PALLADIUM AND PALLADIUM–COPPER COMPOSITE MEMBRANES FOR HYDROGEN SEPARATION

by

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Palladium (Pd) and Pd–copper (Cu) alloy films were applied to porous supports to produce a hydrogen separating membrane. Films were deposited onto porous ceramic (symmetric and asymmetric) and stainless steel tubes using electroless plating. The hydrogen permeabilities and selectivities (ratio of hydrogen to inert gas flux) of the composite membranes were determined at temperatures between 623-1023 K and pressure differentials up to 689.5 kPa. An air purge for 30 minutes at 723 K (followed by an inert gas purge) increased the hydrogen permeability. Membranes were characterized using SEM, EDX, AES, and XRD.

Decline in pure gas separation factor or selectivity (ratio of hydrogen/nitrogen pure gas flux) at high temperature was shown to be due to tin (Sn) at the Pd/ceramic interface. Tin was left over from the sensitizing/activation process required to initiate electroless plating. The low melting point of tin caused destabilization of the film and mechanisms for this process were postulated. A new activation technique using palladium(II) acetate (Pd(O₂CCH₃)₂) in chloroform replaced the activation method involving tin chloride. Membranes activated with Pd acetate and electrolessly plated were stable with regard to selectivity up to 973 K. Hydrogen flux declined above 873 K, apparently due to annealing and textural changes of the Pd film observed in SEM micrographs as loss of surface roughness.

Pd film structure is determined by electroless plating procedures and preparation methods, as well as high temperature treatment conditions. Pd/alumina composite membranes were fabricated by pumping electroless plating solution ("flow system") through the tube lumen. Typically an osmotic pressure gradient was maintained across the tube wall of the porous support by immersion in 6.0 M sucrose solution. The influence of different fabrication procedures on membrane performance was examined by conducting permeability tests at high temperature.

Membranes prepared using the flow system coupled with osmotic pressure appeared to have increased resistance to pore formation at high temperature, presumably
because of the different Pd film microstructure. This plating method resulted in films that appeared to be more dense and impenetrable to gases other than hydrogen in affirmation of previous work\textsuperscript{1-5}. However, more study will be required to verify this conclusion. With fewer voids from which pores could evolve, a denser film might be expected to be more resistant to pinhole formation.

Pd–Cu alloy membranes were made by successive electroless deposition of Pd and then copper onto porous 0.2 \(\mu\text{m}\) \(\alpha\)-alumina microfilters. The resulting membranes were heat treated at 923 K to promote intermetallic diffusion and obtain homogeneous alloy formation. Formation of a bcc phase with increased permeability was not observed at the alloy compositions that were prepared (~34 and 40 atom\% copper). Finally, the future of Pd composite membrane technology was assessed, including suggestions for future topics of research in the field.
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DEDICATION

In memory of Vera Hector, Gemma Morgan, Millard Eakin, William (Bill) English, Drake Dawson, & Ron McDonald.
Pure hydrogen \((\text{H}_2)\) is a valuable industrial material and is consumed on the order of \(500 \times 10^9 \text{Nm}^3/\text{yr}\). It is used for hydrogenations in the chemical process industry, as a blanket gas during the annealing of stainless steel to prevent oxidation and nitriding, as a fuel, cooling fluid, and as a carrier gas during the doping of silicon wafers in the semiconductor industry\(^8,9\). Presently, a major hydrogen sink is for hydrodesulfurization of fuels. It is also used in scientific and military balloons and as rocket fuel.

Separations account for a large fraction of energy use and capital expenditures in the chemical process industry. Current technologies for separating hydrogen consist of solvent absorption, pressure swing adsorption (PSA), cryogenic distillation, and polymer membranes\(^10\). Polymer membranes currently compete with the above technologies to reduce the hydrogen/carbon monoxide (CO) ratio in synthesis gas (syngas), or to recover hydrogen from ammonia reactor effluent, hydroprocessing purge streams, and other petrochemical plant streams\(^11\). Typically comprising hollow fiber modules of various types of polymers (such as polyimide), hydrogen separating polymer membranes can be made very thin but are generally limited to temperatures below 373 K\(^12,13\). Membrane systems have low capital investment although recompression of the permeate is usually required\(^14\).

Inorganic membranes are increasingly being utilized to separate gas mixtures at high temperatures. Some gases preferentially permeate through certain metals, enabling a selective dense metal membrane to be formed. For example, hydrogen has a high permeability in Pd compared to other gases. Oxygen permeates through silver (Ag), enabling the fabrication of an oxygen selective membrane from this metal\(^15-21\). Zeolites, with their well defined pore sizes, have more recently been studied for use as molecular sieving membranes\(^22,23\). Fabrication and characterization of porous membrane materials has been heavily researched in the past decade. Beginning in the late 1980's, porous materials produced from alumina ceramics were heavily studied as potential membrane materials\(^24\). Comprehensive review articles by Lewis\(^25\), Grashoff et al.\(^26\), Hsieh\(^27,28\),
Sarracco\textsuperscript{29}, Armor\textsuperscript{10,12,30-32}, and Shu et al.\textsuperscript{33} cover the basic principles and applications for inorganic membranes and membrane reactors.

Pd membranes are capable of operating at much higher temperatures than polymer membranes, making them ideal for use as a membrane reactor or for recovering hydrogen from high temperature gas streams. Although the concept of a hydrogen separator based on Pd metal has been around for more than a century\textsuperscript{34}, research centering on the development of a technologically and economically feasible hydrogen separating membrane using Pd has skyrocketed in the last decade. While some other metals are more permeable to hydrogen (such as tantalum, Ta), Pd has the distinction of having the highest catalytic activity (except possibly platinum, Pt) for the dissociation of hydrogen into its atomic form. The atomic hydrogen then readily permeates through the metal, while other gases are excluded.

Hydrogen separating membranes have other important technological applications as well. They can be used to recover tritium\textsuperscript{35-43} or they can produce hydrogen gas with impurity levels in the ppb range for use in deposition processes in the computer and aerospace industries\textsuperscript{8}. Tritium (T\textsubscript{2}), the radioactive of the three isotopes of hydrogen, is the fuel in nuclear fusion reactors and a critical component of thermonuclear weapons. Hydrogen (especially T\textsubscript{2})\textsuperscript{44} is costly to produce or to separate from gas mixtures such as reactor effluent or waste streams due to the high capital and energy expenditures associated with compression, heat exchange, cryogenic distillation, and PSA. A robust and selective hydrogen separating membrane could drastically reduce these costs, and ultimately replace traditional unit operations or be integrated into an existing process to recover hydrogen.

Recovery of hydrogen from waste gas or purge streams is a potentially large application of Pd membrane technology\textsuperscript{45,46}. Such streams are typically flared, annually wasting up to 2.5 trillion SCF of hydrogen\textsuperscript{47}. Coal gasification coupled with a Pd membrane could potentially become a large source of hydrogen\textsuperscript{48}. Production of pure hydrogen for fuel cell use is another important function\textsuperscript{47,49-54}. Steam reforming, particularly of methanol, is frequently the source of hydrogen\textsuperscript{9,47,55,56}. In one case, town gas was utilized\textsuperscript{57}. DOE predicts that by 2030 using methanol powered fuel cell vehicles (see Appendix A) could save $42B/yr with a reduction in daily consumption of 2-4 million barrels of oil\textsuperscript{47}. 
Different hydrogen separating membrane materials have been developed in the search for competitive alternatives to costly Pd. These can be categorized as either being based on silica (SiO₂)⁵⁸-⁶⁸, amorphous Pd–Si⁶⁹-⁷³, metal oxides⁷⁴, or on alloys developed for hydrogen storage⁷⁵-⁷⁷. For example, the lanthanum–nickel alloy LaNi₅ is permeable to hydrogen at room temperature and is resistant to thermal cycling⁷⁸. Carbon membranes are preferentially permeable to unsaturated hydrocarbons, CO₂, or H₂S by surface adsorption and flow, facilitating their separation from other gases⁷⁹-⁸⁶. Thus, hydrogen is rejected by the membrane, leaving a hydrogen-rich stream.

Chemical reactions could also be carried out more efficiently in a hydrogen separating membrane reactor⁹¹. By removing product, in this case hydrogen, from the reactor space, thermodynamically limited reactions can be driven towards completion, significantly enhancing conversion over the theoretical equilibrium conversion of the reactor feed stream⁹⁷. Additionally, pure hydrogen recovered on the permeate side of the membrane can be utilized for other purposes. Conversely, adding hydrogen along the length of a reactor can also favorably enhance product yields. Ideally, an endothermic dehydrogenation and an exothermic hydrogenation would be coupled or "conjugated", where each reaction takes place on opposite sides of the catalyst packed membrane reactor⁸⁸-⁹⁷. Thus, hydrogen and heat would be transferred most effectively, as two products are formed while heat is supplied directly where it is needed.

By either adding or removing hydrogen to shift the chemical equilibrium, reactor volume and temperature is lowered⁹⁸, fewer undesirable side products form, and less unreacted feed must be recycled, saving on downstream separation requirements, equipment size, and energy usage. Minimizing reactor surface-to-volume ratio can be especially advantageous in certain situations, for example, in a portable fuel cell electrical generating system or vehicular application. Here, the membrane reactor may be used to efficiently generate pure hydrogen from a liquid fuel for consumption in a fuel cell or other purpose⁵².

Therefore, a robust hydrogen selective membrane has the potential to change the chemical industry by replacing traditional reaction and separation procedures. This could result in tremendous savings in energy consumption and capital investment in equipment. The environmental ramifications include decreased reliance on non-renewable fossil fuel energy sources and the corresponding reduction in greenhouse gas emissions (CO₂) and
other pollutants such as nitrogen and sulfur oxides (NO\textsubscript{x} and SO\textsubscript{x}). Reduction in CO\textsubscript{2} generation would come primarily from increased efficiency, while the use of hydrogen as a transportation fuel (or a hydrogen producing reformer/membrane system) could reduce emissions of other pollutants. Membranes may also play a pivotal role in seasonal energy storage or the so-called hydrogen economy\textsuperscript{99-102}.

However, to be commercially viable, a membrane must possess high flux and selectivity (ability to separate hydrogen from other gases) over a lifetime of years under process conditions, in addition to being affordable\textsuperscript{31,103}. Polymer membranes are economical in some applications, although the higher temperatures of most chemical reactions and many waste gas streams precludes the use of polymer membranes, at least without process modifications such as cooling prior to introduction to the module.

A major drawback to the use of Pd as a membrane material is the high and fluctuating cost of this precious commodity metal and the difficulty in fabricating defect free membranes with Pd films on the order of microns or less\textsuperscript{31}. The use of Pd must be restricted not only due to its high cost, but to maximize the flux through the membrane since permeability is inversely proportional to Pd film thickness. Therefore, reducing Pd use in membrane fabrication has been of foremost consideration.

Many different membrane configurations have been developed in the attempt to minimize Pd film thickness while maintaining membrane integrity and the characteristics of high flux and permselectivity towards hydrogen. Pd films with micron thicknesses or less are readily attainable through the use of a composite membrane. Composite membranes consist of a thin layer of Pd deposited on a porous support. This configuration minimizes the use of Pd, which is imperative from an economic standpoint. Nearly infinite hydrogen selectivity is theoretically possible if a defect-free Pd film can be deposited onto the porous membrane support and a leak-free seal can be made between the inlet and outlet connections and the composite membrane. In addition, the membrane can be operated at high transmembrane pressure differentials because the porous substrate provides mechanical support for the Pd film.

Electroless plating (EP) is often used to deposit Pd films because of its throwing power (coverage of surfaces), ease of implementation, and the ability to deposit on nonconductors. There are many challenges in depositing a thin but impervious (impermeable to gases other than hydrogen) Pd film onto a porous support. First, if the
surface is nonconducting or noncatalytic for electroless deposition, it must be well activated to promote even coverage and good adhesion. Also, the porous support must be relatively smooth and free of macrodefects. It helps if the coefficient of thermal expansion of the support matches that of Pd to reduce stress build up in the deposit\textsuperscript{104}.

EP methods are critical as well. Grainsize and film porosity can vary widely depending on EP bath concentration, composition, and plating temperature\textsuperscript{5,105}. Deposition under an osmotic pressure gradient by conducting EP with a more concentrated solution on the opposite side of the porous support has been found to produce thinner Pd films that are more impenetrable to permeation of gases other than hydrogen\textsuperscript{1-5}.

There are other characteristics of pure Pd that impede the use of Pd membrane technology. These problems have been studied but in most cases acceptable solutions have not yet been found. Long-term stability at high temperatures has been a problem, especially deactivation by carbon under reaction conditions\textsuperscript{31}. Additionally, pure Pd undergoes a phase transition (increase in lattice size) as it absorbs hydrogen, leading to warping and embrittlement, particularly upon thermal cycling\textsuperscript{26}. This effect can be avoided by alloying Pd with a metal that suppresses the critical temperature for the coexistence of these two phases to lower temperatures. Alloys of Pd with silver\textsuperscript{56}, ruthenium (Ru)\textsuperscript{106}, copper\textsuperscript{107}, and other elements achieve this at specific concentrations while maintaining hydrogen permeabilities comparable to or greater than pure Pd. Pd is also susceptible to contamination or irreversible poisoning by common constituents of industrial streams such as sulfur. Alloys of Pd with copper and gold (Au) are resistant to H\textsubscript{2}S\textsuperscript{107-109}, so part of this work focused on making a membrane from the cheaper of these alloys, Pd–Cu.

For a Pd membrane system to replace a conventional practice and be accepted by industry, it must meet the following practical criteria: minimal metal thickness with high separation factor and output per unit volume; steady and predictable performance over a long period of time at high temperature and pressure; potential use in a variety of high-temperature separation and membrane reactor applications; resistance to poisoning by H\textsubscript{2}S, chlorine, CO, and hydrocarbons; the ability to withstand thermal cycling\textsuperscript{10,31,103}. Despite the above hurdles, the special capability of Pd and its alloys to selectively diffuse hydrogen while resisting contamination make it an excellent candidate for a hydrogen separating membrane material. Supported Pd or Pd alloy thin film membranes have been
demonstrated to be a suitable choice of membrane technology with respect to separation factor and high hydrogen throughput.

This work concentrated on improving the preparation methods and the resulting high temperature stability of Pd and Pd–Cu composite membranes. Determining the fundamental nature of Pd composite membrane stability was one of the main goals of this work. Membranes prepared using different methods were tested for extended periods of time at high temperature to assess changes in selectivity and hydrogen permeability. Hopefully, these efforts have moved the art of making Pd composite membranes one step closer to commercial implementation of this technology.

A major focus of this work was to compare the high temperature stability of membranes prepared with the conventional tin chloride sensitizing process to those fabricated using diluted tin sensitizing baths and a new activation procedure. Since membranes prepared by tin sensitizing processes deteriorated when tested at high temperatures, an activation process using Pd acetate was developed that completely eliminated tin contamination from the Pd film. The relationship between preparation methods and stability, as well as other issues affecting high temperature membrane performance will be discussed.

Chapter 2 begins with a brief history of early work in the field. This is followed by an exhaustive literature review on the theoretical aspects of hydrogen permeation in metals, the advantages of Pd alloys, metal deposition processes (including surface preparation and activation techniques), and descriptions of prior Pd membrane fabrication procedures, experimental details and performance. A brief overview of Pd membrane reactors is given as well.

Chapter 3 explains the experimental details, while Chapter 4 describes and compares the permeability, selectivity, and high temperature stability results of membranes activated prior to electroless plating using the traditional tin and Pd chloride or the new Pd acetate activation process.

To minimize Pd film thickness while maintaining high selectivity, membranes were plated by flowing electroless solution through the tube lumen while the tube was submerged in a concentrated fluid (to induce an osmotic pressure gradient). Chapter 5 describes the high temperature performance results for membranes fabricated using this technique. High temperature stability was found to be essential during the preparation of a
Pd–Cu alloy composite membrane, the final subject covered by this research. Chapter 6
gives an account of the fabrication and testing of Pd–Cu alloy membranes.

Chapter 7 summarizes the conclusions reached in this work, and Chapter 8
encompasses suggested avenues of further research to pursue.
2.1 History

Thomas Graham discovered the capacity of Pd to absorb several times its volume of hydrogen in 1866\textsuperscript{34}. This property is now taken advantage of as the basis for some high sensitivity hydrogen detectors\textsuperscript{110-114}, and Pd sometimes serves as a catalyst or membrane electrode in fuel cells\textsuperscript{115-120}. Pd is also endowed with excellent catalytic properties so it is a quintessential ingredient in catalysts for the chemical industry and in automotive catalytic converters. As a platinum group metal, its inert nature and good conductivity has enabled the replacement of some gold microcircuit components with Pd and Pd alloys\textsuperscript{121,122}. Pd has even been purported to produce energy by facilitating the presumably nuclear process of cold fusion\textsuperscript{123}.

The implication that Pd occludes hydrogen was first exploited in 1916 by Snelling who formed hydrogen separating Pd septa\textsuperscript{124}. Apparently, Pd membranes did not receive much further attention until a few companies (Atlantic Refining Company, J. Bishop & Co., Johnson Matthey Metals, and Union Carbide) began using Pd membrane technology to generate hydrogen in the 1960's\textsuperscript{25,46,56,106,125-131}. Since then, small-scale Pd membrane modules have been particularly convenient for producing high-purity hydrogen at remote sites or for industrial or military purposes\textsuperscript{9,26,55,132-139}.

One of the most promising applications of Pd membrane technology is as a Pd membrane reactor (PMR) where chemical reaction and product purification by separation occur simultaneously\textsuperscript{140-145}. Pd membranes are ideal for hydrogenation/dehydrogenation reactions due to the excellent control over hydrogen delivery or removal from the reaction zone. While many genres of reactions and types of separating membranes have been investigated for use as membrane reactors\textsuperscript{146}, significant increases above the theoretical equilibrium conversion can be obtained for hydrogenation and dehydrogenation reactions by using a Pd membrane reactor because of its high permeability and selectivity towards
hydrogen. Gryaznov, Pfefferle, and Wood were the pioneering researchers in this field and dozens have followed since then.

In early work in the U.S. and Soviet Union, relatively thick-walled tubes were employed (>100 μm). Up to the 1980's, Pd membrane technology typically consisted of banks of Pd alloy tubes (particularly PdAg23) with wall thicknesses of at least 100 μm for structural stability (unless otherwise specified, all alloy compositions reported herein are in weight percent, for example, PdAg23 = 23 weight% silver). These foils and tubes were often prepared by induction melting followed by cold working. The nearly perfect selectivity of these membranes enables them to provide very high purity hydrogen for use in the semiconductor manufacturing industry and for separating the isotopes of hydrogen from other gases or each other.

Unfortunately, the cost of Pd foils and tubes is prohibitive for most applications. So, in order to produce a robust and economical means of hydrogen separation on an industrial scale, a thin (<20 μm thick), adherent, nonporous, and durable Pd film must be applied to a permeable support. Abe, Kikuchi, Collins et al., Konno et al., and Uemiya et al. were a few of the initial experimenters to fabricate thin, selective, Pd composite membranes using porous symmetric and asymmetric supports. In the last decade, composite Pd membranes using many different deposition methods and supports have been produced that couple high selectivity with reasonable hydrogen flux.

A large volume of work has been conducted on PMR's and Pd membranes for separating hydrogen. A vast amount of additional work has been published on the interaction of hydrogen with Pd, and about Pd catalysts. An understanding of all the theoretical aspects associated with Pd membrane manufacture and use including hydrogen diffusion in metals, surface activation, and metal deposition processes is essential in developing an effective membrane configuration. Several comprehensive review articles are available, while the background information relevant to this work will be reviewed here.
2.2 Permeability of Hydrogen through Metal Membranes

The importance of Pd as a catalyst as well as a membrane material has prompted many studies on the Pd/hydrogen system. Permeability, $P$, of hydrogen through a metal is a function of diffusivity, $D$ (m$^2$/s) and solubility, $S$ (mol/m$^3$•Pa)$^{190-195}$,

$$P = D \cdot S = \text{mol/m}^2\text{•s•Pa}. \quad (2.1)$$

The addition of some metals such as silver to Pd increases the hydrogen permeability$^{196,197}$. Pd is very permeable to hydrogen but essentially impermeable to other gases, so at least in theory, perfect selectivity can be attained. In practice, purity is limited to tens of ppb due to small amounts of carbon and other impurities that diffuse through the metal lattice and grain boundaries$^{8,198}$.

The driving force for permeation is a difference in hydrogen partial pressure across the metal. Hydrogen permeates through solid metals via what is termed a solution-diffusion mechanism$^{187}$, involving the following steps$^{199}$: diffusion through the boundary layer to the metal surface from the bulk gas; dissociative chemisorption (diatomic hydrogen molecules adsorb on the metal surface and are broken apart into atomic hydrogen$^{200-205}$); absorption into the bulk metal; diffusion to the opposite face; passage from the bulk to the surface; associative desorption (recombination into molecular hydrogen$^{206}$); diffusion away from the surface into the bulk gas. Each process can be described with a forward and reverse rate, for example the dissociative chemisorption of hydrogen$^{199,207}$;

$$H_2(gas) \xrightarrow{k_1P_H} \xleftarrow{k_2c} 2H_{(solid)}, \quad (2.2)$$

where $k_1$ and $k_2$ are the rate constants for adsorption and desorption respectively, $P_H$ is the partial pressure of hydrogen, and $c$ is concentration of hydrogen in the metal (mol/m$^3$).

The surface roughness factor, $\sigma$, is a notable parameter in hydrogen adsorption$^{205,208-211}$. The higher the Pd surface area, the faster the rate of hydrogen uptake. Permeation can be influenced by the surface roughness, the purity of the metal, annealing history, and surface cleanliness$^{158,211}$. Successive oxidation and dehydrogenation of the Pd surface increases the surface area$^{212}$. Mishchenko et al. have thermally diffused zinc into the Pd membrane and then chemically removed it to increase the surface area and increase the hydrogen permeability$^{213-215}$.
Pd and platinum are the most efficient metals for hydrogen adsorption, dissociation or recombination even though their permeabilities are an order-of-magnitude less than that of some of the refractory metals such as tantalum (Ta), vanadium (V), or zirconium (Zr). However, the refractory metals are reactive and are less active for hydrogen dissociation due to rapid passivation by oxygen. Therefore, a Pd (or platinum) film is required on both sides of the membrane as a semi-noble protecting layer as well as a means for dissociating and recombining hydrogen. 

Hydrogen flux will be rate limited by either bulk diffusion or the dissociation or recombination kinetics. A detailed model of the permeation process through Pd was constructed by Ward et al. using rate equations (found in the literature) for each step of the permeation process. Their results showed that for temperatures above 573 K and Pd films as thin as 1 μm, diffusion through the bulk metal is the rate-limiting step. This is consistent with the results of other researchers. At lower temperatures the slow rate of desorption from the low-pressure side hampers flux, while adsorption-limited flux is only encountered at low hydrogen partial pressures (< 10⁻⁸ Torr) or under conditions of excessive contamination. 

External mass transfer resistance, likely to be encountered on the low-pressure side of the membrane, can also reduce hydrogen permeation rate. This is particularly true for very thin membranes (~1 μm) supported on porous supports which offer substantial mass transport resistance. Also, as the metal film becomes thinner, flux tends to become independent of thickness, i.e., surface processes become rate controlling. Percent recovery will then depend on factors such as sweep gas flowrate. 

Assuming equilibrium between the hydrogen molecules in the gas phase and hydrogen atoms dissolved at the interface, atomic hydrogen concentration just within the metal, c, is proportional to the square root of hydrogen pressure;  
\[
c = K_s P_H^{n=0.5} \equiv (\text{mol/m}^3),
\]  
where \(K_s\) is Sieverts' constant (mol/m³•Pa⁻⁰.⁵), and \(P_H\) (Pa) is the partial pressure of hydrogen in the gas phase. Solubility of hydrogen in the lattice is described by Sieverts' constant, \(K_s\). The power dependency, \(n\), describing permeation through the thin metal film is 0.5 because hydrogen diffuses through the metal in the atomic form. This square-root dependence of solubility on pressure is known as Sieverts' law. At
low temperature and high pressure there is significant departure from this relationship. Hydrogen is in the atomic form on the surface and diffuses in the atomic state so that the value of $n$ is 0.5 when bulk diffusion is the rate controlling step for permeation\textsuperscript{180}. When surface processes are rate controlling, due to the presence of contaminants for instance, $n$ has a higher value\textsuperscript{126,222}.

In general, surface effects can be neglected and bulk diffusion is the rate controlling step for permeation through the metal film\textsuperscript{195}. Once inside the metal, Fick's law can be used to describe the steady-state permeation rate or flux of hydrogen through the solid\textsuperscript{199,229,230}:

$$ J = D \frac{dc}{dx} \equiv (\text{mol/m}^2\text{s}). \quad (2.4) $$

Substituting in the relationship for hydrogen concentration in the metal (Sieverts' law), assuming a homogeneous solid so that $D$ in equation 2.4 is independent of hydrogen concentration, and integrating results in:

$$ J = \frac{P}{l} (p_{H,1}^n - p_{H,2}^n) \equiv (\text{mol/m}^2\text{s}), \quad (2.5) $$

where $P$ is the permeability (mol•m/m\textsuperscript{2}•s•Pa\textsuperscript{n}), $l$ is the membrane thickness (m), and $p_{H,1}$ and $p_{H,2}$ are the partial pressures of hydrogen (Pa) on the feed and permeate side respectively.

Inside the metal, hydrogen occupies octahedral sites and exists as a nucleus enveloped by a cloud of semi-bound electrons\textsuperscript{231-233}. Hydrogen electrons partially enter the unfilled d-band of the metal\textsuperscript{228}. The lowest energy pathway for hydrogen diffusion through Pd is from one interstitial site to another\textsuperscript{226,234}. The diffusion coefficient, $D$, the solubility, $S$, and thus the permeability, $P$, are temperature dependent, following the Arrhenius law:

$$ P = P_0 e^{(-E_p / RT)} = D_0 e^{(-E_D / RT)} \cdot S_0 e^{(-E_S / RT)}, \quad (2.6) $$

where $P_0$, $D_0$, and $S_0$ are the permeability, diffusivity, and solubility coefficients, and $E_p$, $E_D$, and $E_S$ are the respective activation energies\textsuperscript{195}. The activation energy for diffusion of hydrogen through Pd is therefore determined by:

$$ E_p = E_D + E_S \quad (2.7) $$

In reality, a metal composite membrane on a porous support will contain defects that affect the mass transfer through it. So transport is really a combination of atomic
diffusion through the metal (solution-diffusion), surface diffusion, Knudsen diffusion, and viscous flow through defects or microcracks. Diffusion of molecular hydrogen along grain boundaries is proportional to \( p_{\text{H}} \) instead of \( p_{\text{H}}^{0.5} \). Knudsen diffusion dominates when the mean free path of the molecule or atom is on the same order as the pore diameter. Then, collisions with the pore wall are of the same frequency as intermolecular collisions and the separation factor is then determined by a ratio of the reciprocal square root of molecular weight:

\[
\alpha_{Ks} = \sqrt{\frac{MW_2}{MW_1}}.
\]

(2.8)

Here, \( \alpha_{Ks} \) is the Knudsen separation factor and \( MW_1 \) and \( MW_2 \) are the molar masses of the lighter and heavier species respectively. Except in some special cases membranes with only Knudsen selectivity are generally not used industrially.

2.2.1 Effects of Contamination

The presence of surface contamination inhibits the hydrogen dissociation reaction and thus the permeability. Contaminants include hydrogen sulfide (H\(_2\)S), chlorine, carbon, CO, and some metals. Chemisorbed surface species raise the energy barrier between the adsorbed and subsurface hydrogen states as well as geometrically block the adsorption sites. One impurity atom may block multiple hydrogen adsorption sites. In most cases, poisoning is reversible by treatment in air, steam or hydrogen.

Air (or oxygen) treatment may increase the hydrogen permeability of Pd by removing impurities. Air may also create an oxide that is then reduced and increases the hydrogen permeability by increasing the surface area and activity for hydrogen dissociation into the atomic form. Many researchers have used air treatment of the Pd membrane as a routine preliminary procedure.

It is thought that hydrogen adsorption is more favorable at certain sites on the metal surface. Despite theoretical studies suggesting that fairly large amounts of surface contamination are required to affect permeability, experimental work suggests that small amounts of contaminants that could preferentially occupy the active sites for hydrogen dissociation may significantly lower permeability. Small amounts of contamination on
either the upstream or downstream surface of the membrane can significantly reduce permeation flux through the membrane211,222.

Coating the Pd film with a more noble metal such as platinum has successfully protected membranes from flux reduction due to the formation of impermeable sulfur compounds at high temperature248,265,266. However, platinum is an order-of-magnitude less permeable to hydrogen than Pd so such composite films have much lower permeabilities than Pd or Pd alloy films. Some Pd–Cu alloys are resistant to sulfur as well107.

Pd readily catalyzes the polymerization of carbon compounds and they can collect on the surface, inhibiting permeability267. Exposure to unsaturated hydrocarbons, alcohols, or carbon monoxide amplifies this problem particularly under reaction conditions31,246,249. Propylene polymerizes especially easily, fouling the membrane surface268. Grease from a vacuum pump is another potential source of carbon. Carbon can diffuse into the metal, and a solid solution of up to 13 atom% can form under the right conditions269-271.

Carbon can destroy the membrane, presumably by diffusing into it or causing it to delaminate from the support through the formation of a supersaturated solid solution249. The exact mechanism for this phenomenon is unclear. Chabot et al. found that CO₂ and CH₄ had limited effect on the hydrogen permeation rate, while Chen et al. observed a 10% reduction in flux in the presence of CH₄ or C₂H₄253,268. In the latter scenario there was no carbon buildup so hydrogen flux reduction was due to chemisorbed impurity molecules interfering with the hydrogen dissociation process.

