palladium, ruggedness to high differential pressure, and chemical stability.

Catalysts Screening in Full Steam Plus Water-Gas Shift Mixture. Catalysts for adsorption and dissociation of molecular hydrogen were tested at ambient pressures in a reaction mixture containing mole fraction compositions of 43.5% steam, 37.3% hydrogen, 16.5% CO_2, 2.2% CO, 525 ppmv H_2S, and balance of N_2 at reactor pressures.

I. INTRODUCTION

A. Review of Program Goals

The overall goal of this Phase I project was to develop and test advanced membranes for separation of hydrogen from complex mixtures of gases. Figure 2 shows schematically one concept envisioned by the CO_2 Capture Project which will require advanced hydrogen separation membranes for successful operation. In this technology, carbon-based fuels are partially oxidized and steam reformed at high temperature into a mixture of syngas, which contains predominantly hydrogen and CO. The carbon monoxide in the syngas is further reacted with steam over a water-gas shift catalyst at temperatures typically between 340 to 440°C (613-713 K) to produce additional hydrogen by the water-gas shift reaction: $CO + H_2O$• • $H_2 + CO_2$. By removing hydrogen through a membrane, the water-gas shift reaction can be driven to near completion at 340 to 440°C without the need for an additional low-temperature water-gas shift catalyst, which typically operates near 200°C (473 K).

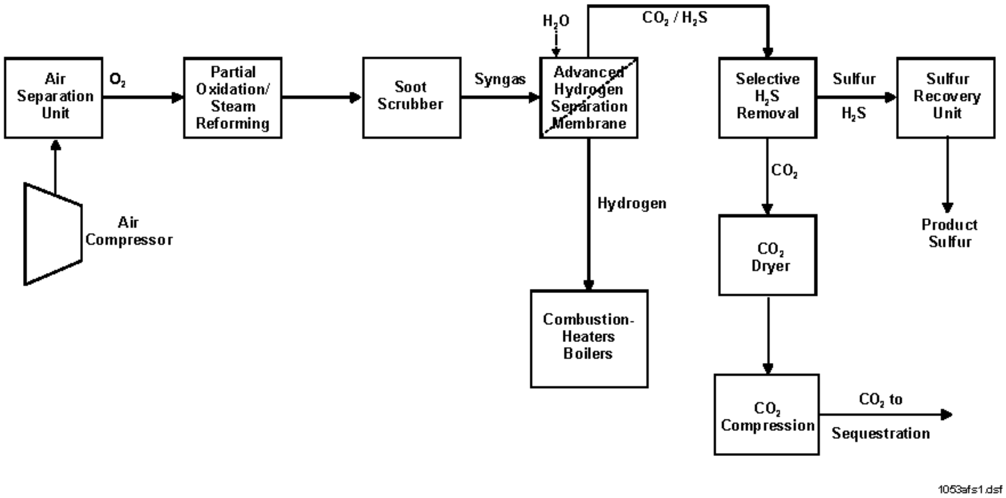


Figure 2. Conceptual CO_2 separation and capture scheme for the Membrane Shift Reactor.

The hydrogen extracted through the membrane can be used as a clean fuel to run turbine engines in integrated gasification combined cycle electric power plants. The retentate containing predominantly CO_2 mixed with H_2S contaminants could be sequestered by the various visions of the CO_2 Capture Project. Successful hydrogen separation membranes would have many potential commercial applications beyond the CO_2 Capture Project and might find use in the chemical and petroleum refining industries or wherever hydrogen extraction or purification of hydrogen are required.

Table 1 lists the original Phase I project targets as outlined by Jan G. J. B. Assink of Shell Global Solutions at the initiation of the Phase I project. For Phase II, the desired pressures are 35 bar absolute on the water-gas shift side (retentate side) of the membrane and 2 bar absolute on the sweep gas side (hydrogen permeate side) of the membrane. Although, in principle, high pressure does not affect the equilibrium of the water-gas shift reaction, because of the equal number of moles of gaseous reactants and products on both sides of the equation, the normal operating pressure of water-gas shift reactors is 35 bar (see, for example, Twigg, 1997). Furthermore, maintenance of high pressure on the retentate side of the membrane is desirable for compression and subsequent sequestration of CO_2.

Table 1.
Phase I Project Goals

Targets	
CO_2 purity	>90%
CO_2 recovery	>90%
H_2 purity	>97%
H_2 recovery	>95%
H_2/CO_2 selectivity	>100
$P_{retentate}$ // $P_{permeate}$	30 bar // 5 bar
pH_2O	15 bar
pH_2S	0.03 bar (1000 ppm)
pCO	7.5 bar

Adapted from (Jan) G. J. B. Assink.

Table 2 lists the target concentrations of steam and the components of the water-gas shift mixture used to test the membranes in the Phase I project. Table 2 also lists the dry mole percent composition of the water-gas shift mixture, which was purchased as a pre-mixed specialty gas in high-pressure gas cylinders from AirGas Corporation. The dry gas was mixed with steam to produce the specified wet gas mixture. Note the high concentration of H_2S of 928 ppmv (part per million by volume) in the dry test mixture. The other minor components of commercial water-gas shift mixtures such as ammonia (NH_3), carbonyl sulfide (COS), hydrogen cyanide (HCN), methane (CH_4), argon (Ar), various hydrocarbons (C_xH_y) and other organic compounds were to be neglected in the Phase I tests. Tests were to be run at pressures of 5, 10 and 15 barg (bar gauge) on the retentate side of the membrane and 0 barg (ambient pressure) on the permeate side of the membrane. Differential pressures across the membranes were thus 5, 10 and 15 bar absolute. Target test temperatures were 250°C, 350°C and 450°C (523 K, 623 K and 723 K). To demonstrate stability of membrane materials, tests were to be run for a minimum of six days.

Table 2.
Specified Mole % Compositions in Water-Gas Shift Mixture

Component	Mole % Wet	Mole % Dry
H_2	37.7	66.7
N_2	0.1	0.18
CO	2.2	3.9
CO_2	16.5	29.2
H_2S	525 ppmv	928 ppmv
H_2O	43.5	--
Total	100%	100%

B. Review of Water-Gas Shift Chemistry

Overview. In principle, all carbon-based fuels including petroleum, natural gas, coal, biomass, and even municipal waste, can be partially oxidized and steam reformed into a mixture of H_2 and CO known as synthesis gas (syngas). For temperatures above about 950°C (1223 K), and for properly adjusted ratios of C : H : O in the reaction mixture, chemical equilibrium can be controlled to overwhelmingly favor production of CO and H_2 over other products such as H_2O and CO_2. If hydrogen is the desired product, the carbon monoxide is reacted with steam at lower temperatures between about 340 to 440°C by the water-gas shift reaction: $CO + H_2O(g)$ • • $H_2 + CO_2$ (see, for example, Twigg, 1997). Extraction of hydrogen through membranes will theoretically shift the equilibrium of the water-gas shift reaction to favor nearly complete reaction of CO. To function, membranes must be designed to be compatible with the very harsh chemical environment of commercial water-gas shift reactors.

