



(51) International Patent Classification:

B01D 69/02 (2006.01) B01D 69/10 (2006.01)

B01D 53/22 (2006.01) B01D 71/80 (2006.01)

(21) International Application Number:

PCT/US2019/042873

(22) International Filing Date:

22 July 2019 (22.07.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/713,436 01 August 2018 (01.08.2018) US

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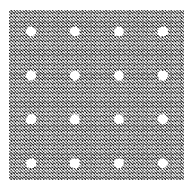
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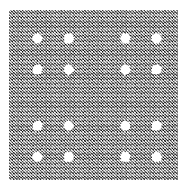
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

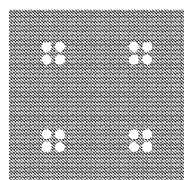
(54) Title: COMPOSITE MEMBRANES COMPRISING AN ISOPOROUS SUPPORT MEMBRANE PREPARED FROM AM-PHIPHILIC BLOCK-COPOLYMERS



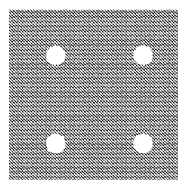
(A)
RELATIVE PERMEANCE = 0.310
CO₂ PERMEANCE = 2,050 GPU



(B)
RELATIVE PERMEANCE = 0.290
CO₂ PERMEANCE = 1,910 GPU



(C)
RELATIVE PERMEANCE = 0.257
CO₂ PERMEANCE = 1,700 GPU



(D)
RELATIVE PERMEANCE = 0.181
CO₂ PERMEANCE = 1,200 GPU

Figure 5

(57) Abstract: The disclosure relates to improved composite membranes for use in separating components in a fluid mixture. The composite membrane comprises an isoporous support layer which provides support to a nonporous selective layer of the composite membrane and which maintains high membrane permeance and selectivity.



Published:

— *with international search report (Art. 21(3))*

**COMPOSITE MEMBRANES COMPRISING AN ISOPOROUS SUPPORT
MEMBRANE PREPARED FROM AMPHIPHILIC BLOCK-COPOLYMERS**

INCORPORATION BY REFERENCE

[0001] All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference.

BACKGROUND

[0002] The disclosure relates to membrane-based fluid separation processes. In particular, the disclosure relates to separation processes using composite membranes comprising a support membrane with an isoporous surface.

[0003] Membrane separation is widely used in molecular separation in fluids. In a membrane separation process, the membrane is situated in between a feed mixture and a permeate mixture. The separation is performed by providing a driving force from the feed side to the permeate side, thereby creating transport through the membrane by permeation. Permeance is a measure of the ability of the membrane to transport a specific molecule and is equal to the inverse of the membrane resistance towards that molecule. Individual molecules have different permeances in the membrane and this creates a separation between molecules.

[0004] There are two basic categories of membranes used to perform molecular separations in fluids: membranes with an asymmetric structure and membranes with a composite structure.

[0005] In asymmetric membranes, a nonporous selective layer seamlessly transitions into a porous substructure consisting of the same material as the selective layer. The membrane may comprise a layer. The membrane may comprise more than one layers.

[0006] In composite membranes, a nonporous selective layer is supported by a porous support membrane consisting of a material different from the selective material. The porous support itself may be asymmetric in pore size distribution across the cross-section of the support. The membrane may comprise a single porous support layer. The membrane may comprise more than one porous support layers.

[0007] Composite membranes are generally used in gas separation applications, pervaporation applications, liquid separation applications, and/or fluid separations. In gas separation applications, both the feed and permeate mixtures are in the gas or vapor state. In pervaporation, the feed mixture is a liquid and the permeate mixture is a gas or vapor. In liquid separations, both the feed and permeate mixtures are in the liquid state.

[0008] The composite membrane configuration is typically developed to allow optimization of the selective layer for permeance and selectivity while simultaneously allowing optimization of the support layer to be mechanically strong and robust. In the last thirty years, improvements in manufacturing techniques had focused on increasing the permeance of composite membranes. This was achieved by making the selective layer thinner and improving the surface of the porous supports to allow micron-scale and even sub-micron scale selective layers to be coated without creating non-selective defects in the selective layer.

[0009] The challenge of making a preferable support layer rests on finding the balance of providing maximum robust mechanical support and having minimum interference with membrane permeability and selectivity, thereby allowing optimized separation performance. Disclosed herein are processes, systems and compositions for preparing support layers of composite membranes using self-assembly properties of block copolymers.

[0010] Previous work in making self-assembly based membranes has focused on improving surface pore structures, such as ensuring uniformity of pore sizes, because the pores are responsible for performing separation. When a self-assembly membrane is used as support for a composite membrane, the pores are not responsible for performing separation. Instead, the uniformity in pore size and pore distribution reduces transport resistance and improves permeance, making it possible to create improved composite membranes.

[0011] Disclosed herein are compositions, systems and processes of manufacturing a support layer of composite membranes and processes of using the same for separation performance. The compositions and processes utilize a self-assembly based membrane as an isoporous support membrane for the preparation of improved composite membranes. Unlike traditional approaches, the disclosed isoporous support membranes is designed to serve as support membrane for nonporous selective layers. The isoporous support membranes have substantially uniformly distributed pores and yield superior result in providing adequate mechanical support without interfering with membrane permeability and/or selectivity.

SUMMARY

[0012] In one aspect, disclosed herein is a composite membrane for separating components in a fluid mixture, the composite membrane comprising an isoporous support layer for supporting a nonporous selective layer, the isoporous support layer comprising: (a) one or more amphiphilic block copolymer; and (b) a plurality of surface pores having substantially uniform distribution, wherein a ratio of the maximum distance to the minimum distance between a surface pore and its closest four neighboring pores is smaller than 3; or (c) a plurality of surface pores having substantially uniform size, wherein a ratio of the maximum diameter to the minimum diameter is smaller than 5; and/or (d) a plurality of surface pores having a density of at least 10^8 pores/cm². The composite membrane may comprise (a) and

(b) and (c) and (d). The composite membrane may comprise (a) and combinations of (b), (c) and (d). The composite membrane may comprise (a) and (b), or (a) and (c) or (a) and (d). The ratio of the maximum distance to the minimum distance distances between one surface pore and its closest four neighboring surface pores may be smaller than 2. The nonporous selective layer may be in contact with the isoporous support layer. In some cases, the isoporous support layer may further comprise a gutter layer between the nonporous selective layer and the isoporous support layer. In some cases, the maximum diameter to the minimum diameter of the surface pores is smaller than 3. In other cases, the maximum diameter to the minimum diameter of the surface pores is smaller than 2. In some cases, the surface pores have a density of at least 10^{10} pores/cm². In some cases, the surface pores have a density of at least 10^{12} pores/cm². The one or more amphiphilic block copolymer comprises a structure of the form selected from X-Y, X-Y-X, and X-Y-Z, wherein X, Y, and Z are selected from a group of polymers consisting of polystyrene, poly-4-vinylpyridine, poly-2-vinylpyridine, polybutadiene, polyisoprene, poly(ethylenestat-butylene), poly(ethylene-alt-propylene), polysiloxane, polyalkyleneoxide, poly-ε-caprolactone, polylactide, polyalkylmethacrylate, polymethacrylic acid, polyaklylacrylate, polyacrylic acid, polyhydroxyethylmethacrylate, polyacrylamide, poly-N-alkylacrylamide, polysulfone, polyethersulfone, polyphenylsulfone, polyetherimide, polyvinylidene fluoride, polyacrylonitrile, cellulose diacetate, cellulose triacetate, and ethylcellulose. In some cases, the isoporous support layer further comprises at least one homopolymer. In some cases, the isoporous support layer further comprises at least one random block copolymer. The selective layer may have a thickness of less than 5 micron. In other cases, the selective layer has a thickness of less than 2 micron. In other cases, the selective layer has a thickness of less than 1 micron. The isoporous support may comprise more than one layer, wherein a first porous layer adjacent to the non-porous top layer

