

# Membranes for Hydrogen Purification: An Important Step toward a Hydrogen-Based Economy

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## Abstract

Production of pure molecular hydrogen is essential to the realization of the proposed “hydrogen economy” that could ultimately provide hydrogen as a clean, renewable source of energy; eliminate the industrialized world’s dependence on petroleum; and reduce the generation of greenhouse gases linked to global warming. A crucial step in obtaining pure hydrogen is separating it from other gaseous compounds—mainly CO<sub>2</sub>—that often accompany hydrogen in industrial chemical reactions. Advanced membrane technology may prove to be the key to the successful, economical production of molecular hydrogen.

Size-sieving glassy polymer membranes can separate H<sub>2</sub> on the basis of its small size. Alternatively, reverse-selective rubbery polymers can expedite the passage and, hence, removal of CO<sub>2</sub> due to its relatively high solubility in such membranes alone or in conjunction with dissociative chemical reactions. Transition-metal membranes and their alloys can adsorb H<sub>2</sub> molecules, dissociate the molecules into H atoms for transport through interstitial sites, and subsequently recombine the H atoms to form molecular H<sub>2</sub> again on the opposite membrane side. Microporous amorphous silica and zeolite membranes comprising thin films on a multilayer porous support exhibit good sorption selectivity and high diffusion mobilities for H<sub>2</sub>, leading to high H<sub>2</sub> fluxes. Finally, carbon-based membranes, including carbon nanotubes, may be viable for H<sub>2</sub> separation on the basis of selective surface flow and molecular sieving. A wide variety of materials challenges exist in hydrogen purification, and the objective of this issue of *MRS Bulletin* is to address those challenges and their potential solutions from basic principles.

**Keywords:** adsorption, carbon, diffusion, energy, film, hydrogen, membrane, metal, polymer, silica, zeolite.

## Introduction

Although hydrogen composes 80% of all known matter in the universe—excluding the elusive “dark matter” whose nature is currently not known—it is not available in its free molecular form on

Earth. Here, it is tied up in the water that covers two-thirds of the planet, in the valuable hydrocarbon deposits that lie under the Earth’s surface, and in countless other compounds. To obtain molecular

hydrogen as a source of fuel requires the development of methods capable of separating hydrogen from carbon, oxygen, nitrogen, and other elements to which it is chemically bound. In some cases, such as in steam reforming of natural gas, described by the reaction



the separation of hydrogen from carbon and oxygen is accomplished on an industrial scale. However, molecular hydrogen is accompanied by CO<sub>2</sub> as a reaction product, which requires another separation step to produce a stream of pure hydrogen.

The challenges of producing hydrogen on an industrial scale are tremendous, but so are the potential rewards: a source of clean, renewable fuel, which produces only water when burned; decreased production of polluting greenhouse gases; and abundant energy for most of the industrialized world, ending our reliance on petroleum resources that are diminishing and becoming increasingly expensive. While much attention has been recently and rightfully paid to H<sub>2</sub> storage and fuel cell development, H<sub>2</sub> separation and purification remain important considerations to achieving a “hydrogen economy.” Furthermore, significant materials advances in membrane technology for H<sub>2</sub> gas separation are needed to drive reductions in existing H<sub>2</sub> production costs. The purpose of this issue of *MRS Bulletin* is to address the materials challenges that exist in hydrogen purification and present examples of the different types of membranes currently being explored for efficient and robust H<sub>2</sub> production.

## The Drive Toward a Hydrogen Economy

In January 2003, a U.S. presidential directive announced the \$1.2 billion Hydrogen Fuel Initiative, which has since generated tremendous interest in a “hydrogen economy” within the United States and catalyzed international cooperation efforts to bring such a global future to fruition. As it is envisioned, this hydrogen economy is one in which molecular H<sub>2</sub> is produced from coal, natural gas, nuclear energy, or renewable sources such as biomass, wind, and solar energy. Following production, H<sub>2</sub> would be distributed and stored, with its eventual use in fuel cells to generate energy, mostly for powering automobiles but also potentially for providing electricity and heat to residential, commercial, and industrial facilities. According to the U.S. Department of Energy (DOE), this overarching objective can be divided into four major research thrusts: production,

distribution/transportation, storage, and fuel cell technology.<sup>1</sup> Clearly, H<sub>2</sub> production—of which purification constitutes a major step—is vital in the eventual adoption of H<sub>2</sub> as an energy source.

Recently more than \$70 USD/barrel, petroleum prices continue an upward trend (see Figure 1a). Since both oil production and refinery capacity in the United States are approaching steady-state, but the consumption of oil is steadily increasing (see Figure 1b), U.S. dependence on foreign petroleum sources has increased substantially—from 35% to 55% since 1973—and is projected to be as high as 68% by 2025.<sup>2</sup> With a growing worldwide population and the emergence of developing nations such as China and India, the demand for dwindling oil reserves will continue to rise. Finally, fossil fuels pose a substantial threat to the environment from the emission of greenhouse gases into the atmosphere, one of the leading causes presumed to be responsible for global warming. Rising global energy requirements, as well as accompanying economic and environmental implications, corroborate a genuine need to explore other energy options such as hydrogen.

