Membranes

Introduction and Current Status

Highly permeable and exquisitely selective membranes are ubiquitous in nature, where they form the outer walls of cells and govern transport of materials into and out of the cell (Doyle, et al. 1998). Synthetic membranes are also widely used in industry as separating devices (Baker 2004). A membrane separates species by selectively permeating certain components of a mixture faster than others through a thin barrier in response to an external driving force, such as a concentration, partial pressure or, more generally, a chemical potential gradient (see Figure **1**).(Wijmans and Baker 1995)

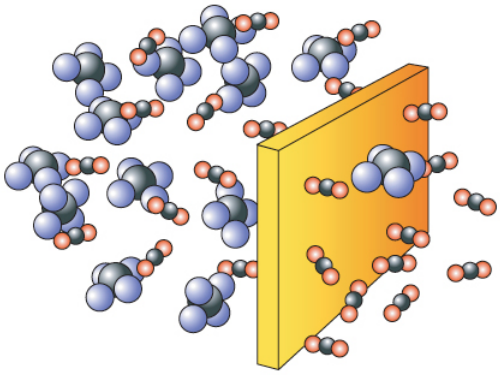


Figure 1. Schematic of a membrane separating a mixture of molecules. Here a mixture of methane (four atoms) and carbon dioxide (three atoms) is depicted, with the CO_2 preferentially passing through the membrane, allowing it to be enriched. Membranes used today are selective for certain components in a mixture, but they cannot exhibit absolute (or 100%) selectivity for a particular component.

Membranes offer a number of inherent advantages over other technologies for separating gases including:

- Low energy use because they can separate species without a phase change
- Simple, passive operation with no moving parts
- Environmentally benign separation without the use of hazardous chemicals
- Small footprint, which is critically important in some applications (e.g., aboard aircraft, spacecraft or on off-shore natural gas platforms)

Figure **2** provides some perspective of these attributes with respect to carbon capture. The photograph shows a gas separation membrane unit being used to remove CO_2 from natural gas. The membranes were installed at this facility after an amine absorption system was taken offline due to corrosion of the columns by the amine solution previously used to remove the CO_2 from the natural gas. The device highlighted in the red box is the membrane system; all other hardware shown in this picture is related to the amine system. This figure provides a compelling

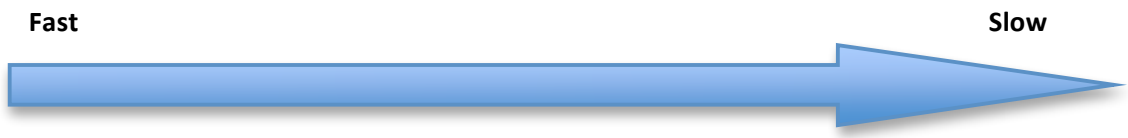
example of the reductions in footprint and process complexity that can be achieved by using membranes relative to amine sorption, a current technology for carbon capture. However, today's membranes have considerable gaps in capabilities for effective gas separation. To capitalize on the very appealing features of membranes as a transformational means of capturing CO_2, O_2, and other gases important to reducing CO_2 emissions, requires development of next-generation membrane materials.

Figure 2. Comparison of a membrane unit with a conventional separation process (i.e., amine sorption system) for removing CO_2 from natural gas. This figure shows the mechanical simplicity of membrane systems as well as their space efficiency relative to other separation processes. Photo courtesy of Air Liquide.

At a molecular level, a variety of mechanisms can affect the separation of gases by a membrane (see Sidebar 1). For example, in polymer membranes, which are the most widely used industrial membranes for gas separations today, gas molecules are separated according to their relative solubility and diffusivity in the polymer (see Sidebar 2). Most polymer membranes in use today sieve small gas molecules based on size, with smaller molecules having higher diffusion coefficients and, in turn, higher permeability coefficients.(Matteucci, et al. 2006) This size sieving gives the order of gas permeability illustrated in Figure 3, which shows smaller molecules being faster (i.e., having higher permeability coefficients) than larger molecules.

Membranes have also been developed that can separate gas molecules based on the relative solubility of the gases in polymers, with more soluble gases being more permeable than those with lower solubility (Baker and Wijmans 1994, Freeman and Pinnau 1997). Gas solubility in a polymer often scales with the critical temperature of the gas (Matteucci, et al. 2006). Such polymers are used industrially to remove organic vapors from air or nitrogen streams (Baker, et al. 1987, Baker 2002) because the membranes are more permeable to the larger, but more soluble organic compounds than to the smaller, but less soluble air gases. Similarly, polymer

membranes that are more permeable to CO_2 than to H_2 are being explored to separate CO_2 from mixtures with H_2 (Lin, et al. 2006).



Gas	H_2O	H_2	H_2S	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8	SF_6
D (Å)	2.65	2.875	3.6	3.325	3.347	3.568	3.817	3.8	4.3	5.5
T_c (K)	647.1	33.3	373.4	304.1	154.6	126.2	190.6	305.3	369.8	318.7

Figure 3. Gas sizes (D), critical temperature (T_c), and common order of permeability coefficients of gas molecules in polymers. Gas molecule diameters for H_2, CO_2, O_2, N_2, and CH_4 are from Robeson et al., which provides an analysis of the gas molecule size most relevant for describing permeation properties in polymers.[1] Gas molecule diameters for the other molecules in this table are kinetic diameters from Breck[2]. Critical temperature data are from Reid et al.[3].

References:

[1] Robeson, L.M., B.D. Freeman, D.R. Paul, and B.W. Rowe, "An Empirical Correlation of Gas Permeability and Permselectivity in Polymers and Its Theoretical Basis," *Journal of Membrane Science*, **341,** 178-185 (2009).

[2] D. W. Breck, Zeolite Molecular Sieves, Wiley-Interscience, New York City, 1974.

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A gas separation membrane typically consists of multiple layers with different functions. A dense, defect-free ultrathin selective layer, of the order of 100nm in thickness or less, performs the molecular separation, while a microporous support structure (substructure) provides mechanical strength and minimal transport resistance. A challenge in making membranes is that the selective layer must be very thin to achieve high flux, and as membranes get thinner, it becomes progressively more difficult to prepare them in a defect-free fashion, that is, without any pinholes or other defects that allow convective (i.e., non-selective) flow of gas through the membrane. In this regard, 1 cm^2 of pinholes in 100 m^2 of membrane (i.e., an area fraction of defects of 1 part in 10^6) is sufficient to destroy selectivity in many membranes, so defects or pinholes in the selective layer must be rigorously avoided to achieve high selectivity. The selective layer and substructure can be made from the same or different materials. Typically, the supporting layer has an asymmetric form with a gradient in porosity from a relatively dense portion in contact with the selective layer to a more open section on the opposite side. An example of a polymeric hollow fiber membrane used today for gas separations is shown in Figure 4.

The thickness of the dense selective layer is very important because it determines the rate at which gases permeate through the membrane, as characterized by membrane permeance. Thinner selective layers translate to higher permeances. High permeance is desirable to reduce the amount of membrane area required to treat a gas stream, and it is particularly important for membrane applications involving very large gas streams, such as those considered for CO_2 capture. Today's membranes produced by solution casting and coating have a minimum selective layer thickness of about 100 nm.

