METHOD OF GAS SEPARATION

The present invention provides a method of separating a target gas species from a mixture of non-amine gas species, the method comprising contacting the mixture of non-amine gas species with a gas separation membrane, the gas separation membrane comprising one or more solid organic ionic plastic crystal (OIPC); creating a difference in pressure across the membrane to facilitate transport of one or more gas species through the membrane so as to provide for a separated gas composition in which the concentration of the target gas species is higher compared with that in the mixture of non-amine gas species; wherein separation of the mixture of non-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid OIPC.
FIELD OF THE INVENTION

The invention relates in general to a method of separating a target gas species from a mixture of non-amine gas species, and more specifically to a method of separating a target gas species from a mixture of non-amine gas species using a gas separation membrane.

BACKGROUND OF THE INVENTION

Separation of target gas species from mixtures of gas species is of significant importance to a large number of industries and is typically aimed at the recovery of valuable gases or to aid in pollution control. Established conventional technologies in this field include cryogenic distillation, swing adsorption techniques (e.g. pressure swing adsorption, vacuum swing adsorption, and temperature swing adsorption), and solvent absorption (e.g. liquid extraction or stripping).

In addition to such conventional technologies, membrane gas separation is establishing itself as a valuable alternative technology for gas separation and is increasingly finding large scale application due to certain inherent advantages of membrane-based separation units over traditional separators. Specifically, gas separation membrane units can offer rapid mass transfer rate and high selectivity towards specific gases, are simple to operate and to install, they can operate under mild pressure and temperature conditions, and do not require use of corrosive and polluting solvents.

The efficiency of a gas separation membrane unit depends largely on the separation performance of the membrane, which itself derives from the characteristics of the specific material from which the membrane is made. Conventional membrane-based separation technologies employ polymer-based membranes in the form of non-porous thin membranes or porous thick membranes. However, while non-porous thin membranes offer
high selectivity towards the target gas species, they often suffer from poor mechanical stability at operative conditions. On the other hand, porous thick membranes offer good mechanical stability and flux rates but typically present lower gas selectivity.

Accordingly, there remains an opportunity to develop a gas separation method that makes use of membranes based on non-conventional materials and offers gas separation with good selectivity while retaining mechanical integrity of the membrane during the separation process.

SUMMARY OF THE INVENTION

The present invention provides a method of separating a target gas species from a mixture of non-amine gas species, the method comprising contacting the mixture of non-amine gas species with a gas separation membrane, the gas separation membrane comprising one or more solid organic ionic plastic crystal (OIPC); creating a difference in pressure across the membrane to facilitate transport of one or more gas species through the membrane so as to provide for a separated gas composition in which the concentration of the target gas species is higher compared with that in the mixture of non-amine gas species; wherein separation of the mixture of non-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid OIPC.

Surprisingly, it has now been found that a gas separation membrane comprising one or more solid OIPCs is differentially permeable to gas species and can be used to effectively discriminate specific gas species contained in a mixture of non-amine gas species in a gas separation process. Without wishing to be limited by theory, it is believed the specific structure of solid OIPCs offers available free volume for the preferential transport of certain gas species relative to others.

Advantageously, the method of the invention is based on a gas separation membrane that combines good selectivity towards the target gas species while maintaining mechanical integrity during the separation.
In addition, OIPCs are characterised by unique plasticity features. Specifically, they are known to undergo at least one solid-solid phase transition before melting. Advantageously such a solid-solid phase transition has been found to afford additional control over the discrimination of the target gas species relative to traditional separation methods. It has now been found that different solid phases of the same OIPC have different permeability to the same gas species. In other words, the gas permeability of a gas species through the structure of an OIPC can change as a result of a solid-solid phase transition of the OIPC.

Accordingly, in one embodiment the method of the invention comprises promoting a solid-solid phase transition in the solid OIPC to change permeability of one or more of the gas species through the structure of the solid OIPC.

In another embodiment, the gas separation membrane consists essentially of one or more solid OIPC.

In a further embodiment, the gas separation membrane further comprises a support for the one or more solid OIPC. This advantageously offers additional mechanical stability to the separation membrane. Also, by selecting a support material that itself offers gas separation capability it is possible to further enhance the efficiency of the separation membrane towards specific gas species.

In another embodiment, the gas separation membrane used in accordance with the invention further comprises a porous material, for example Metal Organic Framework (MOF), Covalent Organic Framework (COF), zeolitic imidazolate frameworks (ZIFs), zeolite, activated carbon material, metal oxide, or a combination of one or more thereof. Advantageously, such porous material can act in synergy with the solid OIPC to enhance the separation performance.

The present invention is also directed to the use of one or more OIPC for separating a target gas species from a mixture of non-amine gas species, wherein separation of the
mixture of non-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid OIPC.

In addition to their surprising gas separation capability, OIPCs advantageously exhibit additional properties such as low to zero flammability, negligible volatility and high thermal stability. Such properties are believed to be particularly advantageous in a variety of industrial activities in which it is required to isolate target gas species from mixtures of production gases for example natural gas production, synthetic fuel production^ bulk inorganic and organic chemicals production, and the likes.

**BR!EF DESCRIPTION OF THE DRAWINGS**

Embodiments of the invention will be now described with reference to the following non-limiting drawings, in which:

Figure 1 shows the permeation rate for CO₂ and ¾ measured using a gas separation membrane made of methylethylpyrrolidinium tetrafluoroborate ([C₂mpyr][BF₄]) in an electrospun polyvinylidene fluoride (PVDF) fibre support;

Figure 2 shows single-gas flux rates as a function of the pressure difference across a gas separation membrane made of [O₄mpyr][BF₄] in an electrospun PVDF fibre support;

Figure 3 shows single-gas flux rates as a function of the pressure difference across a gas separation membrane made of methyldiethylisobutyrophosphorium hexafluorophosphate ([P₆2₂]PF₆) in an electrospun PVDF fibre support;

Figure 4 shows carbon dioxide flux versus transmembrane pressure data for a gas separation membrane made of [C₂mpyr][BF₄] in an electrospun PVDF fibre support, a gas separation membrane made of [P₆2₂]PF₆ in an electrospun PVDF fibre support, and a gas separation membrane made of methypropyropyliTolidinium tetrafluoroborate ([C₂mpyr][BF₄]) in an electrospun PVDF fibre support;
Figure 5 shows $CO_2$ and $N_2$ uptake (mol %) into $([P_{1224}][P_{34}])$; and

Figure 6 shows $CO_2$ uptake (ppni) into diisopropylammonium triflate $[DPA][Tf]$. Some Figures contain colour representations or entities. Coloured versions of the Figures are available upon request.

**DETAILED DESCRIPTION OF THE INVENTION**

The method of the invention separates a target gas species from a mixture of non-amine gas species.

By the expression 'mixture of non-amine gas species' is meant a combination of two or more gas species in which no gas species has the chemical structure $NR_3$, where each $R$ group is independently hydrogen or an organic group (e.g. alkyl). An example of a $NR_3$ gas species is ammonia ($NH_3$).

Apart from being a non-amine, there is no other limitation on the type of gas species used in the method of the invention. For example, the method of the invention may be used in the separation of $N_2$ or $O_2$ from air, separation of $H_2$ from $N_2/34$ and $O_4/34$ mixtures, recovery of $CO$ or $34$ from hydrocarbon gases (e.g. in oil refinery processes), separation of $CH_4$ from the other components of biogas, enrichment of air with $O_2$ for medical or metallurgical purposes, enrichment of ullage with $N_2$ in meeting systems designed to prevent fuel tank explosions, removal of water vapour from natural gas and other gases, removal of $SO_2$, $CQ_2$ and/or $34$ S from natural gas, removal of volatile organic compounds (VOCs) from exhaust streams, or separation of $CO$ and/or $CO_2$ from combustion gases.

