

A method to produce a gas diffusion layer and a fuel cell comprising a gas diffusion layer

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(54) **Title:** A METHOD TO PRODUCE A GAS DIFFUSION LAYER AND A FUEL CELL COMPRISING A GAS DIFFUSION LAYER

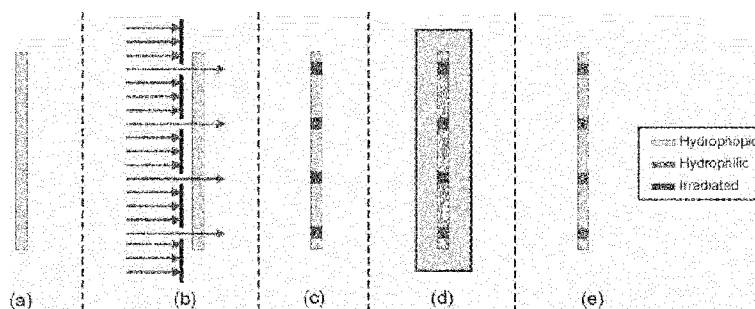


Figure 2

(57) **Abstract:** The present invention discloses a method of manufacturing gas diffusion layers (GDL) with a defined pattern of hydrophobic and hydrophilic regions. The method to produce electrically conductive porous materials with distributed wettability comprises the steps of: a) Coating the external and internal surfaces of a porous base material made of carbon fiber or Titanium with Fluoroethylene-Propylene (FEP) and/or perfluoroalkoxy (PFA) and/or Ethylene-Tetrafluoroethylene (ETFE) or any other hydrophobic polymer; b) Exposing the coated material to irradiation through a blocking mask such that only parts of the coated porous material are exposed; c) Immersing the previously exposed material in a monomer solution and heating to a temperature higher than 45°C, resulting in the graft co-polymerization of monomers on the FEP layer.



A method to produce a gas diffusion layer and a fuel cell comprising a gas diffusion layer

5 The present invention relates to a method to produce a gas diffusion layer and a fuel cell comprising said gas diffusion layer.

10 The idea of engineering water pathways through gas diffusion layers in fuel cells is a permanent topic in the operation of fuel cell stacks.

15 The presence of holes as engineered water pathways has been reported a few times, including *ex situ* and *in situ* measurements to study the effect of this approach. The generated holes having 80µm diameters using a laser and an improved performance in a small scale cell (1 cm²) using this perforated gas diffusion layers has been reported. An improved stability in a 6-cells stack (area of 30 cm²) was reported in which the GDL has been modified in this way, and in an *ex situ* study using environmental scanning electron microscopy (ESEM) water accumulation in perforated GDLs was visualized.

25 Laser perforation of GDLs was also reported. Much larger holes (300 µm) and with a high hole density were used. *In situ* tests using polarization curves and neutron imaging have shown some improvement in certain conditions (low current and low humidity), but also increased mass transport losses for such large holes. Finally, the use of mechanical pinning was reported to create one single hole at specific locations of a single channel fuel cell (under the flow channel or under the land, and near the inlet or outlet of the cell), and the impact of this hole on water distribution was studied.

35 It is the objective of the present invention to provide a method to produce a gas diffusion layer and a fuel cell comprising said gas diffusion layer; said gas diffusion layer allowing higher design flexibility and lower cost.

This objective is achieved according to the present invention by a method to produce electrically conductive porous materials with distributed wettability, comprising the steps of:

- 5 a) Coating the external and internal surfaces of a porous base material made of carbon fiber or Titanium with Fluoroethylene-Propylene (FEP) and/or perfluoroalkoxy (PFA) and/or Ethylene-Tetrafluoroethylene (ETFE) or any other hydrophobic polymer;
- b) Exposing the coated material to irradiation through a
10 blocking mask such that only parts of the coated porous material are exposed;
- c) Immersing the previously exposed material in a monomer solution and heating to a temperature higher than 45°C, resulting in the graft co-polymerization of monomers on the
15 FEP layer.

Compared to the methods known in the prior art, the wettability change using radiation grafting according to the present invention is more cost-effective and allows higher
20 design flexibility. For example, elongated in-plane water pathways cannot be realized using holes. Furthermore, a better durability is obtained due to the covalent bonding of the grafted hydrophilic compound.

