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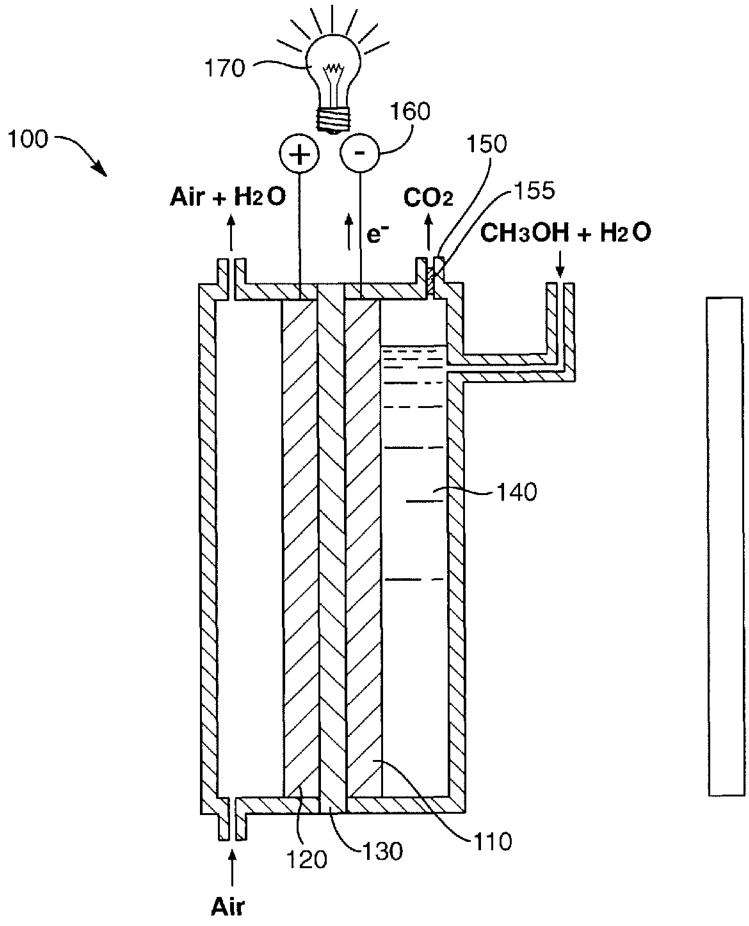
(54) Title: FUEL CELL VENT



(57) Abstract: A fuel cell including a carbon dioxide vent and a vent membrane configured to selectively allow the passage of carbon dioxide gas from within the fuel cell. The vent membrane may include organic hydrocarbons alone or with various additives.

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FUEL CELL VENT

Technical Field

[0001] The present disclosure relates generally to the field of fuel cells. More specifically, the present disclosure relates to fuel cells with improved carbon dioxide vents.

Brief Description of the Drawings

[0002] Understanding that drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with specificity and detail through the use of the accompanying drawings as listed below.

[0003] FIG. 1 is a cross section of a fuel cell with a carbon dioxide vent.

[0004] FIG. 2 shows the skeletal formula of 1,9-decadiene and 1,6-divinyl perfluorohexane.

[0005] FIG. 3 shows the relative permeability and selectivity of a PDMS membrane with added 1,6-divinyl perfluorohexane.

[0006] FIG. 4 shows the relative permeability and selectivity of a PDMS membrane with added 1,9-decadiene.

[0007] FIG. 5 shows the relative permeability and selectivity of a PTMSP membrane with added 1,9-decadiene.

[0008] FIG. 6 shows the relative permeability and selectivity of a PTMSP membrane with added 1,6-divinyl perfluorohexane.

Detailed Description

[0009] It will be readily understood that the components of the embodiments as generally described and illustrated in the figures herein could be arranged and designed in a wide variety of different configurations. Thus, the following more detailed description of various embodiments, as represented in the figures, is not intended to limit the claim scope, but is merely representative of various embodiments. While the various aspects of the embodiments are presented in drawings, the drawings are not necessarily drawn to scale unless specifically indicated.

[0010] As those of skill in the art will appreciate, the principles disclosed herein may be applied to and used with a variety of fuel cell systems including an inorganic or organic fuel cell, direct methanol fuel cell (DMFC), reformed methanol fuel cell, direct ethanol fuel cell, polymer electrolyte membrane fuel cell (PEMFC), microbial fuel cell, reversible fuel cell, formic acid fuel cell, and the like. Furthermore, the present invention may be used in a variety of applications and with fuel cells of various sizes and shapes. For purposes of example only, and not meant as a limitation, the embodiments disclosed herein may be used for electronic battery replacement, mini and microelectronics, car engines, power plants, and as an energy source in many other devices and applications.

[0011] With reference to the accompanying figures, particular embodiments will now be described in greater detail. As shown by FIG. 1, a fuel cell 100 may include an anode 110 and a cathode 120 separated by a proton-exchange membrane (PEM) 130. The anode 110 may be disposed on one side of the PEM 130 and the cathode 120 disposed on the opposite side of the PEM.

