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(54) Title: MEMBRANES AND COATINGS MADE FROM MIXTURES INCLUDING IONIC LIQUIDS HAVING SILIC-
ON-BONDED HYDROLYZABLE GROUPS

(57) Abstract: The present invention relates to silicone compositions made from mixtures including ionic liquids having hydrolys-
able silyl groups. In various embodiments, the present invention provides a method of preparing a silicone composition, the method
including reacting a mixture in a water-miscible solvent in the presence of a condensation catalyst to form a sol, concentrating the
sol to form a wet gel, and drying the wet gel to form a silicone composition; the mixture including (a) an ionic liquid; optionally, (b)
a silane; optionally, (c) a polysiloxane cross-linking agent; optionally, (d) a polydiorganosiloxane; and (e) water; wherein at least
one of optional elements (b) and (c) is included in the mixture. In various embodiments, the present invention provides silicone com-
positions made by the method, membranes and coated substrates including the silicone composition, including supported and unsup-
ported membranes, methods of making the membranes and coated substrates, and methods of using the membranes and coated sub-
strates.



MEMBRANES AND COATINGS MADE FROM MIXTURES INCLUDING IONIC LIQUIDS HAVING SILICON-BONDED HYDROLYZABLE GROUPS

[0001] Ionic liquids (ILs) are salts containing poorly coordinated ions, which can render the melting point of the salts equal to or close to room temperature. Many ionic liquids have even been developed in recent years for applications such as solvents, lubricants, anti-microbial agents, homogeneous and heterogeneous catalysis, treatment of high-level nuclear waste, and metal ion removal.

[0002] The use of membranes to separate gases is an important technique that can be used in many industrial procedures. Examples can include recovery of hydrogen gas in ammonia synthesis, recovery of hydrogen in petroleum refining, separation of methane from other components in biogas synthesis, enrichment of air with oxygen for medical or other purposes, removal of water vapor from natural gas, removal of carbon dioxide (CO₂) from natural gas or biogas, and carbon-capture applications such as the removal of CO₂ from flue gas streams generated by combustion processes.

SUMMARY OF THE INVENTION

[0003] The present invention relates to silicone compositions made from mixtures including ionic liquids having hydrolysable silyl groups (ILHSGs). The present invention provides methods of making the silicone composition and also provides the silicone compositions made thereby. In various embodiments, the present invention provides membranes and coated substrates including the silicone composition, including supported and unsupported membranes, methods of making the membranes and coated substrates, and methods of using the membranes and coated substrates. In some embodiments, the silicone composition is a xerogel or glass.

[0004] The present invention provides a method of preparing a silicone composition. The method includes reacting a mixture in a water-miscible solvent in the presence of a condensation catalyst. The reacting of the mixture forms a sol. The mixture includes (a) an ionic liquid having the formula $Z-Q^+-R^2-SiR^1_mX_{3-m}$. The mixture optionally includes (b) a silane having the formula $R^1_nSiX_{4-n}$. At least one of optional elements (b) and (c) is included in the mixture. The mixture optionally includes (c) a polysiloxane cross-linking agent having an average of at least 3 silicon-bonded X groups per molecule. The mixture optionally includes (d) a polydiorganosiloxane having the formula $X_{3-p}R^1_pSiO(R^1_2SiO)_qSiR^1_pX_{3-p}$. The

mixture also includes (e) water. The method includes concentrating the sol to form a wet gel. The method also includes drying the wet gel to form a silicone composition. The group Q^+ is a cationic organic group including at least one of N, S, and P. At each occurrence X is independently a hydrolyzable group, at each
5 occurrence R^1 is independently C_1 to C_{10} hydrocarbyl, R^2 is C_1 to C_{20} hydrocarbylene, Z^- is a counterion, m is 0, 1, or 2, n is 0 or 1, p is 0, 1, or 2, and q is about 100 to 2000.

[0005] Various embodiments of the present invention have certain advantages over other silicone compositions, including membranes and coated substrates
10 including the same, some of which are surprising. In some examples, the sol-gel process of making the silicone composition is advantageous over other methods of making membranes. In some examples, the reaction conditions of the sol-gel process can be moderate, such as room temperature and ambient pressure. In some examples, the sol-gel method can be a solution coating technique, allowing
15 easy control over rheological properties of the sol and facile tailoring of the coating thickness to specific needs via controlling the concentrations of various ingredients of the sol. For example, in some embodiments, adjusting the amount of solvent used in the mixture can control the speed of deposition, which can affect the porosity of the resulting product. For example, in some embodiments, adjusting the
20 concentration of the cross-linking agent can alter the rheological properties of the sol. In some examples, the sol-gel process can be compatible with many coating configurations and various shapes of substrates, such as for example doctor blade, dip coating, spin coating, slot die coating, and film casting. In some embodiments, since the sols can be well-dispersed colloid suspensions, a high degree of control
25 can be exerted over the chemical homogeneity and microstructure of the membranes. In various examples, the membrane or coated substrate of the present invention can exhibit better permeability and selectivity for particular components in a gas mixture, as compared to other membranes and coated substrates. For example, in various embodiments the membrane or coated
30 substrate can exhibit high CO_2/N_2 and CO_2/CH_4 selectivity, while retaining high permeability.

BRIEF DESCRIPTION OF THE FIGURES

[0006] In the drawings, which are not necessarily drawn to scale, like numerals describe substantially similar components throughout the several views. Like
35 numerals having different letter suffixes represent different instances of

substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0007] FIG. 1 illustrates CH_4/CO_2 selectivity and CO_2 permeability of a

5 membrane versus loading of an ionic liquid in the mixture used to make the membrane, in accordance with various embodiments.

[0008] FIG. 2 illustrates CH_4/CO_2 selectivity and CO_2 permeability of a membrane versus loading of an ionic liquid in the mixture used to make the membrane, in accordance with various embodiments.

10 [0009] FIG. 3 illustrates CH_4/CO_2 selectivity and CO_2 permeability versus loading of polydiethoxysiloxane in the mixture used to make the membrane, in accordance with various embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Reference will now be made in detail to certain claims of the disclosed subject matter, examples of which are illustrated in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which
20 can be included within the scope of the presently disclosed subject matter as defined by the claims.

[0011] References in the specification to “one embodiment,” “an embodiment,” “an example embodiment,” and the like, indicate that the embodiment described can include a particular feature, structure, or characteristic, but every embodiment may
25 not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one of ordinary skill in the art to effect such feature, structure, or characteristic in connection with other
30 embodiments whether or not explicitly described.

[0012] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is
35 explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1%

to 5%" should be interpreted to include not only about 0.1 wt% to about 5 wt%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range.

[0013] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0014] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited.

[0015] Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

Definitions

[0016] The term "about" as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range. When a range or a list of sequential values is given, unless otherwise specified any value within the range or any value between the given sequential values is also disclosed.

[0017] The term "substantially" as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

[0018] The term "independently selected from" as used herein refers to referenced groups being the same, different, or a mixture thereof, unless the context clearly

indicates otherwise. Thus, under this definition, the phrase "X¹, X², and X³ are independently selected from noble gases" would include the scenario where, for example, X¹, X², and X³ are all the same, where X¹, X², and X³ are all different, where X¹ and X² are the same but X³ is different, and other analogous permutations.

[0019] The term "resin" as used herein refers to polysiloxane material of any viscosity that includes at least one siloxane monomer that is bonded via a Si-O-Si bond to three or four other siloxane monomers. In one example, the polysiloxane material includes T or Q groups, as defined herein.

10 **[0020]** The term "radiation" as used herein refers to energetic particles travelling through a medium or space. Examples of radiation are visible light, infrared light, microwaves, radio waves, very low frequency waves, extremely low frequency waves, thermal radiation (heat), and black-body radiation.

[0021] The term "cure" as used herein refers to exposing to radiation in any form, heating, or allowing to undergo a physical or chemical reaction that results in hardening or an increase in viscosity.

[0022] The term "pore" as used herein refers to a depression, slit, or hole of any size or shape in a solid object. A pore can run all the way through an object or partially through the object. A pore can intersect other pores.

20 **[0023]** The term "free-standing" or "unsupported" as used herein refers to a membrane with the majority of the surface area on each of the two major sides of the membrane not contacting a substrate, whether the substrate is porous or not. In some embodiments, a membrane that is "free-standing" or "unsupported" can be 100% not supported on both major sides. A membrane that is "free-standing" or
25 "unsupported" can be supported at the edges or at the minority (e.g. less than about 50%) of the surface area on either or both major sides of the membrane.

[0024] The term "supported" as used herein refers to a membrane with the majority of the surface area on at least one of the two major sides contacting a substrate, whether the substrate is porous or not. In some embodiments, a
30 membrane that is "supported" can be 100% supported on at least one side. A membrane that is "supported" can be supported at any suitable location at the majority (e.g. more than about 50%) of the surface area on either or both major sides of the membrane.

[0025] The term "enrich" as used herein refers to increasing in quantity or
35 concentration, such as of a liquid, gas, or solute. For example, a mixture of gases

A and B can be enriched in gas A if the concentration or quantity of gas A is increased, for example by selective permeation of gas A through a membrane to add gas A to the mixture, or for example by selective permeation of gas B through a membrane to take gas B away from the mixture.

- 5 **[0026]** The term “deplete” as used herein refers to decreasing in quantity or concentration, such as of a liquid, gas, or solute. For example, a mixture of gases A and B can be depleted in gas A if the concentration or quantity of gas A is decreased, for example by selective permeation of gas B through a membrane to take gas B away from the mixture, or for example by selective permeation of gas A through a membrane to add gas A to the mixture.

[0027] The term “solvent” as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

- 15 **[0028]** The term “selectivity” or “ideal selectivity” as used herein refers to the ratio of permeability of the faster permeating gas over the slower permeating gas, measured at room temperature.

- [0029]** The term “permeability” as used herein refers to the permeability coefficient (P_X) of substance X through a membrane, where $q_{mX} = P_X \cdot A \cdot \Delta p_X \cdot (1/\delta)$, where q_{mX} is the volumetric flow rate of substance X through the membrane, A is the surface area of one major side of the membrane through which substance X flows, Δp_X is the pressure difference of the partial pressure of substance X across the membrane, and delta is the thickness of the membrane.

- 25 **[0030]** The term “Barrer” or “Barrers” as used herein refers to a unit of permeability, wherein 1 Barrer = 10^{-11} (cm³ gas) cm cm⁻² s⁻¹ mmHg⁻¹, or 10^{-10} (cm³ gas) cm cm⁻² s⁻¹ cm Hg⁻¹, where “cm³ gas” represents the quantity of the gas that would take up one cubic centimeter at standard temperature and pressure.