comprises an amphiphilic block copolymer and a subsequent porous layer underneath comprises a different block copolymer. In some cases, the isoporous support membrane has a surface porosity of at least 2%. In some cases, the isoporous support membrane has a surface porosity of at least 5%. In some cases, the isoporous support membrane has a surface porosity of at least 10%. In some cases, the isoporous support membrane has a surface porosity of at least 20%. In some embodiments, at least 30% of the surface pores of the isoporous support membrane have a diameter below 1 micron. In some embodiments, at least 30% of the surface pores of the isoporous support membrane have a diameter below 0.3 micron. In some embodiments, at least 30% of the surface pores of the isoporous support membrane have a diameter below 0.1 micron. The fluid mixture may be a gas or vapor mixture. The fluid mixture may be a liquid mixture. The fluid mixture may comprise at least a component A and a component B. In some cases, component A is carbon dioxide. In some cases, component A is helium. In some cases, component A is hydrogen. In some cases, component A is water vapor. In some cases, component A is methane. In some cases, component A is oxygen. In some cases, component A is nitrogen. In some cases, component A is a hydrocarbon vapor. In some cases, component A is sulfur dioxide. In some cases, component A is hydrogen sulfide. In some cases, component A is water. In some cases, component A is ethanol. In some cases, component A is propanol. In some cases, component A is benzene. In some cases, component A is toluene. In some cases, component A is xylene.

[0013] In one aspect, disclosed herein is a process for separating two components, A and B, of a fluid mixture, comprising: (a) passing the fluid mixture across a separation membrane having a feed side and a permeate side, the separation membrane comprises a nonporous selective layer and an isoporous support layer, wherein the isoporous support contains surface pores having substantially uniform distribution, wherein a ratio of the maximum distance to

the minimum distance between a surface pore and its four closet neighboring pores is smaller than 3; (b) providing a driving force for transmembrane permeation; (c) withdrawing from the permeate side a fluid permeate stream enriched in component A compared to the fluid feed mixture; and (d) withdrawing from the feed side a fluid residue stream depleted in component A compared to the fluid mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1. Carbon Dioxide permeance of composite membranes with PDMS top layer of different thicknesses

[0015] Figure 2. Schematic of an idealized composite membrane, showing the top layer and the porous support

[0016] Figure 3. Carbon dioxide permeances of PDMS composite membranes as a function of PDMS top layer thickness for different surface porosities and surface pore radii of the support membrane, as calculated using the correlation of Wijmans and Hao.

[0017] Figure 4. Relative permeance (permeance divided by intrinsic permeance of top layer) of composite membranes as a function of surface porosity of the support.

[0018] Figure 5. Four distributions with average surface porosity of 5%. CO₂ permeance are calculated for a 0.5 micron thick PDMS top layer.

[0019] Figure 6. SEM of the top surface of a support produced by MTR using the traditional phase inversion process.

[0020] Figure 7. Ratio of Largest Distance to Smallest Distance for the four nearest pores for each of the 100 pores in a random distribution. Results shown for ten different distributions (1,000 points total).

DETAILED DESCRIPTION

[0021] The term “fluid” as used herein means a gas, a vapor or a liquid.

[0022] The term “composite membrane” as used herein means a membrane comprising a nonporous selective layer and a support membrane.

[0023] The term “support membrane” as used herein means a porous membrane supporting a nonporous selective layer. The support membrane may be in direct or indirect contact with the nonporous selective layer.

[0024] The term “isoporous support membrane” as used herein means a porous support membrane formed via a combination of amphiphilic block copolymer self-assembly and immersion phase inversion. The isoporous support membrane comprises of one or more amphiphilic block copolymers, or a mixture of one or more amphiphilic polymers with one or more polymers or macromolecules, and can be manufactured to have a higher amphiphilic block copolymer content at one surface compared to the other surface.

[0025] The term “amphiphilic block copolymer” as used herein means a polymer with at least one repeating hydrophilic block and at least one repeating hydrophobic block. The blocks do not vary in length and are not randomly distributed, which leads to the formation of highly ordered structures.

[0026] The term “immersion phase inversion process” as used herein means the process where one or more polymers are dissolved in a solvent system comprising at least one solvent, where the resulting polymer solution is shaped as a thin film either through casting or extrusion, where the thin film is brought into contact with a nonsolvent system containing at least one nonsolvent that is miscible with the solvent, and where a membrane is formed with a porous substructure and a porous or nonporous top layer. This process can produce flat sheet membranes as well as hollow fiber membranes.

[0027] The term “gutter layer” as used herein means a layer of high permeability material placed in between the support membrane and the selective layer.

[0028] The term “selective layer” as used herein means the layer primarily responsible for the selective properties of the composite membrane, consisting of, but not limited to polymers, macromolecules, and inorganic materials.

[0029] A block copolymer consists of at least two different blocks, X and Y, which are coupled together at one specific location in the polymer chain. They are different from random copolymers where segments X and Y are randomly distributed throughout the polymer chain. A block copolymer is called an amphiphilic block copolymer if one of the blocks is hydrophobic and the other block is hydrophilic.

[0030] The present disclosure relates to a process for separating components of a mixture whereby the mixture is passed across an improved separation membrane having a selective nonporous layer supported by an isoporous support membrane, wherein the isoporous support membrane is formed via a combination of amphiphilic block copolymer self-assembly and immersion phase inversion. The mixture may be a gas mixture, vapor mixture, liquid mixture, fluid mixture, or a combination thereof. In some cases, the isoporous support membrane is in contact with the selective nonporous layer. In some cases, the isoporous support membrane is not in contact with the selective nonporous layer.

[0031] The present disclosure also relates to a process for separating two components, A and B, of a mixture such as a gas mixture, vapor mixture, liquid mixture, fluid mixture, or a combination thereof. The separation is carried out by running a stream of the mixture across a membrane that is selective for the desired component to be separated from another component. The desired component to be separated into the permeate may be either

Component A or Component B. The process results, therefore, in a permeate stream enriched in the desired component and a residue stream depleted in that component.

[0032] In some cases, the mixture is fluid mixture comprising gas and/or vapor. In some cases, the mixture is a fluid mixture comprising liquid. In other cases, the mixture is a fluid mixture comprising gas, vapor, and/or liquid.

[0033] As disclosed herein, component A may be a gas, a vapor, or a liquid. Component A may be selected from a group of gases consisting of carbon dioxide, helium, hydrogen, water vapor, methane, oxygen, nitrogen, hydrocarbon vapor, sulfur dioxide, hydrogen sulfide. Component A may be selected from a group of vapor consisting of water vapor and hydrocarbon vapor. Component A may be selected from a group of liquid consisting of water, ethanol, propanol, benzene, toluene, and xylene.

