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(54) **GAS DIFFUSION ELECTRODE SUITABLE FOR USE IN CARBON DIOXIDE ELECTROLYZER AND METHODS FOR MAKING THE SAME**

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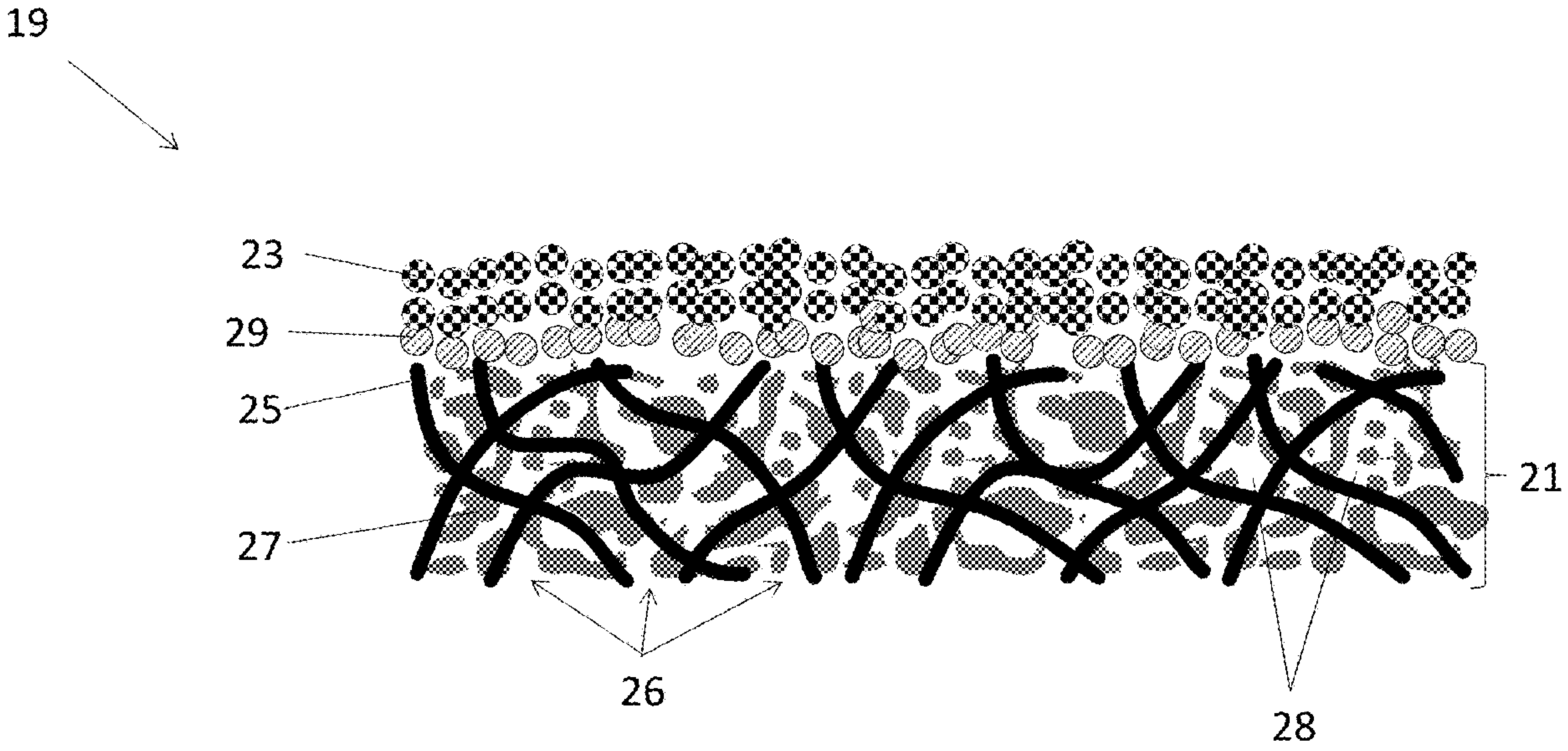
C25B 11/052	(2006.01)

(52) **U.S. Cl.**

CPC ***C25B 11/032*** (2021.01); ***C25B 3/26*** (2021.01); ***C25B 11/052*** (2021.01)

(57) **ABSTRACT**

Gas diffusion electrode suitable for use in carbon dioxide electrolyzer and methods for making the same. According to one embodiment, the gas diffusion electrode may include a gas diffusion layer and a catalyst layer coupled to the gas diffusion layer. The gas diffusion layer, in turn, may include an electron-conductive domain and a non-conductive hydrophobic domain. The electron-conductive domain includes a plurality of pores. The non-conductive hydrophobic domain randomly occupies a portion of the volume of the pores of the electron-conductive domain and is, itself, sufficiently porous to permit gas transport through the electron-conductive domain, for example, by incompletely filling the pores, thereby leaving spaces in the pores, and/or by being made of an inherently porous material. The electron-conductive domain may be in the form of a metal mesh, a carbon paper, or similar structures. The non-conductive hydrophobic domain may be in the form of sintered polymer particles.