Exposure of the membrane to certain metallic vapors or chlorine compounds can irreversibly poison Pd, severely decreasing hydrogen permeability222,245. Mercury from a diffusion pump or metals volatilized during thermal treatment of a catalyst can permanently reduce the hydrogen permeability of a membrane by absorbing into the Pd43,245. It has been noted that impurities next to a brazed joint of a Pd–Ag membrane tube caused failure near the joint43.

2.2.2 Diffusion through Nanostructured Materials

The metal microstructure influences permeability as well. Diffusivity is supposedly greater through nanostructured materials (grainsize < 20 nm) which have a high volume
fraction of grain boundaries than through polycrystalline metal foils\textsuperscript{272-274}. Yet, Koffler et al. found no correlation between grain size and permeability, and some researchers have suggested that a high fraction of grain boundaries actually offer increased resistance to hydrogen permeation. Eastman et al. assert that grain boundaries in nanocrystalline Pd at least have increased hydrogen solubility compared to the bulk metal\textsuperscript{232}. Unannealed nickel has been found to have higher hydrogen permeability due to grain boundary diffusion\textsuperscript{275}. From the apparently conflicting results, it is clear that this topic requires further study.

Some nanostructured materials do appear to have increased permeability\textsuperscript{272,276-280}. Kajiwara et al. found that smaller grains deposited by MOCVD (metal-organic chemical vapor deposition) had higher flux because of the larger effective area for surface diffusion\textsuperscript{281}. This is in contrast to the work of Xomeritakis and Lin who observed the opposite relationship with films deposited by MOCVD\textsuperscript{282}. However, this may have been due to the increased permeation resistance offered by carbonaceous impurities incorporated into the film during the deposition process.

\textbf{2.3 The Alpha to Beta Phase Transition}

Of great concern is the formation of two different Pd hydride phases that occurs with an increase in hydrogen concentration within Pd below the critical temperature of 583 K. Since the overall absorption limit of hydrogen in Pd is 67 atom\% at one atmosphere and 293 K, when the concentration of hydrogen in $\alpha$-Pd hydride phase reaches the solubility limit of 3 atom\%, the hydrogen atoms transition from occupying individual interstices in the $\alpha$ phase to partitioning inside the bulk metal into both the $\alpha$ and the $\beta$-Pd hydride phases\textsuperscript{121}. This is accompanied by distortion of the metal and the production of dislocations due to the coexistence of two face-centered-cubic (fcc) phases with different unit cell sizes of 3.89 and 4.02 Å\textsuperscript{187,198,231,283-285}. Above 583 K only the $\alpha$ phase can exist (corresponding to a lattice constant of 3.89 Å) while the two phases ($\alpha + \beta$) may coexist below this temperature as the octahedral interstices are increasingly occupied by hydrogen atoms\textsuperscript{286,287}.

Therefore, the $\alpha \rightarrow \beta$ phase transition is undesirable because of the internal stress caused by the different lattice constants. Consecutive hydrogen absorption-desorption cycles cause the Pd structure to become disordered\textsuperscript{288}, thus, membranes fabricated from
pure Pd will be destroyed by exposure to hydrogen below the critical point of 573 K and 2 MPa\textsuperscript{26}. Also known as hydrogen embrittlement, the manifestation of this phenomena is warping and destruction of the membrane\textsuperscript{106,159,283}. To avoid this, the membrane must not be exposed to hydrogen below the critical temperature and thoroughly purged with inert gas prior to cooling from high temperature.

\subsection*{2.4 Pd Alloys}

Alloys of Pd possess properties that may help to allay some of the problems experienced by pure Pd membranes\textsuperscript{289}. To begin with, the critical temperature for existence of the $\beta$ phase hydride is lowered in alloys\textsuperscript{287}. Also, the solubility of hydrogen is generally lower in alloys than in pure Pd so less hydrogen can dissolve and cause destructive lattice expansion due to the $\alpha \rightarrow \beta$ phase transition\textsuperscript{290,291}. In addition, the difference between the size of the $\alpha$ and $\beta$ phase lattice constants is closer so less distortion occurs with successive hydrogen absorption-desorption cycles\textsuperscript{106,288}. This helps eliminate membrane rupture due to warping or cracking, particularly failure associated with thermal cycling.

Many Pd alloys are also more permeable to hydrogen including PdAg\textsubscript{25}\textsuperscript{292}, PdCu\textsubscript{40}\textsuperscript{107,293,294}, and PdY\textsubscript{10}\textsuperscript{26,295} (compositions are in weight percent unless otherwise noted). PdRu\textsubscript{6} (atom\%) has a higher permeability at high temperatures than pure Pd and is not subject to embrittlement\textsuperscript{296,297}. Alloys are sometimes more resistant to poisoning by contaminants such as H\textsubscript{2}S, SO\textsubscript{2}, and carbon (coke)\textsuperscript{109,268}. Alloys containing gold or copper are more resistant to sulfur compounds\textsuperscript{108,109}.

Ternary and higher alloys of Pd have been developed to impart high temperature operating capability\textsuperscript{138,298-301}. Addition of alloying elements with higher melting points than Pd results in increased resistance to weakening of the membrane by grain growth. The high melting points of the platinum group metals result in better mechanical properties such as increased high temperature strength\textsuperscript{138}. Russian workers developed what they termed B-series alloys containing 4-6 components, each alloy composition tailored to a specific use\textsuperscript{136,138,298,301}. Alloys with the transition elements or small additions of rare-earths help to maintain the plasticity and texture of the metal\textsuperscript{302}. Although alloys of Pd with Au were found to increase pore formation above 773 K in Pd–Au/alumina composite membranes\textsuperscript{6}, alloys of Pd with silver, nickel, and the platinum group metals have been found to inhibit
embrittlement upon temperature cycling implying that these alloys impart high-temperature resilience.26.

The various alloys studied for their usefulness as hydrogen-permeating membranes are compiled in Table 2.1. Customarily, a specific alloy is tailored to perform a reaction88,144. Often these metals increase the permeability of pure Pd while substantially enhancing its mechanical properties303. For example, PdAg3 is 1.5 times as permeable as pure Pd195. Alloys of Pd often lower the $\alpha \rightarrow \beta$ phase transition temperature by closing the $\alpha/\beta$-Pd hydride miscibility gap that pure Pd has below 573 K232,283,284,304. Alloys with silver, for example, depress the transition to below 350 K and additionally, the two hydride phases have lattice sizes much closer in value than in pure Pd30,305.

The addition of rare earths such as yttrium (Y) and transition metals to Pd increases the mobility of hydrogen because these elements expand the interstitial spacing with their larger atomic radii196,263. Generally, permeability increases with increasing lattice parameter284, although rhodium increases the lattice parameter of the Pd host lattice but decreases the hydrogen diffusion constant by increasing the activation energy for diffusion196. While substitutional alloys may imbue increased permeability, interstitial alloys often decrease hydrogen permeability by blocking hydrogen diffusion paths. In the case of boron, this is presumably caused by distortion of these pathways by the atom in an interstitial position234. Pd–Y alloys have been used to separate hydrogen isotopes401.

The Pd–Ag alloy has been studied extensively because of its higher permeability and increased robustness with regard to thermal cycling. Pd–Ag membrane modules are employed commercially for special applications such as remote hydrogen generation or the ultra-purification of hydrogen9. Albeit better than pure Pd, this alloy has relatively low strength and experiences grain coarsening during extended periods at high temperature136,283. Beyond the increase in lattice parameter due to substitutional alloying, electronic effects such as donation of s and 3d electrons from silver to the collective d band of Pd influence hydrogen diffusivity196,290.

From the literature, Pd–Cu alloys appear to be superior to other alloys. The advantages of the Pd–Cu alloy are its lower cost, enhanced thermal cycling properties, and increased permeability107,109,293,294,305,350. The permeability passes through a maximum around 40% copper. This composition would significantly reduce membrane cost, and this alloy also possesses increased resistance to H2S108,109,350. PdCu40 has been found to be up
Table 2.1 Comprehensive Table of Pd Alloys used as Hydrogen Diffusion Membranes

<table>
<thead>
<tr>
<th>Alloying Element*</th>
<th>References</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Palladium (Pd)</td>
<td>Snelling(^{124}), Lewis(^{187})</td>
<td>Experiences hydrogen embrittlement ((\alpha \rightarrow \beta) phase transition below 310° C)</td>
</tr>
<tr>
<td>Aluminum (Al) 0.1-2.0%</td>
<td>Goltsov(^{306})</td>
<td>Increases mechanical stability, no effect on permeability</td>
</tr>
<tr>
<td>Silver (Ag) 25(^{\circ}/_o)</td>
<td>Hunter(^{292}), Yamamoto(^{307}), Rubin(^{308}), Ehlers(^{309}), Goltsov(^{306,310}), Ackerman(^{311}), Bellanger(^{157-159}), Caga(^{312}), Chabot(^{253}), Connor(^{129}), de Rosset(^{313,314}), Farr(^{315}), Fort(^{316}), Harris(^{317}), Hickman(^{262}), Holleck(^{318}), Jayaraman(^{319}), Jeman(^{243}), Jewett(^{261}), Kikuchi(^{320}), Kishimoto(^{321-323}), Knapton(^{305}), Lanzerstorfer(^{224}), Lewis(^{325,326}), Li(^{327}), Lindsay(^{328}), Makrides(^{197}), Nishikawa(^{152}), O'Brien(^{329}), Parfenova(^{330}), Penzhorn(^{166}), Pugachev(^{195}), Rodina(^{331}), Shu(^{332-335}), Züchner(^{336}), Uemiya(^{180,182}), Ali(^{244,245,337}), El-Sanabury(^{338}), Maruno(^{339}), McLellan(^{340}), Obradovich(^{341}), Ohira(^{342}), Sakamoto(^{343-345}), Serra(^{346}), Trudeau(^{347}), Yang(^{348}), Yeung(^{5}), Yu(^{349}), Edlund(^{350})</td>
<td>Lowers (\alpha \rightarrow \beta) phase transition temp. to below 298 K Coarsening (grain growth) at elevated temps. imparts fragility</td>
</tr>
<tr>
<td>Gold (Au) 5-25%</td>
<td>de Rosset(^{314}), Yamamoto(^{307}), Ehlers(^{309}), Goltsov(^{306}), McKinley(^{108}), Rodina(^{331}), Foo(^{6}), Baier(^{331}), Sakamoto(^{303})</td>
<td>Resistance to corrosive oxidation (high temperature aqueous vapor) and sulfur compounds</td>
</tr>
<tr>
<td>Boron (B) &lt; 10%</td>
<td>de Rosset(^{314}), Allard(^{234}), Knapton(^{305})</td>
<td>Increased permeability</td>
</tr>
<tr>
<td>Cerium (Ce) &lt; 12(^{\circ}/_o)</td>
<td>Doyle(^{304}), Farr(^{315}), Knapton(^{305}), Yoshihara(^{352,353}), Harris(^{354})</td>
<td>Increased permeability and mechanical strength</td>
</tr>
<tr>
<td>Cobalt (Co) 0.1-1%</td>
<td>Yamamoto(^{307}), Batyrev(^{355}), Feenstra(^{287})</td>
<td>Fine crystal structure prevents grain coarsening</td>
</tr>
<tr>
<td>Copper (Cu) 42%</td>
<td>Kikuchi(^{171}), Knapton(^{305}), McKinley(^{107,108}), Piper(^{293}), Mischenko(^{294}), Mikhailenko(^{356}), Uemiya(^{182}), Sakamoto(^{303}), Telegin(^{357}), Vert(^{358}), Edlund(^{109,350})</td>
<td>Increased hydrogen permeability due to bcc phase Resistance to (H_2S)</td>
</tr>
</tbody>
</table>

*weight percent (%) or atom percent (\(^{\circ}/_o\))
<table>
<thead>
<tr>
<th>Alloying Element*</th>
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<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium (In) 1-12%</td>
<td>Goltsov\textsuperscript{310}, Chen\textsuperscript{284}, Knight\textsuperscript{359}, Sakamoto\textsuperscript{360}, Roshan\textsuperscript{361}</td>
<td>Increases strength</td>
</tr>
<tr>
<td>Iron (Fe) 0.1-1%</td>
<td>Yamamoto\textsuperscript{307}, Bryden\textsuperscript{278-280}</td>
<td>Fine crystal structure prevents grain coarsening. H\textsubscript{2}S resistant.</td>
</tr>
<tr>
<td>up to 40%</td>
<td></td>
<td>Small additions promote resistance to high temperature aqueous vapor</td>
</tr>
<tr>
<td>Iridium (Ir)</td>
<td>Yamamoto\textsuperscript{307}</td>
<td>Small additions promote resistance to high temperature aqueous vapor</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>Goltsov\textsuperscript{310}, Gryaznov\textsuperscript{362}, Berseneva\textsuperscript{363}, Volkenshteyn\textsuperscript{364}</td>
<td>Raises the temperature of recrystallization, allowing operation at higher temperatures. Catalytic applications. Does not lower $\alpha \rightarrow \beta$ phase transition.</td>
</tr>
<tr>
<td>&lt;15%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td>Goltsov\textsuperscript{310-365}, Berseneva\textsuperscript{299}</td>
<td>Raises the temperature of recrystallization, allowing operation at higher temperatures.</td>
</tr>
<tr>
<td>0.1-4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel (Ni) 0.1-6%</td>
<td>Yamamoto\textsuperscript{307}, Gryaznov\textsuperscript{366-367}, Noh\textsuperscript{368,369}, Goltsov\textsuperscript{365}, Flanagan\textsuperscript{370}, Kishimoto\textsuperscript{323}, Meng\textsuperscript{371}, Ohira\textsuperscript{342}</td>
<td>Fine crystal structure prevents grain coarsening. Used for dehydrogenation of cyclopentadiene. Catalytic applications.</td>
</tr>
<tr>
<td>Platinum (Pt) 3-10%</td>
<td>Yamamoto\textsuperscript{307}, Goltsov\textsuperscript{306}, Noh\textsuperscript{372-374}, Berseneva\textsuperscript{138,299,300}, Maeland\textsuperscript{375}, Lewis\textsuperscript{376}, Sakamoto\textsuperscript{377}</td>
<td>Small additions promote resistance to high temperature aqueous vapor. Negative influence on permeability but imparts resistance to corrosion or poisoning. Increases thermal stability. Promotes dealkylation of alkyl aromatics.</td>
</tr>
<tr>
<td>Rhenium (Re) 5%</td>
<td>Smirnov\textsuperscript{378,379}, Tylkina\textsuperscript{380}</td>
<td>Small additions promote resistance to high temperature aqueous vapor. Catalytic applications.</td>
</tr>
<tr>
<td>Rhodium (Rh) &lt;10%</td>
<td>Yamamoto\textsuperscript{307}, Gryaznov\textsuperscript{367}, Smirnov\textsuperscript{381}, Noh\textsuperscript{382,383}, Rodina\textsuperscript{384}, Batirev\textsuperscript{385}, Sakamoto\textsuperscript{377}, Artman\textsuperscript{196}, Hoare\textsuperscript{386}, Timofeyev\textsuperscript{387}</td>
<td>Small additions promote resistance to high temperature aqueous vapor. Catalytic applications.</td>
</tr>
</tbody>
</table>

\textit{continued}
<table>
<thead>
<tr>
<th>Alloying Element*</th>
<th>References</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruthenium (Ru) 0.1-12%</td>
<td>Yamamoto(^{307}), Cohn(^{388}), Goltsov(^{306}), Gryaznov(^{366}), Mischenko(^{389,390}), Smirnov(^{378,379,381}), Berseneva(^{138}), Dobrokhotov(^{212,391}), Mikhailenko(^{356}), Avertseva(^{302}), Cabrera(^{298,299}), Darling(^{106}), Gryaznov(^{296}), Karavanov(^{392}), Krasil'nikova(^{393}), Mardilovich(^{394}), Mishchenko(^{304}), Raevskaya(^{395}), Sarylova(^{210}), Batirev(^{385})</td>
<td>Small additions promote resistance to high temperature aqueous vapor. Improved permeability, tensile strength and resistance to embrittlement. Lowers β phase transition temp. Imparts catalytic properties.</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>Itoh(^{69-72}), Lee(^{73}), Sakamoto(^{306}), Zimmerman(^{397})</td>
<td>Amorphous alloy, more permeable</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>Knight(^{359}), Harris(^{317})</td>
<td>Raises the temperature of recrystallization, allowing operation at higher temperatures.</td>
</tr>
<tr>
<td>Tantalum (Ta) 0.1-4%</td>
<td>Goltsov(^{310}), Berseneva(^{299})</td>
<td>Raises the temperature of recrystallization, allowing operation at higher temperatures. Production of isoprene</td>
</tr>
<tr>
<td>Uranium (U) 1-10%</td>
<td>Rubin(^{308})</td>
<td>Imparts high temperature strength without reducing permeability. Operation up to 800° C</td>
</tr>
<tr>
<td>Tungsten (W) 5%</td>
<td>Smirnov(^{379}), Goltsov(^{310,378}), Lobanov(^{398,399}), Berseneva(^{300})</td>
<td>Increases thermal stability. Promotes dealkylation of alkyl aromatics. Raises the temperature of recrystallization, allowing operation at higher temperatures.</td>
</tr>
<tr>
<td>Yttrium (Y), &lt; 12%</td>
<td>Farr(^{315}), Goltsov(^{310}), Avertseva(^{302}), Bryden(^{272,277}), Caga(^{312}), Fort(^{316}), Chen(^{284,304}), Hauptman(^{400}), Knapton(^{305}), Sakamoto(^{343,344,360}), Trudeau(^{347}), Wileman(^{401}), Yoshihara(^{402})</td>
<td>Increased permeability and mechanical strength although more easily oxidized</td>
</tr>
<tr>
<td>Ytterbium (Yb) 8%</td>
<td>Chen(^{403})</td>
<td>Increases solubility and prevents embrittlement</td>
</tr>
</tbody>
</table>
to 1.5 times as permeable as pure Pd at 623 K\textsuperscript{107}. Mishchenko et al. found that PdCu\textsubscript{42} was the Pd–Cu alloy with the highest permeability above 623 K\textsuperscript{294}. Like Pd–Ag, the copper alloy can withstand repeated temperature cycling with much less distortion than pure Pd\textsuperscript{107}, a primary issue in any system that experiences periodic operation at high temperature.

Although the reason for the alloy's increased sulfur resistance has yet to be explained (PdAg\textsubscript{40} is purported to be more noble than pure Pd as well\textsuperscript{121}), the increased permeability of this alloy supposedly depends on the formation of bcc structure by annealing below 873 K\textsuperscript{293}. The increased permeability is attributed to an increase in diffusion coefficient and electronic effects may be responsible for this increased permeability of the alloy\textsuperscript{358,404-406}.

2.5 Methods of Pd Composite Membrane Fabrication

Pd composite membranes may consist of a variety of configurations. Solid tubes or foils may be rolled from the solid metal or from an alloy melt. Thin layers of metal may be deposited onto almost any substrate by physical or chemical vapor deposition. Electroplating can deposit Pd onto a metal substrate more economically than the above methods but for nonconductors such as ceramics another method such as EP or solvated metal atom deposition is required. The basics of each are outlined below.

2.5.1 Physical Vapor Deposition

Physical vapor deposition or PVD is the evaporation of a metal under vacuum and subsequent condensation on the target surface\textsuperscript{407}. Typically a resistively heated wire is a metal source. Samples may be rotated to ensure even coverage. This can be advantageous for deposition onto polymers\textsuperscript{198}.

Although coating thickness is easily controlled using PVD because the metal flux impinges at a certain angle, either substrate rotation must occur during deposition or uneven coating may result. Impingement at an angle can also cause shadowing, or uneven coverage of the surface leading to voids and porosity\textsuperscript{408}. PVD requires the use of costly vacuum chambers, clean conditions, and expensive metal alloy targets. Nonetheless, PVD
can be used to deposit very thin, continuous metal and metal alloy films. Differing sputtering yields often complicate the deposition of alloys. For example, Athayde et al. tried to deposit Pd–Ag24 (atom%) but the film was Pd-rich relative to the sputtering target.

2.5.2 Magnetron Sputtering

A form of PVD, magnetron sputtering takes place when a plasma (glow discharge) induced by a gas (typically argon) introduced into the vacuum chamber dislodges atoms and ions from the metal target to be deposited on the desired surface. The magnetic fields of permanent magnets increase ionization. Ample ionization, high current density, and high sputtering rates are required to deposit a dense, continuous film.

2.5.3 Chemical Vapor Deposition

Often referred to as CVD or metal-organic chemical vapor deposition (MOCVD), this method takes advantage of a compound with a sublimation temperature below the temperature at which it decomposes. CVD of tetraethylorthosilicate (TEOS) or other precursors has been used to form hydrogen separating films on porous glass supports. CVD is a way to deposit oxygen permeable oxide films as well. In the case of composite metal membrane fabrication, the metal-organic material is usually sublimed in a separate chamber from the support to be coated, transported using a carrier gas, and decomposed at the desired surface by reaction with a gas such as hydrogen or by thermal decomposition. Commonly used precursors are Pd (II); acetate, acetylacetonate (acac), hexafluoroacetylacetonate (hfac), and chloride.

A major advantage of CVD is that metal can be more easily deposited within the support pores as opposed to on the surface as is the case with EP and PVD. This enables much thinner Pd films to effectively block the pores of the support. The disadvantages of CVD include contamination of the film with constituents of the metal-organic complex such as carbon. Another problem is buildup of expensive precious metals on non-target surfaces. The metal-organic precursors can also be exorbitant in cost, or if not commercially available, difficult to synthesize.
2.5.4 Electroless Plating

Also known as electrodeless, chemical plating, liquid phase epitaxy, or autocatalytic plating, electroless plating (EP) is the deposition of metals using chemicals as the source of both metal and electrons. EP has been defined as the controlled autocatalytic reduction of metastable metallic salt complexes on target surfaces. EP is autocatalytic in that the deposited metal catalyzes further deposition. A full understanding of its nuances is a key to the production of thin, adherent, pore-free metal films on various substrates.

Presently, the high cost of Pd limits the widespread use of Pd membrane technology. One solution to this problem is to apply a very thin Pd film onto a hydrogen permeable support to form a composite membrane. For widespread commercialization, the amount of Pd utilized to form a selective layer must be minimized even further. The focus of the following discussion is the sensitizing/activation process, the plating bath operatives, and the interplay among the many parameters required for making a thin, stable and selective membrane.

EP has several advantages compared to other deposition techniques. It has excellent throwing-power (coverage) of the plated surface, particularly compared to electroplating whose deposition is sensitive to the current density (electric field) on the substrate. EP can also coat nonconductors with proper surface activation. It requires no expensive electronic equipment, vacuum chambers, metal targets, or metal-organic precursors. The major drawbacks to EP are that it uses highly toxic chemicals and generates hazardous liquid wastes.

EP occurs through an autocatalytic reaction mechanism that is initiated by an activated surface. The substrate is activated prior to the plating operation by seeding the surface with metal crystallites (usually gold, silver, platinum or Pd). This is required to initiate plating and ensure adherence of the film. The metal nucleation sites initiate the EP reaction by catalyzing the decomposition of a reducing agent in the plating bath. EP is autocatalytic because the deposition rate depends on the activity of the metallic Pd being deposited. EP is performed by immersion in a plating bath comprised of the appropriate constituents at the optimum temperature to produce the desired microstructure and plating rate.
EP techniques have been developed for silver\textsuperscript{1,5,33,349,429-431}, gold\textsuperscript{6,421,424,425,432-436}, copper\textsuperscript{419,423,437-493}, nickel\textsuperscript{422,437,494-514}, platinum\textsuperscript{515-518}, Pd\textsuperscript{178,426,436,519-530}, cobalt\textsuperscript{531}, and other metals such as iron and lead\textsuperscript{433}. Despite a report and patent on electroless ruthenium plating\textsuperscript{531,532}, attempts to deposit it have been unsuccessful\textsuperscript{533,534}. Often, the lessons learned from these other electroless deposition systems about adhesion, porosity, and microstructural evolution can be translated into assumptions about electroless Pd plating.

Another method for plating metals for which standard EP baths are not available is by immersion or displacement plating. For example, Pd replaces zirconium because zirconium is less noble than Pd\textsuperscript{525}. One potential problem is that the substrate must also catalyze the EP reaction and some metals are poor catalysts for oxidation of the reducing agent\textsuperscript{426}. Gold is one such metal that requires special plating techniques. For autocatalytic plating to take place, the anodic reaction (decomposition of reducer) must have a less noble potential than that of the cathodic reaction. Gold can be deposited on many metals such as Pd by displacement plating\textsuperscript{6} but only until the metal being coated is completely covered.

\subsection*{2.5.4.1 Surface Preparation}

Prior to any deposition process, the porous support must be cleaned. Organic and inorganic contaminants must be removed to ensure that an adherent, uniform, and defect free deposit can be obtained. Cleaning can be accomplished with a variety of solvents and cleaning agents without altering the membrane characteristics. Typically, substrates are washed in mild detergent, acid, or base, followed by rinsing in deionized water (DI) and an organic solvent such as an alcohol or acetone. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) is another effective cleaning agent.

Adhesion to ceramic substrates may also be enhanced by certain chemical treatments before plating. Etching of alumina has been shown to enhance adhesion\textsuperscript{168,460,535,536}. Soaking in NH\textsubscript{4}F, HF or NaOH cleans and roughens the surface, possibly removing some glassy phase from the alumina such as amorphous silicates\textsuperscript{460,537}. During high temperature processing of the alumina membranes, lower melting glassy phases such as SiO\textsubscript{2} and impurities may segregate to the surfaces between the alumina grains. Dissolution of some of this glassy phase on the surface helps anchor the Pd film by creating a network of pores or pits. Metal/ceramic adhesion of films deposited by EP depends primarily on mechanical
bonding\textsuperscript{497}. Ameen et al. observed that on 96 and 99.5\% $\alpha$-alumina, etching away the vitreous binder components of the alumina with ammonium or sodium fluoride resulted in high pull strengths but destroyed some of the ceramic\textsuperscript{460}. Treatment with HF resulted in low pull strength.

While the above techniques work well for ceramic substrates, metals such as stainless steel require harsher preplating preparation conditions\textsuperscript{8,217,333,526,538-542}. Metals have an omnipresent oxide layer that must be removed. This is accomplished via mechanical cleaning or acid pickling steps. Plating must immediately follow the cleaning step to prevent the oxide layer from reforming. Instead of the standard tin and Pd chloride activation process discussed below, metals are often activated with what is known as a strike\textsuperscript{543,544}. A strike is an acidic metal chloride bath used to remove the oxide layer and electrodeposit a layer of metal active for further metal deposition. Once cleaned and activated, metals can be plated using standard electroless or electroplating.

To convert stainless steel from a hydrophobic to hydrophilic surface, chromic and sulfuric acids with surfactants have been used\textsuperscript{500}. For example, stainless steel was dipped in 25-50\% H\textsubscript{2}SO\textsubscript{4} at 343-353 K for 30 to 75 seconds prior to EP\textsuperscript{526}. This acid pickle (as it is known in the trade) or chemical activation removes contaminants in addition to stripping the oxide layer to expose more active metal for subsequent sensitizing/activation and/or plating\textsuperscript{418}. A stable oxide layer can form if the conditions of this pretreatment are too severe.

2.5.4.2 Activation

After cleaning and before EP, it is necessary to activate the surface of a non-conducting substrate. The most common method for surface activation involves the use of sequential tin chloride sensitizing and Pd chloride activation baths. This forms the metal clusters requisite for initiation of EP\textsuperscript{474,545}. Traditionally, this is accomplished with tin chloride solution followed by activation with PdCl\textsubscript{2}\textsuperscript{520}. Surface activation is primarily for catalyzing the EP reaction because adhesion of the resulting deposit is mostly by mechanical keying with the support\textsuperscript{418,473,476}. The chemistries of sensitizing and activating processes have been thoroughly studied\textsuperscript{428,431,440,441,463-466,468,469,473,496,498,499,543,546-583}. An overview of the procedure follows.
There are two types of activation processes using tin and Pd chloride, either sequential or mixed. In the sequential technique, substrates are immersed in separate tin chloride and PdCl₂ solutions with rinsing in between. Mixed activators consist of a combination of tin and Pd chlorides in one bath. The sequential process will be discussed here because it was used in this work.

The sequential sensitizing-activation procedure begins with immersion in an acidic SnCl₂/SnCl₄ colloidal sensitizing solution followed by acidic PdCl₂ activating solution. The colloidal tin solution is required to anchor the Pd to the surface⁴⁷³. Charbonnier et al. provided a good overview of tin and Pd chloride activation processes and mechanisms as well as relevant literature⁴₄⁸. In that report it was found that tin chemisorbs preferentially onto substrate oxygen followed by Pd attachment via chlorine ions adsorbed on the tin. Although their work involved polymers, the same mechanism can probably be extended to alumina with its surface hydroxyl groups. When the colloidal particles contact the substrate, Sn²⁺ adheres to the surface, probably by a mechanism such as that shown in Figure 2.1 (adapted from Charbonnier et al.⁴₄⁸, Hulteen et al.⁵₈⁴, and Menon and Martin⁵₈⁵):

\[
\begin{align*}
\text{Sn}^{2+} + \text{Pd}^{2+} & \rightarrow \text{Sn}^{4+} + \text{Pd}^0,
\end{align*}
\]

Figure 2.1 Possible mode for sensitizing/activation of alumina surface.