[0012] In the fuel cell 100, a fuel 140 is oxidized at the anode 110, in the presence of a catalyst (*i.e.*, Pt-Ru) and water (H_2O), to produce electrons (e^-), protons (H^+), and carbon dioxide (CO_2). The fuel cell 100 may include a vent 150 to allow the escape of the CO_2 gas. The vent 150 may include a vent membrane 155 designed to provide selective venting of the CO_2 gas. The electrons flow from the anode 110 to the cathode 120 through an external circuit 160 to deliver electrical energy to an attached electrical device or storage device 170. Meanwhile, the protons pass through the PEM 130 and combine with oxygen (O_2) to form water at the cathode 120. The fuel and water can be supplied to the anode through a separate port, as shown by FIG. 1, or may be supplied in an enclosed container holding all the fuel to be used. Ambient air and/or oxygen may flow into the cathode chamber through forced or natural convection. The size of the air-providing inlet and exit may be greatly expanded so as to increase the air flow rate.

[0013] One example of a fuel cell is a direct organic fuel cell which may use hydrocarbon fuels, such as diesel, methanol, ethanol, and chemical hydrides. One embodiment may include a direct methanol fuel cell (DMFC), a type of proton-exchange fuel cell where the methanol fuel is fed directly to the fuel cell. The anode and cathode reactions in a DMFC can be expressed as follows:

$$\text{Anode: } CH_3OH + H_2O \xrightarrow{\text{Pt-Ru}} CO_2 + 6H^+ + 6e^-$$

$$\text{Cathode: } 6H^+ + 6e^- + 1.50_2 \xrightarrow{\text{Pt}} 3H_20$$

[0014] During the oxidation of methanol on the anode side, the production of CO_2 increases the pressure inside the anode fuel compartment. The increasing pressure inside the fuel cell may cause fuel cross-over and decrease the durability of the fuel cell. To avoid this increase in internal pressure, the fuel cell may include an escape vent which allows passage of CO_2 gas generated by the reaction inside the fuel cell. Along with CO_2, the vent may allow fuel to escape which may decrease the efficiency of the fuel cell. To avoid this problem, a selectively permeable membrane may be used in the vent to favor the passage of the CO_2 while limiting the escape of unused fuel. For example, the CO_2 vent membrane may be composed of a hydrophobic material, such as polysiloxane homopolymers such as poly-(diakyl) siloxane, poly-(diethyl) siloxane, poly-(dimethyl) siloxane (PDMS). Other polysiloxane polymers may include poly-(diphenyl) siloxane, poly-(perfluoroalkyl) siloxane, poly-(diglycidoxy) siloxane, poly-(vinylbenzyl) siloxane, poly-(methylmethacryloxy) siloxane, poly-(diaminoalkyl) siloxane, poly-(divinylalkyl) siloxane, and poly-(dichloroalkyl) siloxane.

[0015] Alternatively, the CO_2 vent membrane may be composed of a poly (trialkylsilyl-alkyne) such as poly (trimethylsilyl-1-propyne) (PTMSP) or poly (triethylsilyl-1-propyne) (PTMSP).

[0016] Measuring the selectivity of a CO_2 vent membrane is determined by dividing the permeability of CO_2 through the vent membrane by the permeability of methanol through the vent membrane. The hydrophobicity of the PDMS or PTMSP membranes may be modified through the use of additives to reduce the loss of unused fuel and favor release of CO_2 gas through the vent membrane. The additives may include 1,9-decadiene, 1,6-divinyl perfluorohexane, 1,6-permethyl hexane, 3,3-dimethyl butene, 1,1,1-trifluoro propene, 3,3-dimethyl petn-1,4-diene, and other compounds.

[0017] In one example, the hydrophobic additive 1,6-divinyl perfluorohexane, as shown in FIG. 2, may be added in a range of approximately 10% to 35% by weight to a PDMS solution before casting the membrane to improve the CO_2 selectivity of the membrane. As shown by FIG. 3, and summarized in TABLE 1, an addition of 23%

by weight of 1,6-divinyl perfluorohexane to PDMS yielded a CO_2 vent membrane selectively of approximately 3.33. In yet another example, 1,9-decadiene (FIG. 2) may be added to a PDMS solution in a range of approximately 10% to 35% by weight to optimize membrane selectivity. As shown by FIG. 4 and TABLE 1, 30% by weight of 1,9-decadiene, was added to PDMS giving a CO_2 vent membrane selectivity of 3.88.

TABLE 1

Selectivity Ratio of PDMS Membrane

	PDMS	PDMS	PDMS
Additive	None	1,6-divinyl perlfuoro-hexane	1,9-decadiene
Wt% of additive	0	23%	30%
Pco2	9.30E-10	1.50E-09	3.30E-09
Pmeoh	4.80E-10	4.50E-10	8.50E-10
Selectivity Ratio	1.94	3.33	3.88

[0018] In another embodiment, PTMSP may be used with or without additives to give a higher selectivity for a CO_2 vent membrane. The CO_2 selectivity of a PTMSP membrane alone is approximately 2.48. Alternatively, long-chain alkenes may be mixed with the PTMSP material before casting to improve CO_2 selectivity.

[0019] With reference to TABLE 2 and FIG. 5, the addition of about 14% by weight of 1,9-decadiene to the PTMSP membrane increased the CO_2 vent selectivity to approximately 5.26. With continued reference to FIG. 5, the addition of about 38% by weight of 1,9-decadiene yields a CO_2 selectivity of approximately 7.81. The addition of about 50% by weight of 1,9-decadiene yielded a CO_2 selectivity of approximately 9.78. This is a 297% improvement in CO_2 selectively over a membrane with PTMSP alone and a 404% improvement over the PDMS membrane.

