton conducting.

5

19. The method according to item 20, wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of sulfonated monomers, phosphonated monomers, monomers containing acidic NH, CH, CH₂ groups linked to an electron-withdrawing group, and the salts of the mentioned monomers, and combinations thereof.

10

20. The method according to any of items 20-21, wherein the grafted polymerization product is a precursor, comprising poly(sodium 4-styrenesulfonate) (P4SSNa).

15

21. The method according to any of items 20-22, wherein the acid treated graft copolymer is P(VDF-co-CTFE)-*g*-PSSA.

22. A membrane produced by the method according to any of items 20-23.

20

23. A fuel cell comprising the porous layer according to any of items 1-19.

24. Use of the porous layer according to any of items 1-19 in a fuel cell, a PEM fuel cell, or a DMFC.

25

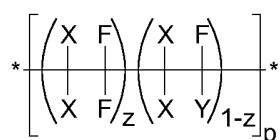
25. Use of the porous layer according to any of items 1-19 in a filter.

References

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- 30 [2] L. Wu et al., Physical Chemistry Chemical Physics 15 (2013), 4870-4887.
- [3] F. He et al., Polymer Testing 30 (2011) 436-441.
- [4] T. Kimura et al., Chemistry Letters 38 (2009) 446-447.
- [5] D. K. Roh et al., Journal of Polymer Science: Part B: Polymer Physics 48 (2010) 1110-1117.

Claims

1. A porous membrane layer comprising a plurality of randomly oriented fibers manufactured by electrospinning,
 5 wherein the fibers comprise a graft copolymer,
 wherein the graft copolymer comprises a backbone and at least one side chain,
 wherein the backbone comprises a partially fluorinated copolymer, and
 wherein at least one side chain of the graft copolymer comprises a
 10 polymerization product of a polymerizable proton donor group or a precursor thereof.
2. The layer according to claim 1, wherein the partially fluorinated copolymer comprises a further halogen other than fluorine, which serves as grafting site for the polymerizable proton donor group or precursor thereof, and/or wherein the
 15 grafting site halogen is selected from the group consisting of chlorine (Cl), bromine (Br), and iodine (I).
3. The layer according to any of the preceding claims, wherein the partially fluorinated copolymer has the chemical structure:



Wherein:

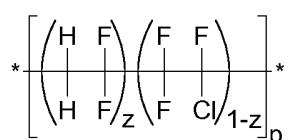
X = H and/or F

Y = Cl and/or Br and/or I

p is the number of repeating units (also known as degree of polymerization)

z is molar fraction and **z** = 0.02-0.98,

- 20 wherein preferably the partially fluorinated copolymer is poly(vinylidene fluoride-co-chlorotrifluoroethylene) with the chemical structure:



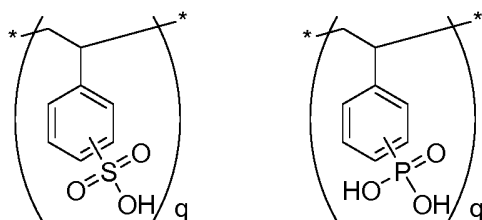
4. The layer according to any of the preceding claims, wherein the polymerizable proton donor group or precursor thereof comprises at least one double bond, which can engage in radical polymerization, and at least one ionic acid group, or at least one acidic group which may be linked to an electron-withdrawing group.

5

5. The layer according to any of the preceding claims wherein the polymerization product of the polymerizable proton donor group is a polystyrene comprising sulfonic acid groups or phosphonic acid groups or combinations thereof.

10

6. The layer according to any of the preceding claims, wherein the polymerization product of the polymerizable proton donor group is a poly(styrenesulfonic acid) or a poly(styrenephosphonic acid) with the chemical structures:



7. The layer according to any of the preceding claims, wherein the grafted side chain is poly(styrenesulfonic acid) obtained from acidic treatment of a grafted side chain of poly(sodium 4-styrenesulfonate).

15

8. The layer according to any of the preceding claims, wherein the graft copolymer is P(VDF-co-CTFE)-g-PSSA, or P(VDF-co-CTFE)-g-P4SSNa.

20

9. The layer according to any of the preceding claims, wherein the layer thickness is below 200 μm , more preferably below 100 μm , and most preferably below 50 μm or below 25 μm and/or wherein the diameter of the fibers is below 500 nm, more preferably below 250 nm, and most preferably below 150 nm.