In one embodiment, the method involves separating $CO_2$ from a mixture of gas species comprising $CQ_2$ and one or more of $N_2$, $H_3$, $CFI4$, $O_2$, $34$ $O$, $H_2S$, $SO_3$, and $NG_3$. In another embodiment, the method of the invention involves separating $CO_2$ from a mixture of $CG_2$.
and N₂, and/or separating CO₂ from a mixture of CO₂ and C₃₄.

The method of the invention provides for a separated gas composition in which the concentration of the target gas species is higher compared with that in the mixture of non-amine gas species. As the efficiency of the gas separation membrane increases so too will the concentration of the target gas species in the separated gas composition.

For avoidance of doubt, any reference herein to 'target gas species' is to be intended as a reference to the one or more gas species that is/are of interest to separate/isolate from the non-amine gas mixture in which they are originally present. In this context, any reference herein to 'gas species' is to be intended as reference to any one (or more than one) gas species present in the non-amine gas mixture, i.e. irrespective of whether it is a (or they are) 'target' gas species.

There is no particular limitation on the concentration of the target gas species in the separated gas composition, provided it is higher compared with that of the target gas species in the mixture of non-amine gas species that was subjected to separation. In some embodiments, the concentration of the target gas species in the separated gas composition is at least 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 10, 20 or 50 times higher compared with that of the target gas species in the mixture of non-amine gas species that was subjected to separation.

The method of the invention is performed using a gas separation membrane which comprises one or more solid organic ionic plastic crystal (OIPC).

The expression 'organic ionic plastic crystal' (OIPC) used herein is intended to mean a salt that (i) contains an organic ion, (ii) is a plastic crystal and (iii) has ionic conductivity of at least 10⁻⁸ S/cm when in its sub-melting phase.

In relation to (i) above, by the salt containing an 'organic ion' is meant a salt having a cation and an anion wherein at least one of the cation and the anion is organic. In this context, by the ion being 'organic' is meant that the ion contains at least one carbon atom.
In one embodiment, both the cation and anion are organic.

In relation to (ii) above, as used herein the expression 'plastic crystal' is meant to indicate that the salt displays at least one temperature-driven solid-solid phase transition before melting. In some cases this phase transition is difficult to observe or the lower temperature phase is difficult to form. In these cases the plastic crystal properties can be indicated by the ionic conductivity of the material in its sub-melting phase.

By the expression 'solid-solid phase transition' is meant a temperature promoted rearrangement of the atomic structure, or parts of the atomic structure, of the OIPC. In the art, different solid phases of an OIPC are also referred to as 'rotator phases', and the solid-solid phase transition of an OIPC is accordingly referred to as 'rotator phase transition'. Those transitions are associated with a temperature promoted onset of rotational or translational motions of the ions (or parts of the ions) resulting in a progressive transformation of the salt structure from a first lattice arrangement to a second arrangement. The second arrangement is characterised by increased disorder, for example rotational disorder whereby all or part of the ion is in rotational motion. When in a plastic phase, the OIPC is more mechanically plastic.

A person skilled in the art would be aware of techniques that can be adopted to measure and characterise a solid-solid phase transition of an OIPC. For the purpose of this application the technique of choice is Differential Scanning Calorimetry (DSC). As it would be known to the skilled person, DSC characterisation is performed at increasing temperatures and allows to obtain a plot of the heat flow into the OIPC versus a reference sample. From this, the heat capacity of the OIPC as a function of the test temperature can also be determined.

In general, a DSC plot allows visualising phase transitions of a material in the form of a discontinuity of the heat flow, versus a reference, at specific temperatures, for example in the form of a spike in the heat flow signal. Accordingly, for the purpose of this application a solid-solid phase transition of an OIPC is characterised by a DSC plot in which a
discontinuity (e.g. a spike) of the heat flow in the sub-melting temperature range is observed. For avoidance of doubt, such discontinuity will be in addition to, and distinct from, the discontinuity arising from the solid-liquid transition of the OIPC (i.e. melting).

5 In relation to (ai) above, the expression ‘ionic conductivity of at least 1G\(^8\) S/cm\(^3\) when in sub-melting phase’ refers to the value of ionic conductivity that is determined by Electrochemical Impedance Spectroscopy (EIS) according to the following procedure. The OIPC is first shaped into a pellet (1 mm thick and 13 mm in diameter) under dry conditions, then sandwiched between two stainless steel blocking electrodes that are looked together. The ionic conductivity is measured by EIS using a frequency response analyzer driven by an impedance measurement software (which would be available to a skilled person). Data is collected over a 10 MHz to 0.1 Hz frequency range and at a temperature at which the OIPC is solid and in the sub-melting phase. The temperature of the cell is controlled using a high-accuracy temperature controller (with accuracy better than ±1°C), with the temperature measured using a thermocouple attached to one of the blocking electrodes. The sample is heated (typically at < 0.5°C/min) and thermally equilibrated (typically for at least 5 minutes) prior to impedance measurement at each temperature point.

20 The chemical nature of the anion and cation that constitute the salt for use in the invention is not particularly limited; provided their combination results in an OIPC that satisfies (i)-(iii) above.

Examples of anions suitable to form the salt used in the invention include BF\(_4^–\), PF\(_6^–\), N(CN)\(_2^–\), (CF\(_3\)SO\(_2\))\(_2^–\)N\(^–\), (FSO\(_2\))\(_2^–\)N\(^–\), OCN\(^–\), SCN\(^–\), dicyanomethanide, carboxamoyl cyanonitroso)methanide, (C\(_2\)F\(_3\)SO\(_2\))\(_2^–\)N\(^–\), (CF\(_3\)S\(_2\))\(_2^–\)C\(^–\), C(CN)\(_3^–\), B(CN)\(_4^–\), (C\(_2\)F\(_3\))\(_3^–\)PF\(_3^–\), alkyl-SO\(_3^–\), perfluoroalkyl-SO\(_3^–\), aryl-SO\(_3^–\), \(\Gamma\), H\(_2\)PO\(_4^–\), HPO\(_4^2^–\), sulfate, sulphite, nitrate, triiluoiOmethanesulfonate, \(p\)-toluenesulfonate, bis(oxalate)borate, acetate, formate, gallate, glycolate, BF\(_3(CN)^–\), BF\(_2(CN)\)\(_2^–\), BF\(_2\)(CN)\(_3^–\), BF\(_3(R)^–\), BP\(_2\)(R)\(_3^–\), BF(R)\(_3^–\) where R is an alkyl group such as Methyl, Ethyl, Propyl etc. and anions made from transition metal complexes, e.g. [Tb(hexafluoroacetyacetone)\(_4^–\)].
In one embodiment, an OIPC suitable for use in the invention comprises a fluorinated anion. The chemical affinity of fluorine with certain gases (e.g. CO₂) can provide for improved solubility of those gases within fluorinated OIPCs relative to non-fluorinated OIPCs. Examples of fluorinated anions suitable for use in the invention include BF₄⁻, PF₆⁻, (CF₃SO₂)₂N⁻, (FSO₂)₂N⁻, BF₃(CN)⁻, BF₂(CN)₂⁻, BF(CN)₃⁻, BF₃(R)⁻, BF₂(R)₂⁻, BF(R)₃⁻ where R is an alkyl group such as Methyl, Ethyl, Propyl etc., (CF₃SO₂)NF, (CF₃SO₂)₂C⁻, (C₂F₅SO₂)₂N⁻, (C₂F₅)₂PF⁻, (C₂F₅PO₂)₂N⁻, (CF₃SO₂)NCN, (CF₃SO₂)N(SO₂F), (CF₃CO)N(SO₂F) and perfluoroalkyl-SO₃⁻.