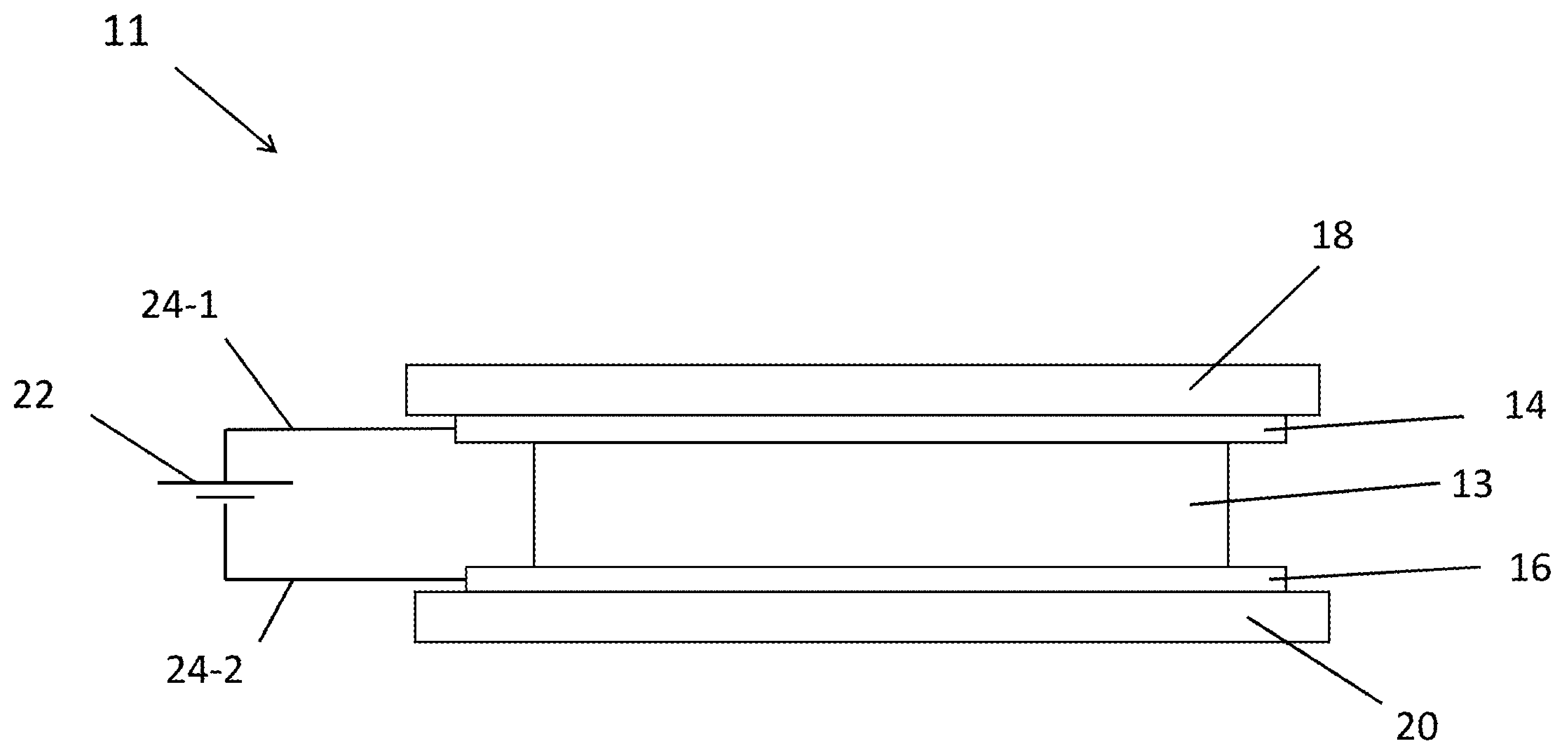


FIG. 1

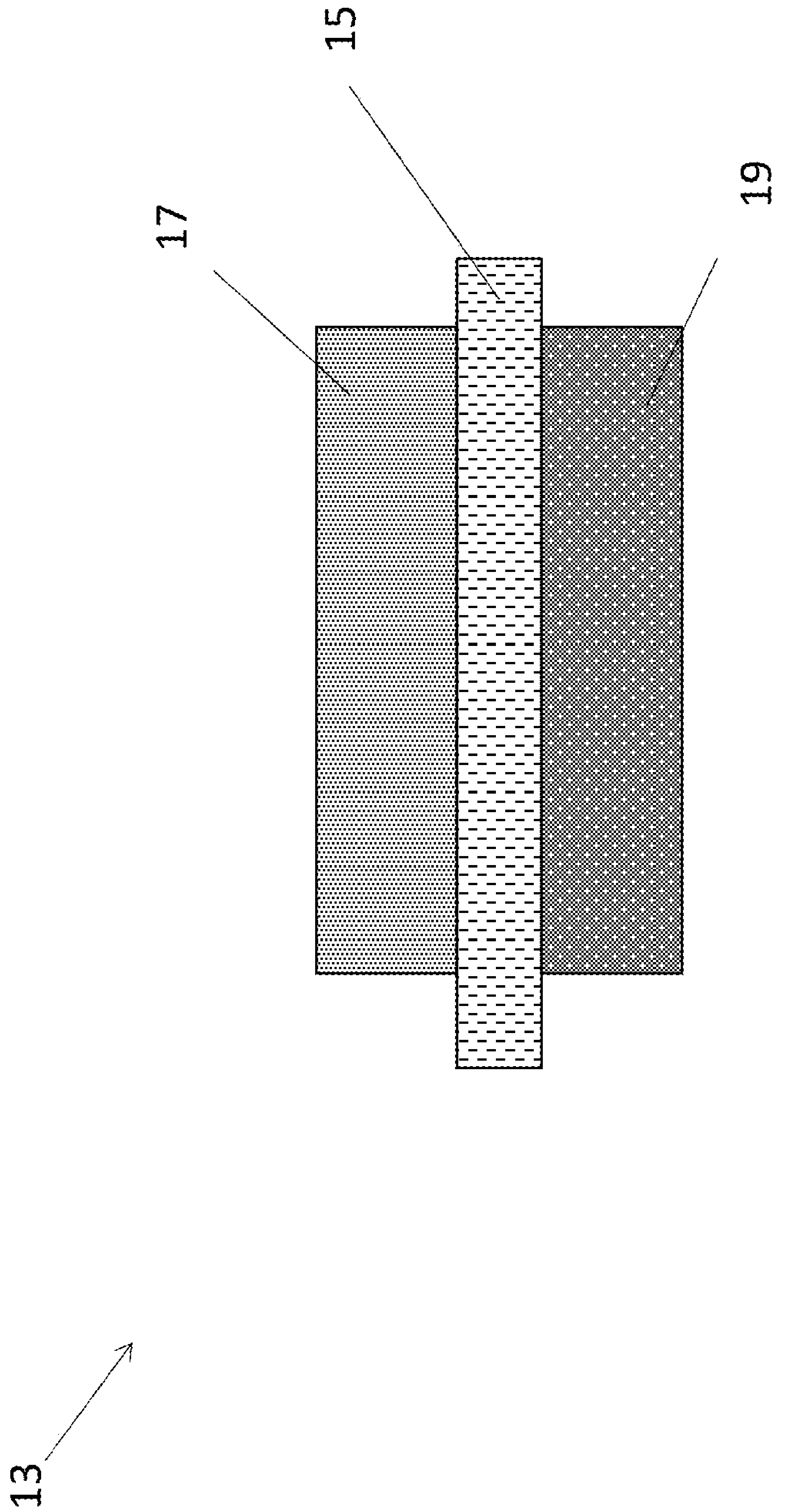


FIG. 2

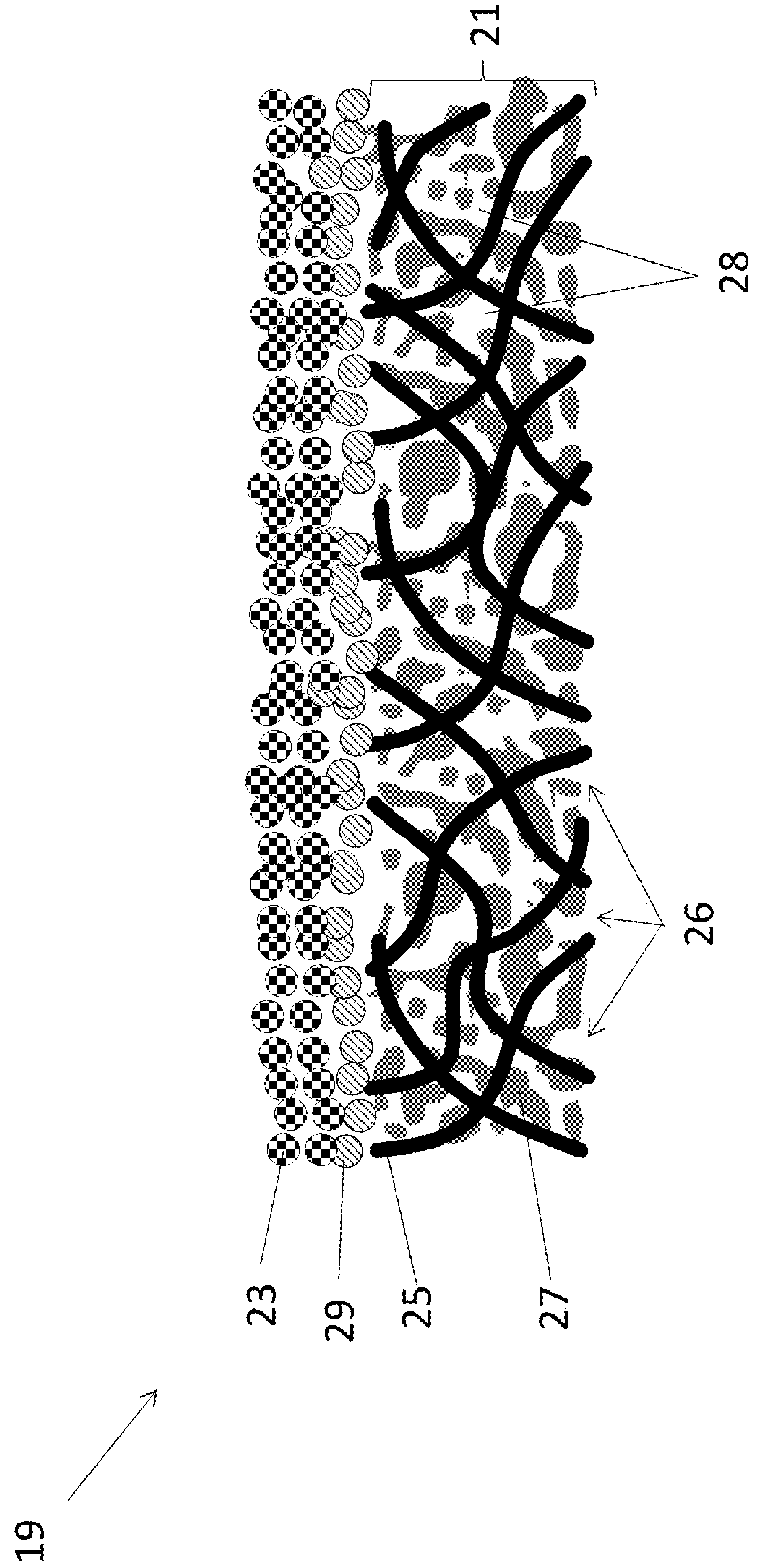


FIG. 3

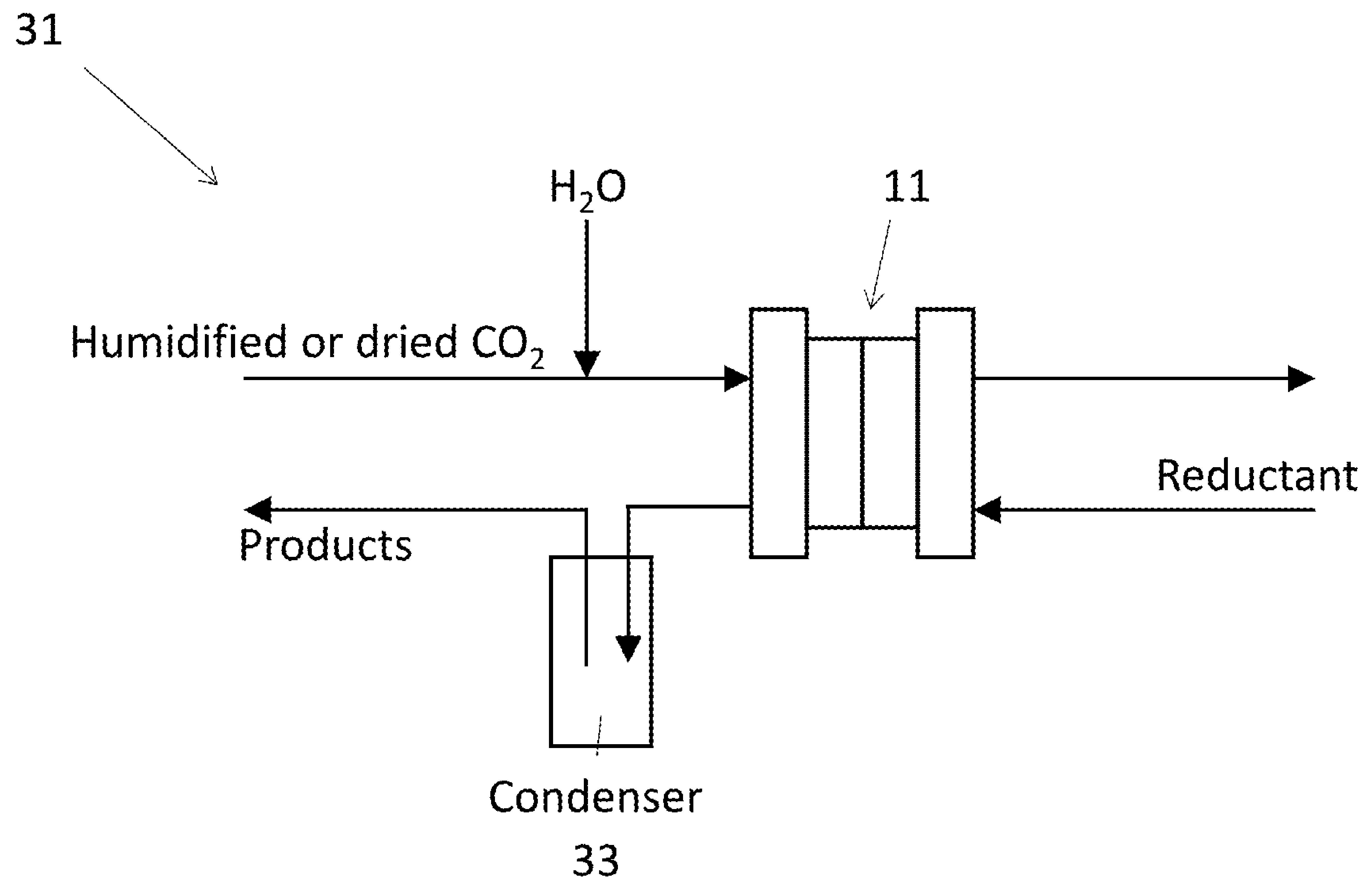

31
H_2O
11
Humidified or dried CO_2
Reductant
Products
Condenser
33

FIG. 4

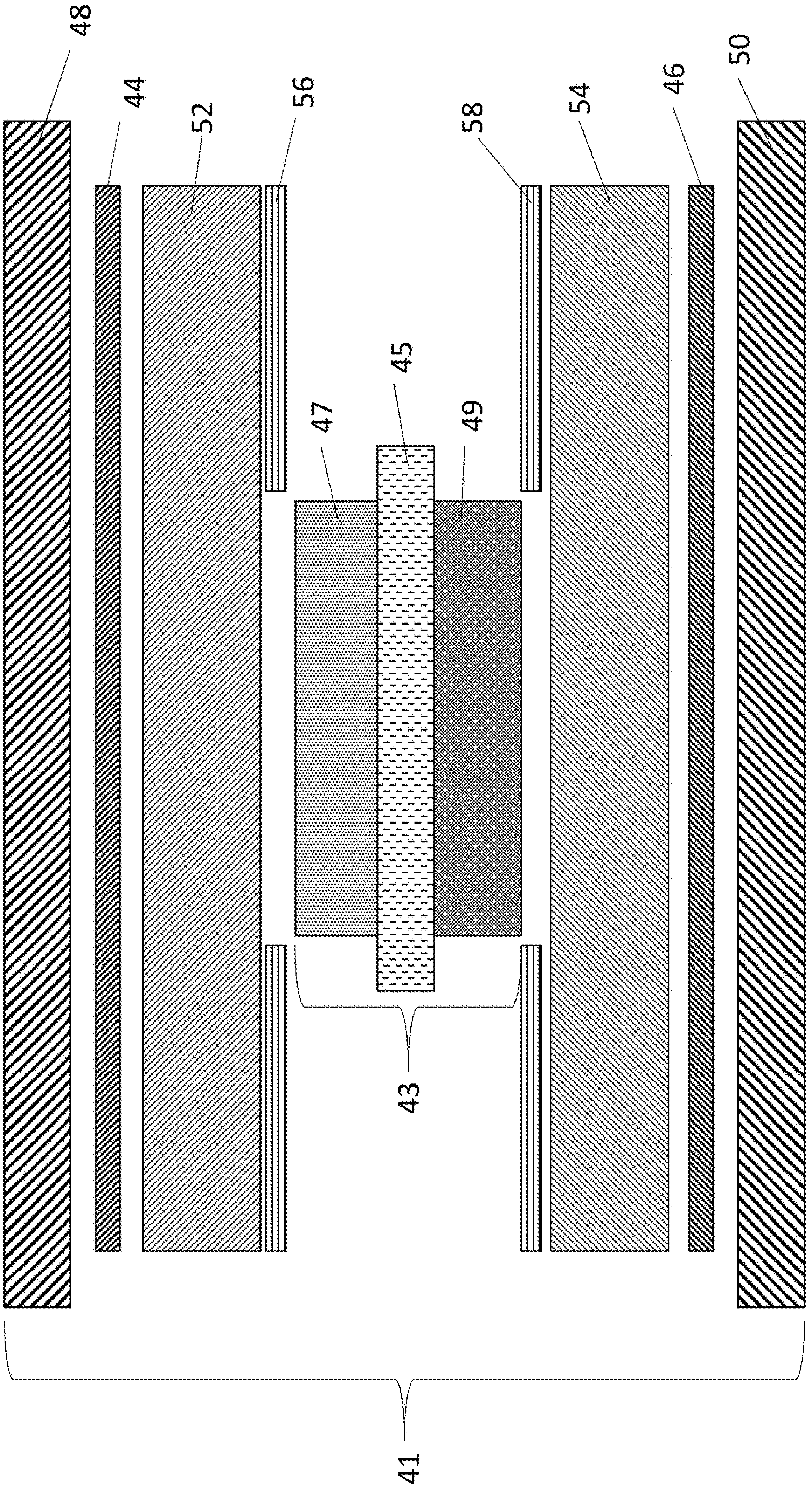


FIG. 5

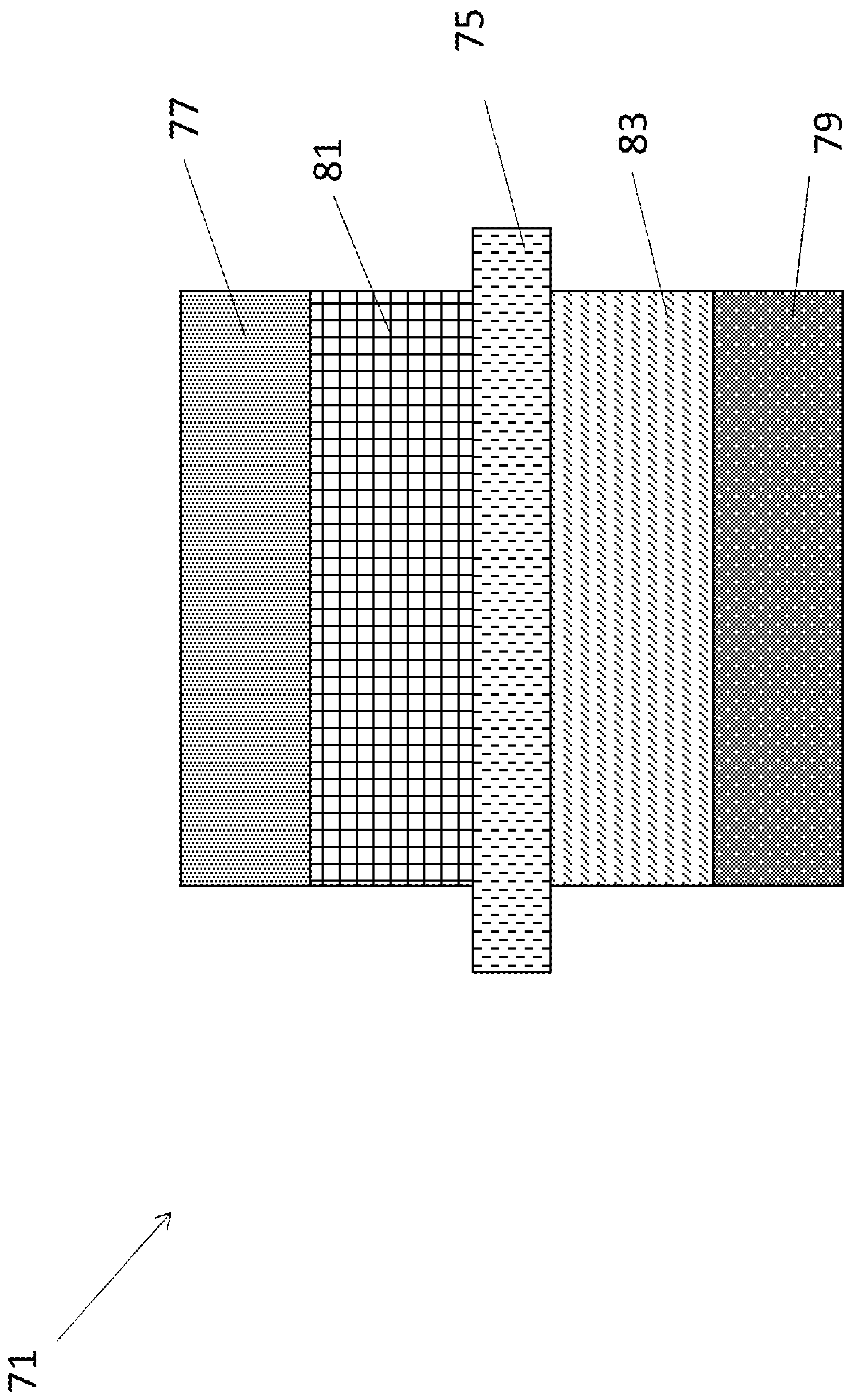


FIG. 6

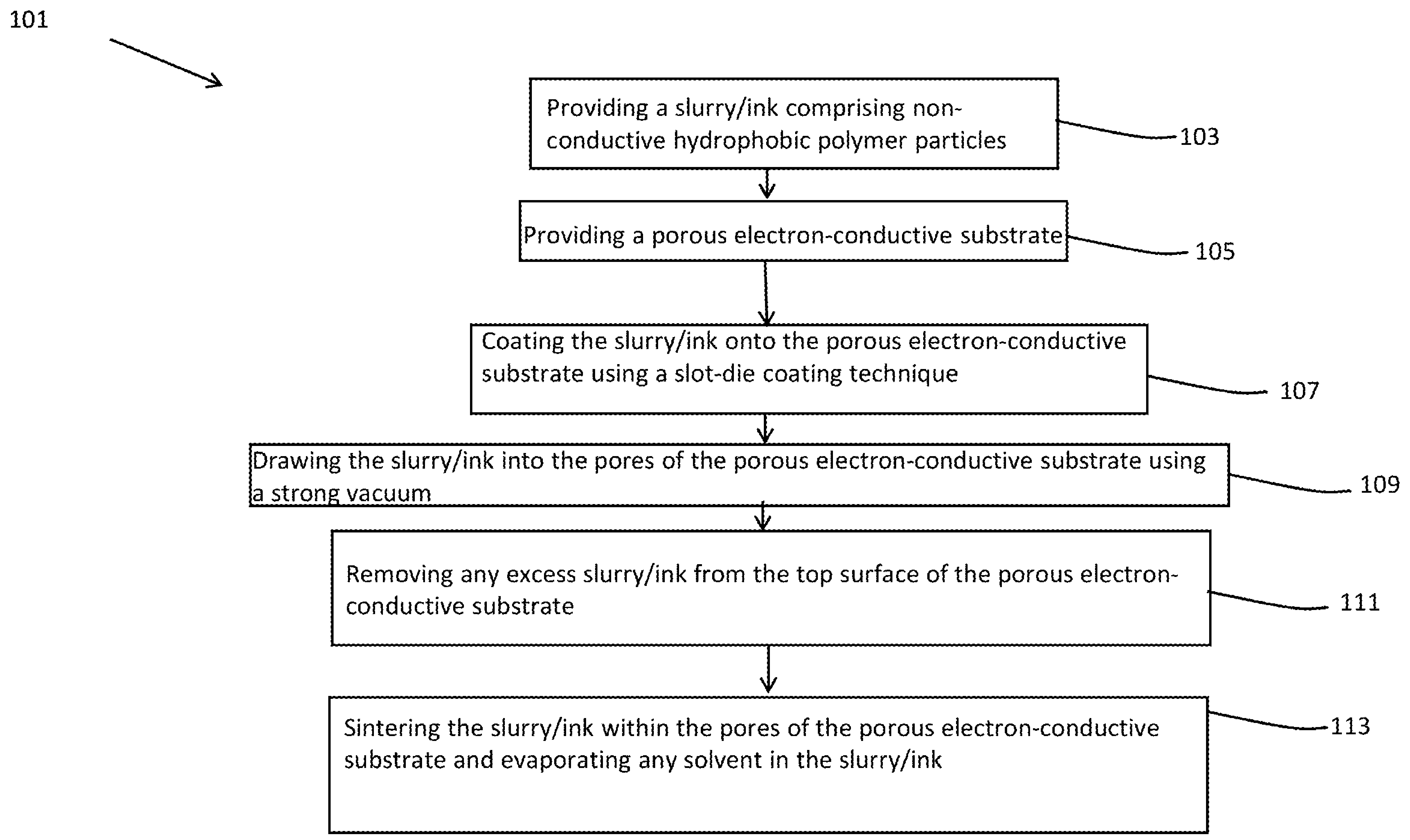

101
Providing a slurry/ink comprising non-conductive hydrophobic polymer particles
103
Providing a porous electron-conductive substrate
105
Coating the slurry/ink onto the porous electron-conductive substrate using a slot-die coating technique
107
Drawing the slurry/ink into the pores of the porous electron-conductive substrate using a strong vacuum
109
Removing any excess slurry/ink from the top surface of the porous electron-conductive substrate
111
Sintering the slurry/ink within the pores of the porous electron-conductive substrate and evaporating any solvent in the slurry/ink
113

FIG. 7

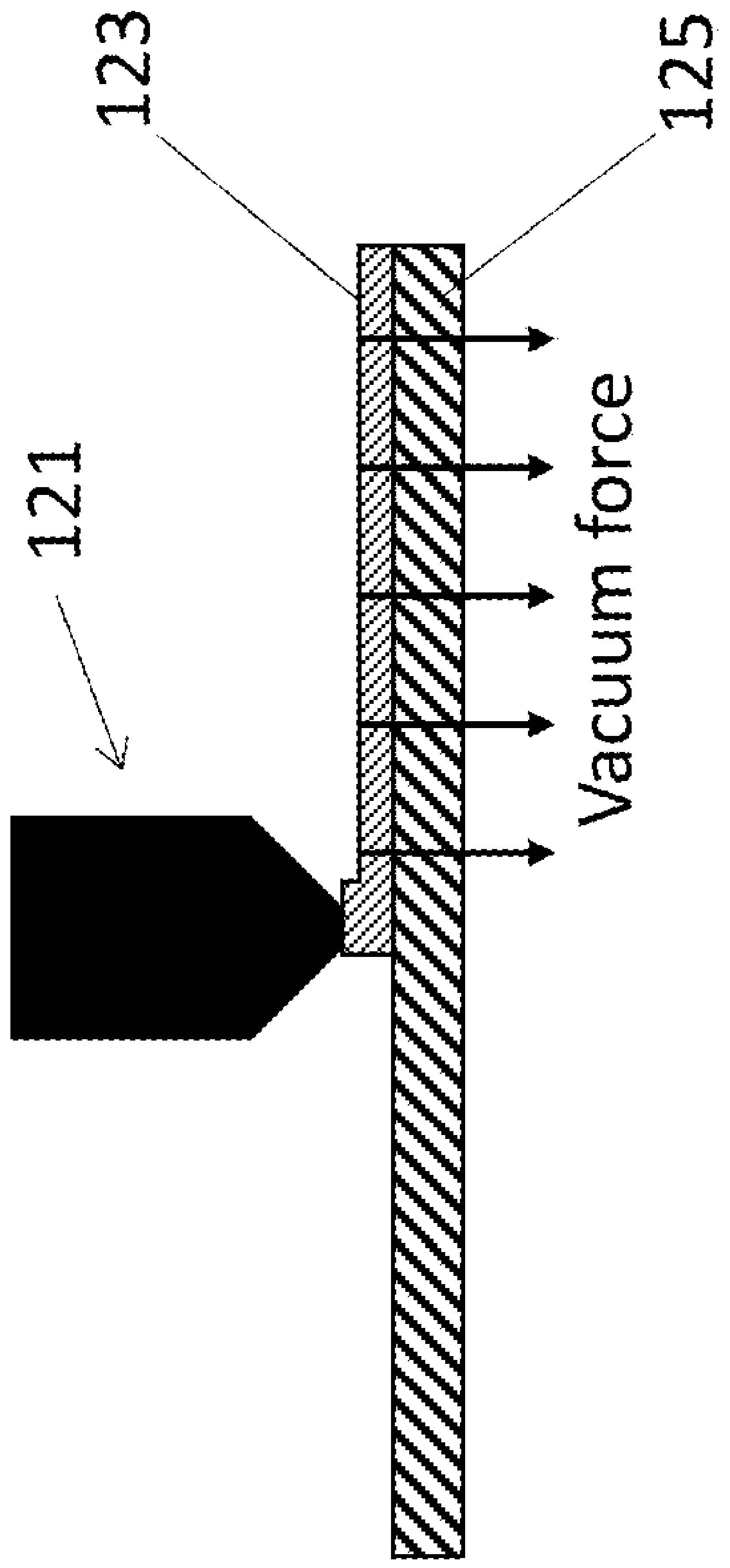


FIG. 8

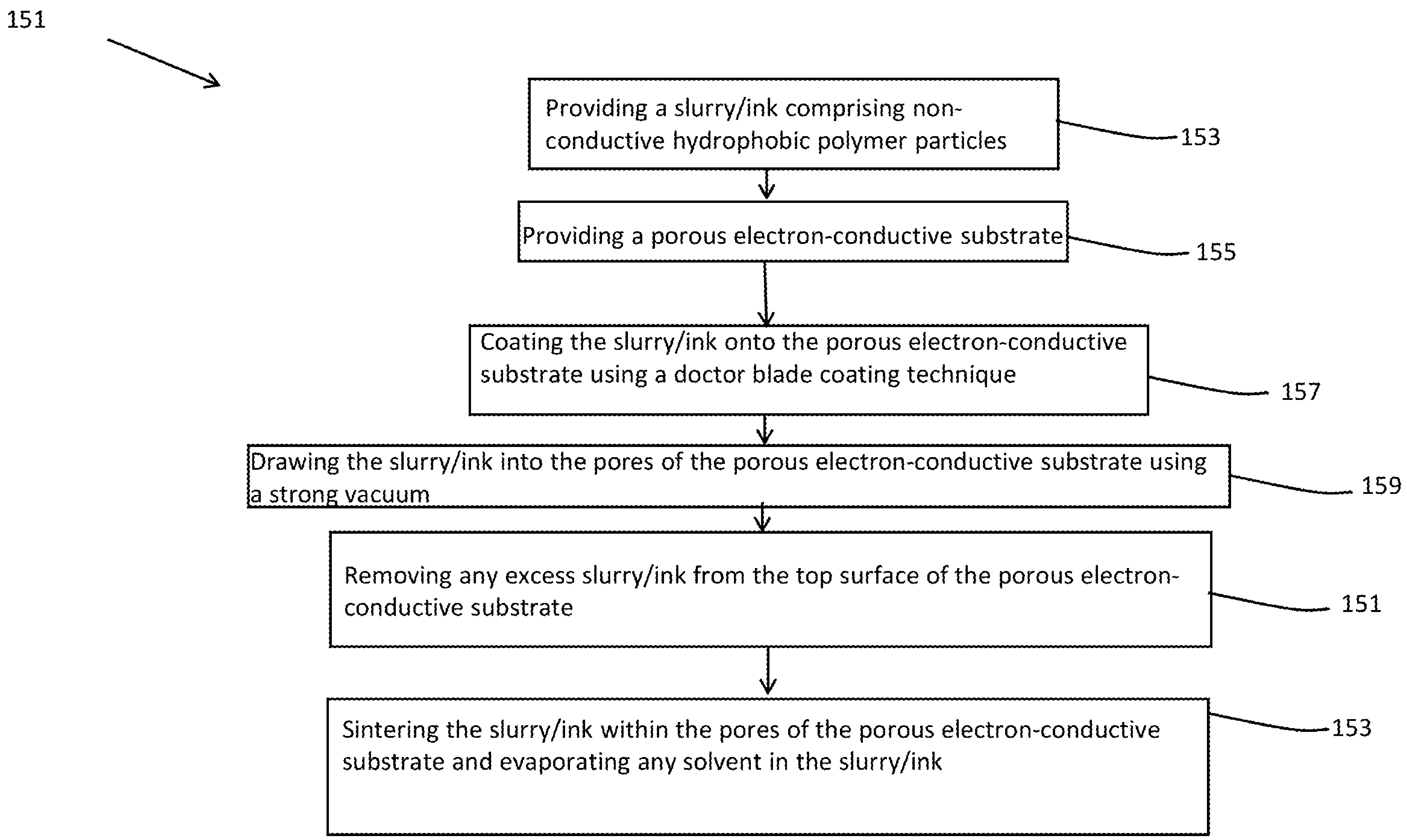

151
Providing a slurry/ink comprising non-conductive hydrophobic polymer particles
153
Providing a porous electron-conductive substrate
155
Coating the slurry/ink onto the porous electron-conductive substrate using a doctor blade coating technique
157
Drawing the slurry/ink into the pores of the porous electron-conductive substrate using a strong vacuum
159
Removing any excess slurry/ink from the top surface of the porous electron-conductive substrate
151
Sintering the slurry/ink within the pores of the porous electron-conductive substrate and evaporating any solvent in the slurry/ink
153