25

10. The layer according to any of the preceding claims, wherein the porosity of the porous microstructure is between 10-80 vol% and/or wherein the porosity of the porous microstructure is interconnected and percolated and/or wherein the porosity comprises micron-sized pores and/or nano-sized pores.

30

11. A method for producing a membrane, comprising the steps of:
- (a) providing a porous, fibrous layer manufactured by electrospinning and comprising a partially fluorinated copolymer comprising at least one halogen other than fluorine,
 - 5 (b) applying surface initiated radical polymerization, preferably SI ATRP, to graft a polymerization product of a polymerizable proton donor group or a precursor thereof, such as a graft copolymer in salt form, and
 - (c) optionally acid treating the graft copolymer, whereby the precursor forms an acidic group, such as sulfonic acid or phosphonic acid, whereby the copolymer
 - 10 becomes proton conducting.
12. The method according to claim 11, wherein the polymerizable proton donor group or precursor thereof is selected from the group consisting of sulfonated monomers, phosphonated monomers, monomers containing acidic NH, CH, CH₂ groups linked to an electron-withdrawing group, and the salts of the
- 15 mentioned monomers, and combinations thereof.
13. The method according to any of claims 11-12, wherein the grafted polymerization product is a precursor, comprising poly(sodium 4-styrenesulfonate) (P4SSNa), wherein preferably the acid treated graft
- 20 copolymer is P(VDF-co-CTFE)-g-PSSA.
14. A fuel cell comprising the porous layer according to any of claims 1-10.