25 With respect to a fuel cell, the objective is achieved according to the present invention by a fuel cell where a gas diffusion layer of the anode side, preferably produced by a method according to any of the preceding claims, comprises hydrophilic parts in order to achieve a distributed
30 wettability and part of channels in an anode flow plate aligned with said gas diffusion layer are connected to a water inlet and flooded with water wherein the water channels and the hydrophilic parts of the GDL form a water supply network used to humidify the fuel cell.

35

Advantageous embodiments of the present invention are listed hereinafter and can be combined in any possible and/or suitable combination:

a) the base material is a porous material is an electrically conductive or non-conductive material;

5 b) the applied coating (a) can be distributed over the thickness in whatever configuration, such as homogeneously distributed over the thickness (high design freedom);

10 c) photon-type radiation is used for irradiation, preferably in an energy range from UV to gamma sources;

d) in addition or alternatively to photon-type radiation, particle beam is used to generate initiators, such as plasma, accelerated and heavy ions;

15 e) the penetration depth of the irradiation is regulated in order to obtained a targeted modification depth, preferably previously produced stacks of various materials, such as gas diffusion layer and microporous layers, can be modified by the targeted modification depth;

20 f) any patterned design can be defined, such us parallel slits or circles;

25 g) lithography methods are used;

h) the monomer solution of step (c) comprises a radically activated monomer resulting in graft copolymerization of a hydrophilic polymer, such us N-nivylformamide, acrylic acid, methacrylic acid, styrene, sufonated styrene, vinylpyridine, 30 glycerol methacrylate among others;

i) the monomer solution is used as a pure liquid or is diluted with a solvent or/and other compounds and one or more additional monomers;

35 j) with an additional step (d) consisting on further exposing the material to solutions and different pressure and temperature conditions in order to pursue additional chemical

reaction to further reduce the contact angle or implement another desired property, such as hydrolysis or sulfonation;

5 k) negative pressures are additionally applied in step (c) to allow the penetration of the solution into the material pores of the porous material;

10 l) a surfactant or any lowering surface tension agents are added to the monomer solution to allow the penetration into the material pores;

m) the porous material is exposed to vapor phase of the monomer or any other mixture of gases;

15 n) the heat removal by water evaporation is sufficient to remove all the heat produced in the fuel cell, suppressing the need of an additional cooling system;

20 o) the water supply network is placed on the cathode side instead of the anode side;

p) the water supply network is used for the supply of water in an electrolyser stack or in a stack of fuel cells.

25 Preferred embodiment of the present invention are hereinafter described in more detail with respect to the attached drawings which depict in:

30 Figure 1 schematically the relation between the pathways for liquid water and for reactant gases in porous materials;

35 Figure 2 schematically a synthesis method according to the present invention for the porous material with patterned wettability;

Figure 3 schematically the distribution of different components in the gas diffusion layer visualized by SEM-EDX;

Figure 4 schematically the fine distribution of water supply using engineered hydrophilic channels in the gas diffusion layer; and

5

Figure 5 schematically a fuel cell stack without coolant channels and using monolithic plates made of carbon (left) or stamped stainless steel (right).

10 The present invention discloses a method of manufacturing gas diffusion layers (GDL) with a defined pattern of hydrophobic and hydrophilic regions. The interest of such materials for fuel cell applications is their potential use on the cathode side to improve the transport of oxygen in presence of liquid

15 water, as discussed in the literature and illustrated in Figure 1. Figure 1 illustrates the relation between the pathways for liquid water and for reactant gases in porous materials. Left: in standard hydrophobic materials. Right: in the new proposed material according to the present invention.

20

A further possibility of application is to use this invention as a help for evaporation cooling in fuel cells and electrolyzers, using the hydrophilic pathways as a help to guide water injection. Other applications relying on porous

25 supports that require through plane conduction of water or any other liquid can benefit from this material, such as microfluidics (dialysis).