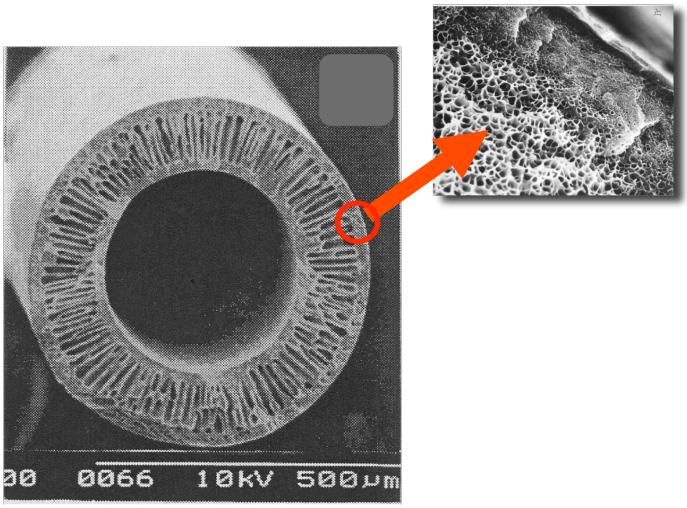

Figure 4. Photomicrograph of a hollow fiber gas separation membrane showing the graded porosity in the wall of the fiber and the ultrathin (~100 nm) separating layer at the outer wall of the fiber. (ref. to D. Wang, K. Li, and W. K. Teo, "Preparation of Poly(ether sulfone) and Poly(ether imide) Hollow Fiber Membranes for Gas Separation: Effect of Internal Coagulant," in ACS Symposium Series Volume 744: Membrane Formation and Modification, I. Pinnau and B.D. Freeman, Editors, pp. 96-109 (1999).

Existing membranes have limitations that hinder their application in CO_2 capture and other important molecular separations. For example, polymeric membranes are subject to a tradeoff relationship where materials tend to have high permeability or high selectivity depending on their chemical structure, but not both high permeability and high selectivity (Freeman 1999, Robeson 1991). This behavior is illustrated in Figure **4** where H_2/N_2 selectivity, α, is presented as a function of H_2 permeability for many polymers. High selectivity is important to improve the degree of separation possible, and high permeability is needed to reduce membrane area required to process a given amount of gas. However, to meet the requirements for efficient and large scale isolation of CO_2, O_2, or other gases from a complex mixture, it is necessary to develop membranes with *both* high selectivity and high permeability—that is, having properties above the upper bound shown in Figure **4**. To achieve such goals will require the development of new classes of membranes, including those made of revolutionary new materials with improved selectivity/permeability characteristics and those incorporating new transport mechanisms.

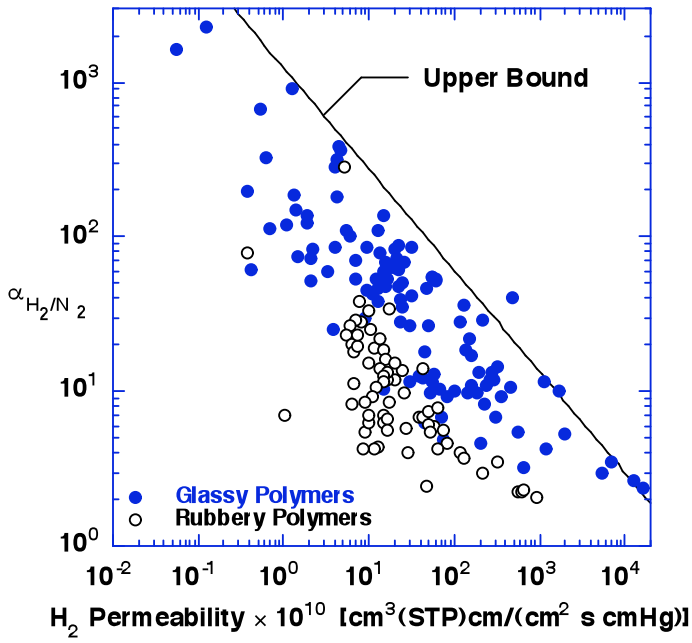

Figure 4. Permeability/selectivity tradeoff as illustrated for the separation of mixtures of hydrogen and nitrogen. Each point on this figure represents the H_2 permeability and H_2/N_2 selectivity of a particular polymer. Generally, polymers that are highly permeable have low selectivity and vice versa. Materials are more permeable to H_2 than to N_2 because H_2 diffusion is faster than N_2 diffusion in polymer membranes. Glassy polymers, which are often more highly size-sieving (i.e., have higher diffusivity selectivity) than rubbery polymers, populate the frontier of this cloud of data points, and the line, called the upper bound, provides a measure of the best known combinations of permeability and selectivity. (Freeman 1999, Robeson 1991) Revolutionary new membranes are needed to achieve permeability/selectivity characteristics that are beyond the upper bound limitations.

Today's membranes have other issues that limit their practical applications for gas separations. In challenging operating environments, such as those expected for CO_2 capture, the performance and mechanical stability of membranes can be compromised. Harmful contaminants in the gas streams as well as high temperatures and/or pressures can all adversely impact the performance and long term productivity of membranes. For example, in polymer membranes, phenomena such as plasticization induced by highly sorbing species reduce the size sieving ability of the membrane. Consequently, gas permeability observed in single gas experiments often appear much more promising than results from real systems that contain mixtures of carbon dioxide and other components—including methane, nitrogen, and hydrogen, among others. In metal membranes, trace components, such as sulfur compounds, poison the membrane surface and ultimately limit transport of the desired molecules. There is a clear need for robust materials that can be fabricated into complex membrane structures while maintaining good transport properties. However, development of these next-generation materials will require new understanding of the separation mechanisms in these material, as well as new strategies for materials synthesis and new capabilities in computational tools to guide the design of robust materials and to model their performance.

Most of today's best performing polymer membranes are highly amorphous, non-equilibrium, glassy polymers. Consequently, another challenge for current membranes is time-dependent behavior caused by physical aging. Figure **5** shows an example of this effect for a polyimide used for nitrogen production from air. Over time, gas permeability of the films decrease (and selectivities increase) significantly, particularly for the thinner films that would be most useful as high flux membranes. This aging behavior is ascribed to densification of the non-equilibrium free volume elements in the polymer that permit molecular transport. However, this aging process is very poorly understood, limiting the likelihood of controlling this undesirable phenomenon. As future gas separation membranes used for CO_2 capture or O_2 enrichment move to thinner and thinner selective layers to maximize gas permeance, preventing the negative effects of aging will be especially important. Thus, understanding, at a fundamental level, the influence of thickness on such non-equilibrium structures will be critical to realize the potential of membrane separations.

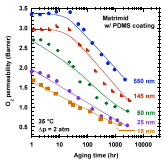

Figure 5. Effect of membrane thickness and time on gas permeability properties of Matrimid®, a glassy polymer.(Rowe, et al. 2009)

Current membranes are typically gradient structures, comprising either multiple layers of different materials (e.g., multi-layer composite membranes), variations in membrane material density through the structure of the membrane (e.g., asymmetric membranes), or both. The development of these structures has evolved in a largely Edisonian fashion. To achieve high performance and maintain integrity in operation, where membranes may be exposed (and respond) to gradients in pressure, temperature, etc., these interfaces between different materials

in a membrane or between regions of different density is critically important. As new membranes are developed, with ever thinner selective layers, the role of the interface on the transport properties and robustness will become even more important. However, there is a large gap in the fundamental understanding of rational manipulation of interface properties to achieve desired structures (e.g., tailored 3-D architecture) while maintaining required robustness and outstanding transport properties.