TABLE 2

Selectivity Ratio of PTMSP Membrane

	PTMSP	PTMSP	PTMSP	PTMSP
Additive	none	1,9-decadiene	1,9-decadiene	1,9-decadiene
Wt% of additive	0%	14%	38%	50%
PCO_2	1.25E-09	1.88667E-09	1.56E-09	1.78E-09
PMeOH	5.04E-10	3.585E-10	2.00E-10	1.82E-10
Selectivity Ratio	2.48	5.26	7.81	9.78

[0020] As shown by FIG. 6, the addition of 1,6-divinyl perfluorohexane to PTMSP also increases the CO_2 vent membrane selectivity. The addition of approximately 14% by weight of 1,6-divinyl perfluorohexane yielded a CO_2 selectivity of greater than 5. The addition of approximately 38% by weight of 1,6-divinyl perfluorohexane yielded a CO_2 selectivity of about 8. The addition of about 50% by weight of 1,6-divinyl perfluorohexane yielded a CO_2 selectivity of greater than 9.

<u>Methods of Preparing Membranes</u>

PDMS Membranes

[0021] A two-part silicone elastomer (base and curing agent) may be used to prepare PDMS membranes. One example of a silicone elastomer is SYLGARD®, available from Dow Corning. The elastomer curing agent is added to the base in the ratio 1:10 (weight %). The mixture may be mechanically stirred for approximately 30 minutes to ensure complete mixing. This is followed by a one-hour degassing step by pulling a vacuum (such as 5 in.Hg, Isotemp Vacuum Oven Model 281A) operating at room temperature. During the stirring process, and before curing the PDMS membrane, 1,9-decadiene, such as is available from Alfa Aesar, or 1,6-divinyl perfluorohexane (97%), such as is abailable from Matrix Scientific, are added as desired. Once the mixture is degassed, it is spin coated on a Teflon® substrate to form a thin film. The membrane may then be cured at approximately 100 °C for about 1 hour. The cured membrane is then peeled off from the substrate and tested for CO_2 selectivity.

PTMSP Membranes

[0022] PTMSP, available from Gelest, Inc. is dissolved in toluene at room temperature and is mixed for approximately one week using rotary mixers. The amount of solvent in the polymer is adjusted to obtain a desired viscosity of the polymer mixture to facilitate easy spin coating. During the production of the PTMSP membrane, 1,9-decadiene, available from Alfa Aesar, or 1,6-divinyl perfluorohexane (97%), available from Matrix Scientific, is added in desired weight ratios during mixing and prior to curing of the base polymer mixture. Thin films of the membrane are then spin coated on a Teflon® substrate. Slow evaporation of the solvent is achieved by placing the cast membrane under approximately 75 PSI gauge pressure while curing at about 60 °C for approximately 3 hours. The resulting membranes are removed from the substrate for testing.

[0023] A fuel cell according to various embodiments disclosed herein may be configured to be stable in various environmental conditions, such as temperature extremes and humidity while maintaining hermeticity and shock and vibration resistance. A fuel cell according to various embodiments may also be configured with the desired input and output connections for a variety of electronic devices. Moreover, the fuel cell may be sized, shaped, and packaged to meet the requirements of the desired electronic device.

[0024] As those of skill in the art will appreciate, the principles of the various embodiments disclosed herein, including a fuel cell with a selective CO_2 vent membrane, may be applied to and used with a variety of hybrid fuel cell systems in which a fuel cell is combined with an energy storage device or other power supply. For example, a fuel cell may be combined with one or more batteries, capacitors, and/or solar cells. The fuel cell may be an inorganic or organic fuel cell, DMFC, reformed methanol fuel cell, direct ethanol fuel cell, proton-exchange membrane fuel cell, microbial fuel cell, reversible fuel cell, formic acid fuel cell, and the like. Furthermore, the present invention may be used in a variety of applications and with fuel cells of various sizes and shapes. For purposes of example only, and not meant as a limitation, the hybrid power system may be used for electronic battery replacement in consumer products, such as smoke alarms, gas detectors (CO_2, Carbon Monoxide, etc.), mini and microelectronics, and as an energy source in many other devices and applications.

[0025] For example, a hybrid power system may include a fuel cell and an energy storage device. The energy storage device may include a battery alone or in combination with a capacitor or other electronic storage devices. The energy storage device may be selected to meet specific storage needs while buffering the fuel cell from peak current activities. The fuel cell may be matched with a number of different storage devices according to the needs of the application. The fuel cell may also be combined with additional electrical power generation devices, such as turbines, solar cells, geothermic power collectors, and thermoelectric devices. When connected with the energy storage device, such as a rechargeable battery, the fuel cell may trickle-charge the battery and keep it powered.

[0026] It should be emphasized that the described embodiments of this disclosure are merely possible examples of implementations and are set forth for a clear understanding of the principles of this disclosure. Many variations and modifications may be made to the described embodiments of this disclosure without departing substantially from the spirit and principles of this disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

Claims

1. A fuel cell comprising:

a carbon dioxide vent;

a vent membrane disposed within the carbon dioxide vent and configured to selectively allow the passage of carbon dioxide gas from within the fuel cell, wherein the vent membrane includes poly siloxane.