Heat Released by the Exothermic Water-Gas Shift Reaction. According to Twigg (Twigg, 1997) of the Catalytic Systems Division of Johnson Matthey and formerly of the Catalysis Centre at Imperial Chemical Industries, the water-gas shift reaction is exothermic with $\Delta H = -41.1\ kJ{\bullet}mol^{-1}$ (at standard thermodynamic conditions). This heat produced by the negative enthalpy of reaction implies that lower temperatures favor conversion of carbon monoxide and steam into carbon dioxide and hydrogen. However, lower temperatures disfavor the kinetics of the reaction. In industrial practice, a compromise is achieved by using a combination of catalysts at both high and low temperatures. The high temperature catalysts convert the bulk of the CO to CO_2 and bring the reaction mixture to equilibrium. However, a few percent of unreacted CO remains in the mixture in the high-temperature equilibrium. To shift the equilibrium in order to favor reaction of the residual CO, the temperature of the reaction mixture is then lowered. In principle, a shift of equilibrium to favor nearly complete conversion of CO also can be obtained by extracting hydrogen through a membrane. A membrane would allow the elimination of the low-temperature water-gas shift catalysts, which are highly susceptible to poisoning by sulfur, and which require removal of sulfur for successful operation. A membrane would also allow complete conversion of CO at the higher temperature and would eliminate the need for heat exchangers for cooling of the reaction mixture.

Water-Gas Shift Temperatures. According to Twigg, the usual inlet temperature for high-temperature shift reactors using fresh high-temperature catalysts of Fe_3O_4/Cr_2O_3 is in the range between 340•C to 360°C (613 K to 633 K). The exothermic heat of reaction increases the catalyst bed and gas exit temperature to about 425°C (698 K). As catalysts age they lose activity, and it usually becomes necessary to increase gas inlet temperature to approximately 400°C (673 K). This results in an exit temperature of about 440°C (713 K). Thus, membrane materials should be designed to withstand a temperature of at least 440°C.

Sulfur Tolerance. The high-temperature water-gas shift catalysts are remarkably robust, having usual lifetimes of 3 to 5 years, although, according to Twigg, there are examples of lifetimes up to 10 years. The high-temperature water-gas shift catalysts use inexpensive magnetite (Fe_3O_4) stabilized by Cr_2O_3, and have been an industry standard since 1912. In addition, the high-temperature water-gas shift catalysts are remarkably tolerant towards high levels of sulfur, such as are present, for example, when coal is gasified. Magnetite reacts with H_2S, to form FeS. The sulfided iron, however, continues to catalyze the water-gas shift reaction, although its activity is reduced to about half that of catalysts containing iron as magnetite. According to Twigg, simply doubling the volume of the catalyst in the catalyst bed compensates for the loss of half of the catalyst activity by sulfur poisoning.

Low-Temperature Catalysts. Due to thermodynamic limitations, the high-temperature water-gas shift conditions allow reduction of concentrations of CO to only about 2 to 4 mol %. Further conversion of CO is accomplished using low-temperature water-gas shift catalysts ($Cu/ZnO/Al_2O_3$), which are typically run at 200°C (limited in practice by the dew point (Twigg,1997)). The copper catalysts reduce the concentration of CO to 0.1 to 0.3 mol %. Although ZnO protects copper to some extent from low levels of sulfur poisoning by formation of ZnS, the low-temperature copper-based water-gas shift catalysts are highly susceptible to poisoning by sulfur. It is unlikely that standard low-temperature water-gas shift catalysts will function at sulfur levels of 525 ppmv (wet) as desired in the Phase I program. However, sulfur tolerant low-temperature water-gas shift catalysts, based on $CoMo/Al_2O_3$, for example, are being developed and are reported in the literature (Lund, 1996; Park, Kim and Lee, 2000).

Advantages of Catalytic Membrane Reactors. Catalytic membrane reactors offer an alternative to the sulfur sensitive low-temperature water-gas shift catalysts for overcoming thermodynamic limitations for CO conversion at high temperatures. From the balanced equation for the water-gas shift reaction, $CO + H_2O(g) \bullet \bullet H_2 + CO_2$, it is evident that removal of hydrogen from the reaction mixture will shift the equilibrium to favor production of CO_2 and to reduce concentrations of CO. Many published works reaffirm both the theoretical and technical feasibility of using catalytic membrane reactor technology in the water-gas shift reaction (see, for example, Criscuoli, Basile and Drioli, 1997, 2000; Criscuoli, Basile, Drioli and Loiacono, 2001; Basile, Criscuoli, Santella and Drioli, 1996; Damle and Dorchak, 1998; and Enick, et al., 2000). Successful membranes would completely eliminate the need for the low-temperature water-gas shift catalysts.

C. Membrane Technical Issues

All membranes and reactor materials must be designed to survive the hostile environment of the water-gas shift reaction. The following lists some of the main technical considerations.

- **Stability Towards High Pressure Steam.** High pressure steam is known to hydrothermally dissolve and deposit many materials, most notably quartz (SiO_2), calcite ($CaCO_3$), siderite ($FeCO_3$), pyrite (FeS), molybdenite (MoS_2), woframite (Fe, Mn)WO_4 and various zeolites and other aluminosilicates. Even metallic gold can be dissolved and re-deposited under fairly mild hydrothermal conditions (200°C). Deposition or redistribution of hydrothermally transported materials can clog and foul porous membranes or poison catalysts. Thus all materials considered for use in the catalytic membrane reactors must be resistant to hydrothermal dissolution, transport and re-deposition.

- **Thermal Stability to at least 440°C (713 K).** The exothermic heat released by the water-gas shift reaction is known to increase the exit gas temperature to about 425°C (698 K) for fresh catalysts and to about 440°C (713 K) for aged catalysts (see Twigg, 1997, p. 303). Thus membranes must be designed to be stable to at least 440°C. An additional margin of safety in the event of temperature excursions would be desirable.

- **Stability Towards Formation of Carbonates by Reaction with CO_2.** If the hydrogen is successfully removed through the membrane, the retentate will contain a high pressure mixture of predominantly CO_2 and steam. This environment will favor formation of carbonates such as $FeCO_3$ (see Lund, 1996), $CaCO_3$, $MgCO_3$, $MnCO_3$, $CuCO_3 \bullet Cu(OH)_2$ (malachite), $NiCO_3$, and $ZnCO_3$. Membrane and catalyst design must take into account possible reaction with CO_2.

- **Resistance to Poisoning by CO.** Carbon monoxide is a well known poison for hydrogen dissociation catalysts such as Pd used on dense hydrogen transport membranes (see Amandusson, Ekedahl and Dannetun, 2000; Amandusson, 2000). Catalysts such as Pd must be supplemented by catalysts which more weakly adsorb CO. Some metals are transported as carbonyls and are deposited in undesired locations in the reactor. For example, volatile metal carbonyls such as $Ni(CO)_4$ and $Fe(CO)_5$ can form by reaction of metals with CO.