FIG. 9

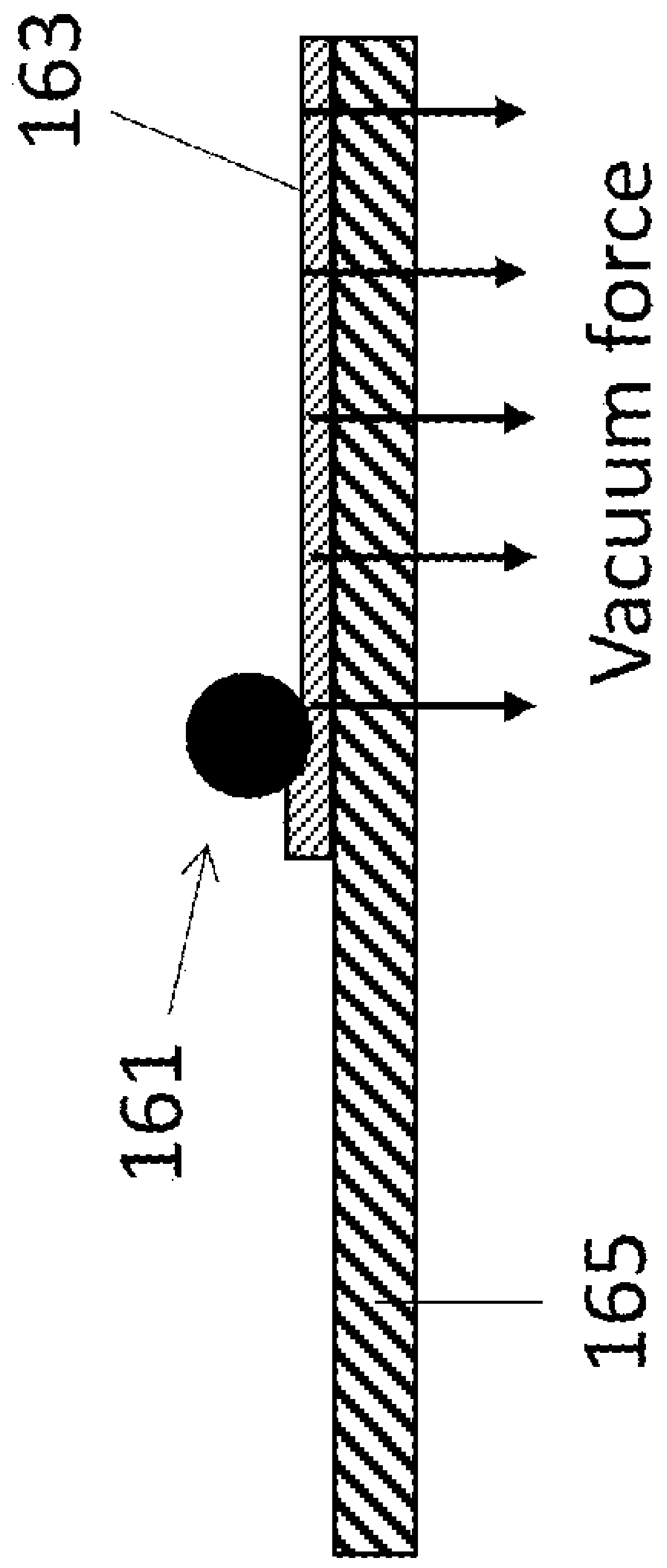


FIG. 10

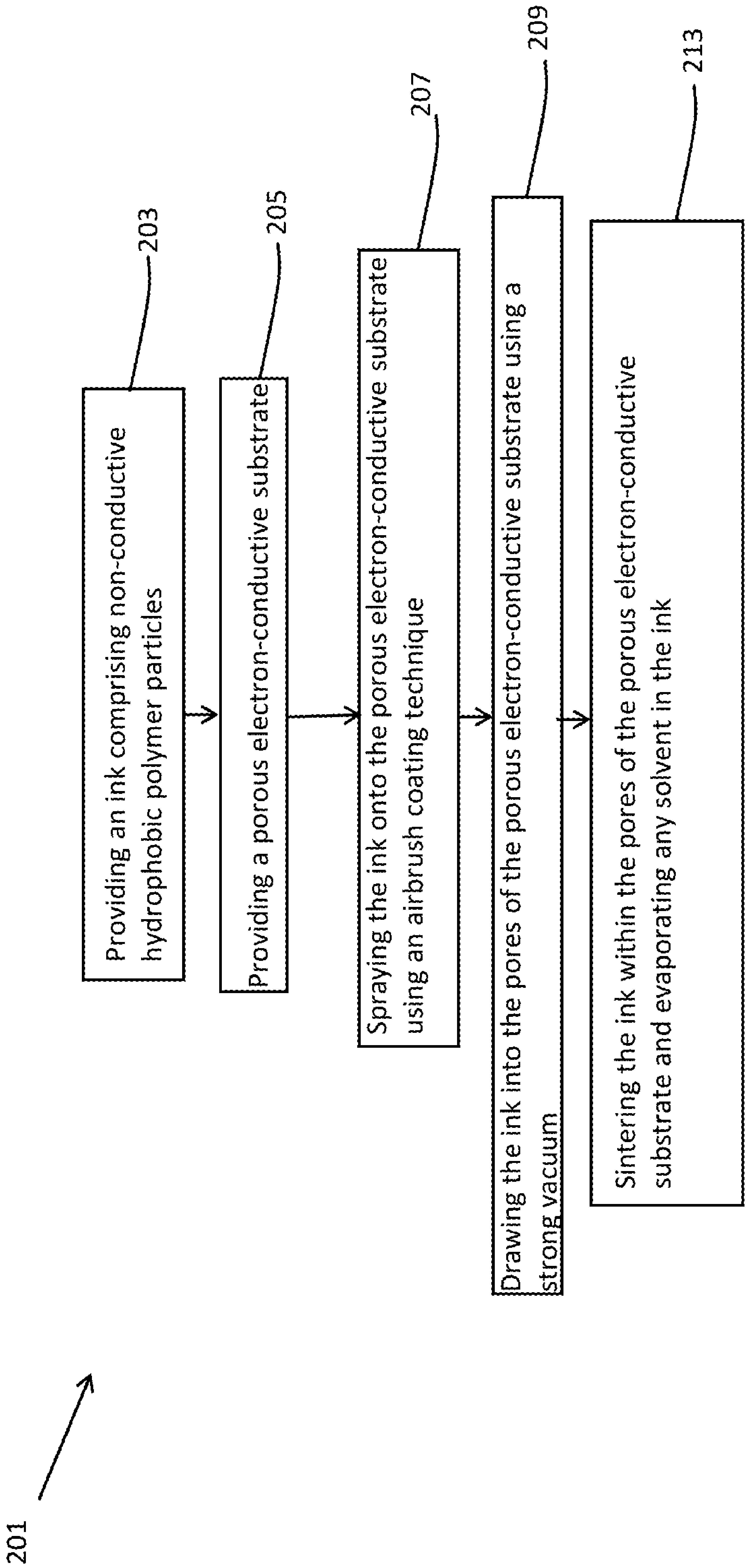

201
203
Providing an ink comprising non-conductive hydrophobic polymer particles
205
Providing a porous electron-conductive substrate
207
Spraying the ink onto the porous electron-conductive substrate using an airbrush coating technique
209
Drawing the ink into the pores of the porous electron-conductive substrate using a strong vacuum
213
Sintering the ink within the pores of the porous electron-conductive substrate and evaporating any solvent in the ink

FIG. 11

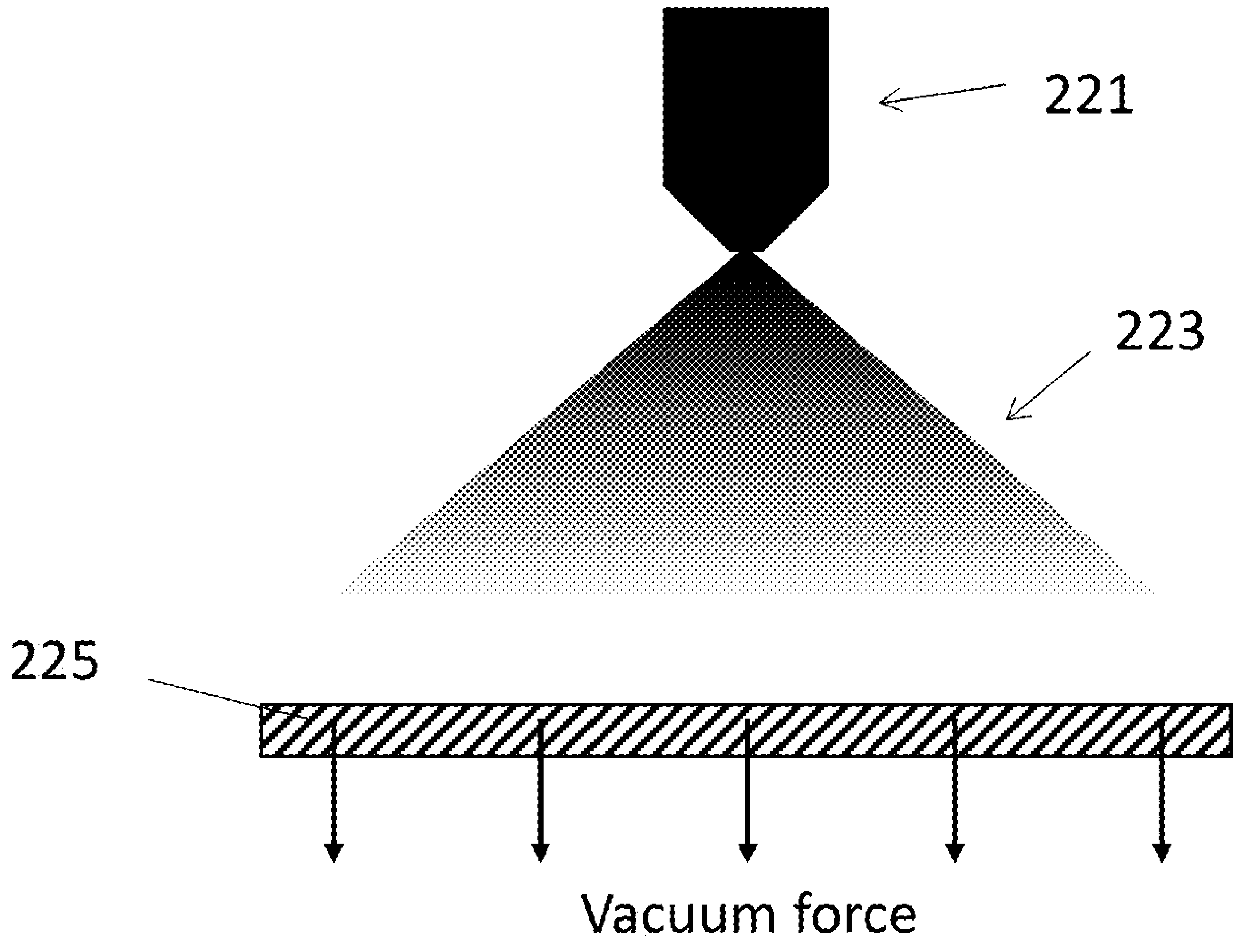


FIG. 12

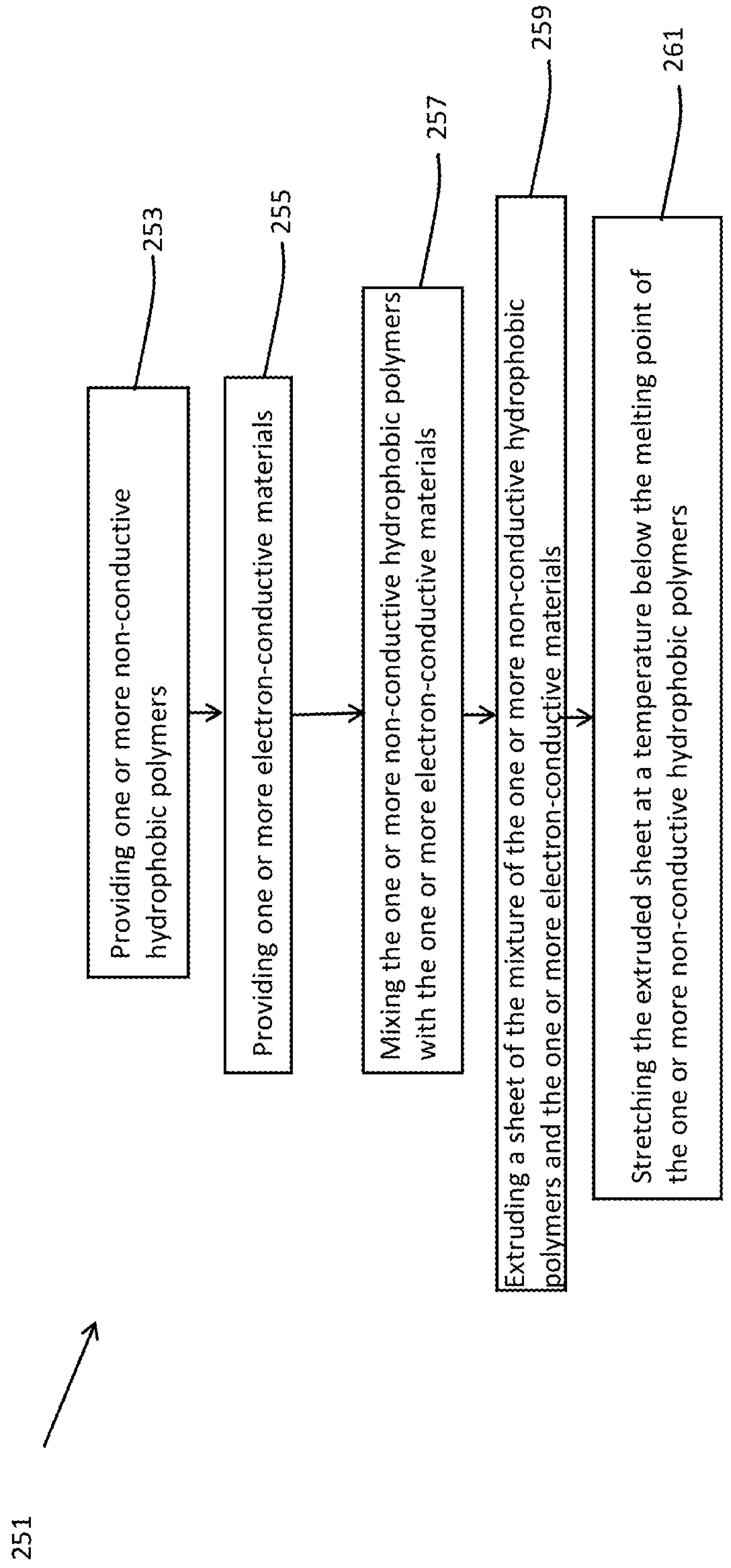

251
253
Providing one or more non-conductive hydrophobic polymers
255
Providing one or more electron-conductive materials
257
Mixing the one or more non-conductive hydrophobic polymers with the one or more electron-conductive materials
259
Extruding a sheet of the mixture of the one or more non-conductive hydrophobic polymers and the one or more electron-conductive materials
261
Stretching the extruded sheet at a temperature below the melting point of the one or more non-conductive hydrophobic polymers