[0031] The term “total surface area” as used herein with respect to membranes refers to the total surface area of the side of the membrane exposed to the feed gas mixture.

- 30 **[0032]** The term “air” as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

[0033] The term “room temperature” as used herein refers to ambient temperature, which can be, for example, between about 15 °C and about 28 °C.

[0034] The term “coating” as used herein refers to a continuous or discontinuous layer of material on the coated surface, wherein the layer of material can penetrate the surface and can fill areas such as pores, wherein the layer of material can have any three-dimensional shape, including a flat or curved plane. In one example, a coating can be formed on one or more surfaces, any of which may be porous or nonporous, by immersion in a bath of coating material.

[0035] The term “surface” as used herein refers to a boundary or side of an object, wherein the boundary or side can have any perimeter shape and can have any three-dimensional shape, including flat, curved, or angular, wherein the boundary or side can be continuous or discontinuous. While the term surface generally refers to the outermost boundary of an object with no implied depth, when the term ‘pores’ is used in reference to a surface, it refers to both the surface opening and the depth to which the pores extend beneath the surface into the substrate.

[0036] The term “mil” as used herein refers to a thousandth of an inch, such that 1 mil = 0.001 inch.

Reacting a Mixture

[0037] In various embodiments, the present invention provides a method of preparing a silicone composition. The method includes reacting a mixture in a water-miscible solvent in the presence of a condensation catalyst to form a sol. The mixture includes an ionic liquid having hydrolyzable groups, and silicon-containing compounds having hydrolyzable groups, such that upon reacting the mixture generates a cross-linked three-dimensional polymeric chemical structure.

The method also includes concentrating the sol to form a wet gel. The method also includes drying the wet gel to form a silicone composition.

[0038] The reaction can occur under any suitable conditions including suitable time, pressure, temperature, and scale. For example, the reaction can occur for about 1 m, 5 m, 10 m, 30 m, 1 h, 2 h, 5 h, 10 h, 1 d, 2 d, 5 d, or about 10 d or more.

For example, the reaction can be performed at less than room temperature, or at about room temperature, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, or at about 200 °C or higher. In some examples, the reaction can be performed at less than ambient pressure, at about ambient pressure, 2 atm, 4 atm, 6 atm, 10 atm, 20 atm, 50 atm, 100 atm, or at about 200 atm or more. In some examples, the reaction can be performed on less than a 1 mg scale, or about 2 mg, 4 mg, 10 mg, 20 mg, 50

mg, 100 mg, 500 mg, 1 g, 2 g, 5 g, 10 g, 20 g, 50 g, 100 g, 500 g, 1 Kg, 2 Kg, 5 Kg, 10 Kg, 20 Kg, 50 Kg, 100 Kg, 500 Kg, or about 1000 Kg or greater scale. The reaction can be conducted with or without stirring or agitation.

[0039] The water-miscible solvent can be any water miscible solvent. In some examples, the water miscible solvent is any C1-C10 alcohol, such as methanol, ethanol, or isopropanol. Examples of water-miscible solvents can include aldehydes such as acetaldehyde; organic acids such as acetic acid, butyric acid, formic acid, and propanoic acid; ketones such as acetone; sulfoxides such as dimethyl sulfoxide; nitriles and isocyanides such as acetonitrile and methyl isocyanide; diols and polyols such as 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, ethylene glycol, 1,3-propanediol, 1,5-pentanediol, propylene glycol, and triethylene glycol, glycerol; alcohols such as 2-butoxyethanol, 1-propanol, 2-propanol, methanol, and furfuryl alcohol; amines such as diethanolamine, methyl diethanolamine, diethylenetriamine, and ethylamine; amides such as dimethylformamide; ethers such as dimethoxyethane and 1,4-dioxane; and heterocycles such as pyridine and tetrahydrofuran.

[0040] Any suitable amount of the water-miscible solvent can be used. In some examples, the water-miscible solvent can be present in about 0.01 wt% to about 99.99 wt%, about 1 wt % to about 99 wt%, or about 5 wt% to about 95 wt%, wherein wt% in this paragraph refers to the percent by weight based on the total weight of the water miscible solvent, the condensation catalyst, and the mixture.

[0041] The condensation catalyst can be any suitable condensation catalyst that promotes hydrolysis of elements of the mixture and subsequent condensation of the products of hydrolysis. For example, the condensation catalyst can be any acid or base. Examples can include organic acids such as formic acid or acetic acid; mineral acids such as hydrochloric acid or sulfuric acid; amines such as ammonia or triethylamine; and other bases such as metal hydroxides like sodium hydroxide or potassium hydroxide; or ammonium hydroxides like ammonium hydroxide or tetraalkyl ammonium hydroxides. In another example, the condensation catalyst can be an organometallic condensation catalyst such as tin compounds, for example dibutyltin dilaurate (DBDLT), stannous octoate, dibutyltin diacetate, dibutyltin diethylhexanoate, dibutyltin dioctanoate, 4-benzyloxyphenyltributylstannane, (dimethylamino)trimethyltin(IV), 1-Methyl-4-(tributylstannyl)-1H-pyrazole, 1-methyl-5-(tributylstannyl)imidazole, 1-methyl-2-(tributylstannyl)pyrrole, 1,3-diacetoxy-1,1,3,3-tetrabutylstannoxane, 1,3-bis(tributylstannyl)benzene, 1,4-bis(tributylstannyl)benzene, 2,2-dibutyl-

- [1,3,2]dioxastannolane, 2-chloro-5-(tributylstannyl)thiazole, 2-(tri-n-butylstannyl)oxazole, 2-tributylstannylthiazole, 2,6-dichloro-3-(tributylstannyl)pyrazine, 2-chloro-5-(tributylstannyl)pyrimidine, 2-(tributylstannyl)pyrazine, 2-(tributylstannyl)furan, 2-(tributylstannyl)thiophene, 2-bromo-5-(tributylstannyl)pyridine, 2-bromo-6-(tributylstannyl)pyridine, 2-chloro-6-(tributylstannyl)pyridine, 2-fluoro-3-(tributylstannyl)pyridine, 2-fluoro-4-(tributylstannyl)pyridine, 2-(tributylstannyl)pyridine, 2-(tributylstannyl)-3-methoxypyrazine, 2-methylthio-5-(tributylstannyl)pyrimidine, 2-tributylstannylbenzo[b]thiophene, 2-(N-boc-amino)-5-(tributylstannyl)thiazole, 2,5-bis(tributylstannyl)thiophene, 3-(tributylstannyl)pyridine, 4-bromo-2-(tributylstannyl)thiazole, 4-(4-(tributylstannyl)phenyl)morpholine, 5-(tributylstannyl)pyrimidine, 5-bromo-2-(tributylstannyl)pyridine, 5,5'-bis(tributylstannyl)-2,2'-bithiophene, 6-methoxy-2-(tributylstannyl)pyrimidine, allenyltributyltin(IV), allyltributylstannane, allyltriphenylstannane, azidotributyltin(IV), azidotrimethyltin(IV), bis(dibutylchlorotin(IV)) oxide, bis(tributylstannyl)acetylene, bis(tributyltin), bis(tributyltin) oxide, bis(tributyltin)sulfide, bis(trimethylstannyl)acetylene, bis[(trimethylsilyl)tributyl]stannyl phosphate, butyltin chloride dihydroxide, butyltin hydroxide oxide hydrate, butyltin trichloride, di-tert-butyltin dichloride, dibutyldimethoxytin, dibutyldiphenyltin, dibutyltin bis(acetylacetonate), dibutyltin dibromide, dibutyltin dichloride, dibutyltin maleate, dibutyltin(IV) oxide, dibutyltin(IV) oxide, dimethyltin dichloride, diphenyltin dichloride, diphenyltin(IV) oxide, ethyl-5-(tributylstannyl)isoxazole-3-carboxylate, ethynyltributylstannane, hexamethylditin, hexaphenylditin(IV), methyltin trichloride, N-methyl-2-(tributylstannyl)indole, N-methyl-4-(tributylstannyl)imidazole, phenyltin trichloride, tetraallyltin, tetrabutyltin, tetraethyltin, tetramethyltin, tetraphenyltin, tetravinyltin, tributyl(1-ethoxyvinyl)tin, tributyl(1-propynyl)tin, tributyl(3-methyl-2-butenyl)tin, tributyl(4,5-dihydrofuran-2-yl)stannane, tributyl(4-chloro)phenylstannane, tributyl(perfluoroethyl)stannane, tributyl(phenylethynyl)tin, tributyl(trimethylsilyl)stannane, tributyl(vinyl)stannane, tributyl(vinyl)tin, tributylphenylstannane, tributylphenylstannane, tributylstannyl trifluoromethanesulfonate, tributyltin bromide, tributyltin chloride, tributyltin cyanide, tributyltin ethoxide, tributyltin hydride, tributyltin iodide, tributyltin isocyanate, tributyltin methoxide, tricyclohexyltin chloride, tricyclohexyltin hydride, triethyltin bromide, trimethyl(phenyl)tin, trimethyl(phenylethynyl)tin, trimethyl(tributylstannyl)silane, trimethyltin bromide, trimethyltin chloride, triphenyltin hydride, triphenyltin hydroxide, or cis-tributyl[2-ethoxyethenyl]stannane.

[0042] Any suitable amount of the condensation catalyst can be used. In some examples, the condensation catalyst can be present in about 0.000,001 wt% to about 50 wt%, about 0.000,1 wt % to about 30 wt%, or about 0.01 wt% to about 15 wt%, wherein wt% in this paragraph refers to the percent by weight based on the total weight of the water miscible solvent, the condensation catalyst, and the mixture.

[0043] Any suitable amount of the mixture can be used. In some examples, the mixture can be present in about 0.000,1 wt% to about 99.999 wt%, about 1 wt % to about 9 wt%, or about 5 wt% to about 95 wt%, wherein wt% in this paragraph refers to the percent by weight based on the total weight of the water miscible solvent, the condensation catalyst, and the mixture.