As used herein, the term 'alkyl', used either alone or in compound words, describes a group composed of at least one Carbon and Hydrogen atom, and denotes straight chain, branched or cyclic alkyl, for example C₁₂₋₂₀ alkyl, e.g. C₄₋₁₀ or C₁₀⁴. Examples of straight chain and branched alkyl include methyl ethyl, n-propyl, isopropyl, n-buty1, sec-butyl, tert-butyl, n-pentyl, 1,2-dimethylpropyl, 1,1-dimethyl-propyl, hexyl, 4-methylpentyl, 1-nethylpentyl, 2-methylpentyl, 3-methylpentyl, Li-dimethylbuty1, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methy1hexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, Octyl, 6-methyleneheptyl, i-methyleneheptyl, i,i,3-p-tetramethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethylloctyl, 1-, 2-, 3- or 4-propylheptyl undecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyleneundecyl, 1-, 2-, 3-, 4-, 5- or 6-propynonyl, 1-, 2-, 3- or 4-butylloctyl, and the like. Examples of cyclic alkyl include mono- or polycyclic alkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and the like.

Where an alkyl group is referred to generally as 'propyl', butyl* etc, it will be understood that this can refer to any of straight, branched and cyclic isomers where appropriate. An
alkyl group may be optionally substituted by one or more optionalksubstituents as herein defined.

The term ‘aryl’ (or ‘carboaryl’) denotes any of single, polynuclear, conjugated and fused residues of aromatic hydrocarbon ring systems (e.g. C₆₋₂₄ or C₆₋₁₈). Examples of aryl include: phenyl, biphenyl, terphenyl, quaterphenyl, naphthyl, tetrahydronaphthyl, anthracenyi, dihydroanthracenyi, benzanthracenyi, dibenzanthraceeiyl, phenanthrenyl, fluorenyl, pyrenyl, idenyl, azulenyl, clirysenyl. Preferred aryl include phenyl and naphthyl. An aryl group may or may not be optionally substituted by one or more optional substituents as herein defined. The term ‘arylene’ is intended to denote the divalent form of aryl

Examples of cations suitable to form the salt used in the invention include: dialkylpyridinium, pyrrolidinium, monoalkylpyrroldinum, dialkylimidazolium, monoalkylammonium, tetraalkylammonium, dialky!ammecium, dialkanolalkylammonium, alkanoieldialkyl ammonium, bis(allylimidazolium), bis(dialkyl)ammonium, bis(aryl)lammoniium, diallylammonium, guanidinium, dialkylamine, dialkylamine, tetraalkyl phosphoniums, alkylammonium, guanidinium, dialkylamine, dialkylamine, dialkylamine, tetraalkyl phosphoniums, alkylammonium, guanidinium, dialkylamine, dialkylamine, dialkylamine, tetraalkyl phosphoniums, etc.

Examples of OIPCs suitable for use in the invention, with include both protic and aprotic types, include N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, N,N-methylene-bis(4-formylphenyl)amine, and N,N-methylene-bis(4-formylphenyl)amine.
diethyl(methyl)(isobutyl)phosphonium bis(fluorosulfonyle)amide, diethyl(methyl)(isobutyl)phosphonium tetrafluoroborate, diethyl(methyl)(isobutyl)phosphonium hexafluorophosphate, methytriethyl)phosphonium bis(fluorosulfonyle)amide, methyl(triethyl)phosphonium bis(trifluoromethylsulfonyle)amide, triisobutyl(methyl)phosphonium hexafluorophosphate, triisobutyl(methyl)phosphonium bis(fluorosulfonyle)amide, triisobutyl(methyl)phosphonium tetrafluoroborate, triisobutyl(methyl)phosphonium thiocyanate, triisobutyl(methyl)phosphonium bis(fluorosulfonyle)amide, dimethylpyrrolidinium bis(fluorosulfonyle)amide, choline dihydrogen phosphate, choline trifluoromethanesulfonate, N,N-dimethylpropylenediammonium triflate, tri(isobutyl)phosphonium bis(trifluoromethanesulfonyle)amide, tri(isobutyl)phosphonium methanesulfonate, tri(isobutyl)phosphonium trifluoromethanesulfonate, tri(isobutyl)ammonium bis(trifluoromethanesulfonyle)amide, tri(isobutyl)phosphonium nitrate, tri(isobutyl)ammonium methanesulfonate, tri(isobutyl)ammonium trifluoromethanesulfonate, tri(isobutyl)ammonium nitrate, 1,2-bis[N-(N'-hexylimidazolium)]ethane bis(hexafluorophosphate), and combinations thereof.

In the method of the invention the OIPC is solid. By the OIPC being 'solid' is meant that the OIPC is in, and maintains, a solid state under the gas separation conditions of temperature, pressure and chemical nature of the gas species being separated, and exhibits a non-zero value of shear modulus at low applied stress. The solid may exhibit plastic flow at values of applied stress above its yield stress. Accordingly, the expression 'solid state' used herein will be understood as being in contrast with 'molten state' or 'solution state' (i.e. dissociated by solvation).

In the method of the invention gas separation is achieved by promoting transport of gas species through a gas separation membrane comprising a solid OIPC. Specifically, gas separation of a mixture of non-amine gas species occurs as a result of one or more gas species permeating through the structure of the solid OIPC,

By the one or more gas species permeating 'through the structure of the solid OIPC' it is
meant that (a) the gas species are transported through the gas separation membrane by passing through the atomic structure of the OIPC, and that in doing so (b) the OIPC maintains its solid state. Accordingly, the structure of the OIPC remains in a solid state during the method of the invention.

In relation to (a) above, without wishing to be limited by theory it is believed permeation of gas species through an OIPC is associated with, and made possible by, presence of defects in the OIPC atomic structure. For example, it is postulated that the permeation occurs through either vacancies in the lattice or through extended defects such as dislocations or grain boundaries within the structure of the solid OIPC.

The presence of defects may also be associated with increased rotational and translational disorder of the ions. The onset of additional disorder when an OIPC undergoes a solid-solid phase transition can also result in a significant increase in the OIPC free volume.

Collectively, it is postulated that all lattice defects within an OIPC makes for a significant amount of excess free volume in addition to the free volume that inherently exists in the OIPC when in its fully packed crystalline form.

In relation to (b) above, the definition is intended to exclude a situation where a gas species, when in contact with the gas separation membrane, dissolves the OIPC. For example, the situation where a solid OIPG liquefies when in contact with an armine-gas such as ammonia.

In contrast, according to the method of the present invention gas separation occurs by one or more of the gas species permeating through the structure of the solid OIPC, with the solid state of the OIPC being maintained throughout the gas separation process.

As use herein, the term 'permeating' and analogous forms such as 'permeateis)' or 'permeation', is intended to mean transport of the gas species through the atomic structure of the solid OIPC. Such transport can be facilitated when a pressure difference exists
the separation membrane.

As a skilled person would know, permeation of gas species through membrane materials is facilitated by the affinity between the gas species and the composition of the membrane. Without wishing to be limited by theory, permeation of gas species through the solid OIPC structure is believed to be facilitated in a similar manner.

During the separation process according to the present invention gas species are believed to be absorbed into the stture of the solid OIPC, diffuse through the OIPC driven by the concentration gradient within the OIPC, and desorb at the lower pressure side.