## The Current Status of Hydrogen Production

On a worldwide basis, 37 billion kg/yr of hydrogen are produced via industrial processes, with steam reforming of natural gas accounting for 80% of the hydrogen generated.<sup>3</sup> Of the total 850 billion m<sup>3</sup>(STP)/yr of H<sub>2</sub> supplied globally, a little over half, 450 billion m<sup>3</sup>(STP)/yr, is produced intentionally, while the remainder results as a

by-product from petrochemical processing at refineries. Besides its potential as an energy source, hydrogen is a versatile chemical with a wide range of commercial uses. It is essential in processes developed for the removal of sulfur from petrochemicals (hydrodesulfurization), as well as for the production of syngas (a mixture composed primarily of CO and H<sub>2</sub>), ammonia, methanol and higher alcohols, urea, and hydrochloric acid. Furthermore, H<sub>2</sub> is routinely employed as a reducing agent for metals in Fischer–Tropsch reactions, a process used to generate hydrocarbon fuels by reacting H<sub>2</sub> and CO in the presence of a transition-metal catalyst, and to modify petroleum products and oils by hydrogenation or hydrocracking.<sup>4–8</sup>

In large-scale chemical plants, such as those currently used to generate H<sub>2</sub>, separation and purification operations account for at least 50%, and sometimes up to 80%, of the capital investment.<sup>9</sup> Consider, for instance, that H<sub>2</sub> obtained from steam reforming of natural gas consumes about 74 MJ/kg of H<sub>2</sub> at ~23 bar on a production basis of 32.2 billion kg/yr. An estimated 470 billion MJ/yr could be saved with only a 20% improvement in the separation/purification train after the reformer.<sup>10</sup> Saved energy translates into reduced production cost, which is synergistic with the ultimate goal of making H<sub>2</sub> economically competitive relative to current gasoline prices.<sup>8</sup> Whether H<sub>2</sub> is produced from foreign or domestic fossil fuel reserves, nuclear energy, or biomass, the need will always exist for efficient ways to separate it from other diluent gases. Advanced membrane technology may prove to be

the most effective means of conducting this separation step.

## Membrane Separation Technology

A membrane is a thin, permeable interface that serves to separate two regions in a chemical system. In biology, the cellular membrane is a porous protecting surface that regulates the transport of molecules into or out of the cell. The net transport of small molecules across a membrane generally requires a driving force, which is provided by a gradient in chemical potential, which relates to concentration, across the membrane. In industrial chemical processes, a membrane can be used to separate compounds based on the size of the molecule, differences in solubility of the molecules in the membrane, dissociative diffusion mechanisms, or other processes.

In this issue of *MRS Bulletin*, we discuss five types of advanced membrane technologies: polymer, metal, silica, zeolite, and carbon. Size-sieving glassy polymer membranes can separate H<sub>2</sub> on the basis of its small size relative to other gases. Alternatively, reverse-selective rubbery polymers can expedite the passage and, hence, removal of CO<sub>2</sub> due to its relatively high solubility in such membranes alone or in conjunction with dissociative chemical reactions. Transition-metal membranes and their alloys can adsorb H<sub>2</sub> molecules, dissociate the molecules into H atoms for transport through interstitial sites, and subsequently recombine the H atoms to form molecular H<sub>2</sub> again on the opposite membrane side. Microporous amorphous silica and zeolite membranes comprising thin films on a multilayer porous support