Currently, all synthetic polymer membranes are processed from solution in organic solvents, using processes such as those presented in **Figure 7**, because this is the only known commercially feasible, large-scale method of making ultrathin gas separation membranes. However, because the membranes are, per force, soluble in organic solvents and organic contaminants are present in many streams that one might wish to separate, the membranes are inherently sensitive to chemical attack while in use. One potential route to resolve this conundrum involves solution processing of materials as soluble precursors and then converting them into highly stable, robust, high performance membranes using an array of methodologies, such as thermal processing,(Park, et al. 2007) or light induced chemical reactions - either by UV, visible, or microwave spectra. Additionally, the use of organic solvents in membrane processing has deleterious effects, contributing significantly to the cost of membrane manufacture and requiring, ultimately, disposal of the solvents, often via environmentally unfriendly processes, such as incineration, which generate CO_2. If solventless strategies could be developed to prepare the 3D architectures required for high performance gas separation membranes, it would provide revolutionary improvements in the efficiency of membrane preparation and provide access to other families of materials that could be used to prepare membranes.

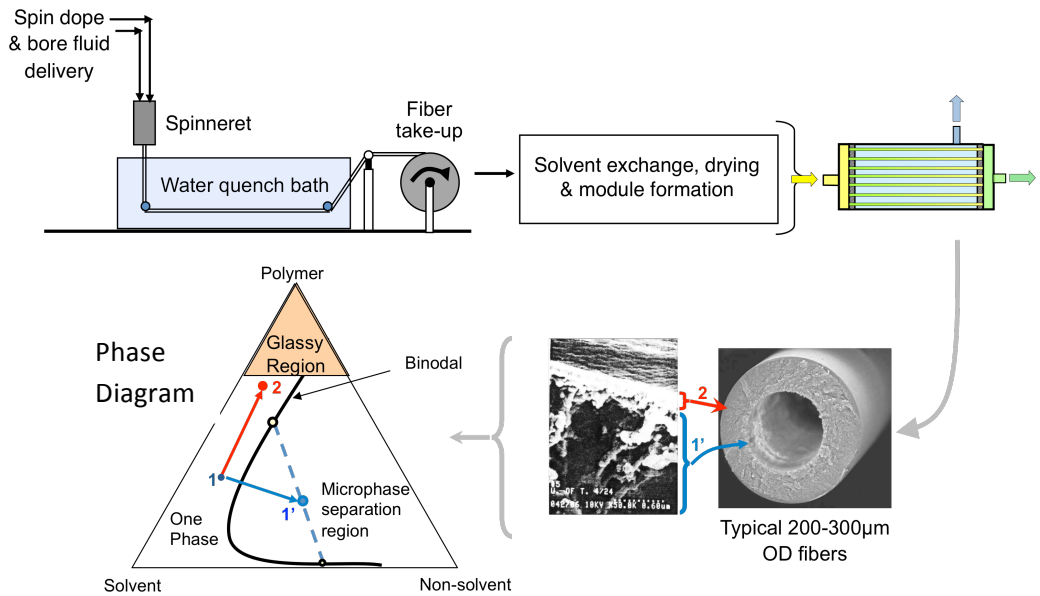

Figure 7. Steps involved in forming asymmetric hollow fiber membranes involves solution processing of polymers to a highly non-equilibrium state. The spin dope (labeled 1 on the phase diagram) contains polymer dissolved in solvent and, potentially, other additives. This dope is fed to a spinneret, and the nascent fiber is extruded into a non-solvent quench bath (typically water), which precipitates a rapid phase separation process (1 ➔ 1' on the phase diagram), to form the porous support structure. After leaving the spinneret and before entering the quench bath, solvent evaporates from the outer surface of the fiber (1 ➔ 2 on the phase diagram), forming the dense skin, which is the selective membrane, and when this skin is quenched in the water bath, the polymer residing in the separating layer is kinetically trapped in a highly non-equilibrium state. Diagram courtesy of Professor W.J. Koros.

To capture 90% of the CO_2 from existing coal-fired power plants, current membrane processes will use about 20% of the electricity generated (Merkel 2010). As such, there is a need to dramatically reduce the energy required for separation to minimize the impact on process requirements. This reduction in energy requirements could be accomplished by breakthroughs in membrane materials with unprecedented transport properties and by harnessing alternative driving forces for separation. The major bottlenecks to reducing the energy required by membranes to efficiently capture carbon are:

- Outperforming the tradeoff between membrane permeability and selectivity
- Lack of chemical and thermal stability of membranes in service
- Rapid aging of ultrathin membranes
- Lack of ability to fabricate controlled membrane architectures

Basic Science Challenges

- Elucidation of the relationship between the nano-scale structure in membranes and separation efficiency.

- Devising new approaches for driving membrane separations, including harnessing alternative driving forces or specific membrane-permeate interactions that can drive membrane-based separation using less energy.
- Understanding the myriad of physical and chemical properties involved in the separation of multicomponent gas mixtures using membranes—including energetics, dynamics and kinetics—that would enable the development of new membrane materials and materials that respond to alternative driving forces (i.e., triggers other than heat and pressure).
- Design of new organic and inorganic membranes with tailored nanostructured three-dimensional architectures that have optimized separation capabilities (both transport and selectivity) and improved stability (i.e., chemical, thermal, and mechanical stability).
- Development of new conceptual frameworks for design of membrane separation systems that are inspired by nature, incorporating self-assembly strategies, multi-functional structures and wholly new approaches to achieve highly selective separations.
- Design of novel membrane materials that would be amenable to solventless processing that could be made highly chemically and thermally resistant.

All of these scientific challenges will require significant advances in characterization tools that will monitor multiple physical and chemical properties simultaneously under realistic conditions. Results from these characterization studies will require advanced computational tools for modeling these complex systems, which can then be used for designing materials, structures and driving forces that will be incorporated in a new generation of membrane separation processes for capturing CO_2.

Conclusions

Membrane technology offers extraordinary promise of low energy, efficient, reliable and environmentally benign gas separation for carbon capture applications. However, to realize this potential, basic research is urgently required to provide revolutionary new membrane materials with controlled architectures, and materials that can respond efficiently to alternative driving forces. Recent advances in synthetic methodologies, nanoscale characterization techniques, hierarchical structure fabrication over many length scales, and molecular simulation and modeling provide unprecedented new opportunities to rationally tailor the next generation of high performance, robust, scaleable membranes for carbon capture.

