Project Title: Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems Using High-Throughput Combinatorial Methods

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ABSTRACT

This report summarizes the work completed under the U.S. Department of Energy Project Award No.: DE-FE0001181 titled “Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems Using High-Throughput Combinatorial Methods.” The project started in October 1, 2009 and was finished September 30, 2014. Pall Corporation worked with Cornell University to sputter and test palladium-based ternary alloys onto silicon wafers to examine many alloys at once. With the specialized equipment at Georgia Institute of Technology that analyzed the wafers for adsorbed carbon and sulfur species six compositions were identified to have resistance to carbon and sulfur species. These compositions were deposited on Pall AccuSep® supports by Colorado School of Mines and then tested in simulated synthetic coal gas at the Pall Corporation. Two of the six alloys were chosen for further investigations based on their performance. Alloy reproducibility and long-term testing of PdAuAg and PdZrAu provided insight to the ability to manufacture these compositions for testing. PdAuAg is the most promising alloy found in this work based on the fabrication reproducibility and resistance to carbon and sulfur. Although PdZrAu had great initial resistance to carbon and sulfur species, the alloy composition has a very narrow range that hindered testing reproducibility.

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EXECUTIVE SUMMARY

Palladium membranes are well known to separate hydrogen. However, in the presence of common industrial stream components such as carbon monoxide and hydrogen sulfide, palladium membranes lose hydrogen flux and purity. Palladium can be alloyed with other metals such as copper, gold, and platinum to increase its chemical tolerance, but traditional one-by-one fabrication and testing methods are slow. Pall Corporation used a combinatorial approach that allows for the investigation of range of ternary alloy compositions at one time. This high-throughput screening method is commonly used in catalyst development, but has not yet been applied to palladium membranes. In this way hundreds of alloys were fabricated and exposed to simulated coal synthesis gas. Based on these experimental results, six alloys were identified for further investigations.

Six palladium-based ternary alloys were deposited on Pall AccuSep® supports by the Colorado School of Mines. The alloys were annealed and pure-gas tested before being shipped to Pall for coal gas testing. The carbon and sulfur resistance of the novel alloys were compared to a palladium-gold alloy, which is one of the best binary alloys for chemical tolerance. The mixed gas testing yielded two stand-out alloys whose results were reproduced. Based on the reproducibly of fabrication and testing performance, PdAuAg was chosen for scale-up and future testing.

INTRODUCTION

The overall objective of this project is to determine the feasibility of operating a Pd-based ternary membrane at high temperatures and pressures for the separation of H_2/CO_2 from coal derived syngas. The main obstacle is finding an alloy composition with the chemical stability to maintain the ability to separate H_2 in the presence of stream contaminants such as CO and H_2S. Recent research has shifted from binary Pd-based membranes to ternary Pd-based membranes. Fabricating and testing each composition using the conventional “one by one” method would require immense amounts time and resources. Pall Corporation utilized a high throughput combinatorial method that involves sputtering Pd and two other metals in a compositional array on a silicon wafer. These wafers were exposed to coal gas with the composition specified by the Southern Company. Visual and analytical inspections of areas that were not discolored by the gas yielded six compositions for further investigation. This report details the results of high-throughput screening technique, fabricating and testing the six identified Pd-based ternary alloy membranes, and reproducing the testing results of the top two performers.

BACKGROUND RESEARCH

The ability for palladium membranes to withstand common contaminants found in coal gasifier feed streams such as hydrogen sulfide and carbon monoxide is a critical step in the path for commercialization. Therefore, chemical stability is emphasized in this background research section. This section will cover topics such as alloying palladium for increased chemical tolerance, combinatorial alloy development methods, gas separation membrane substrate quality, and hydrogen permeation chemical modeling. For a more in-depth look into any of these topics, please refer to Appendix I.

Chemical Stability of Palladium and Palladium-alloy Membranes

Hydrogen sulfide common in coal gasifier effluent streams presents the most serious problem to existing palladium-based membranes since sulfur even in a few parts per million is sufficient to block hydrogen permeation under some operating conditions and premature the life time of a palladium-based membrane system. To increase tolerance to sulfur, researchers have employed Pd-Cu, Pd-Au, Pd-Fe, Pd-Pt binary alloys and few ternary palladium alloys such as Pd-Cu-Ru, Pd-Cu-Rh and Pd-Au-Pt. However, the sulfur tolerance of existing palladium alloys is not yet sufficient for practical applications, especially coal gas hydrogen separation.

Carbon monoxide is also common in coal gas is significantly detrimental to most of existing palladium alloy membranes especially in absence of steam, but it is less critical, compared to sulfur poisoning. Examined palladium alloys include Pd-Ag, Pd-Cu and Pd-Au-Ru. A promising development is partially internal oxidized Pd-Al and Pd-Ag-Al composites which showed improved carbon monoxide resistance. Another interesting investigation is associated with Pd-Y(Gd)-Ag, Pd-Y-Pb(In, Sn) since these materials have high very hydrogen flux and less affinity to carbon monoxide. Temperature for operating palladium membranes can be optimized to mitigate the harmful effects of carbon monoxide, which ranges 350-450^{o}C. Steam can play a role in counteracting carbon monoxide poisoning. This is because water molecules dissociate on palladium membrane surface to form active oxygen species as carbon scavengers. It appears feasible that material approaches along with process conditions can be applied to address carbon issues with palladium-based membranes.

This section begins with a brief summary of the research pertaining to sulfur tolerance and is followed by relevant research on palladium-alloys in the presence of carbon monoxide.

Literature Summary of Hydrogen Permeation of Pd-alloys with Hydrogen Sulfide Present

In the early 1960’s, Union Carbide [1-3] explored palladium alloy membranes for large-scale hydrogen recovery from refinery processes. They systematically assessed the sulfur resistance of Pd, Pd-40Cu, Pd-27Ag and Pd-40Au (wt% alloys) alloy by exposing one millimeter thick foils to 4 – 20 ppmv hydrogen sulfide in hydrogen at 350^{o}C and 75 psig. The membrane samples were onstream for 2-7 days to ensure equilibrium. Their ranking in terms of sulfur tolerance is given as follows.

PdAu40 > Pd > PdCu40 > PdAg27

Even when the concentration of hydrogen sulfide was raised to 20 ppm in the feed gas, the PdAu foil still maintained more than 40% of its sulfur-free hydrogen flux. The authors suggested that a membrane made of pure palladium with a gold enriched surface may have optimum between sulfur tolerance and high hydrogen flux.

M. V. Mundschau et al (2006) [4] reported their investigation of the sulfur tolerance of Pd (20 ppm H_2S), PdCu20 (20 ppm H_2S) and PdAg25 (10 ppm H_2S) at 325°C. Their results suggested the following ranking.

PdCu20 >> Pd > PdAg25

NETL (2003-2010) [5-13] has carefully investigated Pd-Cu alloy system as potential membrane material for coal gas hydrogen separation application. They determined the sulfur resistance of Pd-Cu alloy as a function of its composition under various conditions. Their research work indicates that the PdCu40 alloy foil (BCC crystal and 25 micron thick) completely lost hydrogen permeation in presence of 1000 ppm H_2S at 350°C. It is agreement with Union Carbide. Their post-test surface characterizations by XRD, SEM-EDS and XPS indicate that sulfur contamination was limited to the top surface of the PdCu40 foil and no bulk sulfides were found. In contrast, the pure Pd foil had a palladium sulfide layer of few hundred nanometers thick. Another significant development from their work is that a PdCu20 alloy with FCC structure possesses the best sulfur tolerance among its alloys. In summary, the sulfur tolerance of Pd-Cu alloy can be optimized as a function of its composition and crystal structure; a FCC Pd-Cu alloy has better sulfur tolerance, but a BCC Pd-Cu alloy has higher hydrogen flux.

In all of the research conducted, the presence of small amounts of hydrogen sulfide inhibits hydrogen permeation through Pd-based membranes with some alloys being more affected than others. A general understanding for this inhibition is that sulfur has very high affinity for palladium, meaning a high binding energy of sulfur to palladium. Sulfur has a valence electron structure $3s^2 3p^4$ with two pairs of unshared electrons and electronegativity 2.58 whereas palladium has valence electron configuration of $4d^{10} 5s^0$ with electronegativity 2.20. Several studies have revealed substantial overlap of primarily sulfur p-states with the palladium surface d-band giving rise to a strong covalent bond between the adsorbate and the surface [14-17]. Hydrogen sulfide can dissociatively adsorb on palladium surface and approach saturation monolayer in presence of few ppm sulfur in gas phase. The adsorption is generally very rapid even at room temperature and it has low energy barrier to adsorption and dissociation until a high coverage, for instance above 0.5 ML [14-17].

Once the sulfur is chemisorbed to the surface, it can block hydrogen dissociation sites leading to decreased hydrogen flux. Sulfur adatoms occupy the same surface hollow adsorption site as hydrogen and make at least one hollow site inaccessible for hydrogen adsorption; but it was suggested that the actual surface deactivation per sulfur adatom is larger, comprising about four hydrogen adsorption sites. Sulfur can also form bulk sulfides with metals such as palladium, which have a flux that is four times lower than pure palladium.