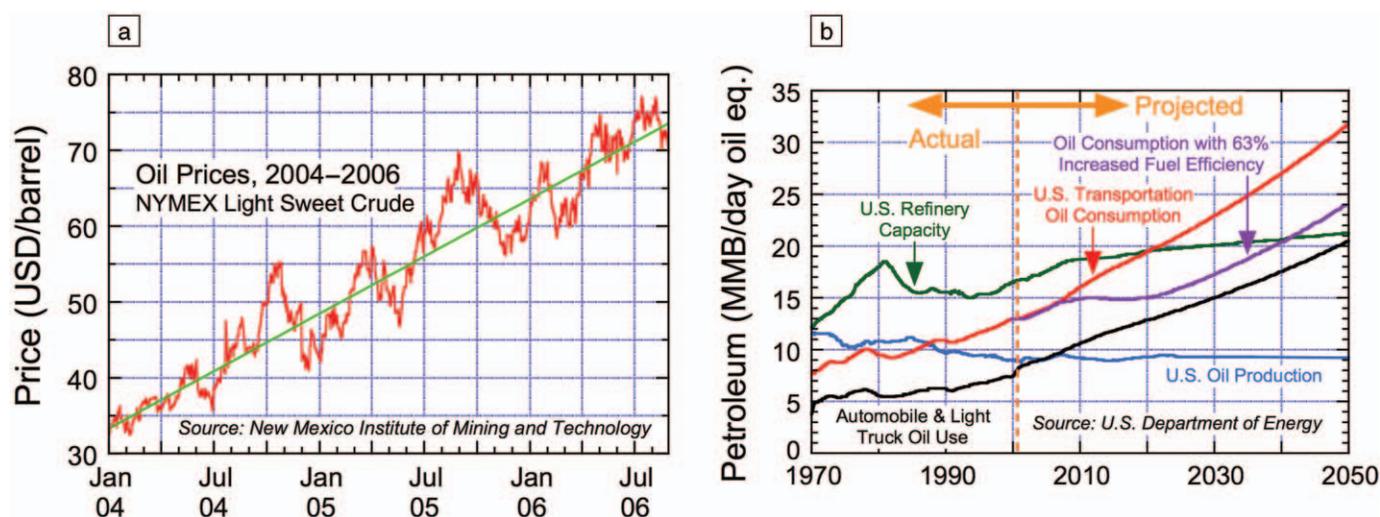


Figure 1. (a) The price of NYMEX light sweet crude oil from January 2004 to August 2006, according to the New Mexico Institute of Mining and Technology. The green line is a linear fit to the data. (Prices taken from <http://octane.nmt.edu/marketplace/prices/>.) (b) Long-range (actual and projected) U.S. dependence on petroleum with time, according to the U.S. Department of Energy.

exhibit good sorption selectivity and high diffusion mobilities for H<sub>2</sub>, leading to high H<sub>2</sub> fluxes. Finally, carbon-based membranes, including carbon nanotubes, may be viable for H<sub>2</sub> separation on the basis of selective surface flow and molecular sieving.

### Polymeric Membranes for Gas Separation

In the past decade, a considerable amount of attention has been paid to polymeric membranes in the application of gas separations. Polymeric membranes such as Polysep systems (UOP) and PRISM systems (Monsanto, Air Products and Chemicals Inc.) are currently used to recover hydrogen from refinery, petrochemical, and chemical process streams.<sup>3</sup> Both examples are based on asymmetric membrane materials, fashioned in either spiral-wound sheet-type contactors (Polysep) or hollow fibers (PRISM) and composed of a single polymer or layers of different polymers, with the active layer being a polyimide. Typically, polymeric membranes are used in lower-temperature hydrogen recovery such as from the tail stream of a pressure swing adsorption (PSA) unit. While the relative temperature sensitivity of polymers compared with dense ceramic or transition-metal membranes is a drawback, polymeric membranes have a number of advantages. Membranes created from polymers are generally less expensive (due to the abundance and price of precursor materials), easier to process, and more mechanically tunable than their inorganic counterparts.

Gas permeation through a dense polymeric membrane is most often described with the solution-diffusion model, given by

$$P = DS, \quad (2)$$

where  $P$  is the permeability coefficient routinely expressed in Barrers:

$$1 \text{ Barrer} = 10^{-10} \text{ m}^3(\text{STP})\text{cm}/(\text{cm}^2 \text{ s cm Hg}). \quad (3)$$

Here,  $D$  is the diffusion coefficient, often given in units of cm<sup>2</sup>/s, and  $S$  is the solubility coefficient in units of cm<sup>3</sup>(gas)/[cm<sup>3</sup>(polymer)cm Hg]. The preferential ability of a polymer membrane to permeate one gas (A) over another gas (B) is referred to as the ideal selectivity ( $\alpha_{A/B}$ ), as can be seen in the following equation:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B}. \quad (4)$$

The ideal selectivity can also be defined as the product of the diffusivity selectivity

and the solubility selectivity of gases A and B. The diffusivity selectivity ( $D_A/D_B$ ) is governed by the size difference of penetrant gases and the size-sieving ability of a polymer material. An important factor that influences the diffusivity selectivity is the available free volume, voids not occupied by polymer chains at nanoscale dimensions through which penetrant gases migrate. In a polymer possessing relatively little free volume, as in the case of glassy polymers, only gas molecules able to fit within existing void regions can diffuse through the membrane. The diffusivity selectivity is also sensitive to temperature conditions: an increase in temperature tends to enlarge void spaces and increase the polymer free volume, thereby increasing the diffusion coefficient of penetrant gases. Solubility selectivity ( $S_A/S_B$ ), on the other hand, is governed by the solubility of gas A relative to the solubility of gas B in the polymer. Typically, solubility increases with increasing size and condensability of a gas penetrant, but decreases with increasing temperature due to reduced chemical interactions.

Glassy polymers ( $T_g > T_{\text{operating}}$ ) are dominated by diffusivity selectivity and thus are often employed to remove lighter gases such as H<sub>2</sub>, whereas rubbery polymers ( $T_g < T_{\text{operating}}$ ) are dominated by solubility selectivity and are therefore often used to remove heavier gases like CO<sub>2</sub>. Here,  $T_g$  denotes the glass-transition temperature of the polymer. As can be seen in Figure 2, polymeric membranes are generally subject to an upper bound, or trade-off, between selectivity and permeability or flux.<sup>11,12</sup> Furthermore, Figure 2a shows why glassy polymers are often preferred over rubbery materials for H<sub>2</sub>-specific separations, given the desire for high product-stream purity, which is a function of the selectivity. Conversely, Figure 2b illustrates why reverse-selective rubbery polymers are preferred for CO<sub>2</sub> removal. The cutting edge of polymeric membrane research takes place when materials are identified or developed that can break the upper limit and achieve both high selectivity and high permeability.