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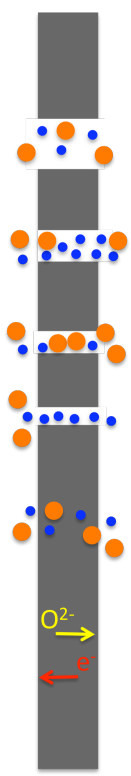
Sidebar 1 – Membrane transport mechanisms

Molecules can move (i.e., permeate) through membranes by a variety of transport mechanisms. The type of transport that occurs is largely dictated by the size of pores or free volume elements in the membrane. The common types of membrane transport are shown schematically in the figure below. In membranes with relatively large pore sizes (>200Å), gas molecules transport by bulk, convective flow. Such membranes have no selectivity for one gas over another. As the membrane pore size decreases, other transport mechanisms, such as Knudsen diffusion and surface flow, can occur. These forms of gas transport, particularly Knudsen diffusion, usually have relatively low selectivity. When the membrane pores are decreased futher and are only slightly larger than gas molecules (~5 Å), molecular sieving can occur. This type of transport can be very selective; however, with today's technologies, it is difficult to make large scale ultrathin membranes with this type of pore structure. Alternatively, gas transport through membranes can occur in the absence of discrete, permanent pores. In this case, gas molecules move through a membrane by solution-diffusion transport. This mechanism involves sorption of the gas into the membrane material followed by diffusion through small, molecular-sized free volume spaces in the membrane. Virtually all polymeric membranes used commercially for gas separations today operate by the solution-diffusion mechanism. A final mechanism of separation can occur in dense inorganic materials, such as perovskites or metals. This mechanism relies on chemical reaction of the gas (e.g., O_2 or H_2) with the membrane material to achieve extremely highly selective transport of targeted gases.

Membrane Transport Mechanisms



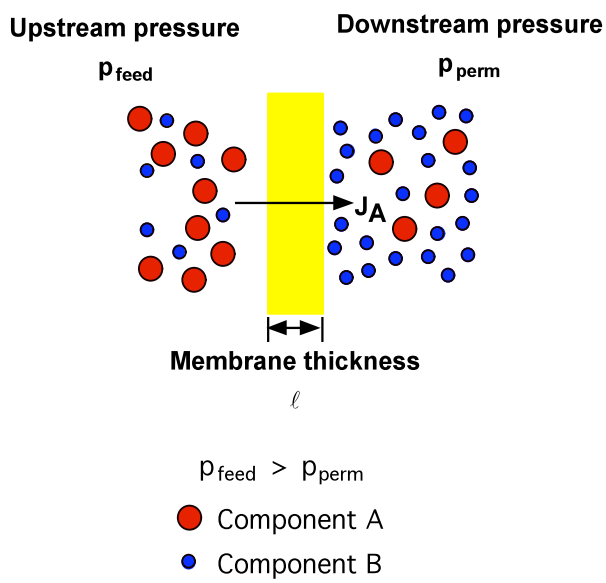
Pore Size (Å)	Transport Mechanism	Comments
>200	Convective Flow	No separation – typical gas filters
λ/D>1* (20-1000)	Knudsen Flow	Very low selectivity – based on $MW^{1/2}$
5 – 10	Surface Flow	Example: microporous carbon with 5-7Å pore size for separation of H_2 from hydrocarbons
<5	Molecular Sieving	Example: carbon membranes with <5Å pores; very high selectivity
Dense (no permanent pores)	Solution-Diffusion	Commercial polymeric gas separation membranes, used mainly for H_2 separation, air separation, and CO_2 removal from natural gas
Dense	Ion Transport Ceramic or Metal (e.g., Pd, Ag) Membranes	Under development for ultrapure H_2, O_2, etc.

*λ = mean free path of gas molecules; D = pore diameter, MW=molecular weight

Sidebar 2 – The Solution-Diffusion Mechanism

Permeability is usually viewed as a material property. The permeability coefficient of a membrane material for specific gas is defined as the steady-state flux of gas through a unit thickness of the membrane under a unit partial pressure driving force. A related parameter used to describe the rate at which gas is transported through a particular membrane is permeance, where permeance is defined as steady-state gas flux divided by the partial pressure driving force, which is equal to permeability of a material divided by the membrane thickness. Thus, membrane permeance can be increased by either using a higher permeability material or reducing the membrane thickness.

Permeability is a key factor in the solution-diffusion mechanism that governs the transport of small gas molecules through all polymers used today as gas separation membranes. In this model, gas molecules first dissolve into the upstream face of a membrane (at high pressure), diffuse through the membrane in the direction of decreasing gas partial pressure and desorb from the lower pressure downstream face of the membrane, as shown in the illustration below.(Matteucci, et al. 2006; Wijmans and Baker, 1995) Within this framework, permeability is a function of the gas solubility (which links the gas concentration in the membrane to the pressure in the adjacent gas phase) and the diffusion coefficient of the gas in the membrane (which is a measure of the gas mobility). The ability of a membrane to separate two gases (e.g., CO_2 and N_2) is often characterized in terms of the ideal selectivity, which is defined as the ratio of the gas permeabilities. Because permeability is equal to solubility times diffusivity and selectivity is the ratio of permability coefficients, the membrane selectivity is a function of both solubility selectivity and the diffusion (or mobility) selectivity.



(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

- Flux of A $\equiv J_A = \dfrac{P_A\,(p_{feed,A} - p_{perm,A})}{\ell}$
- Permeability of A $\equiv P_A = D_A S_A$,
  where $D_A \equiv$ Diffusion coefficient of A
  $S_A \equiv$ Solubility coefficient of A
- Selectivity $\equiv \alpha_{A/B} = \dfrac{P_A}{P_B} = \underbrace{\left(\dfrac{D_A}{D_B}\right)}_{\text{Mobility selectivity}} \underbrace{\left(\dfrac{S_A}{S_B}\right)}_{\text{Solubility selectivity}}$

1. S. Matteucci, Y. Yampolskii, B. D. Freeman and I. Pinnau, Transport of Gases and Vapors in Glassy and Rubbery Polymers, in Y. P. Yampolskii, I. Pinnau and B. D. Freeman (Eds.), Materials Science of Membranes for Gas and Vapor Separation, John Wiley & Sons, Ltd., New York, pp. 1-47, 2006.

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Alternative Driving Forces/Stimuli-Responsive Membranes for Carbon Capture

This is really going in a nice direction, however it needs some further attention. In places it should be expanded. More explanations and examples would be good. Impacts need to be added

Transport processes are driven by chemical potential gradients that create a driving force for separation. Current membrane-based gas separation processes typically use chemical potential gradients in the form of a pressure drop across the membrane. In many instances, membrane separations are not viable due to an inability to economically provide the pressure difference needed. The challenge is to identify alternative driving forces that can be harnessed to drive membrane based separation with lower energy requirements. These driving forces could replace or be used in addition to pressure gradients to lower the energy needed to achieve the desired separation.

BACKGROUND AND MOTIVATION

Current gas separation membrane processes are predominantly driven by a pressure drop across the membrane, as discussed in Sidebar 2. Because pressure has typically been a cost-effective driving force for gas separation, it is most commonly used as the driving force to induce the mass transfer of preferred ions or molecules across membranes. In many large-scale processes, pressure is either already available from unit operations such as gasifiers or can be readily and cost-effectively generated through mature compressor technology.