Literature Summary of Hydrogen Permeation of Pd-alloys with Carbon Monoxide Present

CO is one of the components of coal gas (H_2, CO, CO_2, H_2O and other minors). Its amount depends on gasifier process conditions and additional downstream gas processing, typically in a range of 25-35% at a coal gasifier outlet and down to 1% after being shifted by a catalytic process.

M. Amano et al (1990) [18] analyzed the effects of CO and CO_2 on hydrogen permeation through a pure palladium membrane at 150-450^oC and 0.2-36.8 psia with 10% CO, 50% CO and 50%CO_2 with a balance of hydrogen. A Pd foil had a thickness of 700 microns and 12 mm in diameter. They found that CO inhibited hydrogen permeation below 250^oC and it had no inhibition above 250^oC. In addition, the extent of inhibition significantly increased with the concentration of CO. They observed the same hydrogen solubility constants at each temperature. Therefore, the authors suggested that the deterioration of hydrogen permeation by CO be attributed to the decrease in effective area for H_2 dissociation by the weak adsorption of CO.

F. Gallucci et al (2007) [19] investigated the effect of CO on hydrogen permeation through a pure Pd membrane tube (100 micron thick) with a wide range of CO in hydrogen using H_2-N_2 gas mixture as reference at 250-350^oC and feed pressure 52 psi. It was found that CO molecules remarkably inhibit hydrogen permeation at 250^oC, but not at 350^oC. It is interesting noted that the inhibition of CO to hydrogen permeation is non-linear as a function of CO content in hydrogen. Hydrogen flux rapidly decreased with CO while it was below 15%. In contrast, hydrogen flux gradually approached to the values with H_2-N_2 gas mixtures as CO increased above 15%. The authors hypothesized that it was attributed to the diluting effect by CO.

H. Li et al (2007) [20] used a thin Pd membrane tube to examine the effect of CO on hydrogen permeation and the membrane structure at 320-500^{o}C with H_2-CO gas mixture (CO 20-33%). The membrane was prepared by electroless plating on porous alumina tube and it had a Pd coating of 3 microns thick. They observed three temperature regimes could be recognized considering the effect of CO on hydrogen permeation: 1.) < 350^{o}C CO remarkably inhibited hydrogen permeation; 2.) 350-450^{o}C the inhibition was moderate; 3.) > 450^{o}C the inhibition seems negligible. They also noticed that the inhibition gradually increased with time within 6 hours. And the higher temperature was, the more sharply the inhibition rate with time became. XRD indicated formation of palladium carbide $Pd_{1-x}C_x$ above 450^{o}C. As expected, more palladium carbide phase formed at higher temperature, for instance 500^{o}C. Although palladium carbide phase is metastable under the experimental conditions, its decomposition seems kinetically rather slow. Therefore, palladium carbide phase was accumulating on/in Pd membrane with time, which is consistent with hydrogen permeation decay. Further, palladium carbide phase has litter hydrogen activity.

Combinatorial Methods for High-Throughput Alloy Screening

Combinatorial methods have not yet been adopted for hydrogen separation metal alloy membrane development although it has been successfully practiced by the U.S. chemical and pharmaceutical industries to identify promising new compounds based on the rapid synthesis and evaluation of a large number of material samples.

In a typical combinatorial material development, the characterization tools are used for rapid, high-throughput and automated assessment of single or multiple properties of the large number of samples fabricated together as a combinatorial library [21]. A representative list of materials properties includes chemical, morphological, mechanical, optical, electrical, biological and thermal properties. In any typical of combinatorial experimentation, having the appropriate characterization tool is critical. Without a suitable high-efficiency screening technique, high-throughput synthesis by itself does not provide the information about material properties. For example, when a two million compound library was synthesized with only a 15 ng amount of each compound, the small amount proved to be impossible to analyze using available screening tools. To address a large number of materials-specific properties, a variety of high-throughput characterization tools are required. Ideally, a characterization system for combinatorial materials discovery should be capable of handling small samples with minimal sample preparation requirements and should have rapid turnaround using either serial or parable measurements of library elements during or after the synthesis reaction. It should also have high precision and high accuracy in measurements. In addition, data acquisition, instrument operation and communication among instruments within the discovery cycle should be automated. Data analysis should be effective in handling large amounts of data utilizing either univariate or multivaritate algorithms and should be capable of providing simple transfer functions for the property of interest. Finally, the structure of data management should be clearly laid out and well organized. Good data management schemes should lead to new opportunities in experimental designs, data mining and development of algorithms to correlate data from different characterization tools.

In advanced functional materials, the required performance of a material can become very specific depending on its application. This often means one has to design, develop and tailor screening techniques which are highly specified for individual applications. In many ways, availability of characterization tools determine the scope of one's combinatorial materials studies. In recent decades, a large repertoire of analytic techniques has been adopted as high-throughput characterization tools. Of specific interest to us is chemical imaging methods and instrumentations including various spectroscopic, microscopic, and their combination technologies (laser-induced fluorescence detection, Fourier transform infrared, and Raman spectroscopy), mapping X-ray microdiffractometry, nuclear magnetic resonance, mass spectrometry [22-27].

Substrate Quality for Gas Separations in Palladium-composite Membranes

Thin palladium or palladium alloy films supported on highly permeable, porous metal or/and ceramic substrates are attractive for practical applications because of high hydrogen flux and reduced material cost. Porous stainless steel media and super-permeable refractory metals as supporting substrates offer several advantages of sealing and modulation fabrications. However, it requires an intermediate layer as inter-diffusion barrier and surface morphology control. The technical feasibility has been approved and its optimization / scale-up are yet to be developed. The following physical and chemical properties of substrate materials need to be taken into account.

Both porous ceramic and stainless steel structures have been widely used in the past as the substrates to support thin Pd or Pd alloy films [28, 29]. The main advantages of porous ceramic supports include surface chemical inert and small pore size / uniform pore size distribution. However, the major drawbacks for porous ceramic supports are fragile, susceptible to cracking and difficulty in sealing ceramic to metal parts for process integration. Recently, porous metallic substrates have received considerable attention due mainly to ease of module fabrication and process integration and their closeness of the thermal expansion coefficient to that of Pd and Pd alloys. Contamination from the intermetallic diffusion of metal support and the large pore size / wide pore size distribution presents considerable challenges for depositing thin film with good durability. Therefore, an intermetallic diffusion barrier between Pd film and the support is necessary to build. Methods used to produce the barrier layer include sputtering titanium in a nitrogen atmosphere to form a TiN layer, applying nickel powder followed by sintering combined with the application of a thin gamma-alumina layer by the sol-gel method, depositing zeolite layer by hydrothermal synthesis, and applying ceramic layer by slurry coating, in-situ forming conformal oxide coating by high temperature air treatment. K. Zhang et al (2009) [30] assessed the effectiveness of two types of interdiffusion barriers, one in-situ oxidized metal oxide and the other sol-gel derived mesoporous yttria stabilized zirconia (YSZ). It was noted that the Pd membrane with an in-situ oxidized porous stainless steel was gradually losing hydrogen permeation above 600^{o}C, which resulted from reduction of the oxidized layer by hydrogen. In contrast, the membrane with YSZ as intermediate layer maintained stable hydrogen flux at the same temperature.

Exploring Hydrogen Permeability of Pd-alloys Using Chemical Modeling

Density function theory (one of electronic structure methods) has been increasingly used to investigate hydrogen transport through palladium its alloys and sulfur / carbon adsorption on the membrane surface. It not only helps to understand physics of the phenomena, but also the theoretical computation provide a general guideline to design and select alloying components in complement with emerging high throughput combinatorial alloy development methods. Conventional alloying element screening and optimization methods, i.e. “one at a time” is time consuming and expensive. A recent new development is combinatorial and high throughput method in material science and engineering. Its feature is “many at a time”, which remarkably accelerate material R&D cycling time. This method is being applied for sulfur/carbon resistant Pd-based alloy development through a DOE funded project. In recent years, first principles calculations based on density functional theory (DFT) have been applied to complement well with experimental methods, for instance combinatorial experimentations, for accelerating material development.

DFT calculations have an impressive set of advantages relative to other theoretical tools: they can be applied to arbitrary configurations of atoms including all elements in the periodic table, they provide direct information on the ground state energy of these configurations, and they can be used to predict the precise mechanism of diffusion or reaction events in condensed phases. These advantages are balanced by at least two important caveats. The size of systems that can be treated by DFT is strongly limited by the considerable computational effort involved. Second, DFT calculations are not exact because they involve approximations for electron exchange-correlation effects. It is, therefore, important to establish what level of accuracy can be expected from these calculations.

D. S. Sholl's research group, [31] for a long time, has been using the DFT to study the structures and dynamics of hydrogen in metals. Their studies involved a wide range of hydrogen transport metals including binary and ternary Pd alloys (Pd-Cu, Pd-Cu-X / X: Ti, Zr, V, Nb, Ta, Ru, Rh, Pt, Ag, and Au), binary intermetallics (ZrV_2, $ZrCr_2$, $ZrMn_2$, $ZrFe_2$, and $ZrCo_2$), and amorphous alloys (Fe_3B, ZrNi and ZrNiNb). Of particular interest to this project is the work about ternary metal alloys Pd-Cu-X [32]. Their objective with screening third alloying additive was to increase hydrogen flux of FCC PdCu20 alloy and meantime retain its favorable sulfur resistant surface chemistry. Their calculations suggested Rh can enhance solubility of H. And Pt and Ru are predicted to reduce H solubility, but only lightly. Predicting the effect of additive metals on H diffusion is more difficult than examining solubility. Ru and Rh are predicted to slightly enhance diffusion. Hydrogen permeability is controlled by solubility and diffusion. Accordingly, an initial list of 10 additive metals has been screened down to two particularly promising candidates, Ru and Rh. Certainly the results provide a useful first step towards the application of first principle-based methods to screening ternary alloys for use as hydrogen purification membranes by examining hydrogen solubility and diffusivity.