[0034] Disclosed herein are steps to fabricate composite membranes using polymeric supports that have an isoporous surface and are produced via a combination of phase inversion and self-assembly of block copolymers. This method produces porous surfaces are uniform in pore size, uniform in pore distribution, and have high surface porosities, and thus have preferable features of a support membrane that provides high permeability, high selectivity, and adequate support, and are uniquely suited as porous supports for composite membranes.

[0035] Self-assembly of amphiphilic block copolymers may create highly ordered and uniform structures. For instance, any polymer with two connected but different blocks X and Y will phase separate into different domains, just as a mixture of two different polymers X and Y typically will exhibit phase separation. The block copolymer system will give more ordered structures than the two-polymer system because of the restriction imposed by the physical connection of X and Y. Formation of the block copolymer structure depends on the volume fractions of the blocks. For membrane applications, the structure of most interest is

the “cylinder of X in matrix of Y” structure, which typically will form if the volume fraction of X is between 10% and 40%.

[0036] In some embodiments, the block copolymers used to form the isoporous support includes a structure of the form X-Y or X-Y-X or X-Y-Z, wherein X or Y or Z is selected from one of the polymers comprising polystyrene, poly-4-vinylpyridine, poly-2-vinylpyridine, polybutadiene, polyisoprene, poly(ethylenestat-butylene), poly(ethylene-alt-propylene), polysiloxane, polyalkyleneoxide, poly-ε-caprolactone, polylactide, polyalkylmethacrylate, polymethacrylic acid, polyakdylacrylate, polyacrylic acid, polyhydroxyethylmethacrylate, polyacrylamide, poly-N-alkylacrylamide, polysulfone, polyethersulfone, polyphenylsulfone, polyetherimide, polyvinylidene fluoride, polyacrylonitrile, cellulose diacetate, cellulose triacetate, and/or ethylcellulose.

[0037] Traditional immersion phase inversion process can be applied to solutions that contain a mixture of a block copolymer and a conventional homo-polymer. The resulting membranes may have an “organized surface structure,” but do not quantify porosity, pore sizes or specific level of uniformity.

[0038] Porous membranes with extreme uniform surface pore structures can be obtained by combining self-assembly of amphiphilic block copolymers with the traditional phase inversion process used to make membranes. For a multiple block copolymer, the resulting surface pore structure can be tailored by controlling process conditions such as block copolymer solution composition and evaporation time prior to immersion.

[0039] Formation of an isoporous support can be achieved by using a solution containing a block copolymer with at least one hydrophobic block (majority block) and one hydrophilic block (minority block). The solvent typically is a mixed solvent where the more volatile solvent has the higher affinity for the hydrophobic block. After formation of a thin film of

the solution, a short solvent evaporation time starts self-assembly of the block copolymer at the surface, with the hydrophobic blocks as the continuous phase and the hydrophilic blocks as the dispersed phase. The subsequent water immersion step may orientate and lock in the self-assembly process over the entire membrane surface area and that the phase containing the hydrophilic blocks combines with the water to form micelles. This process only occurs in the region just below the evaporation interface of the film and below this region the isoporous structure transitions into the random porous structure typical of conventional phase inversion membranes. The final structure is obtained through a drying step, which removes the water as well as the residual solvents. The pores in the top surface are the remnants of the micelles from which the water has been removed.

[0040] The parameters that govern the formation of isoporous membranes include parameters that determine whether self-assembly occurs as reported by Rangou et al. These parameters include, but are not limited to, the chemical nature and volume fraction of the blocks in the block copolymer, the total molecular weights of the two blocks, the nature, weight fraction and volatility of the solvents used to dissolve the block copolymer, and the time period allowed for evaporation of the solvents prior to immersion of the block copolymer solution into the aqueous precipitation bath. Other parameters to be controlled are: concentration the block copolymer solution viscosity, humidity during the evaporation step, and temperature of the block copolymer solution and the precipitation bath.

[0041] The isoporous support membranes may be prepared in flat sheet format or in hollow fiber or tubular format, and may be housed in any convenient type of housing and separation unit. Preferably, the isoporous support membranes may be prepared in flat-sheet form and housed in spiral-wound modules. Flat-sheet membranes may also be mounted in plate-and-

frame modules or in any other way. If the membranes are prepared in the form of hollow fibers or tubes, they may be potted in cylindrical housings or otherwise.

[0042] The membrane separation unit may comprise one or more membrane modules. The number of membrane modules required will vary according to the volume of gas to be treated, the composition of the feed gas, the desired compositions of the permeate and residue streams, the operating pressure of the system, and the available membrane area per module. Systems may contain as few as one membrane module or as many as several hundred or more modules. The modules may be housed individually in pressure vessels. Alternatively, the modules may be mounted together with multiple elements in a sealed housing of appropriate diameter and length.

[0043] The membrane separation unit may be operated in any number of different modes, such as cross-flow, co-current, counter-current and with or without addition of an external sweep stream.

[0044] Conventional supports for composite membranes are made by the phase inversion process. This process produces surfaces with a wide distribution in pore size and pore location. Figure 6 shows a high resolution scanning electron microscope (SEM) photo of a support produced via phase inversion, suggesting that composite membranes made with conventional supports suffer from restricted permeances that are even below the permeances predicted by the CFD analysis.

[0045] Porous supports with uniform pore size can be produced using the track etching technique and/or purchased from various sources, including GE Healthcare, Pa, USA. These supports have a uniform pore size, but not a uniform pore distribution and have low surface porosities. Zhu et al reported that composite membranes produced with these porous supports

exhibit significant restriction by the support. Therefore, these supports are rarely used in any commercial composite membranes.

[0046] Ceramic and inorganic porous materials can be formed into porous structures with uniform pore sizes and uniform pore distributions. These materials are orders of magnitude more expensive than polymeric supports. Therefore, these supports are rarely used in any commercial composite membranes.

[0047] Disclosed herein is the utilization of a self-assembly based membrane as an isoporous support membrane for the preparation of improved composite membranes. The separation performance of these composite membranes is determined by the selective material, whereas the isoporous support membrane makes it possible to utilize selective layer thicknesses substantially below one micron and to obtain permeances that exceed the permeances of composite membranes prepared with traditional supports.

[0048] The permeance of composite membranes is improved by inserting a gutter layer in between the support membrane and the primary selective layer. The gutter layer consists of a material that is substantially more permeable, but less selective, than the primary selective layer material. The resulting composite membrane has improved permeances but is less selective than the primary selective layer material.

[0049] In some embodiments, a composite membrane having improved performance, such as high permeability and selectivity, comprises a selective nonporous layer, a gutter layer, and an isoporous support layer. In some embodiments, the isoporous support layer is sufficient to provide improved performance and maintain adequate support, without a gutter layer.

[0050] The isoporous support layer may comprise one or more amphiphilic block copolymers, one or more homo-polymers, one or more random block copolymers, or

combinations thereof. For instance, the isoporous support layer may comprise one or more amphiphilic block copolymers and one or more homo-polymers.

[0051] The isoporous support layer may be manufactured to comprise more than one layer. In some cases, the one or more layers comprise same polymer make up. In some cases, the one or more layers differ in polymer make up. For instance, the top surface and its adjacent layer may comprise an amphiphilic block copolymer whereas a subsequent layer comprises a different type of polymer.

