● Special Issue Trends in Gas Separation Membranes I

New Materials for Selective Gas Separations

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Prof. Noble is the Alfred T. and Betty E. Professor of Chemical Engineering and Co-Director of the NSF MAST Center at the University of Colorado. His research interests involve experimental and theoretical studies of processes that can attain highly selective chemical separations. He is interested in the use of specific interactions that can enhance the selectivity of a separation process. This specific interaction can involve unique solvents such as ionic liquids, reversible chemical complexation, use of external fields (light or electrical), or nanoporous structures (such as zeolites) to provide the selectivity. The main focus of his work has

been on membrane processes with the incorporation of these specific interactions and their application to chemical separations. He currently has 15 patents, over 200 research publications, and 10 textbooks and monographs.

Global Perspectives

Two recent reports provided some very specific guidance and recommendations for membranes with respect to gas separation. A recent NSF workshop on Separations Research Needs for the 21st Century that included a group of academic, industrial and national laboratory experts in separations technologies discussed and identified the future priority separations research needs and opportunities in this important area (Noble and Agrawal, 2005).

Two topics of critical importance and one specific research item from the workshop recommendations directly relate to the general theme of this manuscript.

New Materials

A mass separating agent is key to many separation processes. Thus, advances in new materials have the potential to be translated into mass separating agents with superior properties to those presently used. These properties can include higher loading capacities, better selectivity, improved temperature and pressure range of operation, as well as the ability to tolerate a wide range of chemical environments. In addition, improvements in mechanical properties and chemical resistance can be extremely useful in the construction and operation of separation devices including membranes.

Composite separation systems

The idea of a composite separation system is to combine two or more separating agents into one process. One such approach is to use the properties of two mass separating agents in a synergistic fashion to obtain separation capabilities

that are not available through the use of a single separating agent. As an example, zeolites or other molecular sieves can be incorporated into a polymer membrane to form a new class of membrane called "mixed matrix membranes". The solid phase enhances or alters the polymer membrane selectivity.

The implementation of nanotechnology to prepare very thin and uniform layers on robust layers for membrane applications is a key general need that can be used in a multitude of applications.

One approach is to fabricate composite structures of ionic liquids and lyotropic liquid crystals to obtain ordered materials that have uniform pore sizes and orientations for highly selective separations. The use of thin films requires much smaller quantities of material compared to bulk separation systems (i.e. sorption/desorption) so the cost per unit of gas processed is much lower. The lyotropic liquid crystal phase forms ordered structures with uniform pore sizes on the order of 1-2 nm. The ionic liquid has high solubility selectivity for carbon dioxide. The composite structure provides the mechanical strength of a polymer film combined with the high selectivity of the dispersed phase. There are no previous reports of composite structures using these materials for gas separations.

Target Separations

Some key workshop recommendations that pertain to this topic are:

- Separations associated with carbon dioxide emission in air continues to be a critical environmental and energy

Fig. 1 CO_2/CH_4 flux and selectivity vs. pressure for SAPO-34 membrane.

related issue.

- Hydrogen purification processes have been and will continue to be critical for the drive toward a hydrogen based economy.

A recent National Research Council report (2003) had workshop sessions on separations techniques that were aimed at identifying novel materials and process concepts for CO_2 and hydrogen production. The workshop sessions on separations techniques were aimed at identifying novel materials and process concepts for CO_2 and hydrogen production. The streams from which these gases need to be separated include low-pressure flue gas from the combustion of fossil fuels, and high-pressure streams from the gasification of fossil fuels, in addition to the separation of CO_2 from the atmosphere. Hydrogen was included because efficient and cost-effective purification methods, when coupled with low CO_2 emission generation methods, could enable wide applications of H_2 as fuel.

During the workshop sessions, many potential areas of research in advanced separations techniques were discussed at length. Two that are relevant to this manuscript and a description for their importance are:

1. Nanoscale materials as separation agents;
2. High-temperature membranes;

Nanotechnology offers the potential to make materials with nanometer-sized dimensions. It also allows the predictable fabrication of structures with similar dimensionality. The appeal of these materials and structures is that they can have physical and chemical properties different from those of their larger-scale counterparts.