2. The fuel cell of claim 1, wherein the vent membrane further comprises at least one additive.

3. The fuel cell of claim 2, wherein the additive is a hydrophobic organic compound.

4. The fuel cell of claim 2, wherein the additive is 1,6-divinyl perfluorohexane.

5. The fuel cell of claim 4, wherein the additive 1,6-divinyl perfluorohexane is present in an amount ranging from approximately 10% to 50% by weight.

6. The fuel cell of claim 4, wherein the additive 1,6-divinyl perfluorohexane is present in an amount of approximately 23% by weight.

7. The fuel cell of claim 2, wherein the additive is 1,9-decadiene.

8. The fuel cell of claim 7, wherein the additive 1,9-decadiene is present in an amount ranging from approximately 10% to 50% by weight.

9. The fuel cell of claim 7, wherein the additive 1,9-decadiene is present in an amount of approximately 30% by weight.

10. A fuel cell comprising:

a carbon dioxide vent;

a vent membrane disposed within the carbon dioxide vent and configured to selectively allow the passage of carbon dioxide gas from within the fuel cell, wherein the vent membrane includes a poly (trialkylsilyl-alkyne).

11. The fuel cell of claim 10, wherein the vent membrane includes poly-(trimethylsilyl-1-propyne).

12. The fuel cell of claim 10, wherein the vent membrane further comprises at least one additive.

13. The fuel cell of claim 12, wherein the additive is 1,6-divinyl perfluorohexane.

14. The fuel cell of claim 13, wherein the additive 1,6-divinyl perfluorohexane is present in an amount ranging from approximately 10% to 60% by weight.

15. The fuel cell of claim 13, wherein the additive 1,6-divinyl perfluorohexane is present in an amount of approximately 14% by weight.

16. The fuel cell of claim 13, wherein the additive 1,6-divinyl perfluorohexane is present in an amount of approximately 38% by weight.

17. The fuel cell of claim 13, wherein the additive 1,6-divinyl perfluorohexane is present in an amount of approximately 50% by weight.

18. The fuel cell of claim 12, wherein the additive is 1,9-decadiene.

19. The fuel cell of claim 18, wherein the additive 1,9-decadiene is present in an amount ranging from approximately 10% to 60% by weight.

20. The fuel cell of claim 18, wherein the additive 1,9-decadiene is present in an amount of approximately 14% by weight.

21. The fuel cell of claim 18, wherein the additive 1,9-decadiene is present in an amount of approximately 38% by weight.

22. The fuel cell of claim 18, wherein the additive 1,9-decadiene is present in an amount of approximately 50% by weight.