Nonconducting substrates must be coated with a layer of Sn(II) prior to depositing a layer of Pd for initiating EP. Then, upon immersion in acidic PdCl₂ activating solution, tin binds Pd to the substrate via the reaction:

\[
\text{Sn}^{2+} + \text{Pd}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pd}^0,
\] (2.9)

creating a Pd/Sn alloy on the substrate⁵₈⁵.
The tin should resolubilize in the acidic PdCl₂ solution, but in practice much remains on the surface. Tin-rich surface layers usually cover the active Pd cores. Although activity has been found to depend on the Sn/Pd ratio, excess tin accumulating on top of the Pd crystallites blocks its activity in catalyzing hydrazine decomposition. Interestingly, it was found with nickel (which is similar to Pd) films plated on alumina that pull strength increased with lower concentrations of stannous chloride in the sensitizing solution. Rinsing before plating is required to prevent "drag-in" of the sensitizing and activation bath components into the plating bath. Otherwise, spontaneous decomposition of the bath may occur as the catalyst spreads throughout the solution.

Numerous studies have been performed on the stability of tin sensitizers. Knowledge of these efforts helps us employ sensitizers to their full advantage. For example, tin sensitizers are photosensitive. So, exposure to ultraviolet light should be avoided to prevent photo-oxidation. Oxidation of the colloidal tin sensitizing solution is detrimental to its efficacy and can be mitigated by storing the solution under an inert-gas blanket or by bubbling argon through the solution.

Drying of Pd predeposited onto stainless steel substrates by electroplating has resulted in the formation of divalent Pd oxide (PdO) whereas tetravalent Pd(IV) oxide formed on air-dried activated substrates. Uniform particles of ~500 Å diameter were easily oxidized to both Pd(II) and Pd(IV). Oxides ruin the catalytic properties of the activated substrate. Pd oxide of higher valence appeared to be electroinactive towards hydrazine oxidation although hydrazine reduced Pd(II) oxide to Pd(0) upon immersion in the plating bath. Even oxygen dissolved in the sensitizing or activating solutions can passivate the catalytic sites on the substrate.

Excess tin can be removed from the activated surface by performing a technique called acceleration. This entails briefly soaking the membrane in a solution of H₂SO₄, HCl, EDTA (ethylenediaminetetraacetic acid, C₁₀H₁₆N₂O₈), NaOH, NH₃BF₄, NH₄OH, NH₄F₂, HBF₄, or other complexant to dissolve away excess tin and tin oxides. Water, with a pH of 7, is a poor solvent for tin removal although rinsing in water is not detrimental to coverage of the surface by Pd/Sn catalyst. EDTA is an effective accelerator with the advantage of being non-toxic and usable over a large pH range. Without acceleration, the tin coverage is greater than that of Pd. Tin shields the reactants from the Pd, reducing the catalytic activity by inhibiting hydrogen sorption capability. By removing these
compounds which mask the catalytic activity of the Pd nuclei, the induction time before
initiation of EP is shortened. Pd coverage has been found to remain constant during
acceleration. Membranes have previously been fabricated using this step.

Acceleration can cause rearrangement of the Pd/Sn islands on the activated surface.
After acceleration, high-density particles between 400 and 700 Å were found to be active
for electroless deposition. After activation the tin and Pd compounds existed in the
amorphous state on the substrate surface suggesting many defects, while after acceleration,
fcc structure was detected. This is desirable for film adhesion since Pd has fcc structure.
Increased bonding is obtained when the deposited metal and the substrate or the metal
activator sites on the substrate have a similar crystallographic orientation to facilitate
epitaxial growth.

The state of the Pd crystallites after acceleration depends on the accelerating agent.
NaOH and HCl stripped away the surface layers of tin most effectively leaving almost bare
active nuclei after removing stannous and stannic oxides or hydroxides. Accelerating with
NH₄OH and NH₃BF₄ coagulated the small particles to produce very active high-density
particles. However, the ammonia-based accelerators should be avoided since they result
in less-active Pd-ammonia complexes on the surface.

Before acceleration, drying of the substrate must also be prevented since the active
particles react with oxygen forming difficult to remove compounds that prevent initiation of
metal deposition. None of the accelerators dissolve highly insoluble SnO₂ from a dried
surface. After washing and drying the substrate, tin not in the Pd-Sn core is in the
hydrated stannic oxide state. Acceleration removes tin by a factor of 3 to 10 resulting in a
Pd/Sn ratio of ~3. A Pd/Sn ratio of 6 would result if all tin in just the sheaths were
removed. Tin remaining after activation may dissolve into the electroless bath to be
codeposited with the plating metal.

The structure of the Pd clusters on the substrate that initiate EP may also influence
the structural characteristics of the deposit which are dependent on the nucleation and
growth process. The coverage, adhesion and quality of the film are a function of catalyst
activity. The primary activator deposit strongly affects film growth while bonding
between the film and substrate takes place through metal-oxygen bond formation at the
interface. The morphology of the substrate can be expected to have a strong influence on
the structure of the deposit as well.
Adhesion also depends on the amount of tin and Pd adsorbed on the substrate during sensitizing/activation. Tin reduces adhesion. Furthermore, the higher the surface coverage by the activating metal, the better the coverage by the depositing metal and the less porous the deposit will be. Grain density and size of the metal islands on the substrate affect the catalyst activity. For example, it has been determined that at least 4 to 20 atoms are necessary to initiate electroless nickel plating.

A disadvantage of the Pd/Sn activation process is that contamination of the Pd film with tin from the sensitizing bath may reduce adhesion to the surface and adversely impact the high temperature membrane stability. An alternative for catalyzing alumina surfaces for EP is to use methods ordinarily used for catalyst preparation. Nanoscale Pd clusters on the substrate created by impregnation, incipient wetness, or ion exchange could serve as sites for initiation of EP. This idea was first experimented with by Li et al. who deposited a γ-alumina sol-gel layer containing PdCl₂ onto an α-alumina support to reduce the pore size, catalyze the EP reaction, and fabricate a Pd/composite membrane. Zhao et al. also deposited a Pd-modified boehmite sol to form a γ-alumina layer with smaller pores and to activate the support for electroless deposition. In theory, any technique may be used to deposit a metal seed layer to promote electroless deposition, as long as the metal catalyzes decomposition of the reducing agent.

An alternative method for surface activation also eliminates tin by depositing a metal-organic precursor from solution followed by heat treatment to remove the organic fraction. The new activation technique based on such Pd metallization techniques was developed for the manufacture of electronic components. Gross et al. reported the preparation of Pd thin films by laser direct-write metallization of Pd acetate for the fabrication of microcircuits. The Pd acetate was deposited by soaking the substrate in a chloroform solution. Zhang et al. used a similar technique to activate various surfaces by photochemical decomposition of metal-organic films prior to electroless copper plating. Lasers and ultraviolet light are used for Pd acetate decomposition in these applications to reduce heating of the substrates and to form fine lines or patterns for microcircuits. Previously, Shu et al. have utilized Pd acetate in the membrane activation procedure although this was as a substitute for PdCl₂ in the traditional tin chloride activation process.

In the case of Pd membrane fabrication, ceramic supports are stable at high temperatures. Therefore, a new technique was developed by Schwartz et al. to activate the
ceramic supports that involved the deposition of Pd acetate from solution, followed by heat
treatment to burn off the organic fraction and leave behind Pd particles. Another
advantage of this procedure is the elimination of wastewater generated from rinsing
between the sensitizing and activation baths.

2.5.4.3 Microstructural Evolution

Since the plating rate and film morphology depend on many variables such as
concentration of bath constituents and plating temperature, understanding the fundamentals
of EP is the key to optimizing the conditions for producing usable Pd films. Pd film
structure has been linked to limitations in high temperature stability, resistance to thermal
cycling and minimization of the defect-free film thickness. Beginning film structure is
largely dependent on preparation techniques, with various compositions and concentrations
of plating baths as well as plating conditions strongly influencing subsequent porosity and
stability.

During EP, electrons are released during the anodic partial reaction and consumed
by the cathodic partial reaction:

\[ R^0 \rightarrow R^{z+} + ze^- \quad \text{(anodic)} \quad (2.10) \]
\[ M^{z+} + Ze^- \rightarrow M^0 \quad \text{(cathodic).} \quad (2.11) \]

Here, \( R \) is the reducing agent, \( M \) is the metal, and \( z \) is the number of electrons transferred.

For deposition to occur, the sum of the standard redox potentials \( (E^0) \) of the oxidation and
reduction reactions must be positive and \( \Delta G^0 \) be negative so that the reaction is
thermodynamically favorable. However, if the sum of the redox potentials is too
high, the bath will spontaneously decompose.

Pd EP baths normally consist of a Pd-amine complex stabilized by a chelating or
sequestering agent such as EDTA. Triethyleneamine (C\(_6\)H\(_{15}\)N) has also been used as a
bath stabilizer. Stability dictates the amount of reducing agent that can be added.
According to early work by Rhoda (1958) on the subject, the primary factors influencing
EP of Pd are the metal-ion concentration, temperature, and hydrazine concentration while
amine solvent and stabilizer (EDTA) concentrations are secondary. The pH of the
bath is usually around 11. Controlled deposition of the stabilized bath is accomplished by
the introduction of a suitable reducing agent.
\[ 2Pd(NH_3)_4^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + 8NH_3 + N_2 + 4H_2O. \]  
(2.12)

Vigorous agitation of the plating solution can occur due to gas production. The reaction may also be broken up into anodic and cathodic half-reactions:\(^{333}\)

\[ N_2H_4 + 4OH^- \rightarrow N_2 + H_2O + 4e^-; \]  
(2.13)

\[ 2Pd^{2+} + 4e^- \rightarrow 2Pd^0. \]  
(2.14)

Electroless films form by a sequence of distinct steps\(^{178,182}\). Microstructural evolution takes place with nucleation and ensuing three-dimensional growth from catalytic centers on the surface.\(^{463}\) First, nucleation begins when the Pd on the activated surface catalyzes initial deposition. Then, fine particles grow and these crystals coalesce into large particles on the surface, eventually forming a continuous film. The final grain structure depends on this initial nucleation and growth process as well as the structure of the substrate.\(^{420,463}\)

Metal-ion concentration heavily influences deposition by affecting the nucleation rate. Supersaturation, brought about by higher concentration, increases the nucleation rate resulting in the formation of numerous tiny Pd particles. Possessing high chemical potential, these small particles pack tightly into a dense film to minimize surface energy. With dilute plating baths, crystal growth is faceted due to low supersaturation. In that case, low mass transfer to the surface leads to nucleation inhibited growth. These well-crystallized films adhere better to the substrate but contain pores due to loose packing making them unsuitable as membranes.\(^{105}\)

EP is either diffusion or electrochemically (activation) controlled.\(^{618}\) In diffusion control, mass transport or diffusion of \([\text{PdEDTA}]^2^-\) to the surface followed by reduction after dissociation of the metal complex controls the rate.\(^{619}\) This results in some interdependence of the two partial reactions.\(^{618}\) EP is autocatalytic because the growth rate depends in part on the catalytic activity of the metallic Pd being deposited.\(^{426}\)

Depending on the conditions, diffusion of reactants to the surface, or the reaction on the surface can be rate determining.\(^{490}\) For instance, electroless copper plating rate has been found to be heavily dependent on agitation at low copper concentrations while during operation in kinetically (electron transfer) controlled regimes the rate was zero order with respect to cupric ion concentration. The reaction can be diffusion limited on rough surfaces due to the thicker diffusion layer.\(^{419}\)
Anodic oxidation of reductant is usually under activation process control not affected by agitation of solution while the partial cathodic deposition is usually controlled by diffusion (metal complex transport to the surface)\textsuperscript{545,619}. The two partial reactions are interdependent when they proceed simultaneously \textsuperscript{523,619}. The slower of these two reactions determines the rate of metal deposition. The reaction is said to be under mixed control; diffusional (Pd complex) and electrochemical (hydrazine decomposition kinetics)\textsuperscript{619,620}. Shu found that hydrazine oxidation is the rate limiting step in electroless Pd deposition on stainless steel, i.e. hydrazine adsorption and dehydrogenation controls the rate of Pd deposition\textsuperscript{426}.

The oxidation kinetics of the reducing agent greatly influence EP bath performance. Iacovangelo found that dimethylamine borane (DMAB) is a stronger reducing agent than hydrazine\textsuperscript{421}. However, hydrazine was more effective on Pd and nickel substrates that catalyze its decomposition\textsuperscript{621}. Hypophosphite based baths possessing better stability have also been used successfully\textsuperscript{2,523,524,527}. However hydrazine is a superior reducing agent for Pd membrane fabrication since hypophosphite tends to deposit 3-14 atom\% phosphorous\textsuperscript{523,527} that is incorporated into the film leading to brittleness\textsuperscript{217}. Adsorbed hypophosphite reduced by adsorbed hydrogen leads to codeposition of phosphorous \textsuperscript{527};

\[
H_2PO_2^- \rightarrow P + OH^- + H_2O. \tag{2.15}
\]

In addition to the catalytic activity of the substrate, metal-ion concentration in the plating solution highly influences film microstructure. Since complex concentration is directly proportional to cathodic overpotential, finer grains and coherent films result from the slow release of metal cations from metal complex dissociation\textsuperscript{527}. Therefore, at lower metal-ion concentrations, adhesion is improved because the nuclei are well distributed on the substrate in the initial stages of plating\textsuperscript{426,497}. Indeed, pull strength increases with decreasing metal-ion concentration in the bath\textsuperscript{543}.

Although excess ammonium hinders the tendency of the bath to form hydroxides, as the alkalinity of the bath increases, metal ions can hydrolyze to metal hydroxides that precipitate out\textsuperscript{882}. Also known as Pd black because of its appearance, this fine Pd is sometimes desired on the surface of the Pd membrane since it increases membrane permeability as well as catalytic activity by increasing the metal surface area\textsuperscript{225,622}. Usually bath decomposition is deleterious as it necessitates replacement of the EP solution and plating container.
Temperature has a strong effect on film morphology. The lower the temperature, the larger the crystallites which are formed while faster plating at higher temperatures creates Pd films that are more amorphous with smaller, more closely packed crystallites resulting in a denser structure\textsuperscript{523,524,527,623,624}. Supposedly, the latter is more desirable for producing a thin, defect-free film with higher hydrogen permeability. Better quality deposits have been obtained at higher plating temperatures because compressive stress and lattice strain is reduced\textsuperscript{484}. Expedited nucleation at higher temperature allows the depositing atoms to consolidate into the crystal lattice without strain, resulting in smaller grainsize as well. Deposit hardness depends on the rate of plating with higher rates producing softer, more ductile deposits\textsuperscript{520}. Moreover, if plating rate is too rapid, coating voids may form where swiftly spreading deposition growth fronts coalesce\textsuperscript{497} (although some voids are to be expected). Voids may contain hydrogen from the plating process and cause embrittlement\textsuperscript{443}.

As described above, deposition is usually diffusion controlled while reducing agent decomposition is activation controlled\textsuperscript{620}. So, the higher the reducer concentration, the faster the plating rate, hence smaller crystallites. Zhao et al. found that higher concentrations of hydrazine in the plating bath produced more compact and permselective films\textsuperscript{613}. The increased deposition rate from higher reducer concentration resulted in finer metal particles.

Concentrated baths with high metal content deposit Pd in dense fine-grained films while more dilute baths give a mat appearance. Shu found that the brighter film from a concentrated bath consisted of tightly coalescent surface grains with no crystal habit in contrast to the tapered, loosely-packed crystallite particles obtained from a dilute bath\textsuperscript{105}. The dilute bath with low metal content resulted in large grains separated by voids, suggesting that the concentrated bath is more desirable for creation of a coherent film. However, the film deposited from the dilute bath adhered more strongly to a stainless steel support\textsuperscript{105}.

Concentration of the ligand complexing agent in the bath is of lesser importance in influencing deposition rate and film morphology. The chloride anion of the Pd salt is not completely removed from the coordination sphere of the metal ion but is in equilibrium competition with the organic complexing agent EDTA and solvent molecules for the coordination positions of the metal ions\textsuperscript{382}. The Pd/EDTA complex diffuses through the
boundary layer to the solid-liquid interface and deposits by capturing electrons from the catalytic surface (supplied by oxidation of the reducer), returning to the zero valent, metallic state\textsuperscript{527}. Free metal ions are the product of ligand complex dissociation:

\[(Pd_{m-n}L_n)^{2m-2n} \rightarrow mPd^{2+} + nL^z, \quad (2.16)\]

where \(L\) is the ligand, \(m\) and \(n\) are the metal and ligand coordination numbers respectively, and \(z\) is the charge on the ligand. Using two-dimensional modeling, Shigematsu found that using triethanolamine (\(C_6H_{12}O_3N\)) as the complexant resulted in the least number of voids\textsuperscript{458}.

Stability of the EP bath is imparted from a shift in the reduction potential due to the increased number of coordination positions of the plating-metal atom filled by atoms of the ligand with which it is compounded\textsuperscript{455}. High concentrations of EDTA complexant slow down the metal complex dissociation reaction by decreasing the availability of metal ions to be reduced\textsuperscript{333}. As a strong complexing agent for Pd ions, the dissociation reaction to free Pd ions from stable EDTA-complexed Pd ions becomes the rate-determining step in EP, corresponding to a slow deposition rate\textsuperscript{524}. This is the same as lowering the effective concentration of the metal in solution, promoting the growth of large crystallites\textsuperscript{105}.

Other additions to the plating bath affect plating rate and film structure. The effect of formaldehyde (HCHO) addition to EP baths has been studied by Yeung et al. and the mechanism for its decomposition to formate ion has been studied by Bindra et al. and Horkans et al.\textsuperscript{441,567,620,625}. Formaldehyde oxidation is under kinetic control where the first step is dissociative adsorption into a carbon containing fragment and H\textsuperscript{+}\textsuperscript{441}. Formaldehyde acts as a moderator and produces smaller, more uniform grains. In excess it inhibits plating completely\textsuperscript{2,3}.

Accelerating agents (not to be confused with the step of acceleration and accelerators used during surface activation) such as carbonate compounds speed the plating process and act as secondary buffering agents\textsuperscript{582}. Boric acid has been used as a buffer and has the advantage of also acting as a homogeneous catalyst that lowers the overvoltage for deposition by complexing with the metal\textsuperscript{524}. Boric acid may also increase the nucleation density of the deposit\textsuperscript{626}. With its addition to an EDTA stabilized bath, many tiny nuclei form on the substrate that increase the nucleation density and coverage of the deposit. With TEA (triethanolamine) stabilized baths however, deposit density decreased.
2.5.4.4 Electroless Copper

EP of copper proceeds similarly to electroless Pd albeit with a different reducing agent (commonly formaldehyde, HCHO). Electroless copper has been studied much more extensively than electroless Pd because of its prominence in microcircuit fabrication. The same fundamental principles of surface activation and microstructural evolution with electroless copper generally apply to electroless Pd.

Electroless copper baths are routinely based on copper (II) sulfate ($\text{CuSO}_4 \cdot n\text{H}_2\text{O}$) as the metal source. Commonly used chelating agents include EDTA, and potassium sodium tartrate (Rochelle's salt, $\text{C}_4\text{H}_4\text{KNaO}_6$). These ligands form complexes with the copper (II) ions in solution. Formaldehyde is frequently the reducing agent although DMAB and sodium hypophosphite are also used. Other types of additives increase bath stability and improve wetting.

Deposition occurs by a "multistep catalytic redox mechanism." Copper is an excellent catalyst for formaldehyde oxidation and is much more active than Pd, although Pd does work. The catalytic surface primarily influences the rate of the anodic oxidation of the reducing agent. The overall deposition reaction proceeds when the anodic half reaction (oxidation of formaldehyde) provides the electrons necessary for reduction of the metal ion (the cathodic half reaction):

\[
\text{CuEDTA}^2- + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu}^0 + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{HCOO}^- + \text{EDTA}^4- \quad (2.17)
\]

proceeds when the anodic half reaction (oxidation of formaldehyde) provides the electrons necessary for reduction of the metal ion (the cathodic half reaction):

\[
\text{CH}_2\text{O} + 3\text{OH}^- \rightarrow \text{HCOO}^- + 2\text{H}_2\text{O} + 2e^- \quad \text{or} \quad (2.18)
\]

\[
\text{CH}_2\text{O} + 2\text{OH}^- \rightarrow \text{HCOO}^- + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2 + e^- \quad (2.19)
\]

While formaldehyde and hydroxide are consumed in the formation of methylene glycol anion, hydrogen is formed, the copper complex is reduced, and sulfate and sodium formate build up in the bath.

The pH is an important operating variable since hydroxide ion (OH\(^-\)) is a primary reactant so high pH's are required. A secondary influence of OH\(^-\) concentration is the effect of pH on formaldehyde oxidation. Formaldehyde is in the hydrated state at high pH as methylene glycol and methylene glycol anion:

\[
\text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2 \rightleftharpoons \text{CH}_2(\text{OH})\text{O}^- + \text{H}^+ \quad (2.20)
\]
Since hydrogen is a primary reactant, cleavage of the carbon-hydrogen bond in the adsorbed methylene glycol anion is the rate-determining step. The reaction was found to be first order in methylene glycol anion although diffusion to the substrate was rate limiting at low formaldehyde concentrations.

The stability of electroless copper plating baths is affected by several side reactions. The Cannizarro reaction results in loss of formaldehyde in the bulk solution, especially at high pH:

$$2HCHO + OH^- \rightarrow CH_2OH + HCOO^-,$$  \hspace{1cm} (2.21)

In addition, homogeneous decomposition of the bath can take place by the formation of copper and copper oxide particles that serve as nucleation sites for further breakdown:

$$2Cu^{2+} + HCHO + 5OH^- \rightarrow Cu_2O + HCOO^- + 3H_2O;$$  \hspace{1cm} (2.22)

$$Cu_2O + H_2O \rightarrow Cu + Cu^{2+} + 2OH^-.$$  \hspace{1cm} (2.23)

Dissolved oxygen supplied by aeration can prevent the disproportionation of copper (I) oxide,

$$Cu_2O + \frac{1}{2}O_2 + 2H_2O \rightarrow 2Cu^{2+} + 4OH^-,$$  \hspace{1cm} (2.24)

thus stabilizing the bath. Agitation of the solution during EP usually incorporates sufficient oxygen.

Dissolved oxygen also inhibits nodule formation. In addition to causing bath decomposition, extraneous foreign particles such as dust or copper oxides from decomposition of the solution become charged, settle on, and adhere to the plated surface and are incorporated into the deposit forming nodules. Filtration can trap these particles before they form nodules or cause bath decomposition. Filtration can also inhibit deposition on extraneous surfaces (plate-out).

Stabilizers prevent bath decomposition by adsorbing on extraneous particles in the solution and preventing them from growing larger. Heterocyclic amines such as 2,2'-dipyridyl complex with the copper (I) ions and prevent copper oxide formation because of the stability of the chelate.

Surfactant has the opposite effect of stabilizers, by lowering the interfacial tension and destabilizing the bath. The type and concentration of surfactant can also affect the texture or distribution of crystallographic orientations of the metal film, although entrapped surfactant molecules may have detrimental effects on film properties. Surfactant does
block hydrogen inclusion into the deposit and results in smoother deposits. Adsorbed hydrogen can result in void formation and blistered or discontinuous deposits.

2.5.4.5 Formation of Alloys

Although several researchers have performed electroless codeposition of silver and Pd, controlling the film composition is tricky. Pd–Ag films simultaneously deposited by an EP bath containing both Pd and silver were annealed at 673 K for 150 minutes to obtain an alloy film as confirmed by XRD analysis.

An alternative is to deposit the metals separately and then anneal at much higher temperature. To obtain an alloy film from two distinct metal layers in a reasonable amount of time, a high enough temperature must be utilized to promote complete intermetallic diffusion. Pd–Ag alloy films have been fabricated using such sequential deposition and annealing by several research groups. Pd–Ag films deposited by sequential electroless deposition require much higher temperatures (> 1073 K) to produce a homogeneous film.

2.5.5 Types of Supports

Minimizing use of Pd has been the driving force behind development of composite membrane configurations. A variety of deposition processes and supports have been used. The simplest technique involves compressing a Pd or Pd alloy foil onto a refractory metal foil or a macroporous support such as sintered stainless steel. The primary weakness of Pd/metal composites is that at above 673 K, intermetallic diffusion between the Pd and metal support lowers membrane permeability as the Pd layer diffuses from the surface into the bulk and loses its efficacy for hydrogen dissociation. The interface between the two metals can also offer resistance to hydrogen diffusion. These problems have been overcome by the incorporation of a thin layer (permeable to hydrogen) between the Pd film and the metal support that acts as an impediment to intermetallic diffusion. The other types of supports used in Pd composite membrane fabrication are outlined below.
2.5.5.1 Porous Supports

A common form of Pd composite membrane is a thin Pd film supported by a porous membrane. Ceramics, Vycor glass\(^{2,182,185,276,607}\) or stainless steel are commonly used. Each type of support has its economical and performance tradeoffs. Some advantages of stainless steel are its sturdiness and its ability to be welded. Alumina is resistant to chemical attack and stable at high temperatures.

Pd/ceramic composite membranes are the most prevalent composite due to high permeability, and the ability to withstand high temperatures. Both symmetric and asymmetric ceramic supports have been used\(^{289}\). The tubular geometry is most prevalent but disks are sometimes used. Asymmetric membranes are distinguished by a relatively thin selective layer of very small alumina particles coated on the inner diameter of the tube wall, which consists of much larger particles as shown in Figure 2.2. Mesoporous membranes with pores as small as 50 Å are commercially available. Asymmetric supports have much less resistance to flow since the fairly dense selective layer is very thin relative to the much more porous wall of the tube.

Asymmetric membranes are manufactured by coating the inner diameter of an extruded and fired highly porous support with successive dip-coatings or sol-gel layers of smaller and smaller particles. Curing and firing may be required between each deposition and special treatment processes are required to prevent cracking of the asymmetric layer. Whereas asymmetric membranes work well as supports for Pd membranes due to their smooth inner surface and low resistance to gas flow, the high cost of their multistep manufacturing process makes them relatively expensive compared to other porous supports. Consequently, asymmetric alumina membranes are an order-of-magnitude more expensive than symmetric supports.

Symmetric membranes have the same pore size throughout the wall (Figure 2.3) and are produced in one extrusion and firing sequence. Their much lower cost is the primary advantage of symmetric membranes. The major disadvantage of a symmetric support is its higher resistance to flow. GTC 998 symmetric α-alumina supports are extruded and fired once making them much less costly ($25/ft^2$) than comparable asymmetric ($2120/ft^2$) or stainless steel ($850/ft^2$) supports. They are designated 998 because the alumina is nominally 99.8% pure.
Figure 2.2 Cross-section of an asymmetric, $\alpha$-alumina U.S. Filter T-170 support. The macroporous support (left) has a nominal 12 $\mu$m pore size. The middle layer is $\sim$0.4 $\mu$m and the rightmost layer has a nominally 0.2 $\mu$m pore size. Scalebar 50 $\mu$m.

Figure 2.3 Cross-section of symmetric, $\alpha$-alumina GTC 998 support. Nominal 0.2 $\mu$m pore size. Scalebar is 50 $\mu$m.
Stainless steel supports are fabricated by compressing or sintering together very fine metal particles. The surface roughness of these supports is the limiting factor in obtaining a thin, non-porous Pd film. Although stainless steel based membranes would likely be sturdier and easier to seal (by welding) in an industrial setting than more fragile ceramic supports, their cost is midway between the symmetric and asymmetric ceramics. Table 2.2 offers a comparison of some commercially available porous membrane supports.


<table>
<thead>
<tr>
<th>Material</th>
<th>Suppliers of Porous Support Materials</th>
<th>Cost per Inside Area ($/ft²)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric, α-alumina</td>
<td>Golden Technologies Company, (GTC)</td>
<td>25</td>
<td>0.2 µm pore size</td>
</tr>
<tr>
<td>Symmetric, sintered SS</td>
<td>Mott Metallurgical</td>
<td>850</td>
<td>Small quantities, 0.2 µm</td>
</tr>
<tr>
<td>Asymmetric; α-alumina</td>
<td>U.S. Filter</td>
<td>460</td>
<td>&gt; 100 feet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2120</td>
<td>Small quantities, 0.2 µm</td>
</tr>
</tbody>
</table>

Porous stainless steel supports, with a thermal expansion coefficient close to Pd, are frequently used to form composite membranes. Jarosch et al. used porous Inconel as a support. An advantage of stainless steel is that its coefficient of thermal expansion is similar to that of Pd, leading to increased resistance to thermal cycling. Evidently, the smallest pore size available in a porous tube or disk is 0.5 µm.

It appears that stainless steel supports may require a thicker layer of Pd to form a pore free film than similar porous ceramic supports. This may be due to inherent manufacturing imperfections in the form of large pores or high surface roughness. Shu et al. found that the Mott support required at least 15 µm to form a dense, impervious film. More recently, Mardilovich et al. reported Pd film thicknesses between 20-30 µm on nominal 0.5 µm porous stainless steel supports.

Better results have been obtained on stainless steel supports by using osmotic plating (described above). Yeung et al. obtained a membrane with a hydrogen/nitrogen
selectivity of 100,000. This membrane withstood repeated thermal cycling between 623 and 873 K while membranes prepared using conventional EP did not. The thickness of this membrane was not reported. Li et al. deposited a 10 μm thick Pd film using osmotic plating that had a hydrogen/nitrogen selectivity of over 1000.