However, for post-combustion carbon capture from power plants, the flue gas stream that must be treated is released at near atmospheric pressure and at enormous volumetric flows-- ~2 MMcfm (million cubic feet per minute) for a 550-MWe coal power plant. Flue gas contains a number of components, CO_2, O_2, N_2, H_2O, SO_x, NO_x, and other gases. Notably, 86-88% of the stream is N_2, so the majority of any feed compression energy goes to compressing this diluent from atmospheric pressure to the feed pressure required for membrane separation. This pressure increase requires significant energy input and accounts for much of the cost of electricity (COE) associated with membrane-based processes. An alternative method to create a pressure gradient is the application of a vacuum on the permeate side of membrane. Creating this sub-atmospheric pressure condition for the post membrane flue gas streams can also lead to high energy requirements. The need to reduce the energy required for membrane separations is a critical area of opportunity to provide low energy membrane separations.

Biological membranes take advantage of alternative driving forces, such as pH gradients across membranes to drive protein transport. Additionally, processes that employ light-driven ion transport have been proposed (Khairutdinov 2004). In the proposed system, shown in Figure 1, a spiropyran-crown ether conjugate molecule enhances the diffusion of potassium ions across a membrane. Upon photoisomerization of the molecule to the less stable, more polar form, the molecule more easily travels to the ion-rich interface where an ion is coordinated (i.e., captured) by the molecule. Then, the molecule, which is coordinated with the ion, travels across the membrane and releases the ion at the other interface. Upon release of the ion, the molecule reverts back to its original form, allowing the process to repeat. These examples provide exciting inspiration for identifying new driving forces for gas separations that can be harnessed with synthetic membranes to reduce or remove the need for energy-intensive gas compression or vacuum approaches for concentration of CO_2 from combustion streams, O_2 from air for oxy-combustion, and other applications.

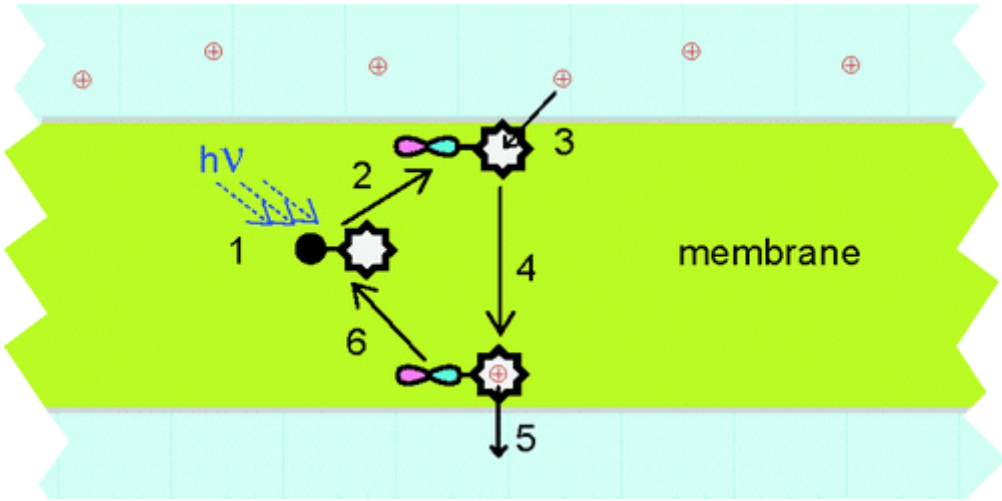

Figure 1. Light-driven transmembrane transport (Khairutdinov 2004).

RESEARCH DIRECTIONS

New classes of gas separation membranes are needed that can harness driving forces in addition to or in lieu of a pressure differential. Driving forces other than pressure can be defined in terms of possible "stimuli" that could be readily available in the external environment and could be used to drive

transport across the membrane. Possible stimuli include thermal and pH gradients, electric and electromagnetic potentials, and sonic/vibrational impulses. For example, membranes have been developed that use an electric potential gradient to create the separation driving force. Additionally, polymer membranes are being developed that control selective transport by response to triggers such as pH, ionic strength, temperature, light, magnetic field, and chemical stimuli (Stuart 2010). To develop these new separation schemes will require new fundamental understanding of the physics influencing separations under alternative driving forces. This understanding will allow entirely new platforms of membrane materials to be developed, with tailored architectures for responding to the driving force and assisting in the separation process.

SCIENTIFIC QUESTIONS AND OPPORTUNITIES

Highly efficient selective small molecule and ion transport through membranes is a key technology needed for gas separations related to both carbon capture and oxy-combustion technologies. Current state-of-the-art polymer membranes generally rely on passive pressure driven transport and are limited by the energy requirement needed to drive the separation, which constitutes a large fraction (~85%) of the parasitic energy cost. State-of-the-art ceramic ion transport membranes for oxygen separation rely on both thermal energy and partial pressure driving force. Novel driving forces for efficient gas separations could result in a dramatic reduction of energy costs that hinder today's membrane separation technologies. Developing such combinations of new membranes and novel driving forces that increase separation efficiencies and lower energy costs would have a huge impact on reduction of CO_2 emmisions formed from combustion. Fundamental research is critically needed to realize the revolutionary impact that will arise from the development of novel chemistries and materials to harness alternative driving forces for energy efficient membrane separations.

Exploit nanostructure in separation efficiency. To develop new separation schemes based on alternative driving forces, revolutionary materials designed at the nanoscale to attain optimal separation efficiencies are needed. Nanoscale features have been shown to dramatically enhance flux and selectivity in pressure-driven polymer membrane separations (Merkel 2002; Park 2007) and electric potential-driven ceramic membrane separations (Maier 2005). Tailoring nanoscale structure is a promising means to enable low energy pathways for selective transport driven by alternative forces. Recent advances in the synthesis of polymers and inorganic materials with nanoscale structural features offer the potential of achieving optimized architectures that respond to external driving forces for efficient gas separations. One can also imagine functionalizing the surface of these materials to add another dimension of optimization. To support the design and synthesis of these nanostructured materials, advanced characterization and computational methods will be required to study these materials under realistic conditions, elucidate and predict mechanisms for gas separations.

Understanding these molecular-level processes will underpin breakthroughs in the utilization of alternatives to pressure/vacuum to drive low energy membrane separations.

Develop new separation functionality triggers. Forces for driving ion and molecule transport across a membrane for carbon capture strategies could take any number of forms, including continuous or pulsed, and could potentially take advantage of environmental conditions at an industrial site including:

- pH-based separation gradient for carbon capture that utilize unique chemistry of CO_2, O_2, and other gases.
- Electromagnetic or magnetorheological gradients
- Electric field/gradient for selective ion or molecular transport
- Sonic/vibrational gradient for selective molecular transport

Much of what we know today about alternative driving forces for separations is based on an Edisonian approach of trial and error. To expedite the discovery and deployment of membrane separations systems consisting of new materials and external triggers requires new computational tools to understand and predict separation of targeted gas molecules or ions at the molecular level. Understanding the structure/performance relationships of these separations systems can drive the development of radically different separation schemes, including the possible advantage of a combination of driving forces in multi-functional membrane materials.