M. P. Hyman et al (2007) [33] examined many palladium alloys (PdMPd, M: Cu, Ag, Au, Co, Ni, Pt, Rh, and Ir). It was suggested that three primary factors determine the binding energies of sulfur on modified Pd surface: a) the position of the d-band center relative to the Fermi level (i.e., the width of the occupied portion of the d-band), b) the density of d-states at the Fermi level, and c) the Fermi energy. The addition of metal that compress the Pd lattice will destabilize the adsorption of sulfur, as well as hydrogen since compressing the Pd lattice shifts the d-band center away from the Fermi level, lowers the Fermi energy, and reduces the density of d-states at the Fermi level. It thus increases the sulfur tolerance. Therefore, 3d transition metals such as Co and Ni may increase the sulfur tolerance of Pd. Introducing ligand effects was found to alter the distribution of the d-states and shift the Fermi level, which eliminates the correlation of the d-band center with the density of states at the Fermi level and the Fermi energy. As a result, the d-band center by itself is a poor metrics of the H_2S reaction energetics for bimetallic surface. For strained Pd(111) without ligand effects, the two metrics correlate, but d-band center shifts derived from ligand effects of an alloying metal do not correlate with the density of states at the Fermi level. The density of states at the Fermi level is an important metric as it indicates the availability of un-occupied states that reduce anti-bonding repulsion. Sulfur adsorption also is somewhat dependent on the Fermi energy because of the repulsion of S-H bonds with Pd d-band. Combining strain with ligand effects was found to lead to unpredictable alteration of the d-band. Therefore, sulfur adsorption on PdMPd surfaces do not accurately predict adsorption on Pd_3M surface. The authors further suggested that sulfur adsorption energies be correlated with lattice constants of metals. It is a simple index for selection of an alloying element for improvement of sulfur tolerance of a Pd alloy. Similar theoretical methods can be applied for study and optimization of CO adsorption on transition metals.

HIGH-THROUGHPUT SCREENING OF ALLOYS

This section is a summary of baseline testing of conventional Pd-Au alloy membranes with coal gas contaminants hydrogen sulfide and carbon monoxide at $400^{o}C$ and 20 psi; use of combinatorial methods to identify S / C resistant Pd alloys; analysis and assessment of the surface quality of porous ceramic-coated substrate; and theoretical calculations of S / C reaction over Pd-Au alloy surface. Emphasis was placed on combinatorial Pd alloy development. For more in-depth information, please refer to Appendix II.

Baseline Testing: pure Pd and Pd-10Au binary alloy

Palladium-Gold (PdAu) alloys have demonstrated promising hydrogen flux performance in the presence of carbon and sulfur species. A PdAu10 (Au 10wt%) alloy membranes have been developed for reformate hydrogen separation at Pall to generate high purity hydrogen. Impact of sulfur upon PdAu10 alloy membranes was determined by hydrogen permeation test with H_2 – H_2S mixed gases at various sulfur concentrations (0.1, 1, 2.5 and 5 ppmv) and temperatures (325, 400 and 500°C). One PdAu10 alloy membrane was tested for one temperature level with addition of hydrogen sulfur in incremental steps from 0.1 up to 5 ppmv. A typical batch of membrane test data is shown in Figure 1. Hydrogen flux at steady state is used to plot against the concentration of H_2S for each temperature. The results are presented in Figure 2. From our membrane test experiments, our findings are:

- Compared to a pure Pd membrane, a PdAu10 alloy membrane had very limited sulfur tolerance. Early literature [1] reported higher sulfur resistance for PdAu40 alloy foil at 350°C. The difference between our result and the reported one may be attributed to the composition of Pd-Au alloy. It appears that increase in Au in Pd-Au alloys may improve sulfur resistance, but it reduces hydrogen flux, too.
- As expected, higher membrane operating temperature mitigated the sulfur inhibition. For instance, in presence of 5 ppm H_2S hydrogen flux at 500°C is almost 6 times as much as that at 325°C.
- Sulfur severely inhibited hydrogen permeation with the concentration of H_2S as low as 0.1 ppm. It is generally accepted that the inhibition is attributed to occupation of sulfur on Pd membrane surface, which is required for dissociation of hydrogen molecules. Therefore, it is industrial practice that H_2S is removed from feed stocks.
- The contaminated membrane surface was partially regenerated once H_2S was removed from hydrogen feed. As shown in Figure 1, hydrogen was back to 75% of the initial value within 3 hours since H_2S feed stopped.

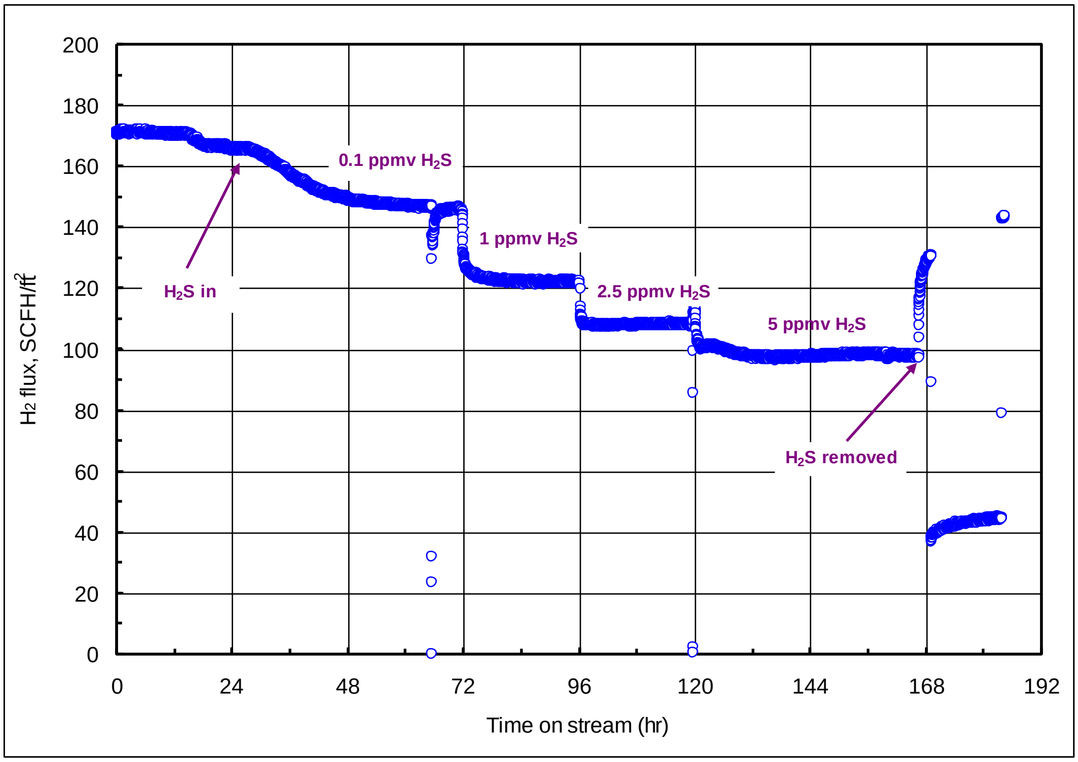

Figure 1. Variation of H2 flux as a function of H2S with time at 500oC for PdAu10 Membrane