### Polymeric Membranes for H<sub>2</sub> Permselective Separation

In the first article in this issue, Perry et al. discuss the historical development of polymeric membranes for hydrogen separation, followed by a detailed mathematical treatment of the diffusivity and solubility parameters involved. They introduce the concepts of "hydrogen-selective" membranes, which allow hydrogen to pass through based on its small size, and "hydrogen-rejective" membranes, which

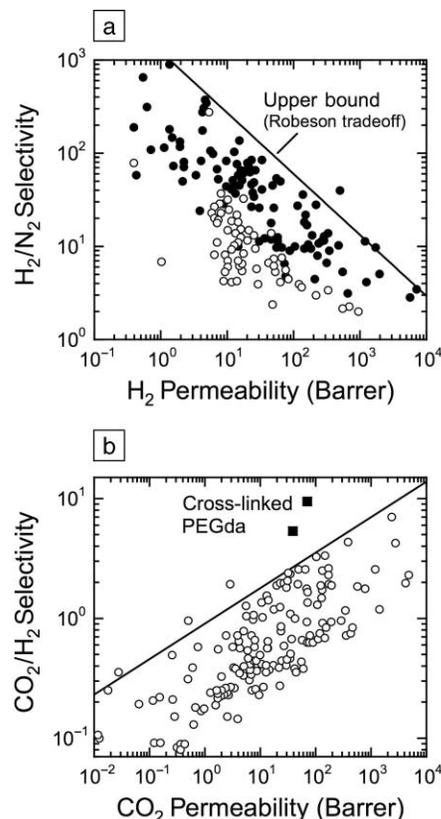


Figure 2. Relationships between (a) H<sub>2</sub>/N<sub>2</sub> selectivity and H<sub>2</sub> permeability<sup>11,12</sup> (adapted from Reference 12 and reproduced with permission from the American Chemical Society) and (b) CO<sub>2</sub>/H<sub>2</sub> selectivity and CO<sub>2</sub> permeability<sup>23</sup> over a wide range of polymers. In (a), rubbery and glassy polymers are depicted by open and filled symbols, respectively, whereas such delineation is not made in (b). The empirical upper bound known as the Robeson tradeoff is identified by the solid line in (a) and (b). Highly CO<sub>2</sub>-selective polyether (PEGda) membranes are identified by filled squares in (b).

favor the passage of higher-solubility molecules such as CO<sub>2</sub> through the membrane while blocking the less-soluble H<sub>2</sub> molecules. As mentioned previously, glassy polymers are often used for the separation of H<sub>2</sub> and CO<sub>2</sub> due to their ability to sieve penetrant gases on the basis of molecular size—and more specifically, the molecular kinetic diameter (see Table I). Since H<sub>2</sub> and CO<sub>2</sub> do not vary significantly in size and since CO<sub>2</sub> has a tendency to be readily soluble in some polymers, separation of these two gases can often be difficult. Furthermore, depending upon the chain structure of a given polymer, CO<sub>2</sub> can act as a plasticizing agent, effectively

**Table I: Light Gas Molecules Commonly Found in H<sub>2</sub> Purification Feed Streams and Their Kinetic Diameters.<sup>10</sup>**

Molecule	Kinetic sieving diameter (nm)
He	0.260
H <sub>2</sub>	0.289
NO	0.317
CO <sub>2</sub>	0.330
Ar	0.340
O <sub>2</sub>	0.346
N <sub>2</sub>	0.364
CO	0.376
CH <sub>4</sub>	0.380

reducing the polymer  $T_g$  and increasing chain mobility, thus increasing its passage through the expanded free volume. As a result, H<sub>2</sub>/CO<sub>2</sub> selectivity only varies between 0.5 and 2.5 over a wide range of polymers.<sup>13</sup>

Despite these findings, novel material advances have been made that have resulted in higher H<sub>2</sub>/CO<sub>2</sub> selectivities. One such study examined the addition of alkyl groups onto novel poly(aryl ether ketone)s at 30°C and 100°C. Inevitably, the addition of alkyl groups in the polymer backbone inhibits chain packing and therefore increases the free volume available for molecular transport, resulting in higher gas permeabilities. Wang et al.<sup>14</sup> found that with increasing alkyl group sizes, the permeabilities of H<sub>2</sub> and CO<sub>2</sub> both increased, but the selectivity between the two gases decreased. Interestingly, however, by increasing the temperature to 100°C, the H<sub>2</sub>/CO<sub>2</sub> selectivity of the polymers likewise increases, along with appreciably improved H<sub>2</sub> permeabilities.

A considerable amount of work has been conducted with polyimides and their derivatives, largely because of their high  $T_g$  and tight chain packing. A study of interest that involves outside-the-box thinking was performed by exposing polybenzimidazole ( $T_g = 435^\circ\text{C}$ ) to temperature ranges that are not normally examined in routine gas transport studies.<sup>15</sup> Pure- and mixed-gas permeabilities have been measured up to 340°C, a temperature at which methanol reforming is usually conducted. For pure gases, the permeability of H<sub>2</sub> reached a maximum of 18 Barrer (at ~250°C), which is relatively low. The corresponding H<sub>2</sub>/CO<sub>2</sub> selectivity is, however, reported to be as high as 20.