POTENTIAL IMPACT

Also include that compression and/or vacuum costs make up a significant fraction of the costs for membrane-based separations

Impact potentially huge b/c coal-fired PC plants in US release ~2 billion tons CO2/yr

Development of more energy-efficient processes

Novel responsive materials w/ new engineering design/applications (storage, biomedical, structural)

New material designs/microstructures

New theories and equipment for molecular and material dynamics

Rapid adoption of cost-effective separation membranes and processes w/ lower parasitic energy penalties

Ability to implement for mobile as well as stationary point sources

Ability to capture CO2 from air

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New membrane materials that integrate specific interactions for improved mass transfer characteristics

New materials are critical for developing membranes with unprecedented efficiency for enrichment of carbon dioxide or oxygen from complex mixtures in various carbon reduction strategies. These new materials may be designed with specific architectures to yield high specificity for transport of target molecules or ions or with catalytic properties for enhancing transport or selectivity. In addition, current membranes perm-selective for carbon dioxide, oxygen or hydrogen suffer from poor stability. The chemical and physical mechanisms that affect membrane stability and transport properties should be studied by combining synthesis of membranes of tailored structure with in-situ monitoring of chemical and physical properties of the membrane under conditions mimicking practical operation.

Background and Motivation

To enable new approaches to carbon capture using membranes, novel inorganic or polymer membranes with high specificity for transport of target molecules (i.e., nitrogen) or ions (i.e., carbonate) are needed as well as better membranes targeting the transport of, for example, CO_2, H_2, and O_2. Membranes incorporating species with specific catalytic properties in membrane bulk phase or surface may substantially enhance the membrane performance and present new opportunities for novel separation/reaction processes for carbon dioxide capture. This Priority Research Direction focuses on new materials that will open opportunities for developing membranes with unprecedented efficiency for use in CO_2 reduction processes.

Research Directions

One approach to creating membranes with high specificity for transport of target molecules relevant to carbon dioxide capture is to design and synthesize membranes that incorporate specific interaction between transport species and membrane material. For example, facilitated transport has been widely studied for both liquid membranes and biological systems [Noble & Koval, 2006]. The concept of incorporating a reversible interaction into the membrane functionality has the potential to enhance both permeability and selectivity. However, membranes based on such concepts have never been reduced to practice for large scale gas separation, despite several decades of reseach efforts to do so. Developing a fundamental understanding of how to *design and control* such selective interactions will be critically important in designing revolutionary new materials to take advantage of selective

interactions with target gases to prepare robust, high flux, high selectivity membranes for carbon capture.

One example of a recently described membrane that selectively transports CO_2 is a dual-phase membrane, with one phase transporting carbonate ion and another phase oxygen ion [Wake, 2009]. CO_2 can permeate through the membrane under a CO_2 pressure gradient or an electrical field gradient. CO_2 on the upstream membrane surface, binds with an oxygen ion, becoming a carbonate ion, which is transported through one phase of the membrane. A reverse reaction on the downstream surface converts carbonate ion to oxygen ion and molecular CO_2, which is released at the downstream surface. An oxygen ion transporting phase, shown in green in the diagram below, moves the oxygen ion from the downstream to upstream surface of the membrane so that it can again transport a molecule of CO_2 across the membrane. The result is a membrane with high specificity for transport of CO_2.

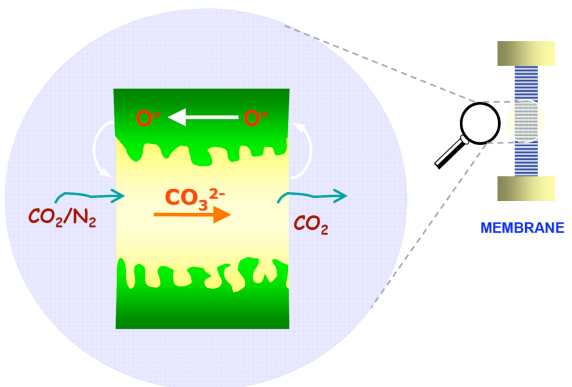

Figure 1 Concept of a carbon-dioxide permeable composite membrane that incorporates interactions between carbonate and oxygen ions with membrane material.

Highly efficient separation or reaction processes for carbon capture can be designed with membranes that transport target molecules and have catalytic properties. Traditionally the catalytic properties are introduced by coating catalytic active species onto a membrane surface, as shown in Figure 2. A limited number of membrane materials with intrinsic catalytic properties do exist. For example, samaria/yttria doped bismuth oxide can selectively transport

oxygen ions and electrons and is catalytically active for converting methane to ethane and ethylene [Akin, 2002]. Design and synthesis of new membrane materials that possess an intrinsic ability to selectively transport target molecules or are endowed with catalytic properties for enhancing transport or reactions related to carbon dioxide capture is urgently needed.

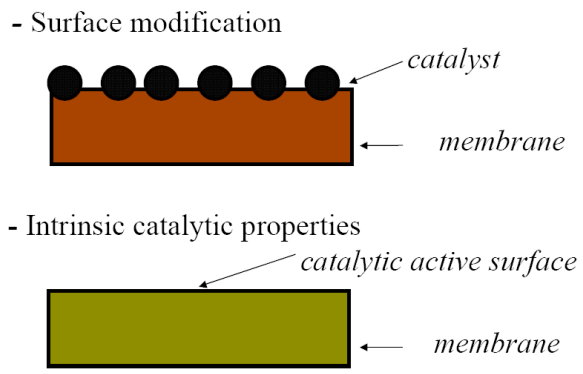

Figure 2 Schematic showing membrane with extrinsic and intrinsic surface catalytic properties

Membranes with high specificity for transport of target molecules can be also realized through development of multi-component composite membranes for synergistic property enhancement. For example, synthesis of stable complexing agents that can selectively separate O_2 from air could result in a membrane with high permeability and selectivity for O_2. These complexes could be a hemoglobin analog or a synthetic chelator that selectively trap and release the target gas molecule or ion. Another example is a novel multicomponent membrane with high selectivity and permeability for a target gas, as shown in Figure 3. This concept is inspired by nature where materials pass through a cell membrane via selective channels. The membrane has a composite structure with highly permeable carbon nanotubes as the support, with polymer filling matrix optimized for chemical, mechanical, and thermal stability. The high perm-selectivity for CO_2 may be achieved through specific interaction between CO_2 and tailored functionalities at the nanotube pore entrance.

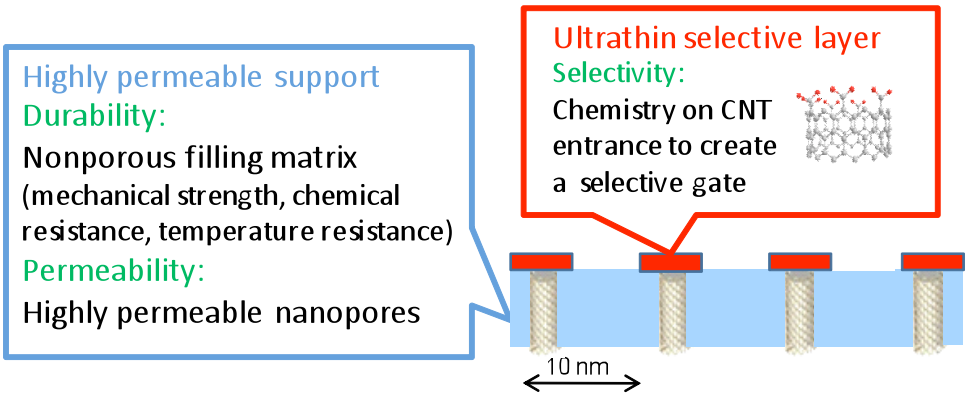

Figure 3 Concept of multi-component membrane with durable high selectivity and permeance for CO_2.