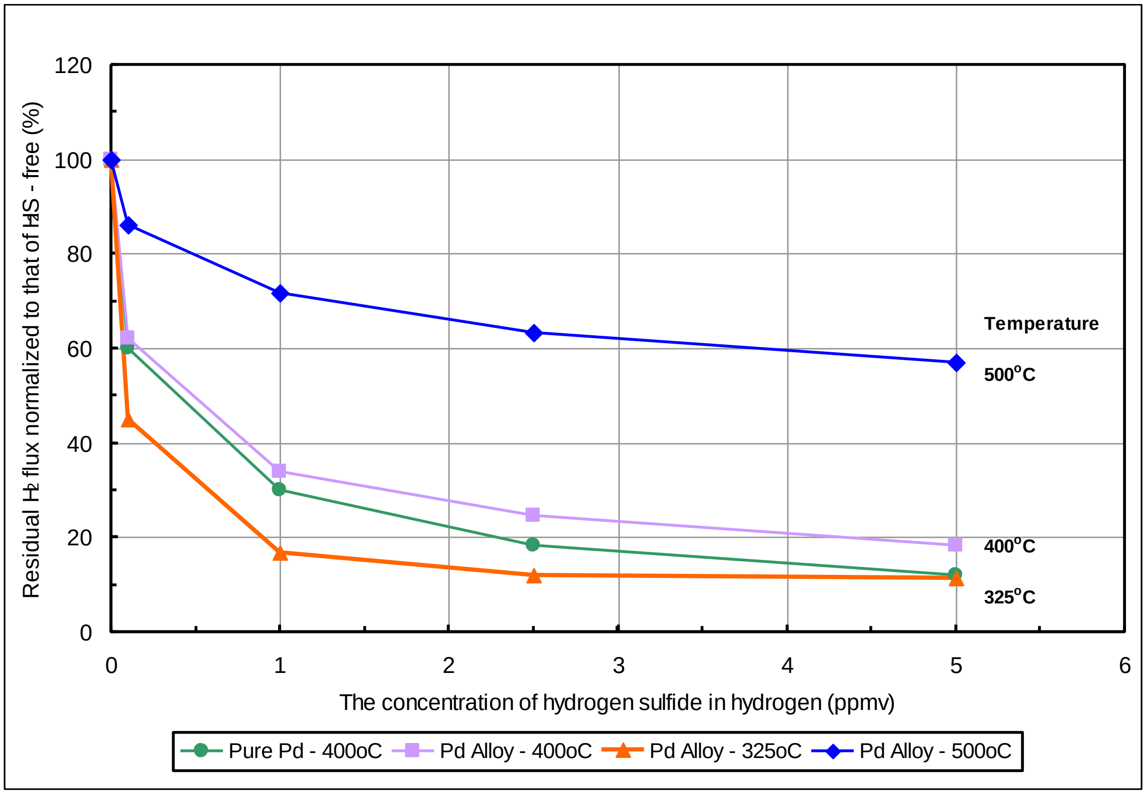

Figure 2. The effect of H2S on hydrogen flux as a function of H2S concentration at 300-500oC for PdAu10 alloy membrane with pure Pd membrane as reference

Description of Equipment and Methods for High-Throughput Screening

The workflow proceeds through four phases that encompass specific functional activities including composition spread fabrication, coal gas exposure, visual screening, and Raman S or/and C mapping.

A multiple target vacuum sputtering system at Cornell University [34] is used for fabrication of composition spreads as shown in Figure 3. The sputter deposition system contains three 2-inch magnetron sputter guns, a 4-inch magnetron sputter gun, and a 1-inch ion gun in the vacuum chamber. A round plate holds three substrate heaters for 3-inch silicon wafer substrate. Any of the three substrates can be brought to any of the three film processing positions, i.e. the ion gun, the 4-inch sputter gun and 2-inch sputter gun. The ion gun is used for substrate cleaning, for instance, to remove the insulating SiO_2 layer from silicon wafers. The 4-inch gun is used most commonly for depositing a tantalum or titanium adhesion layer on silicon substrates prior to the deposition of a composition spread. The three-gun assembly is used for deposition of thin film composition spreads via co-sputtering.

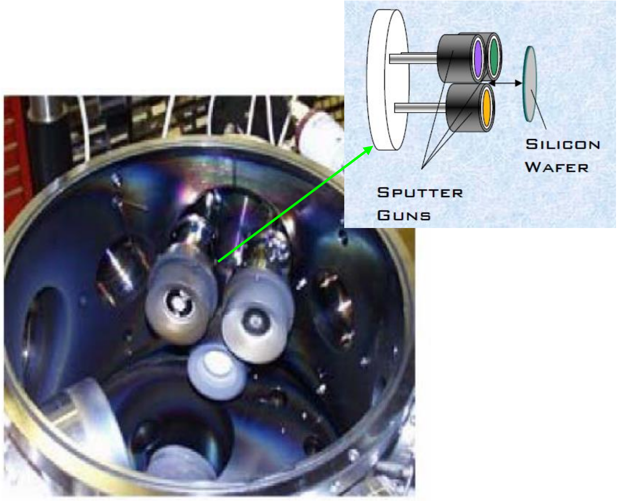

Figure 3. Schematic of a sputtering deposition system at Cornell University

Simulated synthetic coal gas is used to condition thin film compositional spread samples for sulfur / carbon resistance screening. The gas composition was provided by National Carbon Capture Center (NCCC) at Southern Company. It represents a product gas from air blown coal gasifier and consisted of 17.6% H_2, 17.9% CO_2, 2.6% CO, 2.6% H_2O, 59.3%N_2 and 170ppm H_2S. An experimental setup was newly built at Pall to perform coal gas exposure at elevated temperature on the sputtered wafers. It included a SS process tube with quartz liner, furnace, feeding equipment and downstream exhausting system.

Some of the transition metals, for instance silver, tarnish by sulfur and lose metallic shining color. This phenomenon was employed to initial visually survey the corrosion resistance of composition spread in coal gas in presence of hydrogen sulfide. The areas that remain still metallic shining color are identify as sweet spots for further Raman surface S / C mapping to determine their S or/and C resistance. Those spots that expel S or/and C sticking are confirmed as final candidates for membrane fabrication and hydrogen permeation test. The Raman spectro-microscopy was conducted at Georgia Institute of Technology [35].

Experimental results

Eleven composition spreads were fabricated by Bruce van Dover at Cornell University. This batch of the samples focused on how to improve the sulfur / carbon resistance of traditional Pd-Cu, Pd-Ag and Pd-Au alloys by doping third element. The coal gas exposure was conducted at 350^{o}C and pressure slight above atmospheric for 24 hrs. An example of two of these wafers with the sweet spots circled is showed in Figure 4. Those disks with sweet spots were sent to Georgia Institute of Technology for sulfur and carbon surface analysis by Raman spectromicroscopy.

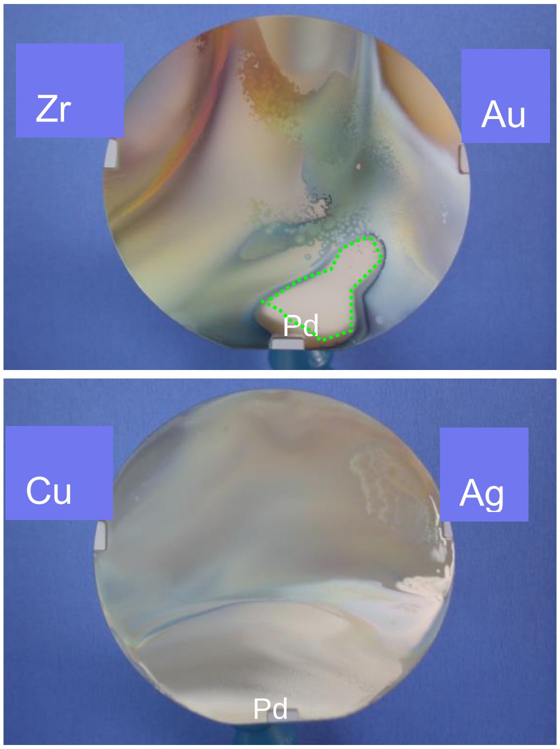

Figure 4. Pictures of coal gas exposed composition spreads

In evaluating the sulfur tolerance of candidate hydrogen permeation alloys using Raman spectroscopy, the main metric is the Raman intensity of bands corresponding to sulfur-sulfur and metal-sulfur bonds. Therefore, the sensitivity of Raman spectroscopy for sulfur surface analysis was first determined at Georgia Institute of Technology. Initially a containing 10-ppm H_2S hydrogen gas was used to condition a pure Pd thin film on 3-inch silicon wafer at 350^{o}C for 3-4 hrs. Multiple Raman spectra were collected from several spots across the sample surface, which are provided in Figure 5. It has been noted that all of Raman spectra collected on thin film compositional spread disks shared a common fluorescence background (very broad modes centered at 200, 350, 540, 730 cm-1) along with an “upward slope” of the spectra with increasing red shift (positive wave numbers). It made difficult to assign bands of Raman spectra of 10 ppm H2S exposed combinatorial samples. To address this issue, our initial attempts were to create SERS effects on film surfaces by spraying 20-nm Ag colloidal particles onto the surface of thin film wafer and thus it would enhance Raman sensitivity. However, the coating process required 300^{o}C baking and it modified samples.