- **Resistance to Poisoning by H_2S.** H_2S reacts with many transition metals to form sulfides. For example, hydrogen dissociation catalysts such as Pd and Ni react with H_2S to form PdS, and NiS which are thermally stable to 950°C (1223 K) and 797°C (m.p.), respectively. Dense membranes must be designed using catalysts which either do not form stable sulfides at reaction conditions, or which form sulfides possessing catalytic activity for hydrogen adsorption and dissociation (such as sulfides of cobalt, molybdenum and tungsten). Sulfur can also segregate to grain boundaries of many structural steels and other materials, causing embrittlement.

- **Resistance to Nitride Formation by Reaction with NH_3.** Many transition metals react with ammonia, cyanide or other fixed compounds of nitrogen and form brittle nitrides. Metals forming nitrides must be coated and protected from nitrogen compounds which may be present in small amounts in the water-gas shift mixture.

- **Mechanical Stability to 35 Bar Absolute and 33 Bar Differential Pressure.** Commercial high-temperature water-gas shift catalysts are typically run at 35 bar absolute pressure. Membranes must be designed to withstand 35 bar on the syngas side of the membrane. If 2 bar absolute pressure is assumed on the sweep gas side, the membrane must be designed to withstand a minimum differential pressure of 33 bar.

- **Resistance of Membranes and Seals to Leaks.** With 33 bar differential pressure, even small pinholes or cracks in membranes and seals will adversely affect membrane selectivity. Catastrophic failure of membranes or seals may occur if materials are embrittled or fail to withstand the differential pressure.

- **Adequate Flux and Selectivity.** Membranes designed to meet the above criteria must be able to extract quantities of hydrogen necessary to meet the goals stated in Table 1, while blocking diffusion of other components in the water-gas shift mixture.

D. Fundamentals of Dense Hydrogen Transport Membranes

Reasons for Choosing Dense over Porous Membranes. Eltron Research Inc. opted to develop dense hydrogen transport membranes rather than porous membranes for a number of reasons. First, there were concerns on whether or not a porous membrane could be made sufficiently defect free to retain the desired pressure differential of up to 33 bar without leaks resulting in a significant pressure drop. Second, there were concerns that the target selectivity could not be achieved if even a small fraction of the pores were too large or if pinholes or defects allowed leaks and Poisseuille flow of all components from the syngas to sweep gas side of the membrane. Finally, there were concerns that because of the high surface area and surface free energy of the porous membranes, that there would be a significant thermodynamic driving force for hydrothermal transport of silica accompanied by plugging of the micro-pores by surface diffusion of silica.

Hydrogen Dissociation Catalyst Required on Hydrogen Source Side. Figure 3 shows schematically the main concepts of dense hydrogen transport membranes. Regardless of whether the dense membrane be a pure metal, a metal alloy, a ceramic, or a metal-ceramic composite, hydrogen molecules must first be adsorbed and dissociated on the surface of the membrane facing the hydrogen source. Many noble metals including Pd, Pt, Ir, and Rh, transition metals such as Ni, Fe, and Co, and metal oxides and some sulfides have inherent catalytic activity for adsorption and dissociation of hydrogen.

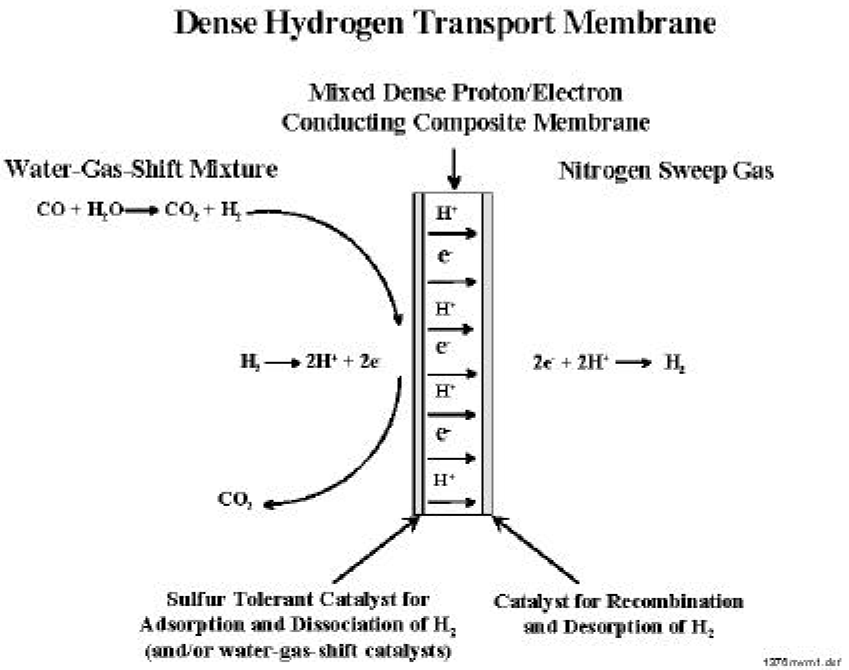


Figure 3. Schematic of a dense membrane for separation of hydrogen from a sulfur contaminated water-gas shift mixture.

Hydrogen Recombination Catalyst Required on Sweep Gas Side. On the sweep gas side of the membrane, the dissociated hydrogen which has diffused through the membrane, must be recombined to form hydrogen molecules, which can then desorb from the surface of the membrane into the sweep gas. From the laws of microscopic reversibility, a catalyst which can dissociate hydrogen molecules will also recombine the hydrogen atoms into hydrogen molecules. Thus, the same catalyst can, in principle, be applied to both sides of the membrane, although in practice, the catalysts will be optimized for the differing environments on the hydrogen source and sink sides of the membrane.

Catalyst Poisoning Considered. In order for hydrogen molecules to adsorb and dissociate on a catalyst surface on the water-gas shift side of the membrane, two adjacent unoccupied surface sites are necessary. If a large fraction of surface sites are occupied by molecules of CO, sulfur, etc., hydrogen cannot adsorb and dissociate, and the catalyst is poisoned. The catalyst on the sweep side of the membrane must also have adjacent, unoccupied surface sites to allow recombination of hydrogen atoms into molecules. To avoid poisoning by components in the water-gas shift mixture, catalysts must be selected or designed which preferentially adsorb and bind hydrogen, and weakly adsorb and bind CO, CO_2, sulfur, etc.

Review of Laws of Diffusion. Hydrogen is transported through dense membranes in a dissociated form and not as molecules. Possible dissociated forms of hydrogen include protons (H^+), neutral hydrogen atoms, hydride ions (H^-), and proton-electron pairs. Diffusion of hydrogen through the dense membranes occurs by completely random atomic motion. For a given atom of hydrogen, it is equally probable, at the atomic level, that the atom will diffuse from the hydrogen source side to the sweep side or visa versa. It is the concentration gradient between the hydrogen source and sweep sides which drives net hydrogen diffusion towards the sweep gas side of the membrane—simply because there is more hydrogen on the source side than the sweep side. For example, if the concentration gradient is composed of a partial pressure of hydrogen on the water-gas shift side of the membrane which is ten times that of the partial pressure of hydrogen in the nitrogen sweep gas, then it is ten times more probable that hydrogen will diffuse from the source to the sink side than visa versa. The greater the concentration gradient between the hydrogen source and sink sides, the greater will be the net hydrogen diffusion across the membrane.