[0052] To make high quality composite membranes it is required that the transport resistance of the support membrane is at least one order of magnitude smaller than the transport resistance of the selective layer. This is because the support membrane resistance essentially is nonselective. This requirement is easily met in most cases because transport in the porous support is by convection whereas transport in the nonporous selective layer is by diffusion, which is much slower.

[0053] As the selective layers of composite membranes become thinner, the membrane permeances may fall below the predictions of the Membrane Permeance equation:

$$\text{Membrane Permeance} = \frac{1}{\text{Membrane Resistance}} = \frac{\text{Selective Layer Permeability}}{\text{Selective Layer Thickness}} \quad (1)$$

In this equation the permeability is expressed in the Barrer unit (10^{-10} cc(STP).cm/cm²/s/cmHg), the selective layer thickness is expressed in micron (10^{-6} m), and the permeance is given in the “gas permeation unit” (10^{-6} cc(STP)/cm²/s/cmHg or GPU). Therefore, a layer with a thickness of one micron and with a permeability of 1 Barrer will yield a permeance equal to one GPU.

[0054] Table 1 and Figure 1 give performance data for nine composite membranes consisting of a polydimethylsiloxane (PDMS) selective layer coated on a polyetherimide support

membrane. The selective layer was applied through a solution dip coating process that avoids penetration of the coating solution into the pores of the support, followed by removing the solvent via evaporation. Each composite membrane has a different thickness of the PDMS layer as was measured with a Filmetrics F20 elipsometer. The permeance of carbon dioxide was measured for all membranes and was plotted in Figure 1 versus the PDMS thickness. The permeability of carbon dioxide in PDMS was 3,300 Barrer and the solid line in Figure 1 represents the permeances as predicted by equation (1). At about 5 micron thickness the permeance started to fall less than predicted. For example, at 1.0 micron thickness the permeance was about 1.6 times less than expected, and at 0.1 micron thickness the permeance was about 6 times less than expected.

Table 1. Carbon Dioxide permeance of composite membranes with PDMS top layer of different thicknesses.

PDMS (micron)	CO2 (gpu)
0.087	5900
0.16	4700
0.23	4900
0.43	3300
0.85	2200
3.2	910
6.5	480
12	280

[0055] Preferably, the thickness of the selective layer is less than 5 micron. The thickness of the selective layer may be less than 2 micron. The thickness of the selective layer may be less than 1 micron. The thickness of the selective layer may be less than 0.1 micron. The thickness of the selective layer may be in the range of between 0.1 and 5 micron.

[0056] The composite membranes all have high CO₂/N₂ selectivity, indicating that the reduced permeances are not due to the presence of the support membrane, which may create

additional resistance to transport. Because support membranes are porous and typically have no significant gas selectivity, which means that any contribution of the support membrane resistance to the composite membrane permeance is likely to reduce the selectivity of the composite membrane.

[0057] However, there is an alternative mechanism that does not reduce the selectivity, and does not rely on the support to have any resistance to transport, but maintain its ability to reduce the permeance of a composite membrane.

[0058] The nonporous part of the support membrane typically has negligible permeability, which means that molecules permeating the non-porous layer can only exit through the porous part of the support. Figure 2 shows a cross-section of the idealized structure of a composite membrane, showing the top layer and the upper part of the porous support with one surface pore.

[0059] Lonsdale et al recognized that this restriction will increase the pathway length for diffusion and will increase the velocity of the molecules near the pore opening (the “funnel” effect). These two effects combined give the top layer a permeance that is smaller than the intrinsic permeance of the layer defined in equation (1). However, Lonsdale et al did not provide accurate magnitude of this effect.

[0060] More recently, Ramon et al have used Computational Fluid Dynamics to analyze the effect. The support membranes used in these simulations have an “ideal” structure, consisting of a uniform distribution of pores of equal radius. The CFD simulations demonstrated that the limited surface porosity of the support membrane reduces the effective permeance and that this restrictive effect increases with decreasing selective layer thickness. Wijmans and Hao performed additional CFD simulations, and were able to accurately correlate the CFD results with the surface porosity of the support membrane and with the

relative thickness of the selective layer, defined as the selective layer thickness divided by the radius of the pores in the support membrane surface. This correlation allows calculation of the reduction in permeance without needing to do more CFD simulations. Examples of permeances predicted for uniform pore size and location through the CFD analysis are given in Figure 3 for different surface porosities and different surface pore radii.

[0061] Support membranes with higher surface porosity and with small surface pores sizes can reduce permeance restriction (Figure 3). An important and unexpected result from additional CFD simulations, performed by Hao et al for non-uniform pore sizes and non-uniform pore distributions, is that deviations from uniformity even more reduces the permeance of the composite membrane. Most notably, at constant average porosity and constant average pore size, the permeance is significantly smaller if the pores are not evenly distributed over the surface area. The permeance also is smaller if the pores are not uniform in size.

[0062] The isoporous support membrane may have a surface porosity of between 1%-99%. The isoporous support membrane may have a surface porosity of at least 2%. The isoporous support membrane may have a surface porosity of at least 5%. The isoporous support membrane may have a surface porosity of at least 10%. Preferably, the isoporous support membrane may have a surface porosity of at least 20%.

[0063] The isoporous support membrane may have surface pores having a diameter below 1 micron. The isoporous support membrane may have surface pores having a diameter below 0.3 micron. Preferably, the isoporous support membrane may have surface pores having a diameter below 0.1 micron. More preferably, at least 30% of the isoporous support membrane may have surface pores having a diameter of the size between 0.01-1 micron.

[0064] A non-uniform distribution of surface pores suggests that the surface contains areas with a porosity above the average porosity value and areas with a porosity below the average. The CFD analysis shows that a decrease in porosity reduces the composite membrane permeance to a greater extent than an equivalent increase in porosity will increase the permeance. This can be seen from the shape of the permeance versus porosity lines in Figure 4 and provides the fundamental reason for why a non-uniform distribution is not desired in a support for a composite membrane.

[0065] Figure 5 shows four different pore distributions, all with the same average surface porosity of 5%. Distributions (a) and (d) are uniform square distributions of pores; the pore radius in (d) is double the radius in (a), and both are covered by the correlation disclosed herein. Distributions (b) and (c) are not uniform distributions, but are also not random and form repeatable patterns for which CFD simulations can be performed easily. Figure 5 gives the relative permeances for the four distributions, as well as the predicted CO₂ permeances if the top layer is a 0.5 micron thick PDMS layer. The sequence (a) to (b) to (c) demonstrates conclusively that a less uniform distribution results in lower permeances. Distribution (d) is the logical end point of the sequence and has the lowest permeance. In distribution (d) every set of four pores has merged into one pore with double radius, which makes it a fully uniform distribution.

[0066] Uniform distributions in a two dimensional surface are either in a square or in a hexagonal configuration. In the square configuration, the distance between a pore and each of its four closest neighboring pores is the same. In the hexagonal configuration, the distance between a pore and each of its six closest neighboring pores is the same. The same will not be true for a non-uniform distribution and this offers a way to quantify the difference between “non-uniform” and “uniform”. Using the web-based random generator www.random.org to

generate the coordinates of each pore within a square grid, ten different random distributions of 100 pores are created. The distance of each pore to its fourth-closest neighbor, as well as the distance to its closest neighbor, and the ratio of the larger distance to the smaller distance are calculated. In any uniform distribution, this ratio is equal to one for every pore.