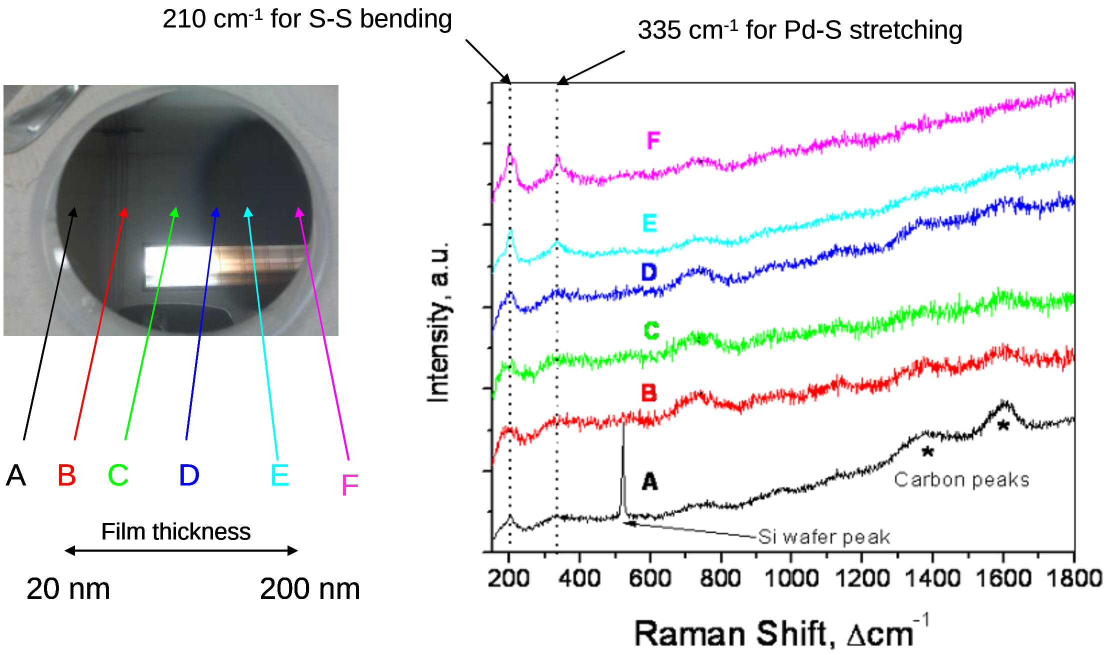

Figure 5. Raman spectra of 10 ppm H2S conditioned pure Pd film

MEMBRANE FABRICATION AND TESTING

Pall Corporation identified six ternary alloys of interest based on the work summarized above. Fabrication of each of these ternary membranes as well as a Pd-Au binary control was completed at the Colorado School of Mines (CSM). The membrane thickness and room temperature leak rate (the quality of the film that determines membrane selectivity) were taken into consideration, but deemed not as important as the composition of the film. CSM was able to consistently utilize electroless plating to deposit Pd, Au, and a few other elements of interest; however, metals they are unable to plate were deposited using magnetron sputtering. The individual layers of each metal were thin (less than one micron) in order to facilitate annealing. The thickness and composition of each layer was estimated gravimetrically and verified using X-ray Fluorescence (XRF). The binary and ternary alloy membranes that are fabricated by sequential deposition require annealing in order to homogenize the metal film. Typically the annealing was done *in-situ* or using a permeation-based annealing method at CSM. After the annealing step, Pall Corporation performed a set of experiments to understand the effect of carbon and sulfur species on H_2 permeation as a function of temperature in a simulated coal gas mixture.

Annealing and Pure-gas Summary

After the desired composition was obtained and verified with X-ray Fluorescence (XRF), the membranes were mounted in a shell-and-tube test housing with Swagelok® fittings at CSM. Flowing N_2 was applied to the membranes during heat up to avoid oxidation and H_2 embrittlement. Membranes were H_2 permeation tested at 400°C at a feed pressure up to 100 psig. After initial permeation measurements were recorded, the membranes were annealed in flowing H_2 at a feed pressure of 5 – 10 psig at a minimum temperature of 500°C for at least 100 hours. Once per day H_2 and N_2 permeation was measured at 20, 60, and 100 psig feed pressures. After the permeation readings leveled out, H_2 permeation was measured up to 600°C and 100 psig. An example of an annealing schedule can be seen in Figure 6 for the PdAuAg alloy membrane.

Figure 6 demonstrates how the H_2 and N_2 fluxes change with time. As the sequential layers begin to diffuse into one another, the fluxes of both gases increase. The increase in N_2 flux is not surprising as high operating temperatures (above 450°C) can lead to defect formation in the film. Although, the H_2 to N_2 selectivity declined during the testing period, it was still high at the end of testing: 2200 at 400°C and 100 psig.

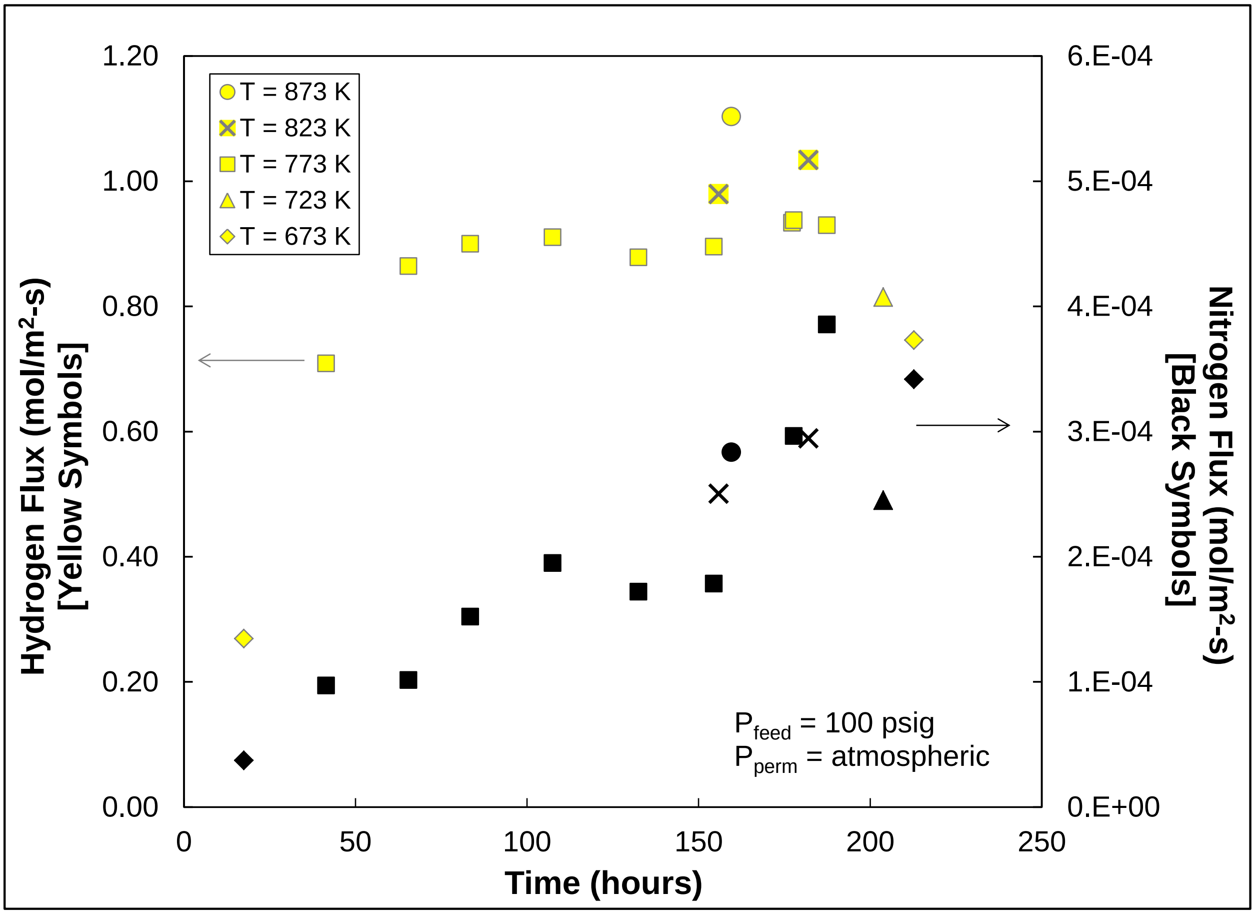

Figure 6. Annealing schedule for alloy composition PdAuAg – demonstration of how H2 and N2 fluxes change with time

Simulated coal syngas testing

The annealed membranes were tested in simulated coal syngas. Table 1 shows the feed gas compositions. The simulated coal syngas values were provided by the Southern Company. The testing procedure was as follows: 24 hours in No Carbon*, 24 hours in simulated syngas without H_2S, 24 hours in simulated syngas with 20 ppm H_2S, and then 24 hours in simulated syngas without H_2S. *The feed gas composition known as "No Carbon" was used to understand the effect of carbon species on membrane performance and was added to the testing procedure partway through testing all of the membranes. The whole testing procedure took place at 500°C before being repeated at 400°C. In all mixed-gas testing, the feed pressure was held at 160 psig.

Table 1. Mixed-gas feed compositions.

Feed Gas	Gas Composition and Testing Conditions	
No Carbon	H_2	36%
	H_2O	3%
	Balance N_2	
Syngas no H_2S	H_2	36%
	CO_2	11%
	H_2O	3%
	CO	1.3%
	Balance N_2	
Syngas with H_2S	H_2	36%
	CO_2	11%
	H_2O	3%
	CO	1.3%
	H_2S	20 ppm
	Balance N_2	

Testing success was based on one main benchmark: that the membrane maintained high H_2 permeance while being exposed to 20 ppm H_2S. A binary PdAu alloy membrane was also tested for comparison. The H_2 permeance during mixed gas testing for each membrane at 500°C is shown in Figure 7.