According to commonly accepted gas separation theories, gas separation, is typically quantified using terms such as ‘permeability’ (P), ‘diffusivity’ (D) and ‘solubility’ (S).

The permeability P of the gas species is correlated to the diffusivity D and the solubility S by the relation:

\[ P = D \times S, \]

where D is a kinetic parameter and S a thermodynamic parameter.

According to the present invention, without wishing to be limited by theory it is believed gas separation occurs as a result of different solubilities in the OIPC of the target gas compared to other gas species in the gas mixture. The diffusivity of the target gas may also be different than that of gas species in the gas mixture. The permeability P of two gases A and B being separated. Thus, this can be determined by measurement of the permeability of the two gases individually then calculated using:

\[ \alpha_{A/B} = \frac{P_A}{P_B} = \left[ \frac{D_A}{D_B} \right] \times \left[ \frac{S_A}{S_B} \right]. \]

For high selectivity, this good diffusivity needs to be combined with high solubility-selectivity for the target gas over another gas, e.g., CO vs. \( \text{N}_2 \).
In one embodiment, the one or more gas species permeating through the structure of the solid OIPC correspond to the target gas species. In such an embodiment, the separated gas composition is collected from a permeate side of the gas separation membrane.

In another embodiment, the one or more gas species permeating through the structure of the solid OIPC do not correspond to the target gas species. In that case, the separated gas composition is collected from a retentate side of the gas separation membrane. In other words, the target gas species is separated as a result of the other gas species in the gas mixture permeating through the solid OIPC.

In one embodiment, the method of the invention further comprises promoting a solid-solid phase transition in the one or more solid organic ionic plastic crystal to thereby change permeability of one or more of the gas species through the structure of the one or more solid organic ionic plastic crystal.

A skilled person would know how to promote a solid-solid phase transition in an OIPC. In one embodiment, the OIPC solid-solid phase transition is promoted by changing the temperature at which the gas separation is effected from a temperature $T_1$ to a temperature $T_2$. There is no limitation as to what are the values of $T_1$ and $T_2$, provided that, when selected from a DSC plot of the corresponding OIPC, $T_1$ and $T_2$ are selected from temperature ranges characterising two different solid phases of the OIPC, as identified in the DSC plot.

In some embodiments, the absolute difference between $T_1$ and $T_2$ is 150°C, 100°C, 75°C, 50°C, 25°C, 10°C, or 5°C.

In some embodiments $T_1$ is a temperature between about 20 and about 30°C, and $T_2$ is a temperature between about 60 and 90°C.

Practical procedures and devices to effect such a temperature change would be known to
the skilled person. These may include, for example, providing means to modify the
temperature of the mixture of non-amine gases contacting the gas separation membrane
(e.g. by way of a heat exchanger that uses heat from another process stream), or providing
the gas separation membrane itself with heating means (e.g. an embedded resistance coil
heater).

As used herein, the expression ‘gas separation membrane’ refers to a material through
which at least two gas species can permeate at different rates. In this context, there is no
limitation to the composition, form, or shape of the ‘gas separation membrane’, provided it
comprises one or more solid OIPC.

In one embodiment, the gas separation membrane consists essentially of one or more solid
OIPC. Membranes according to that embodiment may be of any shape or form, provided
they maintain mechanical stability during gas separation. For example, these membranes
may be formed by pressing the OIPC into sheet or pellet form of varying thicknesses,
which may be in the range of 0.001 to 1 mm.

In another embodiment, the gas separation membrane further comprises a support for the
solid OIPC. There is no particular limitation on the nature or configuration of the support,
as long as it assists with providing mechanical integrity of the gas separation membrane
during the gas separation. The support should also not adversely affect the gas separation.

In one embodiment, the support is in the form of a porous substrate having a first and
second surface region between which the gas species can flow. In such an embodiment the
OIPC is located on at least one of the first and second surface regions to interject the
direction of flow of the gas species.

The porous substrate contains pores that enable gas to flow through the substrate between
the first and second surface regions. By the substrate being ‘porous’ or the substrate
containing ‘pores’ is meant that the substrate contains voids or holes that are suitably
arranged to provide passageways within the substrate that enable the transport of gas
between the first and second surface regions.

The porous substrate may not provide any form of selectivity function of a mixture of gases that passes through it. In other words, the pores within the substrate may be large enough for the mixture of gas species to pass through without undergoing any significant degree of separation. In that case, the porous substrate should provide little if no resistance to gas flow.

Provided the porous substrate can be fabricated into the gas separation membrane in accordance with the invention there is no particular limitation on the shape or dimensions which it may take.

In one embodiment, the porous substrate is in the form of a sheet material or a hollow fibre. Where the porous substrate is in the form of a hollow fibre, for avoidance of any doubt it will be appreciated that the wall structure of the hollow fibre presents as the porous substrate per se. In that case, the inner wall surface of the hollow fibre may be considered to be the first surface region of the porous substrate and the outer wall surface of the fibre may be considered to be the second surface region of the porous substrate, or vice versa.

There is no limitation as to the thickness of the porous substrate. The ‘thickness’ of the substrate is intended to be the distance between the first and second surface region between which the gas species will flow. Generally, the porous substrate will have a thickness ranging from about 0.001 to 1 mm.

In one embodiment, the support is in the form of a matrix within which the one or more solid OIPC is contained.

As used herein, the term ‘matrix’ is intended to mean a secondary solid component of the separation membrane. There is no limitation regarding the nature of the matrix provided the solid OIPC can be distributed throughout the matrix, and that the matrix does not
adversely affect the gas separation. The matrix may provide mechanical integrity to the separation membrane, or facilitate the solubility of gas species in the membrane, thereby aiding the gas separation.

5 In one embodiment, the matrix is homogeneous polymer. For example, the gas separation membrane may be prepared by dispersing the OIPC within monomer which is subsequently polymerised and/or cross-linked to form a polymer matrix within which the OIPC is distributed.

10 Alternatively, the matrix may be in the form of fibres, for example polymer fibres. In that case, the gas separation membrane may be provided from a combination of the solid OIPC and fibres. Such a membrane may be provided by (i) casting a solution of OIPC dissolved in a solvent onto a bundle of fibres, (ii) removing the solvent to form solid OIPC throughout the fibre bundle, and (iii) forming the gas separation membrane by shaping the fibre bundle and solid OIPC into a desired shape. In this context, shaping may be achieved by any means known to the skilled person, for example by compression or kneading. Examples of shapes into which the gas separation membrane may be formed include pellets, discs, and flat sheets.

15 In one embodiment, the fibres are electrospun polymer fibres. Technologies and methodologies for producing electrospun polymer fibres are known to those skilled in the art.

20 In one embodiment the support is made of an inorganic material, for example a ceramic material, for example a metal oxide such as aluminia or silica.

25 In another embodiment the support is made of an organic material, for example polymer.

Examples of polymers suitable for making a support according to the present invention include sulfonic acid polymers such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMP), polyvinylidene fluoride (also known as polyvinylidene difluoride) (PVDF).
sulfonated poly(ether ether ketone) (SPEEK).

In one embodiment, polymers suitable for making a support according to the present invention also assist in the separation of the gas species. Such polymers are known to have porosity characteristics that make them selectively permeable to certain gas species relative to others. When combined with the OIPC to form a gas separation membrane according to the invention these polymers act synergistically with the OIPC in the separation of the target gas species by increasing the solubility or diffusivity of certain gas species in the separation membrane. Depending on the nature of the target gas species, a person skilled in the art would be capable of devising any suitable combination between one or more polymers of this kind and the appropriate OIPC in order to achieve such synergy.