23. The fuel cell of claim 12, wherein the additive is a hydrophobic organic compound.

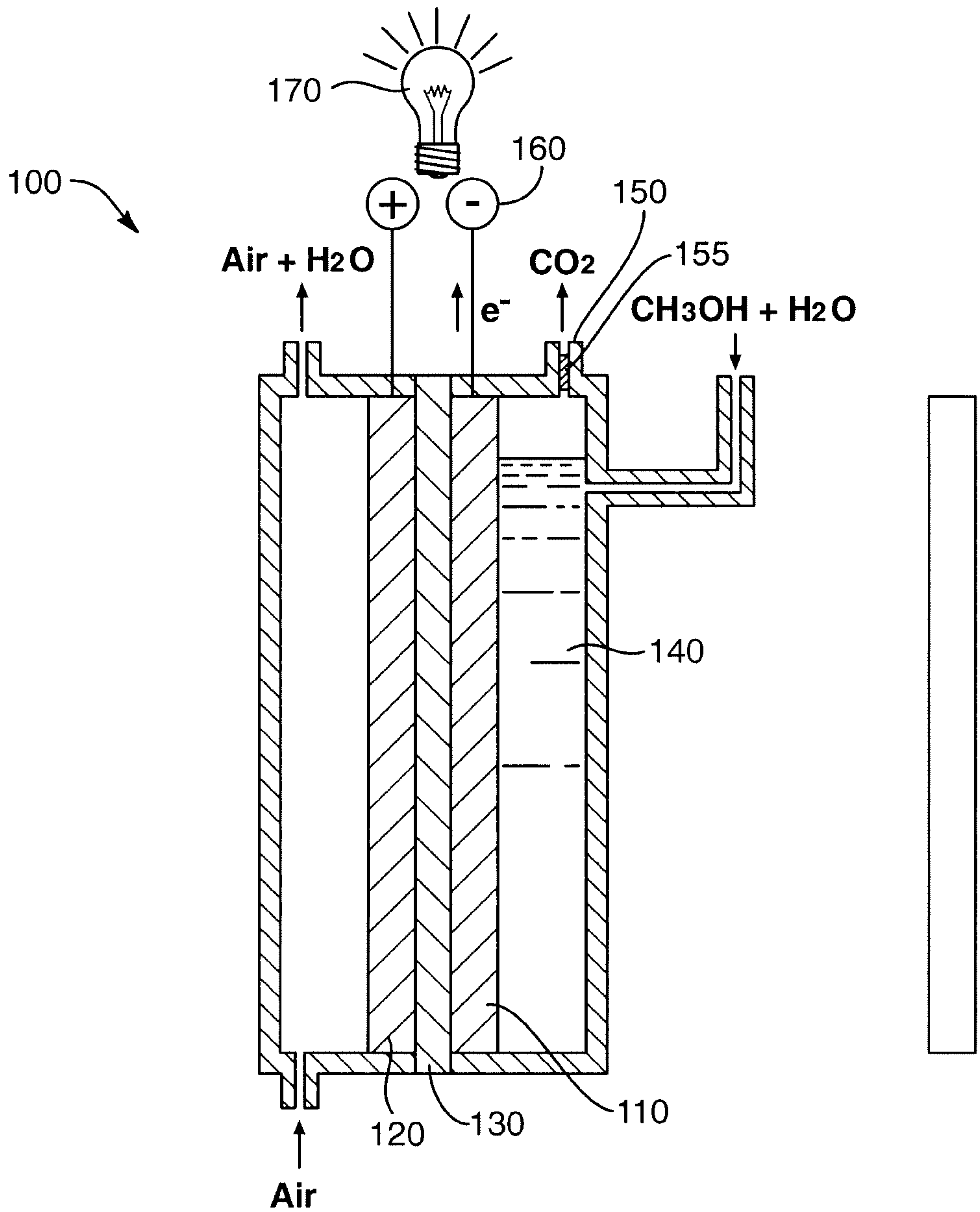
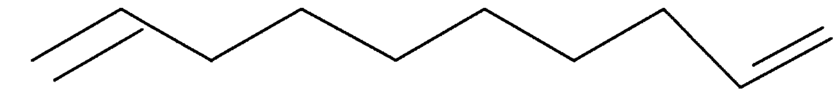
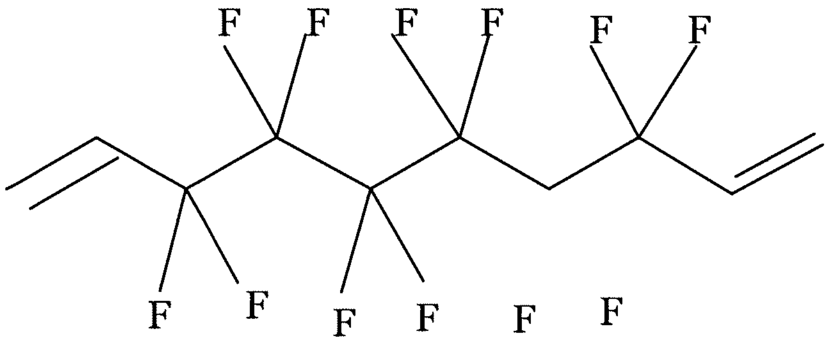


FIG. 1

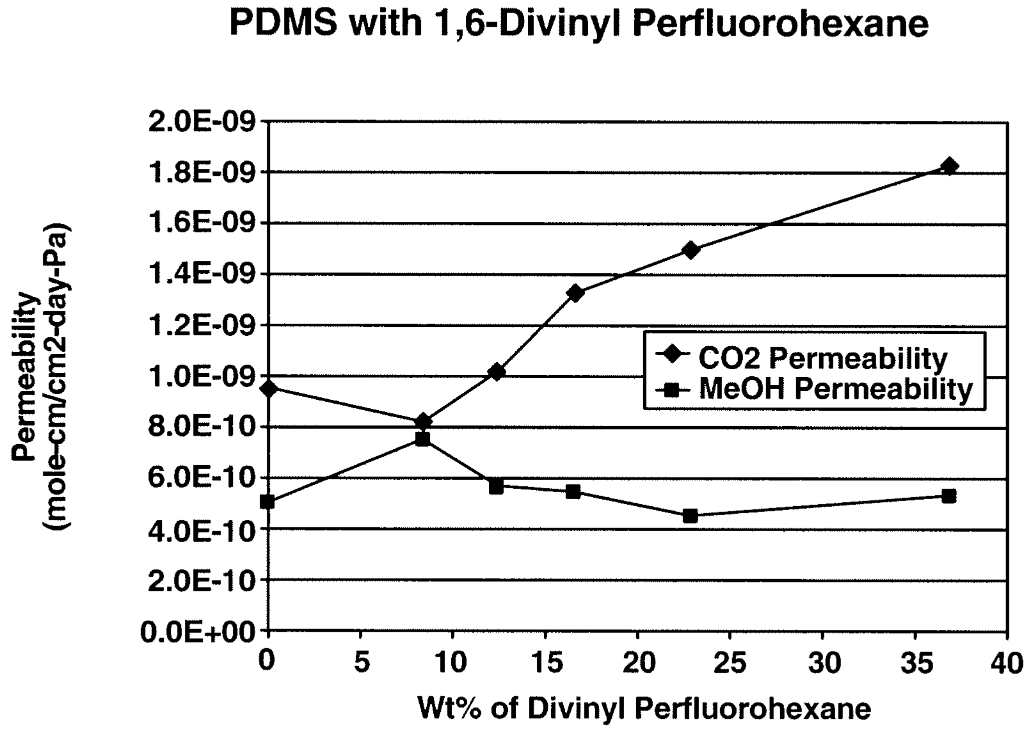


1,9-Decadiene



1,6-Divinyl Perfluorohexane

FIG. 2


PDMS with 1,6-Divinyl Perfluorohexane
Permeability
(mole-cm/cm2-day-Pa)
2.0E-09
1.8E-09
1.6E-09
1.4E-09
1.2E-09
1.0E-09
8.0E-10
6.0E-10
4.0E-10
2.0E-10
0.0E+00
0
5
10
15
20
25
30
35
40
Wt% of Divinyl Perfluorohexane
CO2 Permeability
MeOH Permeability