The average pore size of the stainless steel support can be reduced by mechanically altering its surface. Mardilovich et al. simply abraded the surface to accomplish this while Jemaa et al. used a special technique involving shot peening to accomplish surface pore size reduction of the stainless steel membrane, effectively creating an asymmetric membrane. Jarosch et al. electrodeposited nickel and copper onto a porous Inconel support to reduce the average pore size before electroless plating while Nam et al. decreased the average pore size of a stainless steel membrane by sintering nickel powder onto the surface and electrodepositing a copper layer before electrodeposition of Pd. This enabled the vacuum deposition of a much thinner hydrogen-selective Pd layer of less than 1 μm onto the stainless steel support. With mechanical and chemical treatments, care must be taken to avoid weakening the surface, adversely affecting film adhesion, or actually increasing the surface roughness and pore size of the membrane.

As with Pd on refractory metal supports, Pd on stainless steel also suffers from intermetallic diffusion. Although this appears to take place at higher temperatures (823-873 K), this is still a problem that must be overcome in order to achieve industrial-scale usage. Solutions to this problem are operating at lower temperatures or depositing a porous layer between the Pd and the stainless steel to halt intermetallic diffusion.

Two other less commonly used supports are porous Vycor glass and anodic alumina or Anodiscs (Whatman). These supports are useful for bench scale work to test membranes in principle. Vycor is comprised of silica glass with a fairly uniform 40 Å pore size. It was used in earlier studies to fabricate selective Pd composite membranes but sinters above 823 K causing pore structure collapse. Silica is also unstable under high temperature steam. Very small (200 Å), uniform and straight pores result from anodizing aluminum into alumina.
2.5.5.2 Nonporous Supports

Metals, ion-conducting solids, and polymers are classified as nonporous supports. The main benefit of a nonporous support is the ability to more easily fabricate a leak free membrane. Since the support is solid, a much thinner Pd layer can be used and discontinuities in the Pd layer will not result in defects. Advantages of metal supports include higher hydrogen permeabilities in the case of the refractory metals, and the ability to weld them into a module. Disadvantages often include low permeability in the case of ion-conducting materials such as metal oxides, and intermetallic diffusion of Pd into metallic supports at temperatures above ~673 K.47

A promising composite membrane configuration involves the deposition of a Pd layer (or foil) onto a nonporous base metal foil or tube. Many metals other than Pd are also quite permeable to hydrogen. Nickel permeates hydrogen but at a much slower rate than Pd, while relatively cheap (compared to Pd) refractory metals such as zirconium, niobium (Nb), vanadium, and tantalum are at least an order-of-magnitude more permeable to hydrogen than Pd. Often, refractory metal alloys are more resistant to hydrogen embrittlement as well. However, they are readily oxidized, inhibiting hydrogen dissolution into the bulk metal. A thin surface coating of Pd prevents passivation of the surface and acts as a superior catalyst for hydrogen dissociation into its atomic form. Unfortunately, the problem of intermetallic diffusion plagues this type of composite membrane as well.

Polymers are another class of nonporous support although they are subject to limitations in operating temperature. Metallized polymers have been fabricated for hydrogen separation. Athayde obtained a hydrogen/carbon monoxide separation factor of 100 with a polymer sputter coated with Pd.48

2.6 Prior Work

Pd films have been deposited via a wide variety of techniques. Although many researchers have used EP due to its low cost and simplicity, spray pyrolysis, CVD, physical vapor deposition (PVD) or sputtering, solvated metal atom or co-condensation deposition, and electrodeposition have been utilized for the fabrication of Pd composite membranes.
2.6.1 Electroless Plating

EP is a prevalent form of Pd composite membrane fabrication because of its simplicity and ability to produce good results. The Japanese researchers Konno et al., Hado et al., and Uemiya et al. were the first to create a composite membrane using EP\textsuperscript{185,186}. Many more since then have achieved varying degrees of success\textsuperscript{168,333,349,426,528,613,654,662,667-675}. Hsu and Buxbaum electrolessly deposited Pd onto zirconium to protect it from oxidation and facilitate hydrogen transport through it\textsuperscript{525}.

Huang et al. studied the permeability of 7 and 15 $\mu$m thick Pd films deposited by EP onto $\alpha$-alumina and supported $\gamma$-alumina supports.\textsuperscript{668} Zhao et al. used vacuum infiltration to plate Pd to a thickness of 1 $\mu$m onto a Pd-modified boehmite sol-gel layer\textsuperscript{613}. These membranes peeled during annealing in inert gas so membranes prepared in a batch mode were tested for permeability. The hydrogen/nitrogen ideal separation factor was 23 at a $\Delta$P of 1 atm and 723 K. The EP results of some other researchers has been incorporated into the discussions below.

2.6.2 Physical Vapor Deposition

Peachey et al. studied the purification of hydrogen through a Pd/Ta composite metal membrane\textsuperscript{53,54,648}. To remove the oxide layer before sputtering the foil was ion milled in the same chamber as the sputtering device\textsuperscript{47}. Removal of the oxide layer from both sides of the refractory metal was essential to reduce diffusion resistance through the membrane. The Pd layers increased the permeability of the bare metal foil by ten times. The hydrogen/helium ideal separation factor in their case was 50,000. This high value may be expected with a metal foil. The helium that did leak through probably permeated through grain boundaries or through the membrane seals.

2.6.3 Magnetron Sputtering

Basile fabricated a Pd/alumina membrane using this technique although it was not very permselective because it was deposited on the outside of a ceramic membrane with large pores. Xomeritakis and Lin, and Jayaraman and Lin have formed alloy membranes by this method (discussed below)\textsuperscript{319,676}. Jayaraman et al. sputtered Pd onto asymmetric $\gamma$-
alumina supports to a thickness of 500 nm. At larger thicknesses, intrinsic and interfacial shear stresses caused the film to delaminate. Bryden and Ying formed nanostructured Pd films on porous Vycor glass to obtain a membrane with higher permeability. Apparently they had problems with characterization due to pinholes and delamination.

2.6.4 Chemical Vapor Deposition

Yan et al. were the first to report the formation of a selective Pd composite membrane using CVD. Ward and coworkers formed Pd films using different metal-organic precursors reduced at the support surface in hydrogen gas. Their results were found to be sensitive to deposition temperature, as well as the specific metal-organic precursor.

Xomeritakis et al. have deposited Pd films onto asymmetric γ-alumina supports by counter-diffusion MOCVD. The films they obtained were quite thin (0.5-5 μm) and had some defects since some helium permeated by Knudsen and viscous flow mechanisms. Through counter-flow MOCVD, Pd was deposited within the porous support, potentially reducing problems with embrittlement.

Other researchers such as Meng et al. and Huang et al. have deposited Pd and Pd-alloy films onto asymmetric γ-alumina supports using MOCVD. Meng et al. found that Pd–Ni alloy films (4 μm thick) were more selective and crack-free than pure Pd. Deshpande et al. deposited Pd–Ag films onto γ-alumina (Anodisc) proceeded by sintering of the porous deposit. By using flow-through aerosol assisted CVD, they obtained a dense crystalline film approximately 1 μm thick although none of their films were entirely defect free.

Uemiya's group has demonstrated an important concept in the permeation of hydrogen through Pd membranes by depositing various metals onto porous alumina supports using MOCVD. By partially coating the inner surfaces of pores in alumina with different platinum group metals, they determined that selective surface diffusion of spillover hydrogen plays an important role in mass transfer through the microcracks of thin and discontinuous metal films, even at high temperatures. Other researchers have taken advantage of the high surface mobility of hydrogen on Pd and observed increased
hydrogen permselectivity (greater than Knudsen) through porous ceramic and glass membranes modified with metal particles or coated with sol-gel layers containing metal salts.

More recently, Jun and Lee deposited 2 µm of Pd by MOCVD onto porous stainless steel modified with nickel particles to reduce the pore size to around 0.05 µm. The film required annealing to increase its gas tightness although the Pd diffused into the nickel and iron if the membrane was held above 623 K. The hydrogen/nitrogen ideal separation factor was 1600 at 723 K.

The thin films deposited by CVD often have n values greater than 0.5 and closer to 1. This has been attributed to surface hydrogen dissociation effects becoming more influential in the permeation process. The increased resistance to permeation might be due to organics or other impurities trapped during the deposition process. This might explain the decreasing hydrogen permeability with decreasing grainsize of the CVD films prepared by Xomeritakis and Lin. In that case, contamination at the grain boundaries may have been inhibiting hydrogen permeation.

2.6.5 Other Methods

Other methods of metal film deposition have particular advantages. Electrodeposition can be easily and swiftly carried out on a conducting substrate. Spray pyrolysis and solvated metal atom deposition (SMAD) can be used to deposit thin films. Metal containing sol-gel layers may be deposited on macroporous supports to enhance hydrogen selectivity by blocking defects and facilitating hydrogen surface diffusion.

Amano et al. tested a 1.2 mm thick V–Ni alloy foil with a 0.2 µm coating of Pd deposited by pulse electroplating. Below 473 K, permeability was negatively affected by surface contamination, and cracks developed at 300 kPa of pressure on the feed side. Li et al. deposited a 1.5-2 µm Pd–Ag film by spray pyrolysis of Pd and silver nitrate in a H₂–O₂ flame. However, the ~2 µm thick Pd–Ag film contained defects and the hydrogen/nitrogen selectivity was 24 at 773 K.

Basile et al. prepared a solution of solvated Pd atoms by evaporating Pd and co-condensing it at low temperature in 1-hexene-mesitylene. SMAD of Pd was then carried
out by warming this solution in the lumen of the porous γ-alumina support to promote agglomeration of Pd on the surface. The resulting ~0.1 μm thick film initially had infinite hydrogen/nitrogen selectivity but was not stable for more than 42 h at 595 K. Barbieri et al. also prepared a 0.1 μm film on asymmetric γ-alumina using SMAD that was more selective than a 10 μm film deposited by EP. The originally higher selectivity of the SMAD membrane was attributed to the fact that the electroless film was deposited on the outer surface of a tube with larger pore size. However, the selectivity of the SMAD membrane was still rather low to begin with and declined further during methane steam reforming at 809 K.

2.6.6 Control of Film Microstructure

The importance of Pd film microstructure on composite membrane performance has been recognized and studied by other researchers in the field. Their work has focused on methods of substrate activation and film deposition to control grainsize, adhesion, and film porosity. In turn, these characteristics determine membrane durability, selectivity, and hydrogen permeability.

Shu et al. recognized that film delamination was related to stress in the film caused by the difference in thermal expansion coefficient between the substrate and Pd. They sought to mitigate this problem by first conducting EP with a bath that produced a more porous, stress absorbing, and well anchored layer followed by a more dense, selective layer of Pd. Jayaraman et al. found that films deposited by magnetron sputtering at room temperature peeled from the surface of the porous γ-alumina support at thicknesses greater than 300 nm. In electrodeposition, stress decreases with increasing grainsize and the tensile stress is greatest when the film becomes continuous.

Using pulsed electrodeposition and magnetron sputtering, Bryden and Ying have deposited nanocrystalline Pd and Pd–iron (Fe) films with higher permeability because of a higher percentage of grain boundaries. By alloying Pd with either iron or yttrium they have lowered the critical temperature for the α → β phase transition and also increased the operating temperature where undesirable grain growth occurs in membranes fabricated from these materials.
2.6.7 Pd Alloy Membranes

Preparation of Pd alloys has been accomplished in the past by casting and rolling or induction melting followed by cold working into a foil222,296,389,689. More recent work has involved the use of EP to make Pd alloy membranes with silver98,171,180,333, copper171,182, and gold6. Techniques for codeposition have been developed333,690, although successive single-metal EP depositions followed by annealing are more common due to better alloy composition control98,171,182,333,334,632.

To obtain a homogenous alloy film, various researchers have used differing thermal treatment conditions for sequentially deposited metal films. Shu et al. annealed a codeposited Pd–Ag film for 150 minutes at 673 K and a sequentially deposited Pd–Ag film for 5 hours at 973 K333, while Kikuchi annealed a sequentially deposited Pd–Cu film between 573 and 813 K and a Pd–Ag film between 1073 and 1573 K171,631. Sakai et al., and Kawae et al. annealed Pd–Ag at 1173 K for 2, and 12 hours respectively633,674. However, it seems that from the more recent work of Uemiya that even higher temperatures may be required to achieve homogeneity throughout the film cross-section. In particular, temperatures above the so-called Tamman temperature \(0.5T_m\) where \(T_m\) = melting point of the lower melting point component are necessary, where significant lattice migration can occur691.

Most Pd–Cu alloy membrane work has been carried out using foils (25 \(\mu\)m thick or greater)107,109,293. Apparently, the only group to fabricate Pd–Cu alloy films on porous supports by electroless deposition of Pd and then copper with subsequent annealing was Kikuchi et al.171,182. They annealed under argon at 773 K for 12 hours to form the alloy.

PVD and CVD have also been used to form alloy membranes371. Meng et al. used counter-diffusion CVD to deposit crack-free Pd–Ni films onto porous alumina371. It has been suggested that the effects of hydrogen embrittlement may be reduced or avoided by deposition within the porous support matrix282,680. Schwartz et al. attempted unsuccessfully to create leak-free Pd–Ru alloy films on porous alumina using CVD of Pd and ruthenium acetylacetonates412.

Xomeritakis and Lin, and Jayaraman and Lin deposited Pd–Ag films onto asymmetric \(\gamma\)-alumina supports (3 nm pores) using magnetron sputtering319,676. The ~0.4 \(\mu\)m films densified upon heating to 573 K and exhibited moderate hydrogen/helium
selectivity (> 20). Keeping the substrate at a high enough temperature was found to improve adhesion. Increased hydrogen permeance was observed at larger grainsizes. Another observation they made was that the beginning surface roughness of the support was a key parameter in obtaining a defect free and adherent membrane. One difficulty with PVD is obtaining the desired alloy composition due to differing sputtering yields from an alloy target. This can be overcome by allowing the target surface to reach equilibrium.

Bryden and Ying have experimented with nanocrystalline Pd–Y and Pd–Fe alloys deposited by pulsed electrodeposition and magnetron sputtering. These alloys have better properties than pure Pd with regard to formation of the β-Pd hydride, resistance to hydrogen sulfide poisoning, and increased permeability. Even though PdYg (atom%) is 3.65 times as permeable as PdAg23 (at 573 K and a pressure differential of 689.5 kPa) it was found to be susceptible to surface contamination. The addition of iron and yttrium to Pd stabilized against grain growth so that the higher permeability of the nanostructured alloy material could be maintained at higher temperatures.

2.6.8 Permeability

Before a membrane can be tested for permeability, it must be sealed into a permeation apparatus. This is often one of the most difficult aspects of membrane technology. With metal foils, tubes and stainless steel composite membranes, brazing or welding are easy sealing options. Often, soft metal (such as copper) gaskets are used to seal flat membranes into a permeation cell. With brittle ceramic composite membranes however, trickier solutions are required.

Obtaining a gas tight seal at high temperatures and pressures with interfaces between metals and porous ceramics is nontrivial. Graphite o-rings, ferrules, or gaskets are often employed due to their softness and high temperature resistance. With graphite, operation in an oxidizing atmosphere up to 723 K is permissible. Operation in reducing conditions up to much higher temperatures is possible.

Alternative membrane sealing methods include cermets or ceramic–metal technology. Here, the porous ceramic support is infiltrated with a metal/metal-oxide that strengthens the ceramic and permits brazing to a metal fitting. It is important to obtain
good adhesion or wetting\textsuperscript{695-698} between the metal and ceramic as well as pay attention to the coefficients of thermal expansion of the cermet and the metal fitting. With alumina, cohesion is obtained through interfacial compounds such as Cu/Cu$_2$O/CuAlO$_2$\textsuperscript{694}.

2.6.9 Membrane Stability

The stability and hydrogen permeability of the Pd film and support determine membrane performance and usefulness. For reactions such as methane steam reforming, operation of the membrane at high temperatures (> 823 K) is required. Loss of selectivity towards hydrogen at high temperature has been a problem with composite membranes on both porous ceramic and stainless steel (SS) supports, particularly under dehydrogenation conditions\textsuperscript{246,249,412,657,677}. Decomposition of the membrane is greatly accelerated by coking at temperatures above about 800 K\textsuperscript{246,249,412}.

In the absence of reaction, simultaneous decline in hydrogen flux and increase in the flux of other gases was often observed at temperatures above about 823 K\textsuperscript{657}. While the precise mechanism for this phenomenon has not been elucidated, Yan et al. described it as sintering of the Pd grains\textsuperscript{677}. At or below 673 K, Pd composite membranes seem to be indefinitely stable. However, the ability to withstand temperature cycling is virtually nonexistent with pure Pd films. Alloys are necessary to lower the $\alpha \rightarrow \beta$ phase transition to prevent film warping and destruction.

On porous stainless steel, decrease in hydrogen flux at and above 823 K has been attributed to intermetallic diffusion of constituents from the stainless steel into the Pd film\textsuperscript{657}. Pd deposited onto hydrogen permeable dense metal supports (like vanadium) begins to significantly diffuse at around 673 K\textsuperscript{44,635,638}. One solution to this problem is to deposit a hydrogen permeable barrier between the Pd film and the metal support to inhibit intermetallic diffusion\textsuperscript{334,635,638,640}. Coating the surface of the stainless steel with titanium nitride prior to coating with Pd has also been effective\textsuperscript{334}.

Preparation methods have a strong influence on membrane characteristics. Yeung et al. invented the technique of forming Pd films under an osmotic pressure gradient where EP solution and a much more concentrated solution are on opposite sides of the activated porous support\textsuperscript{1-5}. They have shown that imposing an osmotic pressure gradient in the direction of diffusion mass transfer during EP can provide several benefits including
smaller grainsize, reduction in porosity, and densification of the plated film. Asymmetric 0.2 \( \mu m \) \( \alpha \)-alumina (U.S. Filter T-170), Vycor glass\(^2\), and 0.2 \( \mu m \) sintered stainless steel microfilters (Mott Metallurgical\(^4\)) were used as supports for the Pd composite membranes. It was claimed that Pd membranes prepared using this "osmotic plating" were stable while those prepared conventionally loss selectivity after repeated thermal cycling to 873 K.

2.7 Pd Membrane Reactors

Hydrogen is an essential feedstock in the refining and chemical industries. The chief source of hydrogen is from steam reforming of light hydrocarbons\(^699\). This is used for alcohol synthesis, ammonia production, hydrocracking, hydrotreating, and Fischer-Tropsch synthesis. In a Pd membrane reactor (PMR), thermodynamically equilibrium limited hydrogenation or dehydrogenation reactions can be driven towards the product side by addition or removal of hydrogen from the reactor\(^700,701\). This translates into higher per pass conversion, higher selectivity, a smaller recycle stream, and fewer downstream separations\(^136\). Research on membrane reactors has been summarized in several thorough review articles\(^10,12,27-33,289,701,702\) and the number of studies reported in the literature is impressive.

Unmodified commercially available mesoporous membranes are often selective enough to significantly increase equilibrium-limited reaction conversion\(^140,589,703-708\). However, when permselectivity is determined by Knudsen diffusion, reactant loss to the permeate side can defeat the purpose of the membrane reactor to achieve greater than equilibrium yields\(^709\). A hydrogen permselective PMR may be used to keep two streams of different phases separate. Thus a PMR can alleviate the necessity of separating the catalyst from the product in the case of liquid phase hydrogenations such as in the production of food-grade oils\(^12\).

The PMR may also couple or conjugate reactions where the hydrogen for a hydrogenation is supplied by a dehydrogenation on the opposite side of the membrane\(^88-97,710\). This has been termed a bifunctional Pd membrane reactor\(^710\). Since hydrogenations are generally exothermic, this would supply the heat required by the dehydrogenation. Another way that heat can be supplied by a dehydrogenation is by combusting the generated hydrogen with air on the other side of the membrane\(^147,163,711-713\). Reaction
driven transport is more effective since the driving force for permeation is increased by making the partial pressure of hydrogen close to zero on the permeate side. Many different Pd alloys are used to catalyze specific chemical reactions, although packing a specialized catalyst within the PMR usually augments the relatively low surface area of the membrane itself. Despite such a large volume of work on Pd membrane reactors, they have seen little industrial use.

Certain molecules in a mixture can be selectively hydrogenated in a PMR such as hydrocarbons with higher bond order such as acetylene, ring structures, or those containing sulfur. This phenomenon is explained by the fact that less saturated molecules more easily donate electrons and adsorption transpires with a transfer of electron density to the metal. Molecules preferentially adsorbed on the surface of the Pd film are hydrogenated by atomic hydrogen permeating through the membrane.

Selective adsorption can be advantageous in the production of specialty chemicals where hydrogenation of a valuable feedstock with high selectivity is desired. In addition to conserving chemicals and lowering downstream separation requirements, fewer unwanted byproducts require disposal. Pd membrane technology has the potential to carry out hydrodesulfurization more efficiently or remove acetylene from process streams more efficiently than present technology. Of course a key issue is membrane resistance to fouling by sulfur or polymerization.

Hydrogen permeated through a Pd membrane is also more reactive than molecular hydrogen in the gas phase. In fact, bringing hydrogen into the reaction space through the membrane can multiply the reaction rate relative to feeding hydrogen with the reactant mixture. This is because permeated hydrogen is in a more reactive atomic form or because it prevents the adsorption of species that block reactive sites.

A Pd membrane may be retrofitted to an existing process to increase its efficiency. This ability to augment existing equipment is a major advantage of membrane technology. By connecting a bank of Pd membranes ex-situ between two reactors, it would serve as an interstage hydrogen remover to increase yield in the second reactor. Operating the membrane apart from the reaction zone may also reduce membrane coking.

Since permeability of hydrogen through Pd is inversely proportional to film thickness (see section 2.2.1), the thinner the Pd film the faster the reaction can proceed.
with many thermodynamically equilibrium limited reactions. By minimizing Pd film thickness, higher rates of conversion can be attained. The Pd and Pd alloy foils used in the past were at least twice as thick as the film in a typical Pd composite membrane. A sweep gas can also increase reaction rate by decreasing the hydrogen partial pressure on the permeate side, increasing the hydrogen permeation rate through the membrane. Of course the use of a sweep gas necessitates another separation step.

Adsorption of impurities as well as changes in surface chemical composition due to surface segregation of alloying elements may alter the permeability and catalytic properties of the Pd membrane. Fortunately, when hydrogen is permeated and reacted on a metal film, the permeation rate has a strong influence on preventing the formation of surface compounds that diminish permeability. Once formed however, surface impurities can severely limit flux as described above. Although PMR's have been operated commercially for the production of fine chemicals, there are particular issues associated with PMR operation that still need to be addressed. For instance, the use of existing industrial catalysts may be troublesome due to the different pressure, temperature, and compositional conditions found in the membrane reactor. Catalysts that are not active enough may even limit PMR performance. Conversely, a membrane that is too thick may not have a high enough flux to reach the full potential of the catalyst.

Another problem is that in conventional reactors the presence of hydrogen often prevents carbon buildup and its removal through the membrane results in coking of the catalyst and membrane surface, especially during exposure to unsaturated hydrocarbons. Such carbonaceous and graphitic coatings decrease membrane permeability and may also destroy the Pd film. The mechanism for this is unclear although carbon is known to be able to diffuse into the Pd lattice. Even though the presence of steam in the reactor feed can help lessen this problem, special tuning of catalysts may be required for optimal membrane reactor performance. Steam or air have been reported to attack at the grain boundaries of PdAg (atom%) membranes but there is limited information in the literature about this phenomenon.
2.8 Future of the Technology

As Pd composite membrane films continue to get thinner and thinner, several problems remain. The problem of embrittlement due to the formation of Pd–hydrides can be overcome by the use of alloy membranes. However, the problem of coking (and other contamination) during reactions remains, as does the need to fabricate an extremely thin film in order to decrease capital outlay for an industrial module. Despite these difficulties, the potential for energy savings by the use of Pd composite membranes for hydrogen separation and reaction warrants continued research towards a workable form of the technology\textsuperscript{31}. 
3.1 Introduction

Pd composite membranes were fabricated using porous alumina and stainless steel supports using EP. This chapter describes the experimental details of support preparation, Pd deposition, characterization of the composite membranes by high temperature flux testing, and subsequent morphological and chemical analysis.

3.2 Support Specifications

Tubular, porous alumina microfilters with nominal 0.2 μm pore size, were procured from Golden Technologies Company (GTC, Golden, Colorado). Designated GTC 998, these tubes have an OD of 9 mm, an ID of 6.1 mm, and are fabricated from 99.8% pure α-alumina. Figure 3.1 is an SEM micrograph of the membrane surface. Porous, symmetric stainless steel (type 316) tubes with a pore size of approximately 0.2 μm were procured from Mott Metallurgical Corp. (Farmington, Connecticut). Asymmetric GTC tubes were also plated with Pd. These membranes had a nominal 0.2-0.5 μm pore size in the selective layer supported on a highly porous tube with nominal 12 μm pore size.

Membralox T-170 asymmetric alumina membranes (U.S. Filter Corp., Warrendale, Pennsylvania) with 200 nm pore diameter in the selective layer consist of two sol-gel coatings of α-alumina particles on a highly porous alumina support. The support tube is composed of larger alumina particles with a nominal 12 μm pore size. The layers on top of that, known as gutter layers, reduce the pore size so that the topmost thin and selective layer can be smoothly deposited without pinholes. Other asymmetric membranes used in this work had nominal 100, 50 and 5 nm (50 Å) pore sizes. This γ-alumina selective layer is coated on the inner diameter (lumen) of the tube on top of the two gutter layers with pore sizes of 0.2 and 0.4 μm on the same type of macroporous support with ~12 μm pore size. Cross-sections of these alumina membranes are displayed in Figures 2.2 and 2.3.
3.3 Substrate Preparation

Some of the GTC998 tubes were not quite round by visual inspection. These were rejected because they invariably cracked when attempts were made to seal them into the fittings for high temperature testing. Slightly off-camber tubes worked fine as long as they were perfectly round. It was almost impossible to make them round by glazing. Selected support tubes were cut to 5 or 25 cm lengths with a diamond saw, sequentially cleaned and rinsed ultrasonically in solutions of Alconox detergent, acetic acid, hot water, and 2-propanol\textsuperscript{168}. Table 3.1 lists the cleaning schedule and solution concentrations\textsuperscript{6,734}.

After cleaning, the ends of the ceramic tubes were sealed with one of the following high temperature glazes; (a) Aremco-Seal 617 (Aremco Products, Inc., Ossining, N.Y.), fired at 1145 K for 15 minutes, or (b) Nippon Denki Glass sealing powder GA-13, fired at 1523 K for 60 minutes. When glazing, it was important to paint on an even coating. If the glaze appeared discontinuous or lopsided after firing, it was touched up and refired. Too much glaze tended to globulate during firing.

Stainless steel membranes were ultrasonically cleaned in isopropanol. The ends were either welded to SS Swagelok tube fittings or infiltrated with silver solder to seal the pores.
Table 3.1 Substrate Cleaning Procedure.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Solution Composition</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ultrasonic rinse</td>
<td>deionized water</td>
<td>5 minutes</td>
</tr>
<tr>
<td>ultrasonic alkaline rinse</td>
<td>0.25 g Alconox and 10 mL NH₄OH (28 weight% ammonia) in 500 mL H₂O</td>
<td>5 minutes</td>
</tr>
<tr>
<td>rinse</td>
<td>deionized water</td>
<td>1 minute</td>
</tr>
<tr>
<td>soak</td>
<td>25 weight% acetic acid</td>
<td>5 minutes</td>
</tr>
<tr>
<td>ultrasonic rinse</td>
<td>deionized water</td>
<td>3 minutes</td>
</tr>
<tr>
<td>ultrasonic rinse, repeat</td>
<td>deionized water at 333 K</td>
<td>1 minute</td>
</tr>
<tr>
<td>ultrasonic rinse</td>
<td>isopropanol</td>
<td>5 minutes</td>
</tr>
</tbody>
</table>

3.4 Tin and Pd Chloride Activation

The first activation procedure consisted of immersion for five minutes in an acidic SnCl₂/SnCl₄ ("full strength" sensitizing) bath followed by five minutes in an acidic PdCl₂ (activation) bath with rinsing in deionized water between baths. Rinsing prevented drag out (transfer of activator or sensitizer into the plating bath) which caused precipitation of Pd metal particles. Wrapping the outside of the tube with PTFE tape permitted only the inside surface to be activated and plated. Table 3.2 lists the solution compositions⁶,⁷³⁴.

Table 3.2 Sensitizing and Activating Solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Constituent</th>
<th>Amount</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizer</td>
<td>H₂O</td>
<td>96.25 mL</td>
<td>periodically agitate</td>
</tr>
<tr>
<td></td>
<td>Aged 0.1 M SnCl₄</td>
<td>8.25 mL</td>
<td>to keep homogeneous</td>
</tr>
<tr>
<td></td>
<td>2.6 M acidic SnCl₂</td>
<td>5.5 mL</td>
<td>use fresh solution</td>
</tr>
<tr>
<td>Activator</td>
<td>37 weight% HCl</td>
<td>5 mL</td>
<td>PdCl₂ (99.9% pure) takes several hours to dissolve</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>995 mL</td>
<td>Indefinite shelf life</td>
</tr>
<tr>
<td></td>
<td>PdCl₂</td>
<td>0.267 g</td>
<td></td>
</tr>
<tr>
<td>Aged 0.1 M SnCl₄</td>
<td>SnCl₂•5H₂O</td>
<td>20.9 g</td>
<td>may polymerize and precipitate with time⁵⁵⁰</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>1 L</td>
<td></td>
</tr>
<tr>
<td>2.6 M acidic SnCl₂</td>
<td>SnCl₂•2H₂O</td>
<td>58.7 g</td>
<td>indefinite shelf life</td>
</tr>
<tr>
<td></td>
<td>37 weight% HCl</td>
<td>78 mL</td>
<td></td>
</tr>
</tbody>
</table>
The same activation cycle described above was carried out using full strength tin sensitizer diluted a hundred times ("1/100 strength"). Another technique called acceleration involved soaking the sensitized (full strength tin sensitizer) and activated membrane in 1:1 hydrochloric acid (1 part 37 weight% HCl in 1 part water) for 3 minutes\(^{178,552,573}\). Following a water rinse, the sensitizing-activation-acceleration cycle was repeated to ensure uniform activation. Once the membrane was evenly activated it was immediately transferred into the plating solution (after thorough rinsing) to prevent drying and oxidation that would have diminished the reactivity of the activated surface.