[0044] Reacting the mixture in the water-miscible solvent forms a sol. As used herein, a sol refers to a solution. The sol can be a colloidal solution, including liquids and products of hydrolysis and condensation reactions of the elements of the mixture. At least some of the hydrolyzable groups on elements of the mixture are hydrolyzed during the reaction to form functionalities such as –OH groups which can then condense together to link molecules together via oxygen linkages, also referred to as curing the mixture. The products of hydrolysis and condensation reactions can be polymers in any suitable physical form, ranging from particles of any suitable size to continuous chain-like polymer networks, or any combination thereof.

[0045] The sol is a precursor for the wet gel, wherein the gel is formed at least in part by removing liquids from the sol by concentrating it. As used herein, “wet gel” refers to an integrated network of polymers, wherein the polymers can have any suitable physical form, ranging from particles of any suitable size to continuous chain-like polymer networks, or any combination thereof. In some embodiments, the materials in the sol can continue to react as they form the gel, e.g. the materials in the sol can at least partially cure as they form the gel. In other embodiments, little or no reactions such as continued hydrolysis or condensation reactions occur during the concentrating of the sol. Concentrating the sol can be performed in any suitable fashion, including for example by evaporating at least some of the solvents in the sol. Evaporation can be performed by use of a suitable amount of heat, vacuum, or a combination thereof, for any suitable time. Concentration can be performed at below room temperature, at about room temperature, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, or at about 200 °C or higher. The concentration can be

performed at above atmospheric pressure, or at about 1 atm, 0.1 atm, 0.01 atm, 0.001 atm, 0.000,1 atm, or at or below about 0.000,01 atm. For example, the concentrating can occur for about 1 m, 5 m, 10 m, 30 m, 1 h, 2 h, 5 h, 10 h, 1 d, 2 d, 5 d, or about 10 d or more. In some embodiments, concentrating can be facilitated by allowing a stream of air to pass over the sol for a suitable time.

[0046] The wet gel can be dried to form a silicone composition. The silicone composition includes the hydrolysis and subsequent condensation products formed from the mixture. In some embodiments, the materials in the gel can continue to react as they form the silicone composition, e.g. the materials in the gel can at least partially cure as they form the silicone composition. In other embodiments, little or no reactions such as continued hydrolysis or condensation reactions occur during the drying of the gel to form the silicone composition. Drying the gel can be performed in any suitable fashion, including for example by evaporating at least some of the solvents in the gel. Evaporation can be performed by use of a suitable amount of heat, vacuum, or a combination thereof, for any suitable time. Drying can be performed at below room temperature, at about room temperature, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, or at about 200 °C or higher. The drying can be performed at above atmospheric pressure, or at about 1 atm, 0.1 atm, 0.01 atm, 0.001 atm, 0.000,1 atm, or at or below about 0.000,01 atm. For example, the drying can occur for about 1 m, 5 m, 10 m, 30 m, 1 h, 2 h, 5 h, 10 h, 1 d, 2 d, 5 d, or about 10 d or more. In some embodiments, drying can be facilitated by allowing a stream of air to pass over the gel for a suitable time.

[0047] In some embodiments, concentrating and drying can be discrete steps. In some examples, concentrating and drying can be performed with the same conditions, or with different conditions. In some examples, concentrating and drying can be a single step. Embodiments can encompass methods wherein a wet gel is or is not isolated between steps of concentrating and drying. Likewise, a reaction mixture can fulfill different aspects of the gel to silicone progression in different areas of the gel. For example, as a sol is concentrated some areas can proceed more quickly to the silicone composition while other areas remain as wet gels or sols for different lengths of time. In other examples, the entire reaction mixture proceeds to discrete stages of a gel followed by a silicone composition.

[0048] The silicone composition can have any suitable form. For example, the silicone composition can be a flexible or malleable solid, such as a white, opaque, tough, paper-like film. In some embodiments, the silicone composition can be a

xerogel or a glass. As used herein, a “xerogel” refers to solid formed from a gel by drying. In some examples, a xerogel can be formed from a gel dried with unhindered shrinkage. Xerogels can have high porosity (e.g. about 10% to 80% by volume), high surface area (e.g. about 150-1200 m²/g), and small pore size (e.g. about 0.1-15 nm). Heat treatment of a xerogel can yield a glass. As used herein, a “glass” refers to an amorphous, non-crystalline solid material. Glasses can be optically transparent. In some examples, glasses can be brittle.

Mixture

[0049] The mixture includes (a) an ionic liquid; optionally, (b) a silane; optionally, (c) a polysiloxane cross-linking agent; optionally, (d) a polydiorganosiloxane; and (e) water; wherein at least one of optional elements (b) and (c) is included in the mixture. In some embodiments, both of optional elements (b) and (c) are included in the mixture. In other embodiments, only optional element (b) is included and optional element (c) is not included. In other embodiments, only optional element (c) is included and optional element (b) is not included. The mixture can optionally include any suitable additional material. The mixture can include more than one type of any designated material, for example the mixture can include two different types of ionic liquid, or three different types of polydiorganosiloxane.

[0050] Any suitable amount of the ionic liquid (a) can be used. In some examples, the element ionic liquid can be present in the mixture from about 0.01 wt% to about 99 wt%, about 1 wt % to about 50 wt%, or about 5 wt% to about 40 wt% of the mixture, wherein wt% in this paragraph refers to the percent by weight based on the total weight of mixture elements (a), (b), (c), and (d).

[0051] Any suitable amount of the silane (b) can be used. In some examples, the silane can be present in the mixture from about 0 wt% to about 99 wt%, about 5 wt % to about 60 wt%, or about 10 wt% to about 35 wt% of the mixture, wherein wt% in this paragraph refers to the percent by weight based on the total weight of mixture elements (a), (b), (c), and (d).

[0052] Any suitable amount of the polysiloxane cross-linking agent (c) can be used. In some examples, the polysiloxane cross-linking agent can be present in the mixture from about 0 wt% to about 99 wt%, about 1 wt % to about 30 wt%, or about 5 wt% to about 15 wt% of the mixture, wherein wt% in this paragraph refers to the percent by weight based on the total weight of mixture elements (a), (b), (c), and (d).

[0053] Any suitable amount of the polydiorganosiloxane (d) can be used. In some examples, the polydiorganosiloxane can be present in the mixture from about 0

wt% to about 99 wt%, about 30 wt % to about 90 wt%, or about 50 wt% to about 80 wt% of the mixture, wherein wt% in this paragraph refers to the percent by weight based on the total weight of mixture elements (a), (b), (c), and (d).

- [0054]** Any suitable amount of water (e) can be used. In some examples, the
 5 water can be present in the mixture from about 0.000,1 wt% to about 99 wt%, about 1 wt % to about 90 wt%, or about 5 wt% to about 80 wt% of the mixture, wherein wt% in this paragraph refers to the percent by weight based on the total weight of mixture elements (a), (b), (c), (d), and (e).

Ionic Liquid

- 10 **[0055]** The mixture can include (a) an ionic liquid. The ionic liquid has hydrolyzable silyl functionalities, groups such as alkoxysilyl groups, allowing for hydrolysis and subsequent cross-linking in certain embodiments. The ionic liquid can have the formula $Z-Q^+-R^2-SiR^1_mX_{3-m}$. The group Q^+ can be a cationic organic group including at least one of N, S, and P. At each occurrence X can be
 15 independently a hydrolyzable group. At each occurrence R^1 can be independently C_1 to C_{10} hydrocarbyl. The substituent R^2 can be C_1 to C_{20} hydrocarbylene. The variable m can be 0, 1, or 2.

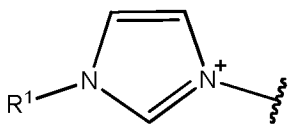
- [0056]** As used herein, "hydrolyzable group" refers to any substituent X that can undergo a hydrolysis reaction with water to give a hydroxyl group. For example, a
 20 compound R-X can undergo hydrolysis to give R-OH and H-X. For example, X can be any alkoxy group, such as a C_1 - C_{10} alkoxy group, branched or linear, such as methoxy, ethoxy, propoxy, i-propoxy, t-butoxy, n-butoxy, s-butoxy, and the like; a halogen, such as bromide, chloride, fluoride, or an iodide; a carboxylate such as acetate; or a heteroester such as an organophosphorus ester or an organosulfur
 25 ester.

- [0057]** At each occurrence R^1 can be independently C_1 to C_{10} hydrocarbyl, can be branched, linear or cyclic, can be aliphatic, unsaturated, conjugated, or aromatic, and can include alkyl such as methyl, ethyl, propyl, n-butyl, t-butyl, s-butyl; alkenyl such as ethenyl or propenyl; alkynyl; cycloalkyl such as hexanyl; or aromatic such
 30 as phenyl.

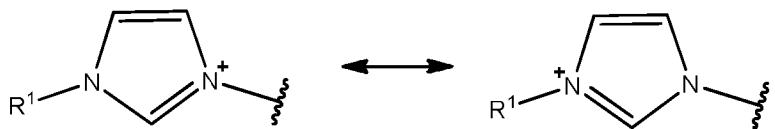
[0058] The variable m can be 0, 1, or 2. For example, $-SiR^1_mX_{3-m}$ can be $-SiX_3$, $-SiR^1X_2$, or $-SiR^1_2X$.