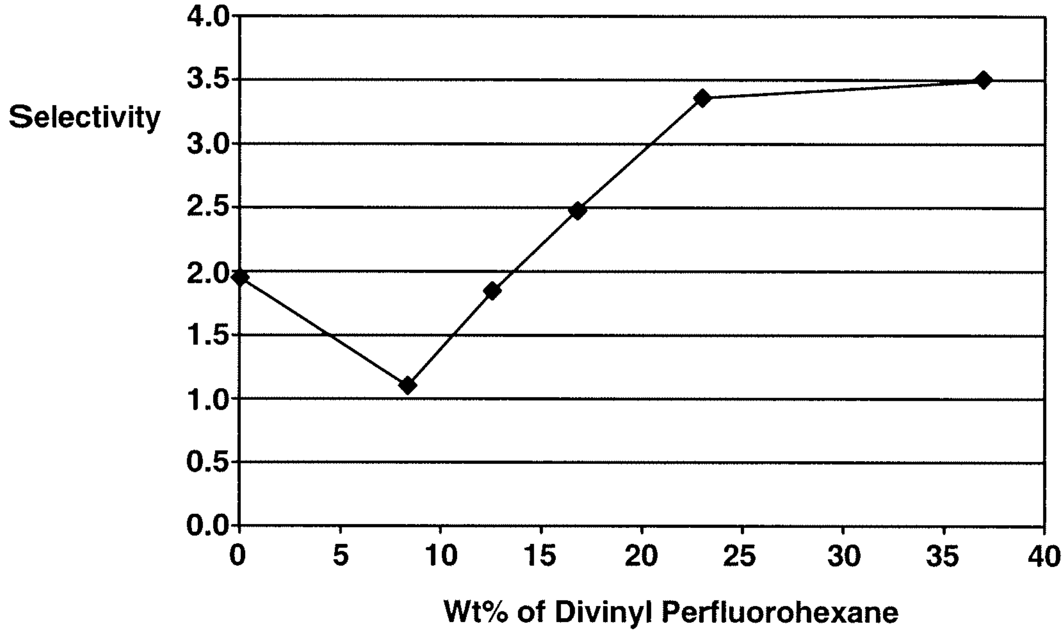

Selectivity
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
35
40
Wt% of Divinyl Perfluorohexane