The proposed method to synthesize such a material is based on

30 radiation induced graft polymerization. The originally hydrophobic material is exposed to a beam which is masked in certain regions. Alternatives to define the exposed regions are to use lithography or a scanning pencil beam. The regions which have been exposed are "activated". Consequently the

35 graft copolymerization process will occur only in these regions. The synthesis process is summarized in Figure 2. Figure 2 shows the synthesis method according to the present invention for the porous material with patterned wettability. (a): Base porous material (hydrophobized). (b): Irradiation

using a mask. (c): Locally irradiated base material. (d): Impregnation with grafting solution. (e) Resulting material with patterned wettability.

5 Currently, the realization of a first GDL hydrophobized using Fluoro-Ethylene-Propylene and with localized grafting of Acrylic Acid as a hydrophilic compound has been demonstrated. For this example a gas diffusion layer commercially available Toray TPGH-090 was coated with 30% weight of FEP and sintered.
10 The material was then irradiated with an electron beam of 1.5 MeV energy and 50.0 kGy dose. A mask of 2 mm thickness stainless steel was used with drilled slits of 500 μm . The irradiated material was placed into a reactor of 50 mL and 50 mbar pressure. The grafting solution (15% vol Acrylic acid in
15 water) was pumped in after 60 min of nitrogen bubbling. The reaction was brought to a temperature of 60°C.

The distribution of the different components visualized by SEM-EDX is shown in Figure 3. The current method uses vacuum
20 for a correct wetting of the material with the grafting solution, but the process can be realized in an also cost effective way, for example using a surfactant or vapor phase grafting. Figure 3 shows SEM-EDX mappings of a gas diffusion layer hydrophobized using FEP and locally grafted with Acrylic
25 Acid according to the present invention. Left: C (carbon) signal showing the carbon fibers. Middle: F (fluorine) signal showing the distribution of coating. Right: Na (sodium) signal showing the grafted Acrylic Acid, after exchange in NaOH for visualization purposes.

30

It is believed that this method is of significant interest, since the performance of the fuel cell is improved by the use of this material. Moderate additional costs are expected due the simplicity of the process and the low cost of the
35 chemicals involved.

General thoughts on patentability

- In particular, the use of FEP as hydrophobizing agent prior to grafting is not published yet. The use of FEP is

a critical part of the process due to better radiation resistance and grafting kinetics of this material compared to the PTFE normally used for hydrophobization. The patent application therefore covers all GDL using FEP
5 as hydrophobizing agent which is grafted afterwards.

In addition, the implementation of the evaporation cooling concept using the material above can be realized. The direct injection of liquid water in a fuel cell for the purpose of
10 humidification and cooling has important advantages:

- Operation of the cell with dry gases, suppressing the bulky and costly external humidifiers
- Efficient cooling, potentially suppressing the need for an additional coolant circulation

15 The practical implementation of evaporation cooling is difficult. Our studies on differential cells have shown that, on the local scale, humidification from the anode side is much more effective than from the cathode side. However, due to the
20 permeation through the membrane and the electro osmotic drag, water injected in the anode inlet will be transported to the cathode side. Figure 4 shows fine distribution of water supply using engineered hydrophilic channels in the GDL. Below the
25 water soaked hydrophilic regions, hydrogen is transported to the electrode through the hydrophobic micro-porous layer (MPL) usually present in fuel cells.

The present invention now uses a design that provides some of the channels on the anode side (for example, each 3rd channel)
30 as water supply channels being completely flooded with water (these supply channels are connected to another manifold than the hydrogen supply channels). To transport the water efficiently to the regions between the water supply channels, elongated hydrophilic water pathways are created in the GDL
35 (using the method described above). To avoid gas bubbling into the water supply channels, those can optionally be covered by a hydrophilic region as illustrated in Figure 4. As the transport of gas is not very critical on the anode side, a significant portion of the GDL volume (e.g. 50% or even 75%)

can be used for the transport of water. Besides their role in distribution the water away from the water supply channels, the finely spaced hydrophilic channels are appropriate to increase the water surface for a more efficient evaporation.

5

The key interest of the present invention resides in the fact that the use of the common components can be maintained and nothing is particularly added compared to the classical fuel cell technology. The extra cost of the present GDL modification method is offset by the system cost reduction due to the suppression of external humidifiers. Even further, if the evaporation cooling is, as targeted, sufficient to remove all the heat produced, a further cost and size reduction by suppressing the coolant circulation and by using monolithic separator plates can be realized. Such a design is illustrated in Figure 5. Due to these advantages, the present idea has a large potential compared to the existing designs for evaporation cooling. Figure 5 illustrates a stack based on the present idea, without coolant channels and using monolithic plates made of carbon (left) or stamped stainless steel (right).