- [0059]** The substituent R^2 can be C_1 to C_{20} hydrocarbylene, can be branched, linear or cyclic, can be aliphatic, unsaturated, conjugated, or aromatic, and can include alkyl such as methylene, ethylene, propylene, butylene; alkenylene such as ethenylene or propenylene; alkynylene; cycloalkylene such as hexanylene; or aromatic such as phenylene. In some examples, R^2 can be $-R^5-Ar-R^5-$, wherein at each occurrence R^5 can be independently a single bond or C_{1-10} alkylene and Ar can be a C_{4-10} divalent cycloalkyl, aryl, heterocyclyl, or heteroaryl group. For example, R^2 can be a divalent methylphenyl, methylphenylmethyl, phenyl methyl, methylcyclohexyl, and the like.
- [0060]** The group Z^- can be any suitable counterion for Q^+ , such as any suitable anion. The group Z^- can serve as a counterion for a single Q^+ , or for two or more Q^+ . In some examples, Z^- can be a halide, such as fluoride, chloride, bromide, or iodide. In other examples, Z^- can be nitrate, hydrogen sulfate, dihydrogen phosphate, bicarbonate, nitrite, perchlorate, iodate, chlorate, bromate, chlorite, hypochlorite, hypobromite, cyanide, amide, cyanate, hydroxide, permanganate, an acid anion such as acetate or formate, or anions with negative charges greater than -1 such as oxide, sulfide, nitride, arsenate, phosphate, arsenite, hydrogen phosphate, sulfate, thiosulfate, sulfite, carbonate, chromate, dichromate, peroxide, or oxalate.
- [0061]** The group Q^+ can be any suitable cationic organic group including at least one of N, S, and P. For example, Q^+ can be an ammonium group, a phosphonium group, or a sulfonium group. For example Q^+ can be $R^1_a M^{+}$, wherein $M^+ = N^+, P^+, \text{ or } S^+$, provided that when M^+ is N^+ or P^+ , a is 3, and when M is S^+ , a is 2. For example, Q^+ can be $R^1_3 P^+$ or $R^1_3 N^+$. For example, Q^+ can be $R^1_2 S^+$. In some examples, Q^+ can be $R^1_a Y^+$, wherein Y^+ is a heterocyclic ring bearing a positive charge, the heterocyclic ring including at least one N, S, or P, and a is 1, 2, or 3. Y^+ can be any suitable heterocyclic ring, and can be substituted by any suitable number of organic substituents. For example, Y^+ can be a heteroaromatic ring. Heterocyclic rings can be saturated or unsaturated, aromatic or nonaromatic, can include rings having 5 to 20 ring members, including fused rings. Heterocycles including N, S, or P can include any suitable number of N, S, or P atoms such as 1,

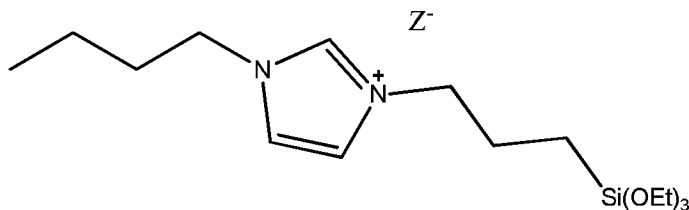
2, 3, or 4 N, S, or P atoms or any combination thereof. In addition, heterocycles can include any other heteroatom, such as O or B. In various embodiments, Y^+ can be pyrrolidinium, pyridinium, pyrimidinium, pyrazolium, benzimidazolium, imidazolium, triazolium, tetrazolium, azepanium, azepinium, benzazepanium, thiazolium, isothiolium, tholium, benzthiazolium, phospholium, phosphorinolum, oxazolium, oxathiazolium, and the like. In some examples, the heterocyclic ring is bound to the $-R^2-SiR^1_mX_{3-m}$ at a heteroatom in the heterocyclic ring. In some examples, a is 1 and R^1Y^+ is an imidazolium illustrated as



One of ordinary skill in the art will readily recognize that the positive charge in an imidazolium is distributed at least between the nitrogen atoms, as illustrated by the following resonance structures:

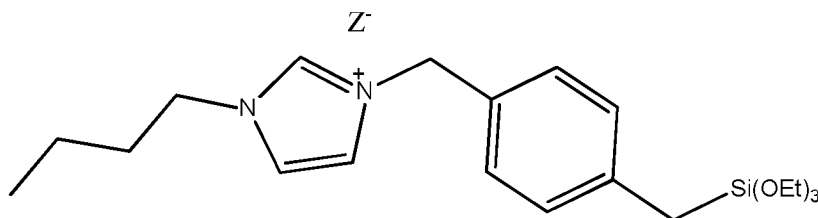


[0062] For example, in various embodiments, the ionic liquid is



15

or



Silane

[0063] The mixture optionally includes (b) a silane having the formula $R^1_nSiX_{4-n}$. In some embodiments, the mixture includes the silane. In other embodiments, the mixture does not include the silane. The mixture includes at least one of optional

elements (b) and (c). The silane can be any suitable silane. At each occurrence R^1 can be independently C_1 to C_{10} hydrocarbyl, as defined herein. At each occurrence X can be independently a hydrolyzable group, as defined herein. The variable n can be 0 or 1. The silane can be R^1SiX_3 or SiX_4 . In some examples, the silane is tetraethyl orthosilicate, tetramethyl orthosilicate, methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, methyltriethoxysilane, and the like.

Polysiloxane Cross-Linking Agent

[0064] The mixture optionally includes (c) a polysiloxane cross-linking agent having an average of at least 3 silicon-bonded X groups per molecule. In some embodiments, the mixture does include element (c). In other embodiments, the mixture does not include element (c). The mixture includes at least one optional elements (b) and (c). The cross-linking agent can be any suitable cross-linking agent. Each siloxane group can be M, D, T, or Q. The cross-linking agent can be linear or resinous. Aside from X and other siloxane groups, each silicon atom of the polysiloxane can be substituted by any suitable substituent, such as a halide or an organic group, such as R^1 , a C_1 to C_{10} hydrocarbyl, as defined herein. At each occurrence X can be independently a hydrolyzable group, as defined herein. Each individual silicon atom of the cross-linking agent can have 2, 1, or 0 silicon-bonded X groups. The polysiloxane crosslinking agent can have an average of about 3 to 50,000 silicon-bonded X groups per molecule, about 3 to 10,000, about 3 to 1000, about 3 to 100, about 3 to 10, or an average of about 3 to 5 silicon-bonded X groups per molecule. In some embodiments, element (c) can be a poly(dialkoxysiloxane) including about 5 to 95% (w/w) SiO_2 , or about 20 to 90%, or about 30 to 70%, or about 40 to 60%, or about 45 to 55%, or about 48 to 52% (w/w) SiO_2 . In some embodiments, element (c) can be a polydiethoxysiloxane.

Polydiorganosiloxane

[0065] The mixture optionally includes (d) a polydiorganosiloxane having the formula $X_{3-p}R^1_pSiO(R^1_2SiO)_qSiR^1_pX_{3-p}$. In some embodiments, the mixture does include element (d). In other embodiments, the mixture does not include element (d). Element (d) can be any suitable polydiorganosiloxane having the formula $X_{3-p}R^1_pSiO(R^1_2SiO)_qSiR^1_pX_{3-p}$. At each occurrence X can be independently a hydrolyzable group, as defined herein. At each occurrence R^1 can

be independently C₁ to C₁₀ hydrocarbonyl, as defined herein. The variable p can be 0, 1, or 2; thus element (d) can have the formula X₃SiO(R¹₂SiO)_qSiX₃, X₂R¹₁SiO(R¹₂SiO)_qSiR¹₁X₂, or XR¹₂SiO(R¹₂SiO)_qSiR¹₂X. The variable q can be about 50 to 4000, about 100 to 2000, about 300 to 1500, or about 600 to 900. In some examples, q is about 800. In some examples, element (d) is a trimethylsiloxy-terminated polydimethylsiloxane.

Water

[0066] The mixture includes (e) water. The water can be of any suitable purity.

Membrane

[0067] In one embodiment, the present invention provides a membrane that includes the silicone composition. In another embodiment, the present invention provides a method of forming a membrane. In some embodiments, the membrane can be formed directly of the silicone composition, for example the sol can be gelled and dried on a substrate wherein the silicone composition can remain and be used as a membrane. In other embodiments, the silicone composition can be processed in some fashion, such as ground or crushed. The processed silicone composition can be directly formed into a membrane by processing steps such as pressing or heating or a combination thereof. In another example, the processed silicone composition can be laminated to supports such as polymer supports, such as nylon or polypropylene membrane filters, by use of suitable laminating techniques such as hot press. In another example, the processed silicone composition can be subsequently integrated into a composition that formed the membrane via a drying or curing process.

[0068] The present invention can include the step of forming a membrane. The membrane can be formed on at least one surface of a substrate. For any membrane to be considered “on” a substrate, the membrane can be attached (e.g. adhered) to the substrate, or be otherwise in contact with the substrate without being adhered. The substrate can have any surface texture, and can be porous or non-porous. The substrate can include surfaces that are not coated with a membrane by the step of forming a membrane. All surfaces of the substrate can be coated by the step of forming a membrane, one surface can be coated, or any number of surfaces can be coated.

[0069] The step of forming a membrane can include two steps. In the first step, the composition that forms the membrane, such as the mixture or a curable composition that includes the processed silicone composition, can be applied to at

least one surface of the substrate. In the second step, the applied composition that forms the membrane can be cured to form the membrane. In some embodiments, the curing process of the composition can begin before, during, or after application of the composition to the surface. The curing process transforms the composition that forms the membrane into the membrane. The composition that forms the membrane can be in a liquid state, for example a sol. The membrane can be in a solid state, for example a dried gel or a cured composition formed from a mixture including a processed dried gel.

[0070] The composition that forms the membrane can be applied using conventional coating techniques, for example, immersion coating, spin coating, dipping, spraying, brushing, roll coating, extrusion, screen-printing, pad printing, or inkjet printing.

[0071] Curing the composition can be the reacting, concentrating, and drying steps described herein. In an embodiment wherein the composition that forms the membrane is a curable composition that includes processed silicone composition, curing the composition that forms the membrane can include the addition of a curing agent or initiator such as, for example, a hydrosilylation catalyst. In some embodiments, the curing process can begin immediately upon addition of the curing agent or initiator. The addition of the curing agent or initiator may not begin the curing process immediately, and can require additional curing steps. In other embodiments, the addition of the curing agent or initiator can begin the curing process immediately, and can also require additional curing steps. The addition of the curing agent or initiator can begin the curing process, but not bring it to a point where there composition is cured to the point of being fully cured, or of being unworkable. Thus, the curing agent or initiator can be added before or during the coating process, and further processing steps can complete the cure to form the membrane.

[0072] Curing the composition that forms the membrane can include a variety of methods, including exposing the composition to ambient temperature, elevated temperature, moisture, or radiation. In some embodiments, curing the composition can include combination of methods.

[0073] The membrane of the present invention can have any suitable thickness. In some examples, the membrane has a thickness of from about 1 μm to about 20 μm . In some examples, the membrane has a thickness of from about 0.1 μm to about 200 μm . In other examples, the membrane has a thickness of from about 0.01 μm to about 2000 μm .