FIG. 3

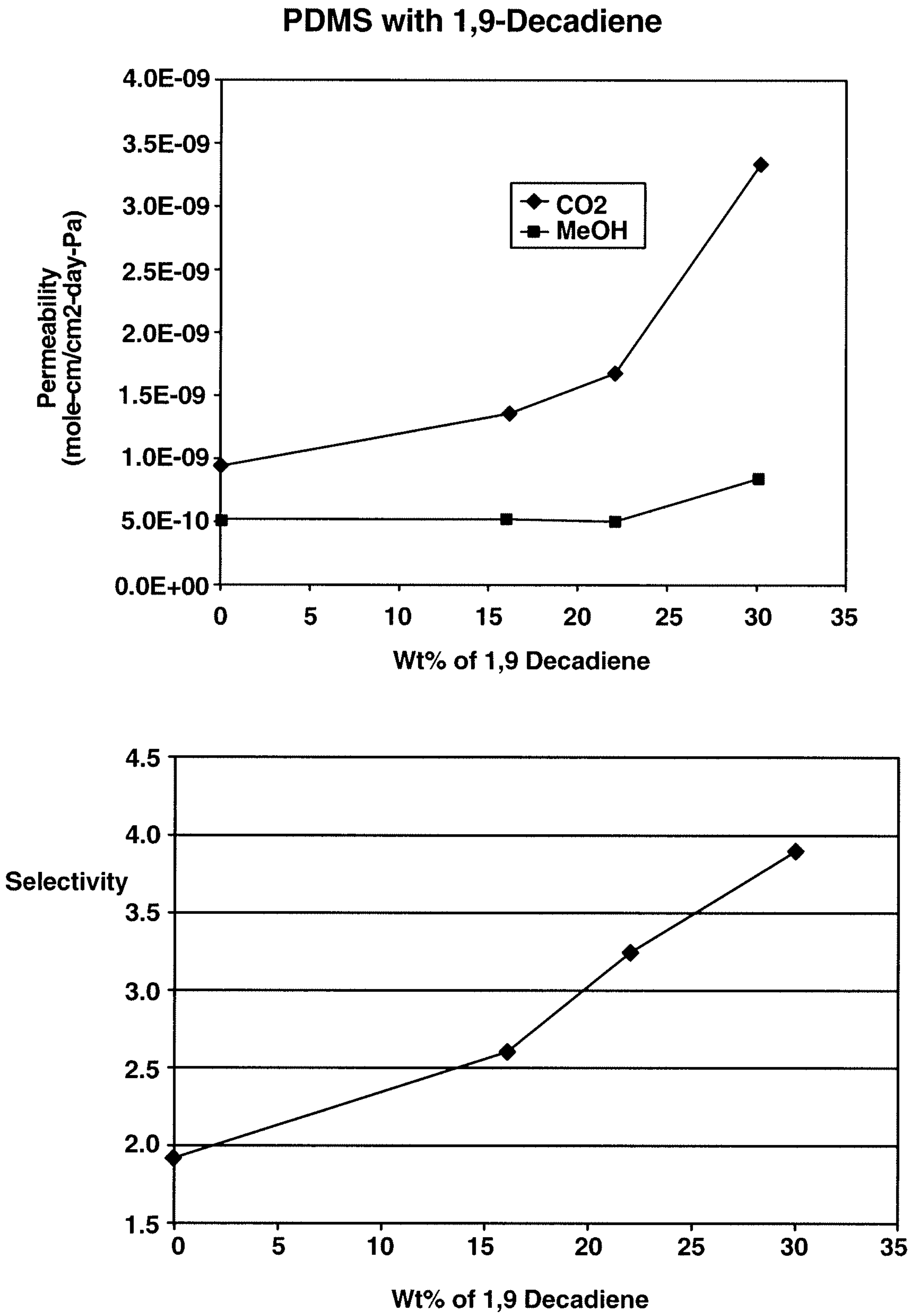

PDMS with 1,9-Decadiene
Permeability (mole-cm/cm2-day-Pa)
4.0E-09
3.5E-09
3.0E-09
2.5E-09
2.0E-09
1.5E-09
1.0E-09
5.0E-10
0.0E+00
CO2
MeOH
0
5
10
15
20
25
30
35
Wt% of 1,9 Decadiene
Selectivity
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Wt% of 1,9 Decadiene