Nanoscale porous structures with minimum irregularities in the molecular path may significantly increase the molecular flux through the pores. Methods to design and construct such structures and their incorporation into defect-free membranes are research opportunities. Nanoscale membranes

Table 1 Gas sorption and sorption selectivity values for different RTILs

RTILs	CO_2	CH_4	N_2	Sorption Selectivity @ 40°C	
	H (atm)	H (atm)	H (atm)	CO_2/CH_4	CO_2/N_2
[emim][dca]	95 ± 3	1960 ± 120	4850 ± 700	21 ± 1	51 ± 8
[emim][Tf ₂ N]	46 ± 1	550 ± 14	1160 ± 80	12 ± 0.5	25 ± 2
[emim][CF ₃ SO ₃]	71 ± 2	1200 ± 54	2680 ± 240	17 ± 1	38 ± 4
[hmim][Tf ₂ N]	40 ± 1	352 ± 7	938 ± 30	8.7 ± 0.2	23 ± 1

that are thermally and mechanically stable and that do not require a support or that can utilize a support that is not flux-limited will represent a major technology breakthrough.

Another promising area of research is in the design of high-temperature, stable porous structures that have the porous space filled with functionalized molten salts. The molten salts would perform the separation, taking advantage of facilitated transport mechanisms since the molten salts need to operate under minimum pressure differential. These structures will require stable, nonvolatile molten salts with high permeance and good selectivity.

Our Research Related to This Topic

Zeolite Membranes

Because of their well-defined and narrow nanoscale pore size distributions, zeolite membranes can potentially separate mixtures of molecules that are difficult to separate by more conventional means because of their similar physical properties (boiling points, molecular weight, chemical reactivity). H_2 from CO and CO_2 is particularly interesting as the large differences in kinetic diameters between H_2 (0.289 nm) and CO_2 (0.330 nm), provide the potential to make a zeolite membrane ideal for this separation. Additionally, CO and H_2S , major contaminants for polymer electrolyte membrane fuel cells (PEMFCs), have even larger kinetic diameters, 0.376 and 0.360 nm, and therefore would be expected to have even lower flux rates through a H_2 selective zeolite membrane.

We have reported that SAPO-34 membranes selectively separate CO_2 from CH_4 (Li et al., 2004,2005). The SAPO-34 is a silicoaluminophosphate having the composition $\text{Si}_x\text{Al}_y\text{P}_z\text{O}_2$ where $x = 0.01 - 0.98$, $y = 0.01 - 0.60$, $z = 0.01 - 0.52$, and $x + z = y$.

Almost all studies of gas separations in zeolite membranes have used relatively low feed pressures, but feed pressures may be as high as 7 MPa in industrial applications. As shown in Fig. 1, CO_2 was separated from CH_4 with higher selectivities than reported previously for SAPO-34 membranes, and at

Fig. 2 Schematic representations of some common LLC phases formed by amphiphiles in H_2O .

Fig. 3 Formation of cross-linked H_{II} phase nanocomposites using taper-shaped LLC monomers.

Table 2 Transport properties of light gases in H_{II} and disordered membranes of cross-linked 1.

Gas	Film Morphology	P^a	P_{Dis}/P_{HII}	S^b	S_{Dis}/S_{HII}	D^c	D_{Dis}/D_{HII}
CO_2	Disordered	6.9 ± 0.10	1.3	1.17 ± 0.07	0.7	4.4 ± 0.34	1.9
	H_{II}	5.2 ± 0.12		1.68 ± 0.09		2.3 ± 0.19	
N_2	Disordered	0.32 ± 0.02	1.7	0.06 ± 0.01	1.0	4.6 ± 0.52	1.6
	H_{II}	0.19 ± 0.01		0.06 ± 0.01		2.8 ± 0.20	
O_2	Disordered	1.3 ± 0.03	1.7	0.09 ± 0.01	0.9	11 ± 1.70	1.7
	H_{II}	0.77 ± 0.02		0.10 ± 0.01		6.3 ± 0.17	
CH_4	Disordered	0.66 ± 0.01	1.7	0.21 ± 0.02	1.0	2.5 ± 0.22	1.8
	H_{II}	0.40 ± 0.03		0.22 ± 0.04		1.4 ± 0.22	
H_2	Disordered	7.2 ± 0.10	1.6				
	H_{II}	4.4 ± 0.13					

^a Permeability in Barrers, units of $10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$

^b Gas solubility in units of $\text{cm}^3 (\text{STP}) / (\text{cm}^3 \cdot \text{atm})$

^c Diffusivity values $\times 10^8$ with units of cm^2 / s

Error bars represent plus or minus one standard deviation

higher pressures than used previously for zeolite membranes.