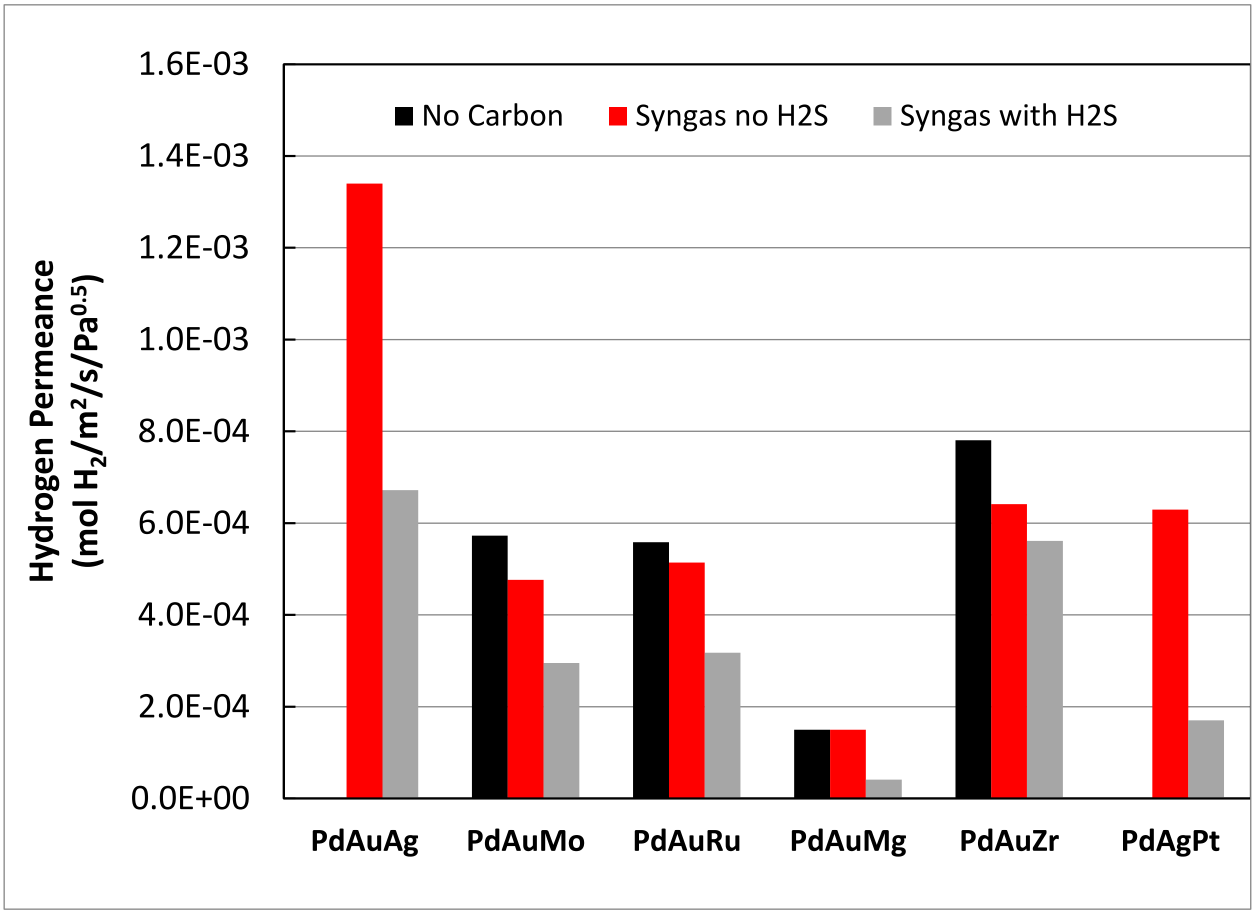

Figure 7. Effect of carbon and sulfur species at 500°C

***The PdAuAg and PdAgPt tests took place before we planned to account for the carbon inhibition**

Carbon Inhibition at 500°C

The difference between the black and red bars in Figure 7 is the amount the H_2 permeance is inhibited due to the presence of carbon species. From this data, we can rank the alloys in terms least affected by carbon to the most affected with the amount the permeance is reduced in parenthesis:

PdRuAu (8%) < PdMoAu (18%) < PdZrAu (19%) < PdAu (26%)

The ability of the novel ternary alloy compositions to be less affected in the presence of carbon compared to the benchmark PdAu alloy is encouraging.

Sulfur Inhibition at 500°C

The resistance to sulfur species can be seen in the difference in H_2 permeance in syngas with and without H_2S (the difference between the red and grey bars in Figure 7). This comparison allows us to rank the alloys from most affected to least affected with the amount the permeance is reduced in parenthesis:

PdZrAu (12%) < PdAu (27%) < PdRuAu, PdMoAu (38%) < PdAuAg (50%)
< PdMgAu (72%) < PdAgPt (75%)

Only one novel ternary alloy had better resistance to H_2S at 500°C than PdAu.

The testing procedure was repeated for 400°C and the permeation results are shown in Figure 8. Although the trends are similar, they are worth discussing.

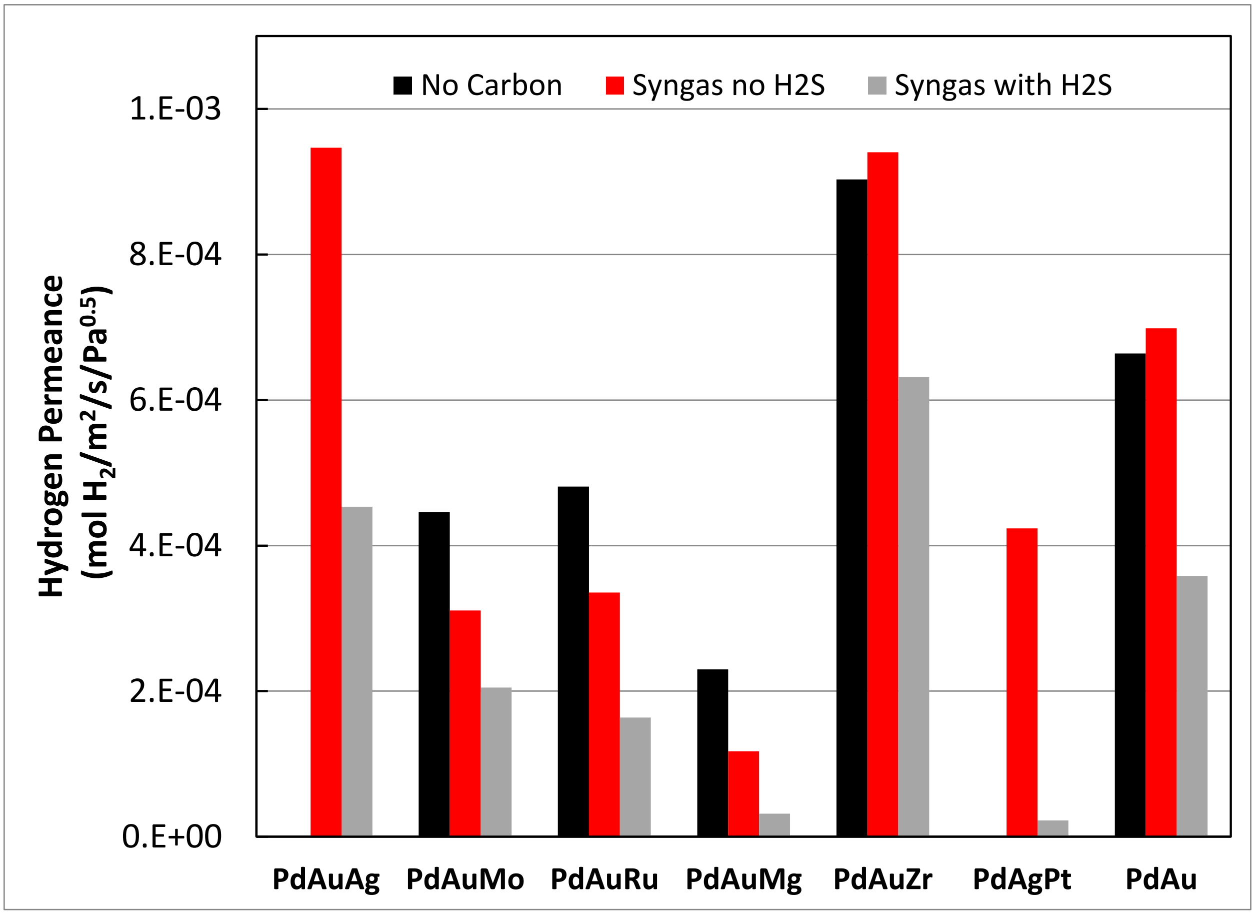

Figure 8. Effect of carbon and sulfur species at 400°C

Carbon Inhibition at 400°C

The carbon inhibition can be found by comparing the H_2 permeance when there is no carbon species (the black bars) to the feed gas containing carbon species (the red bars). Unlike the data at 500°C, there are a few alloys that exhibited slightly higher permeance in the carbon species: PdAu and PdZrAu. The remaining alloys can rank in terms least affected by carbon to the most affected with the amount the permeance is reduced in parenthesis:

PdRuAu, PdMoAu (30%) < PdMgAu (49%)

It is interesting that the two alloys most affected by carbon at 500°C were the least affected at 400°C (PdZrAu and PdAu), and the opposite trend is true for PdRuAu and PdMoAu. Unfortunately, the absolute H_2 permeance of PdRuAu and PdMoAu are too low to further investigate the reasoning behind this behavior.

Sulfur Inhibition at 400°C

The ability to withstand 20 ppm H_2S in syngas can be found by comparing the red and grey bars in Figure 4. From this, we can sort the alloys from most affected to least affected with the amount the permeance is reduced in parenthesis:

PdZrAu (10%) < PdMoAu (34%) < PdAu (49%) < PdRuAu (51%)
< PdAuAg (52%) < PdMgAu (73%) < PdAgPt (95%)

Two ternary alloys retained more of their H_2 permeance than the benchmark PdAu and a two had a similar decreases of about 50%.