Diffusion behavior is summarized mathematically by Fick's First Law of Diffusion:

$$J = -Ddc/dx$$

where J is the flux of hydrogen across the membrane in $mol \cdot m^{-2} \cdot s^{-1}$
dc is the concentration gradient of molecular hydrogen across the membrane in $mol \cdot m^{-3}$
dx is the membrane thickness in m
and D is the diffusivity, in $m^2 \cdot s^{-1}$, which is an intrinsic property of each solid material.

The negative sign implies that net flux is in the direction towards the lower concentration. The concentration gradient, dc, equals $c_f - c_p$, where c_f is the concentration of molecular hydrogen in the gas phase on the feed or retentate (water-gas shift) side of the membrane in $mol \cdot m^{-3}$, and c_p is the concentration of molecular hydrogen in $mol \cdot m^{-3}$ in the gas phase on the permeate (nitrogen sweep) side of the membrane.

From Fick's First Law it is evident that the hydrogen flux, J, will be increased by maximizing the hydrogen concentration gradient, dc, across the membrane by maximizing hydrogen concentration, c_f, on the hydrogen source side of the membrane and minimizing the hydrogen concentration, c_p, on the hydrogen sink side of the membrane by rapid flow of sweep gas. Hydrogen flux will also be increased by minimizing the membrane thickness, dx, (Note that hydrogen flux is inversely proportional to membrane thickness.) and by choosing membrane materials which inherently possess the highest diffusivity, D, for hydrogen. The diffusivity, D, is a function of temperature and is related to the velocities and jump distances which atoms achieve in the materials.

Relation of Sievert's Law to Fick's First Law of Diffusion. The actual concentration of hydrogen on the surfaces of a dense membrane can be different from the concentration of hydrogen in the gas phase. The actual driving force for diffusion across the membrane will be the concentration gradient within the membrane. The maximum concentration of hydrogen in the dense membrane will be on the surface of the membrane facing the hydrogen source, and the minimum will be on the surface facing the hydrogen sink.

One approximation for the concentration of hydrogen on the surfaces can be given by Langmuir's Isotherm. Assuming dissociative adsorption of hydrogen on the surface to occur, two surface sites are required to accommodate two hydrogen atoms. Adsorption of hydrogen can be represented by the equation:

H_2 + 2 (adsorption sites) • •2 H(adsorbed).

The rate of hydrogen adsorption will be proportional to the partial pressure of hydrogen in the gas phase and the square of the number of empty adsorption sites on the membrane surface, and can be written thus:

$$\text{rate(adsorption)} = k_1 p_{H2}(1-\theta)^2$$

where k_1 is the rate constant for adsorption, p_{H2} is the partial pressure of H_2 in the gas phase above the membrane and θ is the fraction of the surface covered by hydrogen. The term $(1-\theta)$ is the fraction of the surface uncovered by hydrogen. The rate of desorption from the surface is given by:

$$\text{rate(desorption)} = k_{-1}\theta^2,$$

where k_{-1} is the rate constant for desorption of hydrogen.

At equilibrium, the two rates are equal and thus:

$$k_1 p_{H2}(1-\theta)^2 = k_{-1}\theta^2.$$

Solving for θ, the surface coverage, gives:

$$\theta = (k_1/k_{-1})^{1/2} p_{H2}{}^{1/2}/(1 + (k_1/k_{-1})^{1/2} p_{H2}{}^{1/2}).$$

If the pressure is low and 1 » $(k_1/k_{-1})^{1/2} p_{H2}{}^{1/2}$, then $\theta = (k_1/k_{-1})^{1/2} p_{H2}{}^{1/2}$.

It is thus seen that the coverage of hydrogen on the membrane surface will be proportional to the square root of the hydrogen pressure. From this, one can see the origin of the square root dependence on flux according to Sievert's Law:

$$J = P_e^{*} \cdot l^{-1}(p_f^{0.5} - p_p^{0.5})$$

where P_e^{*} is the permeability in $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$, l is the membrane thickness in m, and p_f and p_p are the partial pressures of hydrogen in Pa on the feed and permeate side of the membrane.

However, if the pressure is high, $1 \ll (k_1/k_{-1})^{1/2} p_{H2}^{1/2}$ and $\theta = 1$. The surface will become saturated with hydrogen at some pressure, and the flux will no longer be a function of pressure, but will remain a constant. Thus at very high partial pressure of hydrogen the equation for hydrogen flux may become J = constant.

The Langmuir Adsorption Isotherm assumes that all surface sites are identical and that the heat of adsorption does not change with coverage. In practice, the surface of the membranes will be heterogeneous and heats of adsorption will vary with hydrogen coverage. The pressure dependence may then be a function of pressure to some power other than 0.5 ($p^{1/n}$) or the pressure dependence may be logarithmic. These alternatives would be valid only for the lower pressure range. At pressures above saturation, the hydrogen flux would again be constant, and independent of pressure.

Fick's First Law of Diffusion can be converted into Sievert's Law by writing:

$$J = - P_e^{*} \cdot l^{-1}(p_f^{0.5} - p_p^{0.5})$$

where J is the flux of hydrogen across the membrane in $mol \cdot m^{-2} \cdot s^{-1}$
l is the membrane thickness in m
P_e^{*} is the permeability in $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$
p_f is the partial pressure of molecular hydrogen on the feed, f, side in Pa
and p_p is the partial pressure of molecular hydrogen on the permeate, p, side in Pa

The permeability, P_e^{*}, (in $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$) is related to the diffusivity, D, (in $m^2 \cdot s^{-1}$) by the equation: $P_e^{*} = D \cdot S$, where S is the solubility of hydrogen in the membrane material in $mol \cdot m^{-3} \cdot Pa^{-0.5}$ (see, for example, Paglieri and Way, 2002). As in the case of diffusivity, the permeability is also a function of temperature and is an inherent property of each material. Because the hydrogen flux through a membrane is directly proportional to the permeability of the material, it is highly desirable to chose membrane materials with the highest permeabilities for hydrogen.

E. Cermet and Supported Thin Film Strategies

Cermets. Cermets (ceramic-metals) are made by sintering together fine powders of both ceramic and metal to form dense continuous matrices of both ceramic and metal. Figure 4 shows a cross section of a dense cermet fabricated at Eltron Research Inc. for the early Phase I tests. The coefficients of thermal expansion were sufficiently well matched to allow fabrication and testing without formation of cracks formed by thermal stress.

Cermets have a great advantage over metal foils in that, like ceramics, they can be extruded as tubes. In the Phase I research, flat disks were used in the tests. The composite ceramic-metal membranes eliminate the hydrogen embrittlement problem encountered using pure metal films.