Examples of polymers known to have porosity characteristics that make them selectively permeable to certain gas species include substituted polyacetylenes (e.g. poly (1-(trimethylsilyl)-1-piOyne) (PTMSPs), poly (1-idimethyl-f3propylsilyl)-i-propyne), poly (1-(dimethyl-n-butylsilyl) l-1 -propyne), poly (1-phenyl-1-1 -propyne)poly (dipheilyaeetylene), poly (i-butylaCetylene), poly [1-phenyl-2-j7-trimethylsilylphenyl-acetylene), poly (1-phenyl -2^-hydroxypheny]-acetylene), co-polymers thereof, or any mixtures thereof), poly(ethylene oxides), polyamides, polyimides, polysulfoiies, polycarbonates, polarylates, poly(phenyleneoxide) s, polyanilines, thermally rearranged polymers, and polymers of intrinsic microporosity (PIMs) (e.g. polyptalocyanines, polyspirobismdanes, polybenzidioxanes, or any combination thereof), and any combinations thereof.

When the gas separation membrane comprises a support, the OIPC will typically constitute at least 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, or 90% of the membrane total weight. In one embodiment, the OIPC constitutes between 5% to 95%, 10% to 95%, 20% to 95%, 30% to 95%, 40 to 95%, 50% to 95%, 60% to 95%, 70% to 95%, 80% to 95%, or 90% to 95% of the membrane total weight. In another embodiment, the OIPC constitutes between 5% to 75%, 10% to 75%, 20% to 75%, 30% to 75%, 40 to 75%, 50% to 75%, 60% to 75%, or 70% to 75% of the membrane total weight. In another embodiment, the
OIPC constitutes between 5% to 50%, 10% to 50%, 20% to 50%, 30% to 50%, or 40% to 50% of the membrane total weight.

In one embodiment, the gas separation membrane further comprises a porous material, for example a nanoporous material.

As used herein, the expression 'porous material' means a material containing voids, and specifically voids that allow passage of gas species through the material. As used herein, the expression 'nanoporous' material refers to a material that in its native state has a porosity deriving from voids or cavities which smallest dimension is not larger than 100 nm.

The porous material may act synergistically with the OIPC in the separation of the target gas species by increasing the solubility of diffusivity of certain gas species in the separation membrane relative to the separation membrane absent the porous material.

Examples of suitable porous material include Metal Organic Framework (MOF), a Consens Organic Framework (COF), a zeolite, an activated carbon material, a metal oxide, or any combination thereof.

Examples of MOFs suitable for use in the present invention include calixarene-based MOFs, heterocyclic azolate-based MOFs, metal-cyanide MOFs, and any combination thereof. Specific examples of MOFs that are suitable for use in the present invention include those commonly known in the art as CD-MOF-1, CD-MOF-2, CD-MQF-3, CPM-13, FJi-F, FMOF-i, HKUST-1, IRMOF-1, IRMOF-2, IRMOF-3, IRMOF-6, IRMOF-8, IRMOF-9, IRMOF-13, IRMOF-20, JUC-4S, JUC-62, MIL-101, MIL-103, MIL-125, MIL-53, MIL-88 (including MIL-88A, MIL-88S, MIL-88C, MIL-88D series), MOF-5, MOF-74, MQF-177, MOF-210, MQF-200, MOF-205, MOF-505, MOROF-2, MOROF-1, NOTT-100, NOTT-101, NOTT-1Q2, NOTT-1:03, NOTT-105, NOTT-106, NOTT-107, NOTT-109, NOTT-110, NOTT-111, NOTT-112, NOTT-113, NGTT-114, NQT-T-140, NU-100, rho-ZMOF, PCN-6, PON-6', PCN9, PCN10, PCN12, PCN12', PCN14, PCN16,
Further examples of MOFs suitable for use in the present invention are disclosed in WO 2010/075610, the content of which is included herein as reference in its entirety.

Examples of COFs suitable for use in the present invention include those commonly known in the art as COF-1, COF-5, COF-6, CGF-8, COF-10, COF-42, COF-66, COF-43, COF-102, COF-103, COF-105, COF-108, COF-202, COF-30Q, CQF-366, triazine-based COFs (e.g. CTF-1, CTF-2), TP-COF, NiPoCOF, NiPc-BDTA-COF, ZnP-CQF, CuP-COF, H2P-COF, HHTP-DPB-CGF, ZnPc-PPE-COF, PPy-COF, D=A GOF, CTC-COB, and any combinations thereof.

Further examples of COFs suitable for use in the present invention and details on their synthesis are disclosed in X. Feng et al, Chemical Society Reviews 2012, Vol. 41, Pages 6010–6022, the content of which is included herein as reference in its entirety.

Examples of zeolites suitable for use in the present invention include zeolite A (e.g. Na, K, Ag, Mg, Ca forms), zeolite X (e.g. Na, Li, Ca, Ba form), mordenite (e.g. Na, H, Ca form), chabazite (e.g. Na, Ca form), elinoptilolite (e.g. K, Ca form), silicalite, and any combination thereof.

Examples of activated carbon suitable for use in the present invention include powdered activated carbon (R 1, PAG), granular activated carbon (GAG), extruded activated carbon (EAC), bead activated carbon (BAG), impregnated carbon (e.g. iodine, silver, and cations such as Al, Mn, Zn, Pe, Li, Ca impregnated carbon), and any combination thereof.
Examples of metal oxides suitable for use in the invention include aluminium oxide, chromium(ii) oxide, chromium(iii) oxide, chromium(iv) oxide, chromium(vi) oxide, cobalt(ii) oxide, cobalt(iii) oxide, cobalt(iii) oxide, copper(ii) oxide, copper(iii) oxide, iron(ii) oxide, iron(iii) oxide, iron(iii) oxide, lithium oxide, magnesium oxide, manganese(ii) oxide, manganese(iii) oxide, manganese(iv) oxide, manganese(vii) oxide, nickel(ii) oxide, nickel(iii) oxide, silicon dioxide, tin(ii) oxide, tin(iv) oxide, titanium dioxide, zinc oxide, and any combination thereof.

If used, the porous material may constitute at least 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, or 90% of the total weight of the membrane, or between 0.5% to 50%, 1% to 30%, 1% to 20%, 1% to 10%, or 1% to 5% of the total weight of the membrane.

The method of the invention comprises creating a difference in pressure across the membrane to facilitate transport of one or more gas species through the membrane.

Techniques for creating such a differential pressure across a gas separation membrane are well known to those skilled in the art, and are not particularly limited to any specific technique provided it results in a differential pressure across the membrane.

For example, opposing sides of a membrane may be isolated from each other (in terms of gas flow) and the mixture of gas species to be separated applied under pressure to one side of the membrane. In practice this may achieved in separation modules of the kind known in the art, examples of which include flat sheet modules (e.g. plate-and-frame and spirally-wound modules) and tubular modules (e.g. fine capillaries or tubes housed like a shell and tube heat exchanger).

As a person skilled in the art would know, pressure conditions suitable in the invention may be expressed in terms of pressure ratio R:

$$ R = \frac{P_r}{P_p} $$

Where $P_r$ and $P_p$ are, respectively, the absolute pressure at the retentate and permeate side.
of the gas separation membrane, measured at the corresponding surface of the separation membrane.

There is no particular limitation to the values of pressure ratio suitable for use in the invention, provided there is a difference in pressure across the membrane to facilitate transport of one or more gas species through the membrane.