The present invention provides a significant advantage compared to other proposed ideas due to the following features:

25

- The use of an industrially available irradiation method (e-beam) and low cost chemicals, providing a cost advantage to other proposed methods (e.g. deposition inkjet or screen printing)
- 30 - The use of a chemical modification method with a better durability as compared to other physical deposition methods
- Compared to some of the methods (e.g. perforation), the present design offers a significantly higher flexibility for the design of the hydrophilic area/volumina of a gas diffusion layer.

35

On the evaporation cooling (application) disclosure, the significant advantage of the present inventions resides in the

fact that no additional layer is included, and that no layer is significantly bulkier or expensive than in classical fuel cell designs (as opposed, for example, to the water transport plates of the UTC design). Thus, the following advantages are

5 realizable:

- Reduced stack and system cost, which is critical for automotive applications
- Reduced system size (= increase of power density), which is essential as well for automotive applications

10

Patent Claims

1. A method to produce electrically conductive porous materials with distributed wettability, comprising the steps
5 of:
- a) Coating the external and internal surfaces of a porous base material made of carbon fiber or Titanium with Fluoroethylene-Propylene (FEP) and/or perfluoroalkoxy (PFA) and/or Ethylene-Tetrafluoroethylene (ETFE) or any other hydrophobic polymer;
 - 10 b) Exposing the coated material to irradiation through a blocking mask such that only parts of the coated porous material are exposed;
 - c) Immersing the previously exposed material in a monomer solution and heating to a temperature higher than 45°C,
15 resulting in the graft co-polymerization of monomers on the FEP layer.
2. The method according to claim 1, wherein the base material is a porous material is an electrically conductive or non-
20 conductive material.
3. The method according to any of the preceding claims, wherein the applied coating (a) can be distributed over the thickness in whatever configuration, such as homogeneously
25 distributed over the thickness.
4. The method according to any of the preceding claims wherein photon-type radiation is used for irradiation, preferably in an energy range from UV to gamma sources.
30
5. The method according to any of the preceding claims wherein particle beam is used to generate initiators, such as plasma, accelerated and heavy ions.
- 35 6. The method according to any of the preceding claims wherein the penetration depth of the irradiation is regulated in order to obtained a targeted modification depth, preferably previously produced stacks of various materials, such as gas

diffusion layer and microporous layers, can be modified by the targeted modification depth.

7. The method according to any of the preceding claims,
5 wherein any patterned design can be defined, such us parallel slits or circles.

8. The method according to any of the preceding claims,
wherein lithography methods are used.

10

9. The method according to any of the preceding claims,
wherein the monomer solution of step (c) comprises a radically
activated monomer resulting in graft copolymerization of a
hydrophilic polymer, such us N-nivylformamide, acrylic acid,
15 methacrylic acid, styrene, sulfonated styrene, vinylpyridine,
glycerol methacrylate among others.

10. The method according to any of the preceding claims,
wherein the monomer solution is used as a pure liquid or is
20 diluted with a solvent or/and other compounds and one or more
additional monomers.

11. The method according to any of the preceding claims,
wherein with an additional step (d) consisting on further
25 exposing the material to solutions and different pressure and
temperature conditions in order to pursue additional chemical
reaction to further reduce the contact angle or implement
another desired property, such us hydrolysis or sulfonation.

30 12. The method according to any of the preceding claims,
wherein negative pressures are additionally applied in step
(c) to allow the penetration of the solution into the material
pores.

35 13. The method according to any of the preceding claims,
wherein a surfactant or any lowering surface tension agents
are added to the monomer solution to allow the penetration
into the material pores.

14. The method according to any of the preceding claims, wherein the porous material is exposed to vapor phase of the monomer or any other mixture of gases.

5 15. A fuel cell where a gas diffusion layer of the anode side, preferably produced by a method according to any of the preceding claims, comprises hydrophilic parts in order to achieve a distributed wettability and part of channels in an anode flow plate aligned with said gas diffusion layer are
10 connected to a water inlet and flooded with water wherein the water channels and the hydrophilic parts of the GDL form a water supply network used to humidify the fuel cell.