[0074] The membrane of the present invention can be selectively permeable to one substance over another. In one example, the membrane is selectively permeable to one gas over other gases or liquids. In another example, the membrane is selectively permeable to more than one gas over other gases or liquids. In one embodiment, the membrane is selectively permeable to one liquid over other liquids or gases. In another embodiment, the membrane is selectively permeable to more than one liquid over other liquids. In some examples, the membrane has an ideal CO₂/N₂ selectivity of at least about 15-55, for example at least about 20, at least about 30, at least about 40, or at least about 50. In some examples, the membrane has a CO₂/CH₄ selectivity of at least about 1-30, such as at least about 5, at least about 10, at least about 15, or at least about 20. In some embodiments, with a CO₂/N₂ mixture for example, the membrane has a CO₂ permeability coefficient of at least about 50-4000 Barrers, such as about 50 Barrers, 100, 150, 200, 500, 1000, 1500, 2000, 2500, 3000, 3500, or about 4000 Barrers. In some embodiments, with a CO₂/CH₄ mixture for example, the membrane has a CO₂ permeability coefficient of at least about 50-4000 Barrers, such as about 50 Barrers, 100, 150, 200, 500, 1000, 1500, 2000, 2500, 3000, 3500, or about 4000 Barrers.

[0075] The membrane of the present invention can have any suitable shape. In some examples, the membrane of the present invention is a plate-and-frame membrane, a spiral wound membrane, a tubular membrane, a capillary fiber membrane or a hollow fiber membrane. The membrane can be a continuous or discontinuous layer of material. In some embodiments, the membrane may be used in conjunction with a liquid that enhances gas transport, such as in a membrane contactor (e.g. a device that permits mass transfer between a gaseous phase and a liquid phase across a membrane without dispersing the phases in one another).

Unsupported Membrane

[0076] In some embodiments of the present invention, the membrane is unsupported, also referred to as free-standing. The majority of the surface area on each of the two major sides of a membrane that is free-standing is not contacting a substrate, whether the substrate is porous or not. In some embodiments, a membrane that is free-standing can be 100% unsupported. A membrane that is free-standing can be supported at the edges or at the minority (e.g. less than 50%) of the surface area on either or both major sides of the membrane. The support for

a free-standing membrane can be a porous substrate or a nonporous substrate.

Examples of suitable supports for a free-standing membrane can include any

examples of supports given herein. A free-standing membrane can have any

suitable shape, regardless of the percent of the free-standing membrane that is

5 supported. Examples of suitable shapes for free-standing membranes include, for example, squares, rectangles, circles, tubes, cubes, spheres, cones, and planar sections thereof, with any thickness, including variable thicknesses.

[0077] A support for a free-standing membrane can be attached to the membrane

in any suitable manner, for example, by clamping, with use of adhesive, by melting

10 the membrane to the edges of the substrate, or by chemically bonding the

membrane to the substrate by any suitable means. The support for the free-

standing membrane can be not attached to the membrane but in contact with the

membrane and held in place by friction or gravity. The support can include, for

example, a frame around the edges of the membrane, which can optionally include

15 one or more cross-beam supports within the frame. The frame can be any suitable

shape, including a square or circle, and the cross-beam supports, if any, can form

any suitable shape within the frame. The frame can be any suitable thickness. The

support can be, for example, a cross-hatch pattern of supports for the membrane,

where the cross-hatch pattern has any suitable dimensions.

20 **[0078]** In some embodiments, a free-standing membrane is made by the steps of

coating or applying a composition onto a substrate, curing the composition, and

partially or fully removing the membrane from the substrate. After application of the

composition to the substrate, the assembly can be referred to as a laminated film or

fiber. During or after the curing process the membrane can be at least partially

25 removed from at least one substrate. In some examples, after the unsupported

membrane is removed from a substrate, and the unsupported membrane is

attached to a support, as described above. In some examples, an unsupported

membrane is made by the steps of coating a composition onto one or more

substrates, curing the composition, and removing the membrane from at least one

30 of the one or more substrates, while leaving at least one of the one of more

substrates in contact with the membrane. In some embodiments, the membrane is

entirely removed from the substrate. In one example, the membrane can be peeled

away from the substrate. In one example, the substrate can be removed from the

membrane by melting, subliming, chemical etching, or dissolving in a solvent. In

35 one example, the substrate is a water soluble polymer that is dissolved by purging

with water. In one example, the substrate is a fiber or hollow fiber, as described in US 6,797,212 B2.

[0079] In examples that include a substrate, the substrate can be porous or nonporous. The substrate can be any suitable material, and can be any suitable shape, including planar, curved, solid, hollow, or any combination thereof. Suitable materials for porous or nonporous substrates include any materials described above as suitable for use as porous substrates in supported membranes, as well as any suitable less-porous materials. In some examples, the membrane can be heated, cooled, washed, etched or otherwise treated to facilitate removal from the substrate. In other examples, air pressure can be used to facilitate removal of the membrane from the substrate.

Supported Membrane or Coated Substrate

[0080] In some embodiments of the present invention, the membrane is supported on a porous or highly permeable non-porous substrate. A supported membrane has the majority of the surface area of at least one of the two major sides of the membrane contacting a porous or highly permeable non-porous substrate. A supported membrane on a porous substrate can be referred to as a composite membrane, where the membrane is a composite of the membrane and the porous substrate. The porous substrate on which the supported membrane is located can allow gases to pass through the pores and to reach the membrane. The supported membrane can be attached (e.g. adhered) to the porous substrate. The supported membrane can be in contact with the substrate without being adhered. The porous substrate can be partially integrated, fully integrated, or not integrated into the membrane.

[0081] A coating can be formed on the at least one porous surface of the substrate or on the at least one surface of the highly permeable non-porous substrate, e.g. by coating the at least one porous surface with the mixture or a curable composition that includes the processed silicone composition. Alternately, a porous or highly permeable non-porous substrate can be placed in contact with the formed coating before, during, or after curing of the coating. In some examples, a porous substrate can have its pores filled at the surface to provide a smooth surface for formation of a membrane; after formation of the membrane, the composition filling the pores can be dried or otherwise removed or shrunk to restore the porosity of the substrate. In some examples, the supported membrane is made in a manner identical to that disclosed herein pertaining to a free-standing membrane, but with the additional

step of placing or adhering the free-standing membrane on a porous substrate to make a supported membrane.

[0082] The porous substrate can be any suitable porous material known to one of skill in the art, in any shape. For example, the substrate can be a filter. The porous substrate can be woven or non-woven. The porous substrate can be a frit, a porous sheet, or a porous hollow fiber. For example, the at least one surface can be flat, curved, or any combination thereof. The surface can have any perimeter shape. The porous substrate can have any number of surfaces, and can be any three-dimensional shape. Examples of three-dimensional shapes include cubes, spheres, cones, and planar sections thereof with any thickness, including variable thicknesses. The porous substrate or highly permeable non-porous substrate can be smooth, be corrugated or patterned, or have any amount of surface roughness. The porous substrate can have any number of pores, and the pores can be of any size, depth, shape, and distribution. In one example, the porous substrate has a pore size of from about 0.2 nm to about 500 μm . The at least one surface can have any number of pores. In some examples, the pore size distribution may be asymmetric across the thickness of the porous sheet, film or fiber.

[0083] Suitable examples of porous substrates include porous polymeric films, fibers or hollow fibers, or porous polymers or any suitable shape or form. Examples of polymers that can form porous polymers suitable for use as a porous substrate in embodiments of the present invention include those disclosed in U.S. Patent No. 7,858,197. For example, suitable polymers include polyethylene, polypropylene, polysulfones, polyamides, polyether ether ketone (PEEK), polyarylates, polyaramides, polyethers, polyarylethers, polyimides, polyetherimides, polyphthalamides, polyesters, polyacrylates, polymethacrylates, cellulose acetate, polycarbonates, polyacrylonitrile, polytetrafluoroethylene and other fluorinated polymers, polyvinylalcohol, polyvinylacetate, syndiotactic or amorphous polystyrene, KevlarTM and other liquid crystalline polymers, epoxy resins, phenolic resins, polydimethylsiloxane elastomers, silicone resins, fluorosilicone elastomers, fluorosilicone resins, polyurethanes, and copolymers, blends or derivatives thereof. Suitable porous substrates can include, for example, porous glass, various forms and crystal forms of porous metals, ceramics and alloys, including porous alumina, zirconia, titania, and steel.

Method of Separating Gas Components

[0084] The present invention also provides a method of separating gas components or water vapor in a feed gas mixture by use of the membrane

described herein. The method includes contacting a first side of a membrane with a feed gas mixture to produce a permeate gas mixture on a second side of the membrane and a retentate gas mixture on the first side of the membrane. The permeate gas mixture is enriched in the first gas component. The retentate gas mixture is depleted in the first gas component. The membrane can include any suitable membrane as described herein.

[0085] The membrane can be free-standing or supported by a porous or permeable substrate. In some embodiments, the pressure on either side of the membrane can be about the same. In other embodiments, there can be a pressure differential between one side of the membrane and the other side of the membrane. For example, the pressure on the retentate side of the membrane can be higher than the pressure on the permeate side of the membrane. In other examples, the pressure on the permeate side of the membrane can be higher than the pressure on the retentate side of the membrane.

[0086] The feed gas mixture can include any mixture of gases. For example, the feed gas mixture can include hydrogen, carbon dioxide, nitrogen, ammonia, methane, water vapor, hydrogen sulfide, or any combination thereof. The feed gas can include any gas known to one of skill in the art. The membrane can be selectively permeable to any one gas in the feed gas, or to any of several gases in the feed gas. The membrane can be selectively permeable to all but any one gas in the feed gas.

[0087] Any number of membranes can be used to accomplish the separation. For example, one membrane can be used. The membranes can be manufactured as flat sheets or as fibers and can be packaged into any suitable variety of modules including hollow fibers, sheets or arrays of hollow fibers or sheets. Common module forms include hollow fiber modules, spiral wound modules, plate-and-frame modules, tubular modules and capillary fiber modules.

[0088] In embodiments, the membrane can be used to separate liquids. In some embodiments, the membrane can be used to separate a gas from a liquid. In another embodiment, the membrane can be used to separate a liquid from a gas. In another example, the membrane can be used to separate a gas from a gas that contains a suspended solid or liquid. In another example, the membrane can be used to separate a liquid from a liquid that contains a suspended or dissolved solid or gas.

[0089] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to the examples given herein.