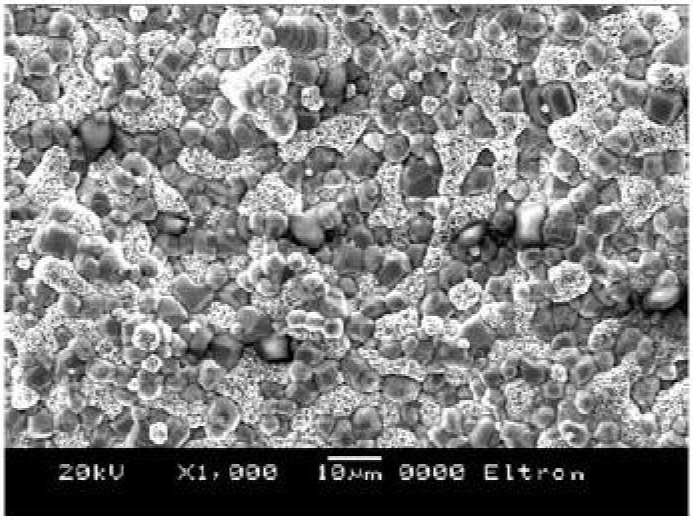


Figure 4. **Cermets (ceramic-metals) are made by sintering together ceramic and metal powder to form dense continuous matrices of both metal and ceramic. Both metals and ceramic are chosen for high proton transport. Metal and ceramic are lattice matched to minimize strain and dislocations. A cross section of the membrane is shown.**

Supported Thin Film Strategies. Because hydrogen flux is inversely proportional to the thickness of the membrane, it is desirable to make the dense membranes as thin as possible. Because thin films (of the order of microns) cannot withstand differential pressures of 33 bar, the strategy is to support the thin dense film atop a thick porous ceramic support. The thick porous support is designed to withstand the required differential pressures while not significantly reducing the flux of molecular hydrogen.

Figure 5 is a Scanning Electron Microscope (SEM) image of a fine porous membrane layer sintered onto a substrate of the same material but with larger pore and particle size. The coarser porous substrate is made with thickness of the order of millimeters to withstand the desired differential pressure. Pores in the substrate are 1-2 or more microns in diameter to allow rapid diffusion of molecular hydrogen in the gas phase. The fine porous layer, which is less than 8 microns in thickness, has pores and ceramic particles which are both sub-micron in size. The fine porous layer acts as a support for a dense membrane layer. *Alternatively, the fine porous layer can be replaced with a thin layer of cermet, which forms a dense membrane.*

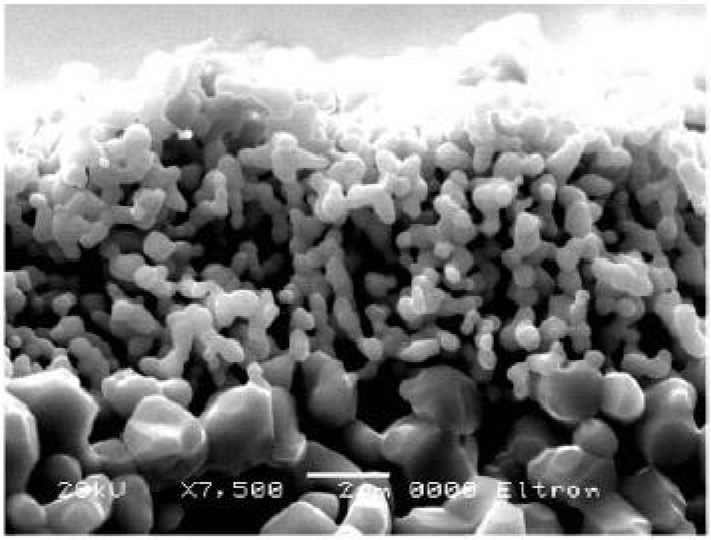
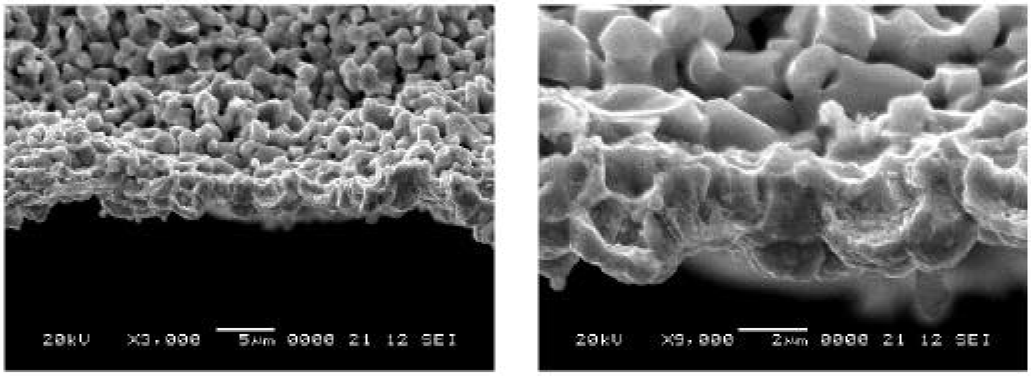


Figure 5. **Image shows a fine porous layer of ceramic sintered atop a ceramic substrate of larger pore size and particle size. The substrate with larger pore size allows more rapid diffusion of hydrogen and is designed with a thickness to withstand large differential pressures. The fine porous layer acts as a substrate for metals used in the dense composite. Note the 2 micron bar scale showing that pores and particles in the top layer are sub-micron in size.**

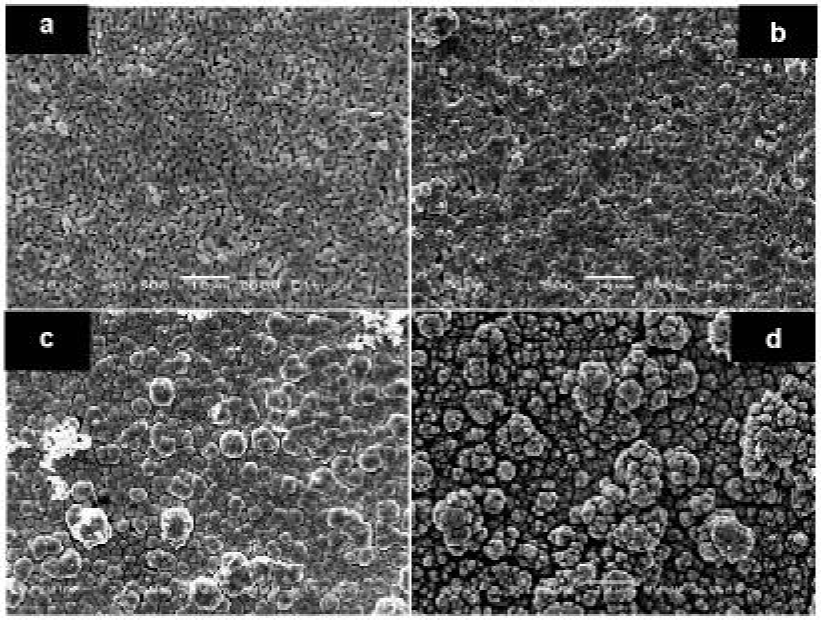
Figure 6 shows SEM images at two magnifications, of a cross section of a 3 micron thick metal film deposited atop a ceramic support. As in the case of the cermets, the ceramic substrate and metal layer are lattice matched to minimize interfacial stress, dislocations and cracks. Lattice matching also aids nucleation and growth of the metal atop the ceramic substrate.