While research has been conducted with poly(amide-imide) block copolymers,<sup>16</sup> the emerging concept of polyimide

mixed-matrix composite materials has provided some promising results in gas permeation studies. Yong et al.<sup>17</sup> reported that combinations of polyimide (Matrimid<sup>®</sup>), zeolite materials, and 2,4,6-triaminopyrimidine (TAP) at 35°C yield relatively good He/CO<sub>2</sub> selectivity results (He is often used to emulate H<sub>2</sub> due to its comparable size and inert nature). While the permeabilities are relatively low, the results illustrate that the incorporation of particles typically used for size-sieving H<sub>2</sub> can generate a composite material (see Figure 3) capable of improved selectivity. Smaihl et al.<sup>18</sup> generated hybrid imide-siloxane systems containing silica particles to achieve both high H<sub>2</sub> permeabilities and selectivities. Other noteworthy materials advances include polymer laminates such as a multilayer polysulfone/silicone rubber composite membrane yielding a high H<sub>2</sub>/N<sub>2</sub> selectivity at 50°C,<sup>19</sup> incorporation of a poly(ethylene oxide) layer into a polysulfone/silicone rubber composite, resulting in a H<sub>2</sub>/N<sub>2</sub> selectivity that is higher than the selectivity of any one of the integrated components at 35°C,<sup>20</sup> and alumina-supported styrene divinylbenzene with high H<sub>2</sub>/CH<sub>4</sub> selectivities.<sup>21</sup> Unfortunately, none of these studies provide CO<sub>2</sub>

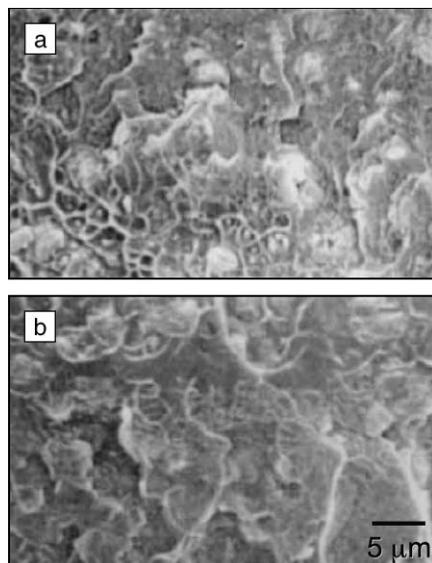
data, so their overall value remains speculative at this point.

### Polymeric Membranes for CO<sub>2</sub> Permselective Separation

Carbon dioxide is a highly permeable gas, largely because it is an acid gas with a quadrupolar moment and high solubility in a number of polymers, particularly rubbery polymers that possess polar chemical species. Such reverse-selectivity can be used to promote CO<sub>2</sub> migration into the permeate stream, leaving H<sub>2</sub> pressurized in the retentate stream. The net result is removal of the CO<sub>2</sub> contaminant and recovery of the H<sub>2</sub> product at high pressure, thereby eliminating the need for costly H<sub>2</sub> recompression prior to use or storage. These membranes have resulted in CO<sub>2</sub>/H<sub>2</sub> selectivities as high as ~10 in a polyphosphazene composed of poly(dichlorophosphazene) modified with 2-(2-methoxyethoxy)ethanol.<sup>22</sup> Similar<sup>23,24</sup> and, depending on temperature, even higher<sup>24,25</sup> CO<sub>2</sub>/H<sub>2</sub> selectivities have been measured in cross-linked poly(ethylene glycol) diacrylate (PEGda) membranes, as shown in Figure 2b.

In the second article in this issue, Hägg and Quinn examine one type of hydrogen-rejective membrane referred to as a polymeric facilitated transport membrane. These membranes selectively permeate CO<sub>2</sub> by means of a reversible chemical reaction between the penetrant gas and the membrane material. In addition, the membrane provides a barrier to H<sub>2</sub> permeation. A wide range of polymeric materials have been investigated, including ion-exchange resins, hydrophilic polymers blended with CO<sub>2</sub>-reactive salts, polyelectrolytes, fixed-site carrier polymers, and biologically inspired materials.

Some glassy, high-free-volume polymers are inherently CO<sub>2</sub>-selective, but their more attractive characteristic is their unusually high gas permeabilities. Poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-methyl-1-pentyne) (PMP), and poly(*tert*-butylacetylene) (PTBA), all substituted polyacetylenes, possess H<sub>2</sub> permeabilities of ~19,000 Barrer, 5800 Barrer, and 300 Barrer, respectively, but their CO<sub>2</sub>/H<sub>2</sub> selectivities are all only ~2 at 25°C.<sup>26,27</sup> A random copolymer composed of tetrafluoroethylene and poly[2,2-bis(trifluoro-methyl)-4,5-difluoro-1,3-dioxole] (TFE/BDD, 87/13 mol basis), as well as Teflon<sup>®</sup>, both exhibit H<sub>2</sub> permeabilities of over 3000 Barrer. However, they exhibit even lower CO<sub>2</sub>/H<sub>2</sub> selectivities (slightly greater than 1 at 25°C).<sup>28,29</sup> Most of these membranes, along with polydimethylsiloxane (PDMS), are better suited for the removal of larger organic vapors