FIG. 13

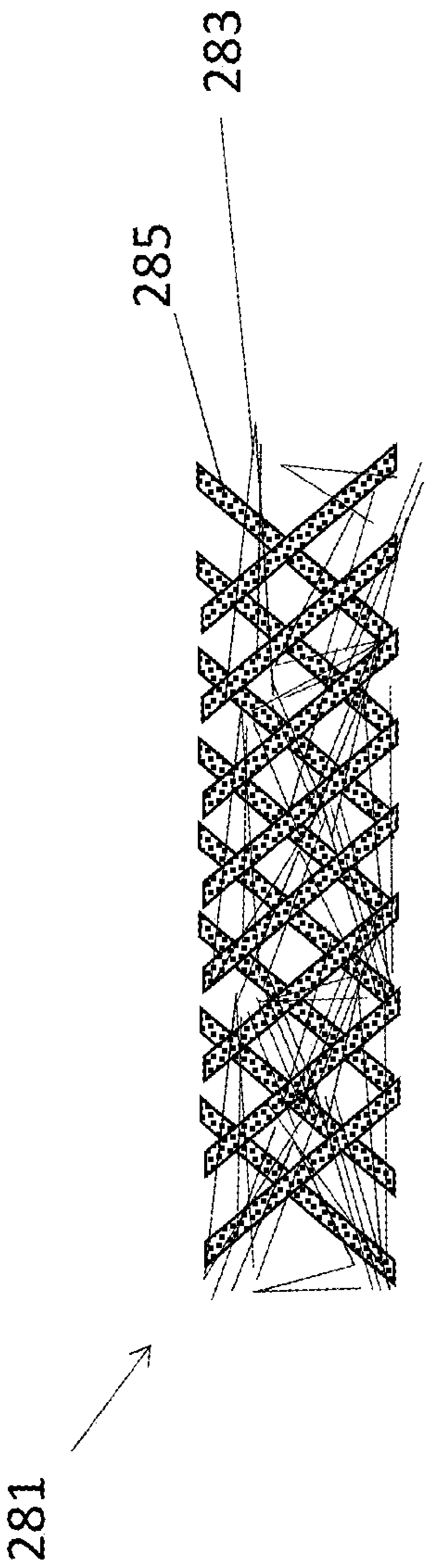


FIG. 14

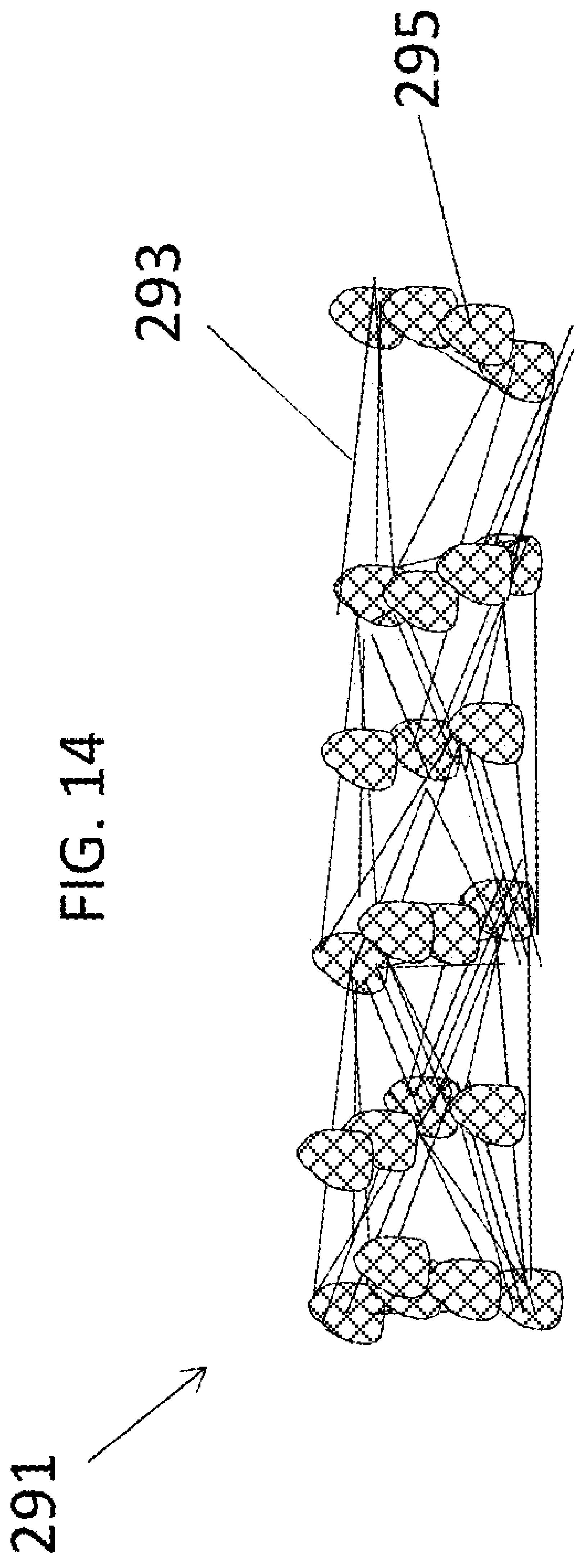


FIG. 15

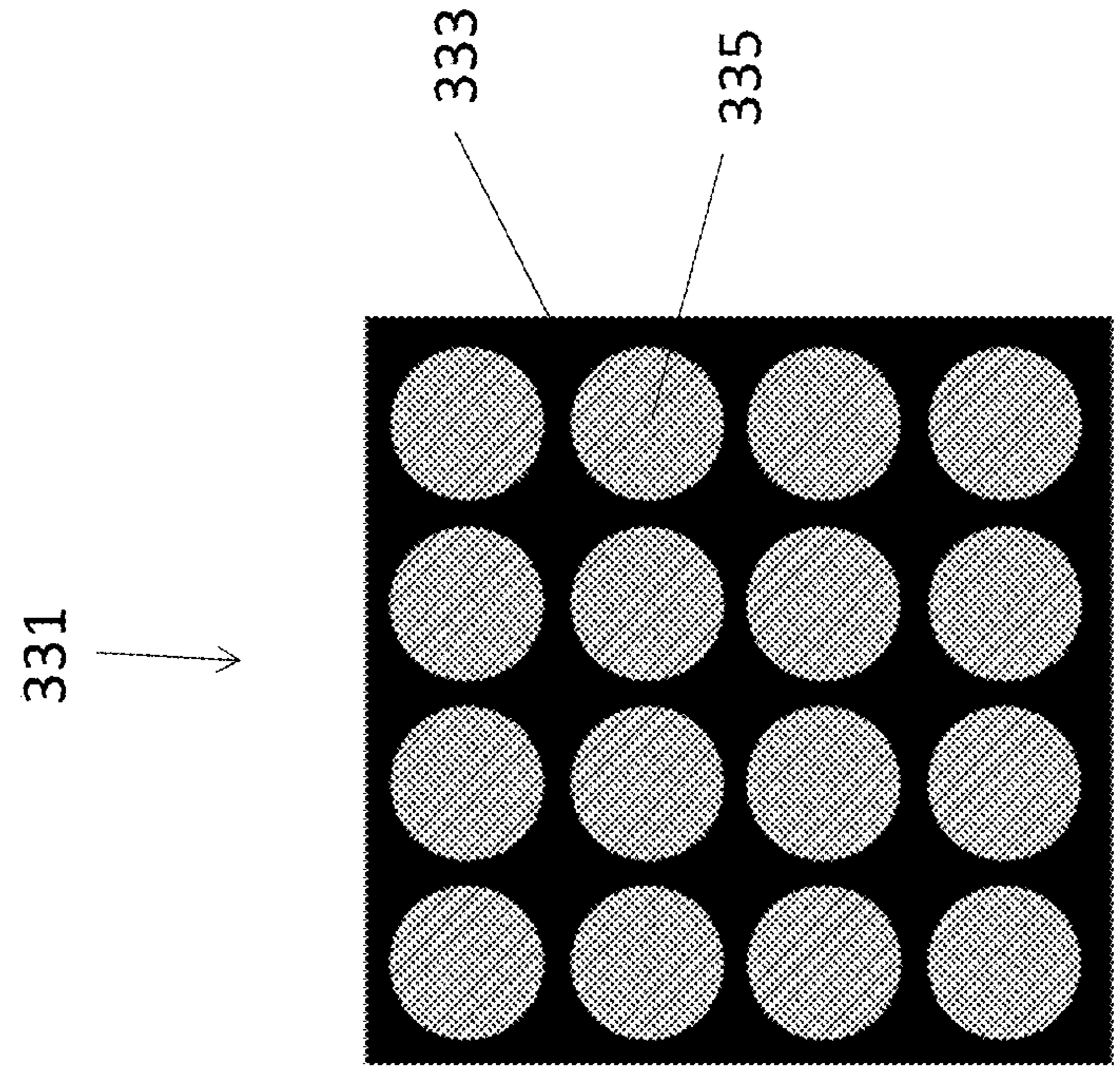


FIG. 17

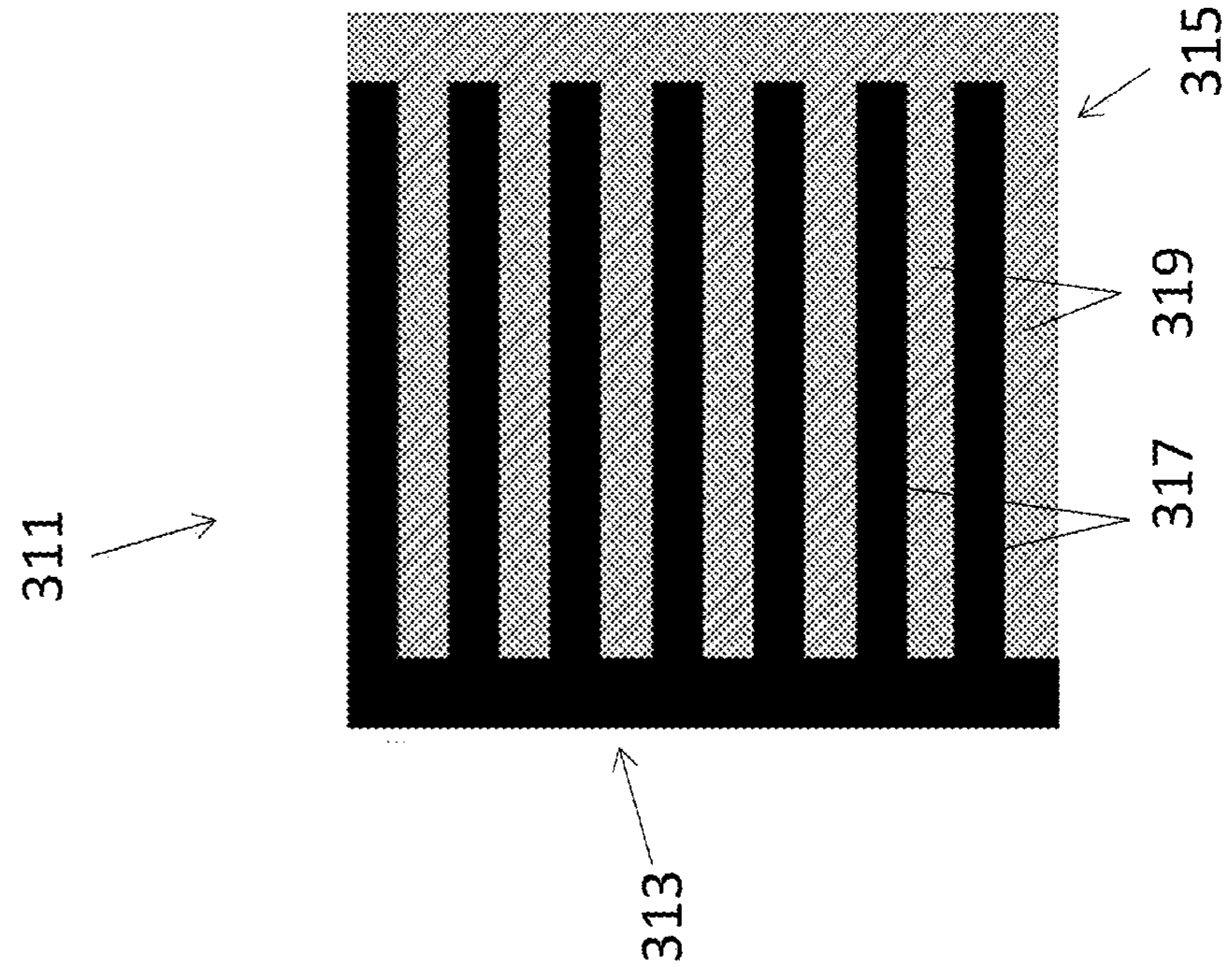


FIG. 16

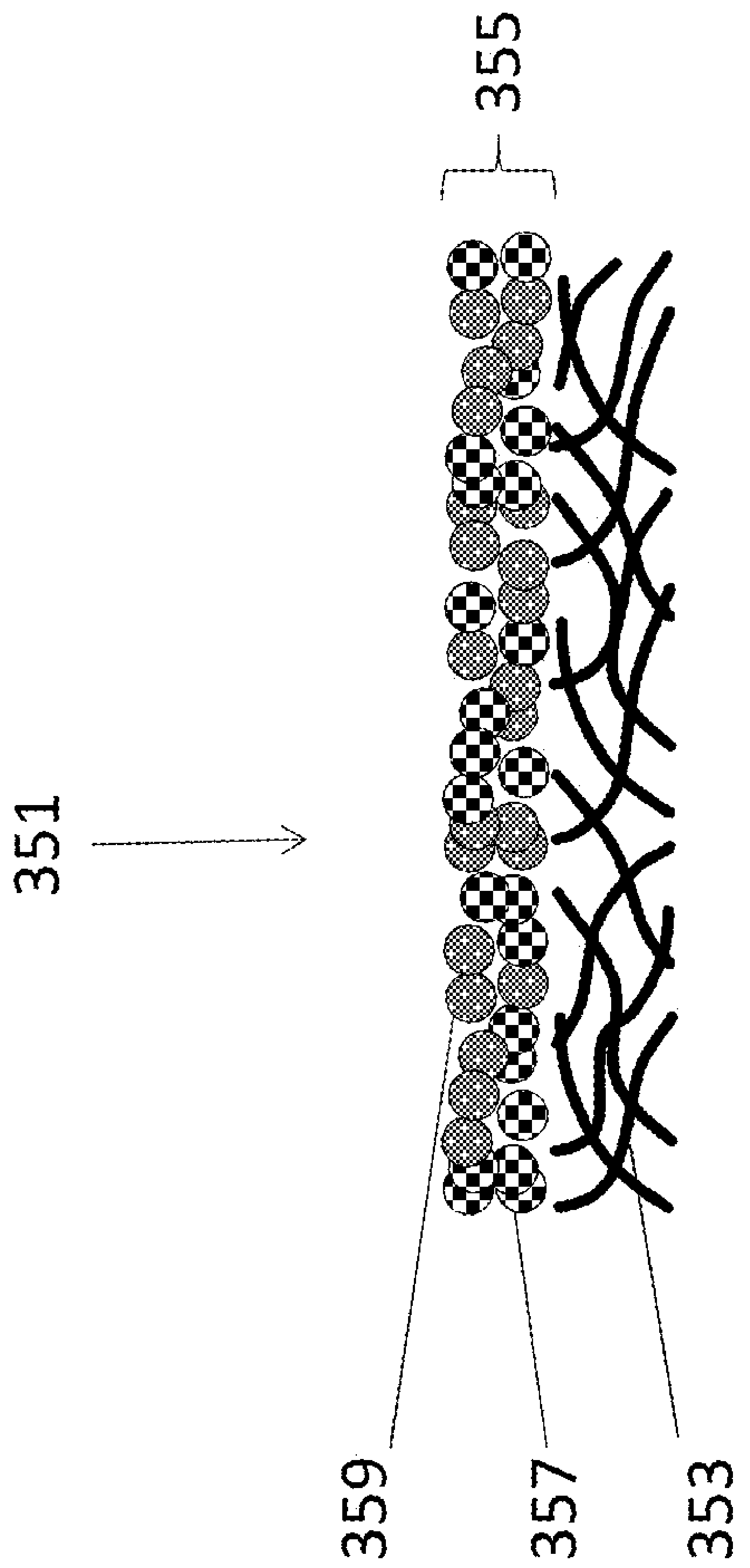


FIG. 18

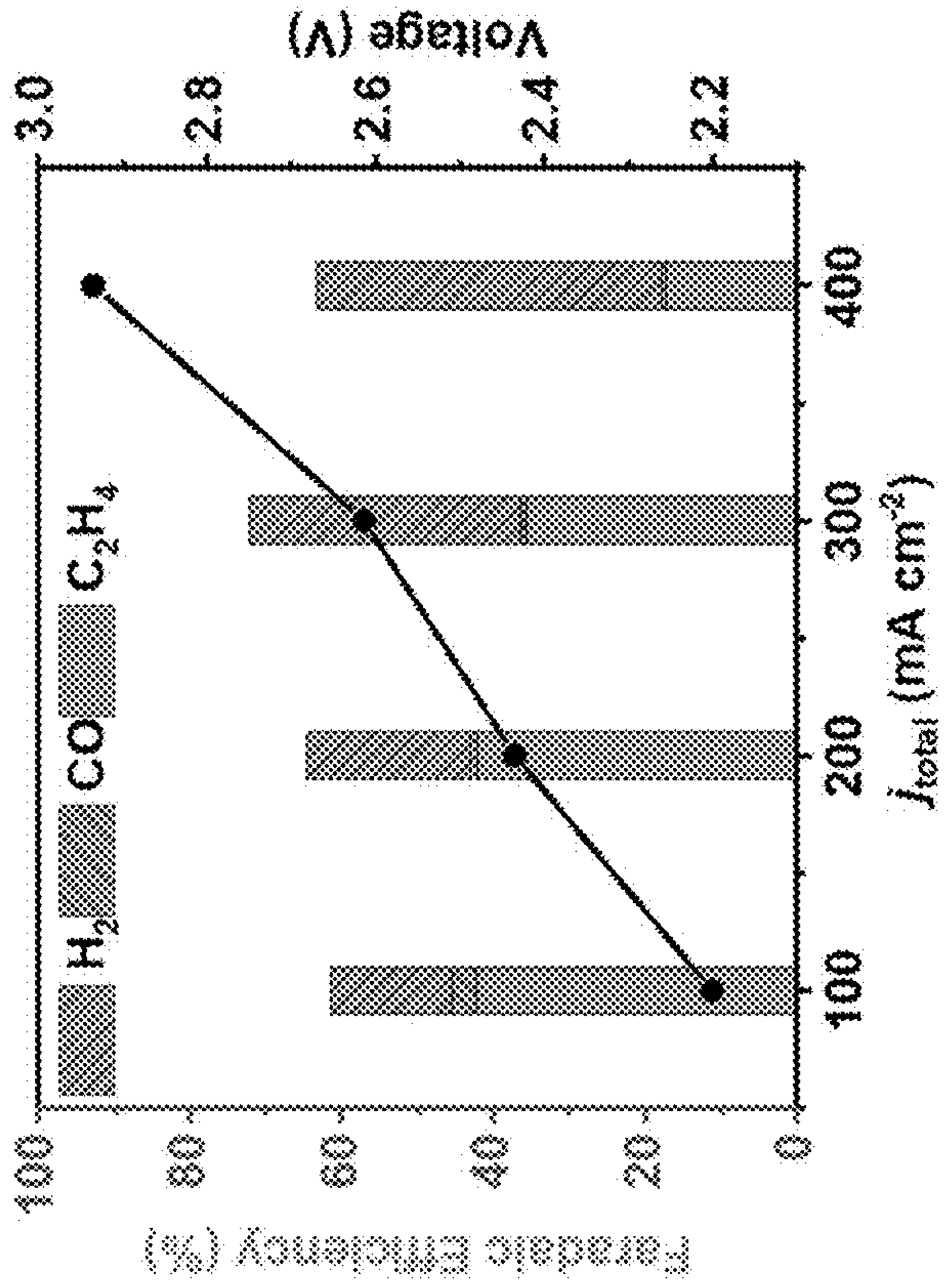

Faradaic Efficiency (%)
0
20
40
60
80
100
Voltage (V)
2.2
2.4
2.6
2.8
3.0
j_{total} (mA cm^{-2})
100
200
300
400
H$_2$
CO
C$_2$H$_4$

FIG. 19

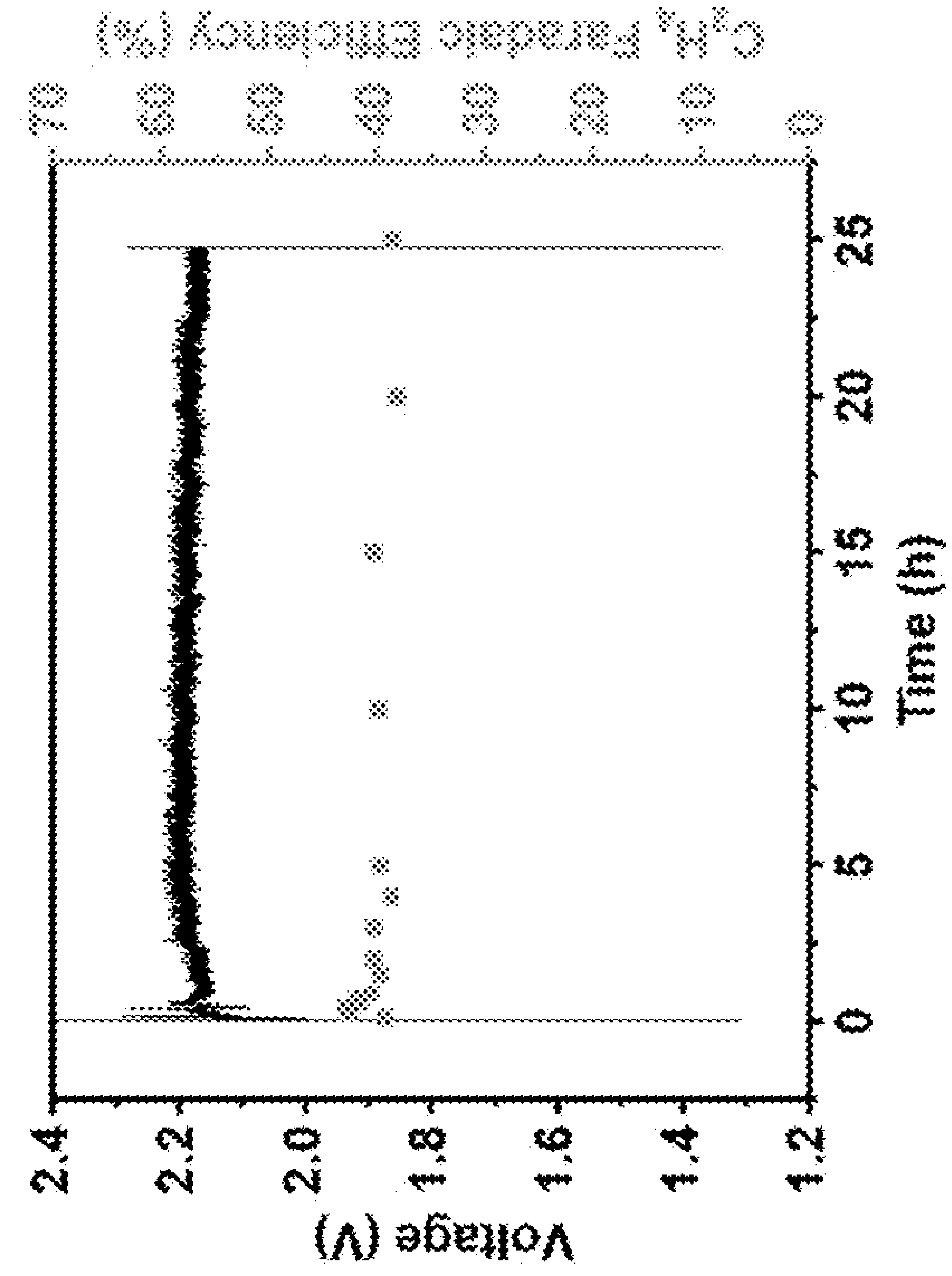

Voltage (V)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Time (h)
0
5
10
15
20
25
C$_2$H$_4$ Faradaic Efficiency (%)
0
10
20
30
40
50
60
70

FIG. 20

GAS DIFFUSION ELECTRODE SUITABLE FOR USE IN CARBON DIOXIDE ELECTROLYZER AND METHODS FOR MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. 119(e) of U.S. Provisional Patent Application No. 63/403,338, inventors Tianyu Zhang et al., filed Sep. 2, 2022, the disclosure of which is incorporated herein by reference.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under DE-EE0009421 awarded by the Department of Energy, Energy Efficiency and Renewable Energy (DOE EERE). The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] The present invention relates generally to electrochemical cells, such as electrolyzers and fuel cells, and relates more particularly to a novel gas diffusion electrode suitable for use in a carbon dioxide electrolyzer, to a membrane electrode assembly comprising said gas diffusion electrode, to a carbon dioxide electrolyzer comprising said membrane electrode assembly, and to methods for fabricating said gas diffusion electrode, said membrane electrode assembly, and said carbon dioxide electrolyzer.