In one embodiment, the pressure ratio \( R \) is in the range \( 1 < R \leq 10,000 \), \( 1 < R < 10,000 \), \( 1 < R \leq 5,000 \), \( 1 < R < 5,000 \), \( 1 < R < 250 \), \( 1 < R \leq 100 \), \( 1 < R < 100 \), \( 1 < R \leq 5 \), \( 1 < R < 2 \). In some embodiments, the pressure ratio \( R \) is in the range \( 2 < R < 10,000 \), \( 2 < R \leq 1,000 \), \( 2 < R < 750 \), \( 2 < R < 500 \), \( 2 < R < 250 \), \( 2 < R \leq 100 \), \( 2 < R < 50 \), \( 2 < R \leq 25 \), \( 2 < R \leq 10 \), or \( 2 < R \leq 5 \). In some embodiments, the pressure ratio \( R \) is in the range \( 5 < R \leq 10,000 \), \( 5 < R \leq 1,000 \), \( 5 < R < 750 \), \( 5 < R \leq 500 \), \( 5 < R \leq 250 \), \( 5 < R \leq 100 \), \( 5 < R \leq 50 \), \( 5 < R \leq 25 \), or \( 5 < R \leq 10 \). In some embodiments, the pressure ratio \( R \) is in the range \( 10 < R \leq 10,000 \), \( 10 < R \leq 1,000 \), \( 10 < R \leq 750 \), \( 10 < R \leq 500 \), \( 10 < R \leq 250 \), \( 10 < R \leq 100 \), \( 10 < R \leq 50 \), \( 10 < R \leq 25 \), or \( 10 < R < 25 \). In some embodiments, the pressure ratio \( R \) is in the range \( 25 < R \leq 10,000 \), \( 25 < R \leq 1,000 \), \( 25 < R \leq 750 \), \( 25 < R \leq 500 \), \( 25 < R \leq 250 \), \( 25 < R < 100 \), or \( 25 < R < 50 \).

There is no particular limitation as to the operative temperature at which gas separation is effected, provided the GIPC is solid at that temperature. In one embodiment, the temperature is between about 20°C and 120°C.

The present invention also provides for the use of one or more GIPC for separating a target gas species from a mixture of non-amine gas species, wherein separation of the mixture of ion-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid OIPC.

Specific embodiments of the invention will now be described with reference to the following non-limiting examples,
EXEMPLARY

The examples described herein include gas permeation measurements performed on single gas species, which are indicative of the relative permeability of the same gases when separated from a mixture containing those gas species. This approach is supported by the reports of J. B. Alexopoulos et al. Polymer 10 (1969) 265-269, and is commonly used in the field (see for example Hassan et al. Journal of Membrane Science 104 (1995) 27-42, Tome et al. Journal of Membrane Science 428 (2013) 260-266).

EXAMPLE 1

Synthesis of OIPCs

Synthesis of methyllethylisobutylphosphonium hexafluorophosphate \([\text{[P}^{12}\text{S}_{4}\text{][P}^{3}\text{4}]\) was performed according to the procedure described in detail in Journal of Materials Chemistry (2011) 21, 7640-7650, the content of which is incorporated herein in its entirety.

Syntheseses of the methyllethylpyrroldinium tetrafluoroborate ([C\(_3\)mpyr][BF\(_4\)]) and methylpropylpyrrolidinium tetrafluoroborate ([C\(_3\)mpyr][BF\(_4\)]) were performed according to the procedure described in detail in Electrochimica Acta 46 (2001) 1753–1757, the content of which is incorporated herein in its entirety.

Synthesis of dipropylaminoniuna niflate ([DPA][Tf\(_2\)]) which is a protic OIPC, was performed by adding slowly one mole of aqueous solution of triflic acid to one mole of dipropylamine cooled in an ice bath. After the addition, the contents were stirred for another 30 minutes and then the mixture dried on a rotary evaporator at 70°C. The solid product was further dried at room temperature by storage in a vacuum desiccator.
EXAMPLE 2

**Synthesis of OIPC/polymer fibre gas separation membranes**

Poivynylidene fluoride (PVDF) mats were made using ©leetrospun PVDF fibres as described in *Journal of Materials Chemistry A* 3 (2015) 6038-6052, the content of which is incorporated herein in its entirety. Pellets of 12.5mm diameter were punched from the resulting mats, for use in the membrane.

[C\textsubscript{2}mptyr][BF\textsubscript{4}]/PVDF membranes were made by preparing a solution of 1:5 w/w OIPC in methanol and casting the solution onto the PVDF mats obtained as described above. The mass of the PVDF fibres was 4mg and the mass of OIPC used was 1.3mg, giving a total dry mass of 23mg after removal of the methanol. The membranes were dried in a vacuum oven overnight at 55°C before pressing. The thickness of the membrane was 150μm, prepared by pressing the pellet on a 1 ton press for 1/2 an hour at 70°C.

[C\textsubscript{3}mptyr][BF\textsubscript{4}]/PVDF membranes were made by preparing a solution of 1:5 w/w OIPC in ethanol and casting the solution onto the PVDF mats described above. The mass of the PVDF fibre was 2mg and the mass of OIPC used was 9mg, giving a total dry mass of 11mg after removal of the ethanol. The membranes were dried in a vacuum oven overnight at 55°C before pressing. The thickness of the membrane was 71μm, prepared by pressing the pellet on a 1 ton press for 1/2 an hour at room temperature.

[P\textsubscript{1224}][PF\textsubscript{6}]/PVDF membranes were made by preparing a solution of 1:5 w/w OIPC in ethanol and casting the solution onto the PVDF mats described above. The mass of the PVDF fibre was 4mg and the mass of OIPC used was 20mg, giving a total dry mass of 24mg after removal of the ethanol. The membranes were dried in a vacuum oven overnight at 55°C before pressing. The thickness of the membrane was 143μm, prepared by pressing the pellet on a 1 ton press for 1/2 an hour at room temperature.
EXAMPLE 3

Set up of gas permeability measurements using OIPC/polymer fibre membranes

Permeation measurements were performed using a permeation apparatus based, in construction and valve placement, on the one described in detail in *Journal of Membrane Science* 428 (2013) 260-266, the content of which is incorporated herein in its entirety.

The gas contacting surfaces were all stainless steel with Swageloic fittings and Viton o-rings. The feed- and permeate-side pressure transducers were both Keller Series 35X HT absolute-range transducers with a 4-20 mA output and a compensated temperature range of 20-120°C. The feed tank was 2200 ml with a 0-10 Bar(abs) transducer and the permeate tank was 35 ml with a 0-1 Bar(abs) transducer. A type-k thermocouple was used to measure the temperature, and the vacuum used was 4 x 10^-2 mBar. This apparatus was housed in a Binder BF 115 Model incubator with temperature control from 5°C above room temperature to 100°C, with 0.2°C accuracy. Transducer and thermocouple outputs were recorded using an MCC USB-2404-UI model data acquisition unit with 24-bit resolution.

In a typical experiment, the sample was mounted in the sample holder which was positioned between the feed and permeate tanks and which was constructed in such a way as to prevent circumvention of the mounted membrane by the gas. In other words, if a gas moves from the feed tank to the permeate tank, it must necessarily have flawed through the mounted membrane. After mounting, vacuum was drawn on both sides of the membrane in preparation: for the first permeation experiment. The apparatus was then allowed to equilibrate at the desired experimental temperature and left under vacuum overnight before introducing the penetrant gas and beginning the experiment.