*Figure 3. Scanning electron microscopy cross sections of (a) a Matrimid<sup>®</sup>/4A zeolite (0.38-nm pore size)/TAP (1.00/0.43/0.21 by weight) composite membrane and (b) a Matrimid<sup>®</sup>/13X zeolite (0.74-nm pore size)/TAP (1.00/0.43/0.14 by weight) composite membrane, with He/N<sub>2</sub> selectivities of 1282 and 575, respectively. (Adapted from Reference 17 and reproduced with permission from Elsevier Science.)*

over light gases such as hydrogen,<sup>30</sup> although PDMS does exhibit a CO<sub>2</sub>/H<sub>2</sub> selectivity of ~4.3 at 35°C.<sup>31</sup>

## Inorganic Membranes for H<sub>2</sub> Purification

Much effort has recently been devoted to the synthesis of inorganic membranes because of their potential applications in the domains of gas separation, pervaporation, and reverse osmosis, as well as in the development of chemical sensors and catalytic membranes.<sup>32–36</sup> Inorganic membranes, which possess good thermal stability and chemical inertness, enjoy several important advantages over polymer membranes for many industrial applications. Improvements continue to focus on areas of membrane integrity and manufacturing costs.

## Alloys and Metals

Metallic materials are of great interest for hydrogen-selective membranes.<sup>10</sup> The article by Sholl and Ma describes metal membranes for high-temperature applications. The physical mechanism of H<sub>2</sub> permeation through metal membranes is quite different from porous membranes: metal membranes function by adsorbing and dissociating gaseous H<sub>2</sub> on the metal surface exposed to the feed stream and subsequent diffusion of atomic H through interstitial sites in the metal. Recombination of atomic H into H<sub>2</sub> on the downstream membrane side completes the transport of H<sub>2</sub> across the membrane. Because of this mechanism, metal membranes can achieve essentially perfect selectivity for H<sub>2</sub> when exposed to gas mixtures, because transport of species other than hydrogen through the membrane is restricted to defects in the film. Effective membranes can be prepared by depositing thin metal films on macroporous supports. These membranes can be 100% selective toward hydrogen since hydrogen is transported in dissociated form, which yields ultrapure hydrogen with little or no greenhouse gas contamination. Despite such performance, porous membranes can still be useful to drive the reaction. More work is needed to explore practical opportunities in this area. Of the metals currently of interest, Pd remains the most promising for H<sub>2</sub>-selective membranes, even with its mechanical limitations, including embrittlement, cracks, pinhole film defects, delamination, and sulfur sensitivity.<sup>10,32,37–42</sup>

Furthermore, for Pd membranes to be economically attractive in H<sub>2</sub> separations, they have one major shortcoming that must be addressed prior to their wide-scale implementation in industrial processes:

their flux must be improved by a factor of 2–4 for use in steam reformers or water–gas shift (WGS) reactors.<sup>10</sup> As a result, current research is focused on the consistent preparation of thin Pd films, measuring ~5 μm thick, that can still afford high selectivity. Thin Pd membranes deposited on porous supports, such as porous alumina or porous metal, are able to withstand the operating conditions typical of H<sub>2</sub> manufacture processes. Sol-gel processing<sup>43</sup> and chemical vapor deposition (CVD)<sup>39,40,44</sup> have thus far been the methods of choice to prepare such thin films. Sol-gel modification provides good selectivity and permeability, in contrast to CVD methods, which yield membranes with reduced permeability but enhanced selectivity. The sol-gel method, however, suffers from poor reproducibility. A variety of synthetic methods have been reported in addition to those already listed,<sup>44,45</sup> including electroless plating,<sup>10,45–49</sup> where films exhibit high permeances for long operational times while retaining H<sub>2</sub>/N<sub>2</sub> selectivities on the order of 1000.

## Silicas and Zeolites

High-temperature porous membranes (e.g., silica, silicalites, and zeolites) have also been investigated for applications in steam reforming,<sup>51,52</sup> dry reforming,<sup>53–55</sup> and WGS reactions.<sup>56,57</sup> These materials eliminate the need for scarce precious metals. In addition, they are less expensive and exhibit higher permeances than Pd-based membranes. Moreover, they are inert to H<sub>2</sub> embrittlement. Verweij et al. discuss microporous amorphous silica and zeolite membranes synthesized as thin films on a multilayer porous support. The membranes possess a network of connected micropores measuring ~0.5 nm in diameter. Favorable combinations of sorption selectivity and diffusion mobility in the membrane materials lead to high H<sub>2</sub> fluxes and good selectivity with respect to other gases. The membranes also show potential for application in H<sub>2</sub> separation under harsh conditions. Amorphous silica membranes exhibit very high H<sub>2</sub> fluxes because they can be made very thin, but all-silica MFI-type zeolite (termed silicalite) membranes are expected to demonstrate better operational stability. To make the membranes a viable option, improvements are needed to reduce the occurrence of membrane defects, decrease manufacturing costs, and enhance reproducibility and operational stability.