[0067] Figure 7 shows the ratios for the ten different random distributions; for each distribution the pores are sorted from the smallest ratio (which cannot be smaller than one) to the largest ratio. The difference between the random distributions and the uniform distribution wherein the ratio is at least 1 for all pores in the uniform distribution. In some cases, the ratio is at least 2 for all pores in the uniform distribution. In some cases, the ratio is at least 3 for all pores in the uniform distribution. In some cases, the ratio is at least 5 for all pores in the uniform distribution. In some cases, the ratio is at least 10 for all pores in the uniform distribution. Preferably, the ratio is at a range between 0.1-20 for all pores in the uniform distribution.

[0068] Preferably, the distances between one surface pore and its four closest neighboring surface pores substantially fulfill the condition that the ratio of the maximum distance to the minimum distance is smaller than 10. The distances between one surface pore and its four closest neighboring surface pores substantially fulfill the condition that the ratio of the maximum distance to the minimum distance is smaller than 3. The distances between one surface pore and its four closest neighboring surface pores substantially fulfill the condition that the ratio of the maximum distance to the minimum distance is smaller than 2.

[0069] Preferably, the diameters of the surface pores substantially fulfill the condition that the ratio of the maximum diameter to the minimum diameter is smaller than 10. The diameters of the surface pores substantially fulfill the condition that the ratio of the maximum diameter to the minimum diameter is smaller than 5. The diameters of the surface pores

substantially fulfill the condition that the ratio of the maximum diameter to the minimum diameter is smaller than 3. The diameters of the surface pores substantially fulfill the condition that the ratio of the maximum diameter to the minimum diameter is smaller than 2.

[0070] The density of the surface pores of the isoporous support may be between 10^7 pores/cm²- 10^{15} pores/cm². Preferably, the density of the surface pores of the isoporous support is at least 10^8 pores/cm². The density of the surface pores of the isoporous support is at least 10^{10} pores/cm². The density of the surface pores of the isoporous support is at least 10^{12} pores/cm².

WHAT IS CLAIMED IS:

1. A composite membrane for separating components in a fluid mixture comprising an isoporous support layer for supporting a nonporous selective layer of a separating membrane, the isoporous support layer comprising:
 - (a) one or more amphiphilic block copolymer; and
 - (b) a plurality of surface pores having substantially uniform distribution, wherein a ratio of the maximum distance to the minimum distance between a surface pore and its closest four neighboring pores is smaller than 3; or
 - (c) a plurality of surface pores having substantially uniform size, wherein a ratio of the maximum diameter to the minimum diameter is smaller than 5; or
 - (d) a plurality of surface pores having a density of at least 10^8 pores/cm².
2. The composite membrane of claim 1, wherein the ratio of the maximum distance to the minimum distance distances between one surface pore and its closest four neighboring surface pores is smaller than 2.
3. The composite membrane of claim 1, wherein the nonporous selective layer is in contact with the isoporous support layer.
4. The composite membrane of claim 1, further comprising a gutter layer between the nonporous selective layer and the isoporous support layer.
5. The composite membrane of claim 1, wherein the maximum diameter to the minimum diameter of the surface pores is smaller than 3.
6. The composite membrane of claim 1, wherein the maximum diameter to the minimum diameter of the surface pores is smaller than 2.

7. The composite membrane of claim 1, wherein the surface pores have a density of at least 10^{12} pores/cm².
8. The composite membrane of claim 1, wherein the one or more amphiphilic block copolymer comprises a structure of the form selected from X-Y, X-Y-X, and X-Y-Z.
9. The composite membrane of claim 8, wherein X, Y, and Z are selected from a group of polymers consisting of polystyrene, poly-4-vinylpyridine, poly-2-vinylpyridine, polybutadiene, polyisoprene, poly(ethylenestat-butylene), poly(ethylene-alt-propylene), polysiloxane, polyalkyleneoxide, poly-ε-caprolactone, polylactide, polyalkylmethacrylate, polymethacrylic acid, polyaklylacrylate, polyacrylic acid, polyhydroxyethylmethacrylate, polyacrylamide, poly-N-alkylacrylamide, polysulfone, polyethersulfone, polyphenylsulfone, polyetherimide, polyvinylidene fluoride, polyacrylonitrile, cellulose diacetate, cellulose triacetate, and ethylcellulose.
10. The composite membrane of claim 1, further comprising at least one homo-polymer.
11. The composite membrane of claim 1, further comprising at least one random block copolymer.
12. The composite membrane of claim 1, wherein the selective layer have a thickness of less than 1 micron.
13. The composite membrane of claim 1, wherein the isoporous support comprises a first amphiphilic block copolymer layer and a second amphiphilic block copolymer layer.

14. The composite membrane of claim 1, wherein the isoporous support layer has a surface porosity of at least 5%.
15. The composite membrane of claim 1, wherein the isoporous support layer has a surface porosity of at least 10%.
16. The composite membrane of claim 1, wherein the isoporous support layer has a surface porosity of at least 20%.
17. The composite membrane of claim 1, wherein at least 30% of the surface pores of the isoporous support layer have a diameter below 0.1 micron.
18. The composite membrane of claim 1, wherein the fluid mixture is a gas or vapor mixture.
19. The composite membrane of claim 1, wherein the fluid mixture is a liquid mixture.
20. The composite membrane of claim 1, wherein the fluid mixture comprises at least component A and component B.
21. The composite membrane of claim 20, wherein component A is carbon dioxide.
22. The composite membrane of claim 20, wherein component A is helium.
23. The composite membrane of claim 20, wherein component A is hydrogen.
24. The composite membrane of claim 20, wherein component A is water.
25. The composite membrane of claim 20, wherein component A is oxygen.
26. The composite membrane of claim 20, wherein component A is nitrogen.
27. The composite membrane of claim 20, wherein component A is a hydrocarbon.
28. The composite membrane of claim 20, wherein component A is sulfur dioxide.
29. The composite membrane of claim 20, wherein component A is hydrogen sulfide.
30. A process for separating two components, A and B, of a fluid mixture, comprising:

(a) passing the fluid mixture across a separation membrane having a feed side and a permeate side, the separation membrane comprises a nonporous selective layer and an isoporous support layer, wherein the isoporous support layer comprises an amphiphilic block copolymer and contains surface pores having substantially uniform distribution, wherein a ratio of the maximum distance to the minimum distance between a surface pore and its four closet neighboring pores is smaller than 3;

(b) providing a driving force for transmembrane permeation;

(c) withdrawing from the permeate side a fluid permeate stream enriched in component A compared to the fluid mixture; and

(d) withdrawing from the feed side a fluid residue stream depleted in component A compared to the fluid mixture.