[0004] The efficient electrochemical conversion of carbon dioxide into valuable carbon-based fuels and chemicals is desirable both for reducing carbon emissions and for storage of renewable electricity. In many instances, the electrochemical conversion of carbon dioxide into valuable products is accomplished using a carbon dioxide electrolyzer. Typically, such a carbon dioxide electrolyzer includes a membrane electrode assembly. The membrane electrode assembly, in turn, often includes an ion exchange membrane positioned between a cathode and an anode. In order to promote a reaction rate that is suitable for carbon dioxide conversion on an industrial scale, the cathode is typically in the form of a gas diffusion electrode. Such a gas diffusion electrode typically includes a catalyst layer and a gas diffusion layer. The catalyst layer functions as the reaction zone (i.e., where the electrochemical reduction of carbon dioxide actually occurs). By contrast, the gas diffusion layer, which may be, for example, a filamentary structure defining a plurality of pores, functions as the mass transport pathway for supplying carbon dioxide reactant to the catalyst layer. In many cases, the gas diffusion layer is made of a carbon material in order to provide high electron conductivity, which is necessary for the electrochemical reaction to proceed. However, because carbon materials typically tend to be hydrophilic, which, as discussed below, is undesirable, the surface of the carbon material making up the gas diffusion layer is commonly coated with a thin layer of a fluorinated material, for example, 5-30 wt % of one or more fluorinated polymers, such as polytetrafluoroethylene (PTFE), to increase the hydrophobicity and gas transport efficiency of the gas diffusion layer. Therefore, gas diffusion layers of the type described above operate by having electrons conducted through the solid carbon material of the gas diffusion layer and by having gas phase reactants and products transported through the pores defined by the hydrophobically-coated surface of the carbon material making up the gas diffusion layer.

[0005] Ideally, a membrane electrode assembly comprising a gas diffusion electrode is designed to minimize electrolyzer resistance and to increase energy efficiency. However, a membrane electrode assembly comprising a gas diffusion electrode as described above is susceptible to low carbon dioxide transport efficiency during long-term operation due to one or more of the following reasons: (1) carbon-based gas diffusion layers that are coated with a hydrophobic fluorinated polymer gradually lose hydrophobicity over time due to an erosion of the hydrophobic coating and, thus, become deficient in preventing flooding of the cathode catalyst layer with water; (2) the carbon material providing the structure of the gas diffusion layer tends to oxidize over time and, thus, to wear down; (3) water pressure at the cathode catalyst layer gradually builds up as water migrates from the anode side to the cathode side, eventually breaking the pores of the gas diffusion electrode; and (4) the hydrogen evolution reaction, which competes with the reduction of carbon dioxide at the cathode catalyst layer, turns some of the liquid water present at the cathode into hydrogen gas, resulting in a net fluid flux from the catalyst layer to the flow channels of the gas diffusion layer, thereby hindering the diffusion of carbon dioxide towards the catalyst layer. As can be appreciated, when flooding of the cathode with water occurs, the availability of carbon dioxide at the cathode decreases, thereby resulting in low carbon dioxide reduction selectivity.

[0006] One approach that has been taken to addressing the above-described gas transport efficiency problem has been to provide a gas diffusion electrode that comprises an ePTFE (expanded polytetrafluoroethylene) membrane, which is a porous hydrophobic structure. In such a gas diffusion electrode, a catalyst layer is loaded on top of the ePTFE membrane, followed by coating a layer of conductive carbon material for electron conduction. Consequently, as can be appreciated, a gas diffusion electrode comprising an ePTFE membrane of the above-described type decouples the gas transport and electron conduction functions since the carbon dioxide reactant diffuses through the ePTFE membrane whereas electrons are conducted through the conductive carbon material coating. Because, unlike conventional carbon-based gas diffusion membranes, the hydrophobicity of an ePTFE membrane does not wane over time, a gas diffusion electrode employing an ePTFE membrane intrinsically solves the hydrophobicity degradation problem of conventional gas diffusion electrodes. However, the problems of water pressure building up in the catalyst layer and of net gas flux from the cathode layer to the flow channel due to the hydrogen evolution reaction have not been solved. These problems can have a significant impact on the amount of carbon dioxide that reaches the cathode layer and, thus, can significantly limit the amount of carbon dioxide that is electrochemically converted.

[0007] Accordingly, there is a need for an alternative gas diffusion electrode that addresses the issue of flooding.

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a novel gas diffusion electrode that is suitable for use in a carbon dioxide electrolyzer.

[0009] It is another object of the present invention to provide a gas diffusion electrode as described above that overcomes at least some of the shortcomings associated with at least some existing gas diffusion electrodes.

[0010] It is still another object of the present invention to provide a gas diffusion electrode as described above that is easy to manufacture and easy to use.

[0011] Therefore, according to one aspect of the invention, there is provided a gas diffusion electrode suitable for use in a carbon dioxide electrolyzer, the gas diffusion electrode comprising (a) a gas diffusion layer, the gas diffusion layer comprising (i) an electron-conductive domain, the electron-conductive domain having a thickness and comprising a plurality of pores, and (ii) a non-conductive hydrophobic domain, the non-conductive hydrophobic domain having a thickness ranging from about 10% to about 100% of the thickness of the electron-conductive domain, the non-conductive hydrophobic domain randomly occupying a portion of the volume of the pores of the electron-conductive domain, the non-conductive hydrophobic domain being porous to permit gas transport through the gas diffusion layer; and (b) a catalyst layer, the catalyst layer being coupled to the gas diffusion layer.

[0012] In a more detailed feature of the invention, the non-conductive hydrophobic domain may comprise at least one of an ether polymer, an acrylic polymer, a fluorocarbon polymer, a polystyrene polymer, a poly(vinyl chloride) polymer, and a poly(N-vinylpyrrolidone) polymer.

[0013] In a more detailed feature of the invention, the non-conductive hydrophobic domain may comprise at least one of a fiber, a particle, a pellet, and a rod.

[0014] In a more detailed feature of the invention, the non-conductive hydrophobic domain may comprise a particle, and the particle may have a size ranging from about 1 nm to about 1 mm.

[0015] In a more detailed feature of the invention, the non-conductive hydrophobic domain may have a size ranging from about 5 nm to about 100 μm.

[0016] In a more detailed feature of the invention, the non-conductive hydrophobic domain may comprise at least one of a fiber and a rod, and the non-conductive hydrophobic domain may have a diameter ranging from about 1 nm to about 1 mm and a length ranging from nanometer to centimeter scale.

[0017] In a more detailed feature of the invention, the non-conductive hydrophobic domain may have a diameter ranging from about 5 nm to about 100 μm.

[0018] In a more detailed feature of the invention, the electron-conductive domain may comprise carbon, the non-conductive hydrophobic domain may have a mass, the electron-conductive domain may have a mass, and the mass of the non-conductive hydrophobic domain may range from about 30 wt % to about 600 wt % of the mass of the electron-conductive domain.

[0019] In a more detailed feature of the invention, the electron-conductive domain may comprise at least one of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0020] In a more detailed feature of the invention, the electron-conductive domain may comprise at least one of a paper, a foam, a felt, a sinter, a cloth, and a mesh.

[0021] In a more detailed feature of the invention, the electron-conductive domain may be coated with at least one hydrophobic polymer with a loading ranging from about 0.1 wt % to about 40 wt % of the electron-conductive domain.

[0022] In a more detailed feature of the invention, the electron-conductive domain may have a thickness ranging from about 0.5 μm to about 2 mm.

[0023] In a more detailed feature of the invention, the gas diffusion electrode may further comprise an interlayer, the interlayer may be disposed between and in direct contact with each of the gas diffusion layer and the catalyst layer, and the interlayer may be porous and electron-conductive.

[0024] In a more detailed feature of the invention, the interlayer may have a thickness ranging from about 5 nm to about 30 μm.

[0025] In a more detailed feature of the invention, the interlayer may comprise at least one of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0026] In a more detailed feature of the invention, the interlayer may be coated with one or more hydrophobic materials with a weight ratio of about 5 wt % to about 40 wt % of the interlayer.

[0027] In a more detailed feature of the invention, the interlayer may comprise a mixture of electron-conductive particles and hydrophobic polymer particles.

[0028] In a more detailed feature of the invention, the hydrophobic polymer particles may be present in the interlayer at a mass ratio ranging from about 5 wt % to about 200 wt % of the electron-conductive material particles.

[0029] In a more detailed feature of the invention, the catalyst layer may comprise at least one of copper, silver, gold, carbon, bismuth, iron, boron, nitrogen, oxygen, fluorine, aluminum, silicon, phosphorus, sulfur, chromium, manganese, cobalt, nickel, zinc, gallium, selenium, molybdenum, ruthenium, rhodium, palladium, iridium, and platinum.

[0030] In a more detailed feature of the invention, the non-conductive hydrophobic domain may comprise a porous hydrophobic particle.

[0031] In a more detailed feature of the invention, the porous hydrophobic particle may have a particle size of about 1 nm to about 1 mm.

[0032] In a more detailed feature of the invention, the porous hydrophobic particle may have at least one internal pore, with a pore diameter ranging from about 50 nm to about 5 μm.

[0033] In a more detailed feature of the invention, the porous hydrophobic particle may be made by cryo-milling a bulk quantity of a porous material into powder.

[0034] In a more detailed feature of the invention, the porous hydrophobic particle may comprise at least one of polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyvinyl chloride (PVC).

[0035] According to another aspect of the invention, there is provided a method of fabricating a gas diffusion electrode, the method comprising the steps of (a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises (i) providing a slurry, the slurry comprising at least one hydrophobic material and at least one organic solvent; (ii) providing an electron-conductive substrate, the electron-conductive substrate having a thickness and comprising a plurality of pores; (iii) loading the slurry into the pores of the electron-conductive substrate; and (iv) sintering the slurry, whereby the solvent evaporates, forming a non-conductive hydrophobic domain within the pores of the electron-conductive substrate, the non-conductive hydrophobic domain having a thickness ranging from about 50% to about 100% of the thickness of the electron-conductive domain, the non-conductive hydrophobic domain configured to permit gas transport through the electron-conductive substrate; and (b) positioning a catalyst layer over the gas diffusion layer.

[0036] In a more detailed feature of the invention, the loading step may comprise one of screen printing, doctor blade coating, slot-die coating, vacuum filtration coating, and airbrush coating.

[0037] In a more detailed feature of the invention, the slurry may further comprise at least one of water and one or more binders.

[0038] In a more detailed feature of the invention, the loading step may comprise airbrush coating, and the airbrush coating may be conducted at a pressure ranging from about 0.5 bar to about 15 bar.

[0039] In a more detailed feature of the invention, the pressure may range from about 2 bar to about 6 bar.

[0040] In a more detailed feature of the invention, the sintering step may be performed at a temperature no greater than the melting point of the at least one hydrophobic material.

[0041] In a more detailed feature of the invention, the temperature may be about 0° C. to about 50° C. below the melting point temperature of the at least one hydrophobic material.

[0042] In a more detailed feature of the invention, the sintering step may be performed at a pressure ranging from about 0 lb. to about 5000 lbs.

[0043] In a more detailed feature of the invention, the method may further comprise the step of positioning an interlayer directly between the catalyst layer and the electron-conductive substrate.

[0044] In a more detailed feature of the invention, the interlayer positioning step may comprise at least one of spraying, screen printing, doctor blade coating, vacuum filtration coating, compression coating, and slot-die coating.

[0045] According to yet another aspect of the invention, there is provided a gas diffusion electrode made by the above method.

[0046] According to still yet another aspect of the invention, there is provided a method of fabricating a gas diffusion electrode, the method comprising the steps of (a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises (i) providing at least one non-conductive hydrophobic polymer; (ii) providing at least one electron-conductive material; (iii) mixing the at least one non-conductive hydrophobic polymer and the at least one electron-conductive material to form a mixture; (iv) extruding the mixture to form a sheet; (v) stretching the sheet at a temperature below the melting point of the at least one non-conductive hydrophobic polymer to form pores for gas transport through the sheet; and (b) positioning a catalyst layer over the gas diffusion layer.

[0047] In a more detailed feature of the invention, the stretching may comprise at least one of uniaxial stretching and biaxial stretching of the sheet.

[0048] In a more detailed feature of the invention, a mass ratio of the at least one electron-conductive material to the at least one non-conductive hydrophobic polymer may range from about 15 wt % to about 300 wt %.

[0049] In a more detailed feature of the invention, the mass ratio may be from about 50 wt % to about 200 wt %.

[0050] In a more detailed feature of the invention, the at least one electron-conductive material may be one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0051] In a more detailed feature of the invention, the at least one electron-conductive material may be one or more of a fiber, a particle, a pellet, and a rod.

[0052] In a more detailed feature of the invention, the at least one electron-conductive material may have a particle size ranging from about 1 nm to about 1 mm.

[0053] In a more detailed feature of the invention, the at least one electron-conductive material may be at least one of a fiber and a rod, and the at least one electron-conductive material may have a diameter ranging from about 1 nm to about 1 mm and a length ranging from the nanometer scale to the centimeter scale.

[0054] In a more detailed feature of the invention, the temperature may be the melting point temperature of the at least one non-conductive hydrophobic polymer.

[0055] In a more detailed feature of the invention, the mixture may further comprise a lubricating agent and a pore former.

[0056] In a more detailed feature of the invention, the stretching may comprise stretching at a ratio ranging from about 2:1 to about 40:1.

[0057] According to a further aspect of the invention, there is provided a gas diffusion electrode made by the above method.

[0058] According to yet a further aspect of the invention, there is provided a method of fabricating a gas diffusion electrode, the method comprising the steps of (a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises (i) providing a first gas diffusion layer piece, the first gas diffusion layer piece being porous and electron-conductive; (ii) providing a second gas diffusion layer piece, the second gas diffusion layer piece being porous, non-conductive and hydrophobic, wherein the first gas diffusion layer piece and the second gas diffusion layer piece are complementarily shaped to mate with one another in the same plane; (iii) mating together the first gas diffusion layer piece and the second gas diffusion layer piece; and (b) positioning a catalyst layer over the gas diffusion layer.

[0059] In a more detailed feature of the invention, the first gas diffusion layer piece and the second gas diffusion layer piece may form an interdigitated construction.

[0060] In a more detailed feature of the invention, the first gas diffusion layer piece may comprise a transverse opening, and the second gas diffusion layer piece may be dimensioned to mate with the transverse opening.

[0061] In a more detailed feature of the invention, the gas diffusion layer may have a uniform distribution of one or more electron-conductive areas and one or more non-conductive, hydrophobic areas.

[0062] In a more detailed feature of the invention, each of the first gas diffusion layer piece and the second gas diffusion layer piece may have an area, and a ratio of the areas of the first and second gas diffusion layer pieces may range from about 1:2, respectively, to about 2:1, respectively.

[0063] In a more detailed feature of the invention, the first gas diffusion layer piece may comprise at least one of carbon paper, metal foam, metal mesh, and metal paper.

[0064] In a more detailed feature of the invention, the second gas diffusion layer piece may comprise at least one of a fluoropolymer film and a polyvinyl chloride film.

[0065] In a more detailed feature of the invention, the first and second gas diffusion layer pieces may have similar thicknesses.

[0066] According to still a further aspect of the invention, there is provided a gas diffusion electrode made by the above method.

[0067] According to still yet another aspect of the invention, there is provided a method for fabricating a gas diffusion electrode, the method comprising the steps of (a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises (i) providing a porous electron-conductive substrate, the porous electron-conductive substrate having an outer surface; (ii) preparing a slurry, the slurry comprising a random mixture of at least one electron-conductive material, at least one non-conductive hydrophobic polymer material, and at least one solvent; and (iii) coating the outer surface of the porous electron-conductive substrate with the slurry, which, upon drying, forms a porous coating on the outer surface of the porous electron-conductive substrate; and (b) positioning a catalyst layer over the porous coating of the gas diffusion layer.

[0068] In a more detailed feature of the invention, a volume ratio of the at least one electron-conductive material to the at least one non-conductive hydrophobic polymer material may range from about 9:1, respectively, to about 1:3, respectively.

[0069] In a more detailed feature of the invention, the porous coating may have a thickness ranging from about 1 μm to about 200 μm.

[0070] In a more detailed feature of the invention, the at least one electron-conductive material may have a particle size from about 10 nm to about 5 μm.

[0071] In a more detailed feature of the invention, the at least one non-conductive hydrophobic polymer material may have a particle size of from about 20 nm to about 200 μm.

[0072] In a more detailed feature of the invention, the coating step may comprise at least one of doctor blade coating, slot-die coating, bar-coating, and screen printing.

[0073] In a more detailed feature of the invention, the method may further comprise, prior to the coating step, pre-coating the electron-conductive substrate with at least one hydrophobic material to a weight percentage of about 0.1 wt % to about 40 wt %.

[0074] According to still yet a further aspect of the invention, there is provided a gas diffusion electrode made by the above method.

[0075] The present invention is also directed at novel methods for fabricating a gas diffusion layer, a membrane electrode assembly, and an electrochemical cell, such as an electrolyzer or fuel cell.

[0076] For purposes of the present specification and claims, various relational terms like “top,” “bottom,” “proximal,” “distal,” “upper,” “lower,” “front,” and “rear” may be used to describe the present invention when said invention is positioned in or viewed from a given orientation. It is to be understood that, by altering the orientation of the invention, certain relational terms may need to be adjusted accordingly.

[0077] Additional objects, as well as aspects, features, and advantages, of the present invention will be set forth in part in the description which follows, and in part will be obvious from the description or may be learned by practice of the invention. In the description, reference is made to the accompanying drawings which form a part thereof and in which is shown by way of illustration various embodiments for practicing the invention. The embodiments will be described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that structural changes may be made without departing from the scope of the invention. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is best defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0078] The accompanying drawings, which are hereby incorporated into and constitute a part of this specification, illustrate various embodiments of the invention and, together with the description, serve to explain the principles of the invention. The drawings are not necessarily drawing to scale, and certain components may have undersized and/or oversized dimensions for purposes of explication. In the drawings wherein like reference numeral represents like parts:

[0079] FIG. **1** is a simplified side view of a first embodiment of an electrochemical cell constructed according to the present invention;

[0080] FIG. **2** is a simplified section view of the membrane electrode assembly shown in FIG. **1**;

[0081] FIG. **3** is a simplified section view of the cathode shown in FIG. **2**;

[0082] FIG. **4** is a simplified schematic view of a first embodiment of a system constructed according to the present invention for converting carbon dioxide into products like ethylene, the system including the electrochemical cell of FIG. **1**;

[0083] FIG. **5** is a partly exploded simplified section view of a second embodiment of an electrochemical cell constructed according to the present invention;

[0084] FIG. **6** is a simplified section view of an alternative membrane electrode assembly to the membrane electrode assembly of FIG. **2**;

[0085] FIG. **7** is a flowchart depicting a first embodiment of a method according to the present invention for fabricating a gas diffusion layer of the type shown in FIG. **3**;

[0086] FIG. **8** is a schematic depiction of a gas diffusion layer being made by the slot-die technique of FIG. **7**;

[0087] FIG. **9** is a flowchart depicting a second embodiment of a method according to the present invention for fabricating a gas diffusion layer of the type shown in FIG. **3**;

[0088] FIG. **10** is a schematic depiction of a gas diffusion layer being made by the doctor blade technique of FIG. **9**;

[0089] FIG. **11** is a flowchart depicting a third embodiment of a method according to the present invention for fabricating a gas diffusion layer of the type shown in FIG. **3**;

[0090] FIG. **12** is a schematic depiction of a gas diffusion layer being made by the airbrush technique of FIG. **11**;

[0091] FIG. **13** is a flowchart depicting a fourth embodiment of a method according to the present invention for fabricating a gas diffusion layer of the type shown in FIG. **3**;

[0092] FIG. **14** is a schematic depiction of a gas diffusion layer made by the stretching technique of FIG. **13**;

[0093] FIG. **15** is a schematic depiction of an alternative gas diffusion layer made by the stretching technique of FIG. **13**;

[0094] FIG. **16** is a top view of a first alternative gas diffusion layer to the gas diffusion layer shown in FIG. **3**, the first alternative gas diffusion layer being constructed according to the present invention;

[0095] FIG. **17** is a top view of a second alternative gas diffusion layer to the gas diffusion layer shown in FIG. **3**, the second alternative gas diffusion layer being constructed according to the present invention;

[0096] FIG. **18** is a simplified section view of a third alternative gas diffusion layer to the gas diffusion layer shown in FIG. **3**, the third alternative gas diffusion layer being constructed according to the present invention;

[0097] FIG. **19** is a graph depicting the Faradaic efficiencies of carbon dioxide reduction products and corresponding cell voltages versus the applied total current densities for the test described in Example 1; and

[0098] FIG. **20** is a graph depicting the cell voltages and corresponding Faradaic efficiencies of carbon dioxide reduction products versus time for the test described in Example 2.