15 16. The fuel cell according to claim 15, wherein the heat removal by water evaporation is sufficient to remove all the heat produced in the fuel cell, suppressing the need of an additional cooling system.

20 17. The fuel cell according to claim 15 or 16 wherein the water supply network is placed on the cathode side instead of the anode side.

25 18. The fuel cell according to any of the preceding claims 16 to 18, wherein the water supply network is used for the supply of water in an electrolyser stack or in a stack of fuel cells.

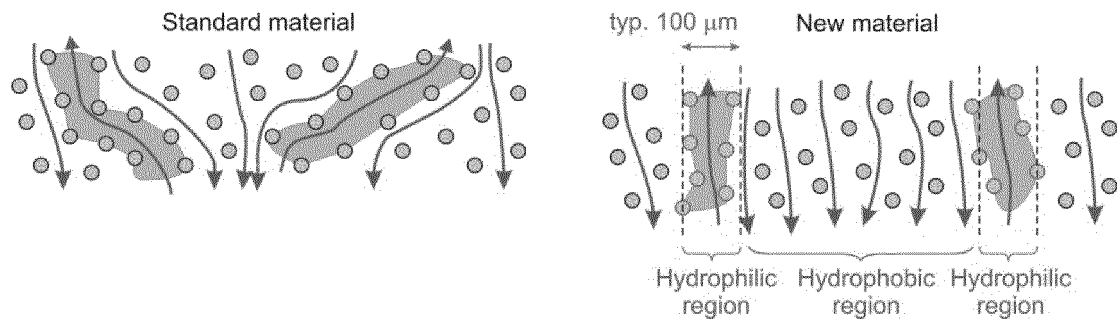


Figure 1