### 3.5 Pd Acetate Activation

Dr. John Collins developed this technique at Sandia National Laboratory, Albuquerque, New Mexico\(^ {412}\). The membranes were soaked in a 0.05 M Pd acetate solution in chloroform for 3 minutes and allowed to dry. Organics were removed by heating up to 673 K under nitrogen followed by a ramp to 723 K at 1 K per minute under air. After a nitrogen purge, hydrogen was flowed for a couple of hours and the tubes were furnace cooled.

For the new procedure, the outside of the ceramic support was wrapped in PTFE tape, then the tube was dip-coated for 3 minutes in a 0.05-0.2 M solution of Pd acetate in chloroform, dried, calcined at 673 K and hydrotreated at 723 K\(^ {412,587}\). The heating scheme consisted of a ramp to 673 K under nitrogen, air exposure during ramp to 723 K, nitrogen purge (for safety), followed by a 2 hour soak and cooling under flowing hydrogen. The heat treatment schedule that was used is shown in Figure 3.2. The membranes were metallic gray after this treatment process.

Stainless steel membranes were activated with either a sulfuric-acid pickle (100% H\(_2\)SO\(_4\) at 353 K for 60 s), or the conventional tin/Pd chloride activation process. The membranes were then rinsed with deionized water immediately followed by immersion in the EP bath. The membranes were plated using the standard electroless Pd process.
Following surface activation, the membranes were plated with Pd using the electroless plating recipe listed in Table 3.3. The ammonia based electroless plating bath used PdCl₂ as the metal source and hydrazine (N₂H₄) as the reducing agent. The membrane was wrapped with PTFE tape and placed in a 20-mL glass vial containing 18 ml of plating solution. The 1.0 M hydrazine solution was added at this time (0.25 ml). The cap was screwed on loosely to allow gaseous products of the plating reaction to escape and the vial was partially submerged in a constant temperature bath maintained at 345 K. For most of the membranes, the plating solution was changed every hour. The PTFE or vial was replaced if Pd had deposited on either of them during the plating cycle. While plating some membranes, hydrazine was added incrementally to compensate for decomposition and more effectively utilize the Pd.

During plating in the continuous "flow system", the membranes were submerged in 6.0 M sucrose solution (Figure 3.3). A Masterflex peristaltic pump (Cole Parmer...
Table 3.3 Electroless Pd Plating Bath

<table>
<thead>
<tr>
<th>Solution</th>
<th>Constituent</th>
<th>Amount</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating bath</td>
<td>Na₂EDTA</td>
<td>1.75 g</td>
<td>plating begins with hydrazine addition</td>
</tr>
<tr>
<td></td>
<td>Pd-ammine complex</td>
<td>25 mL</td>
<td>Indefinite shelf life without hydrazine</td>
</tr>
<tr>
<td></td>
<td>1.0 M N₂H₄</td>
<td>0.25 mL</td>
<td></td>
</tr>
<tr>
<td>1.0 M N₂H₄</td>
<td>35 weight% hydrazine, N₂H₄</td>
<td>10 g</td>
<td>handle with great care</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>99.5 mL</td>
<td></td>
</tr>
<tr>
<td>Pd-ammine complex</td>
<td>PdCl₂ stock solution</td>
<td>1000 mL</td>
<td>let sit for a few days and filter</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>120 mL</td>
<td>indefinite shelf life</td>
</tr>
<tr>
<td></td>
<td>NH₄OH</td>
<td>715 mL</td>
<td></td>
</tr>
<tr>
<td>PdCl₂ stock solution</td>
<td>deionized water</td>
<td>980 mL</td>
<td>let sit for several hours to dissolve</td>
</tr>
<tr>
<td></td>
<td>37 weight% HCl</td>
<td>20 mL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PdCl₂</td>
<td>10 g</td>
<td>99.9% pure</td>
</tr>
</tbody>
</table>
• Construct apparatus in hood or very well ventilated area.

• Ceramic tubes must be activated prior to plating.

• Gaseous NH₃ produced by plating reaction.

• Reducing agent, N₂H₄, is toxic.

Figure 3.3 Schematic of Flow System.
Instrument Co., Vernon Hills, IL) was used to circulate the solution through the tube lumen while PTFE or nylon compression fittings and PTFE tape were used to attach the membrane to food-grade plastic Tygon tubing. Five times the plating bath volume and hydrazine was used for plating cycles of one hour. The direction of solution flow was reversed periodically and the solution was replaced hourly with warm deionized water rinsing between cycles. Volume of plating solution depended on plating duration and the number of membranes being plated.

A hot plate/magnetic stirrer and Erlenmeyer flask were used to maintain the plating bath temperature at a constant value, usually between 328 and 345 K in the flow system. The lower temperature helped to prevent Pd from plating out on the plastic tubing. The tubing was replaced if Pd was present. Temperature was measured frequently with a PTFE wrapped Omega Type K thermocouple. Up to two 25-cm membranes at a time were plated in series as shown in Figure 3.3. After plating with either method, the membranes were rinsed, soaked for several hours to overnight in 340 K water (to remove sucrose, plating solution, and other impurities), rinsed, dried at 353 K, and weighed. The Pd film thickness was estimated by dividing the weight difference between the plated and unplated membrane by the plated surface area and density of Pd (11.96 g/cm³). SEM images were also used to estimate film thickness.

3.7 Electroless Copper

Since immersion of copper metal in electroless Pd plating solution resulted in the displacement plating of Pd, Pd was plated first followed by electroless copper. Thus, the predeposited Pd catalyzed the decomposition of formaldehyde to initiate electroless copper plating. The electroless copper baths used to make membranes are reported in Table 3.4. Plating was carried out after wrapping the membrane in PTFE tape, cleaning it, and attaching it to a PTFE compression fitting using either PTFE tape or a rubber o-ring. The open end of the tube was placed in the electroless plating solution in a beaker suspended in a constant temperature bath. The solution was circulated through the tube lumen using a peristaltic pump. Osmotic plating was also conducted. Post-plating procedures were the same as for Pd. The preparation details for each membrane are given in Chapter 6.
Table 3.4 Electroless Copper Plating Baths.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Constituent</th>
<th>Concentration</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Plating Bath 1(^{449})</td>
<td>CuSO(_4)·5H(_2)O</td>
<td>0.04 M</td>
<td>9.9872 g/L</td>
</tr>
<tr>
<td></td>
<td>Na(_2)EDTA</td>
<td>0.08</td>
<td>29.776 g/L</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde (37%)</td>
<td>0.04</td>
<td>3.003 mL/L</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>pH=12.5</td>
<td></td>
</tr>
<tr>
<td>Cu Plating Bath 2(^{457})</td>
<td>CuSO(_4)·5H(_2)O</td>
<td>0.04</td>
<td>9.9872 g/L</td>
</tr>
<tr>
<td></td>
<td>Na(_2)EDTA</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Formaldehyde (37%)</td>
<td>0.04</td>
<td>3.003 mL/L</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>pH=12.5</td>
<td></td>
</tr>
<tr>
<td>(surfactant)</td>
<td>Triton X-100</td>
<td></td>
<td>50 mg/L</td>
</tr>
<tr>
<td>(stabilizer)</td>
<td>2,2-bipyridyl</td>
<td></td>
<td>10 mg/L</td>
</tr>
<tr>
<td>Cu Plating Bath 3(^{456})</td>
<td>CuSO(_4)</td>
<td>0.025</td>
<td>6.225 g/L</td>
</tr>
<tr>
<td></td>
<td>CuSO(_4)·5H(_2)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na(_2)EDTA</td>
<td>0.054</td>
<td>20.0988 g/L</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde (37%)</td>
<td>0.187</td>
<td>14.039 mL/L</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>0.50</td>
<td>20 g/L</td>
</tr>
<tr>
<td></td>
<td>Triton X-100</td>
<td></td>
<td>25 mg/L</td>
</tr>
<tr>
<td></td>
<td>2,2-bipyridyl</td>
<td></td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Cu Plating Bath 4(^{478})</td>
<td>CuSO(_4)·5H(_2)O</td>
<td></td>
<td>7.8218 g/L</td>
</tr>
<tr>
<td></td>
<td>Na(_2)EDTA</td>
<td>0.08</td>
<td>40 g/L</td>
</tr>
<tr>
<td></td>
<td>Glycine</td>
<td>0.02</td>
<td>5 g/L</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>pH=12.4</td>
<td>16 g/L</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde (37%)</td>
<td>0.187</td>
<td>16 mL/L</td>
</tr>
<tr>
<td>(surfactant)</td>
<td>Triton X-100</td>
<td></td>
<td>50 mg/L</td>
</tr>
<tr>
<td>(stabilizer)</td>
<td>2,2-bipyridyl</td>
<td></td>
<td>10 mg/L</td>
</tr>
</tbody>
</table>
3.8 High Temperature Testing Procedures

Membrane characterization experiments began with an ambient (room) temperature leak test conducted with nitrogen, followed by high temperature gas permeation experiments conducted with hydrogen, nitrogen, and helium. To perform high temperature tests for thermal stability and permeability, the membranes were carefully sealed into stainless steel Swagelok fittings with graphite ferrules. Breakage was avoided (by learning the hard way) by tightening the fitting incrementally and frequent leak checking at ambient temperature. This was performed by pressurizing the membrane lumen with nitrogen at 689.5 kPa and submersion in an alcohol/water mixture to check for leaks from the membrane or end seals. Alcohol has a lower surface tension than water, enabling the detection of pores at lower pressure\(^{735}\). This revealed leakage from the graphite seals or the membrane. If the former were observed, the compression fittings were carefully tightened with intermittent leak checking until there were no leaks from the fittings. If very few or no bubbles emerged from the membrane (less than a couple of cm\(^3/\)min), it was tested at high temperature.

If the membrane had very few or no leaks it was loaded into a stainless steel tube and centered in a furnace. Single gas permeability tests were conducted at transmembrane pressure differentials up to 689.5 kPa using hydrogen, nitrogen and helium between 673 and 1023 K. The system for measuring gas permeation is shown in Figure 3.4. A type K thermocouple centered within the inner diameter of the membrane measured temperature. The membrane was centered in the furnace inside a 2.54 or 3.81-cm OD stainless steel or dense alumina shell sealed with PTFE ferrules and stainless steel compression fittings.

Brooks mass flow controllers metered gas flow or it was controlled manually with a needle valve. All gases were nominally 99.999% pure (UHP grade) and were used without further purification. Permeate pressure (shell side) was local atmospheric pressure (~83 kPa). Gas flowrates were measured using bubble flowmeters. These values were converted to STP and pure gas fluxes were calculated.

Since the ferrules used to seal the stainless steel shell were made of PTFE to facilitate loading and unloading the membrane, copper tubing was wound around the fitting and cooling water was circulated using a peristaltic pump. Otherwise the ferrules softened
Figure 3.4 System for permeation experiments.
and could leak. Stainless steel ferrules were used on the 2.54 cm tube to alleviate this problem.

The membrane was heated (and cooled) at 1 K/min. under helium purge. To avoid embrittlement of the Pd film, hydrogen was not introduced until 623 K, well above the critical temperature for the $\alpha \rightarrow \beta$ phase transition. Before continuing the permeation tests, some membranes were exposed to flowing air at 623, 673 or 723 K for 30 minutes between 207-690 kPa to activate the Pd surface and facilitate removal of impurities or carbonaceous material. Some membranes were deliberately not treated with air to see if any high temperature stability problems resulted.

No sweep gas was used on the permeate side during the permeation experiments. With the 1.5" ID stainless steel shell, it took several minutes to reach an equilibrium flowrate. The sweep side was purged with helium after testing with hydrogen, otherwise back-permeation of hydrogen to the tube side through the membrane resulted in a negative flux for a period of time.

Data was collected by taking two or three measurements of the pure gas flowrate within a several minute time period at a given pressure and averaging the values. For example, three nitrogen flowrate data points collected within a five minute timeframe had values of 13.1, 13.0, and 12.9 cm$^3$/min. The average of these three data points was obviously 13.0 cm$^3$/min while the standard deviation was 0.1 cm$^3$/min. (0.8% of the mean). Small deviations were typically observed with the flow measurements.

Upon completion of high temperature permeability tests, the membrane was cooled at 1 K/min. under inert gas. Final measurements of inert gas flux through the membrane were then made at room temperature. After removal of the membrane from the permeation apparatus, it was visually inspected to determine if leaks originated from the membrane or the fittings by performing another ambient temperature leak test under isopropanol/water.

The first Pd–Cu alloy membrane was sectioned and heat treated at 773 and 873 K for 12 hours under flowing helium. SEM, EDX and XRD were then performed. Further Pd–Cu alloy membranes were heat treated in-situ to observe the influence of temperature on intermetallic diffusion and permeability.
3.9 Membrane Analysis

The tested membranes were broken and scanning electron microscopy (SEM) was used to study film morphology and estimate Pd film thickness. To determine the presence and atomic compositions of contaminants, energy dispersive analysis of X-rays and Auger electron spectroscopy were used for elemental analysis. Grain size was calculated using the Scherrer equation and X-ray diffraction data.

3.9.1 Scanning Electron Microscopy

Specimens were prepared by attaching samples to metal buttons with carbon paint or tape and loaded into the vacuum chamber (SEM, JEOL 840). Specimens were made conducting by coating with gold or carbon. The film morphology was observed by scanning over large portions of the film surface and cross-section at both low and high magnifications. Film thicknesses were obtained by averaging measurements made from several micrographs taken at different locations.

3.9.2 Energy-Dispersive X-Ray Analysis

Samples were the same as those for SEM but coated with carbon instead of gold for elemental analysis (Noran 5500).

3.9.3 Auger Electron Spectroscopy

Samples were prepared using gloves to avoid contamination, secured to the sample holder and loaded into the apparatus (Perkin-Elmer PHI 600 Scanning Auger Multiprobe). The beam voltage was 5.0 kV. Ion milling was conducted by introducing argon into a relatively high pressure region in which it is ionized by collisions with electrons. At an electron emission current of 25 mA, an argon pressure of $5 \times 10^3$ Pa, and an acceleration potential of 3 kV, the removal rate is ~75 Å/min. It should be noted that without standards, the error in the atomic compositions could be as high as 20%, hence the terminology semi-quantitative was used to describe the results.
3.9.4 X-Ray Diffraction

X-ray diffraction (XRD) was conducted using a Rigaku model RU-200 diffractometer with a 1° graphite divergence slit. The x-ray beam was filtered with a graphite crystal monochromater to obtain Cu_Kα radiation. Pd film samples were mounted on glass slides using double sided tape. Care was taken to flatten the films as much as possible. Scanning was typically conducted over the angular range from 20 to 90° 2θ to sample the first five Bragg peaks (111-222). A step size of 0.02° and count time of 2 or 4 seconds per step were used.

Materials Data Inc. (MDI) software was used to convert the data for plotting and determination of peak widths at half-maximum intensity. The data was further analyzed using PeakFit software (Jandel Scientific) to more accurately calculate peak areas and peak widths at half maximum intensity. This involved fitting a curve to the data and separating out the Cu_Kα2 peak when possible. All of the peaks were fit with a superposition of Pearson functions in which the width parameters of the peaks in the separated sub-pattern were forced to be shared.

X-ray line broadening analysis (XLBA) was used to estimate grainsize (t). This technique derives from the Scherrer equation and is applicable up to t of ~100 nm:

\[ t = \frac{K\lambda}{\beta_\text{r} \cos \theta} \]  

(3.1)

Here, the constant K was taken as 0.9, θ is the Bragg angle in radians, and for Cu_Kα radiation the wavelength, λ, is 1.54056 Å. The integral pure diffraction broadening, β_r, was derived from the experimental peak width (breadth) B, and the instrumental broadening, b:

\[ \beta_\text{r} = (B^2 - b^2)^{1/2} \]  

(3.2)

For this particular instrument, b varies according to the line width calibration curve determined by using a well-crystallized National Institute of Standards (NIST) LaB₆ standard. When the Cu_Kα₁ and Cu_Kα₂ peaks were combined as was the case at lower values of 2θ, the value of b was taken as 0.17. At higher values of 2θ, the value of b was determined from the calibration curve. The first five Pd peaks were used to calculate t, and the results averaged to obtain the final value. Alloy compositions were calculated assuming a linear variation in d-spacing shift with composition. See Appendix B for a sample
calculation.

3.10 Safety Procedures

Some important safety measures were undertaken to avoid exposure to toxic chemicals and to prevent explosions. The EP solutions are highly toxic, containing chemicals that are corrosive, carcinogenic, and mutagenic. Hydrazine, formaldehyde, chloroform and aqua regia are particularly noxious. The harmful effects of Pd compounds may not even be fully known. Therefore, gloves and safety goggles were worn at all times during chemical handling. All work was conducted in the fume hood as well. When electroless plating was carried out in the ventilated explosion room, the EP solutions were transferred in the fume hood and tightly capped before carrying them to the explosion room. A nylon tube attached to the rubber stopper transported fumes from the Erlenmeyer flask directly to the vent.

Hydrogen is a very explosive gas and great care was taken in its use. Air and hydrogen were never mixed in the membrane at high temperature. This was ensured by keeping a constant flow through the membrane with pressure on the tube side and at least a few cubic centimeters of flow per minute. When the air purge was conducted, an inert gas purge was conducted for several minutes before and after. Unless necessary, hydrogen was not run overnight through the membrane and the bottle was checked to be sure that hydrogen did not run out unattended. An electronic or liquid leak detector was used to detect the escape of any flammable gases from the permeation apparatus.

The permeation apparatus was constructed of stainless steel because of its durability. Quartz would be optimal from a contamination standpoint, but it has the potential of breaking and releasing hydrogen at high temperature inside the furnace. Because of the PTFE ferrules in the stainless steel Swagelok fittings on the ends of the shell side permeate collecting tube, care was taken not to pressurize it to more than a couple of atmospheres. This prevented the ends from blowing off, especially above 423 K where the PTFE tended to soften. Stainless steel ferrules were used on the 2.5 cm permeation tube.
4.1 Membrane Preparation Methods

Every step in the fabrication of the membrane can be important to its final quality and attention to detail is critical. Typically, researchers have used asymmetric macroporous ceramic membranes as supports while we have primarily utilized cheaper, symmetric membranes obtained from Golden Technologies Company, Inc. (GTC, Golden, Colorado). Symmetric porous alumina supports were chosen for study because they are significantly cheaper to produce than asymmetric supports. However, symmetric supports have the disadvantage of higher resistance to flow. Therefore, membranes fabricated with GTC 998 supports generally had lower fluxes in comparison to Pd composite membranes on porous asymmetric supports\textsuperscript{168,412}.

The non-conducting alumina substrates were sensitized with tin chloride solution followed by activation with PdCl\textsubscript{2} solution in order to seed the inner membrane surface with Pd nuclei. The sequence sensitization, activation, acceleration was repeated until the ceramic (or stainless steel) substrate is uniformly activated. This was determined qualitatively by observing the uniformity in color of the substrate. After one or two sensitization/activation cycles, the GTC alumina tubes turned uniformly dark brown inside. In an attempt to reduce the amount of tin chloride used in the sensitizing step, the sensitizer was diluted 100 times. After several sensitizing-activating-rinsing cycles, the inner surface of the ceramic membrane appeared light brown or cream colored instead of dark brown.

Although both the T-170 and GTC 998 tubes were fabricated with \(\alpha\)-alumina, a distinct difference in the appearance of the two surfaces was observed after the sensitizing/activation procedure. The T-170 tubes took several cycles (at least 4) to acquire a uniformly colored surface moderately dark brown in color. In contrast, after one or two sensitization/activation cycles the GTC 998 tubes turned uniformly dark black. This
difference in appearance was thought to qualitatively be related to the amount of tin present among the Pd on the surface. We have observed that over a few months the sensitizer made from the aged 0.1 M SnCl₄ solution (see Chapter 2, p. 27) became less potent, although both types of supports have been sensitized and activated simultaneously for comparison to eliminate this variable.

The asymmetric Membralox supports also appeared brown inside, but not as dark as the symmetric GTC 998 tubes after the same number of activation cycles. Differences in ease of activation may be due to slightly different chemical properties of the inner surfaces between the symmetric and asymmetric supports. Different surface chemistry may be due to the presence of various constituents in the alumina such as silica. By using sensitizing solution diluted a hundred times, the GTC 998 tubes also reach a light tan color close to the appearance of the T-170 tubes after one or two steps using full strength tin sensitizer.

Another technique called acceleration to remove the tin after the sensitization/activation sequence before EP has been used to fabricate membranes. More specifically, a chemical solution such as HCl, NaOH, or EDTA that will complex the tin away from the palladium-tin alloy on the substrate is used. Acceleration was also used to reduce the amount of tin left on the ceramic before EP. In this procedure, an acid, base or complexant such as EDTA removes excess tin or tin chlorohydroxide from the catalyzed surface. Supposedly, this removes the tin layer and leaves clusters of Pd nuclei for initiation of EP. During acceleration, a black material was seen to dissolve away, leaving the surface shiny and metallic in appearance. After treatment with 1:1 HCl, the inner surface of the GTC 998 tube was a silver/gray color.

Elimination of tin entirely from the plating process was accomplished by activating with Pd acetate. The tubes appeared brownish-gray after activation using the Pd-acetate technique. EP was then performed as before. The membranes described in this chapter were all plated using the batch system. Typical Pd film morphologies are shown in the SEM micrographs of Figure 4.1.

A porous stainless steel tube prepared using a sulfuric-acid strike (100% H₂SO₄ at 353 K for 60 s) and rinsed became coated with Pd black upon plating. In fact, we were unable to make any of stainless steel membranes leak-free even after depositing up to 20 μm Pd. To enhance wetting of the stainless steel (and hopefully increase adhesion of the Pd film), a surfactant solution containing phosphoric acid was used to clean another
Figure 4.1 SEM micrographs of some surfaces and cross sections of Pd films deposited onto GTC 998 supports using the batch system. (a-d) Surfaces. (e-f) Cross sections.
stainless steel tube. However, the deposited Pd film was not less porous. Previously, it has taken 20 hours of EP to obtain an impervious film on stainless steel\cite{333}. Our efforts to duplicate the Pd/stainless steel composite membrane results of other researchers have been unsuccessful, possibly due to our substrate preparation techniques or plating methods. The irregular particle size of the substrate makes it difficult to obtain a continuous film with less than 20 μm of Pd without modifying the surface of the support\cite{658}. This may be due to inherent manufacturing defects in the form of large pores since the technology has not been able to produce less than a nominal 0.2 μm pore size.

Only a few Pd composite membranes were fabricated using the asymmetric US Filter membranes as well. The high temperature test results were not very reliable because of poor selectivity and/or leaks in the shell side of the permeation apparatus. Comparisons are made below to the performance of Pd composite membranes on asymmetric US Filter supports prepared by Collins et al.\cite{168,246,412,734} This work focused primarily on fabricating Pd composite membranes using the GTC 998 supports.

Many EP baths have been utilized; ours was chosen to maximize plating rate and bath stability. Plating was conducted between 313-348 K. Higher temperature or the addition of too much hydrazine resulted in spontaneous bath decomposition and Pd plating out on the walls of the bath container, tubing and PTFE, as well as the formation of very finely divided Pd particles. At our usual plating temperature of 345 K the reaction was fairly rapid, close to being unstable.

4.2 Characterization

In our experiments, the traditional method of calculating Pd film thickness by the weight difference before and after plating, overestimated thickness. Even though membranes were soaked in hot deionized water after plating, plating solution may have remained trapped in the pores of the ceramic support. Sometimes, large Pd nodules (several times the film thickness) that formed on the films contributed to weight gain without constituting a significant part of the film itself, resulting in calculated thicknesses greater than the actual, effective thickness. It is possible that particles in the electroless bath contributed to nodule formation\cite{477}.
Therefore, scanning electron microscope (SEM) micrographs of the film cross-section were used for more accurate estimates of thickness. Values were obtained by averaging measurements made from several micrographs taken at different locations. The thickness values reported in this paper were determined in this manner, although thicknesses calculated by weight difference are listed in Table 4 where the results for all membranes tested are summarized. The standard deviations are included. From the statistical analysis, it is apparent that there was a considerable amount of deviation in the thickness values obtained by SEM measurements (up to 55% of the measured value but usually around plus or minus 25%).

In an effort to quantify the elements remaining after activation, the porous alumina supports were activated by the various methods involving tin chloride and the ceramic was analyzed before EP. As expected, amount of tin varied according to preparation technique as shown in Figure 4.2, a graphical representation of the semi-quantitative EDX results (atom%). Since EDX does not detect oxygen, the atomic compositions were normalized by calculating the amount of oxygen with the assumption that all of the aluminum was in the form of alumina. A Pd/Sn ratio of 0.4 was found on the surface. This result was comparable to the findings of Kim et al., who measured a Pd/Sn ratio of 1.5 (with chlorine also present) at the interface between the substrate and an electroless copper deposit. EDX analysis of a tin and Pd chloride activated 0.2 μm asymmetric US Filter tube indicated the presence of 0.8 atom% Pd, 2.5% tin, 37% aluminum, (55% oxygen), 2.0% chlorine, and 3.0% sodium.

From our data, chlorine was present on the alumina surface. For comparison to a membrane electrolessly plated and then tested at high temperature, the Pd film was peeled from the ceramic support of Membrane 1 (analysis of the Pd film is discussed below), and the alumina was analyzed (Figure 4.2). This membrane was prepared using full strength tin sensitizer and tested up to 823 K for 12 days. No chlorine was detected by EDX. It was either removed during electroless plating or driven off during high temperature testing. Also, there was less tin on this ceramic surface presumably because it diffused into the Pd film during the high temperature permeation test, or it was on the alumina particles stuck to the Pd film when it was peeled off.

Furnace permeation tests were used to characterize the membranes for permeability, selectivity, and stability at high temperatures by measuring single-gas fluxes and
Table 4. Membrane Specifications.

<table>
<thead>
<tr>
<th>Sensitizing Technique</th>
<th>No.</th>
<th>Calculated Thickness</th>
<th>SEM Est. Thickness</th>
<th>Flux Data</th>
<th>Air purge</th>
<th>H Flux at 723 K*</th>
<th>Selectivity at 723 K*</th>
<th>SEM Images</th>
<th>Heated to (K)</th>
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<tr>
<td>Full-strength</td>
<td>6.8 μm</td>
<td>3.1 μm ±0.4 μm</td>
<td>Fig. 4.3</td>
<td>Yes</td>
<td>0.125 mol/m²s</td>
<td>5</td>
<td>Fig. 4.4</td>
<td>873 K</td>
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</tr>
<tr>
<td>Full-strength</td>
<td>9.3</td>
<td>9.4 ±3.7</td>
<td>Fig. 4.3</td>
<td>Yes</td>
<td>0.114</td>
<td>12</td>
<td>Fig. 4.5</td>
<td>823</td>
<td></td>
</tr>
<tr>
<td>Full-strength</td>
<td>10.3</td>
<td>7.9 ±1.7</td>
<td>Fig. 4.3</td>
<td>Yes</td>
<td>0.0947</td>
<td>39</td>
<td>Fig. 4.6</td>
<td>823</td>
<td></td>
</tr>
<tr>
<td>Full-strength</td>
<td>14.1</td>
<td>11.3 ±6.2</td>
<td>Fig. 4.3</td>
<td>Yes</td>
<td>0.148</td>
<td>∞</td>
<td>Fig. 4.6</td>
<td>823</td>
<td></td>
</tr>
<tr>
<td>Full-strength 1</td>
<td>19.6</td>
<td>16.7 ±7.3</td>
<td>Fig. 4.7</td>
<td>Yes</td>
<td>0.188</td>
<td>34</td>
<td>Fig. 4.8</td>
<td>823</td>
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<tr>
<td>1/100-strength 2</td>
<td>19.3</td>
<td>16.4 ±3.3</td>
<td>Fig. 4.9</td>
<td>Yes</td>
<td>0.153</td>
<td>200</td>
<td>Fig. 4.10</td>
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<td>1/100-strength 3</td>
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<td>26.8 ±7.6</td>
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<td>73</td>
<td>Fig. 4.12</td>
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<td>Accelerated 4</td>
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<td>Fig. 4.13</td>
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<td>51</td>
<td>Fig. 4.14</td>
<td>873</td>
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<td>Pd acetate 5</td>
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<td>Fig. 4.15</td>
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<td>Not meas.</td>
<td>9.3 ±4.9</td>
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<td>Fig. 4.19</td>
<td>873</td>
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<tr>
<td>Pd acetate 7</td>
<td>23.9</td>
<td>21.1 ±4.0</td>
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<td>40</td>
<td>Fig. 4.21</td>
<td>1023</td>
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*ΔP = 689.5 kPa, selectivity = hydrogen flux/nitrogen flux. Selectivities for Membranes 1-4 obtained by linear interpolation between values at 673 and 773 K.
Figure 4.2 EDX results showing amounts of Sn, Pd and chlorine remaining on the substrate after preparation for electroless plating. Included for comparison are the results for the substrate of Membrane 5 (prepared using full strength Sn sensitizer), after plating with Pd and permeation testing up to 823 K.
hydrogen/nitrogen pure gas separation factors. Dependence of flux on pressure drop was
determined to help quantify the resistance of the porous symmetric support through a
transport model of the supported film. Gas permeabilities and hydrogen/nitrogen ideal
selectivities (ratio of pure gas permeabilities) were determined in experiments conducted
with single gases. More precisely, the term ideal separation factor ($\alpha_{\text{ideal}}$) or permeability
ratio (permselectivity) should be used, but for the sake of brevity, selectivity will be
defined as the hydrogen to nitrogen flux ratio\(^2\):

$$\alpha_{\text{ideal}} = \frac{F_H}{F_N}$$

(4.1)

A sweep gas was not used because in industry, it makes the membrane process less
attractive by necessitating another separation step. Although the use of vacuum would
appear to enhance the performance of a membrane process as well, this is generally not
feasible in the industrial setting either\(^3\).