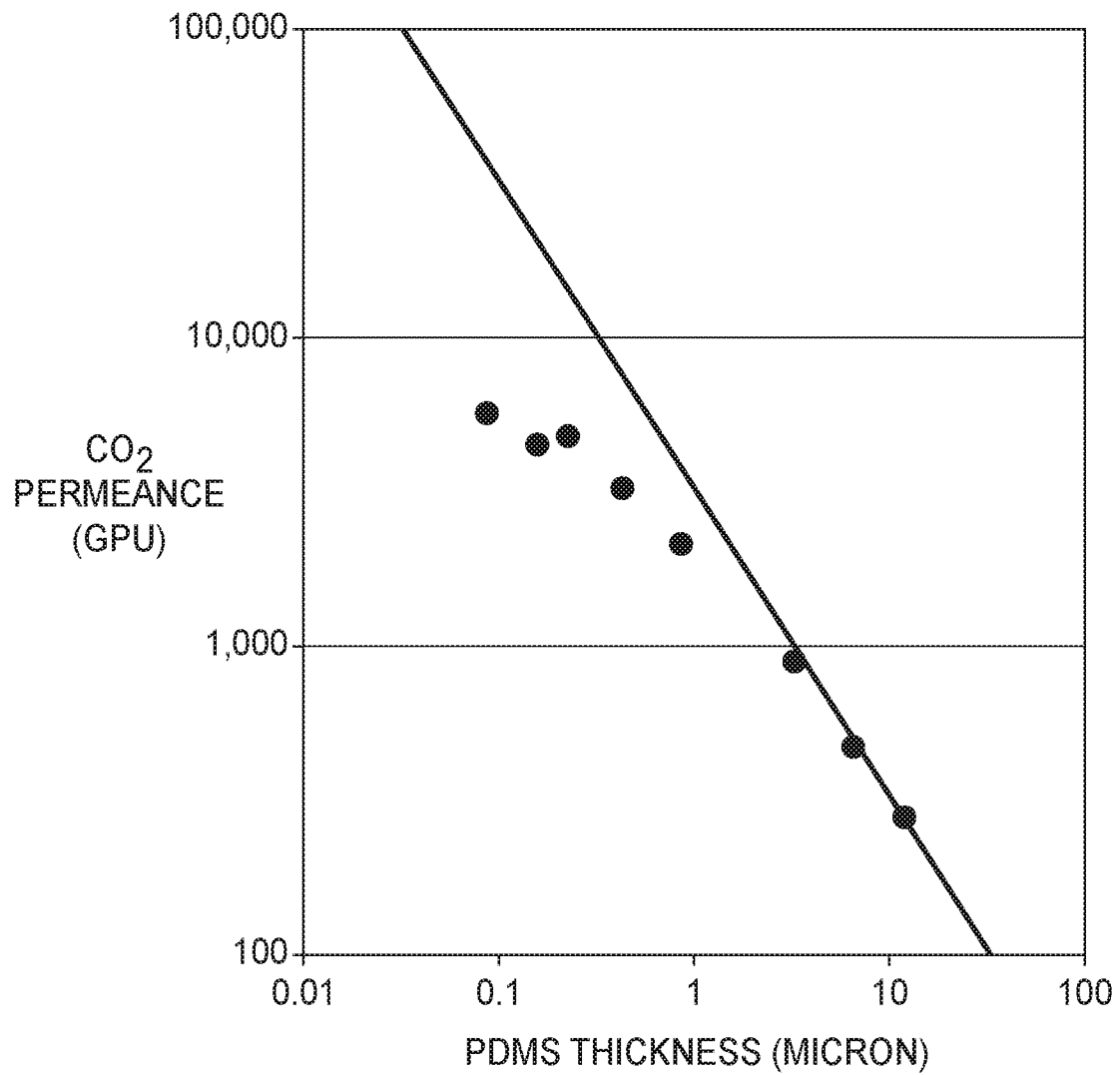


Figure 1

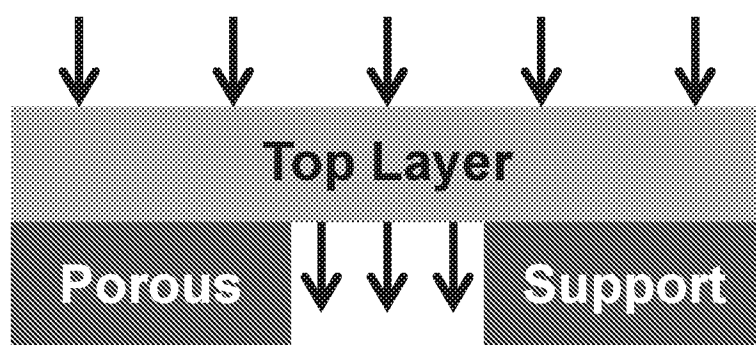


Figure 2

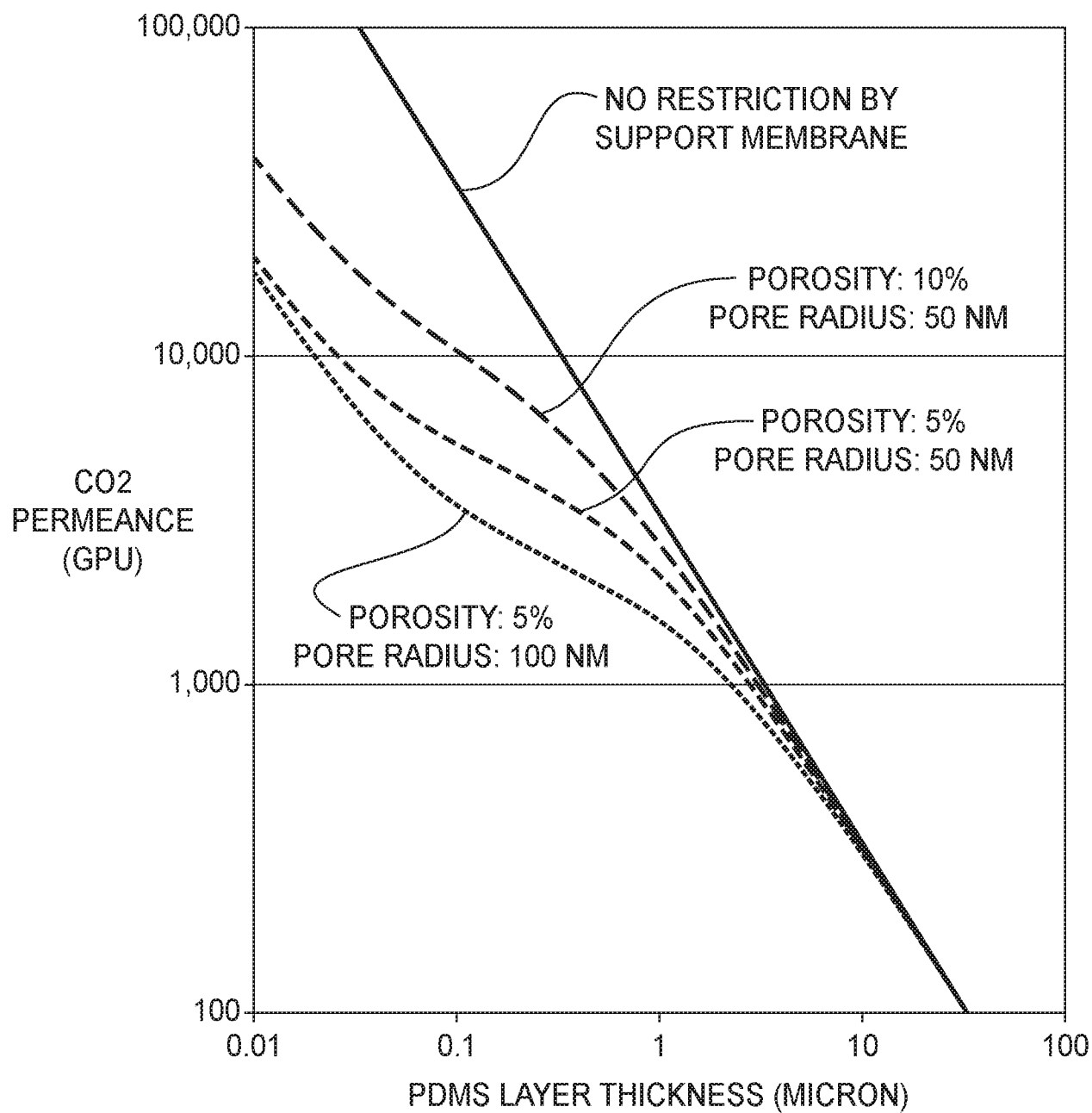


Figure 3

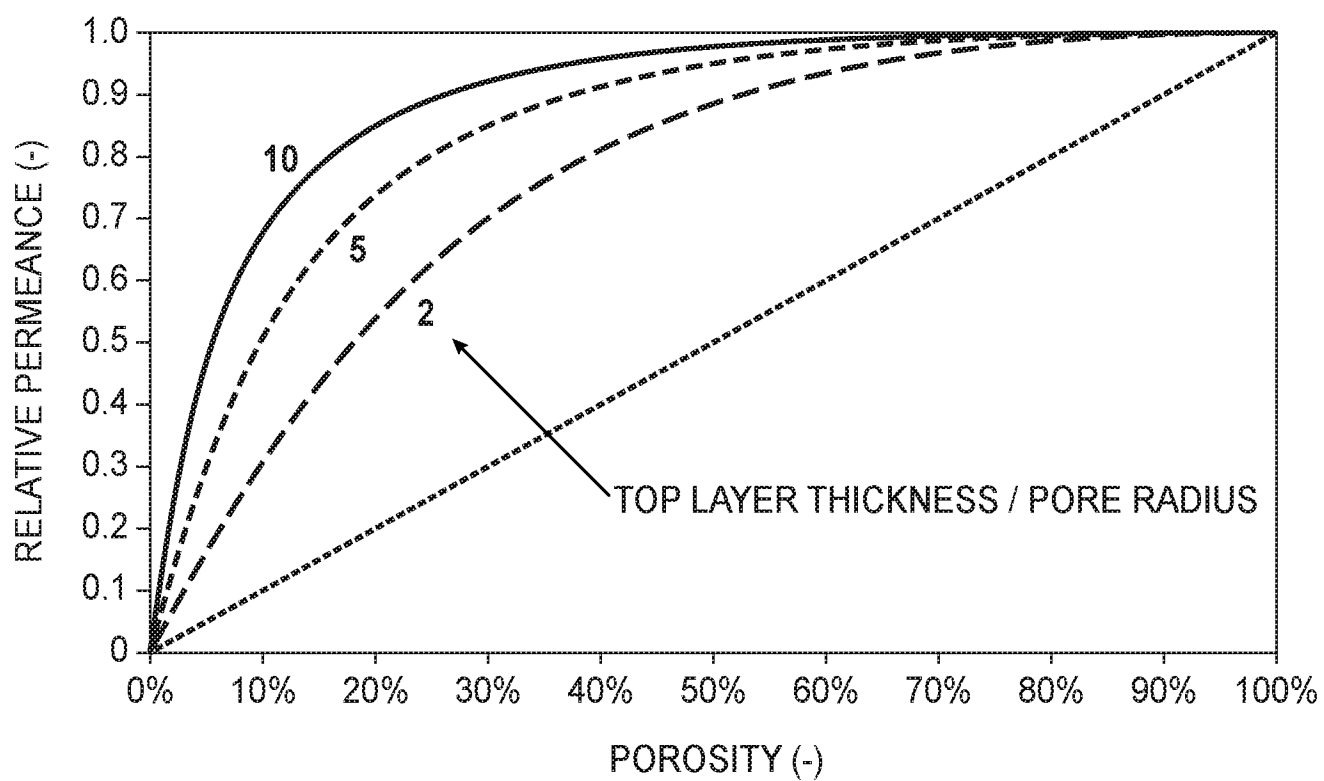
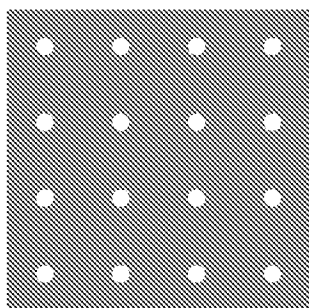
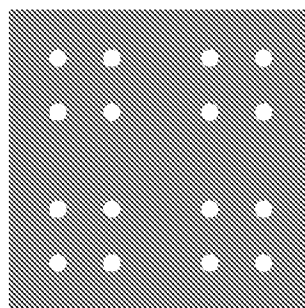


Figure 4



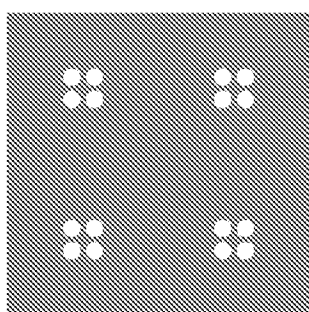
(A)

RELATIVE PERMEANCE = 0.310
CO₂ PERMEANCE = 2,050 GPU



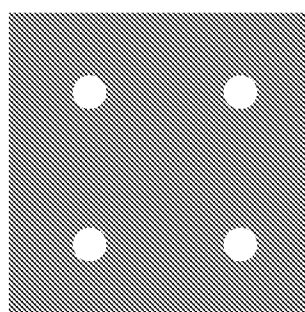
(B)

RELATIVE PERMEANCE = 0.290
CO₂ PERMEANCE = 1,910 GPU



(C)