FIG. 4

PTMSP with 1,9-Decadiene

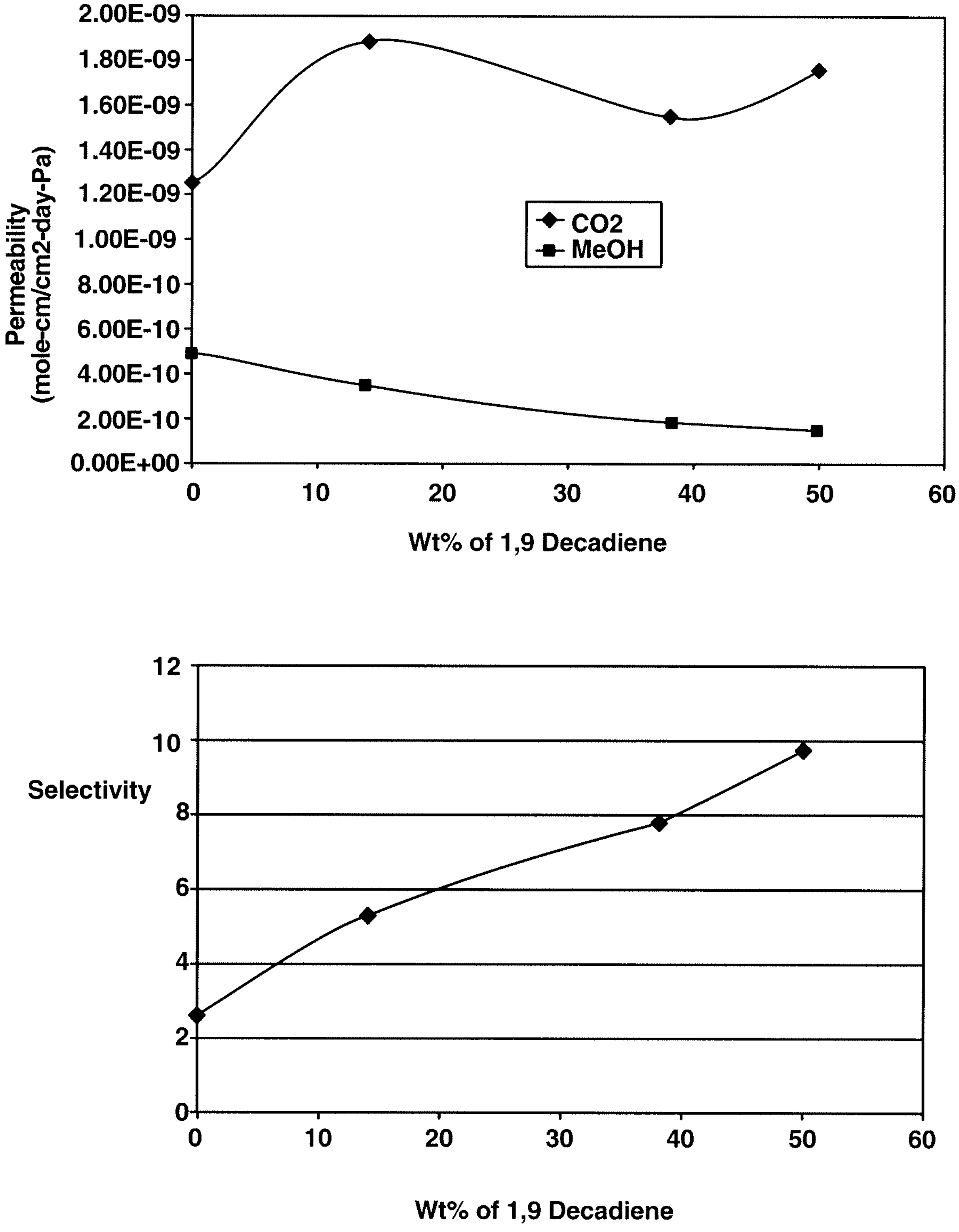


FIG. 5

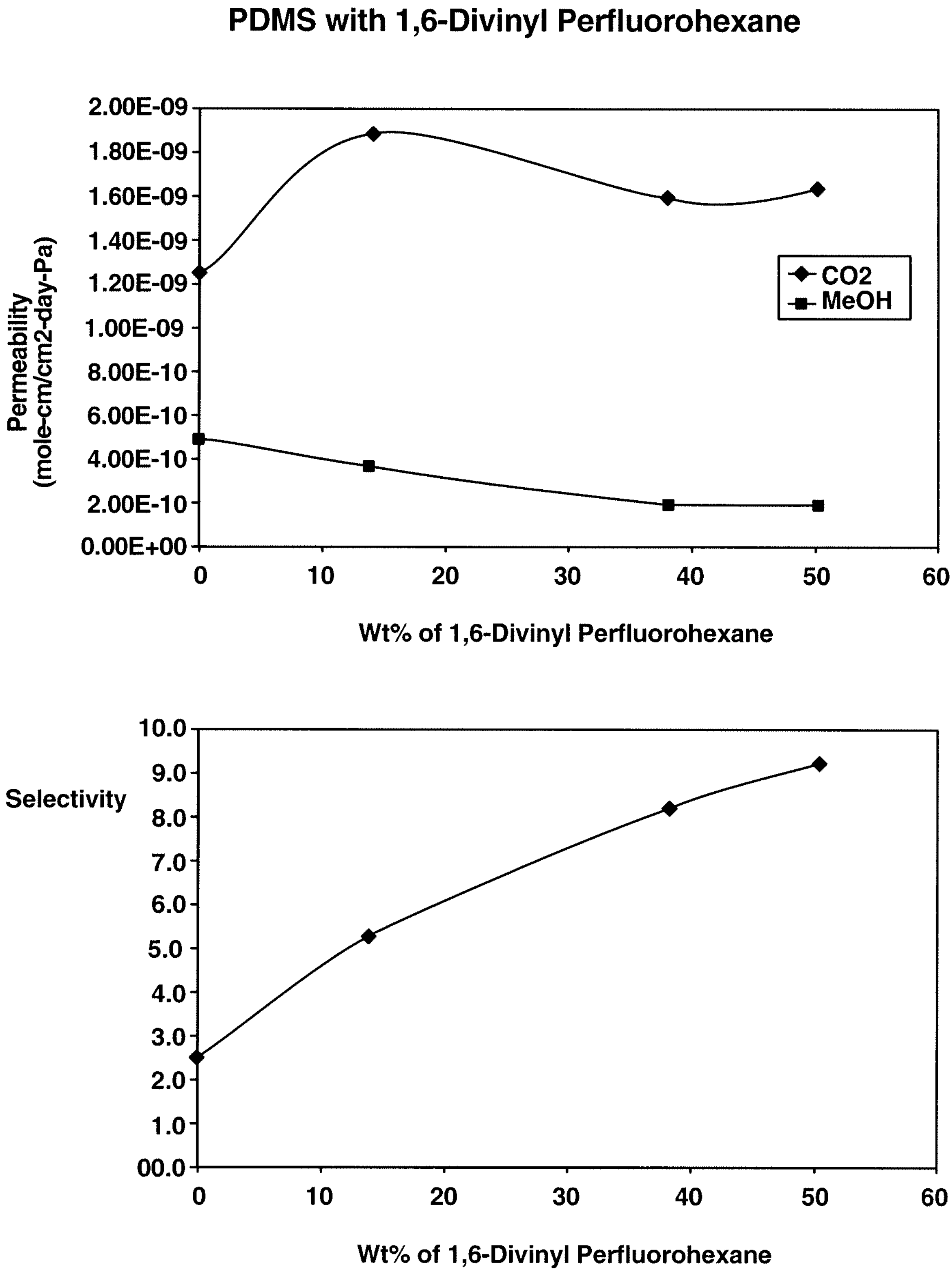

PDMS with 1,6-Divinyl Perfluorohexane
Permeability (mole-cm/cm2-day-Pa)
2.00E-09
1.80E-09
1.60E-09
1.40E-09
1.20E-09
1.00E-09
8.00E-10
6.00E-10
4.00E-10
2.00E-10
0.00E+00
0
10
20
30
40
50
60
CO2
MeOH
Wt% of 1,6-Divinyl Perfluorohexane
Selectivity
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
00.0
0
10
20
30
40
50
60
Wt% of 1,6-Divinyl Perfluorohexane

FIG. 6