Many existing membranes that selectively transport CO_2, oxygen or hydrogen have poor chemical, thermal or mechanical stability. For example, perovskite type ceramic ionic transport membranes offer high oxygen flux but suffer from surface contamination, bulk phase segregation or mechanical rupture during operation, especially under conditions of large oxygen partial pressure gradients. Hydrogen permeable ceramic or metal membranes also have severe problems of surface contamination that causes a decline in permeation flux and a change in surface catalytic properties during use. Key chemical and physical mechanisms that affect membrane stability and transport properties need to be understood so that membranes with improved properties can be developed. New tools are required to study membranes at realistic conditions, allowing in-situ monitoring of chemical and physical properties of the bulk and surface of the membrane. Coupled with new tools for modeling these mechanisms, new membranes with vastly enhanced stability could be developed.

Scientific Questions and Opportunities

Polymeric materials that separate gases through the solution diffusion mechanism have dominated membrane technology for the past 30 years; however, new materials that take advantage of new transport mechanisms offer opportunities for significant advancements in carbon capture. For example, facilitated transport and mixed ionic-electronic conducting ceramic membranes may achieve near infinite selectivity for CO_2, O_2 or H_2 by tuning chemical interactions with high specificity for target molecules. Recent reports have demonstrated the efficacy of this approach for several challenging applications, including olefin/paraffin separations, oxygen and hydrogen purification and carbon dioxide rejection. However,

significant fundamental advances in the design of new composite membranes are required to design membranes with high specificity for selective transport of target molecules relevant to carbon capture.

- Advances in the understanding of the role of kinetics and microstructure must be achieved to create membranes that react reversibly with these molecular or ion species.
- New approaches for synthesis of composite membranes would enable the development of stable, high throughput membranes utilizing interactive components, such as ionic liquids.
- Discovery of new mechanisms not envisioned in the past to selectively transport target molecule such as nitrogen across membranes.

Potential Impact

The research areas outlined above seek novel insight into material stability and specific membrane/gas interactions to design next generation carbon-capture membranes with long life and outstanding transport performance. They also have the potential to make significant impacts on other fields such as fuel cell technology and membrane reactors. For example, the fundamental understanding and control of membrane material stability can foster the synthesis of novel, highly stable membranes and reveal synergistic material combinations that couple high transport rates with unprecedented selectivity. As a result, infinite selectivity and high permeance may be achieved at much lower temperatures than with current mixed-conducting membranes. Also, the ability to tailor chemical and physical interactions may enable stable and exquisite membrane selectivity for ionic and neutral species at the moderate temperatures typical of post-combustion flue gases. New insight into material properties, synergies between bulk and surface properties, and newly discovered pathways for property-driven design may inspire novel synthetic strategies. Finally, incorporation of functionalities with catalytic activity into membrane structures may provide alternative routes for fuel and/or flue gas conversion into useful products or benign byproducts.

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CRAFTING HIERARCHICAL ENVIRONMENTS IN MATERIALS TO MANIPULATE CARBON DIOXIDE

Abstract

(TBW)

Sam, could you draft the abstract for this section? BDF

Background and Motivation

One of the great challenges in materials design is to identify rational structure-building pathways across scales to support complex functions and integration of needed physical properties. Such hierarchical structures of materials exist in the most sophisticated materials of biological systems, but have not yet been translated to synthetic structures except in very primitive forms. The crafting of such structures with the target of managing molecules of carbon dioxide could have a deep environmental impact for the globe. The strategies toward this goal could use innovation on scalable top down fabrication of the hierarchical structures or use programmed self-assembly of components, such as small molecules, polymers, ions, or nanoparticles. The key question is, what structures will fundamentally change our ability to manipulate a molecule over a broad range of functions? These functions span from the simplicity of efficient diffusion into a solid structure from the gas phase to the enormous challenge of managing its reversible adsorption or chemical reaction on walls and confined spaces of the hierarchical structures. From the standpoint of fundamental chemistry, this challenge will clearly require the development of new catalytic and supramolecular chemistry; some of it possibly inspired by the enzymatic management of carbon dioxide in biology. From the materials chemistry perspective, highly efficient membranes will require materials with graded free volume architectures and surface chemistries to manipulate carbon dioxide in three dimensional environments.

Efficient strategies to create such spatial structural heterogeneities in a single macroscopic construct are effectively undeveloped in materials science. A model structure could be a highly porous surface in a macroscopic structure that readily accepts carbon dioxide and shuttles it into confined spaces that reversibly chemisorb carbon dioxide or react with it. Engineering the release of molecules (e.g., CO_2) after shuttling them to another environment is needed; for example, to provide feedstock for an algae farm or synthetic conversion into useful molecules or materials. Chemical reaction of CO_2 within a hierarchical material may require shuttling the molecule through a catalytic process as different forms of carbon.

The development of new membranes, whether for use in carbon capture and storage (CCS) or other processes, requires new approaches and significant fundamental advances in understanding the material function. The required advances span broad materials classes, including polymers, inorganic solids, composites, fluids, as well as capacities to shape their structure and organizational architecture over length scales that bridge from the atomic level to macroscopic limits. It requires new capacities to harness specific chemical interactions, systems of chemistry, and transport dynamics. It requires new conceptual frameworks for design. It requires new durable systems and means of synthesis and processing to construct them. There also exists a critical opportunity to expand the design rules for membrane materials beyond traditional models to form factors that bridge enabling molecular features to complex, yet deterministically articulated, 3D organizations. It stands as a grand challenge for research to provide new materials that exhibit transport features of atomic/molecular architecture, structural dynamics, and physico-chemical phenomena.

Research Directions

Self-assembly. A natural question is to ask what could *self-assembly*, biology's main manufacturing tool, offer to the development of these strategies. The current scientific platform of self-assembly is mainly centered around designed molecules that create nanostructures driven by noncovalent interactions. Departing from this relatively simple, though not completely developed platform, has been slow since transitioning from nanostructures to hierarchical macroscopic constructs with self-assembly requires complex dynamic processes that create the structure. Self-assembly can be a pathway dependent process. An example is known in which molecules assemble into a bilayer nanoscale membrane with two domains, one amorphous and one ordered that separate two liquids, leading to osmotic events that build additional layers through diffusion. Permeability and mechanical behavior not only differ in the various compartments of this hierarchical membrane but change as a function of time as the membrane grows further from simple reagents. One additional level of complexity in this type of membranous structure is its decoration with functions that can catalyze or react with molecules in specific compartments. The chemistry used in building this variety of hierarchical structure by self-assembly could combine both organic and inorganic chemistry. Creative work in this area of materials synthesis could integrate supramolecular nanostructures, covalent and supramolecular polymers, metal organic frameworks, and ceramic-like lattices. As we approach 2020, materials heterogeneous in both architecture and composition could offer surprising ways of manipulating carbon dioxide, a molecule we should regard as both a challenge and an opportunity.