A single gas was tested at a time. Between experiments using the same gas, a time greater than or equal to ten times the 'time-lag' was allowed to elapse, during which time a vacuum was maintained on both sides of the membrane. The 'time-lag' approach is

For example, if the 'time-lag' was ten minutes, meaning it took ten minutes to reach a Steady State of flux across the membrane, then the membrane was kept under vacuum for one hundred minutes between the conclusion of one permeation experiment and the commencement of the next permeation experiment provided the gas type had not been changed.

In the case that gas type was changed between permeation experiments, the membrane was kept under vacuum overnight before the next permeation experiment was started.

**EXAMPLE 4**

*Gas permeability measurements using OIPCpolymer fibre membranes*

Data shown in Figure 1 were obtained using a [C_{2}mpyr][BF_{4}]/PVDF polymer fibre gas separation membrane obtained according to the procedure described in Example 2 (90°C), on an instrument consisting of a large feed tank and a small permeate tank separated by the gas separation membrane. A transmembrane pressure gradient is established by pressurising the feed tank with a single gas species at a time and pulling a vacuum on the permeate tank. Gas flux through the membrane is measured by monitoring the increase in pressure in the permeate tank.

Figure 1 is a graph plotting the change in permeate tank pressure over time. A gas species will tend to follow the pressure gradient from the feed tank, across the membrane, and into the permeate tank. As this occurs, the permeate tank pressure increases. The graph shows that $G_2$ permeates through the [C_{2}mpyr][BF_{4}]/PVDF polymer fibre membrane at a higher rate than nitrogen.
Data shown in Figure 2 were obtained using a [C2mpyr][BF4]/PVDF polymer fibre gas separation membrane obtained according to the procedure described in Example 2, at 35°C over a pressure range of 1 to 2 Bar and using the same setup use to obtain the data shown in Figure 1. The graph in Figure 2 plots single-gas flux rates as a function of the pressure difference across the membrane. One curve from Figure 1 becomes a single point on this graph. The representation of information in Figure 2 allows more precise calculation of flux rates because they can be normalized against changes in transmembrane pressure. This representation is useful when flux rates for a particular gas are very low. The membrane in use is the same as was used to produce the data in Figure 1 and when these data are fitted (blue line), they show that the flux of nitrogen causes an increase of approximately 6 nBar per second per Bar of transmembrane pressure.

Data shown in Figure 3 were obtained using a [P1224][PF6]/PVDF polymer fibre gas separation membrane obtained according to the procedure described in Example 2, at 35°C and at a pressure range of 1 to 5 Bar. The graph depicted in Figure 3 shows the same representation of data as Figure 2. The data show consistent increase in flux as the transmembrane pressure is increased to 5 Bar, which was the highest pressure tested. From the ratio of the fitted slopes of the individual gas species, a selectivity of 23 is calculated.

Data shown in Figure 4 were obtained using a [C3mpyr][BF4]/PVDF polymer fibre gas separation membrane, a [C2mpyr][BF4]/PVDF polymer fibre gas separation membrane, and a [P1224][PF6]/PVDF polymer fibre gas separation membrane, in a test performed at 35°C. Figure 4 shows the same representation of data as in Figures 2 and 3, but with a log-scale on the y-axis and with new data from the [C3mpyr][BF4]/PVDF polymer fibre gas separation membrane. The graph highlight an enhancement in flux rates as transmembrane pressure increases in the case of the [C3mpyr][BF4]/PVDF polymer fibre gas separation membrane.
EXAMPLE 5

Gas Absorption tests using OIPCs

A smaller experimental setup consisting of a small main volume and an isolated sample chamber was constructed using similar components used for the permeability apparatus described in Example 3. The main volume and the sample chamber were isolated by a valve. The sample was held under vacuum at the desired temperature overnight and the main volume was pressurized. The experiment was started by opening the valve which separated the main volume and the sample chamber, thereby introducing the gas to the sample. This is initially recorded by the instrumentation as a sharp drop in head pressure as the gas from the main volume fills the volume of the sample chamber, followed by the curve corresponding to uptake of the gas by the sample. This drop in head pressure was measured over time as the sample absorbed the gas.

Figure 5 shows gas uptake data measured using [P₁₂₂₄][P₃₄]. The GIPC was placed in a small chamber and exposed to vacuum overnight between experiments. A single-gas (either CO₂ or N₂) was then introduced and the change in head pressure was recorded for several hours. This was performed at both 35 and 45°C. The plot of Figure 5 shows a larger reduction in head pressure under a carbon dioxide atmosphere than under a nitrogen atmosphere, which is consistent with selective absorption of CO₂ over N₂.

Figure 6 shows gas uptake data measured using Dipropylammonium triflate ([DPA][Tf]), using the same procedure adopted to obtain the data shown in Figure 5. In the chemical structure of [DPA][Tf] the cation has a mobile proton. This is in contrast to the OIPCs used in the tests described in relation to Figures 1-5, which do not have mobile protons on the cation. The data in Figure 6 shows the ability of dipropylammonium triflate to absorb CO₂.

Every formulation- or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated. Specific names of compounds are
intended to be exemplarily, as it is known that one of ordinary skill in the art can name the same compounds differently.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word 'comprise', and variations such as 'comprises' and 'comprising', will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or inclination derived from it), or to aity matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A method of separating a target gas species from a mixture of non-amine gas species, the method comprising:
   contacting the mixture of non-amine gas species with a gas separation membrane, the gas separation membrane comprising one or more solid organic ionic plastic crystal (©IPC);
   creating a difference in pressure across the membrane to facilitate transport of one or more gas species through the membrane so as to provide for a separated gas composition in which the concentration of the target gas species is higher compared with that in the mixture of non-amine gas species;
   wherein separation of the mixture of non-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid ©IPC.

2. The method of claim 1, further comprising promoting a solid-solid phase transition in the solid OIPC to change permeability of one or more of the gas species through the structure of the solid OIPC.

3. The method of claim 1 or 2, wherein the one or more solid OIPC comprises an anion selected from BF$_4^-$, PF$_6^-$, N(CN)$_2^-$, (CF$_3$SO$_2$)$_2$N$, (FSO$_2$)$_2$N$, OCN$, SCN$, dicyanamethanide, carbamoyl cyanamido(nitroso)methanide, (C$_2$F$_5$SO$_2$)$_2$N$, (CF$_3$SO$_2$)$_3$C$, C(CN)$_3^-$, B(CN)$_4^-$, (C$_2$F$_3$)$_3$PF$_5^-$, alkyl-SO$_3^-$, perfluoroalkyl-SO$_3^-$, aryl-SO$_3^-$, I, H$_2$PO$_4^-$, HPO$_4^{2-}$, sulfate, sulphite, nitrate, trifluoromethanesulfonate, p-toluenesulfonate, bis(oxalate)borate, acetate, formate, gallate, glycolate, BF$_3$(CN)$^-$, BF$_2$(CN)$_2^-$, BF(CN)$_2^-$, and Tb(hexafluoroacetylacetone)$_4^-$.

4. The method of any one of claims 1 to 3, wherein the one or more solid OIPC comprises a cation selected from dialkylpyrrolidinium, pyridinium, monoalkylpyrrQidifflum, diaikjiimidazolium, monoalkylammonium, imidazolium, tetraalkylammonium, quaternary ammonium, trialkylammonium, dialkylaurnomum, dialkanolaikjadmonium, aikanoldialkylammonium, bis:(alkylimicazolium),...
bis(dialkyl)ammonium, bis(trialkyl)ammonium, diallylammonium, dialkanolammonium, alkylalkanolammonium, alkylallylammonium, guanidinium, diazabicyclooctane, tetraalkyl phosphoniums, trialkylphosphoniums, trialkylsulfoniums, tertiarysulfoliniums, imidazolinium, cholinium, formamidinium, formadinium, bicyclic (spiro) ammonium, pyrazolium, benzimidazolium, dibenzylammonium, caffeineum, piperazinium, dialkyl(amine)ammonium, alkyl(diamino)ammonium, triaminoammonium, aminopyrroldidium, and aminimidazolium.