DETAILED DESCRIPTION OF THE INVENTION

[0099] As noted above, the presence of excess water at the cathode catalyst layer of a carbon dioxide electrolyzer can significantly limit the amount of carbon dioxide that reaches the cathode catalyst layer and, thus, can significantly reduce the amount of carbon dioxide that is reacted by the carbon dioxide electrolyzer. The present invention is directed, at least in part, at a novel gas diffusion electrode that may be suitable for ameliorating the foregoing problem. In particular, as will be discussed further below, the gas diffusion electrode of the present invention may comprise a novel gas diffusion layer and a catalyst layer coupled to the novel gas diffusion layer. More specifically, in at least one embodiment, the novel gas diffusion layer may comprise (i) an electron-conductive domain, the electron-conductive domain comprising a plurality of pores, and (ii) a non-conductive (i.e., electron non-conductive) hydrophobic domain, the non-conductive hydrophobic domain randomly (i.e., non-uniformly) occupying a portion of the volume of the pores of the electron-conductive domain, the non-conductive hydrophobic domain, itself, being porous to permit gas transport through the gas diffusion layer. Alternatively, in another embodiment, the novel gas diffusion layer may comprise an electron-conductive domain and a non-conductive hydrophobic domain, wherein each of the electron-conductive domain and the non-conductive hydrophobic domain is porous and wherein the electron-conductive domain and the non-conductive hydrophobic domain are complementarily shaped to collectively form a planar structure. Alternatively, in another embodiment, the novel gas diffusion layer may comprise (i) an electron-conductive domain, the electron-conductive domain comprising a pair of opposing surfaces and a plurality of pores designed for gas transport between the pair of opposing surfaces; and (ii) a porous layer positioned over one of the opposing surfaces of the electron-conductive domain, the porous layer comprising a random mixture of electron-conductive materials and non-conductive hydrophobic materials.

[0100] The present invention is also directed, at least in part, at a membrane electrode assembly that includes a gas diffusion electrode as described above and is further directed, at least in part, at an electrochemical cell, such as a fuel cell or electrolyzer (e.g., carbon dioxide electrolyzer), that includes such a membrane electrode assembly. Moreover, the present invention is additionally directed, at least in part, at methods for fabricating the gas diffusion layer of such a gas diffusion electrode, as well as to methods for fabricating the gas diffusion electrode, itself, to methods for fabricating a membrane electrode assembly comprising the aforementioned gas diffusion electrode, and to methods for fabricating an electrochemical cell, such as a fuel cell or electrolyzer, comprising the aforementioned membrane electrode assembly.

[0101] Referring now to FIG. **1**, there is shown a simplified side view of a first embodiment of an electrochemical cell constructed according to the present invention, the electrochemical cell being represented generally by reference numeral **11**. Details of electrochemical cell **11** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **1** and/or from the accompanying description herein or may be shown in FIG. **1** and/or described herein in a simplified manner.

[0102] Electrochemical cell **11** may be a fuel cell or electrolytic cell but is preferably a carbon dioxide electrolyzer designed, for example, to convert carbon dioxide into carbon-containing materials, such as, but not limited to, ethylene. Electrochemical cell **11** may comprise a membrane electrode assembly **13**, which is discussed in greater detail below. Electrochemical cell **11** may further comprise a first current collector **14**, a second current collector **16**, a first endplate **18**, a second endplate **20**, and a voltage source **22**, all of which may be conventional. First current collector **14** and second current collector **16** may be coupled to membrane electrode assembly **13** on opposite sides thereof. In addition, first current collector **14** and second current collector **16** may be electrically coupled to voltage source **22** through leads **24-1** and **24-2**, respectively. First endplate **18** may be positioned above and coupled to first current collector **14**, and second endplate **20** may be positioned below and coupled to second current collector **16**.

[0103] Although not shown, electrochemical cell **11** may further comprise various gaskets, frames, and gas transport structures of the type conventionally used in electrochemical cells, particularly carbon dioxide electrolyzers.

[0104] Where, for example, electrochemical cell **11** is a carbon dioxide electrolyzer, carbon dioxide may be delivered to the cathode side of membrane electrode assembly **13**, and a suitable reductant, such as a potassium hydroxide solution, may be delivered to the anode side of membrane electrode assembly **13**. As a result of electrolysis, the carbon dioxide supplied to electrochemical cell **11** may be reduced to ethylene or the like.

[0105] Referring now to FIG. **2**, there is shown a simplified section view of membrane electrode assembly **13**. Details of membrane electrode assembly **13** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG.

2 and/or from the accompanying description herein or may be shown in FIG. 2 and/or described herein in a simplified manner.

[0106] Membrane electrode assembly (MEA) **13**, which may be a zero-gap membrane electrode assembly, may comprise an ion exchange membrane **15**, an anode **17** positioned on one side of, and in direct contact with, ion exchange membrane **15**, and a cathode **19** positioned on the opposite side of, and in direct contact with, ion exchange membrane **15**. Ion exchange membrane **15**, which functions as a separator and ion conductor between anode **17** and cathode **19**, may be an ion exchange membrane of the type typically used in a carbon dioxide electrolyzer. More specifically, ion exchange membrane **15** may be, for example, a proton exchange membrane, an anion exchange membrane, or a bipolar membrane, with anion exchange membranes and bipolar membranes being preferred and with anion exchange membranes being particularly preferred.

[0107] Anode **17** may comprise an anode of the type conventionally used in a carbon dioxide electrolyzer or otherwise used to target an electrochemical oxidation reaction, such as the oxygen evolution reaction (OER). For example, the anode may be a piece of metal foam that is catalytically active for anode reactions, or the anode may be a piece of metal foam having a surface on which active catalysts are deposited, or the anode may be a gas diffusion electrode comprising a porous transport layer and a catalyst layer.

[0108] Referring now to FIG. **3**, cathode **19**, which may be a gas diffusion electrode, may comprise a gas diffusion layer **21** and a catalyst layer **23**. Gas diffusion layer **21**, in turn, may comprise an electron-conductive domain **25** and an electron non-conductive (i.e., non-conductive) hydrophobic domain **27**. Electron-conductive domain **25** may comprise any type of porous, electron-conductive structure and, thus, may be similar to a conventional or non-conventional electron-conductive gas diffusion layer. As such, examples of structures suitable for use as electron-conductive domain **25** may comprise, for example, an electron-conductive mesh, woven (e.g., cloth) or felt material, paper, or disc, a porous graphite film, a metal foam, a metal sinter, or combinations thereof. Materials suitable for use in making the above types of structures may include carbon and/or one or more metals including, but not limited to, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0109] Electron-conductive domain **25** may include a plurality of intrinsic pores or channels **26** suitable for gas transport therethrough. In the present embodiment, electron-conductive domain **25** may be a unitary member consisting of a single piece of material, such as a single sheet of carbon paper or a single piece of a metal mesh; however, it is to be understood that, alternatively, electron-conductive domain **25** could be made by joining together a plurality of separate pieces of material, for example, by lamination or otherwise, to form a coherent structure. Also, it is to be understood that, although, in the embodiment shown, electron-conductive domain **25** is shown as a network of filamentary structures, electron-conductive domain **25** need not be formed from filamentary structures.

[0110] Electron-conductive domain **25** may range in thickness from about 0.5 μm to about 2 mm, with a preferred thickness ranging from about 1 μm to about 200 μm.

[0111] Electron-conductive domain **25** may optionally be coated with one or more hydrophilic polymers, with a loading that may range from about 0.1 wt % to about 40 wt % of electron-conductive domain **25**, and preferably from about 5 wt % to about 30 wt % of electron-conductive domain **25**.

[0112] Non-conductive hydrophobic domain **27** may comprise one or more hydrophobic materials randomly occupying a portion of the volume of the pores **26** of electron-conductive domain **25**. Non-conductive hydrophobic domain **27** may, itself, be sufficiently porous to permit gas transport through gas diffusion layer **21**, by virtue of non-conductive hydrophobic domain **27** incompletely filling pores **26**, thereby leaving spaces **28** in pores **26**, and/or by virtue of non-conductive hydrophobic domain **27** being made of an inherently porous material. The porous and hydrophobic features of non-conductive hydrophobic domain **27** may allow for high gas permeability and may repel water by capillary action. Moreover, the comparatively large quantity of material used to form non-conductive hydrophobic domain **27**, as opposed to the amount of hydrophobic material conventionally used to provide a thin film on electron-conductive domain **25**, may help to ensure that gas diffusion layer **21** can function in the long term with a minimal decrease in hydrophobicity. In addition, the non-conductive feature of non-conductive hydrophobic domain **27** may counter the electro-wetting phenomenon encountered with conventional gas diffusion electrodes.

[0113] Materials suitable for use in forming non-conductive hydrophobic domain **27** may include, for example, one or more hydrophobic polymers, such as, but not limited to, one or more of ether polymers, acrylic polymers, fluorocarbon polymers, polystyrene polymers, poly(vinyl chloride) polymers, and poly(N-vinylpyrrolidone) (PVP) polymers. Such materials may take the physical form of, for example, one or more of a fiber, a particle, a pellet, a rod, and the like. When, for example, the hydrophobic material used to form non-conductive hydrophobic domain **27** is in the form of a particle, the particle size may range from about 1 nm to about 1 mm, with a preferred particle size ranging from about 5 nm to about 200 nm. On the other hand, when the hydrophobic material used to form non-conductive hydrophobic domain **27** is in the form of a fiber or a rod, the fiber or rod may have a diameter ranging from about 1 nm to about 1 mm, preferably from about 5 nm to about 30 μm, and may have a length ranging from the nanometer to centimeter scale.

[0114] Where, for example, electron-conductive domain **25** is made of carbon, the mass of the hydrophobic polymer making up non-conductive hydrophobic domain **27** versus the mass of electron-conductive domain **25** may range from about 30 wt % to about 600 wt %, with a preferred range being from about 200 wt % to about 400 wt %.

[0115] Non-conductive hydrophobic domain **27** may have a thickness that is equal to or less than that of electron-conductive domain **25**, with the thickness of non-conductive hydrophobic domain **27** ranging from about 5% to about 100% of that of electron-conductive domain **25**, preferably about 10% to about 100% of that of electron-conductive domain **25**, and more preferably about 50% to about 100% of that of electron-conductive domain **25**. In this manner, by having the thickness of electron-conductive domain **25** be at least as great as the thickness of non-conductive hydrophobic domain **27**, one may ensure that gas diffusion layer **21** may conduct electrons across its entire thickness

[0116] It is to be understood that, although, in the embodiment shown in FIG. **3**, the hydrophobic material used to form non-conductive hydrophobic domain **27** is randomly positioned within pores **26** of electron-conductive domain **25** and is not additionally used to uniformly coat the filamentary structures of electron-conductive domain **25**, one could position hydrophobic material within pores **26** of electron-conductive domain **25** and could additionally uniformly coat the filamentary structures of electron-conductive domain **25** with a thin film of hydrophobic material. For example, electron-conductive domain **25** may be coated with one or more hydrophobic polymers, with a loading ranging from about 0.1 wt % to about 40 wt %, preferably from about 5 wt % to about 30 wt %.

[0117] After the hydrophobic material used to form non-conductive hydrophobic domain **27** is loaded into pores **26** of electron-conductive domain **25**, the hydrophobic polymer may be sintered. The sinter temperature may be around the melting point of the hydrophobic polymer, preferably about 0° C. to about 50° C. below the melting point of the hydrophobic polymer, more preferably about 10° C. to about 30° C. below the melting point of the hydrophobic polymer. The sinter pressure applied may range from about 0 lb. to about 5000 lbs.

[0118] Cathode **19** may further comprise an interlayer **29**, which may be one or more layers positioned between gas diffusion layer **21** and catalyst layer **23** and which may serve to increase the electron-conductivity of cathode **19**. Interlayer **29** may comprise one or more electron-conductive materials including, but not limited to, carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass. Interlayer **29** may additionally comprise one or more hydrophobic materials, preferably one or more hydrophobic polymer materials of the types described above. In one embodiment, interlayer **29** may comprise a first layer of electron-conductive materials coated with a second layer of hydrophobic materials, with the hydrophobic materials constituting about 5 wt % to about 40 wt %, preferably about 5 wt % to about 30 wt % of the electron-conductive materials. In another embodiment, interlayer **29** may comprise a single layer that may be a mixture of electron-conductive material particles and hydrophobic polymer particles, and the mass ratio of hydrophobic polymer particles to electron-conductive material particles may range from about 5 wt % to about 200 wt %.

[0119] Interlayer **29**, which may be formed by one or more deposition techniques including spraying, screen printing, doctor blade coating, vacuum filtration coating, compression coating, and slot-die coating, may have a thickness that may range from about 5 nm to about 30 μm, preferably from about 5 nm to about 100 nm.

[0120] Catalyst layer **23**, which may be conventional in composition and structure and which may be formed using conventional techniques, may be deposited or otherwise positioned directly over interlayer **29**. For example, catalyst layer **23** may be a layer of catalyst particles coated on top of interlayer **29** to a thickness ranging from 100 nm to 10 μm. Alternatively, catalyst layer **23** may comprise, for example, catalyst particles loaded onto a substrate layer, which are then coated together onto interlayer **29**. The catalyst layer may comprise one or more of copper, silver, gold, carbon, bismuth, iron, boron, nitrogen, oxygen, fluorine, aluminum, silicon, phosphorus, sulfur, chromium, manganese, cobalt, nickel, zinc, gallium, selenium, molybdenum, ruthenium, rhodium, palladium, iridium, and platinum.

[0121] It is to be understood that interlayer **29** could be omitted (depending, for example, on the electron conductivity of electron-conductive domain **25**) and that, in such a case, catalyst layer **23** could be positioned directly on top of gas diffusion layer **21**.

[0122] Referring now to FIG. **4**, there is schematically shown one embodiment of a system for converting carbon dioxide into products like ethylene, the system being constructed according to the present invention and being represented generally by reference numeral **31**. Details of system **31** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **4** and/or from the accompanying description herein or may be shown in FIG. **4** and/or described herein in a simplified manner.

[0123] System **31** may comprise electrochemical cell **11**. As can be seen, water and a dry or humidified stream of carbon dioxide may be delivered to the cathode of electrochemical cell **11**, and a suitable reductant, such as a potassium hydroxide solution, may be delivered to the anode of electrochemical cell **11**. The resulting products may then flow from electrochemical cell **11** to a condenser **33** for separation or purification of the products.

[0124] Referring now to FIG. **5**, there is shown a partly exploded simplified section view of a second embodiment of an electrochemical cell constructed according to the present invention, the electrochemical cell being represented generally by reference numeral **41**. Details of electrochemical cell **41** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **5** and/or from the accompanying description herein or may be shown in FIG. **5** and/or described herein in a simplified manner.

[0125] Electrochemical cell **41** may be a fuel cell or electrolytic cell but is preferably a carbon dioxide electrolyzer designed, for example, to convert carbon dioxide into carbon-containing materials, such as, but not limited to, ethylene. Electrochemical cell **41** may be similar in many respects to electrochemical cell **11** and may comprise a membrane electrode assembly **43**, which may be similar or identical to membrane electrode assembly **13**. To this end membrane electrode assembly **43** may comprise an ion exchange membrane **45**, which may be similar or identical to ion exchange membrane **15**, an anode **47**, which may be similar or identical to anode **17**, and a cathode **49**, which may be similar or identical to cathode **19**.

[0126] Electrochemical cell **41** may further comprise a first current collector **44**, which may be similar or identical to first current collector **14**, and a second current collector **46**, which may be similar or identical to second current collector **16**. First current collector **44** and second current collector **46** may be electrically coupled to a voltage source (not shown). In addition, electrochemical cell **41** may further comprise a first endplate **48**, which may be similar or identical to first endplate **18**, and a second endplate **50**, which may be similar or identical to second endplate **20**. First endplate **48** may be positioned directly above and coupled to first current collector **44**, and second endplate **50** may be positioned directly below and coupled to second current collector **46**.

[0127] Electrochemical cell **41** may further comprise a first bipolar plate **52** and a second bipolar plate **54**, both of which may be conventional. First bipolar plate **52** may be positioned between, and in direct contact with each of, first current collector **44** and anode **47** of membrane electrode assembly **43**. Second bipolar plate **54** may be positioned between, and in direct contact with each of, second current collector **46** and cathode **49** of membrane electrode assembly **43**.

[0128] Electrochemical cell **41** may further comprise a first gasket **56** and a second gasket **58**, both of which may be conventional. First gasket **56** may be positioned on the anode side of membrane electrode assembly **43**, and second gasket **58** may be positioned on the cathode side of membrane electrode assembly **43**.

[0129] Electrochemical cell **41** may be used in a fashion analogous to that for electrochemical cell **11**.

[0130] Referring now to FIG. **6**, there is shown a simplified section view of an alternative membrane electrode assembly to membrane electrode assembly **13**, the alternative membrane electrode assembly being constructed according to the present invention and being represented generally by reference numeral **71**. Details of membrane electrode assembly **71** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **6** and/or from the accompanying description herein or may be shown in FIG. **6** and/or described herein in a simplified manner.

[0131] Membrane electrode assembly **71** may be similar in certain respects to membrane electrode assembly **13**. To this end, membrane electrode assembly **71** may comprise an ion exchange membrane **75**, which may be similar or identical to ion exchange membrane **15**, an anode **77**, which may be similar or identical to anode **17**, and a cathode **79**, which may be similar or identical to cathode **19**.

[0132] On the other hand, whereas membrane electrode assembly **13** is designed for use in a zero-gap electrolyzer, membrane electrode assembly **71** is designed for use in a flow electrolyzer. Accordingly, membrane electrode assembly **71** may further comprise an anode buffer layer **81** and a cathode buffer layer **83**, each of which may be used to flow electrolyte therethrough. Anode buffer layer **81**, which may be conventional, may be positioned between and in direct contact with each of ion exchange membrane **75** and anode **77**, and cathode buffer layer **83**, which may be conventional, may be positioned between and in direct contact with each of ion exchange membrane **75** and cathode **79**.

[0133] Gas diffusion layer **21**, which may be used in the construction of cathode **19**, cathode **49**, and cathode **79**, may be made by a number of different techniques. Some of these techniques are discussed below.

[0134] For example, referring now to FIG. **7**, there is shown a flowchart depicting a first embodiment of a method according to the present invention for fabricating a gas diffusion layer like gas diffusion layer **21**, the method being represented generally by reference numeral **101**. Details of method **101** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **7** and/or from the accompanying description herein or may be shown in FIG. **7** and/or described herein in a simplified manner.

[0135] Method **101** may comprise a step **103** of providing a slurry or ink comprising non-conductive hydrophobic polymer particles. Such a slurry/ink may comprise one or more types of non-conductive hydrophobic polymer particles dispersed in an organic solvent. Examples of non-conductive hydrophobic polymers that can be used for such particles may include ether polymers, acrylic polymers, fluorocarbon polymers, polystyrene polymers, poly(vinyl chloride) polymers, and poly(N-vinylpyrrolidone) (PVP) polymers. The particle size may range from about 1 nm to about 1 mm. If the non-conductive hydrophobic polymer is in fiber or rod form, the diameter of the fiber or rod may range from about 1 nm to about 1 mm whereas the length may range from the nanometer to centimeter scale. Where the polymer particle size is beyond 10 um, the particle, itself, may include internal pores. A pore former and lubricant agent may be applied.

[0136] Method **101** may further comprise a step **105** of providing a porous electron-conductive substrate. (It is to be understood that, although step **105** is shown in the present embodiment as occurring after step **103**, step **105** may occur before step **103** or concurrently with step **103**.) The porous electron-conductive substrate may comprise a material, such as, but not limited to, carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass. The porous electron-conductive substrate may be in the form of a structure, such as, but not limited to, paper, foam, felt, sinter, cloth, and mesh. The thickness of the porous electron-conductive substrate may range from about 0.5 μm to about 2 mm and may be, for example, 1 μm, 90 μm, 200 μm, 300 μm, and 1 mm. A hydrophobic treatment may be applied to the surface of the porous electron-conductive substrate to increase the water breakthrough pressure. In addition to, or independently of, the foregoing, a hydrophilic treatment may be applied to some area of the porous electron-conductive substrate to facilitate water flow along the substrate material.