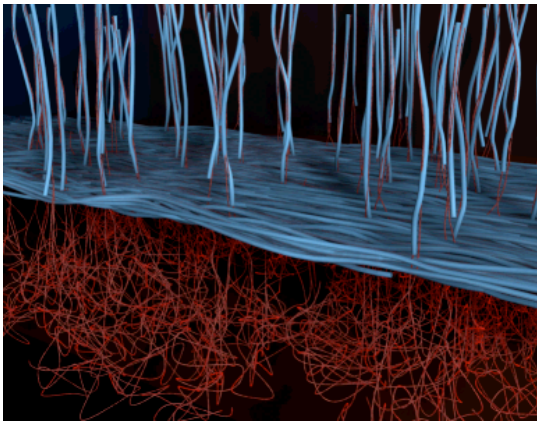

Figure 1. A hierarchical membrane formed from molecular constituents via a

Materials chemistry. Membranes provide a powerful and enabling means to affect separations in complex fluid streams, with beneficial qualities for adoption within CCS processes. High transport rates and for selectivity are key attributes in such separations. There remain significant challenges in developing useful membranes for CCS, nonetheless. Membranes may have stabilities (thermal, mechanical, or chemical) that limit the scope of their application. The optimization of selectivity can also lead to a direct degradation of the permeance, leading to an unacceptable scaling of the size required for a systems level architecture. The properties of membrane separators are also strongly impacted by processing, leading to impacts on their evolution during use. Progress is required that will enable new ways to harness these essential attributes in ways that will broadly expand the capabilities of membrane materials. First, advances are required that will allow precise constructions of heterogeneous architectures that best support gas transport, including careful selection of the chemistry and composition of materials. Polymers might be selected in contexts related to segmental interactions that could be exploited to mediate solubility and diffusivity. Specific compositions of oxides might be adopted because of how they influence thermal expansion or vacancy densities. There remains, though, a significant need and opportunity to further develop the chemistry of membrane materials in ways that harness either chemical mechanisms or specific forms of interaction to influence permeation rates and selectivity. Research is needed to develop important classes of membrane materials more fully enabling systems of chemistry that could more broadly enable CCS separations, in particular for both CO_2 post combustion separations and O_2 separations for oxyfuel combustion scenarios. In each case, membrane chemistries are desired that could broadly extend the range of what is possible within separations of this type. This work must deliver these capabilities within materials that are robust to application specific conditions. Materials are need that facilitate transport via specific but easily reversible interactions. Materials that allow facilitated *uptake, transport, and release*—would transform what is possible in membrane technology and provide a model that follows more closely the inspirational membrane mediated transport of small molecules in biological systems. To fully adopt this analogy within membrane separations technology requires new capacities to precisely tailor molecular interactions in a hierarchy with dynamics (e.g. conformational) that is currently impossible in synthetic materials.

Hierarchical 3D organization at the mesoscale of transport. There is a significant need to fundamentally change the scope of possibilities for the form factors of membrane separation materials. One notable example involves the desirability of providing means to minimize the "footprint" of a membrane separator by integrating them in form factors that extend beyond traditional 2D motifs of current technology—thin films, hollow fiber bundles, etc.—adopting instead more effective, space saving 3D designs that most efficiently mediate separations needed for CCS. General methods that could be used to prepare materials structures of this type with broad compositional and molecular variability, will fundamentally transform systems level capabilities. This latter challenge is one that cannot be addressed by conventional forms of synthesis or processing. It is one that is, however, timely for redress via advances exploiting synergies of top down and bottom up means of materials construction for function—the design of structure for function by assembly and new/emerging means of 3D micro and nanoscale fabrication. Each has a useful and empowering role to play.

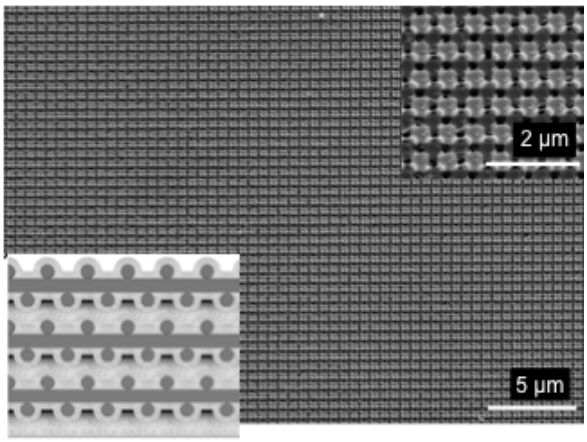

Figure 2. A bicontinuous mesoporous polymer monolith prepared by a large area, low cost phase contrast lithography.

The length scales addressed by assembly overlap those addressable by physical forms of processing—new means of patterning and fabrication that allow deterministic 3D organizations of materials. New phase contrast and interference lithographies, as well as rapidly advancing methods of deterministic assembly and net form direct write fabrication, are providing important means to prepare complex integrated 3D architectures. There is a significant opportunity to develop these and other approaches to provide useful new ways to prepare structures that will provide robust and previously impossible capabilities for membrane-based separations. Specific opportunities where research might be developed include the development of new methods for preparing 3D organizations embedding, gradient systems (e.g. density or composition), hierarchically porous materials, asymmetric and/or heterogeneously integrated polymer networks. It remains a challenge and an opportunity to develop design rules that maximize both the capacity and specificity of membrane based separations. To reduce the footprint of a membrane for a separation one conceptually could fold a 2D film into a mesoporous, but precise 3D form embedding a system of channels. The construction of such systems remains a frontier experimental challenge and the development of computational methods for optimizing the properties of folded materials forms will require significant progress in topological mathematics.

Scientific Questions and Opportunities

The dominating scientific questions that research must address are several fold.

- Fundamental understanding of assembly in technological materials relative to the models provided by biology remain relatively primitive. With increased knowledge of nature's examples, significant opportunities exist to expand the range of capabilities and forms of materials to which it can be applied as well as to develop it as a broadly enabling paradigm for functional design.
- Significant advances in synthetic approaches are needed to expand capabilities for fabrication of 3D nano and microscale architectures. Today's technologies for such structures are generally complex and limited as to enable classes and organizations of materials.
- The ability to design useful *device level* 3D form factors for membrane separation materials is at best limited. In biology, many of the most effective membrane-mediated separation/transport processes involve complex, non-planar articulations of structure that are highly optimized to support function. Achieving similar levels of sophistication in technological materials appears to be a rich and important opportunity for progress in materials.
- The exploitation of molecular/atomistic underpinnings of structural dynamics as enabling components of mesoscale transport dynamics has yet to enter its infancy and progress remains limited by the fact that there are no current approaches to theory that can predictively or usefully bridge disparate but entwined features of this sort.
- Molecular designs of facilitating membrane materials remain far too limited, as does the scope of enabled chemistry.

When taken together, the points raised above suggest significant opportunities to realize significant advances in the separations capabilities of membrane separation materials.

Potential Impact

Multifunctional hierarchical structures generated by self-assembly could have both specific and broader impact on energy related technologies. In the specific case of carbon dioxide capture, this new genre of materials would offer new options in carbon dioxide management. The options could include the integration of separation, sequestration, recycling, and chemical transformation in various combinations not currently available with known solid materials or liquids. This field is a great science investment because many energy related technologies would benefit from it as well. For example, the ideal architectures for photovoltaic or photocatalytic solar cells would benefit enormously from hierarchical structures. An example would be single constructs that block electrons or holes in some domains, but conduct both efficiently in separate regions of the hierarchical structure. In photocatalysis, domains could be structured to absorb photons across the solar spectrum, and other domains of the same material could support catalysts for water splitting reactions and other useful chemical transformations.