General Methods

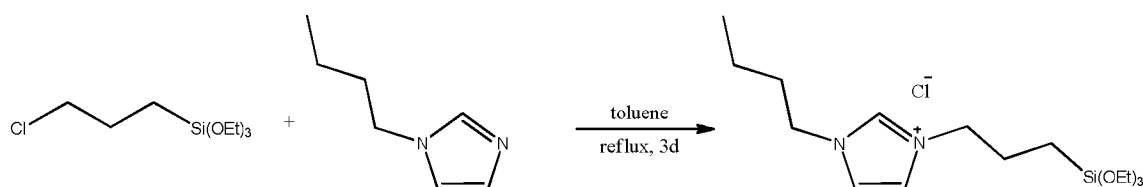
5 [0090] **Gas permeation test.** Gas permeability coefficients and ideal selectivities in a binary gas mixture were measured using a permeation cell including upstream (feed/retentate) and downstream (permeate) chambers that were separated by the membrane. The upstream chamber had one gas inlet and one gas outlet. The downstream chamber had one gas outlet. The upstream chamber was maintained
10 at 100 psig pressure and was continuously supplied with a suitable mixture of CO₂ gas and CH₄ gas (molar ratio of CO₂:CH₄=85:15, unless otherwise noted) at a flow rate of between 150-180 standard cubic centimeters per minute (sccm). The membrane was supported on a stainless-steel filter disk with a diameter of 55 mm. The membrane area was defined by a placing a silicone rubber gasket with a
15 diameter of 50 mm (Exotic Automation & Supply) on top of the membrane. The downstream chamber was maintained at ambient pressure and was connected to a 6-port injector equipped with a 1-mL injection loop. On command, the 6-port injector injected a 1-mL sample into a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The amount of gas permeated through the
20 membrane was calculated by calibrating the response of the TCD detector to the gases of interest. The reported values of gas permeability and selectivity were obtained from measurements taken after the system had reached a steady state in which the permeate side gas composition became invariant with time.

[0091] Permeability of gas component i can be calculated by the following
25 equation: $P_i = V \cdot \delta / (A \cdot t \cdot \Delta p)$, whereas P_i is the permeability for a gas i in a given membrane, V is the volume of gas which permeates through the membrane, δ is the thickness of the membrane, A is the area of the membrane, t is time, Δp is the pressure difference of the gas i at the retentate and permeation side. Ideal selectivity (α) of gas pair i and j is determined by $\alpha = P_i / P_j$. Permeance (M) is normalized
30 permeability of gas components: $M_i = P_i / \delta$.

Example 1. Synthesis of 1-(3-triethoxysilylpropyl)-3-butylimidazolium chloride (IL1).

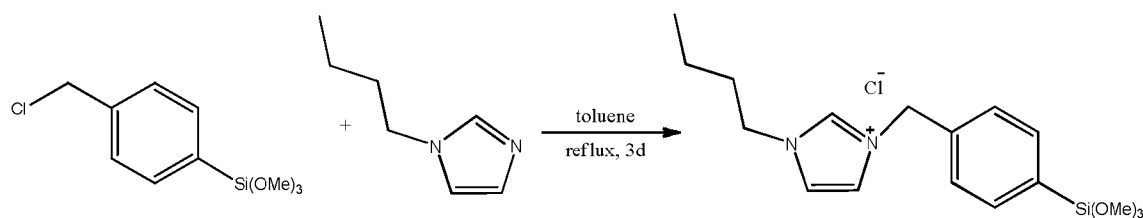
[0092] 1-Butylimidazole (13.67 g, 0.11 mol) and (3-chloropropyl)triethoxysilane (25.60 g, 0.11 mol) were refluxed in toluene (80 mL) for three days. The mixture was triturated with hexanes (100 mL). The hexanes layer was then decanted and
35 the process was repeated twice. Solvent was removed under high vacuum at 40 °C

overnight. IL1 was obtained as a golden yellow oil. The ^1H NMR spectrum conformed to the desired structure. Yield: 38.27 g (100%).



5 Example 2. Synthesis of 1-(p-(trimethoxysilyl)benzyl)-3-butylimidazolium chloride (IL2).

[0093] 1-Butylimidazole (12.46 g, 0.1 mol) and (p-(chloromethyl)phenyl)trimethoxysilane (24.68 g, 0.1 mol) were refluxed in toluene (80 mL) for three days. The mixture was triturated with hexanes (350 mL). The
 10 hexanes layer was then decanted and the process was repeated twice. Solvent was removed under high vacuum at 40 °C overnight. IL2 was obtained as a dark brown yellow oil. The ^1H NMR spectrum conforms to the desired structure. Yield: 28.20 g (75.9%).



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Example 3. Fabrication of sol-gel membranes by co-hydrolyzing IL1 with TEOS.

[0094] To a mixture of IL1 (10.14 g) obtained in Example 1 and tetraethyl orthosilicate (3.28 g, TEOS) was added water, concentrated ammonia (30% wt), and absolute ethanol. The molar ratio of solutes in the clear solution was
 20 TEOS:water:ammonia:ethanol = 10:960:96:80. The solution was stirred vigorously for 30 minutes and was left standing still at room temperature for 5 days. The clear sol was heated to 90 °C and volatiles were removed by an air stream. The viscous liquid was then heated to 120 °C to further remove volatiles. Finally the sol was gelled at 180 °C to afford a transparent glass. Yield: 6.58 g (102.2%, potentially
 25 evidencing remaining ethoxy groups). T_g : 1.5 °C. TGA onset temperature: 273 °C. Ash content (calcined at 800 °C): 36.8 %. Theoretical ash content: 42%.

[0095] The gel was crushed and grounded into a fine powder. The powder was pressed into free standing and continuous membranes by a Carver hot press. The

gel can also be laminated to polymer supports by the hot press, such as nylon and polypropylene membrane filters.

Example 4. Fabrication of sol-gel membrane via condensation cure.

- [0096] To a solution of IL1 (0.41 g) and polydiethoxysiloxane (0.11 g, PDEOS, 23.0-23.5% Si (w/w), 48-52% SiO₂ (w/w) equivalent) in isopropyl alcohol (10 mL) and ethanol (5 mL) was added a solution of trimethylsiloxy-terminated polydimethylsiloxane (0.71 g, PDMS, room temperature viscosity = 65,000 cSt.) and dibutyltin dilaurate (24.5 mg, DBDLT) in tetrahydrofuran (5 mL). Water (180 μ L) was added. The cloudy mixture was heated to 80 °C for 3 hours. The clear solution was distributed into several Teflon Petri dishes. Solvent was evaporated in a fume hood slowly (~3-4 hours), to provide a wet gel. The thin films were cured in an oven at 85 °C, to provide a membrane, which was a flexible, white, opaque, tough, paper-like film. Chemical compositions and gas separation performances were summarized in the table below:

15

PDMS wt%	PDEOS wt%	IL1 wt%	Ideal selectivity (CO ₂ /CH ₄)	CO ₂ Permeability (CO ₂ /CH ₄ , Barrer)	Ideal selectivity (CO ₂ /N ₂)	CO ₂ Permeability (CO ₂ /N ₂ , Barrer)
56.6%	8.8%	32.7%	14.92	136.28	30.67	122.54

Example 5. Variation of IL1 loading.

- [0097] Following the general procedure of Example 4, average chemical compositions of membranes and their separation performance with various IL1 loadings can be seen in the table below. The results given for IL1 loadings of 10% are the average of at least two parallel measurements, and the results given for IL1 loadings of 20% and 33% are the average of at least three parallel measurements. IL1 loading at 0% and further increase of the IL1 loading to 40% and 50% resulted in tacky and discontinuous films.

PDMS wt%	PDEOS wt%	IL1 wt%	Ideal selectivity (CO ₂ /CH ₄)	CO ₂ Permeability (Barrer)
75%	13%	10%	3.31	997.37
67%	11%	20%	9.7	182.5
56%	9%	33%	12.7	81.3

25

Example 6. Analysis of IL1 loading.

[0098] The dependence of the gas separation performance on IL1 content as measured in Examples 4 and 5 is graphically depicted in FIG. 1. FIG. 1 illustrates CH₄/CO₂ selectivity and CO₂ permeability of a membrane versus loading of IL1 in the mixture used to make the membrane. The CO₂ selectivity of the membranes increased when the IL1 loading increased, while the permeability of CO₂ and CH₄ decreased and leveled off at about 10-20%.

Example 7. Sol-gel membrane made using IL2 and variation of IL2 loading.

[0099] Following the general procedure of Example 4, chemical compositions of membranes and their separation performance with various IL2 loadings can be seen in the Table below. The results given are the average of at least two parallel measurements. The gas mixture used in this experiment was CO₂:CH₄ = 50%:50% mole.

PDMS wt%	PDEOS wt%	IL2 wt%	Ideal selectivity (CO ₂ /CH ₄)	CO ₂ Permeability (Barrer)
75.1%	12.3%	9.9%	4.06	1538.08
66.5%	11.0%	20.1%	7.98	210.15
56.1%	9.1%	32.8%	5.29	177.23

[00100] The dependence of the gas separation performance on IL2 content is graphically depicted in FIG. 2. FIG. 2 illustrates CH₄/CO₂ selectivity and CO₂ permeability of a membrane versus loading of IL2 in the mixture used to make the membrane. FIG. 2 illustrates CH₄/CO₂ selectivity and CO₂ permeability of a membrane versus loading of an ionic liquid in the mixture used to make the membrane. The CO₂ selectivity of the membranes generally increased when the IL2 loading increased, with the highest selectivity measured at about 20.1% IL2, while the permeability of CO₂ and CH₄ decreased and leveled off at about 10-20%. Membranes containing IL2 generally showed lower selectivity than membranes with IL1 at comparable IL loading level.

Example 8. Dependence of gas separation performance on PDEOS content.

[00101] Following the general procedure of Example 4, chemical compositions of membranes and their separation performance with various PDEOS loadings with about 30% IL1 can be seen in the table below. At 8% PDEOS, no continuous thin

films could be obtained. No higher loading than 15% was attempted, as higher loading of PDEOS led to a decline of the selectivity.

PDMS wt%	PDEOS wt%	IL1 wt%	Ideal selectivity (CO ₂ /CH ₄)	CO ₂ Permeability (Barrer)
57%	9%	32%	13.3	131.9
56%	12%	30%	11.74	31.10
53%	15%	30%	8.17	118.10

[00102] The dependence of the gas separation performance on PDEOS content is graphically depicted in FIG 3. FIG. 3 illustrates CH₄/CO₂ selectivity and CO₂ permeability versus loading of polydiethoxysiloxane in the mixture used to make the membrane. The loading of the crosslinker, PDEOS, was found have an impact on selectivity. Increase of PDEOS led to decline of the selectivity, while the impact of PDEOS on CO₂ permeability was less clear.

[00103] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments.