[0137] Method **101** may further comprise a step **107** of coating the slurry/ink onto the porous electron-conductive substrate using a slot-die method.

[0138] Method **101** may further comprise a step **109** of drawing the slurry/ink into the pores of the porous electron-conductive substrate using a strong vacuum. (A vacuum filtration method may alternatively be used to draw the slurry/ink into the pores of the porous electron-conductive substrate when preparing the gas diffusion layer on a small scale.)

[0139] Method **101** may further comprise a step **111** of removing any excess slurry/ink from the top surface of the porous electron-conductive substrate. The thickness of the porous hydrophobic polymer domain formed by the slurry/ink may range from 5 to 100% of the thickness of the porous electron-conductive substrate. The mass of the hydrophobic polymer versus the mass of the porous electron-conductive substrate may range from about 30 wt % to about 600 wt %.

[0140] Method **101** may further comprise a step **113** of sintering the slurry/ink within the porous electron-conductive substrate and evaporating the solvent in the slurry/ink, whereby spaces are left in the pores of the electron-conductive substrate for gas transport. The sintering temperature is preferably about 0° C. to about 50° C. below the melting point of the hydrophobic polymer, more preferably about 10° C. to about 30° C. below the melting point of the hydrophobic polymer. A pressure of about 0 to about 5000 lbs. may be applied.

[0141] Referring now to FIG. **8**, there is schematically shown a gas diffusion layer being made according to method

101. More specifically, slot die **121** can be seen depositing a layer **123** of slurry/ink on top of porous electron-conductive substrate **125**, and a vacuum force is being used to draw layer **123** into the pores (not shown) of porous electron-conductive substrate **125**.

[0142] Referring now to FIG. **9**, there is shown a flowchart depicting a second embodiment of a method according to the present invention for fabricating a gas diffusion layer like gas diffusion layer **21**, the method being represented generally by reference numeral **151**. Details of method **151** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **9** and/or from the accompanying description herein or may be shown in FIG. **9** and/or described herein in a simplified manner.

[0143] Method **151** may be similar in many respects to method **101** and, in this regard, may comprise a step **153**, which may be similar or identical to step **103** of method **101**, a step **155**, which may be similar or identical to step **105** of method **101**, a step **159**, which may be similar or identical to step **109** of method **101**, a step **161**, which may be similar or identical to step **111** of method **101**, and a step **163**, which may be similar or identical to step **113** of method **101**. By contrast, method **151** may differ from method **101** in that method **151** may comprise, instead of step **107** of method **101**, a step **157** in which the slurry/ink may be coated onto the porous electron-conductive substrate using a doctor blade coating technique, instead of slot-die coating technique.

[0144] Referring now to FIG. **10**, there is schematically shown a gas diffusion layer being made according to method **151**. More specifically, doctor blade **161** can be seen being used to coat a layer **163** of slurry/ink on top of porous electron-conductive substrate **165**, and a vacuum force is being used to draw layer **163** into the pores (not shown) of porous electron-conductive substrate **165**.

[0145] It is to be understood that techniques similar to slot-die coating and doctor-blade coating, such as, but not limited to, screen printing, may alternatively be used to impregnate the pores of a porous electron-conductive substrate with a slurry of a non-conductive polymer.

[0146] Referring now to FIG. **11**, there is shown a flowchart depicting a third embodiment of a method according to the present invention for fabricating a gas diffusion layer like gas diffusion layer **21**, the method being represented generally by reference numeral **201**. Details of method **201** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **11** and/or from the accompanying description herein or may be shown in FIG. **11** and/or described herein in a simplified manner.

[0147] Method **201** may comprise a step **203** of providing an ink comprising non-conductive hydrophobic polymer particles. Such an ink may comprise one or more types of non-conductive hydrophobic polymer particles in a suitable solvent. Examples of non-conductive hydrophobic polymers that can be used for such particles may include ether polymers, acrylic polymers, fluorocarbon polymers, polystyrene polymers, poly(vinyl chloride) polymers, and poly (N-vinylpyrrolidone) (PVP) polymers. The particle size may range from about 1 nm to about 1 mm. If the non-conductive hydrophobic polymer is in fiber or rod form, the diameter of the fiber or rod may range from about 1 nm to about 1 mm whereas the length may range from the nanometer to centimeter scale. One or more binders may also be included in the ink.

[0148] Method **201** may further comprise a step **205** of providing a porous electron-conductive substrate. (It is to be understood that, although step **205** is shown in the present embodiment as occurring after step **203**, step **205** may occur before step **203** or concurrently with step **203**.) The porous electron-conductive substrate may comprise a material, such as, but not limited to, carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass. The porous electron-conductive substrate may be in the form of a structure, such as, but not limited to, paper, foam, felt, sinter, cloth, and mesh. The thickness of the porous electron-conductive substrate may range from about 0.5 μm to about 2 mm and may be, for example, 1 μm, 90 μm, 200 μm, 300 μm, and 1 mm. A hydrophobic treatment may be applied to the surface of the porous electron-conductive substrate to increase the water breakthrough pressure. In addition to, or independently of, the foregoing, a hydrophilic treatment may be applied to some area of the porous electron-conductive substrate to facilitate water flow along the substrate material.

[0149] Method **201** may further comprise a step **207** of spraying the ink into the pores of the porous electron-conductive substrate using an airbrush printing method. Strong gas pressure may be used for the aforementioned airbrush printing method. Such gas pressure may range from about 0.5 bar to about 15 bar, depending on the strength of the porous electron-conductive substrate, and, in some instances, may range from about 2 bar to about 6 bar. In addition, a vacuum may also be applied in a step **209**. The mass of the hydrophobic polymer applied versus the mass of the porous electron-conductive substrate may range from about 50 wt % to about 600 wt %.

[0150] Method **201** may further comprise a step **213** of sintering the ink within the porous electron-conductive substrate and evaporating the solvent in the slurry/ink, whereby spaces are left in the pores of the electron-conductive substrate for gas transport. The sintering temperature is preferably about 0° C. to about 50° C. below the glass transition temperature of the hydrophobic polymer, more preferably about 10° C. to about 30° C. below the glass transition temperature of the hydrophobic polymer. A pressure of about 0 to about 5000 lbs. may be applied.

[0151] Referring now to FIG. **12**, there is schematically shown a gas diffusion layer being made according to method **201**. More specifically, air brush **221** can be seen depositing a layer **223** of ink onto porous electron-conductive substrate **225**, and a vacuum force is being used to draw layer **223** into the pores (not shown) of porous electron-conductive substrate **225**.

[0152] Referring now to FIG. **13**, there is shown a flowchart depicting a fourth embodiment of a method according to the present invention for fabricating a gas diffusion layer like gas diffusion layer **21**, the method being represented generally by reference numeral **251**. Details of method **251** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **13** and/or from the accompanying description herein or may be shown in FIG. **13** and/or described herein in a simplified manner.

[0153] Method **251** may comprise a step **253** of providing one or more non-conductive hydrophobic polymers.

Examples of the one or more non-conductive hydrophobic polymers may include ether polymers, acrylic polymers, fluorocarbon polymers, polystyrene polymers, poly(vinyl chloride) polymers, and poly(N-vinylpyrrolidone) (PVP) polymers.

[0154] Method **251** may further comprise a step **255** of providing one or more electron-conductive materials. (It is to be understood that, although step **255** is shown in the present embodiment as occurring after step **253**, step **255** may occur before step **253** or concurrently with step **253**.) The one or more electron-conductive materials may be selected from, for example, one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass, and may be in the form of, for example, one or more of fibers, particles, pellets, rods, and the like. The particle size of the one or more electron-conductive materials may range from about 1 nm to about 1 mm. If the electron-conductive materials are in fiber or rod form, the diameter of the fiber or rod may range from about 1 nm to about 1 mm whereas the length may range from the nanometer to centimeter scale.

[0155] Method **251** may further comprise a step **257** of mixing the one or more non-conductive hydrophobic polymers and the one or more electron-conductive materials. The mass ratio of the one or more electron-conductive materials versus the one or more non-conductive hydrophobic polymers may range from about 15% to about 300%, preferably from about 50% to about 200%.

[0156] A lubricating agent may be added so that the mixture forms a paste that can then be extruded into a sheet at a temperature beyond the melting point of the one or more non-conductive hydrophobic polymers.

[0157] Method **251** may further comprise a step **259** of extruding a sheet of the mixture formed in step **257**.

[0158] Method **251** may further comprise a step **261** of uniaxially or biaxially stretching the sheet at a temperature that is below the melting point of the one or more non-conductive hydrophobic polymers, preferably about 20° C. lower than the melting point of the one or more hydrophobic polymers. The stretching ratio may range between 2:1 and 40:1. The lubricating agent will be volatilized during the stretching process.

[0159] Referring now to FIG. **14**, there is schematically shown a gas diffusion layer made according to method **251**, the gas diffusion layer being represented generally by reference numeral **281**. Details of gas diffusion layer **281** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **14** and/or from the accompanying description herein or may be shown in FIG. **14** and/or described herein in a simplified manner.

[0160] As can be seen, gas diffusion layer **281** may comprise a non-conductive hydrophobic component, which, after stretching, forms a porous hydrophobic membrane structure **283**. Gas diffusion layer **281** may additionally comprise a conductive material **285** in fiber form, which spans the thickness of the aforementioned porous hydrophobic membrane structure **283**. In this manner, gas may be transported through the porous hydrophobic membrane structure **283** whereas electrons may be conducted through the thickness of conductive material **285**.

[0161] An alternative embodiment to gas diffusion layer **281** is shown in FIG. **15** and is represented generally by reference numeral **291**. Details of gas diffusion layer **291** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **15** and/or from the accompanying description herein or may be shown in FIG. **15** and/or described herein in a simplified manner.

[0162] Gas diffusion layer **291** may be similar to gas diffusion layer **281** in that gas diffusion layer **291** may comprise a porous hydrophobic membrane structure **293**, which may be similar or identical to porous hydrophobic membrane structure **283** of gas diffusion layer **281**. On the other hand, gas diffusion layer **291** may differ from gas diffusion layer **281** in that gas diffusion layer **291** may comprise a conductive material **295** in pellet form whereas, as noted above, gas diffusion layer **281** may comprise a conductive material **285** in fiber form.

[0163] Referring now to FIG. **16**, there is shown a top view of a first alternative gas diffusion layer to gas diffusion layer **21**, the first alternative gas diffusion layer being constructed according to the present invention and being represented generally by reference numeral **311**. Details of gas diffusion layer **311** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **16** and/or from the accompanying description herein or may be shown in FIG. **16** and/or described herein in a simplified manner.

[0164] Gas diffusion layer **311** may comprise a first gas diffusion layer piece **313** and a second gas diffusion layer piece **315**. First gas diffusion layer piece **313** and second gas diffusion layer piece **315** may be complementarily shaped to mate with one another in the same plane so as to form a complete gas diffusion layer structure. First gas diffusion layer piece **313** may comprise a porous electron-conductive gas diffusion material, such as, but not limited to, carbon paper, metal foam, metal mesh, or metal paper. Second gas diffusion layer piece **315** may comprise a porous non-conductive hydrophobic gas diffusion material, such as, but not limited to, an expanded polytetrafluoroethylene (e-PTFE) membrane, an expanded polyvinylidene fluoride (e-PVDF) membrane, or other porous hydrophobic non-conductive materials such as polymer films (e.g., fluoropolymer film, polyvinyl chloride film), meshes, woven structures, packed particles and so on. First gas diffusion layer piece **313** and second gas diffusion layer piece **315** preferably have a similar thickness. As can be seen, in the present embodiment, gas diffusion layer **311** has an interdigitated construction, with first gas diffusion layer piece **313** and second gas diffusion layer piece **315** having mating pluralities of fingers **317** and **319**, respectively.

[0165] Preferably, when first gas diffusion layer piece **313** and second gas diffusion layer piece **315** are assembled, the porous electron-conductive and porous non-conductive hydrophobic areas are distributed relatively evenly such that the area ratio between the electron-conductive area and the non-conductive area may vary from about 1:2 to about 2:1. In the present embodiment, first gas diffusion layer piece **313** and second gas diffusion layer piece **315** may alternate at a 1 mm interval. Based on the accuracy of manufacturing, the interval can be as low as 300 μm.

[0166] Referring now to FIG. **17**, there is shown a top view of a second alternative gas diffusion layer to gas diffusion layer **21**, the second alternative gas diffusion layer being constructed according to the present invention and being represented generally by reference numeral **331**. Details of gas diffusion layer **331** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **17** and/or from the accompanying description herein or may be shown in FIG. **17** and/or described herein in a simplified manner.

[0167] Gas diffusion layer **331** may comprise a first gas diffusion layer piece **333**. First gas diffusion layer piece **333** may comprise a porous electron-conductive gas diffusion material, such as, but not limited to, carbon paper, metal foam, metal mesh, or metal paper. One or more transverse pinholes or openings, which in the present embodiment are circular, are provided in first gas diffusion layer piece **333**.

[0168] Gas diffusion layer **331** may further comprise a plurality of second gas diffusion layer pieces **335**, each of which may comprise a porous non-conductive hydrophobic gas diffusion material, such as, but not limited to, an expanded polytetrafluoroethylene (e-PTFE) membrane, an expanded polyvinylidene fluoride (e-PVDF) membrane or other porous hydrophobic non-conductive materials such as polymer films (e.g., fluoropolymer film, polyvinyl chloride film), meshes, woven structures, packed particles and so on. Second gas diffusion layer pieces **335** may be appropriately sized and shaped to mate with, or fill, the transverse pinholes of first gas diffusion layer piece **333** so as to form a complete gas diffusion layer structure. First gas diffusion layer piece **333** and second gas diffusion layer pieces **335** preferably have similar thicknesses.

[0169] Referring now to FIG. **18**, there is shown a simplified section view of a third alternative gas diffusion layer to gas diffusion layer **21**, the third alternative gas diffusion layer being constructed according to the present invention and being represented generally by reference numeral **351**. Details of gas diffusion layer **351** that are discussed elsewhere in this application or that are not critical to an understanding of the invention may be omitted from FIG. **18** and/or from the accompanying description herein or may be shown in FIG. **18** and/or described herein in a simplified manner.

[0170] Gas diffusion layer **351** may comprise a porous electron-conductive substrate **353**. Porous electron-conductive substrate **353** may comprise any of the porous electron-conductive materials discussed above including, but not limited to, an electron-conductive mesh, woven (e.g., cloth) or felt material, paper, or disc, a porous graphite film, a metal foam, a metal sinter, or combinations thereof.

[0171] Gas diffusion layer **351** may further comprise a microporous layer **355** positioned directly on top of porous electron-conductive substrate **353**. Microporous layer **355**, which may have a thickness of about 1 μm to about 200 μm, may comprise a random mixture of one or more electron-conductive materials **357** and one or more non-conductive hydrophobic polymer materials **359**. Materials suitable for use as the one or more electron-conductive materials **357** and the one or more non-conductive hydrophobic polymer materials **359** may include any of the respective materials described above. The volume ratio between the one or more electron-conductive materials and the one or more non-conductive hydrophobic polymer materials may vary from about 9:1 to about 1:3. The particle size of the one or more electron-conductive materials may vary from about 10 nm to about 5 μm, and the particle size of the one or more non-conductive hydrophobic materials may vary from about 20 nm to about 200 μm.

[0172] To fabricate gas diffusion layer **351**, one may prepare a slurry/ink comprising the one or more electron-conductive materials, the one or more non-conductive hydrophobic polymer materials, and one or more solvents. A binder may also be included in the slurry/ink. After the slurry/ink is uniformly mixed, the slurry/ink may be coated on top of porous electron-conductive substrate **353** by bar-coating, slot-die coating, doctor blade coating, or screen printing and then may be allowed to dry. Prior to such coating, porous electron-conductive substrate **353** may be pretreated with a hydrophobic material. In contrast with some of the techniques discussed above, the present fabricating technique does not involve applying a vacuum to draw the slurry/ink into porous electron-conductive substrate **353**. Instead, the slurry/ink forms a microporous layer on top of the porous electron-conductive substrate, thereby forming a two-layer structure.

[0173] As noted above, in some instances, the non-conductive hydrophobic polymer used in the present invention may, itself, be inherently porous. The particle size of such a porous non-conductive hydrophobic polymer particle may vary from about 1 μm to about 1 mm and may have internal pores with a pore diameter that may vary from about 50 nm to about 5 μm. Preferably, the particle size of such a porous non-conductive hydrophobic polymer particle is about 100 μm and its pore diameter varies from about 200 nm to about 5 μm. Such a porous non-conductive hydrophobic polymer particle may be prepared by cryo-milling a piece of porous non-conductive hydrophobic polymer film (e.g. polytetrafluoroethylene film, polyvinylidene fluoride film, polyvinyl chloride film, etc.) into a powder.

[0174] It is to be understood that the gas diffusion electrode of the present invention is not limited to use in carbon dioxide electrolyzers and may also be suitable for use in other electrochemical energy conversion reactions involving reactants and products in multiple phases, such as, but not limited to, N_2 reduction reaction, O_2 reduction reaction, H_2 oxidation reaction, O_2 evolution reaction, and H_2 evolution reaction.

[0175] It is also to be understood that the gas diffusion electrode of the present invention is not limited to use in a cathode and may also be used in anode. However, where the gas diffusion electrode of the present invention is used as an anode, the electron-conductive material cannot be carbon.

[0176] The following examples are given for illustrative purposes only and are not meant to be a limitation on the invention described herein or on the claims appended hereto.

EXAMPLE 1

[0177] An electrochemical carbon dioxide reduction performance test was conducted using an MEA electrolyzer comprising a gas diffusion electrode of the present invention. More specifically, the gas diffusion electrode was made by airbrushing a hydrophobic polymer slurry into a carbon-based gas diffusion layer, followed by spraying a layer of copper to form a catalyst layer. The gas diffusion electrode was then assembled with a VERSOGEN anion exchange membrane (Versogen, Newark, DE) and a stainless-steel paper-based Ni—Fe catalyst electrode to make the MEA. During electrolysis, a dry carbon dioxide stream with a flow rate of 100 sccm was fed to the cathode chamber, while a 1 mL min^{-1} of 1 M KOH electrolyte was introduced to the anode chamber. The electrolyzer was tested in galvanostatic mode. A constant current density ranging from 100 to 400 mA cm^{-2} was applied to the electrolyzer while the voltage and flue gas component was monitored online. As shown in FIG. **19**, the present gas diffusion electrode achieved 42% C_2H_4 selectivity at a total current density of 200 mA cm^{-2} and a cell voltage of 2.44 V.

EXAMPLE 2

[0178] A stability test was conducted under a total current density of 100 mA cm^{-2}. The test condition was the same as the one described above in Example 1. As shown in FIG. **20**, the gas diffusion electrode maintained over 40% C_2H_4 selectivity for over 24 h without observable selectivity degradation. Moreover, the cell voltage maintained at 2.19 V for over 24 h, and no observable increase was detected.

[0179] Some additional comments, features, aspects and/or observations relating to one or more embodiments of the present invention are provided below.

[0180] In one embodiment, the gas diffusion electrode (sometimes alternatively referred to as a water management gas diffusion electrode) may comprise (1) a gas diffusion domain comprising a hydrophobic, and non-conductive polymer, (2) an electron-conductive material network, (3) an optional, thin, porous, electron-conductive interlayer, and (4) a catalyst layer.

[0181] The gas diffusion domain may comprise, for example, one or more of ether polymers, acrylic polymers, fluorocarbon polymers, polystyrene polymers, poly(vinyl chloride) polymers, and poly(N-vinylpyrrolidone) (PVP) polymers.

[0182] The hydrophobic material may be in the form of one or more of a fiber, a particle, a pellet, a rod, and so on.

[0183] When the hydrophobic material is in the form of a particle, the particle size may range from about 1 nm to about 1 mm, with a preferred particle size ranging from about 5 nm to about 200 nm.