Overall Membrane Performance

PdAuAg and PdZrAu alloy membranes demonstrated the highest H_2 permeance of the ternary alloys identified for carbon and sulfur resistance in the simulated coal syngas with 20 ppm H_2S. Both alloy compositions maintained a similar or higher absolute H_2 permeance in the presence of H_2S than a PdAu binary alloy at both temperatures examined.

Repeat testing of top performing alloy compositions

The annealed membranes were tested in simulated coal syngas. Table 1 shows the feed gas compositions. The simulated coal syngas values were provided by the Southern Company. The testing procedure was as follows: 24 hours in No Carbon*, 24 hours in simulated syngas without H_2S, 24 hours in simulated syngas with 20 ppm H_2S, and then 24 hours in simulated syngas without H_2S. *The feed gas composition known as "No Carbon" was used to understand the effect of carbon species on membrane performance and was added to the testing procedure partway through testing all of the membranes. The whole testing procedure took place at 500°C before being repeated at 400°C. In all mixed-gas testing, the feed pressure was held at 160 psig.

PdAuAg Repeat Testing

Six PdAuAg alloys were fabricated and pure-gas tested to understand how sensitive the hydrogen permeability is to changes in alloy composition. The results are seen in Figure 9. A few of the membranes tested had very high hydrogen permeability, while some had lower permeability suggesting that small compositional changes can have a large effect on the hydrogen permeabily.

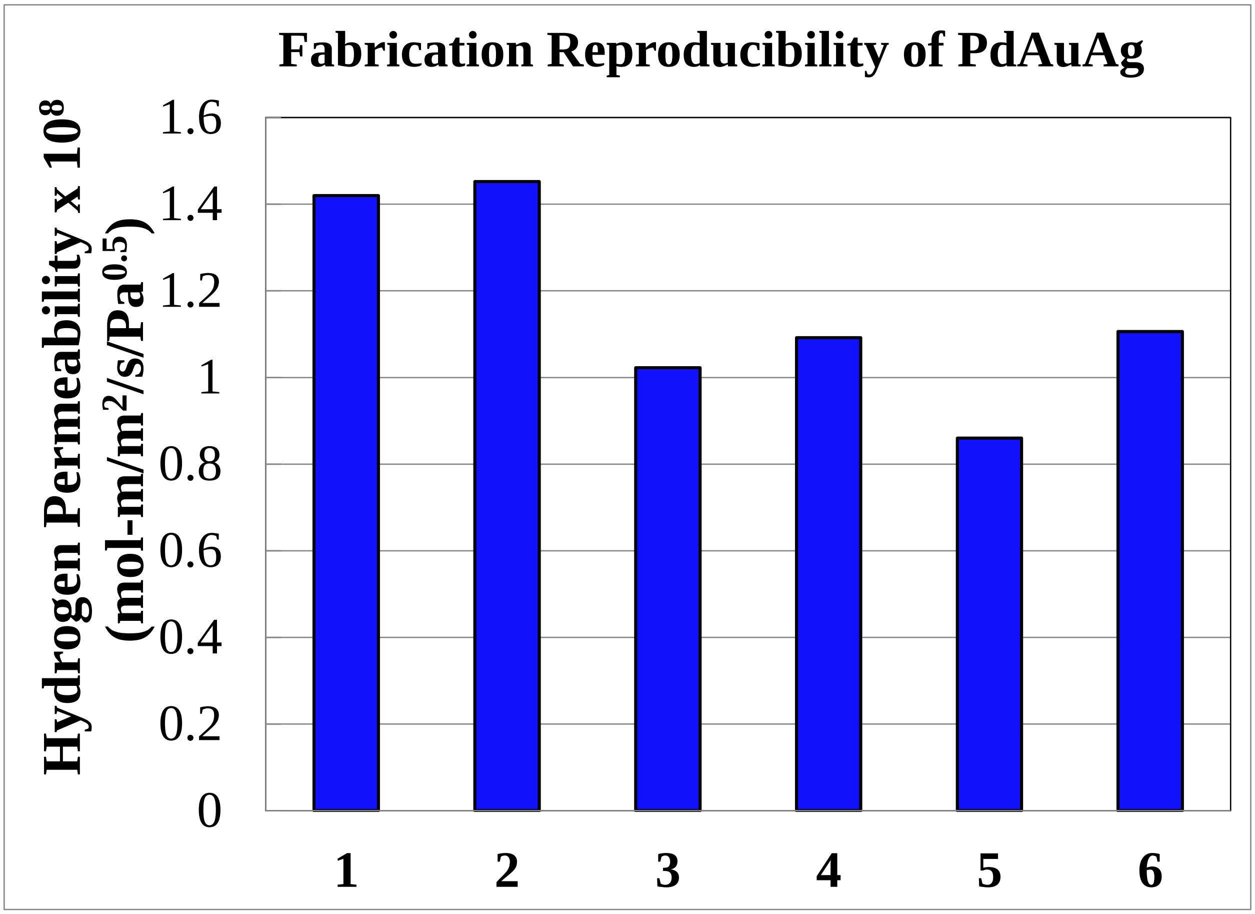

Figure 9. Pure-gas Testing of PdAuAg at 500°C

Three of these membranes were tested in mixed-gas experiments. The results can be seen in Figure 10. All of the membrane drop to similar permeances in mixed-gas, which is very promising for scaling up this alloy composition.

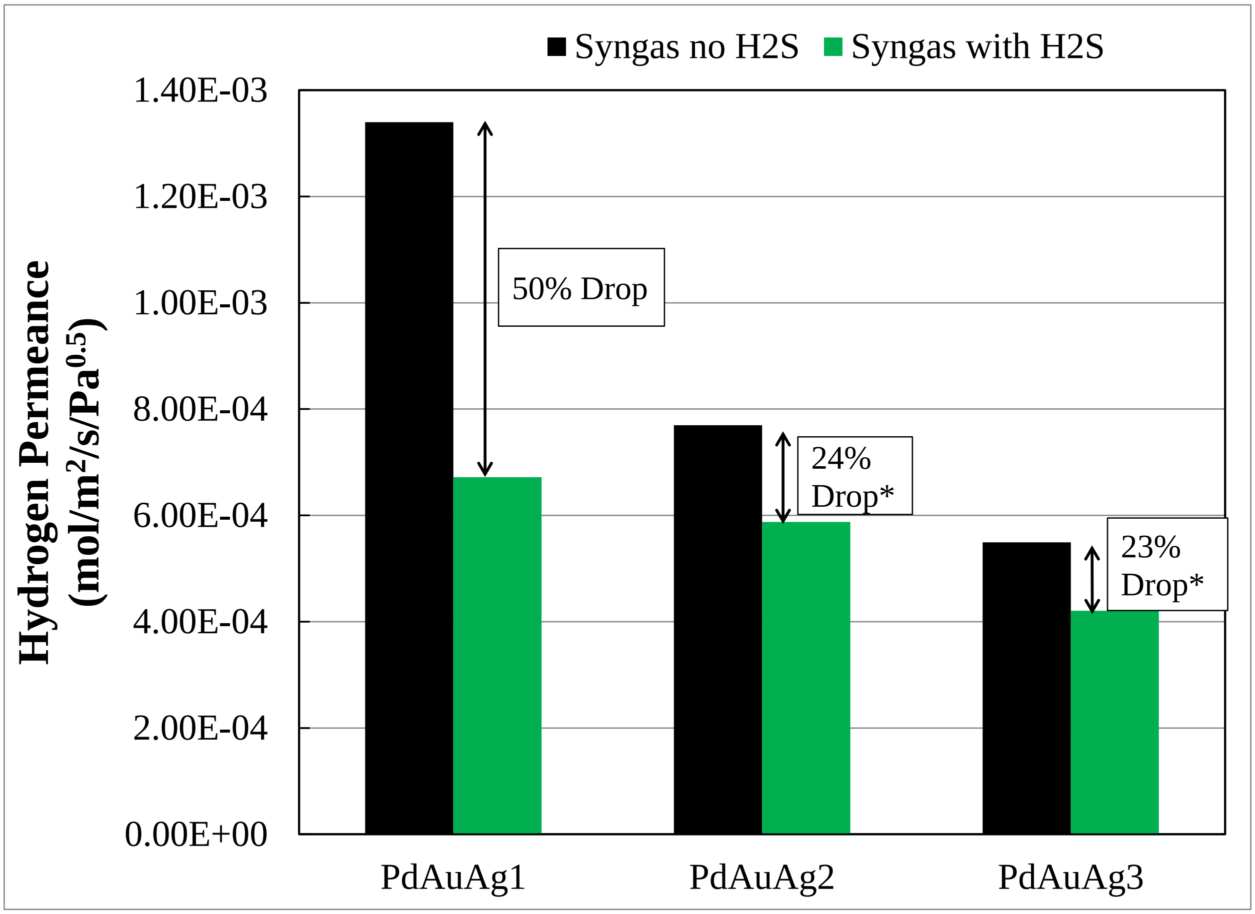

Figure 10. Mixed-gas Testing of PdAuAg at 500°C
***Changed feed gas composition to be DOE test protocol for H2 separating membranes (condition 2b, but with 20 ppm H_2S instead of 30)**

PdZrAu Repeat Testing

Six PdZrAu alloys were fabricated; however, only three were pure-gas tested to understand how sensitive the hydrogen permeability is to changes in alloy composition. The other three films were not adhered well to the supports which lead to peeling of the film. The results are seen in Figure 11. Although the PdZrAu membranes all had similar fluxes, the repeatability was not good enough to justify more testing on this particular alloy. The ICP-MS results show that the composition window for carbon and sulfur tolerance is too narrow to make PdZrAu a viable alloy for manufacturing.