5. The method of any one of claims 1 to 4, wherein the one or more solid OIPC is selected from N,N-methylethylpyrroloidinium tetrafluoroborate, N,N-methylpropylpyrroloidinium tetrafluoroborate, dimethylpyrroloidinium tetrafluoroborate, dimethylpyrroloidinium thiocyanate, N,N-ethylmethylpyrroloidinium thiocyanate, tetramethylammonium dicyanamide, tetraethylammonium dicyanamide, N,N-methylethylpyrroloidinium bis(trifluoromethanesulfonyl)amide,
diethyl(methyl)(isobutyl)phosphonium bis(fluorosulfonyl)amide, diethyl(methyl)(isobutyl)phosphonium tetrafluoroborate, diethyl(methyl)(isobutyl)phosphonium hexafluorophosphate, methyl(triethyl)phosphonium bis(fluorosulfonyl)amide, methyl(triethyl)phosphonium bis(trifluoromethylsulfonfonyl)amide, triisobutyl(methyl)phosphonium hexafluorophosphate, triisobutyl(methyl)phosphonium bis(fluorosulfonyl)amide, triisobutyl(methyl)phosphonium tetrafluoroborate, triisobutyl(methyl)phosphonium thiocyanate, triethyl(methyl)phosphonium bis(fluorosulfonyl)amide, methylthiopropylpyrroloidinium bis(fluorosulfonyl)amide, dimethylpyrroloidinium bis(fluorosulfonyl)amide, choline dihydrogen phosphate, choline trifluoromethanesulfonate, N,N-dimethylpropylenediammonium triflate.

25 tri(isobutyl)phosphonium bis(trifluoromethanesulfonfonyl)amide, tri(isobutyl)phosphonium methanesulfonate, tri(isobutyl)phosphonium trifluoromethanesulfonate, tri(isobutyl)ammonium bis(trifluoromethanesulfonfonyl)amide, tri(isobutyl)phosphonium nitrate, tri(isobutyl)ammonium methanesulfonate, tri(isobutyl)ammonium trifluoromethanesulfonate, tri(isobutyl)ammonium nitrate, 1,2-bis[N-(N'hexylimidazolium)]ethane bis(hexafluorophosphate), and combinations thereof.
6. The method of any one of claims 1 to 5, wherein the separation membrane comprises a support for the one or more solid OIPC.

7. The method of claim 6, wherein the support is a porous substrate.

8. The method of claim 6, wherein the support is in the form of fibres.

9. The method of claim 8, wherein the fibres are polymer fibres.

10. The method of claim 9, wherein the polymer is selected from poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMP), Polyvinylidene fluoride (PVDF), sulfonated poly(ether ether ketone) (SPEEK), a substituted polyacetylene, a polyethylene oxide, a polyamide, a polyimide, a polysulfone, a polycarbonate, a polyarylate, a poly(phenyleneoxide), a polyaniline, a thermally rearranged polymer, a polymer of intrinsic microporosity (PIM), and any combinations thereof.

11. The method of any one of claims 8 to 10, wherein the fibres are electrospun polymer fibres.

12. The method of any one of claims 6 to 11, wherein the solid OIPC constitutes between 5% to 95% of the total weight of the gas separation membrane.

13. The method of any one of claims 1 to 12, wherein the separation membrane further comprises a nanoporous material.

14. The method of claim 13, wherein the nanoporous material is selected from a Metal Organic Framework (MOF), a Covalent Organic Framework (COF), a Zeolite Imidazolate Framework (ZIFs), a zeolite, an activated carbon material, a metal oxide, and any combination thereof.

15. The method of claim 13 or 14, wherein the nanoporous material constitutes
between 0.5% to 50% of the total weight of the membrane.

16. The method of any one of claims 1 to 15, wherein the difference in pressure across the membrane provides for a pressure ratio $R$ in the range $1 < R \leq 10,000$.

17. The method of any one of claims 1 to 16, wherein the mixture of non-amine gas species comprises $CO_2$.

18. The method of any one of claims 1 to 17, wherein $CO_2$ is separated from a mixture of gas species comprising $CO_2$ and one or more of $\frac{3}{4}$ $H_2$, $C_2H_4$, $O_2$, $H_2O$, $\frac{3}{4}S$, $SO_2$, and $NO_x$.

19. The method of claim 18, wherein $GO_2$ is separated from a mixture of $CO_2$ and $N_2$ or $C(\frac{3}{4})$ and $CH_4$.

20. Use of one or more solid organic ionic plastic crystal (OIPC) for separating a target gas species from a mixture of non-amine gas species, wherein separation of the mixture of non-amine gas species is promoted by one or more of the gas species permeating through the structure of the one or more solid OIPC.
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5

Figure 6
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/04 (2006.01)  B01D 53/22 (2006.01)  B01D 71/06 (2006.01)

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)

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)

WIPO; EPODOC; TXTE; TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPES, TXPEEA, TXPUSEA, TXPUSEA1, TXPUSEB, TXPWEOA; INSPEC; IPC and CPC Marks: IC/CC: B01D53/04, B01D53/22, B01D53/46, B01D53/48, B01D53/50, B01D53/52, B01D53/54, B01D53/62, B01D67, B01D69, B01D71/06/L0W, B01D2253/20/L0W, B01D53/228; keywords: membrane, frame-work, matrix, organic plastic crystal, plastic crystal, organic crystal, OIPC, polyionic liquid, separate, absorb, gas, air, N2, nitrogen, oxygen, methane, carbon monoxide, carbon dioxide, hydrogen sulphide, O2, CH4, CO, CO2, H2S, pyrrolidinium tetrafluoroborate, pyrrolidinium thiocyanate, ammonium dicyanamide, methanesulfonylamide, phosphonium, fluorosulfonylamide, dihydrogen phosphate, methanesulfonate, ammonium triflate, ammonium nitrate, hexafluorophosphate and similar search terms; Esp@enet, Google Scholar, ScienceDirect & Google Patents using similar search terms, "Applicant/Inventor name search"; "DEAKIN UNIVERSITY, MONASH UNIVERSITY/PRINGLE, Jennifer M., FORSYTH, Maria, MCDONALD, Jonathan Lane, MACFARLANE, Douglas Robert through AusPat and Esp@enet. Applicant(s)/Inventor(s) name searched in all internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Documents are listed in the continuation of Box C</td>
<td></td>
</tr>
</tbody>
</table>

|  X | Further documents are listed in the continuation of Box C |  X | See patent family annex |

| *  | Special categories of cited documents: | "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 |
|"A" | document defining the general state of the art which is not considered to be of particular relevance | "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 |
|"E" | earlier application or patent but published on or after the international filing date | "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 |
|"L" | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "&" | document member of the same patent family |
|"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 |

Date of the actual completion of the international search 21 October 2015

Date of mailing of the international search report 21 October 2015

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au

Authorised officer

Debashis Roy
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262256125

Form PCT/ISA/210 (fifth sheet) (July 2009)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 2007/01 19302 A1 (RADOSZ et al.) 31 May 2007 Abstract; paragraphs [0002], [0006], [0012]; claims 1-2, 5-9</td>
<td>1-20</td>
</tr>
</tbody>
</table>
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Publication Number</td>
<td>Publication Date</td>
</tr>
</tbody>
</table>

End of Annex