Membranes were well characterized during high temperature flux tests to determine
their permeability, selectivity and stability. Table 4 consists of a compilation of the high
temperature test results. The results of prior work on symmetric GTC 998 supports are
included for comparison (the first four full-strength membranes\(^6\). In prior work using
symmetric GTC 998 supports, test conditions were held constant to determine the influence
of thickness on flux and selectivity at high temperature\(^6\). These membranes were prepared
using the full strength tin sensitizer and Pd chloride activation sequence followed by EP.
Pd film thicknesses varied between 3 and 11 $\mu$m (as measured from SEM micrographs).
Hydrogen and nitrogen flux data for these membranes as a function of temperature and time
online are shown in Figures 4.3-6.

The graphs clearly illustrate some important trends in the data. Hydrogen flux
through the membrane rose with each increase in temperature up to 823 K, while nitrogen
flux generally increased with both time and temperature. Also, the hydrogen flux
decreased with increasing membrane thickness, as expected since hydrogen flux should be
inversely proportional to Pd film thickness. It is not readily apparent upon comparison of
the data, but the thicker the membrane, the greater the ratio of hydrogen to nitrogen flux or
selectivity.

In addition, regardless of membrane thickness, the nitrogen flux at 823 K increased
significantly with time resulting in a loss of selectivity. It is important to note that the
percent increase in nitrogen flux at 823 K was greater for the thicker membranes even
Figure 4.3 Flux data for membrane prepared using full strength tin sensitizer. $\Delta P = 689.5 \text{ kPa}$. Pd film thickness $\approx 3 \text{ \textmu m}$. 
Figure 4.4 Flux data for membrane prepared using full strength tin sensitizer. ΔP = 689.5 kPa. Pd film thickness = 9 μm.
Figure 4.5 Flux data for membrane prepared using full strength tin sensitizer. $\Delta P = 689.5$ kPa. Pd film thickness $= 8 \mu$m.
Figure 4.6 Flux data for membrane prepared using full strength tin sensitizer. $\Delta P = 689.5$ kPa. Pd film thickness $\approx 11 \mu m$. 
though the final selectivity was also higher for these membranes. Thus, the mechanism leading to a decline in membrane performance is occurring in both membranes with relatively thin Pd films as well as those with thicker films. The fact that hydrogen flux for the 8-μm thick membrane was less than that for the 11-μm thick membrane may be due to surface contamination. Hydrogen permeation through Pd is quite sensitive to adsorbed impurities.

The 3 μm thick membrane (Figure 4.3) experienced a drop in both hydrogen and nitrogen flux at 873 K. This may have been due to morphological changes in the Pd film in the form of grain boundary loss or the closure of microvoid channels left over from electroless plating, restricting pathways for gaseous diffusion. The nitrogen flux continued to increase however, even upon cooling to lower temperature (673 K).

SEM micrographs taken of the Pd films after testing showed annealing or sintering of the surface and the formation of pores or holes (Figures 4.7-4.9). These simultaneous processes resulted in loss of permeability to hydrogen that was not offset by its increased diffusion through pores. This can explain the tendency for the nitrogen permeation rate to increase, even as the hydrogen flux leveled off or declined. Yan et al., have observed this phenomenon on a thinner (~2 μm) Pd membrane on α-alumina prepared by MOCVD. When this membrane was cycled between 273 and 773 K, the concurrent increase in nitrogen flux and decrease in hydrogen flux was attributed to sintering of the Pd grains. Xomeritakis and Lin suggested that Pd film densification was the result of the elimination of intercrystalline space at higher temperatures.

The results for these four membranes served as a jumping off point for continued investigations into the mechanisms for selectivity decline and pore formation. Four more membranes were fabricated similarly and tested. However, the high temperature flux data contained too much variability due to leaks from either the membrane end seals or the shell side of the permeation apparatus. Therefore this data was not particularly useful and was discarded.

Once experience had been gained with the testing procedures and data could be collected without unexplained fluctuations, insight could be gained into the mechanisms influencing high temperature behavior. Figure 4.10 displays hydrogen and nitrogen flux data versus time for Membrane 1, prepared using the full strength tin sensitizer and Pd chloride activation sequence. This membrane had a Pd film thickness of 17 μm (as
Figure 4.7 SEM micrographs of membrane prepared using full strength tin sensitizer and tested up to 873 K. Pd film thickness ≈ 3 μm.
Figure 4.8 SEM micrographs of membrane prepared using full strength tin sensitizer and tested up to 823 K. Pd film thickness = 8 μm. (a) Surface. (b-c) Cross sections of Pd film on porous alumina support. (d) Cross section of Pd film with alumina particles adhering to its underside.
Figure 4.9 SEM micrographs of two different membranes prepared using full strength tin sensitizer and tested up to 823 K. (a-b) Surface and cross section. Pd film thickness ≈ 9 μm. The white particles in (a) are probably alumina debris from when the membrane was fractured for analysis. (c-d) Surface and cross section. Pd film thickness ≈ 11 μm.
Figure 4.10 Flux data for Membrane 1, prepared using full strength tin sensitizer. $\Delta P = 689.5$ kPa. Pd film thickness = 17 $\mu$m.
estimated from SEM micrographs). It was held at each temperature (723, 773, and 823 K) to observe what effect, if any time had on performance. The steady increase and leveling off in hydrogen flux during the first couple days of membrane testing, as seen on the graph, is believed to be caused by the removal of contaminants by the permeating hydrogen\textsuperscript{211}. The membrane was held at 723 and 773 K for about two weeks and one week respectively in order to determine if pores would form at these temperatures.

Whereas at 723 and 773 K the hydrogen and nitrogen fluxes reached steady-state values without pore formation, after a few days at 823 K the hydrogen flux increased only slightly while nitrogen flux increased steadily. The membrane essentially failed at this temperature when the separation factor fell to around the Knudsen level, indicating dominance of the Knudsen separation mechanism through pinholes in the Pd film or leaks in the graphite ferrules. The membrane was cooled at 1 K/min., removed from the furnace, and leak checked under isopropanol/water using nitrogen at 7 atm. Many bubbles were observed over the entire surface indicating leaks from the Pd film instead of the graphite seals. SEM micrographs (Figure 4.11) revealed pores in the film. Sintering of the surface occurred compared to the unheated film displayed in Figure 4.1.

Other researchers have observed pinhole formation in Pd membranes, however, this was associated with operation in hydrocarbon streams\textsuperscript{246,249,412}. Several composite membranes prepared on asymmetric 0.2 μm Membralox T-170 α-alumina supports using tin chloride activation experienced defect formation within twelve hours of operation at 798 K\textsuperscript{246,412}. The reason given for the failure of these membranes was that carbon deposited during propane dehydrogenation experiments (particularly from the cracking of propylene) diffused into the films, causing stress and forming holes. A control experiment was conducted by heating a membrane under hydrogen or inert gas up to 848 K\textsuperscript{739}. No degradation of the membrane or loss of permselectivity was observed, so it is expected that this particular mechanism of chemical degradation due to carbon deposition was not a factor during testing of the GTC alumina based membranes of our present study.

Prior work with Pd membranes on T-170 supports has demonstrated that they also exhibit a loss in selectivity during operation between 773 and 873 K\textsuperscript{168,734}. The membranes were prepared using full strength tin sensitizer and EP using the same solution compositions as in our study. Pd film thicknesses ranged between 11 and 19 μm. Heating from 773 to 823, or 823 to 873 K resulted in a decrease in hydrogen/nitrogen and
Figure 4.11  SEM micrographs of Membrane 1 (prepared using full strength tin sensitizor) after testing up to 823 K. Pd film thickness = 17 μm. (a-b) Pd film morphology. (c) Close-up of pore. (d) Cross-section of Pd film on ceramic support. Notice voids.
hydrogen/helium selectivity. Loss in hydrogen/nitrogen selectivity ranged from around 10% up to 50%. Complete membrane failure was not observed because time on line was generally less than a few days.

We postulated that tin was enhancing morphological change of the Pd films at high temperature, causing the formation of pores that reduced the selectivity. Further efforts focussed on reducing and eliminating tin from the membrane preparation procedures and conducting high temperature tests to study the performance of these membranes. Membrane 2, prepared using sensitizer diluted 100 times ("1/100 strength"), behaved similarly to the membranes prepared using full strength tin sensitizer. It had a Pd film thickness of 16 µm and the selectivity dropped to around the Knudsen level at 873 K (Figure 4.12). Pores formed in this membrane as well as visible in Figure 4.13.

Another membrane (No. 3) was prepared using 1/100 strength sensitizer except the Pd film was about twice as thick (27 µm). The selectivity decreased from around 70 at 773 K, to about 25 at 823 K with the rise in nitrogen flux as shown in Figure 4.14. However, instead of falling after increasing the temperature to 873 K, the selectivity stayed above 25 for a week. It did not drop to Knudsen selectivity, presumably because of its relatively thick Pd film.

Some other features of the graph of the results for Membrane 3 are worthy of more detailed explanation. For example, the steady state hydrogen flux increased with increasing temperature as was expected since hydrogen permeation through Pd increases exponentially with temperature. However, at 873 K, hydrogen flux decreased after the initial increase. This was most likely due to annealing, resulting in a loss of Pd surface area for hydrogen dissociation and subsequent permeation. After only a few days at 923 K, upon returning to 823 K the hydrogen flux was reduced to almost half of its previous value at this temperature.

SEM micrographs (Figure 4.15) confirmed that the surface morphology had changed compared to the unheated state. Notice that the surface has become smoother compared to the rough, cauliflower-like appearance of a typical, unheated Pd film (Figure 4.1). The cracks seen may have been an artifact of cooling too fast since the final selectivity was approximately 40 prior to cooling. Typically the membranes are heated and cooled at the rate of 1 K/min. In this case, the furnace was shut off and allowed to cool faster. Actually, during cooling in any manner the thin Pd film may develop defects that
Figure 4.12 Flux data for Membrane 2, prepared using 1/100 strength tin sensitizer. $\Delta P = 689.5$ kPa. Pd film thickness $= 16$ $\mu$m.
Figure 4.13  SEM micrographs of Membrane 2, prepared using 1/100 strength tin sensitizer and tested up to 823 K. Pd film thickness = 16 μm. (a) Surface of Pd film. (b-c) Cross sections.
Figure 4.14 Flux data for Membrane 3, prepared 1/100 strength Sn sensitizer. ΔP = 689.5 kPa. Pd film thickness ≈ 27 μm.
render the membrane useless due to the $\alpha \rightarrow \beta$ phase transition or differences in thermal expansion coefficient between Pd and the support.

A similar reduction in hydrogen flux at high temperature was observed by Mardilovich et al. who attributed loss of hydrogen flux to metallic interdiffusion between the Pd film and the porous stainless steel support. Changes in the structure of the Pd layer was another reason given by Mardilovich for the decrease in hydrogen flux. They experimented with 19-28 $\mu$m thick Pd films tested at 50 K intervals between 623 and 973 K for 5 hours at each temperature. At 823 K and above, hydrogen flux declined while nitrogen flux increased.

Figure 4.15 SEM micrographs of Membrane 3, prepared using 1/100 strength tin sensitizer and tested up to 923 K. Pd film thickness $\approx 27 \mu$m. (a) Surface of Pd film. (b) Cross-section.

Although interdiffusion may have reduced hydrogen flux in their case through the formation of less permeable compounds between Pd and the stainless steel support, our work suggests that another effect (such as rearrangement of the Pd film) also influences the decrease in hydrogen flux since alumina and Pd do not interact at these temperatures. Yeung et al. found that exposure of a Pd/SS composite membrane to ethane
dehydrogenation at 773 K resulted in a loss of hydrogen permeability. In this case it was not clear if this was a chemical effect or the result of metallic interdiffusion.

Other possible explanations for the annealing effect include the formation of Pd oxides or other compounds due to impurities in the test gases or the formation of less permeable Pd-Sn compounds at the Pd/ceramic interface. Below 923 K, oxygen can chemisorb on Pd. Antoniazzi et al. found that impurities such as sulfur may segregate from the bulk metal, particularly at high temperatures, to block surface adsorption sites and lower hydrogen permeability by impeding the entry and exit of hydrogen. However, tin could have the same effect, especially if it was in the oxidized state. The only impurities other than tin (except for carbon) detected during EDX and AES analysis of the membrane films were nitrogen and chlorine (between 1 and 6 atom%). These were likely remnants from the EP bath. Alternatively, annealing of the film could be closing off avenues for hydrogen permeation or surface diffusion along microcracks and grain boundaries. The nitrogen flux through Membrane 3 decreased after treatment at 923 K, supporting the latter hypothesis.

Membrane 4 was prepared using acceleration in the sensitizing and activating process and had a film thickness of 15 μm. Once again, the selectivity decreased noticeably at 823 K (by about 25%, from 46 to 34) and appreciably at 873 K (from 34 to 20, or 40%). Figure 4.16 demonstrates that reducing the temperature to 723 K after four days of operation at 873 K resulted in a recovery of the level of flux originally obtained at 723 K and that the increase in nitrogen flux was arrested. SEM revealed some pores on the surface (Figure 4.17).

The EDX data (Figure 4.2) suggest that degree of membrane failure may be correlated to the amount of tin on the ceramic support. For example, membranes prepared using full strength tin chloride sensitizer, experienced a drop in selectivity (increase in nitrogen flux) at 823 K while membranes prepared using 1/100 strength tin solution or acceleration exhibited less severe decline in selectivity, and failed at higher temperatures.

AES analysis confirmed that tin had diffused into the Pd film at the Pd/alumina interface of Membrane 1 (prepared using full strength tin sensitizer and tested up to 823 K). The film was peeled off of the ceramic, and after removing the ubiquitous carbon layer by sputtering away ~240 Å, the atomic composition was 89.7% Pd, 1.9% tin, 1% oxygen,
Figure 4.16 Flux data for Membrane 4, prepared using acceleration. ΔP = 689.5 kPa. Pd film thickness ≈ 15 μm.

Figure 4.17 SEM micrographs of Membrane 4, prepared using acceleration and tested up to 873 K. Pd film thickness ≈ 15 μm. (a) Surface of Pd film. (b) Cross section.
1.4% chlorine, 5.7% nitrogen with a trace of carbon. Sputtering another ~200 nm into the film, the composition was 98.3% Pd and 1.6% tin.

Also, there is a definite correlation between Pd film thickness and film stability. For membranes around 10 μm in thickness or less, significant microstructural change of the Pd surface was observed after 3 days at 823 K as the films became smoother and openings formed. From SEM micrographs (Figures 4.7-4.9), the Pd had annealed extensively and numerous pores were visible.

Membranes of greater thickness also experienced textural changes of the Pd film surface and reductions in selectivity were observed. The particular pores seen in Figures 4.11 and 4.13 may not have extended to the ceramic support but indicate that some mechanism was acting to increase the porosity of the film via the formation of channels or holes. Dwell time at 823 K also affected the degree of selectivity decline. However, all membranes prepared using full strength or 1/100 tin chloride sensitizer and held at 823 K for more than several days failed to some extent, with the magnitude of selectivity drop depending on the film thickness.

Using the Pd acetate technique to activate the surface prior to EP produced membranes with greater stability and less selectivity loss at temperatures above 823 K. Figure 4.18 displays the results for Membrane 5, plated to a film thickness of 10 μm. Nitrogen flux remained fairly constant during a week at 823 K, corresponding to a selectivity of 56. Upon cooling to lower temperatures, the hydrogen fluxes at 773 and 723 K were higher than they were prior to treatment at 823 K, indicating that significant structural changes in the Pd film did not take place. The SEM micrographs (Figure 4.19) show the surface morphology with some pores visible. These pores probably did not extend throughout the film since the nitrogen leak rate remained constant. The cross-sections show large nodules that were formed during EP.

The results for Membrane 6 (approximately 9 μm thick) are plotted in Figure 4.20. From the plot, hydrogen flux dropped and nitrogen flux increased at 873 K, which caused an 18% drop in selectivity, from 57 to 47. The original flux was not restored upon returning to 823 K, probably due to annealing of the Pd film as discussed above. Treatment with air at this time (see Figure 4.20) did not restore the original permeability. The membrane performed well considering how long it was at high temperature (12 days) and the thickness of the Pd film.
Figure 4.18 Flux data for Membrane 5, prepared using Pd acetate. $\Delta P = 689.5 \text{kPa}$. Pd film thickness $= 10 \mu m$. \[ \text{Hydrogen Flux (mol/m}^2\text{s)} \]

\[ \text{Nitrogen Flux (mol/m}^2\text{s)} \]
Figure 4.19 SEM micrographs of Membrane 5 prepared using Pd acetate and tested up to 823 K. Pd film thickness = 10 μm. (a-b) Surface. (c-d) Cross sections of Pd film on porous alumina support.
Figure 4.20 Flux data for Membrane 6, prepared using Pd acetate. $\Delta P = 689.5 \text{ kPa}$. Pd film thickness $\approx 9 \mu\text{m}$. 

![Graph showing flux data for Membrane 6, prepared using Pd acetate.](image-url)
It was observed that after permeation tests with nitrogen the hydrogen flux was reduced considerably. Figure 4.21 displays data points illustrating the recovery of hydrogen flux after running nitrogen. The SEM micrographs revealed a smooth relatively pore-free surface (Figure 4.22). Evidently some annealing of the surface had occurred that explained the observed reduction in hydrogen flux after going from 873 to 823 K (see Figure 4.20).

A thicker membrane prepared using Pd acetate possessed excellent stability. Membrane 7 was approximately 21 µm thick and exhibited stable nitrogen flux up to 1023 K as shown in Figure 4.23. The annealing effect is also clearly seen with this membrane and appears to be expedited at higher temperatures along with loss of hydrogen permeability. Nitrogen flux slowly increased at 1023 K, concurrently with a decrease in hydrogen flux. Then, as the membrane failed, hydrogen flux increased as nitrogen flux increased rapidly.

However, upon cooling to lower temperatures the nitrogen flux through Membrane 7 dropped and at 723 was lower than any previous value for this membrane. Hydrogen flux dropped as well since the film had annealed. Although the mechanism for this apparent resealing of leaks requires further study, it may be due to permeation through the graphite seals in the stainless steel fittings. The fittings have a higher coefficient of thermal expansion than the ceramic membrane, so at high temperature, gas could begin to leak through. Lowering the temperature would contract the metal fitting, recompressing the graphite ferrule around the ceramic tube. This mode of leakage appears to be different from the failure mechanism observed with membranes prepared using tin chloride. Once selectivity dropped with those membranes, it was not restored at lower temperatures due to the formation of pores, visible in the SEM micrographs.

SEM micrographs of Membrane 7 are exhibited in Figure 4.24. Annealing of the surface occurred, and only a few pores were visible. From this observation and the high temperature permeation results, it is readily apparent that replacing the conventional tin chloride activation process with Pd acetate produces membranes capable of operating for longer periods and at temperatures 100 to 150 K higher.

The methods to dilute the sensitizer or remove tin after its application to the substrate apparently lessened the problem of membrane failure but substantial selectivity decline was still observed at 823 or 873 K. Several possible explanations for this
Figure 4.21 Flux data for Membrane 6, prepared using Pd acetate, showing recovery of hydrogen flux after nitrogen permeation testing. T = 873 K, ΔP = 689.5 kPa. Pd film thickness = 9 μm.

Figure 4.22 SEM micrographs of Membrane 6 prepared using Pd acetate and tested up to 873 K. Pd film thickness = 9 μm. (a) Surface. (b) Close-up of pore.
Figure 4.23 Flux data for Membrane 7, prepared using Pd acetate. $\Delta P = 689.5$ kPa. Pd film thickness $\approx 21$ µm.
Figure 4.24 SEM micrographs of Membrane 7 prepared using Pd acetate and tested up to 1073 K. Pd film thickness ≈ 21 µm. (a-b) Surface. (c-d) Cross sections.
phenomenon include: (a) Tin or chlorine adsorbed during sensitizing/activation, or EP bath constituents could be trapped at the Pd/alumina interface and within the film during electroless deposition and induce the formation of porosity by hastening rearrangement of the Pd film. These contaminants might also weaken the Pd/alumina bond, causing the film to delaminate; (b) Since tin has a low melting point (505 K), it could be enhancing metallic diffusion along the grain boundaries, widening channels for diffusion of gases; (c) The mismatch in thermal expansion coefficient between Pd and alumina could result in film cracking or delamination; (d) Residual porosity in the Pd film produced during EP could easily transform into pores. We believe that all four of these processes play a role in the observed pore formation and selectivity decline.

Research on the Pd-Sn system in the catalyst and microelectronic fields may provide some insight into what may be occurring at the Pd-Sn/alumina interface. At high temperature, metallic intermixing may be driven by strain relief as well as surface energy minimization. Incorporation of tin into the Pd film may result in delamination and leak formation from loss of adhesion to the alumina support caused by diffusion swelling or buckling (as seen in Pt-Sn) due to the size difference between Pd and tin.

Pd-Sn intermetallic compounds and surface alloys with larger lattice parameters than pure Pd form readily at elevated temperatures. Above 573 K, diffusion of tin into Pd is expedited and above 800 K, an orthorhombic Pd$_2$Sn surface alloy structure can form. This is the same temperature range where we observed membrane failure. Tin may also preferentially diffuse along grain boundaries, hastening pore formation.

Pd-Au alloy films (~10 μm thick) prepared by using full strength tin sensitizer and EP on GTC symmetric alumina membranes exhibited pore formation at 823 K that was more rapid than with pure Pd membrane films of the same thickness. Drop in selectivity was hastened by increasing Au content. This was attributed to enhanced metallic diffusion of gold, which has a lower melting point than Pd (1338 vs. 1828 K). Interdiffusion of Pd and Au has been observed at temperatures as low as 525 K in catalysts although the small crystallites of catalysts should be expected to behave differently than a continuous film. However, since tin has a melting point of 505 K, it would be expected for any tin present on the Pd film to have a similar effect, even though the amount of tin was only a few percent at most at the Pd/alumina interface. This conclusion is consistent with our
observations that membranes activated with tin chloride experience a loss in selectivity at 823-873 K, while membranes activated with Pd acetate do not, or if they do, it is much less.

Mismatch in thermal expansion coefficient between the Pd and alumina support has not been ruled out as the origin of membrane failure. Restoration of the permselectivity of Membrane 7 upon lowering the temperature as discussed above may have been from the opening of diffusion paths due to stress induced by mismatch in thermal expansion coefficient, which then closed when the stress was relieved by returning to a lower temperature. Shu et al. have attempted to alleviate this problem by forming the Pd film using two different plating baths which create different structures. The first bath deposits a more firmly anchored but porous film in order to help absorb stress from mismatch in thermal expansion while the second bath deposits a denser, selective layer.

The problem may be one of adhesion as well. In general, metals wet ceramics poorly although wetting can be improved by the presence of an oxide layer between the metal film and the ceramic. However, in the present system of high temperatures and reducing conditions, tin may be expected to be in the metallic form and not promoting adhesion of the Pd film to the alumina support.

Finally, EP may be creating Pd films that contain voids, possibly due to the incorporation of impurity particles or plating around gas bubbles. For example, during electroless copper deposition it has been noted that grain boundary voids are prone to form. When heated, such residual porosity could consolidate into larger pores as the film rearranges, enhanced by the presence of tin. This process may be the source of the pores seen in many of the SEM images. Wunderlich et al. used high resolution electron microscopy (HREM) to image nanovoids formed at the grain boundaries and even within the grains of sintered nanocrystalline Pd.

Hydrogen can be absorbed during EP as well, resulting in stress and microcracks due to the \( \alpha \rightarrow \beta \) phase transition. Trapped hydrogen may form pockets within the metal as well. Adjusting EP bath composition or plating temperature and plating under an osmotic pressure gradient to form a denser film may help to eliminate these problems.

Many researchers have used an oxidation/reduction cycle to activate the Pd surface for experiments. In this work, hydrogen flux increased up to 75% after the air purge (Figures 4.12, 4.16, 4.18 and 4.20), consistent with the findings of other
researchers\textsuperscript{267,311}. Other than facilitation of contaminant removal, a likely explanation for these increases is that formation and subsequent reduction of \textit{Pd(II)} oxide (PdO) by hydrogen resulted in nanocrystallites of Pd with higher activity or surface area for hydrogen dissociation\textsuperscript{225,260}. From the preceding results of numerous high temperature tests of membranes prepared by different activation methods, no correlation between air purge and membrane stability could be made.

4.3 Conclusions

Strong evidence was presented suggesting that activation of the alumina membrane with tin/Pd chloride for electroless deposition resulted in a decline in hydrogen/nitrogen separation factor at temperatures of 823 K and above. Termed instability, the drop in selectivity often manifested itself with the formation of porosity in the Pd film that was thought to be caused or accelerated by the presence of tin at the interface between the Pd film and the porous alumina support.

This argument was bolstered by the observation of increased stability when the traditional electroless plating activation method using tin chloride was replaced with a procedure utilizing Pd acetate. These membranes were stable with respect to nitrogen flux up to temperatures of 973 K except a decline in hydrogen flux was attributed to annealing of the Pd film. The objective was met of preparing a Pd composite membrane that maintained its selectivity at high temperature.
5.1 Membrane Preparation Methods

Preparation methods also play an important role in Pd film stability. Yeung et al. have postulated that conducting electroless plating under an osmotic pressure gradient produces composite membranes that are more resistant to rearrangement at high temperature. Osmotic plating involves plating with a concentrated solution (such as 6 M sucrose) on the opposite side of the membrane as the electroless solution. The resulting film is denser in appearance and more impervious to gases other than hydrogen.

The following describes the fabrication and high temperature performance of membranes prepared using the osmotic plating technique and activated with either tin chloride or Pd acetate. The objective was to determine if this technique had any advantages over the batch plating method. For example, the goal was to find out if osmotic plating created membranes that would maintain selectivity at higher temperatures or have increased selectivity for the same Pd film thickness.

Membranes were prepared using the flow system with osmotic pressure, similar to the methods practiced by Yeung et al. The flow system with no osmotic pressure gradient, i.e. with the tube exposed to air resulted in aggregates of Pd crystallites (10 μm grains) which did not form an impervious film. However, Shu et al. have fabricated a permselective Pd composite membrane by circulating the electroless plating solution through a support exposed to air. We have found Pd flakes circulating in the plating solution while plating in the flow system in air, consistent with the findings of Yeung et al. So from here on, flow system implies use of osmotic pressure.

Advantages of the flow system include ease of scale-up to longer tube lengths and the ability to plate several membranes in series or parallel (see Figure 3.3). Simultaneously plating two 25-cm tubes has been simply accomplished. In fact, longer membranes
typically had better selectivities, possibly due to the contribution of leaks at the ends of the membrane, incurred while tightening the compression fittings. Often, visual inspection during the ambient temperature leak tests revealed leakage from the area at the edge of the glaze at the membrane end. This leakage may have originated inside the membrane at the interface between the Pd film and the end-sealing glaze. Pd did not adhere well to the glaze, and the glaze did not appear to be activated during any of the activation procedures.

After plating in the flow system, a membrane was broken for SEM analysis. There appeared to be no difference in film thickness from one end of the membrane to the other as expected since the reaction is relatively slow compared to the plating solution circulation rate through the tube. Mass transfer analysis gave a Reynolds number of 145 for the plating flowrate of 41 cc/min. This is completely within the laminar flow regime. Hindrance of mass transfer to the surface has been known to result in rougher, conical growths.

Pd films prepared under an osmotic pressure gradient appeared denser and more compact or finer grained compared to films prepared without osmotic pressure as shown in Figure 5.1. This morphology was believed to result from the osmotic pressure compacting the film against the support. The osmotic pressure was also thought to radially enhance mass transfer to the surface of the membrane where deposition took place. Pumping the solution through the inner diameter of the tube also increased the flow of reactants to the plating surface. Increased mass transfer to the Pd film should result in faster deposition, smaller crystal size, and a gas-tight film.

5.2 Characterization

Permeation tests demonstrated that osmotic plated membranes maintain respectable hydrogen selectivities during operation at high temperatures for extended periods of time. Some of the important test parameters are listed in Table 5. Figure 5.2 displays the results for Membrane 8, prepared using tin chloride sensitizer and osmotic plating. It was estimated to be 15 μm thick from SEM micrographs (Figures 5.3 and 5.1).

An air purge was conducted at 723 K to remove organic contaminants from the membrane (such as residual sucrose trapped in the pores of the ceramic support), resulting in greatly increased permeability. The membrane experienced a 15% drop in selectivity.
Figure 5.1 Comparison of membranes prepared by batch electroless plating (a-c) or electroless plated using the flow system with osmotic pressure (d-f).
Table 5. Specifications for Membranes Fabricated using Osmotic Plating in the Flow System.