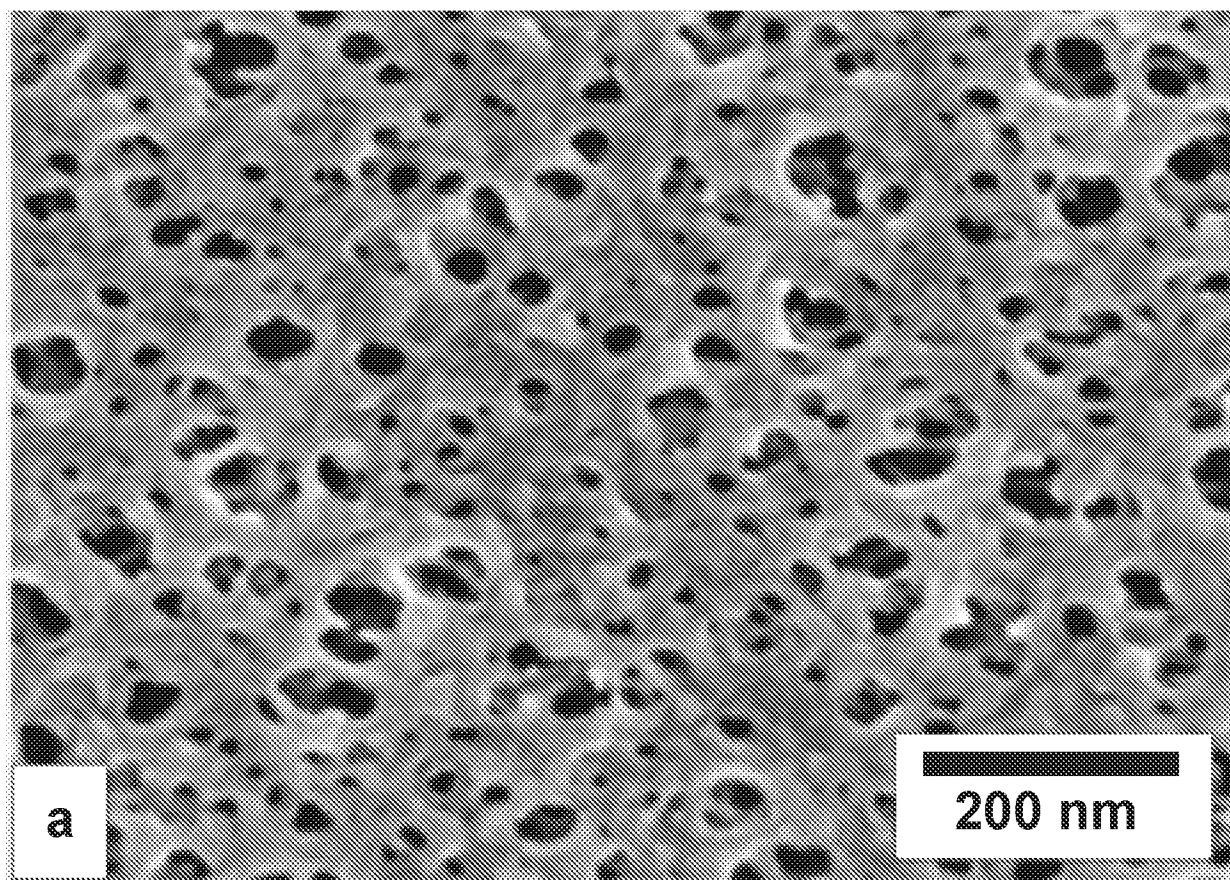
RELATIVE PERMEANCE = 0.257
CO₂ PERMEANCE = 1,700 GPU



(D)

RELATIVE PERMEANCE = 0.181
CO₂ PERMEANCE = 1,200 GPU

Figure 5



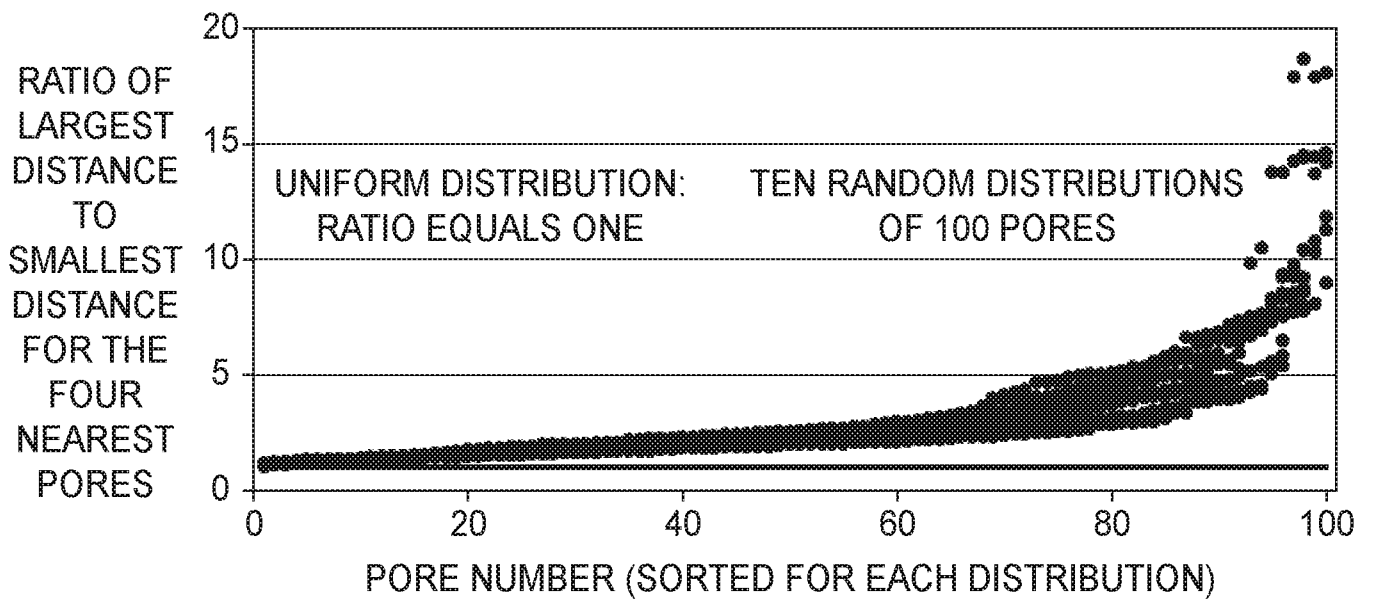


Figure 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/042873

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D69/02 B01D53/22 B01D69/10 B01D71/80 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	J.G. WIJMANS ET AL: "Influence of the porous support on diffusion in composite membranes", JOURNAL OF MEMBRANE SCIENCE, vol. 494, 1 November 2015 (2015-11-01), pages 78-85, XP055626390, NL ISSN: 0376-7388, DOI: 10.1016/j.memsci.2015.07.047 the whole document ----- -/--	1-30
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 2 October 2019		Date of mailing of the international search report 10/10/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Hennebrüder, K

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2019/042873

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	ROBERTO NISTICÒ: "Block copolymers for designing nanostructured porous coatings", BEILSTEIN JOURNAL OF NANOTECHNOLOGY, vol. 9, 29 August 2018 (2018-08-29), pages 2332-2344, XP055626415, DOI: 10.3762/bjnano.9.218 abstract Section: Critical considerations on p. 2340 to p. 2341 2; p. 2337 left col. 1; figures 1b, 6,7	1-30
Y	----- SUZANA PEREIRA NUNES: "Block Copolymer Membranes for Aqueous Solution Applications", MACROMOLECULES, vol. 49, no. 8, 26 April 2016 (2016-04-26), pages 2905-2916, XP055593819, WASHINGTON, DC, UNITED STATES ISSN: 0024-9297, DOI: 10.1021/acs.macromol.5b02579 abstract Introduction 2, Final remarks	1-30
Y	----- MARYAM RADJABIAN ET AL: "Influence of Solvent on the Structure of an Amphiphilic Block Copolymer in Solution and in Formation of an Integral Asymmetric Membrane", ACS APPLIED MATERIALS & INTERFACES, vol. 9, no. 37, 15 February 2017 (2017-02-15), pages 31224-31234, XP055626428, US ISSN: 1944-8244, DOI: 10.1021/acsami.6b15199 abstract; figures 2,3,5 p. 31231	1-30
Y	----- AYSE ASATEKIN ET AL: "Self-Assembled Polymer Nanostructures for Liquid Filtration Membranes: A Review", NANOSCIENCE AND NANOTECHNOLOGY LETTERS, vol. 7, no. 1, 1 January 2015 (2015-01-01), pages 21-32, XP055626420, US ISSN: 1941-4900, DOI: 10.1166/nnl.2015.1930 abstract page 25, right-hand column, paragraph 2 -----	1-30