Figure 7 shows top views of metal deposition atop a ceramic substrate. Figure 7a shows the uncovered ceramic substrate before deposition of the metal. Figure 7b shows the surface after the initial nucleation of a few islands of metal. Figure 7c shows completion of a dense metal layer. Figure 7d shows three-dimensional growth of the metal layer after completion of the continuous film.



Cross Section of Metal Layer Electrolessly Deposited Atop a Porous Ceramic

Figure 6. **Scanning electron microscope images at two magnifications of a three micron thick metal layer deposited atop a fine porous layer of ceramic. Metal and ceramic are lattice matched to minimize strain and dislocations and to aid nucleation and growth of the metal on the ceramic. Metal layer is at bottom of images.**



Electroless Deposition of Metal Atop a Ceramic Support

Figure 7. **a) Ceramic surface before metal deposition. b) Nucleation of a few metal islands. c) A continuous palladium film atop the ceramic. d) Additional deposition of metal producing a three-dimensional growth morphology which increases surface area and enhances hydrogen adsorption.**

F. Strategies for Sulfur Tolerant Catalysts

The large quantities of H_2S in the water-gas shift mixture, as indicated in Tables 1 and 2, imply that sulfur tolerant hydrogen dissociation catalysts must be applied to the water-gas shift side of the dense membrane. Because palladium sulfide is thermally stable to 950°C (1223 K), palladium membranes are expected to be poisoned when exposed to the water-gas shift mixture at temperatures below 440°C. Alternatives to palladium are platinum and iridium, which have sulfides which thermally decompose at 300°C and 250°C, respectively. The platinum and iridium catalysts may escape poisoning by sulfur if the membranes are operated above their respective sulfide decomposition temperatures and if the equilibrium concentration of sulfides on their surfaces remains low. CoS/MoS_2, a well known hydrodesulfurization catalyst, and sulfided molybdenum have also been considered in the literature. For example, Lund (1996) and Park, Kim and Lee (2000) have demonstrated that these catalysts operate as sulfur resistant catalysts for the water-gas shift reaction. The known sulfur tolerant high-temperature water-gas shift catalyst, Fe_3O_4/Cr_2O_3, and its cobalt analog, Co_3O_4/Cr_2O_3, were also considered as sulfur tolerant hydrogen dissociation catalysts in the Phase I project.

Hydrogen dissociation catalysts on the water-gas shift side of the membrane must also be tolerant towards poisoning by carbon monoxide. Table 3, adapted from the work of Benzinger (1991), compares desorption energies for CO for selected metals. Metals with high desorption energies for CO are most likely to be poisoned by CO. From Table 3, metals such as Ag, Cu and Co would offer the best resistance to poisoning by CO. However, metals such as Ag, Ni and Pd will react with H_2S in the gas mixture and form sulfides. Copper, cobalt and platinum offer the best compromise between sulfur and CO poisoning resistance.

Table 3.
Desorption Energies of Carbon Monoxide (kJ/mol)

Metal	Crystal Face	ΔH_{ad}
Ag	(111)	25
Cu	(100)	70
Co	(0001)	105
Ni	(100)	109
Ni	(111)	109
Pt	(111)	126
Pt	(100)	134
Pd	(111)	142
Pd	(100)	151

Table 4.
Hydrogen Desorption Energies (kJ/mol)

Metal	Crystal Face	D(M-H)
Ag	(111)	218
Pt	(100)	247
Pt	(111)	247
Co	(0001)	251
Co	(1010)	251
Cu	(111)	251
Ni	(110)	259
Ni	(100)	263
Ni	(111)	264
Pd	(111)	259
Pd	(100)	268
Pd	(110)	268

Materials Facing Hydrogen Sink Side of Membrane. On the hydrogen sink side of the membrane it is desirable to have materials with the lowest possible desorption energies for hydrogen. Table 4, adapted from Benzinger (1991), lists hydrogen desorption energies for some selected materials. Other common metals such as Fe, W, Mo, Nb, and Ru have hydrogen desorption energies ranging from 276 to 293 kJ•mol^{-1}. From Table 4 it is evident that silver would be the best material (assuming that sulfur does not reach the silver from the water-gas shift side of the membrane). The second best material would be platinum, which might resist sulfur for temperatures above 300°C.

II. EXPERIMENTAL PROCEDURES AND APPARATUS

A. Membrane Testing at Ambient Pressure

Construction of Six Reactor Stations for Ambient Pressure Tests. Figure 8 shows the six reactor stations which were built for testing the membranes at ambient pressures. Because of safety concerns over toxic levels of hydrogen sulfide, carbon monoxide and carbonyl sulfide, special safety precautions were necessary, and four reactor systems were designed and built with stainless steel gas handling systems rated for hydrogen sulfide and with special ventilation

Figure 8. Six new reactor stations built for testing membranes at ambient pressure. On the left are two stations designed to measure hydrogen flux under ideal conditions in the absence of catalyst poisons using purified mixtures of hydrogen and helium in the feed stream. On the right are four reactors which were used for testing membranes in the presence of the sulfur contaminated water-gas shift mixture and steam at ambient pressure. These four systems were designed to contain and vent H_2S, COS, and CO in the event of leaks. In the center are two gas chromatography instruments used for measuring hydrogen concentration on the permeate side of the membranes.

systems for confining and removing the gases in the event of a leak. Two reactors were also built to handle high purity hydrogen and helium gas mixtures only in order to avoid contamination of membranes by sulfur and other catalyst poisons. These two reactors were used to test membranes under ideal conditions of pure hydrogen and to measure the maximum possible hydrogen flux through the membranes. These reactors were also used to check membranes and seals for leaks.

Most of the high cost components, such as the reactor ovens, oven controls, power supplies, thermocouple controls, bubble meters, gas handling equipment, carbon monoxide detectors, gas chromatography apparatus, computers and software, were already on hand at Eltron Research, and were simply incorporated into the new apparatus without purchase cost to the project.

Apparatus for Measuring Hydrogen Flux in the Absence of Sulfur. Figure 9 shows a close-up view of the two reactors used for measuring hydrogen flux under ideal conditions using only hydrogen and helium in the feed stream and argon in the sweep stream. The purpose of these reactors is to measure the maximum hydrogen flux possible from the membranes in the absence of the complicating effects of H_2S, steam, CO, CO_2 and other components of the water-gas shift mixture, which may poison or degrade the membrane catalysts. Once hydrogen flux values were measured under ideal conditions, flux values were measured under the water-gas