<table>
<thead>
<tr>
<th>Sensitizing Technique</th>
<th>No.</th>
<th>Calculated Thickness</th>
<th>SEM Est. Thickness</th>
<th>Flux Data</th>
<th>Air purge</th>
<th>H Flux at 723 K*</th>
<th>Selectivity at 723 K*</th>
<th>SEM Images</th>
<th>Heated to (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-strength 8</td>
<td>8</td>
<td>20.3</td>
<td>15.3 μm ± 6.4 μm</td>
<td>Fig. 5.2</td>
<td>Yes</td>
<td>0.125 mol/m²·s</td>
<td>59</td>
<td>Fig. 5.3 and 5.1f</td>
<td>873</td>
</tr>
<tr>
<td>Pd acetate 9</td>
<td>9</td>
<td>25.7</td>
<td>18.4 ±7.7</td>
<td>Fig. 5.4</td>
<td>Yes</td>
<td>0.128</td>
<td>32</td>
<td>Fig. 5.5 and 5.6</td>
<td>1023</td>
</tr>
<tr>
<td>Full-strength 10</td>
<td>10</td>
<td>9.4</td>
<td>11.1 ±3.8</td>
<td>Not shown</td>
<td>Yes</td>
<td>0.217 (ΔP = 517 kPa)</td>
<td>79</td>
<td>Not shown</td>
<td>923</td>
</tr>
<tr>
<td>Pd acetate 11</td>
<td>11</td>
<td>11</td>
<td>Not meas.</td>
<td>Not shown</td>
<td>Yes</td>
<td>0.416 (at 623 K)</td>
<td>1200</td>
<td>Not shown</td>
<td>623</td>
</tr>
</tbody>
</table>

*ΔP = 689.5 kPa, selectivity = hydrogen flux/nitrogen flux.
Figure 5.2 Flux data for Membrane 8 activated using full strength tin sensitizer and osmotically plated. Pd film is 15 μm thick.
Figure 5.3 SEM micrographs of Membrane 8. Activated using tin and Pd chloride, electroless plated under an osmotic pressure differential, and tested up to 873 K. (a-b) Surface of membrane. (c-f) Cross sections. (f) Close-up of void.
from 63 to 53 over a three-day period in going from 773 to 823 K (at a ΔP of 690 kPa). The fact that the selectivity was still 59 after five days at 873 K suggested that the method of applying the Pd film was an important variable since membranes prepared using full strength tin chloride sensitizing always experienced a more significant drop in selectivity (or failure) at either 823 and/or 873 K. Hydrogen flux decreased and nitrogen flux increased slightly during several days of operation at 873 K before the membrane was taken to lower temperatures.

Comparing Membrane 8 to other membranes of similar thickness fabricated in the batch system (Membranes 1, 2, and 4) revealed that the hydrogen flux at 723 K was lower than these three membranes but the nitrogen flux was lower than two of the three other membranes as well. The selectivity of 59 at 723 K (ΔP = 690 kPa) was within the expected range. The permeability of this membrane may have been lower because of the different structure imparted by plating in the flow system or because of impurities from osmotic plating blocking the pores.

The nitrogen flux through Membrane 8 increased by 27% at 823 K. Membranes of similar thickness as Membrane 8 that were activated using tin chloride and electroless plated without osmotic pressure experienced similar increases in nitrogen flux at 823 or 873 K (see Chapter 4). In contrast to these membranes, the nitrogen flux for Membrane 8 was fairly constant at 873 K (5% increase). It is likely that the osmotic plating process imparted the apparently heightened stability of Membrane 8.

Since porosity in the Pd film may transform into pores or channels for diffusion of inert gas through the membrane, the denser film created by osmotic pressure may better resist structural rearrangement upon heating to high temperature. The flow of electroless plating solution through the tube lumen may have also swept away gas bubbles adhering to the surface that could cause "skip plating" or a discontinuous film. Perhaps the increased stability of Membrane 8, prepared using full strength tin sensitizer, was because some of the tin was dissolved away during the initial stages of plating due to the heightened mass transfer in the flow system. However, Kim et al. found that tin dissolved into the plating solution was redeposited with the metal being plated343.

The surface morphology of Membrane 8 (Figure 5.3a,b) had changed during exposure to 873 K in comparison to the unheated samples shown in Figure 5.1. Images of the film cross-section show the presence of voids. It is not known whether these were
formed during the permeation testing or are an artifact of electroless plating, although the cross-sections of the unheated films pictured in Figure 5.1 contain some small voids. Perhaps these agglomerate at high temperature. Despite the presence of these pores in Membrane 8, the selectivity was still 49 at 873 K.

A membrane fabricated using Pd acetate activation and osmotic plating remained fairly impervious to nitrogen at temperatures up to 1023 K as shown in Figure 5.4. Membrane 9 was 18 μm thick (as determined from SEM micrographs) and had an increase in helium flux at 823 K of 11%. Helium flux data was used because not enough nitrogen data points were collected (helium leak rate usually closely follows nitrogen leak rate so this should be an accurate representation). Compared to Membranes 1, 2, and 4, the hydrogen flux was somewhat lower as expected because Membrane 9 was thicker. The nitrogen flux was within the expected range.

The ideal separation factor at 923 K and a ΔP of 690 kPa (after hydrogen flux leveled off) was 36. At 923 K and above, however, hydrogen flux declined while nitrogen flux increased significantly. This was ascribed to annealing or rearrangement of the Pd film so that it becomes less permeable to hydrogen; concurrently some porosity or leaks must have formed diffusion pathways for nitrogen. Loss of surface roughness may have reduced the catalytic ability of Pd to dissociate hydrogen or grain growth may have resulted in the disappearance of more permeable grain boundaries. Another explanation for the decrease in hydrogen flux was surface contamination. This would inhibit the hydrogen dissociation reaction and retard surface diffusion. Further investigation of the reason for hydrogen flux decline at high temperatures is necessary to completely understand what was occurring.

In any case, the permeability of Membrane 9 was not restored upon returning to 923 K after exposure to 1023 K for 9 days. Notwithstanding, compared to membranes prepared without osmotic pressure, less decline in hydrogen flux was observed with this membrane at 823 and 873 K. In fact, the selectivity increased from 32 to 46 in going from 723 to 823 K when the membrane was first heated up. The SEM micrographs of Figure 5.5 show the annealed surface and some pores that were formed. The film apparently follows the contours of the underlying porous support.

Some of the cross-sections of Membrane 9 in Figure 5.6 contain pores (e,f). The other film cross-sections in Figure 5.6 appear to be much less porous. The pores may have
Figure 5.4 Flux data for Membrane 9, prepared using Pd acetate. $\Delta P = 689.5$ kPa. Pd film thickness = 18 $\mu$m.

Figure 5.5 SEM micrographs of the surface of Membrane 9, tested up to 1023 K.
Figure 5.6 SEM micrographs of cross sections of Membrane 9, tested up to 1023 K.
formed when the membrane was fractured for SEM analysis, but they appear to have formed during the high temperature permeation experiment. Such large pores have not been observed in SEM micrographs of Pd films that have not been subjected to high temperature flux testing.

Membrane 10 was 25.3 cm long, activated using tin chloride with acceleration, and osmotically plated to a thickness of 11 μm. Unfortunately a power outage while the membrane was at 773 K caused the temperature to fall to 453 K causing loss in selectivity and the data from further experiments had to be discounted. The flux and selectivities before then are worth discussing. At 723 K and a transmembrane pressure differential of 517 kPa (the mass flow controllers could not produce a high enough flowrate to test at the usual ΔP of 690 kPa), the hydrogen flux was 0.217 mol/m²·s and the selectivity was 79. These values were some of the highest seen for any membrane in this work. Possible explanations for the increased hydrogen flux of this longer tube are discussed below.

Membrane 11 was also 25.3 cm long and was tested by an external party (D.J. Edlund of Northwest Power Systems, Bend, Oregon). At 623 K the selectivity was 1200 and the hydrogen flux was 0.416 mol/m²·s (Table 5). The flux would be expected to be even higher than this at 723 K. There are a few probable reasons why the flux and selectivity for this membrane were much higher than for the other membranes tested. The first reason may be related to the way that flux was calculated. The membrane area used in that calculation was the area of the Pd film coated on the inner diameter of the membrane. The glaze on the shorter tubes (5-6 cm long) often covered up to half of the outer surface. It had been assumed that the resistance of the support was negligible (< 10% of resistance to flow) and that the gases flowed around the glaze without resistance. This assumption must be reevaluated. Future work should involve better characterizing the influence of the GTC 998 support on permeation characteristics if they will continue to be used. In the longer tube, the glazed area covered a much smaller fraction of the outer surface area.

Another reason the flux was so high is that the Pd film was relatively thin. If the thickness as calculated by the weight difference gave a result of 11 μm, then the actual thickness would undoubtedly be less. This is because the membrane was plated in the flow system with sucrose as the osmotic fluid and inevitably some gets trapped in the pores resulting in a calculated thickness value greater than the actual.
There are at least two likely reasons for the increased selectivity of Membrane 11. The first possibility was that a more defect free Pd film was created during osmotic plating and the second likelihood was that any leaks around the end seals or leaks at the interface in the tube lumen between the Pd film and the glaze would be drowned out in the large volume of flux from the long expanse of membrane. Very often while tightening membranes into the stainless steel Swagelok fittings, a very faint crackling noise was heard. This was almost unavoidable because even with the use of a fresh graphite ferrule the fittings had to be tightened enough so that they did not leak. Before the crackling noise was heard, the membranes often did not leak at all, while afterwards gas bubbles appeared during the room temperature leak check under methanol/water.

Therefore, the attachment of the fittings was believed to cause some delamination of the Pd film or else microcracks in the glaze. Supporting evidence included the observation that during the room temperature leak check, gas frequently emanated from the interface at the glaze and the porous tube (on the outside of the membrane), indicating a pinhole or discontinuity in the Pd film near the end of the membrane tube.

Other chemicals may be used to create an osmotic pressure gradient. Schwartz et al. used calcium chloride (CaCl₂) and created a membrane with a very low nitrogen leak rate. However, the hydrogen flux was very low as well due to contamination by calcium as shown by AES. Therefore, these results demonstrated that while electroless plating under a CaCl₂ osmotic pressure gradient produced membranes more impervious to nitrogen, sucrose was better from the standpoint of Pd film contamination.

In fact, Schwartz et al. and Collins and Way generally obtained much higher selectivities (> 500) and permeabilities using asymmetric Membralox supports than the Pd composite membranes of this study fabricated using the GTC 998 supports. The increased flux is likely due to the decreased resistance of the asymmetric support. Explanations for the increased selectivity include the possibility that the selective inner alumina layer of the Membralox support contains fewer large defects or pores than the GTC support, i.e. it is less rough. The sequential processes involved in applying the asymmetric ceramic layer may result in a smoother inner surface, requiring less Pd to plug the pores. Another likelihood is that because the bulk of the Membralox tube is highly porous, consisting of approximately 12 μm particles, this would allow the viscous 6.0 M sucrose
solution to better penetrate the tube wall, increasing the osmotic pressure driving force. These two factors probably enabled the deposition of a more defect-free film.

An attempt was made to correlate membrane performance with grainsize. A discussion and presentation of the pertinent XRD results is presented in Appendix C.

5.4 Conclusions

From the four membranes prepared in the flow system with osmotic pressure, verification of the postulate that membranes prepared under osmotic pressure develop fewer pinholes and are more stable than membranes plated in the batch mode during operation at high temperature was inconclusive. Osmotic plating obviously results in different film morphology, and also appears to be beneficial with regard to increased stability, but further experimentation must be carried out to affirm this since these conclusions were based on only a small number of membranes.

The contribution of defects at the ends of the tubes was found to potentially be a major source of inert gas permeation. The leaks were thought to be created when the fittings were attached to the membrane and tightened. Could the increased selectivity of the longer membrane tubes be credited to osmotic plating or the fact that any leaks in the end seals or ends of the membrane would be less noticeable with the longer membranes than in the shorter membranes? Obviously, the next experiments to conduct would be to batch plate two 25 cm long membranes activated by either tin/Pd chloride or Pd acetate and test them at high temperature until they fail (up to 1023 K). If osmotic plating in the flow system is truly beneficial, these membranes should exhibit lower selectivities and experience larger increases in nitrogen flux at temperatures of 823 K and above. The mechanism for the formation of the porosity seen in Figure 5.6e,f is unclear and requires additional study as well.
PREPARATION OF PALLADIUM–COPPER ALLOY MEMBRANES FOR HYDROGEN SEPARATION

6.1 Introduction

The problems of embrittlement and surface contamination experienced by pure Pd may be overcome by the use of alloy membranes. According to the work of several researchers, PdCu_{42} has the highest permeability of the Pd–Cu alloys (up to 1.5 times as permeable as pure Pd at 623 K) (Ref. 107). A bcc alloy phase is credited with this increased permeability because it has much lower activation energy for hydrogen diffusion. Hydrogen/metal interaction is weaker on the alloy surface resulting in greater mobility compared to pure Pd (Ref. 406).

According to work by Piper and McKinley, the more permeable bcc alloy phase is only formed under certain conditions (Ref. 107,293). McKinley observed its slow formation during permeation tests at 623 K while Piper more thoroughly characterized the system and determined that temperatures below 873 K were necessary to accomplish formation of any of the more permeable bcc alloy phase. According to permeability measurements, the most permeable composition is very close to 42 weight percent copper. Above around 47 weight% copper an ordered bcc phase can solely exist while a two-phase (fcc and bcc) alloy may be present at compositions between 36 and 47%. Both Piper and McKinley as well as Mishchenko et al. noted that the transition between the two structures could be slow (on the order of weeks at 623 K), and that the presence of hydrogen increased the transformation rate (Ref. 294).

Additionally, the alloy has increased resistance to thermal cycling and contamination by H_2S (Ref. 108,109). The reason for the enhanced nobility of this alloy with regard to sulfur resistance is not well understood, but is most likely related to the electronic structure of the alloy. Although the hydrogen solubility data around the α → β phase transition for the particular alloy composition of interest here has evidently not been
measured, the critical temperature for formation of the β phase in the 20 atom% Pd–Cu alloy is lowered by more than 200 K\textsuperscript{303}.

The primary objective for this segment of this work was to prepare a PdCu\textsubscript{42} film on the GTC 998 support. Once that was achieved, the permeability and selectivity would be determined, as well as the resistance of the membrane to thermal cycling.

6.2 Membrane Preparation Methods

The preparation of a Pd–Cu alloy membrane film can essentially be divided into three distinct steps. First, the proper amounts of Pd and copper must be individually deposited by EP to reach the target composition of about 42 weight% copper. The main complication in that procedure is the uncertainty involved in calculating film thickness by the weight difference method. Secondly, annealing to form a homogeneous alloy must be accomplished (see §2.6.7). Since Pd and copper are miscible across the entire range of solid solutions, this should not be a difficult task. The problem is reaching a high enough temperature for intermetallic diffusion to transpire at a reasonable rate while staying at a low enough temperature to preserve the integrity of the membrane.

The final challenge is to convert the homogeneous Pd–Cu alloy into the more permeable bcc phase. As outlined in the previous section, this can only take place below 873 K, while annealing to form a homogeneous alloy requires temperatures in excess of 873 K. Therefore, in theory, annealing to form the homogeneous alloy and annealing to form the bcc phase should be conducted at different temperatures above and below 873 K respectively.

Alloy deposition from bimetal EP baths is difficult to control\textsuperscript{333} so we chose to sequentially deposit Pd and copper followed by annealing to form an alloy film. Proper heat treatment of the alloy film as described above should result in the desired bcc phase\textsuperscript{107,293,754,755}. To deposit the copper film onto the Pd, various electroless copper baths were experimented with to find one that was stable and deposited copper at a reasonable rate (see Table 3.4). EP of copper onto a Pd/alumina composite membrane (GTC 998 support) was necessary because the electroless Pd solution replaced copper by displacement plating.
For the first membrane (Membrane Cu-1), Bath 1 was used to deposit approximately 12 μm of copper (as calculated by the weight difference method) onto the existing 20 μm (estimated) of Pd on this 25 cm GTC 998 support. It had been activated before electroless Pd deposition using tin and Pd chloride with acceleration in 1:1 HCl. Membrane Cu-2 was plated using electroless copper Baths 2 and 3. During plating, it was submerged in 6 M sucrose in an attempt to help plug any defects in the Pd film with the depositing copper. Membrane Cu-2 was tested for high temperature permeability with approximately 10 μm of copper on top of 47 μm of Pd (activated prior to deposition using the standard tin and Pd chloride).

The first three baths were depositing copper too slowly so Bath 4 was tried. Another problem that was encountered is that Pd is not an especially active catalyst for the electroless copper plating reaction. Accordingly, the Pd surface had to be properly prepared before EP. In the course of experimenting with ways to clean and activate the Pd surface, it was found that 50% HNO₃ (nitric acid) passivated the Pd with a seemingly permanent oxide layer. The oxide layer was not catalytically active towards electroless copper deposition. A quick immersion in aqua regia (82% HCl and 18% HNO₃ by volume) removed some of this oxide layer. Copper deposition was then possible but did not appear to be uniformly coating the surface (this is also called skip plating). Work on this particular membrane was halted and another Pd/alumina membrane was selected to be copper plated.

Membrane Cu-3 had a base Pd film of nominally 20 μm and was plated using Bath 4 to a copper layer thickness of 15 μm. Before electroless copper deposition it was cleaned in hot 5% HNO₃. This seemed to clean the surface well for EP. After plating it had only a few leaks during the ambient temperature leak check so it was tested at high temperature. The specifications of the three Pd–Cu membranes fabricated are listed in Table 6.

### 6.3 Characterization

Membrane Cu-1 was broken during the attempt to seal it into the Swagelok compression fittings. It therefore served as a source of sacrificial sections to be heat treated at various temperatures and analyzed. These pieces were heated to either 773 or 873 K for
Table 6. Pd–Cu Membrane Specifications.

<table>
<thead>
<tr>
<th>Sensitizing Technique</th>
<th>No.</th>
<th>Calculated Thickness of Pd (μm)</th>
<th>Calculated Thickness of Copper (μm)</th>
<th>SEM Est. Thickness of Pd (μm)</th>
<th>Flux Data</th>
<th>Air purge</th>
<th>Highest Selectivity*</th>
<th>SEM Images</th>
<th>Heated to (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerated</td>
<td>Cu-1</td>
<td>20</td>
<td>12</td>
<td>21.6 ±2.4</td>
<td>broken</td>
<td>Yes</td>
<td>13.7</td>
<td>not shown</td>
<td>various</td>
</tr>
<tr>
<td>Full-strength</td>
<td>Cu-2</td>
<td>10</td>
<td>47</td>
<td>27.6 ±8.5</td>
<td>Figure 6.3</td>
<td>Yes</td>
<td>11</td>
<td>Figure 6.5</td>
<td>723 K</td>
</tr>
<tr>
<td>Pd acetate</td>
<td>Cu-3</td>
<td>20</td>
<td>15</td>
<td>30.3 ±7.6</td>
<td>Figure 6.6</td>
<td>Yes</td>
<td>11</td>
<td>not shown</td>
<td>923 K</td>
</tr>
</tbody>
</table>

*ΔP = 689.5 kPa, selectivity = hydrogen flux/nitrogen flux.
12 hours under helium and analyzed afterwards with XRD and EDX to determine if a homogeneous film was created.

The XRD analysis of the metal films (Figure 6.1) demonstrated that an alloy membrane was formed upon heat treatment at 873 K in comparison to the unheated sample. However, the bottom of the membrane contained 12 atom% less copper than the top (Figure 6.2). Appendix B contains an example of how the atomic compositions were calculated from the XRD results with the assumption of a linear variation in d-spacing with compositional change. Evidently, not enough time was allowed for formation of an alloy of uniform composition. The section heated to 773 K for 12 hours (not shown) still exhibited strong peaks for both Pd and copper with no indication of alloy formation.

The above results demonstrated the potential for Pd–Cu alloy membranes to be prepared by sequential electroless deposition followed by annealing at high temperature. Further work focused on annealing in situ to observe the changes in hydrogen permeability as the alloy formed at various temperatures. Membrane Cu-2 was therefore tested at 623 and 723 K. Figure 6.3a displays hydrogen and nitrogen flux data versus time online where it can be seen that at 623 K the hydrogen flux was very low and it increased quickly to a steady state value at 723 K. At this point, it was thought that the intermetallic diffusion was complete due to the leveling off of permeation flux.

The low flux at 623 K was expected because copper is very poor at dissociating hydrogen and also has low permeability. The increase in flux at 723 K was not surprising because the Tamman temperature \(0.5T_m\), where \(T_m\) = melting temperature) for this system is 679 K, given the relatively low melting point of copper (1358 K). The Tamman temperature indicates where significant lattice migration can occur\(^{691}\). The leveling off of hydrogen flux was interpreted as the formation of a homogeneous alloy. Further testing (Figure 6.3b) showed that 100 K changes between 623 and 723 K did not affect hydrogen or nitrogen flux and that an air purge at 723 K resulted in a hydrogen flux increase of 26%. Furthermore, decreasing the temperature to 373 K caused the nitrogen flux to increase drastically and the membrane failed as the selectivity fell to the value expected from Knudsen diffusion.

XRD analysis of Membrane Cu-2 indicated that an alloy of approximately 34 atom% copper had formed on the side of the film where the copper had been deposited (Figure 6.4). Another alloy phase of 85 atom% copper also formed and a slight copper hue
Figure 6.1 XRD results for the Pd–Cu film of Membrane Cu-1. Film thickness ≈ 22 μm.
(a) As electrolessly deposited. (b) Annealed at 873 K for 12 hours under helium. The PdCu alloy is approximately 34 atom% copper.
Figure 6.2 XRD results for bottom of the Pd–Cu film of Membrane Cu-1, annealed at 873 K for 12 hours under helium. The PdCu alloy is approximately 22 atom% copper.
Figure 6.3 Flux data for Membrane Cu-2. Film thickness = 30 μm. (b) (Data continued).
Figure 6.4 XRD results for Membrane Cu-2. (a) Top of Pd–Cu film. The PdCu alloy is approximately 33 atom% copper. The CuPd alloy is approximately 15 atom% Pd. (b) Bottom.
could be seen on the surface of the membrane film. However, no copper was detected by XRD or EDX on the bottom of the film (the side adhering to the porous alumina support). The existence of a layer of pure Pd is a possible explanation for why the membrane failed at 373 K as the $\alpha \rightarrow \beta$ Pd-hydride phase transition most likely caused delamination of the film.

A reasonable interpretation of the results for Membrane Cu-2 is that the copper film was probably even thinner than 10 μm and quickly diffused into the Pd at 723 K. SEM micrographs of the cross-section are shown in Figure 6.5. The film was relatively thick which explains the low flux of this membrane compared to the thinner Pd membranes described previously (Chapters 4 and 5). Although the thicknesses of the Pd and copper layers were calculated to be 47 and 10 μm respectively, from the SEM micrographs the film was 28 μm thick. The presence of large growths and nodules on the surface as well as plating solution or sucrose trapped in the porous support were the likely weight contributions leading to this discrepancy. The copper deposit was also visible in the micrographs as a spongy looking coating on the Pd surface (Figure 6.5).

Membrane Cu-3 was annealed in situ as well. This membrane was activated using Pd acetate and plated in batch mode. The thickness determined from SEM micrographs was 30 μm and the estimated composition was 36 weight% copper as calculated from the thicknesses of the deposited Pd and copper layers. It was hoped that during annealing the Pd and copper layers of this membrane would result in an alloy closer to the desired composition of 42 weight% copper.

At 623 and 673 K only slight increases in hydrogen flux were observed with time (Figure 6.6a) with a modest increase at 723 K. This is in contrast to Membrane Cu-2 where hydrogen flux increased dramatically at 723 K. That Cu-3 had a thicker copper layer is one plausible explanation for this difference in behavior. The hydrogen permeability would be expected to increase greatly when Pd began to diffuse to the surface and a thicker film would increase the time required for this to occur. Indeed, the hydrogen flux did begin to climb, although not as steeply as for Cu-2, after Cu-3 was held at 723 K for a couple of days.

At 773 K, hydrogen flux began to increase steadily, although not as quickly as observed for Membrane Cu-2 at 723 K. Nitrogen flux decreased at 623 K and increased at 773 K. After 5 days at 773 K, hydrogen flux had almost tripled from 0.013 to 0.037
Figure 6.5 SEM micrographs of Membrane Cu-2, prepared using acceleration and tested up to 723 K. (a) Surface of Pd film. (b-d) Cross sections.
Figure 6.6 Flux data for Membrane Cu-3, prepared using Pd acetate and batch plated. 
\[ \Delta P = 689.5 \text{ kPa} \]. Pd film thickness \( \approx 30 \mu\text{m} \). (b) (Data continued).
mol/m²•s. At this time, hydrogen flux again leveled off and the temperature was increased to 823 K to promote further intermetallic diffusion. As with previous membranes, after permeating nitrogen, hydrogen flux took a certain period of time to rebound to its steady state value.

A loss in hydrogen permeability was observed at 823 K (Figure 6.6b), potentially due to textural changes resulting in a smoother Pd film surface or a decrease in grain boundary area due to annealing. Although such decreases were previously noted at temperatures at or above 873 K, since copper has a lower melting point than Pd it could be expected to lower the temperature for atom migration and changes in film texture or morphology. As with pure Pd, other explanations include the formation of an oxide layer or adsorption of impurities on the surface. Upon returning to 723 K however, the hydrogen flux was more than twice what it had been previously at this temperature. So the film had become more permeable to hydrogen (at lower temperatures) during the annealing process.

Then, Membrane Cu-3 was dropped back to 723 K (at 1 K/min.) to conduct an air purge for 40 minutes at 690 kPa (exposing the graphite seals to oxygen above 723 K leads to their degradation). The membrane was then taken to 873 K to continue annealing at a higher temperature. It should be noted in Figure 6.6a that at this temperature no decrease in hydrogen flux due to annealing was observed and that the nitrogen flux increased and leveled off. After hydrogen flux plateaued once again the temperature was increased by 50 K whereupon the hydrogen flux increased slowly while nitrogen leak rate appeared to remain constant.

The membrane was held at 923 K for 14 days and then taken to lower temperatures in 50 K intervals (Figure 6.6b). Since Aremco-Seal 617 was used as the end-seal glaze, 923 K was the maximum operating temperature. However, it can be concluded that annealing at temperatures at or higher than 923 K will be required in order to obtain a homogeneous alloy film. This was because it could probably be assumed that if the hydrogen flux continued to rise at a given temperature then intermetallic diffusion was still ongoing. The hydrogen flux increased significantly in going from 873 to 923 K (Figure 6.6b), suggesting that the film was not completely homogeneous at 873 K. All of the pure Pd membranes exhibited hydrogen flux decline at temperatures at or greater than 873 K while the hydrogen flux for Membrane Cu-3 remained constant at 923 K.
Upon cooling to lower temperatures, selectivity decreased with each 50 K drop in temperature. This was due to the decline in hydrogen flux at each temperature and the concurrent increase in nitrogen flux. Here, nitrogen flux probably increased due to mismatch in thermal expansion coefficient between the Pd film and the ceramic support in contrast to nitrogen flux increases at high temperature most likely caused by the formation of pores.

When the membrane was removed from the furnace, the room temperature leak check showed bubbles emanating from both the membrane itself and the fittings. The difference in thermal expansion coefficient between the stainless steel Swagelok fitting and the ceramic membrane tube probably resulted in the leaks from the fittings. The leakage from the membrane was not surprising given the low selectivity ~10 throughout most of the course of testing.

There were also copper flakes inside the membrane tube that had separated from the metal film coating the membrane. It was likely that the bond between the copper and the Pd was not very strong, possibly due to the presence of a thin oxide layer. It was also possible that the stress in the electroless copper layer caused it to delaminate sometime during high temperature testing. On most of the membrane film, the copper appeared to have diffused into the Pd film.

XRD analysis was employed to determine the composition of the film once high temperature testing was completed (Figure 6.7). The estimated atomic composition of the Pd rich phase was 40 atom% (28 weight%). Analysis of both the top and bottom resulted in this composition, suggesting that the film was homogeneous. This was not the case from visual inspection (described above), although the majority of the film appeared to be the same color (light gray). Some copper rich phase (10 atom% Pd) was also picked up by XRD analysis of the top of the film, albeit this was probably some of the aforementioned copper that had separated from the film and proved difficult to remove from the sample prepared for the XRD analysis. The relatively low permeability of the membrane might be partially explained by the failure to reach the target composition of 42% copper.
Figure 6.4 XRD results for Membrane Cu-2. The PdCu alloy on both the top and bottom of the film is approximately 40 atom% copper. (a) Top of Pd–Cu film. CuPd alloy is approximately 10 atom% Pd. (b) Bottom.
6.4 Conclusions

The potential advantages of using a Pd–Cu alloy membrane instead of pure Pd for increased resistance to thermal cycling and H₂S contamination were recognized and outlined. While no enhancement in resistance to embrittlement or increase in flux or selectivity over pure Pd membranes was demonstrated by this work, the significant achievement here was the fabrication of a Pd–Cu alloy film on a porous alumina support. The key objective of forming a Pd–Cu alloy by annealing a successively deposited layer of Pd and then copper was met by annealing at 923 K. Although the concept of forming an alloy membrane by this technique was shown to be possible, further optimization needs to be carried out. For example, the annealing process was not complete since some copper rich phases remained. The hydrogen fluxes and selectivities of the two membranes tested were also relatively low compared to the pure Pd membranes (see Chapters 4 and 5).