Ionic Liquids

Recent research has focused on room temperature Ionic Liquids (ILs) as novel, benign solvent replacements for volatile organic compounds traditionally used in chemical processing including liquid membranes (Scovazzo et al., 2002, 2004). ILs combine into one solvent system a number of unique properties. ILs have high thermal stability, high ionic conductivity, negligible vapor pressure and are non-flammable. Unlike traditional organic media, IL's properties may be adjusted via chemical alteration of the cation or anion to produce application specific compounds. Many ILs are liquids over a wide temperature range with some known melting points as low as -96°C and some liquid ranges in excess of 300°C . High coulombic forces constrain the IL constituents and thus, the ILs exert practically no vapor pressure

above the liquid surface. These features have led to current investigations of ILs as alternative media for a variety of applications that use organic solvents.

We have previously shown that regular solution theory can explain the solubility behavior of gases in imidazolium-based ILs (Camper, 2004, 2005). This provides the basis for determining the solubility selectivity for various gas pairs in an IL. Table 1 below shows the solubility for the gases of interest measured in four different ILs. Note that the solubility increases as H decreases. Recent results show that the diffusion coefficients are very similar so selectivity is based on solubility differences (Camper, 2005). This is in contrast to gas separation using glassy polymers where the selectivity is based on differences in diffusivity.

Polymerizable Lyotropic Liquid Crystals

Lyotropic liquid crystals (LLCs) are amphiphilic molecules containing a hydrophobic organic tail section and a

	P (Barrers)	S (cc / cc LLC / atm)	D (cm ² /s)
CO ₂	5.5	1.5	2.8E-08
N ₂	0.21	0.035	5.4E-08
O ₂	0.84	0.078	8.4E-08
CH ₄	0.44	0.20	1.7E-08
H ₂	4.9		

LLC-Na⁺ Properties for Light Gases

	P _a / P _b	S _a / S _b	D _a / D _b
CO ₂ / N ₂	27	48	0.58
O ₂ / N ₂	4.1	2.4	1.8
CH ₄ / N ₂	2.1	6.2	0.35
CO ₂ / CH ₄	13	7.9	1.6
H ₂ / N ₂	24		
CO ₂ / H ₂	1.1		

LLC-Na⁺ Separation Performance

hydrophilic headgroup, which self-assemble in the presence of water or other hydrophilic species into highly ordered, yet fluid phase-separated assemblies with specific nanometer-scale hydrophilic domains. Depending on the shape of the constituent LLCs and the interfacial curvature energy of the system monodisperse hydrophilic domains ranging in structure from lamellae to cylindrical channels to three-dimensionally interconnected pores with dimensions in the 1–10 nm size range can be formed (Fig. 2). By making polymerizable analogs of LLC mesogens, it has been possible to stabilize the various LLC assemblies with retention of phase microstructure via photo-initiated radical cross-linking (Gin et al., 2005).

Cross-linked LLC networks exhibiting an ordered cylindrical nanostructure show promise as a novel platform for polymer-based, next-generation gas separation membranes. The H_{II} nanostructure, when compared to a membrane with the same chemical compositions but lacking an ordered nanostructure, has been observed to significantly influence the solubility of CO₂ and retard the diffusion for all gases (Table 2). As a result, CO₂-based separations were more favorable in the H_{II} membrane. For separations not involving CO₂, there was no observed difference in any ideal gas separation factor, as the permeability of each gas increased by the same factor.

The gas separation performance of a crosslinked LLC-Na⁺ salt membrane exhibiting the inverted hexagonal H_{II} phase (see Fig. 2&3) are shown below. These results show that the LLC phase also demonstrates selectivity based on solubility differences. The incorporation of ILs, with higher diffusion coefficients (approx. two orders of magnitude higher) and solubility selectivity should enhance both the selectivity and flux.

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(Received 16 January 2006 ;

Accepted 20 January 2006)