[00104] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[00105] Embodiment 1 provides a method of preparing a silicone composition, the method comprising: reacting a mixture in a water-miscible solvent in the presence of a condensation catalyst to form a sol, the mixture comprising (a) an ionic liquid having the formula $Z^+Q^-R^2-SiR^1_mX_{3-m}$; (b) optionally, a silane having the formula $R^1_nSiX_{4-n}$; (c) optionally, a polysiloxane cross-linking agent having an average of at least 3 silicon-bonded X groups per molecule; (d) optionally, a polydiorganosiloxane having the formula $X_{3-p}R^1_pSiO(R^1_2SiO)_qSiR^1_pX_{3-p}$; and (e) water; concentrating the sol to form a wet gel; and drying the wet gel to form a

silicone composition; wherein Q^+ is a cationic organic group comprising at least one of N, S, and P, at each occurrence X is independently a hydrolyzable group, at each occurrence R^1 is independently C_1 to C_{10} hydrocarbyl, R^2 is C_1 to C_{20} hydrocarbylene, Z^- is a counterion, m is 0, 1, or 2, n is 0 or 1, p is 0, 1, or 2, q is about 100 to 2000, and at least one of optional elements (b) and (c) is included in the mixture.

[00106] Embodiment 2 provides the method of Embodiment 1, wherein the silicone composition is a xerogel or glass.

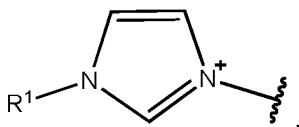
[00107] Embodiment 3 provides the method of any one of Embodiments 1-2, wherein the cross-linking agent (c) is a poly(dialkoxysiloxane) comprising from 20 to 90% (w/w) SiO_2 .

[00108] Embodiment 4 provides the method of any one of Embodiments 1-3, wherein Q^{+-} is $R^1_a M^{+-}$, wherein $M^+ = N^+, P^+, \text{ or } S^+$, provided that when M^+ is N^+ or P^+ , a is 3, and when M is S^+ , a is 2.

[00109] Embodiment 5 provides the method of any one of Embodiments 1-3, wherein Q^{+-} comprises $R^1_a Y^{+-}$, wherein Y^+ is a heterocyclic ring bearing a positive charge, the heterocyclic ring comprising at least one N, S, or P, and a is 1, 2, or 3.

[00110] Embodiment 6 provides the method of Embodiment 5, wherein the heterocyclic ring is bound to the $-R^2-SiR^1_m X_{3-m}$ at a heteroatom in the heterocyclic ring.

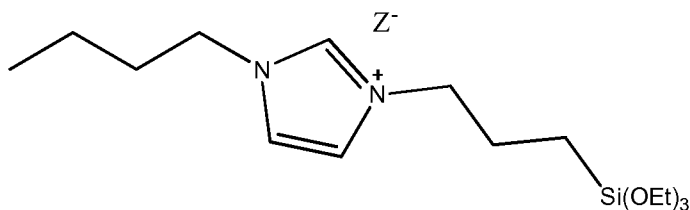
[00111] Embodiment 7 provides the method of any one of Embodiments 5-6, wherein a is 1 and $R^1 Y^{+-}$ is



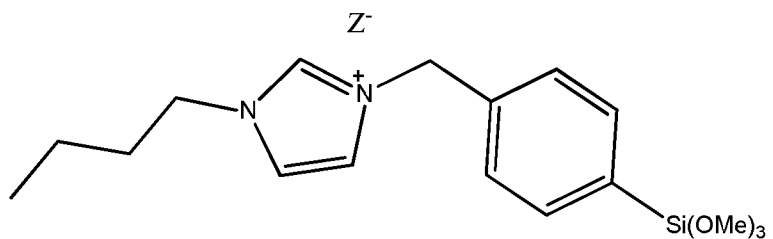
[00112] Embodiment 8 provides the method of any one of Embodiments 1-7, wherein at each occurrence R^1 is independently C_1 to C_{10} alkyl.

[00113] Embodiment 9 provides the method of any one of Embodiments 1-8, wherein R^2 is $-R^5-Ar-R^5-$, wherein at each occurrence R^5 is independently a single bond or C_{1-10} alkylene and Ar is a C_{4-10} divalent cycloalkyl, aryl, heterocyclyl, or heteroaryl group.

[00114] Embodiment 10 provides the method of any one of Embodiments 1-3 and 5-9, wherein the ionic liquid is at least one of



and



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[00115] Embodiment 11 provides the method of any one of Embodiments 1-10, wherein at each occurrence X is independently -OR⁴, wherein R⁴ is C₁ to C₁₀ hydrocarbyl.

10 [00116] Embodiment 12 provides a silicone composition prepared according to the method of any of Embodiments 1-11.

[00117] Embodiment 13 provides an unsupported membrane comprising the silicone composition prepared according to the method of any one of Embodiments 1-12, wherein the membrane is free-standing.

15 [00118] Embodiment 14 provides the unsupported membrane of Embodiment 13, wherein the membrane has a thickness of from 0.1 to 200 μm.

[00119] Embodiment 15 provides the unsupported membrane of any one of Embodiments 13-14, wherein the membrane is selected from a plate membrane, a spiral membrane, tubular membrane, and hollow fiber membrane.

20 [00120] Embodiment 16 provides a coated substrate, comprising: a substrate; and a coating on the substrate, wherein the coating comprises the silicone composition prepared according to the method of any one of Embodiments 1-11.

[00121] Embodiment 17 provides the coated substrate of Embodiment 16, wherein the substrate is porous and the coating is a membrane.

[00122] Embodiment 18 provides the coated substrate of any one of Embodiments 16-17, wherein the porous substrate is a frit comprising a material selected from glass, ceramic, alumina, and a porous polymer.

[00123] Embodiment 19 provides a method of separating gas components in a feed gas mixture, the method comprising contacting a first side of a membrane comprising the silicone composition prepared according to the method of any one of Embodiments 1-11 with a feed gas mixture comprising at least a first gas component and a second gas component to produce a permeate gas mixture on a second side of the membrane and a retentate gas mixture on the first side of the membrane, wherein the permeate gas mixture is enriched in the first gas component.

[00124] Embodiment 20 provides the method of Embodiment 19, wherein the permeate gas mixture comprises carbon dioxide and the feed gas mixture comprises at least one of nitrogen and methane.

[00125] Embodiment 21 provides the apparatus or method of any one or any combination of Embodiments 1-20 optionally configured such that all elements or options recited are available to use or select from.

CLAIMS

We claim:

1. A method of preparing a silicone composition, the method comprising:
reacting a mixture in a water-miscible solvent in the presence of a
condensation catalyst to form a sol, the mixture comprising

(a) an ionic liquid having the formula $Z-Q^+-R^2-SiR^1_mX_{3-m}$;

(b) optionally, a silane having the formula $R^1_nSiX_{4-n}$;

(c) optionally, a polysiloxane cross-linking agent having an average
of at least 3 silicon-bonded X groups per molecule;

(d) optionally, a polydiorganosiloxane having the formula X_3-

$pR^1_pSiO(R^1_2SiO)_qSiR^1_pX_{3-p}$; and

(e) water;

concentrating the sol to form a wet gel; and

drying the wet gel to form a silicone composition;

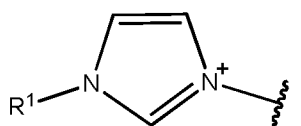
wherein Q^+ is a cationic organic group comprising at least one of N, S, and P, at each occurrence X is independently a hydrolyzable group, at each occurrence R^1 is independently C_1 to C_{10} hydrocarbyl, R^2 is C_1 to C_{20} hydrocarbylene, Z^- is a counterion, m is 0, 1, or 2, n is 0 or 1, p is 0, 1, or 2, q is about 100 to 2000, and at least one of optional elements (b) and (c) is included in the mixture.

2. The method of claim 1, wherein the silicone composition is a xerogel or glass.

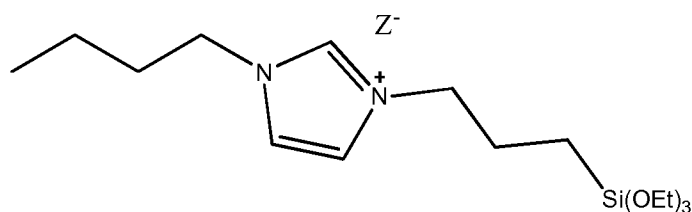
3. The method of any one of claims 1-2, wherein the cross-linking agent (c) is a poly(dialkoxysiloxane) comprising from 20 to 90% (w/w) SiO_2 .

4. The method of any one of claims 1-3, wherein Q^{+-} is $R^1_aM^{+-}$, wherein M^+ is N^+ , P^+ , or S^+ , provided that when M^+ is N^+ or P^+ , a is 3, and when M is S^+ , a is 2.

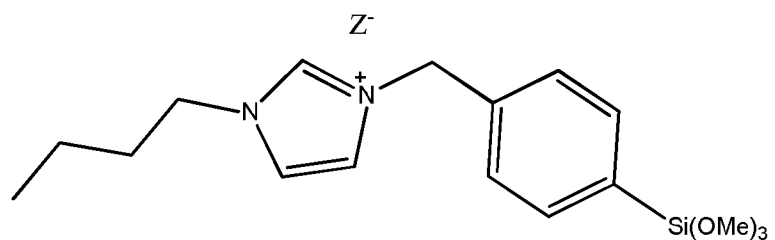
5. The method of any one of claims 1-3, wherein Q^{+-} comprises $R^1_a Y^{+-}$, wherein Y^{+-} is a heterocyclic ring bearing a positive charge, the heterocyclic ring including at least one N, S, or P, and a is 1, 2, or 3.
6. The method of claim 5, wherein the heterocyclic ring is bound to the $-R^2-SiR^1_m X_{3-m}$ at a heteroatom in the heterocyclic ring.
7. The method of any one of claims 5-6, wherein a is 1 and $R^1 Y^{+-}$ is