Important parameters to consider in preparing an alloy membrane were determined to be control of alloy composition by depositing appropriate amounts of each metal during sequential electroless plating, soaking at a high enough annealing temperature for a long enough period of time. Formation of the more permeable bcc Pd–Cu alloy phase by holding below 873 K (as indicated in the literature) was not observed. Although the objective of depositing Pd and then copper to reach a final composition of ~42 weight% copper was not achieved, it was found that by soaking the membrane in hot water after plating to remove absorbed impurities from the porous support resulted in a more accurate estimate of metal film thickness by the weight difference method.

The results suggested that temperatures at or above 923 K were obligatory in order to reach a state of homogeneity from the originally distinct electrolessly deposited Pd and copper layers. Albeit the bcc alloy phase was not formed under these conditions, or even thereafter at lower temperatures, probably because the copper composition was too low. Now that some of the basic principles for preparation of composite alloy membranes by electroless plating have been demonstrated in practice, fabrication of thinner alloy membranes should be easily accomplished. Testing the thermal cycling and contaminant resistance of Pd–Cu membranes should follow.
Pd/alumina composite membranes were prepared using activation schemes that varied the amount of tin present at the metal/ceramic interface. During testing at 823 or 873 K, the hydrogen/nitrogen pure gas permeability ratio (selectivity) declined since nitrogen flux increased with time. Porosity was evident in SEM micrographs of the Pd film surface. The presence of tin at the Pd/alumina interface contributed to a decline in selectivity at 823 K regardless of film thickness. The amount of time it took for selectivity to fall at 823 K was found to be proportional to Pd film thickness and the same mechanism that caused decline in selectivity was operating regardless of thickness. It was difficult to ascertain the exact influence of film thickness, time on line, or activation method on membrane performance since the effects of each variable were superimposed.

A Pd acetate activation procedure activated the surface well for electroless plating. The new procedure eliminated tin chloride entirely from membrane fabrication resulting in stable nitrogen flux for at least a week at temperatures up to 973 K. This supported the hypothesis that tin is detrimental to film stability at high temperature. Other factors affecting high temperature performance were elucidated. For instance, an air purge conducted at 723 K resulted in increased hydrogen flux, while irreversible changes in film structure due to annealing at 873 K and above negatively impacted hydrogen flux.

Fabrication of Pd composite membranes using EP under an osmotic pressure gradient (osmotic plating) was found to be advantageous, particularly when utilized on substrates activated by Pd acetate instead of tin and Pd chloride. These techniques in conjunction produced thinner, more permselective films that seemed to be more resistant to morphological change or pore formation during high temperature permeation tests than membranes activated using tin chloride sensitizer and deposited by conventional batch EP methods. However, further experiments will need to be conducted to clarify whether the heightened performance was due to the plating method or because longer tubes were used whose high hydrogen flux masked leaks contributed by Pd film delamination at the glazed
ends. Nonetheless, osmotic plating apparently produced fewer voids and pores in the Pd film, resulting in better stability at high temperatures. Some pores did form at high temperature (≥ 873 K) as observed by SEM, although the mechanism for their formation was unclear.

Pd–Cu alloy films were prepared on porous α-alumina supports by sequential electroless deposition of Pd and then copper. Although the fluxes and selectivities of these composite membranes were relatively low, the principle of forming an alloy film through the intermetallic diffusion of two distinct metal layers was demonstrated. Temperatures of 923 K or above were determined to be necessary to obtain compositional homogenization of the bimetal film. Optimization of film composition to obtain the most permeable alloy consisting of 42 weight% copper, can be assisted by soaking the membrane in water after electroless plating to remove impurities from within the porous support. This will lead to more accurate weight measurements for thickness estimations of the Pd and copper layers.

In attempts to fabricate a membrane from Mott Metallurgical porous stainless steel tubes, it was found that it takes much more palladium (~20 μm) to obtain a leak free film than on porous ceramic. The films were either not thick enough to effectively plug the pores of the support, the Pd film itself was inherently porous from the electroless plating process, or leak tight end seals were not made.
Chapter 8
RECOMMENDATIONS FOR FUTURE WORK

8.1 Justification for Continued Study

The potential for huge energy and capital savings in the chemical process industry warrants continued research into Pd composite membranes with thinner films, higher selectivities, improved robustness with regard to thermal cycling or embrittlement, and resistance to poisoning by contaminants. Significant reduction in the Pd film thickness on various supports has been achieved in the last decade. A better understanding of the processes used during fabrication is prerequisite for continued advancements in the field.

8.2 Remaining Hurdles to Overcome

There are many interesting and challenging aspects of Pd composite membranes to study including thin films, nanostructured materials, microstructural evolution, grain growth, hydrogen permeation mechanisms, porous support fabrication, surface chemistry, alloy formation, etc. A multidisciplinary approach to solving these technical problems involving chemists, material scientists, and engineers will be essential to make the most progress.

Although some very thin, permeable and permselective Pd composite membranes have been fabricated, several difficulties still inhibit commercial implementation of Pd membrane technology. These problems include embrittlement and cracking due to the $\alpha \rightarrow \beta$ Pd hydride phase transition$^{131}$, poisoning or fouling due to the presence of sulfur or unsaturated carbon compounds in the operating stream$^{244-246,249}$, and inability to withstand temperature cycling. The exact mechanism of membrane failure is not completely understood at this time and should be the subject of further study. Also, in order to be accepted by industry, membranes must have a lifecycle of at least months or years under
process conditions. Foremost, the thickness of the Pd film must be reduced even further. A selective Pd layer on the order of a micron or less would be preferable.

8.3 Specifics to Investigate

Further endeavors should focus on creating as robust a Pd alloy membrane as possible and using it to conduct reaction experiments. One of the most important aspects of Pd membrane fabrication is EP techniques, and their development should be the focus of a fair percentage of future study. The effects of temperature and concentration of bath constituents on film structure, adhesion and porosity should continue to be explored.

Another idea for depositing a thin film would be to conduct EP with the plating solution on one side and a solution containing the reducing agent on the other side of the porous support. That way, metal would be deposited only at the interface where the two solutions meet inside the membrane.

More specifically, osmotic pressure should be used in future work to produce a thin and impervious film and alloys will be utilized to impart resilience towards temperature cycling as well as increased permeability. It has been demonstrated that membranes prepared using EP under an osmotic pressure gradient are thinner and more stable at high temperature. Osmotic plating conserves Pd by increasing film density while reducing film thickness so less metal is required to form a leak-free film. Henceforth, membranes should be fabricated using this technique rather than in simple batch EP baths.

The relationships between surface preparation methods and the characteristics of electrolessly deposited films remain to be explored. For example, what is the effect of activation catalyst coverage on Pd film nucleation, microstructure, porosity and adhesion? Activation methods should continue to be improved. Different heat treatment schedules for the Pd acetate activation technique could influence the Pd crystallite size, activity, and resulting adhesion of the Pd film to the support. Instead of heating to remove the organic fraction, the Pd acetate might also be reduced by immersion in a reducing agent such as hydrazine. Of course, any process involving tin should be avoided unless membrane operation at low temperatures (< 773 K) is intended.

Since sealing the membranes into the metal compression fittings tends to create leaks in the Pd film at the ends of the tube, perhaps the fittings should be attached to the
glazed ends of the tube before electroless plating. This way, the ceramic is pre-stressed and there will be less chance for the Pd film to be delaminated during tightening of the fittings. Also, if the tube breaks, then the effort of conducting electroless plating will not have been wasted.

Given that Pd is subject to embrittlement, alloys that lower the $\alpha \rightarrow \beta$ phase transition temperature should be used. In particular, Pd alloyed with ruthenium should be prepared as well as Pd–Cu alloys. If electroless ruthenium turns out to be impossible, adding a small amount of ruthenium salt to the electroless Pd bath may cause ruthenium to be incorporated into the film during deposition. Parameters for the creation of an alloy film should be optimized. Development of an electroless plating process for simultaneous deposition of Pd–Cu alloys would eliminate the need for high temperature annealing.

Membranes should be characterized with regard to flux, high temperature stability, catalytic activity, resistance to poisoning, and resilience with regard to thermal cycling. Mixed-gas tests should be performed to determine if any selectivity enhancement occurs because of hydrogen occupying the microcracks and grain boundaries, preventing permeation of other gases. To determine thermal cycling resistance, numerous excursions between room temperature and least 673 K should be undertaken with permeation measurements at each extreme. Decrease in selectivity will indicate loss of adhesion or formation of pores, while SEM analysis will reveal any structural changes.

In addition to SEM, analysis of membranes with other instruments such as XRD, and AES should become routine. XRD analysis can reveal changes in Pd grainsize or reveal phases that may influence permeability characteristics. Through consistent XRD analysis of tested membranes, a more thorough understanding might be gained of how hydrogen permeates through metals. This is important information if tailoring the morphology by EP techniques or annealing at specific conditions for increased permeability is to be pursued. Although inroads into the design of nanostructured materials may produce stable metal films with potentially much higher hydrogen permeabilities, more work on nanostructured materials is required to firmly establish their increased permeability.

Even with the use of UHP gases (99.999% pure), some apparent surface poisoning effects were observed during testing at high temperature. After permeating nitrogen or helium, hydrogen flux decreased but was recoverable to the prior level after a period of
time. Other researchers in the field have noted this and blamed it on contamination although a full explanation has not yet been given\(^{660}\). AES or XPS analysis of the surface for impurities could be conducted after observation of this phenomenon. However, if the problem is a carbon layer, it may not be possible to differentiate between carbon deposited at high temperature and the carbon contamination layer normally seen on samples exposed to atmosphere for even brief lengths of time. In any case, to reduce the possibility of oxygen or moisture in the gases from affecting membrane performance, oxygen and moisture traps should be installed.

Of course in real world situations, gas streams may contain a variety of impurities that have the potential to poison the membrane surface or at least impede hydrogen permeation. Contamination by carbon or sulfur containing materials is an important consideration for operation with most chemical processes. The reversibility of poisoning or fouling of the membranes from compounds present in gas streams should be evaluated. Regenerating or preventative measures can be developed.

This work showed that at least a few microns of Pd are required to form a permselective Pd film on the symmetric GTC 998 supports (at least with the present activation and deposition methods). Accordingly, membranes should be prepared using asymmetric ceramic supports, particularly those with 50 Å pore size. Although these membranes are costlier, their higher permeability, and the likelihood of requiring much less Pd to form a defect-free coating may offset the higher cost of such supports. However, adhesion of films to these supports has been problematic\(^{676}\) and a new activation or electroless deposition method promoting stronger bonding may be required. Therefore, deposition methods other than EP should be tried. Solvated metal atom deposition (SMAD, see §2.6.5) should be experimented with further for it may be promising for depositing a very thin and selective Pd film on mesoporous supports.

Future work should include further attempts to fabricate a leak-free film on porous stainless steel supports. The use of stainless steel supports may be advantageous from the standpoint of durability and ease of welding them into a module. Cermets (ceramic-metal) materials should be studied to obtain a means of welding metal infiltrated porous ceramic membranes\(^{86,693}\). Specific recommendations for reducing the pore size of the stainless steel supports include either mechanically modifying the surface or depositing a smooth and more selective intermediate layer between the support and the Pd film. This may include a
porous ceramic or a hydrogen permeable metal deposited by sol-gel, dip coating, CVD, or sputtering.

Preparation of membranes in clean room conditions might be worth the effort in order to try and eliminate the microscopic particles that may create defects in the thin Pd film. Similar measures taken during the fabrication of membranes comprised of amorphous silica films on porous γ-alumina supports demonstrated that dust particles might be fouling the surface, therefore hampering the deposition of a defect-free thin film\textsuperscript{63}. Furthermore, high purity chemicals may also prevent defects in the as-is electrolessly plated film, or prevent defects from forming in the film during annealing due to codeposited impurities\textsuperscript{659}. Foreign particles have been shown to cause nodule formation so passing the EP solution through a submicron filter during plating is also recommended\textsuperscript{477}.

Characterization of the Pd film surface area and pore size distribution may be worthwhile. This might be accomplished by Brunauer-Emmett-Teller (B.E.T.) analysis using nitrogen adsorption at 77 K\textsuperscript{608,683}. Surface areas before and after high temperature testing as well as of the supports themselves could indicate any loss or gain in surface area due to high temperature annealing or porosity formation respectively. Small-angle neutron scattering (SANS) might also be employed to determine more about the Pd film structure such as an estimation of free volume, void space, and vacancies\textsuperscript{793}.

Many of the courses of research suggested above should become routine practices. Increased amount of routine characterization needs to be carried out. For example, it may take a large collection of XRD data on many different membranes, to come to any conclusions about the influence of electroless plating methods or annealing conditions on grainsize and the subsequent effect on hydrogen permeability. SEM microscopy is essential to view the surface and see how the Pd film morphology varies.

8.4 Outlook

The prospects for emergence of a viable Pd composite membrane configuration look better every year. Starting with a porous ceramic support with 50 Å pores, it seems reasonable that a very thin Pd film could be deposited to create a defect free membrane, (at least in theory). Researchers working with stainless steel supports are obtaining thinner and more selective Pd membranes through surface modifications of the stainless steel
support membrane prior to using special metal deposition techniques\textsuperscript{661}. Pd/refractory-metal membranes have equal or greater fluxes than Pd films on porous supports despite the relatively thick refractory metal layer\textsuperscript{794}. Therefore, Pd composite membrane technology might revolutionize hydrogen reactions and separations, and with research to overcome the technical and engineering challenges, commercial use may be as soon as a decade away. This would help utilize the world's energy resources in a more efficient, environmentally sustainable manner.
GLOSSARY

**Membrane Nomenclature**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>asymmetric</td>
<td>a membrane material comprised of a highly porous layer coated with a very thin layer, with smaller, more selective pores or that is dense but permselective for a specific molecule</td>
</tr>
<tr>
<td>Knudsen diffusion</td>
<td>mobility of molecules through pores of the same order as molecular diffusion path lengths resulting in selectivity based on the square roots of molecular weight</td>
</tr>
<tr>
<td>lumen</td>
<td>the inner diameter of a tube</td>
</tr>
<tr>
<td>microporous</td>
<td>a material with pores smaller than 2 nm (IUPAC definition)</td>
</tr>
<tr>
<td>mesoporous</td>
<td>a material with pores between 2-5 nm (IUPAC definition)</td>
</tr>
<tr>
<td>macroporous</td>
<td>a material with pores larger than 5 nm (IUPAC definition)</td>
</tr>
<tr>
<td>symmetric</td>
<td>a membrane material consisting of the same pore size throughout</td>
</tr>
<tr>
<td>flux</td>
<td>volume passing through the membrane per unit area and time</td>
</tr>
<tr>
<td></td>
<td>permeability a function of solubility and diffusivity; flow per area, time, driving force through a membrane of known thickness (^2)</td>
</tr>
<tr>
<td>permselectivity</td>
<td>a measure of the ability for a membrane to separate two different molecules or atoms</td>
</tr>
<tr>
<td>solution-diffusion</td>
<td>a permeation mechanism whereby the permeant molecule or atom diffuses through a membrane material by first dissolving</td>
</tr>
</tbody>
</table>

**Plating Nomenclature**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>osmotic plating</td>
<td>carrying out a liquid phase deposition process with a more concentrated liquid on the opposite side of the porous support to create an osmotic pressure driving force for plating solution permeation through the support</td>
</tr>
<tr>
<td>flow system</td>
<td>conducting a deposition process by pumping the plating solution</td>
</tr>
</tbody>
</table>
strike
an acidic metal-containing solution used to clean and activate an
electrically polarized metal surface

pickle
an acid cleaning step to remove impurities and oxides from a metal
surface prior to electroless plating or electroplating

plate-out
undesired electroless deposition of metal onto extraneous surfaces

drag-in
transfer of one solution into another on a surface to be plated,
usually with detrimental effects on the second solution

shot peening
bombarding the surface of a porous material to alter its surface
properties, in general, to decrease the pore size

throwing power
a qualitative term describing the ability of a deposition process to
uniformly coat a surface

overpotential
Bockris "departure of electrode potential from the equilibrium value
due to the slowness of one of the steps of the electrode reaction

List of Symbols

\( S \)  solubility = (mol/m^3•Pa)
\( D \)  diffusivity = (m^2/s)
\( P \)  permeability = (mol•m/m^2•s•Pa)
\( K_s \)  Sieverts' constant = (mol/m^3•Pa)
\( c \)  concentration = (mol/m^3)
\( p \)  partial pressure
\( F \)  flux = (mol/m^2•s)
\( E \)  activation energy = (J/mol)
\( l \)  membrane thickness = (m)
\( T_m \)  melting point = (K)
\( t \)  grainsize (nm)
\( L \)  ligand
\( M \)  metal
\( E^o \)  standard redox potential = (V)
\( z \)  number of electrons transferred
\( R \)  
\( \text{gas constant} = (8.314 \text{ J/mol}\cdot\text{K}) \)

\( n \)  
\( \text{power dependency of pressure driving force for hydrogen permeability} \)

\( K \)  
\( \text{constant in Scherrer equation} = 0.9 \)

\( b \)  
\( \text{instrumental broadening (degrees)} \)

\( B \)  
\( \text{experimental peak width (degrees)} \)

\( \text{MW} \)  
\( \text{molecular weight} = (\text{g/mol}) \)

**Greek Symbols**

\( \alpha \)  
\( \text{phase of Pd with low hydrogen solubility} \)

\( \beta \)  
\( \text{phase of Pd with high hydrogen solubility} \)

\( \sigma_s \)  
\( \text{surface roughness factor} \)

\( \alpha_{Kn} \)  
\( \text{Knudsen selectivity} \)

\( \alpha_{\text{ideal}} \)  
\( \text{ideal separation factor or permselectivity, a ratio of the pure gas fluxes} \)

\( \theta \)  
\( \text{Bragg angle} = (\text{radians}) \)

\( \lambda \)  
\( \text{wavelength} = (\text{Å}) \)

\( \beta_i \)  
\( \text{integral pure diffraction broadening (radians)} \)

**Subscripts**

\( 1 \)  
\( \text{upstream, high pressure side} \)

\( 2 \)  
\( \text{permeate or downstream, low pressure side} \)

\( i \)  
\( \text{species i} \)

\( s \)  
\( \text{surface} \)

\( H \)  
\( \text{hydrogen} \)

\( m \)  
\( \text{metal coordination number} \)

\( n \)  
\( \text{ligand coordination number} \)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF</td>
<td>standard cubic feet</td>
</tr>
<tr>
<td>PSA</td>
<td>pressure swing adsorption</td>
</tr>
<tr>
<td>DI</td>
<td>deionized water</td>
</tr>
<tr>
<td>EP</td>
<td>electroless plating</td>
</tr>
<tr>
<td>ICE</td>
<td>internal combustion engine</td>
</tr>
<tr>
<td>PMR</td>
<td>palladium membrane reactor</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>XLBA</td>
<td>x-ray line-broadening analysis</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive x-ray analysis</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>electric vehicle</td>
</tr>
<tr>
<td>PEMFC</td>
<td>proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>SS</td>
<td>stainless steel</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethylorthosilicate</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>MOCVD</td>
<td>metal-organic chemical vapor deposition</td>
</tr>
<tr>
<td>SMAD</td>
<td>solvated metal atom deposition</td>
</tr>
</tbody>
</table>
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General consensus in the scientific community has been reached that the potentially disastrous consequences of global warming or the greenhouse effect may only be remedied by drastically curtailing the production of greenhouse gases. Carbon dioxide (CO₂) is the primary human generated greenhouse gas of concern, due to its large volume of emissions worldwide. Internal combustion engines (ICE's) in motor vehicles constitute one of the largest fractions of the CO₂ generated by human activity.

With the forthcoming industrialization of less developed countries, and the expanding growth of the global economy and population, the need for swift, clean and safe personal transportation will steadily increase. Worldwide car population is projected to double in the next 20 to 30 years, obviously offsetting any gains in fuel efficiency and emission controls. Tightening of environmental laws is apt to continue as mounting pressures on the natural resources of the environment become severe and the implementation of environmentally sustainable practices becomes necessary. Air pollution is already an unhealthy problem in airsheds surrounding major cities everywhere. To reduce production of CO₂ and other pollutants, vehicles must be redesigned for fuel efficiency and minimal emissions. These are important considerations because it is paramount to reduce the environmental impacts associated with energy extraction and use, especially with increasing global pressure on petroleum reserves.

There are a few potentially workable prototype vehicles suitable for large-scale production that are more energy efficient and create less pollution. Energy is supplied from various sources for these so-called new generation of vehicles or hypercars including batteries, hydrogen, liquids derived from renewable biomass, (such as alcohols), solar panels, and fuel cells. Vehicles with combinations of power systems are called hybrids. These vehicles reduce emissions by burning cleaner fuels and/or making the most efficient...
use of fuel or energy. In practice, solar powered vehicles remain a novelty. However, battery powered electric vehicles (eV's) are becoming more prevalent with the development of more energy dense storage battery technology.

One advantage of an eV is that it can be charged during off-peak hours from a power plant or renewable energy source. Although the energy on the grid often originates from carbon based fuels such as coal or natural gas, a large central power plant is significantly more efficient than an ICE. Plus, pollutants are more easily treated at a power plant. In operation, eV's are quieter and waste no power when stalled in traffic. Less noise pollution from roads would improve quality of life. Also, with regenerative braking technology, energy that is normally lost can be recovered during braking for increased efficiency. The primary disadvantage of eV's is the environmental problems associated with battery production, recycling, and disposal. The weight of the batteries as well as their replacement cost are also major considerations.

The fuel cell/electric hybrid vehicle is an attractive option possessing similar range and performance attributes to ICE vehicles\textsuperscript{51}. Fuel cell vehicle efficiencies may be as high as 30-40\% while ICE vehicles are presently around 15\%.\textsuperscript{799} This is because the fuel cell output is primarily electrical energy while the ICE produces some mechanical power and a lot of waste heat.

For power a liquid fuel, such as methanol, would react with steam over a catalyst bed, yielding hydrogen, carbon dioxide, and traces of carbon monoxide. The purified hydrogen would react with air in a proton exchange membrane fuel cell (PEMFC) to power an electric motor. During idling, batteries may be charged for later assistance with accelerating and starting. PEMFC's are lightweight, power dense, and operate at fairly low temperatures ($\sim 353$ K). They consist of a polymer electrolyte membrane that is permeable to $H^+$ ions, sandwiched between the two electrodes. Although the amount of platinum catalyst required within the polymer membrane has been drastically reduced, it is still a major cost of the PEMFC module\textsuperscript{758}.

Only recently have advancements in the technological and economical aspects made the fuel cell even close to being feasible for mass production. Presently, the higher cost of hydrogen and alcohols as fuels as well as the cost of fuel cell modules limits commercial use. Development of a compact module for generating electricity has hinged on factors such as a durable and compact fuel cell, high yield catalysts for producing hydrogen from
liquid fuels, and an effective system for preventing impurities from affecting fuel cell performance. Hydrogen is a very clean fuel, however its distribution and storage in either the liquid or compressed gaseous form would require prohibitive capital investment. Meanwhile, the extensive infrastructure already exists for liquid fuel distribution. Coupled with the fact that hydrogen storage cylinders are heavy and bulky, on-board generation of hydrogen from a liquid fuel seems to be an attractive option.

Despite the possibility of superior efficiency, fuel cells have several drawbacks yet to be overcome. Fuel cells have a warm-up period and respond poorly to the need for impulse power. Coupling with a battery or flywheel alleviates these problems although batteries add weight and cost to the vehicle. Toyota and Daimler-Chrysler have demonstrated that methanol can be converted to hydrogen in an on-board reactor for fuel cell consumption. Arthur D. Little is working on a portable partial oxidation reactor for conversion of gasoline and air into a hydrogen rich product for fuel cell use. The optimal reactor combines reforming and partial oxidation. Although reforming is more efficient, partial oxidation is better for meeting impulse power requirements, and can provide the heat necessary for reforming, particularly during start-up.

The other critical problem is that feed impurities such as sulfur compounds and CO easily poison the fuel cell, drastically reducing its power output. On-board purification of hydrogen to remove CO to the less than 20 ppm essential for fuel cell use can be accomplished in a number of ways including preferential catalytic oxidation of the CO to CO$_2$ in a preferential oxidation (PROX) reactor, low temperature shift reaction of CO and steam to hydrogen and carbon dioxide, catalytic methanation, adsorption on a regeneratable getter, PSA, or membrane separation.

An effective hydrogen separating membrane can also be used to prevent CO from poisoning the catalyst in the fuel cell. A membrane reactor/separator eliminates the need to remove CO in an inefficient PROX reactor following the reformer. Amphlett et al. calculated that the size of the partial oxidation reactor is on the same order as the reformer, increasing the attractiveness of alternative CO removal techniques such as a Pd membrane. Plus, some loss in efficiency is incurred as some of the hydrogen is converted to water although the catalyst is quite selective. Lægsgaard Jørgensen et al. conducted methanol reforming in a PMR at 20 atm and studied the effect of CO on membrane reactor performance.
Pd composite membranes are a promising technology for integration into a reaction and/or separation process involving hydrogen. Such membranes possess high flux and selectivity as well as the ability to operate at high temperatures and pressures. These characteristics make Pd membranes suitable for incorporation into a fuel cell vehicle system. The potential applications range beyond vehicular fuel cells. Stationary fuel cells operating at much higher temperatures are often insensitive to impurities although a PMR providing hydrogen from fuels such as natural gas or coal gas could increase their efficiency. Unfortunately, significant hurdles remain to commercial implementation of Pd membranes, particularly with regard to cost and thermal cycling resistance, critical considerations in a vehicle.
APPENDIX B

EXAMPLE OF ALLOY COMPOSITION CALCULATION FROM XRD RESULTS

Pd–Cu alloy compositions were calculated from XRD d-spacings by assuming a linear shift with composition. Table B contains the XRD data for the (111) Pd and copper peaks of the top of Membrane Cu-2. Figure B is the XRD pattern with the raw tabulated data.

Table B. XRD Results for Top of Membrane Cu-2, (111) Peak.

<table>
<thead>
<tr>
<th></th>
<th>Palladium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing $^02$</td>
<td>2.246 Å</td>
<td>2.088 Å</td>
</tr>
<tr>
<td>measured d-spacing</td>
<td>2.1913 Å</td>
<td>2.1101 Å</td>
</tr>
</tbody>
</table>

From the shift in the Pd peak, the copper composition was estimated by linear interpolation:

$$Atom\% \text{ Copper} = \frac{2.246 - 2.1913}{2.246 - 2.088} = 0.346 \times 100\% = 35\%$$
Figure B. Raw XRD data.
APPENDIX C

COMPILATION AND DISCUSSION OF XLBA RESULTS

The XRD results were used to calculate grain size using XLBA and the Scherrer equation (see §3.9.4) for all the Pd films analyzed are reported in Table C. As can be seen from the results, heat treatment history influenced grain size. While X-ray diffraction analysis of the Pd films could not determine if any correlation exists between hydrogen permeability and Pd grain size, several observations could be made. First of all, the films were textured with a strong (111) orientation after plating and kept this alignment after heating as well. Some electroless copper deposits have exhibited (111) orientation as well, with larger grain size at the top surface than the bottom of the film443.

As expected, there were changes in grain size upon annealing at high temperature. After heating to 1023 K, the top grain sizes of Membranes 7 and 9 doubled (Table C). An interesting feature to note is of the grain size of the bottom of these, Membrane 9 only increased slightly from the typical bottom grain size of an unheated film. These observations notwithstanding, XRD analysis on more membranes as well as further analysis of the existing XRD and flux data is necessary before any correlations can be made between grain size and hydrogen permeability.

If films with smaller grain size turn out to possess higher permeability, grain growth may be inhibited by addition of a metal to Pd above the solubility limit so that segregation of the alloying metal to the grain boundaries prevents grain coarsening272,276-280. A drawback of this may be that the alloying metal is prone to oxidation or is less active than Pd in breaking the H-H bond. Operation at lower temperatures may be required to prevent grain coarsening.
Table C. Grainsizes of Selected Membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Plating Method</th>
<th>Heated to (K)</th>
<th>Top* (nm)</th>
<th>Top (111) (nm)</th>
<th>Bottom* (nm)</th>
<th>Bottom (111) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTC-21</td>
<td>19.3 µm</td>
<td>flow</td>
<td>345 K</td>
<td>25 nm</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GTC-20.4</td>
<td>6.3</td>
<td>batch</td>
<td>345</td>
<td></td>
<td>22</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Membr. 10</td>
<td>(11)</td>
<td>flow</td>
<td>345</td>
<td>23</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-1</td>
<td>(12)</td>
<td>batch</td>
<td>723</td>
<td>28</td>
<td>38</td>
<td>33</td>
<td>43</td>
</tr>
<tr>
<td>GTC-17.1</td>
<td>16.5</td>
<td>batch</td>
<td>823 (?)</td>
<td>63</td>
<td>65</td>
<td>26</td>
<td>35</td>
</tr>
<tr>
<td>GTC-17.4</td>
<td>16.5</td>
<td>batch</td>
<td>623 (?)</td>
<td>64</td>
<td>&gt; 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membr. 7</td>
<td>(21)</td>
<td>batch</td>
<td>1023</td>
<td>73</td>
<td>&gt; 100</td>
<td>38</td>
<td>64</td>
</tr>
<tr>
<td>Membr. 9</td>
<td>(18)</td>
<td>flow</td>
<td>1023</td>
<td>67</td>
<td>&gt; 100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Average of the first 5 peaks

†Determined by weight difference, values in parenthesis determined by SEM