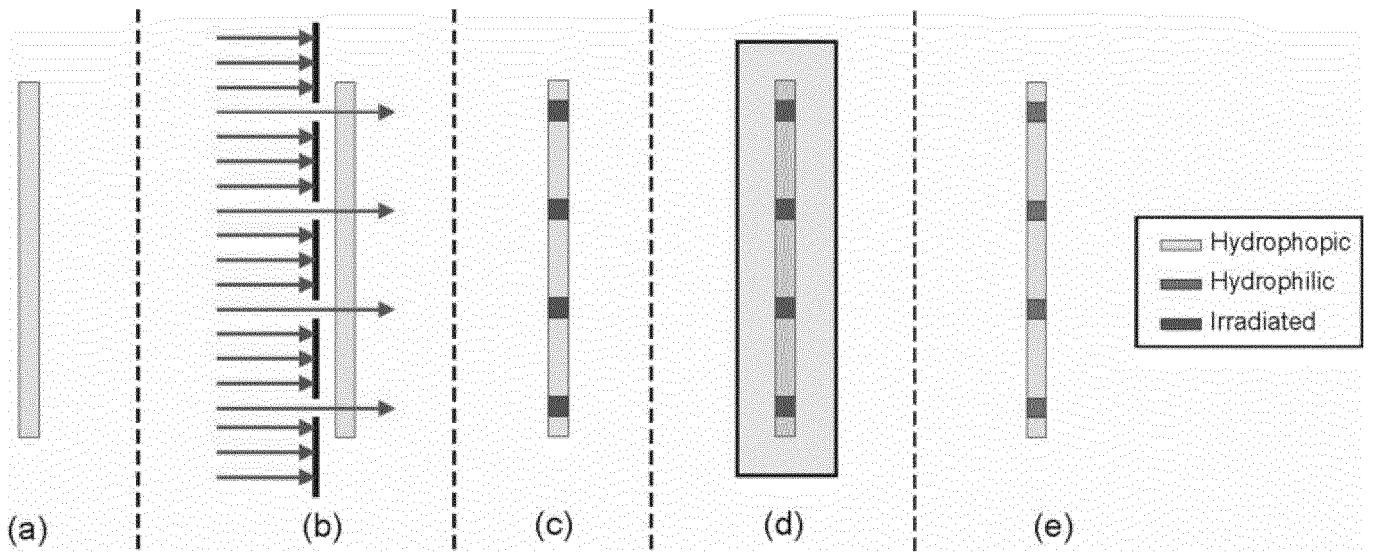


Figure 2

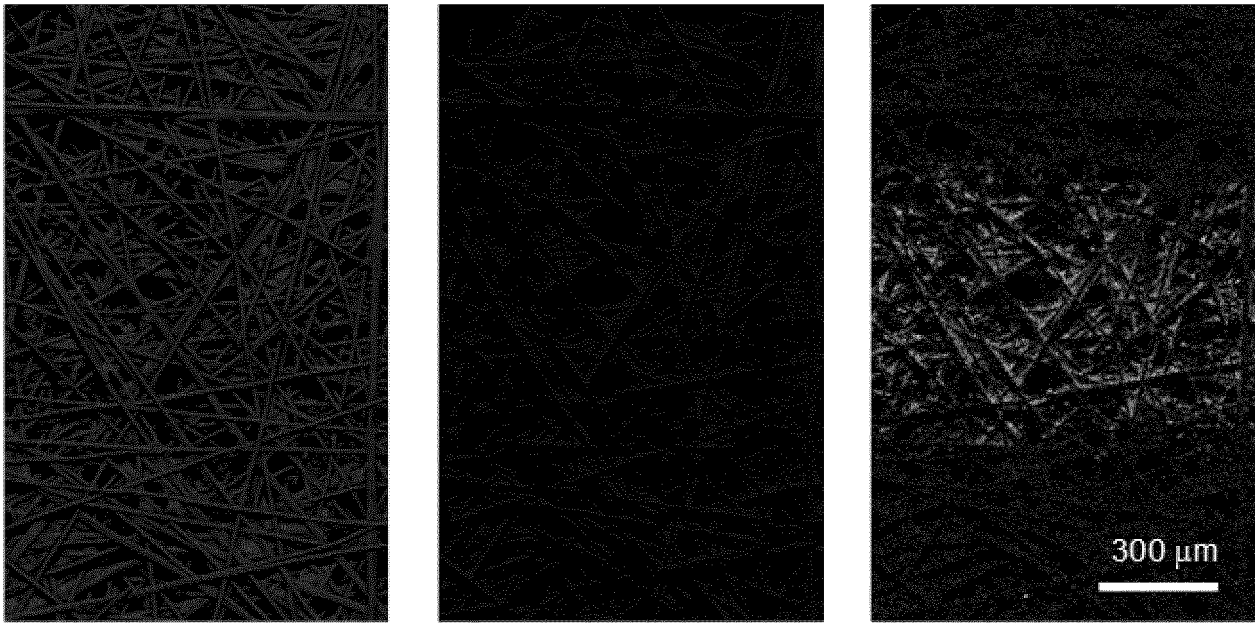


Figure 3

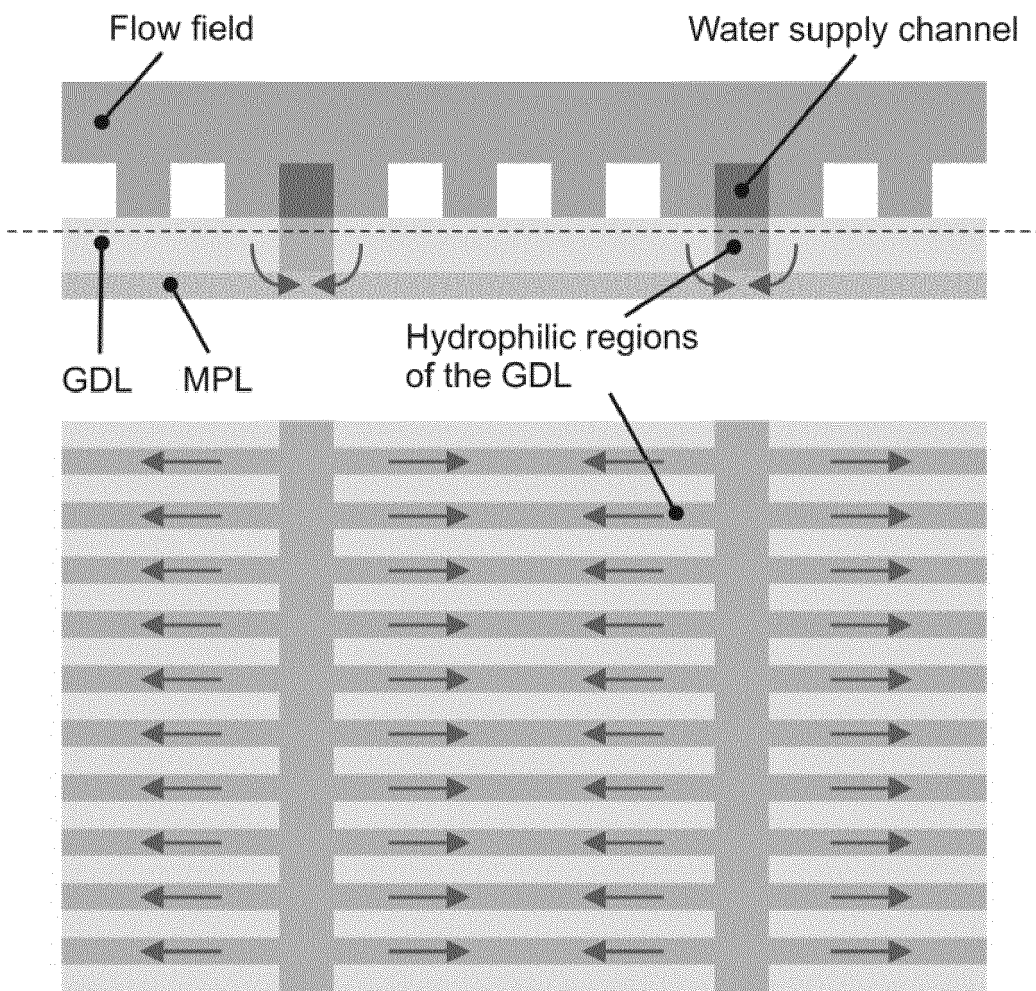


Figure 4

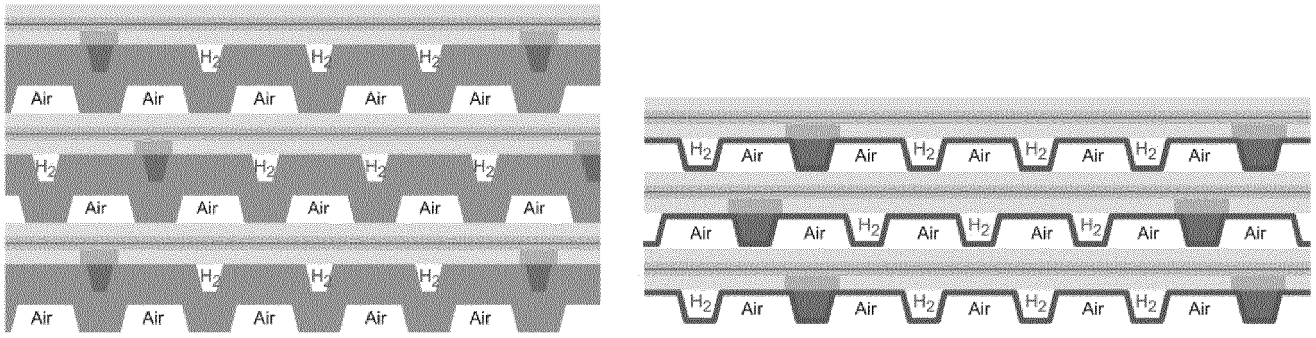


Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/069284

A. CLASSIFICATION OF SUBJECT MATTER
 INV. H01M8/02 H01M8/04
 ADD. H01M8/10

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 1 947 722 A1 (DAINIPPON INK & CHEMICALS [JP]) 23 July 2008 (2008-07-23) paragraph [0014]; claim 1	1-18
A	EP 1 693 101 A1 (SCHERRER INST PAUL [CH]) 23 August 2006 (2006-08-23) claim 1	1-18
X	WO 2014/061280 A1 (PANASONIC CORP [JP]) 24 April 2014 (2014-04-24) abstract & US 2014/329167 A1 (OKANISHI TAKEOU [JP] ET AL) 6 November 2014 (2014-11-06) paragraphs [0404], [0405]; figure 16; example 6	15

Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search 11 December 2015	Date of mailing of the international search report 22/12/2015
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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 Koessler, Jean-Luc
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2015/069284

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