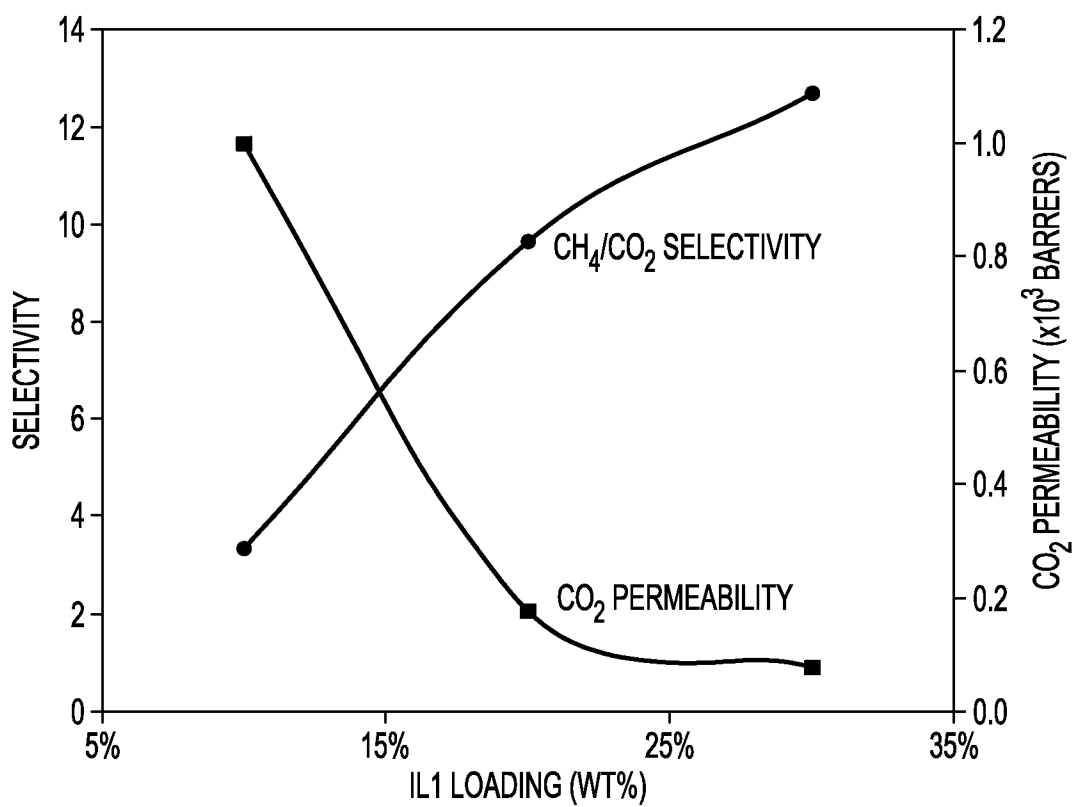
8. The method of any one of claims 1-7, wherein at each occurrence R^1 is independently C_1 to C_{10} alkyl.
9. The method of any one of claims 1-8, wherein R^2 is $-R^5-Ar-R^5-$, wherein at each occurrence R^5 is independently a single bond or C_{1-10} alkylene and Ar is a C_{4-10} divalent cycloalkyl, aryl, heterocyclyl, or heteroaryl group.
10. The method of any one of claims 1-3 and 5-9, wherein the ionic liquid is at least one of



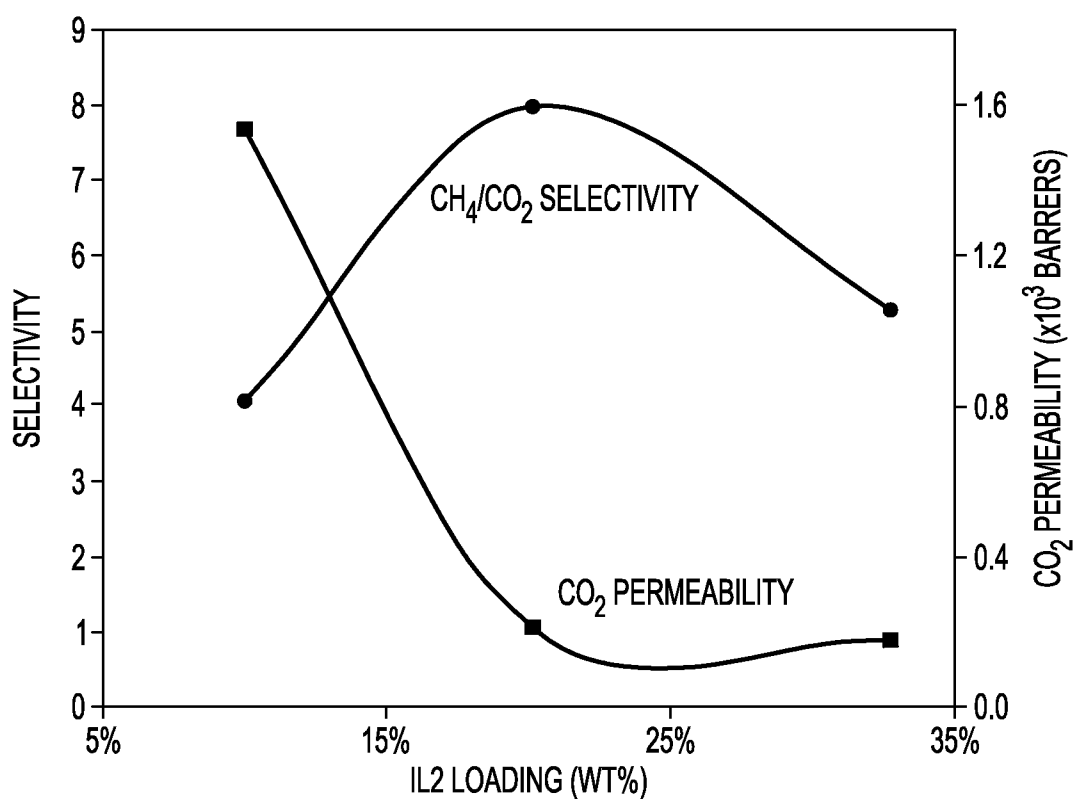
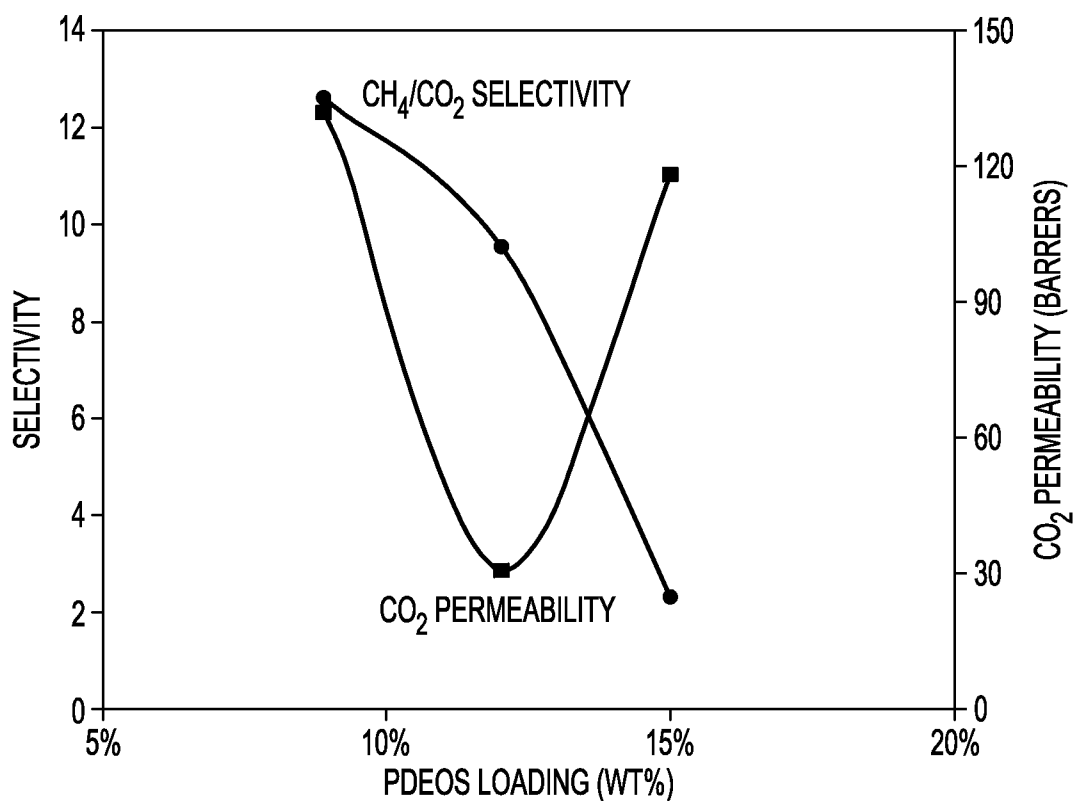
and



11. The method of any one of claims 1-10, wherein at each occurrence X is independently -OR⁴, wherein R⁴ is C₁ to C₁₀ hydrocarbyl.
12. A silicone composition prepared according the method of any of claims 1-11.
13. An unsupported membrane comprising the silicone composition prepared according to the method of any one of claims 1-12, wherein the membrane is free-standing.
14. A coated substrate, comprising:
a substrate; and
a coating on the substrate, wherein the coating comprises the silicone composition prepared according to the method of any one of claims 1-11.
15. A method of separating gas components in a feed gas mixture, the method comprising contacting a first side of a membrane comprising the silicone composition prepared according to the method of any one of claims 1-11 with a feed gas mixture comprising at least a first gas component and a second gas component to produce a permeate gas mixture on a second side of the membrane and a retentate gas mixture on the first side of the membrane, wherein the permeate gas mixture is enriched in the first gas component.
16. The method of claim 15, wherein the permeate gas mixture comprises carbon dioxide and the feed gas mixture comprises at least one of nitrogen and methane.

*FIG. 1*

2/2

*FIG. 2**FIG. 3*

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/052701

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/14 B01D71/70 C08J3/075 C08G77/26 C08G77/28
C08G77/30 C08L83/04

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 C08J C08G C08L

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RAJKUMAR KORE ET AL: "Synthesis of triethoxysilane imidazolium based ionic liquids and their application in the preparation of mesoporous ZSM-5", CATALYSIS COMMUNICATIONS, vol. 18, 1 February 2012 (2012-02-01), pages 11-15, XP055089292, ISSN: 1566-7367, DOI: 10.1016/j.catcom.2011.11.012	12-14
Y	page 12, paragraph 2.2; figure 2	1-11
A	-----	15,16
Y	US 2012/024778 A1 (MINEHARA HIROKI [JP] ET AL) 2 February 2012 (2012-02-02)	1-11
A	example 1	12-16

☐

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

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"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

20 November 2013

Date of mailing of the international search report

28/11/2013

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/052701

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012024778 A1	02-02-2012	AU 2010231859 A1	13-10-2011
		CN 102378645 A	14-03-2012
		EP 2415515 A1	08-02-2012
		KR 20120013308 A	14-02-2012
		SG 174896 A1	28-11-2011
		US 2012024778 A1	02-02-2012
		WO 2010113656 A1	07-10-2010