To date, the most promising results for a membrane separation with steam reforming have been achieved with a silica zirconia composite membrane prepared by sol-gel coating.<sup>51</sup> However, the presence of

water vapor may significantly affect the performance of these silica membranes over time, particularly if operated at relatively low temperatures.<sup>10</sup> Recent studies on silica-based zeolite membranes (see Figure 4) have confirmed that H<sub>2</sub>O adsorption at temperatures >100°C interferes with H<sub>2</sub> selectivity by enhancing CO<sub>2</sub> permeance.<sup>58</sup> Microporous silicas are very promising due to their low cost, high stability, and high permeance. Recently, these membranes have also yielded exceptional H<sub>2</sub> selectivities, with the best H<sub>2</sub>/N<sub>2</sub> selectivities exceeding 10,000 for membranes prepared by CVD.<sup>10,58–61</sup> An extension of silica membrane research is the development of hybrid metal-coated silica systems, such as the Al-coated SiO<sub>2</sub> permselective membranes reported by Oyama.<sup>61</sup> They are likewise prepared by CVD of a thin SiO<sub>2</sub> layer on a porous alumina substrate, resulting in a non-continuous network of solubility sites. The submicrometer-thick silica-on-alumina composite motif uses progressive size gradation, thereby promoting enhanced permeability of hydrogen over CO<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub>.

Another method for avoiding costly and fragile Pd for H<sub>2</sub> purification relies on the use of nanoporous membranes. Zeolite membranes in particular combine pore size and shape selectivity with the inherent mechanical, thermal, and chemical stability necessary for long-term operation. The effective pore size distribution of the zeolite membrane, and hence its separation performance, is intrinsically governed by the choice of the zeolitic phase.<sup>62–65</sup> This applies when molecular-size-exclusion sieving is dominant and no other diffusion pathways bypass the network of well-defined zeolitic channels (otherwise, viscous flow through grain boundaries prevails). The optimum thickness of the zeolite film is always a compromise between separation performance and overall transmembrane flux and should be tailored to the needs of the application envisioned. Very thin (~0.5 μm) *H*-galloaluminosilicate ZSM-5 type (MFI) membranes on alumina have recently been synthesized<sup>66</sup> and found to exhibit high fluxes [He permeance of ~80 × 10<sup>-7</sup> mol/(m<sup>2</sup> s Pa)] coupled with separation factors essentially in the Knudsen diffusion regime (He/SF<sub>6</sub> ≈ 0.9 Knudsen factor). Large-surface-area MFI membranes have been grown with a high success rate and exhibit good selectivity characteristics (H<sub>2</sub>/SF<sub>6</sub> > 3 Knudsen factor) but low H<sub>2</sub> permeance, on the order of 1.5 10<sup>-8</sup> mol/(m<sup>2</sup> s Pa).<sup>67</sup>

Due to the need for carbon sequestration associated with H<sub>2</sub> production from fossil fuels, zeolite membranes selective

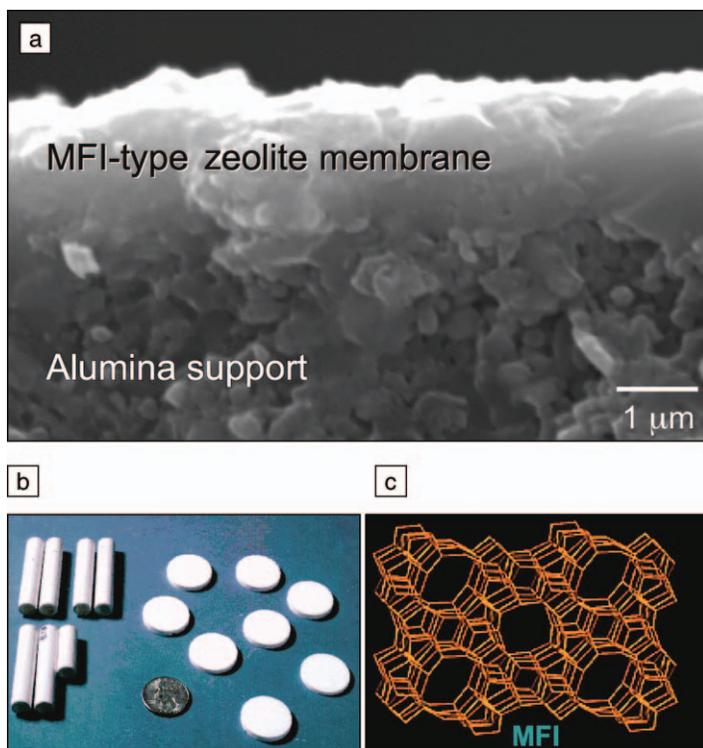


Figure 4. (a) Scanning electron microscopy cross section of an MFI-type zeolite membrane on an alumina support.<sup>58</sup> (b) The membrane ceramic supports<sup>58</sup>; (c) the MFI structure. (Adapted from the IZA database website, [www.iza-structure.org/databases/](http://www.iza-structure.org/databases/).)

for CO<sub>2</sub> gas separations have also been studied and include the faujasite (FAU) and the silica/aluminophosphate (SAPO-4) framework families. For example, Dong and co-workers<sup>68</sup> reported that the addition of water vapor to the CO<sub>2</sub>/N<sub>2</sub> feed gas drastically reduced CO<sub>2</sub> and N<sub>2</sub> permeances and altered the membrane selectivity at low temperature (<80°C), but enhanced CO<sub>2</sub> selectivity at elevated temperature (140–200°C). Noble and Falconer<sup>69</sup> have likewise demonstrated that their SAPO-4 zeolite membranes can be used to separate CO<sub>2</sub> from CH<sub>4</sub> under a variety of pressures and temperatures, with high selectivities at 30 atm and 50°C.