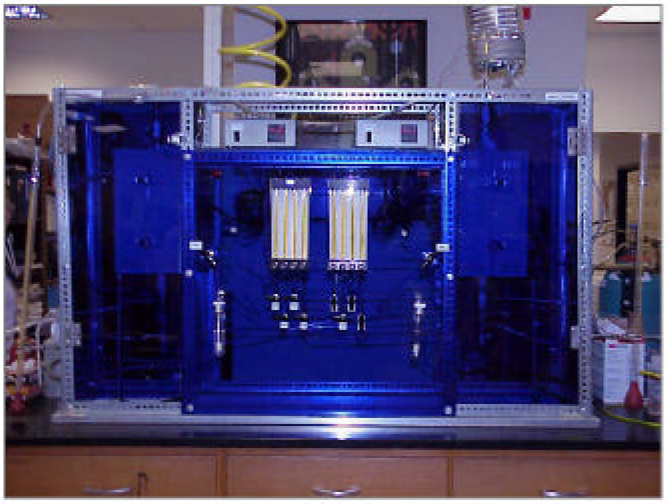


Figure 9. Two reactor stations constructed for measuring hydrogen flux through membranes under ideal conditions using purified hydrogen plus helium mixtures. A hydrogen/helium mixture was streamed past one side of the membrane and pure argon carrier gas was streamed past the opposite side of the membrane. Hydrogen and helium concentrations were measured in the argon exhaust by gas chromatography. Leaks, if any, were detected using the helium. Hydrogen flux measurements revealed the maximum flux of hydrogen possible through the membranes under ideal conditions of pure hydrogen and in the absence of complicating factors in the water-gas mixture. After passing tests in these reactors, membrane types were tested in the sulfur contaminated water-gas shift mixture.

shift mixture at ambient pressures, and the poisoning and degradation of the membranes noted. These reactors were also used to test membranes and seals for leaks by measuring helium concentration in the argon sweep gas.

In these reactors, a mixture of approximately 85 volume % H_2 and 15 volume % helium was streamed past one side of the membrane, and pure argon sweep gas was streamed past the opposite side of the membrane. The concentration of hydrogen and helium in the argon sweep gas was measured by gas chromatography. The total flow of exhaust gas at ambient conditions was measured with a bubble meter, which is a primary flow standard. From the total flow of the exhaust stream of the argon sweep gas and from the concentration of hydrogen and helium in the sweep gas, the volumes of hydrogen and helium which have diffused through the membrane or possible leak paths were calculated.

The purpose of the helium in the hydrogen was to test for possible leaks in the membranes and seals. If the membranes and seals were not accurately checked for leaks, high flux of hydrogen through leak paths can be erroneously assigned to efficiency of the membrane. If cracks, pores or other defects are present in the membranes or seals, helium will diffuse through these leak paths at a rate just slightly less than that of hydrogen. (Given the same concentration gradient, helium will diffuse more slowly than hydrogen by approximately the square root of two because the atomic mass of helium is approximately twice that of molecular hydrogen.) Helium does not diffuse through defect-free dense membranes.

If any helium leak was detected due to defective seals or membrane, the membranes were rejected. The ultimate goal at Eltron Research was to produce dense membranes and seals with negligible helium leak in order to produce 100% selectivity for hydrogen. However, the project goal specified 3% allowed contamination of the hydrogen. After the membrane fabrication technique was proven to produce membranes with target hydrogen flux, the membranes were tested under the more rigorous conditions of the sulfur contaminated water-gas and steam mixture.

Tube type furnaces surrounded the reactors and were capable of heating the membranes and gas mixtures from room temperature to over 1000°C, if necessary, although most of the tests were limited to the range of 340 to 450°C. The systems shown in Figure 9 are designed to contain and quickly vent hydrogen out of the building in the event of a leak and to keep concentrations of hydrogen below explosion limits. System leaks were constantly monitored by measuring nitrogen in the reactor exhaust. At the flow rates of hydrogen which were used, the total chemical energy which could be released in the event of a catastrophic mixing of hydrogen with air was equivalent to only 15 Watts. The explosion potential was minimal, even in the worst case scenario of the reactor wall cracking, and the hydrogen igniting by the hot walls of the oven.

Apparatus for Testing Membranes in the Presence of Sulfur Contaminated Water-Gas Shift Mixtures. Figure 10 shows a close-up view of the four reactor units built for testing the membranes at ambient pressures in the specified water-gas shift mixture and in the presence of steam. Specifications for the wet mole % water-gas shift mixture were specified by ChevronTexaco, and cylinders of the corresponding dry mixture were ordered from AirGas Corporation. The wet and dry compositions of the water-gas shift mixture are listed in Table 2. The apparatus shown in Figure 10 was equipped with four peristaltic pumps for dispensing the required water into the dry gas mixture. The pumps were calibrated by weighing the mass of water dispensed while the water was in the liquid phase. The water was then vaporized to steam and mixed with the dry water-gas shift mixture.

Figure 10. **The four reactor stations built which were used to test the membranes under steam and water-gas shift gas components at ambient pressures. The cabinets and exhaust vents were designed to contain and vent toxic H_2S, CO and COS in the event of a leak in the gas lines. Carbon monoxide sensors placed within the cabinets sound an alarm in the event that CO levels exceed safety guidelines. Air flow in the cabinets and vents is calculated to dilute H_2S in the exhaust to levels below OSHA allowed guidelines. Calibrated peristaltic pumps were used to inject liquid water, which was converted into steam and mixed with the dry components of the water-gas shift mixture.**

To meet gas supplier guidelines for safe handling of H_2S and the other toxic gases (CO and COS), 304 type stainless steel tubing and components were used throughout the gas handling system. Special gas regulators rated for H_2S were purchased. Detectors for CO, which sound an alarm in the event of a gas leak, were placed within the cabinets. Detectors for CO were set to sound before CO levels exceed OSHA recommended guidelines *within* the cabinets. In the event of a leak in the gas lines, the gas should be confined within the cabinets and vented out of the building.

Air flow through the cabinets and through the ventilation pipes seen on the top of the cabinets is sufficient to dilute the H_2S to levels which meet OSHA guidelines of 10 ppm for worker safety, *even within the exhaust vents*. The ventilation system also kept gas concentrations below explosion limits in the event of a catastrophic leak. The compressed gas cylinders containing the dry mixture of the water-gas shift gas were contained within ventilated gas cabinets, which vent gases out of the building in the event of a leak in the cylinders or gas regulators.

Considerable thought was also put into safety concerns about toxicity of carbonyl sulfide, COS, which can theoretically form from the components of the water-gas shift mixture at the temperatures used in the study. Conclusions were made that the air flow through the cabinets would reduce concentrations to OSHA allowed levels. Because of the toxic and explosive nature of the test gases, it was deemed prudent to build these stations to specifications which will safely accommodated any worst-case scenarios.

B. Membrane Testing at High Pressure

Figure 11 shows the containment facility which surrounds two high pressure reactors for testing hydrogen separation membranes. The containment facility was designed to capture and vent gases in the event of a reactor leak. Figure 12 shows one of the two high pressure reactors within the containment facility. The high pressure reactors were designed to operate up to 900°C (1173 K) and 300 psi (20 bar) differential pressure. Furnaces surround the reactor tubes, and a pressure relief valve is at the top of each unit. Tests were run at 5, 10 and 15 barg on the retentate side of the membrane and 0 barg on the permeate side of the membrane. Tests at high differential pressure were run typically in the temperature range between 340-450°C.

Preliminary tests were run using hydrogen and helium in the feed stream and nitrogen in the sweep stream. Tests under ideal-hydrogen-helium mixtures were used to determine maximum hydrogen flux through the membrane materials at pressure and to prove that membrane materials could survive 15 bar differential pressure without helium leak.

High Pressure Hydrogen Separation Membrane Reactors used at Eltron Research Inc.