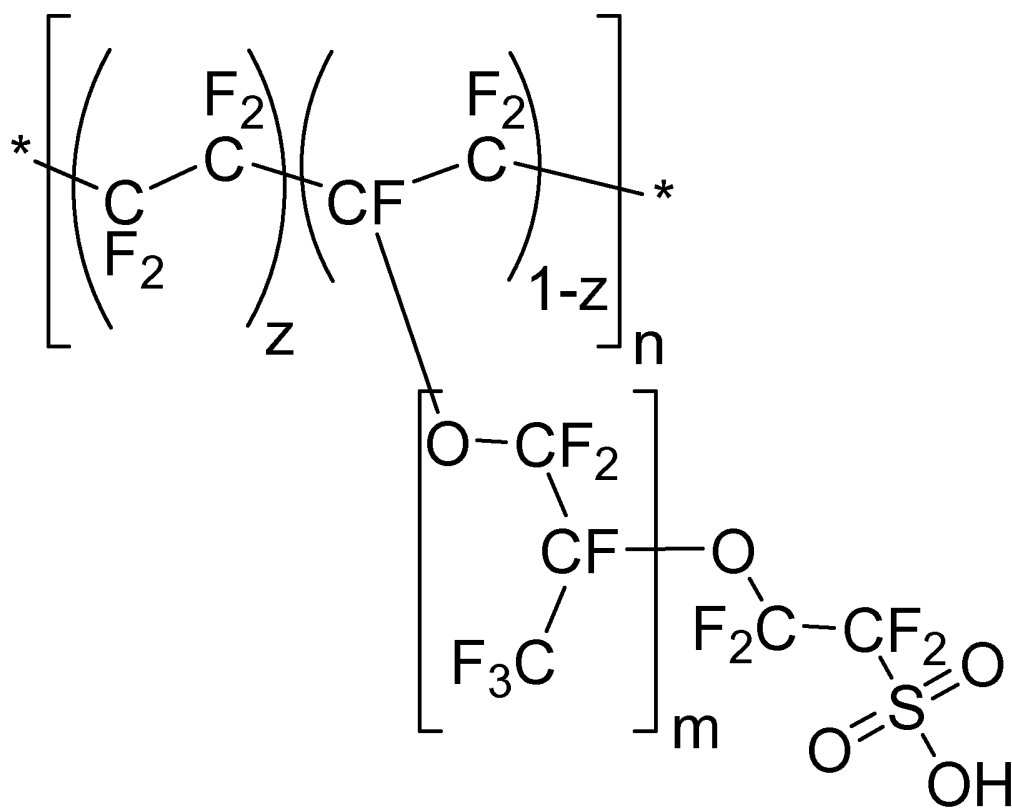


Fig. 1

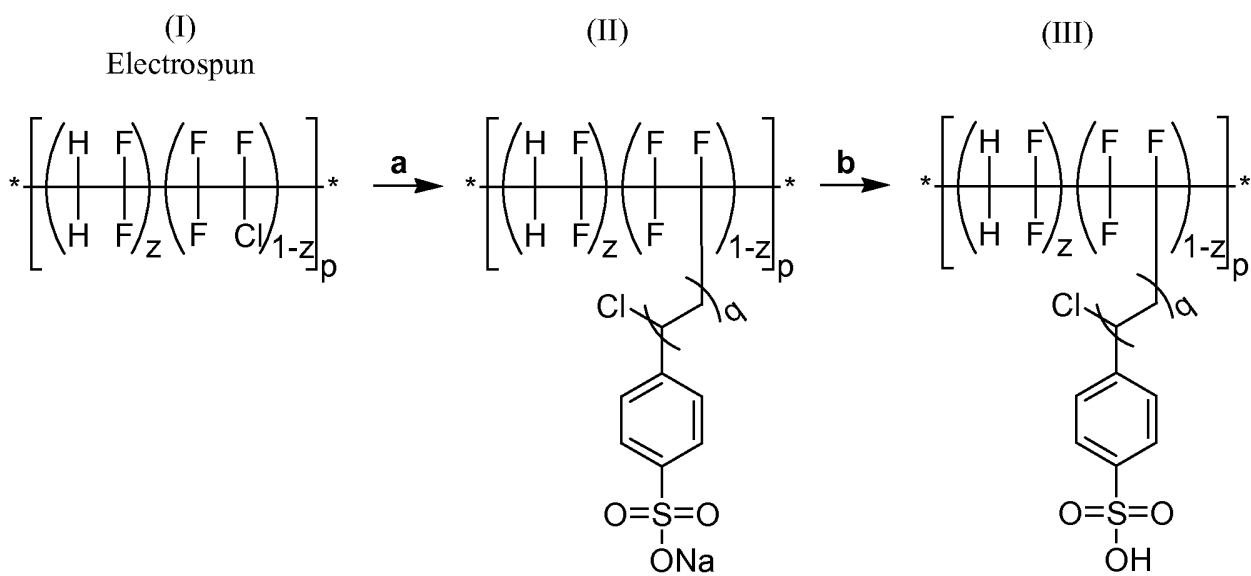


Fig. 2

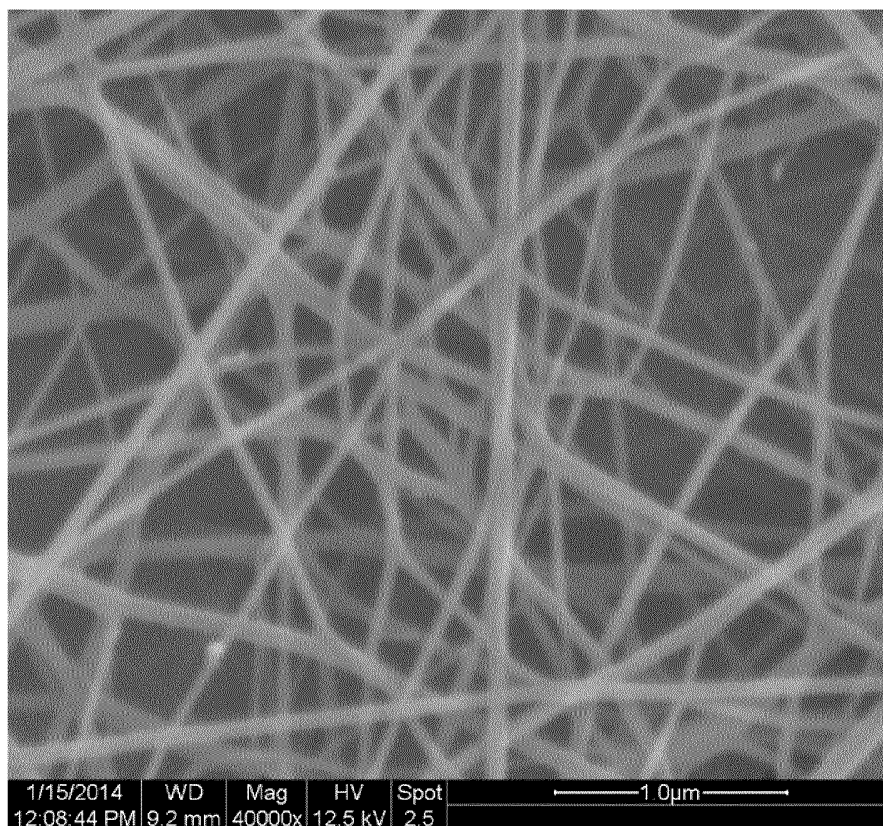


Fig. 3

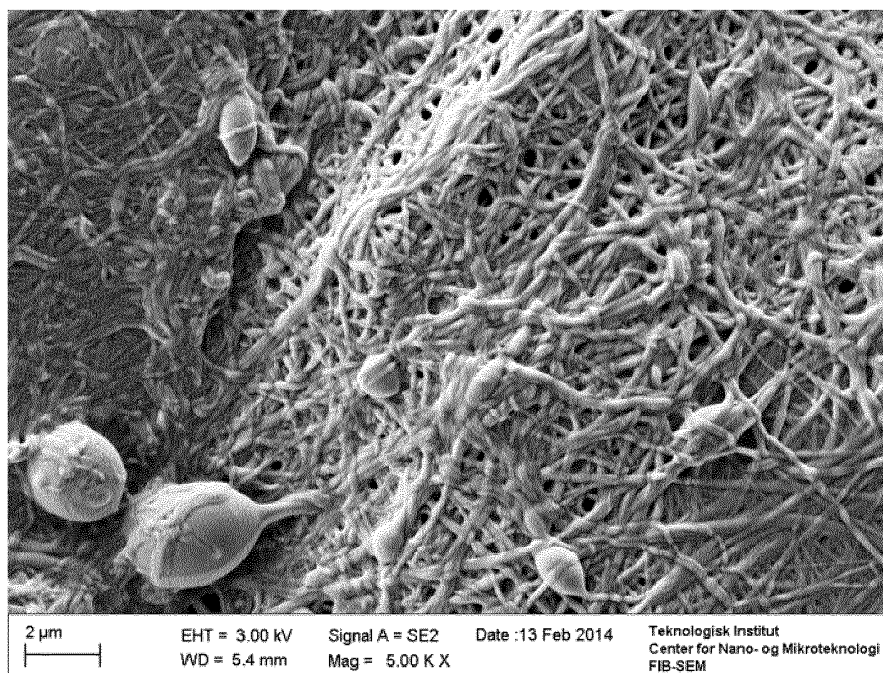


Fig. 4

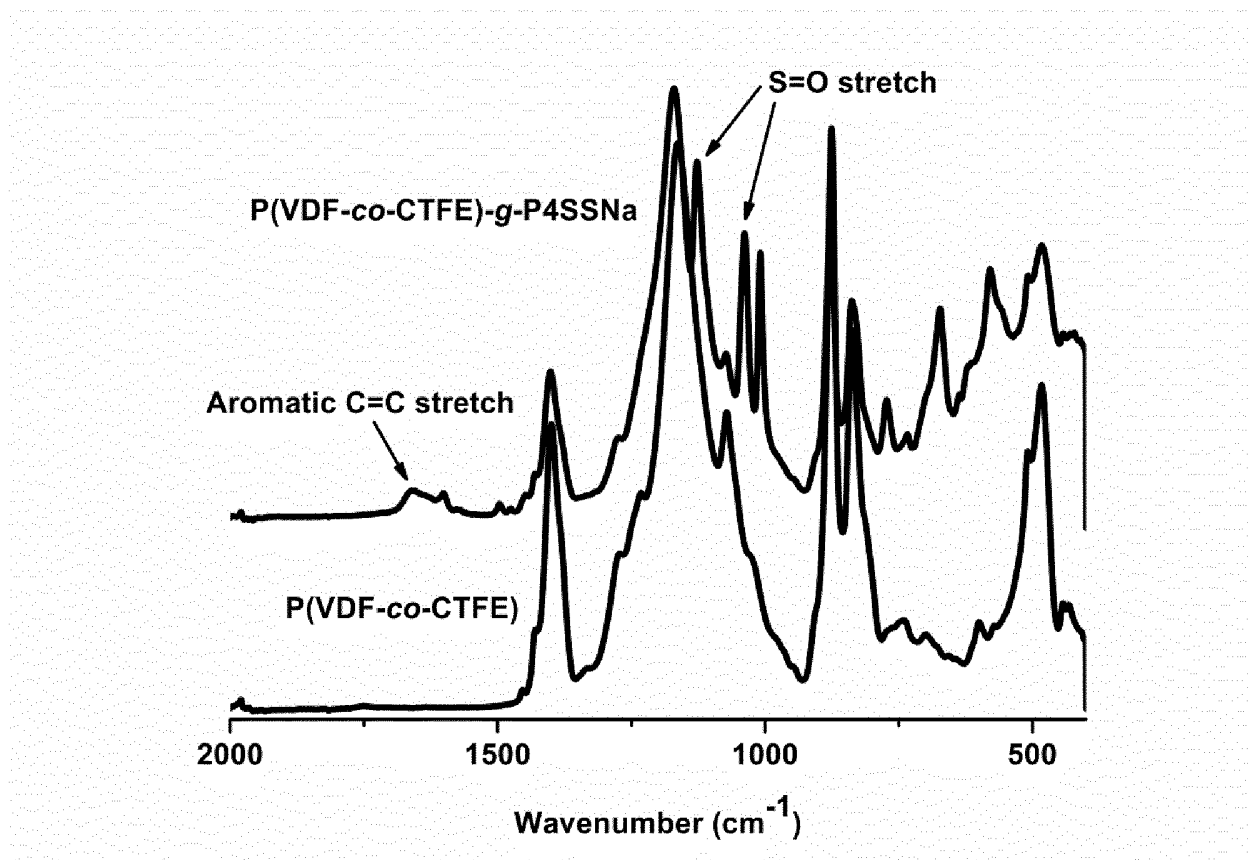


Fig. 5

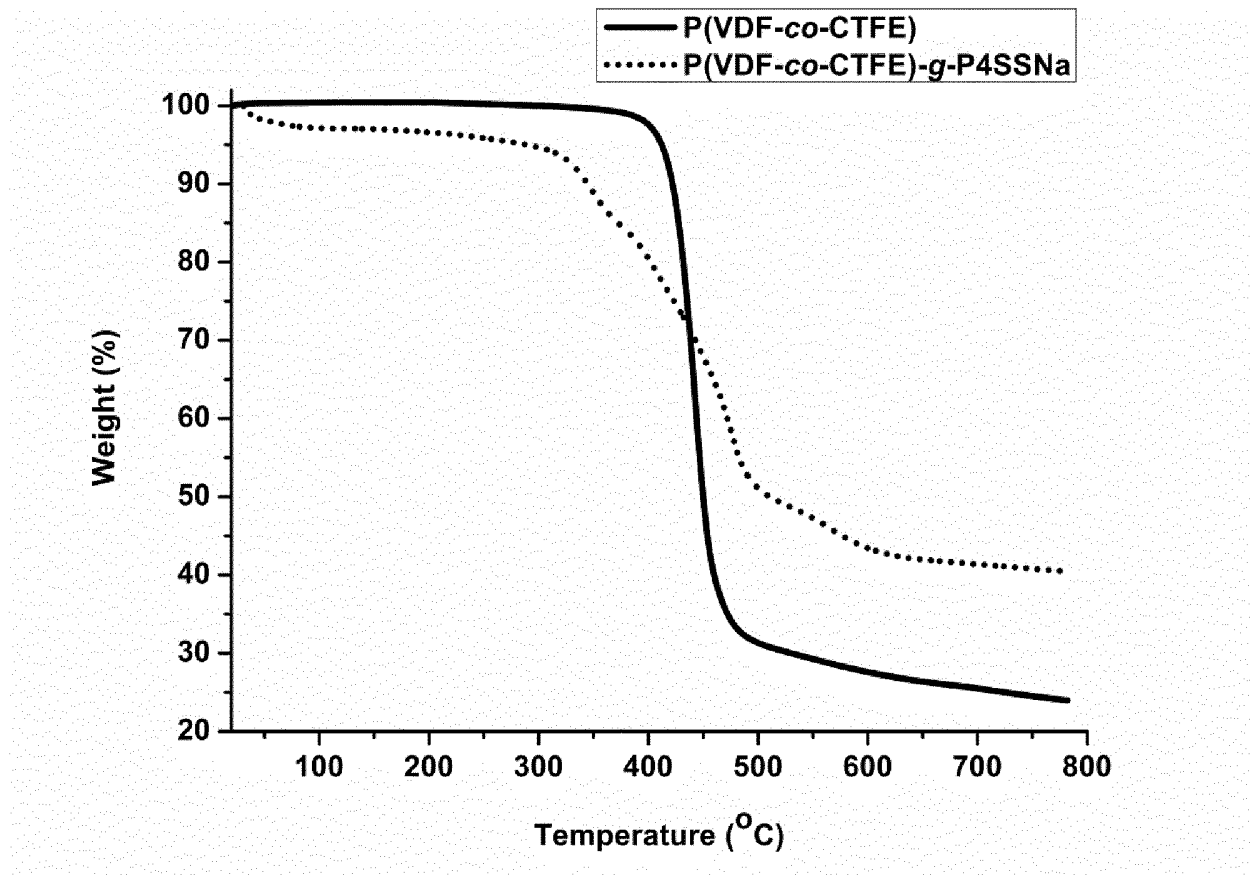


Fig. 6

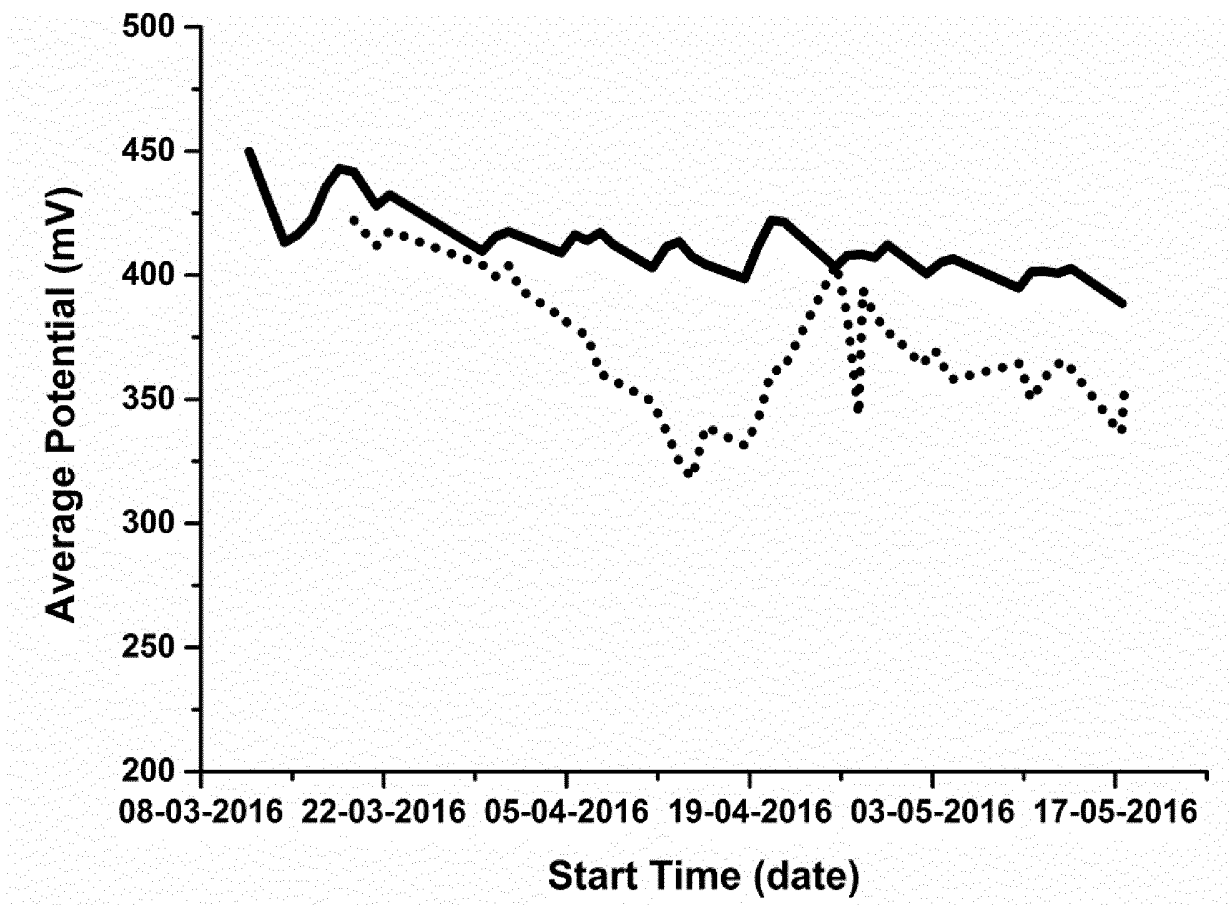


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2016/061395

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01D67/00 B01D71/76 B01D71/78 B01D71/82 C08J5/22
 C08F255/02 C08F259/08 H01M8/10 B01D71/28 B01D71/34
 B01D71/30

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)
 B01D C08J C08F 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	KR 2009 0130566 A (KYUNGPOOK NAT UNIV IND ACAD [KR]) 24 December 2009 (2009-12-24) abstract claims 1-7 ----- -/--	1,4-6,9, 10,14 2,3,7,8, 11-13

Further documents are listed in the continuation of Box C. 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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Date of the actual completion of the international search 10 October 2016	Date of mailing of the international search report 24/10/2016
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lançon, Eveline
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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/061395

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