### Carbon-Based Membranes

In her article, Pietraß discusses the use of carbon membranes and carbon nanotubes (CNTs) as hydrogen separation devices. Carbon membranes have been prepared as unsupported or supported materials. Typical precursors are organic polymers that are converted to pure carbon materials by treatment at high temperature in an inert atmosphere (carbonization). Among the unsupported membranes, capillary tubes or hollow fibers and flat membranes have been fabricated to date.

Selective surface flow (SSF<sup>TM</sup>) membranes were introduced in 1993 by Rao and Sircar.<sup>70</sup> These porous carbon membranes are formed by cross-linking and subsequent carbonization of poly(vinylidene chloride)-acrylate terpolymer latex polymer. The permeability of hydrogen in a mixture with hydrocarbons was reduced by several orders of magnitude over that of pure hydrogen, indicating that hydrocarbon-selective adsorption hindered the pore diffusion of hydrogen, thus making these membranes extremely promising for hydrogen separation. The advantages of these membranes are multi-fold. Since adsorption occurs on the high-pressure side, the partial pressure of the component to be adsorbed can be low, and the partial pressure gradient across the membrane does not need to be high to achieve satisfactory separation. The driving force for mass transfer across the membrane is the difference in the concentration of the adsorbed species.

In addition, carbon nanotubes are being investigated for possible use in hydrogen separation. The unique porous structure of an array of CNTs that can be millimeters long at diameters of molecular dimensions has prompted studies to investigate transport through these tubes. The

smoothness of the interior in defect-free nanotubes gives rise to greater transport capacity than conventional carbon-based membranes. Hydrogen separations are expected to be effective for very small nanotube diameters.

### Conclusions

Worldwide, various membranes composed of diverse materials have been and continue to be studied and optimized for the robust and economically efficient large-scale production of H<sub>2</sub>. Each type of membrane possesses strengths and current weaknesses.<sup>8</sup> However, strides are being continually reported to improve each membrane type to eventually meet the H<sub>2</sub> energy goals established by the U.S. Department of Energy and its global counterparts.

While polymeric membranes have come a long way over the past decade, it is obvious that more work is required to create competitive technologies that will help reduce production costs for a sustainable hydrogen economy. In the short term, polymeric membranes must be further developed for either H<sub>2</sub>- or CO<sub>2</sub>-selective applications. Ideally, H<sub>2</sub>-selective membranes should exhibit H<sub>2</sub>/CO<sub>2</sub> selectivities that exceed 15–20 at 200°C, which is the current range for commercial membranes, whereas CO<sub>2</sub>-selective membranes (which could likewise benefit air revitalization technologies) should target CO<sub>2</sub>/H<sub>2</sub> selectivities that are double the current commercial membranes. Greater stability and improved performance at elevated temperatures (e.g., at syngas conditions of 200°C) would significantly benefit the involvement of polymer membranes in commercial H<sub>2</sub> activities. Long-term research strategies should be examined for mixed-matrix membranes and the development of organic-inorganic hybrid materials that could yield unexpected, but highly desirable, properties.<sup>71</sup> Polymeric membranes possess a great deal of potential, provided novel concepts are conceived to meet both short-term and long-term hydrogen separation goals.

Inorganic membranes hold the potential for full and near-term industrial implementation due to their tunable nature and high-temperature/high-pressure stability. However, a few materials-related hurdles remain. Concerns associated with these materials include increasing the selectivity and flux for metal membranes as well as reproducibility in porous membranes. Compared with organic membranes, inorganic membranes are currently expensive to manufacture. Introduction into large-scale production facilities is, however, anticipated to result in more competitive costs approaching \$1100 USD/m<sup>2</sup>.

The marriage of H<sub>2</sub>-selective membranes with advances in materials-related nanotechnology, including nanotube synthesis and designer nanoporosity, holds tremendous promise for the development of stable inorganic membranes capable of achieving the gas separation goals necessary to ultimately realize a hydrogen economy.

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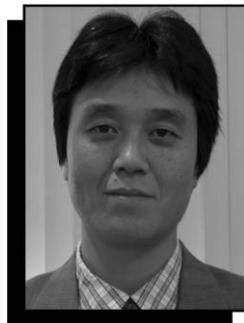


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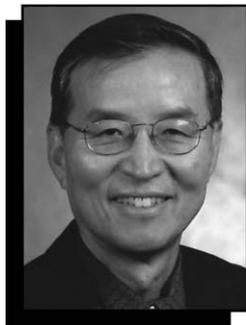
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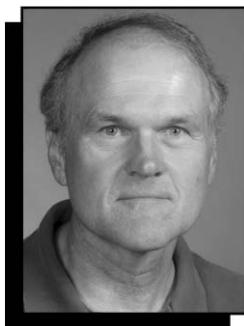
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**David S. Sholl**

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