[0184] When the hydrophobic material is in the form of a fiber or a rod, its diameter may range from about 1 nm to about 1 mm whereas its length may range from nanometer to centimeter scale. A preferred diameter may range from about 5 nm to about 30 μm.

[0185] The thickness of the porous, hydrophobic, polymer domain may range from about 5% to about 100% of the electron-conductive material network thickness, with a preferred range for the thickness of the porous, hydrophobic, polymer domain being from about 50% to about 100% of the electron-conductive material network thickness.

[0186] When the electron-conductive material is carbon, the mass of the hydrophobic polymer versus the mass of the electron-conductive material network may range from about 30 wt % to about 600 wt %, with a preferred range being from about 200 wt % to about 400 wt %.

[0187] The electron-conductive material network may comprise one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0188] The electron-conductive material network, which is porous, may be in the form of one or more materials like paper, foam, felt, sinter, cloth, mesh, and so on.

[0189] The electron-conductive material network may be coated with one or more hydrophobic polymers with a loading ranging from about 0.1 wt % to about 40 wt %, with a preferred range being from about 5 wt % to about 30 wt %.

[0190] The electron-conductive material network may be coated with one or more hydrophilic polymers with a loading ranging from about 0.1 wt % to about 40 wt %, with a preferred range being from about 5 wt % to about 30 wt %.

[0191] The electron-conductive material network may range in thickness from about 0.5 μm to about 2 mm, with a preferred range for the thickness of the electron-conductive material network being from about 1 μm to about 200 μm.

[0192] The thickness of the electron-conductive material network may be equal to or greater than the thickness of the porous hydrophobic gas diffusion domain.

[0193] The thickness of the optional interlayer, when present, may range from about 5 nm to about 30 μm, with a preferred range for the optional interlayer, when present, being from about 5 nm to about 100 nm.

[0194] The optional interlayer may comprise one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0195] The optional interlayer may be coated with one or more hydrophobic materials with a weight ratio of about 5 wt % to about 40 wt %, with a preferred range being from about 5 wt % to about 30 wt %.

[0196] The optional interlayer may comprise a mixture of electron-conductive material particles and hydrophobic polymer particles. The mass ratio of the hydrophobic polymer particles to electron-conductive material particles may range from about 5 wt % to about 200 wt %.

[0197] The catalyst layer may comprise one or more of copper, silver, gold, carbon, bismuth, iron, boron, nitrogen, oxygen, fluorine, aluminum, silicon, phosphorus, sulfur, chromium, manganese, cobalt, nickel, zinc, gallium, selenium, molybdenum, ruthenium, rhodium, palladium, iridium, and platinum.

[0198] When using a screen printing, doctor blade, slot-die, vacuum filtration, or airbrush technique to fabricate the water management gas diffusion electrode, a hydrophobic material slurry may comprise one or more hydrophobic materials, water, one or more organic solvents, and one or more binders.

[0199] When using an airbrush technique to fabricate the water management gas diffusion electrode, the airbrush pressure may range from about 0.5 bar to about 15 bar, with a preferred pressure ranging from about 2 bar to about 6 bar.

[0200] When fabricating the water management gas diffusion electrode, the hydrophobic polymer may be sintered after being loaded into the electron-conductive material network.

[0201] The sinter temperature may be around the glass transition temperature of the hydrophobic polymer, with a preferred range being about 0° C. to about 50° C. below the glass transition temperature of the hydrophobic polymer, and more preferably about 10° C. to about 30° C. below the glass transition temperature of the hydrophobic polymer.

[0202] The sinter pressure may range from about 0 lb. to about 5000 lbs.

[0203] The interlayer may be loaded by one or more techniques including spraying, screen printing, doctor blade, vacuum filtration, compression, and slot-die.

[0204] The water management gas diffusion electrode may alternatively be fabricated by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material.

[0205] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the mass ratio of electron-conductive material to hydrophobic polymer may range from about 15 wt % to about 300 wt %, with a preferred range being from about 50 wt % to about 200 wt %.

[0206] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the electron-conductive material may be one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

[0207] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the electron-conductive material may be in the form of one or more of a fiber, a particle, a pellet, a rod, and so on.

[0208] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the particle size of the electron-conductive material may range from about 1 nm to about 1 mm. If the electron-conductive materials are in fiber or rod form, the diameter may range from about 1 nm to about 1 mm whereas the length may range from the nanometer scale to the centimeter scale.

[0209] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the hydrophobic polymer membrane may be uniaxially or biaxially stretched at a temperature below the melting point of hydrophobic polymer, with a preferred temperature being the glass transition temperature of the hydrophobic polymer.

[0210] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, a lubricating agent and a pore former may be added.

[0211] When fabricating the water management gas diffusion electrode by uniaxial or biaxial stretching of a hydrophobic polymer membrane embedded with electron-conductive material, the stretching ratio may range from about 2:1 to about 40:1.

[0212] The water management gas diffusion electrode may be used as a gas diffusion electrode for a CO_2-reduction reaction, an N_2-reduction reaction, an O_2-reduction reaction, an O_2-evolution reaction, an H_2-evolution reaction, and an H_2-reduction reaction.

[0213] The water management gas diffusion electrode may be fabricated by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate.

[0214] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the two pieces of substrate may be cut into a patterned shape.

[0215] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the distribution of the electron-conductive area and the non-conductive, hydrophobic area should be uniform.

[0216] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the ratio of the electron-conductive area to the non-conductive area may vary from about 1:2, respectively, to about 2:1, respectively.

[0217] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the electron-conductive substrate may comprise one or more of carbon paper, metal foam, metal mesh, and metal paper.

[0218] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the non-conductive porous hydrophobic substrate may comprise one or more of a fluoropolymer film and a PVC film.

[0219] When fabricating the water management gas diffusion electrode by matching or mating together a piece of an electron-conductive substrate and a piece of a non-conductive, porous, hydrophobic substrate, the electron-conductive and non-conductive materials preferably have similar thicknesses.

[0220] The water management gas diffusion electrode may alternatively be fabricated by co-coating a random mixture comprising (i) hydrophobic, non-conductive particles/materials; and (ii) electron-conductive particles/materials on top of an electron-conductive substrate.

[0221] When fabricating the water management gas diffusion electrode by co-coating a random mixture comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials on top of an electron-conductive substrate, the volume ratio of the electron-conductive particles to the non-conductive hydrophobic particles may vary from about 9:1, respectively, to about 1:3, respectively.

[0222] The thickness of the random mixture layer comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials may vary from about 1 μm to about 200 μm.

[0223] The particle size of the electron-conductive materials in the random mixture layer comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials may vary from about 10 nm to about 5 μm.

[0224] The particle size of the non-conductive hydrophobic materials in the random mixture layer comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials may vary from about 20 nm to about 200 μm.

[0225] When fabricating a water management gas diffusion electrode by co-coating a random mixture comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials on top of an electron-conductive substrate, techniques including one or more of doctor blade, slot-die, bar-coating, and screen printing may be used to apply the random mixture layer.

[0226] When fabricating a water management gas diffusion electrode by co-coating a random mixture comprising hydrophobic, non-conductive particles/materials and electron-conductive particles/materials on top of an electron-conductive substrate, the substrate may be pre-coated with one or more hydrophobic materials with a weight percentage of about 0.1 wt % to about 40 wt %.

[0227] With respect to the various water management gas diffusion electrodes discussed above, the hydrophobic particle/material, itself, may be porous.

[0228] The particle size of the aforementioned porous hydrophobic particle may vary from about 1 μm to about 1 mm. Such a particle may have internal pores, with a pore diameter that may vary from about 50 nm to about 5 μm.

[0229] The aforementioned porous hydrophobic particle may be made by cryo-milling a bulk quantity of porous material into powder.

[0230] Materials that may be used for the porous hydrophobic particles may include polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyvinyl chloride (PVC).

[0231] The embodiments of the present invention described above are intended to be merely exemplary and those skilled in the art shall be able to make numerous variations and modifications to it without departing from the spirit of the present invention. All such variations and modifications are intended to be within the scope of the present invention.

What is claimed is:

1. A gas diffusion electrode suitable for use in a carbon dioxide electrolyzer, the gas diffusion electrode comprising:

(a) a gas diffusion layer, the gas diffusion layer comprising

(i) an electron-conductive domain, the electron-conductive domain having a thickness and comprising a plurality of pores, and

(ii) a non-conductive hydrophobic domain, the non-conductive hydrophobic domain having a thickness ranging from about 10% to about 100% of the thickness of the electron-conductive domain, the non-conductive hydrophobic domain randomly occupying a portion of the volume of the pores of the electron-conductive domain, the non-conductive hydrophobic domain being porous to permit gas transport through the gas diffusion layer; and

(b) a catalyst layer, the catalyst layer being coupled to the gas diffusion layer.

2. The gas diffusion electrode as claimed in claim **1** wherein the non-conductive hydrophobic domain comprises at least one of an ether polymer, an acrylic polymer, a fluorocarbon polymer, a polystyrene polymer, a poly(vinyl chloride) polymer, and a poly(N-vinylpyrrolidone) polymer.

3. The gas diffusion electrode as claimed in claim **1** wherein the non-conductive hydrophobic domain comprises at least one of a fiber, a particle, a pellet, and a rod.

4. The gas diffusion electrode as claimed in claim **3** wherein the non-conductive hydrophobic domain comprises a particle and wherein the particle has a size ranging from about 1 nm to about 1 mm.

5. The gas diffusion electrode as claimed in claim **4** wherein the non-conductive hydrophobic domain has a size ranging from about 5 nm to about 100 μm.

6. The gas diffusion electrode as claimed in claim **3** wherein the non-conductive hydrophobic domain comprises at least one of a fiber and a rod and wherein the non-conductive hydrophobic domain has a diameter ranging from about 1 nm to about 1 mm and a length ranging from nanometer to centimeter scale.

7. The gas diffusion electrode as claimed in claim **6** wherein the non-conductive hydrophobic domain has a diameter ranging from about 5 nm to about 100 μm.

8. The gas diffusion electrode as claimed in claim **1** wherein the electron-conductive domain comprises carbon, wherein the non-conductive hydrophobic domain has a mass, wherein the electron-conductive domain has a mass, and wherein the mass of the non-conductive hydrophobic domain ranges from about 30 wt % to about 600 wt % of the mass of the electron-conductive domain.

9. The gas diffusion electrode as claimed in claim **1** wherein the electron-conductive domain comprises at least one of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

10. The gas diffusion electrode as claimed in claim **1** wherein the electron-conductive domain comprises at least one of a paper, a foam, a felt, a sinter, a cloth, and a mesh.

11. The gas diffusion electrode as claimed in claim **1** wherein the electron-conductive domain is coated with at least one hydrophobic polymer with a loading ranging from about 0.1 wt % to about 40 wt % of the electron-conductive domain.

12. The gas diffusion electrode as claimed in claim **1** wherein the electron-conductive domain has a thickness ranging from about 0.5 μm to about 2 mm.

13. The gas diffusion electrode as claimed in claim **1** further comprising an interlayer, the interlayer being disposed between and in direct contact with each of the gas diffusion layer and the catalyst layer, the interlayer being porous and electron-conductive.

14. The gas diffusion electrode as claimed in claim **13** wherein the interlayer has a thickness ranging from about 5 nm to about 30 μm.

15. The gas diffusion electrode as claimed in claim **13** wherein the interlayer comprises at least one of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

16. The gas diffusion electrode as claimed in claim **13** wherein the interlayer is coated with one or more hydrophobic materials with a weight ratio of about 5 wt % to about 40 wt % of the interlayer.

17. The gas diffusion electrode as claimed in claim **13** wherein the interlayer comprises a mixture of electron-conductive particles and hydrophobic polymer particles.

18. The gas diffusion electrode as claimed in claim **17** wherein the hydrophobic polymer particles are present in the interlayer at a mass ratio ranging from about 5 wt % to about 200 wt % of the electron-conductive material particles.

19. The gas diffusion electrode as claimed in claim **1** wherein the catalyst layer comprises at least one of copper, silver, gold, carbon, bismuth, iron, boron, nitrogen, oxygen, fluorine, aluminum, silicon, phosphorus, sulfur, chromium, manganese, cobalt, nickel, zinc, gallium, selenium, molybdenum, ruthenium, rhodium, palladium, iridium, and platinum.

20. The gas diffusion electrode as claimed in claim **1** wherein the non-conductive hydrophobic domain comprises a porous hydrophobic particle.

21. The gas diffusion electrode as claimed in claim **20** wherein the porous hydrophobic particle has a particle size of about 1 nm to about 1 mm.

22. The gas diffusion electrode as claimed in claim **21** wherein the porous hydrophobic particle has at least one internal pore, with a pore diameter ranging from about 50 nm to about 5 μm.

23. The gas diffusion electrode as claimed in claim **20** wherein the porous hydrophobic particle is made by cryomilling a bulk quantity of a porous material into powder.

24. The gas diffusion electrode as claimed in claim **20** wherein the porous hydrophobic particle comprises at least one of polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyvinyl chloride (PVC).

25. A method of fabricating a gas diffusion electrode, the method comprising the steps of:

(a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises
  providing a slurry, the slurry comprising at least one hydrophobic material and at least one organic solvent;
  providing an electron-conductive substrate, the electron-conductive substrate having a thickness and comprising a plurality of pores;
  loading the slurry into the pores of the electron-conductive substrate; and
  sintering the slurry, whereby the solvent evaporates, forming a non-conductive hydrophobic domain within the pores of the electron-conductive substrate, the non-conductive hydrophobic domain having a thickness ranging from about 50% to about 100% of the thickness of the electron-conductive domain, the non-conductive hydrophobic domain configured to permit gas transport through the electron-conductive substrate; and
(b) positioning a catalyst layer over the gas diffusion layer.

26. The method as claimed in claim **25** wherein the loading step comprises one of screen printing, doctor blade coating, slot-die coating, vacuum filtration coating, and airbrush coating.

27. The method as claimed in claim **26** wherein the slurry further comprises at least one of water and one or more binders.

28. The method as claimed in claim **26** wherein the loading step comprises airbrush coating and wherein the airbrush coating is conducted at a pressure ranging from about 0.5 bar to about 15 bar.

29. The method as claimed in claim **28** wherein the pressure ranges from about 2 bar to about 6 bar.

30. The method as claimed in claim **25** wherein the sintering step is performed at a temperature no greater than the melting point of the at least one hydrophobic material.

31. The method as claimed in claim **30** wherein the temperature is about 0° C. to about 50° C. below the melting point of the at least one hydrophobic material.

32. The method as claimed in claim **25** wherein the sintering step is performed at a pressure ranging from about 0 lb. to about 5000 lbs.

33. The method as claimed in claim **25** further comprising the step of positioning an interlayer directly between the catalyst layer and the electron-conductive substrate.

34. The method as claimed in claim **33** wherein the interlayer positioning step comprises at least one of spraying, screen printing, doctor blade coating, vacuum filtration coating, compression coating, and slot-die coating.

35. A gas diffusion electrode made by the method of claim **25**.

36. A method of fabricating a gas diffusion electrode, the method comprising the steps of:

(a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises
  providing at least one non-conductive hydrophobic polymer;
  providing at least one electron-conductive material;
  mixing the at least one non-conductive hydrophobic polymer and the at least one electron-conductive material to form a mixture;
  extruding the mixture to form a sheet;
  stretching the sheet at a temperature below the melting point of the at least one non-conductive hydrophobic polymer to form pores for gas transport through the sheet; and
(b) positioning a catalyst layer over the gas diffusion layer.

37. The method as claimed in claim **36** wherein the stretching comprises at least one of uniaxial stretching and biaxial stretching of the sheet.

38. The method as claimed in claim **36** wherein a mass ratio of the at least one electron-conductive material to the at least one non-conductive hydrophobic polymer ranges from about 15 wt % to about 300 wt %.

39. The method as claimed in claim **38** wherein the mass ratio is from about 50 wt % to about 200 wt %.

40. The method as claimed in claim **36** wherein the at least one electron-conductive material is one or more of carbon, copper, iron, stainless steel, silver, gold, nickel, aluminum, molybdenum, zinc, titanium, and brass.

41. The method as claimed in claim **36** wherein the at least one electron-conductive material is one or more of a fiber, a particle, a pellet, and a rod.

42. The method as claimed in claim **41** wherein the at least one electron-conductive material has a particle size ranging from about 1 nm to about 1 mm.

43. The method as claimed in claim **41** wherein the at least one electron-conductive material is at least one of a fiber and a rod and wherein the at least one electron-conductive material has a diameter ranging from about 1 nm to about 1 mm and a length ranging from the nanometer scale to the centimeter scale.

44. The method as claimed in claim **36** wherein the temperature is the melting point temperature of the at least one non-conductive hydrophobic polymer.

45. The method as claimed in claim **36** wherein the mixture further comprises a lubricating agent and a pore former.

46. The method as claimed in claim **36** wherein the stretching comprises stretching at a ratio ranging from about 2:1 to about 40:1.

47. A gas diffusion electrode made by the method of claim **36**.

48. A method of fabricating a gas diffusion electrode, the method comprising the steps of:

(a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises
  providing a first gas diffusion layer piece, the first gas diffusion layer piece being porous and electron-conductive;
  providing a second gas diffusion layer piece, the second gas diffusion layer piece being porous, non-conductive and hydrophobic, wherein the first gas diffusion layer piece and the second gas diffusion layer piece are complementarily shaped to mate with one another in the same plane; and
  mating together the first gas diffusion layer piece and the second gas diffusion layer piece; and
(b) positioning a catalyst layer over the gas diffusion layer.

49. The method as claimed in claim **48** wherein the first gas diffusion layer piece and the second gas diffusion layer piece form an interdigitated construction.

50. The method as claimed in claim **48** wherein the first gas diffusion layer piece comprises a transverse opening and wherein the second gas diffusion layer piece is dimensioned to mate with the transverse opening.

51. The method as claimed in claim **48** wherein the gas diffusion layer has a uniform distribution of one or more electron-conductive areas and one or more non-conductive, hydrophobic areas.

52. The method as claimed in claim **48** wherein each of the first gas diffusion layer piece and the second gas diffusion layer piece has an area and wherein a ratio of the areas of the first and second gas diffusion layer pieces ranges from about 1:2, respectively, to about 2:1, respectively.

53. The method as claimed in claim **48** wherein the first gas diffusion layer piece comprises at least one of carbon paper, metal foam, metal mesh, and metal paper.

54. The method as claimed in claim **48** wherein the second gas diffusion layer piece comprises at least one of a fluoropolymer film and a polyvinyl chloride film.

55. The method as claimed in claim **48** wherein the first and second gas diffusion layer pieces have similar thicknesses.

56. A gas diffusion electrode made by the method of claim **48**.

57. A method for fabricating a gas diffusion electrode, the method comprising the steps of:

(a) forming a gas diffusion layer, wherein said gas diffusion layer forming comprises
  providing a porous electron-conductive substrate, the porous electron-conductive substrate having an outer surface;
  preparing a slurry, the slurry comprising a random mixture of at least one electron-conductive material, at least one non-conductive hydrophobic polymer material, and at least one solvent;
  coating the outer surface of the porous electron-conductive substrate with the slurry, which, upon drying, forms a porous coating on the outer surface of the porous electron-conductive substrate; and
(b) positioning a catalyst layer over the porous coating of the gas diffusion layer.

58. The method as claimed in claim **57** wherein a volume ratio of the at least one electron-conductive material to the at least one non-conductive hydrophobic polymer material ranges from about 9:1, respectively, to about 1:3, respectively.

59. The method as claimed in claim **58** wherein the porous coating has a thickness ranging from about 1 μm to about 200 μm.

60. The method as claimed in claim **58** wherein the at least one electron-conductive material has a particle size from about 10 nm to about 5 μm.

61. The method as claimed in claim **58** wherein the at least one non-conductive hydrophobic polymer material has a particle size of from about 20 nm to about 200 μm.

62. The method as claimed in claim **58** wherein the coating step comprises at least one of doctor blade coating, slot-die coating, bar-coating, and screen printing.

63. The method as claimed in claim **58** further comprising, prior to the coating step, pre-coating the electron-conductive substrate with at least one hydrophobic material to a weight percentage of about 0.1 wt % to about 40 wt %.

64. A gas diffusion electrode made by the method of claim **57**.

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