Figure 11. Containment facility designed to capture and vent gases from high pressure units in the event of leaks. Mass flow controllers are seen on the left.

High Pressure Test Apparatus Used for Hydrogen Transport Membranes

Figure 12. One of two high pressure reactors dedicated to testing hydrogen transport membranes. The unit shown is designed to operate at up to 900°C (1173 K) and 300 psi (20 bar) differential pressure. Furnace surrounds reactor tube. A pressure relief valve is at the top of the unit.

Summary Of Data Collecting And Data Handling

After synthesis of new membrane materials and after fabrication of new composite membranes, the next step was to check dense membranes for possible leaks and to measure hydrogen flux under ideal conditions at ambient pressures. Only after proof was obtained showing that dense membranes had negligible leak and were capable of high permeability for hydrogen, were further tests conducted at high differential pressures and under water-gas shift plus steam mixtures.

Initial tests were run as follows: After sealing membranes to support tubes, a mixture of approximately 85 vol. % H_2 and 15 vol. % He was streamed past the hydrogen feed side of the membrane (retentate side) and pure argon was streamed pasted the permeate side of the membrane. Total feed flow of gases on each side of the membrane was approximately 150 $mL{\bullet}min^{-1}$ (ambient). Feed flow was determined using calibrated rotameters. Rotameters were, in turn, calibrated using bubble-meters. Exhaust flow rates were measured directly at ambient pressure and temperature using bubblemeters. For all calculations, flow rates at ambient pressure and temperature were converted to standard pressure and temperature (STP) of 1 atm and 273 K. Temperatures of the membrane reactor tubes were set using a temperature programmable tube-type furnace. Temperatures were measured using thermocouples. The tube-type furnaces could be operated from room temperature to over 1000°C.

Samples of gas from the permeate exhaust were injected into a gas chromatography apparatus and the concentrations of hydrogen and helium in the argon sweep gas were determined. The gas chromatography peak areas were calibrated using hydrogen-helium standard gas mixtures which were purchased as specialty gases from AirGas Corporation. Argon, rather than nitrogen was used as the sweep gas, in order to detect possible air leaks in the gas lines. Before experiments could be performed, it was always necessary to prove that no nitrogen (or oxygen) was present due to leak in the gas lines. Oxygen, if present could consume hydrogen, skewing results, and air leaks imply probable escape of hydrogen from gas lines.

If helium was detected in the permeate exhaust, implying a mechanical defect in the membrane or seal, the membrane was rejected. Data for hydrogen permeation was considered reliable only if the helium leak was absent. It was assumed if membranes were impermeable to helium, that they would also be impermeable to non-hydrogen gases in the water-gas shift mixture.

From the total flow rate of the permeate exhaust in $mL{\bullet}min^{-1}$ measured by bubblemeters, and from the fraction of hydrogen in the exhaust flow as known from the hydrogen concentration, measured by gas chromatography, the flow rate of hydrogen in the permeate exhaust was calculated. In the absence of leaks, the flow rate of hydrogen (converted to STP) in the permeate exhaust must be identical to the flux of hydrogen through the membrane. Dividing the flow rate of hydrogen in $mL{\bullet}min^{-1}$ (STP) by the geometric area of the membrane in cm^2 gives the hydrogen flux through the membrane in units of $mL{\bullet}min^{-1}{\bullet}cm^{-2}$ (STP). These units of flux were converted into SI units of flux ($mol{\bullet}s^{-1}{\bullet}m^{-2}$) using conversion factors of 22,414 mL H_2 = 1 mol H_2, 1 min = 60 s, and 10,000 cm^2 = 1 m^2.

With flow rates and pressure kept constant, values of hydrogen flux, J, were determined as a function of temperature. Typically at least six gas samples were injected into the gas chromatography apparatus at each of seven temperatures to gain reasonable statistics (i.e., approximately 42 data points were collected to generate each data plot).

With hydrogen flux, J, determined at various temperatures, the diffusivity, D, was calculated at each temperature using Fick's First Law of Diffusion, $J = -Ddc/dx$, as described in the introduction. The membrane thickness is known, and the concentration of hydrogen on each side of the membrane is known, so that values of J, dc and dx, can be substituted into Fick's First Law of Diffusion and the equation solved for D at each temperature. Values of diffusivity are characteristic for each membrane material, and comparison of diffusivities of the various membrane materials can be used to rank the relative merit of each membrane material. Membrane materials with the highest diffusivities will ultimately yield the highest values for hydrogen flux at given experimental conditions.

With values of diffusivity, D, determined at several temperatures, the activation energy for hydrogen diffusion, E_{act}, and the Arrhenius pre-exponential factor, D_0, are found from the Arrhenius equation, $D = D_0e^{-Eact/RT}$, by plotting lnD vs. 1/T. The slope of the plot is equal to $-E_{act}/R$, where R is the ideal gas constant. The y-intercept is equal to $\ln D_0$. Such plots should give reliable values for the activation energy for hydrogen diffusion, without making any assumptions as to the pressure dependence of hydrogen flux.

If Sievert's Law holds, then the hydrogen flux will be proportional to the square root of the partial pressures of hydrogen according to the equation: $J = P_e^* \cdot l^{-1}(p^{0.5}_{feed} - p^{0.5}_{permeate})$. This is a good assumption for dense membranes which are not too thin to be limited by surface kinetics, and if there are no pinhole leaks in the membrane and seal which follow pressure laws to the first power of p, and if thick porous layers do not limit diffusion, which also follow pressure laws to the first power of p.

Knowing the concentration of hydrogen on both sides of the membrane, and knowing the ambient pressure on both sides of the membrane, the partial pressure of hydrogen on each side of the membrane is easily calculated. With the membrane thickness, l, known, and the hydrogen flux, J, measured, the equation $J = P_e^* \cdot l^{-1}(p^{0.5}_{feed} - p^{0.5}_{permeate})$ is solved for the hydrogen permeability, P_e^*, for each temperature.

With values of hydrogen permeability, P_e^*, determined at several temperatures, the activation energy for hydrogen diffusion, E_{act}, and the Arrhenius pre-exponential factor, P_0, are found from the Arrhenius equation, $P_e^* = P_0e^{-Eact/RT}$ by plotting ln P_e^* vs. 1/T. The slope of the plot is equal to -Eact/R, where R is the ideal gas constant. The y-intercept is equal to $\ln P_0$. If the energy of activation of such plots agrees with energies of activation by plotting natural logarithms of diffusivities, this is partial evidence that Sievert's Law holds and that hydrogen flux is proportional to the square root of the partial pressures of hydrogen. Permeabilities like diffusivities are also characteristic of each membrane material, and can be compared to determine the relative merit of each membrane material.

Values of permeance for each individual temperature are found by dividing values of permeability by the membrane thickness in meters. The SI units of permeability are $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$ and those of permeance are $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$. The pre-exponential factor Q_0, desired by the consortium, is found by dividing the pre-exponential factor, P_0, in units of $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$ by the membrane thickness in meters. Units of Q_0 are also $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$ as are the individual values of permeance at each temperature. Values of permeance can be compared as a figure of merit between membranes and takes into account the thickness of an individual type of membrane as well as the material of the membrane.

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