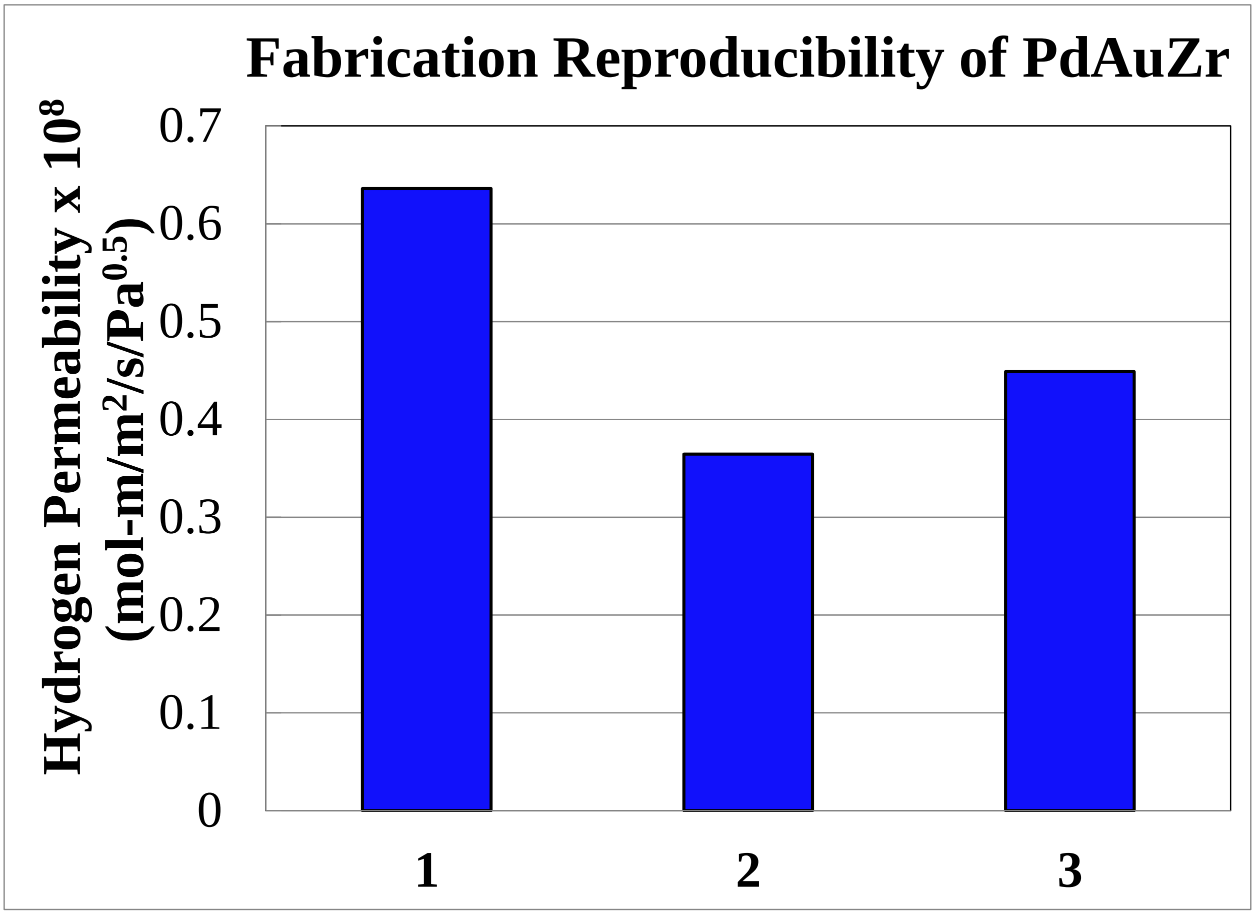

Figure 11. Pure-gas Testing of PdZrAu at 500°C

CONCLUSIONS

High-throughput combinatorial screening of Pd-based alloys is a great starting point for alloy selection. It allows for quick screening of novel compositions instead of the tedious fabrication, testing, and analysis of each membrane i.e. conventional one-by-one processing. Based on the screening, six alloys were chosen for fabrication. Fabrication was completed using a combination of electroless deposition and magnetron sputtering. The metals were deposited in a layered structure, therefore annealing to form a homogeneous (or as close as possible to homogeneous) was important. Most of the annealing was done in-situ during hydrogen permeation. Once stable hydrogen fluxes were observed, the membranes were assumed to be annealed.

Based on the pure and mixed-gas testing results, PdAuAg and PdZrAu were the top performing alloys in terms of chemical resistance and hydrogen permeability. Additional membranes of each composition were fabricated and tested in order to gain insight to the reproducibility of the results. PdZrAu alloy proved to be difficult to fabricate and failed upon the introduction of hydrogen sulfide in the mixed-gas testing. Small changes in the composition (verified by inductively coupled mass spectrometry), proved to be detrimental to the carbon and sulfur tolerance. This demonstrates why reciprocal testing is important to understand commercial feasibility. PdAuAg alloys tested had variability in hydrogen permeability, but all alloys tested demonstrated good carbon and sulfur resistance. The compositional window for carbon and sulfur tolerance is much wider for PdAuAg than PdZrAu.

RECOMMENDATIONS

Combining alloy screening with hydrogen permeability using hydrogenography would be more useful as some of the selected alloys had very low hydrogen permeability despite their high chemical tolerance. Further testing of PdAuAg in different amounts of sulfur, different gas mixtures, as well as time scales will be useful before large-scale manufacturing. It would be beneficial to reproduce other identified ternary compositions to see if the sulfur and carbon tolerance improves by changing alloying compositions.

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APPENDIX I: LITERATURE REVIEW

This appendix presents a literature review of the project research topics that include surface effects of coal gas components with emphasis on hydrogen sulfide and carbon monoxide; high throughput combinatorial alloy development; palladium-based membrane substrate quality and characterizations; and hydrogen permeation chemical modeling. The review was prompted by the need to understand previous work on palladium-based membranes and to provide the-status-of the art. The literature search was carried out with ScienceDirect® database by key words, palladium membranes, palladium alloys, palladium membranes and sulfur poisoning, palladium membranes and carbon poisoning.

Background of Palladium-Based Membrane Technology

It is well established that dense palladium and palladium alloy membranes are permeable for hydrogen [1-3]. Over the past 50 years, palladium alloy membranes have been developed into a technology that, in some instances, is used in practice [4]. Illustrations include the ultra-purification of hydrogen for use in semiconductor manufacturing process and hydrogen generators for remote or small-scale usage. Commercial palladium-based membranes are made of palladium-silver alloys in tubular form. Johnson Matthey [5] supplies both commercial systems on markets. Power+Energy Inc [6] is also now a supplier for hydrogen purification palladium-based membrane units.

There has been a resurgence of interest in palladium-based membrane technology in recent two decades, largely due to their unmatched potential as hydrogen selective membranes for membrane reactor application in hydrogen production and pre-combustion carbon capture [7-11]. Particular applications include membrane reformer and membrane water gas shift reactor. E. Kikuchi (1997) [12] and S. Uemiya (2004) [13] reviewed this topic. Of special interest to U.S. is generation of hydrogen from the nation’s most abundant fossil fuel, coal, by gasification process. Hydrogen permeable membranes are an integral part of tomorrow’s coal gasification plants being promoted by the U.S. DOE Vision 21 program. Palladium-based membranes have been demonstrated to be promising candidates for hydrogen / carbon dioxide separation. However, a critical technical hurdle impeding palladium membrane development is its susceptibility to poisoning or deactivation by contaminants present in gasifier effluent streams, for instance, hydrogen sulfide and carbon monoxide. These contaminants significantly inhibit hydrogen flux or/and premature the membrane life time. Furthermore, for palladium membranes to be economically attractive in large scale hydrogen separation, their flux must be improved by several factors. As a result, recent research efforts have been addressing strategies for fabricating thinner membrane layers, as well as identifying alloy compositions with improved comparability with coal gas chemical environment, which will be reviewed in detail as follows. A comprehensive review of palladium membranes and their application to membrane reactor has been provided by J. N. Armor (1989) [14], J. Shu et al (1991) [15], R. Dittmeyer et al (2001) [16] and S. N. Paglierl et al (2002) [17]. More recently, this topic has been reviewed in a book Inorganic Membranes for Energy and Fuel Applications edited by A. C. Bose (2009) [4].

Hydrogen transport through palladium-based metal membrane is generally envisioned as following an atomic transport mechanism. Assuming transport from the high hydrogen pressure surface to the low pressure surface, the atomic transport process follows several sequential steps:

- Dissociative adsorption of hydrogen molecules onto the membrane surface;
- Transition of atomic hydrogen from the surface into bulk metal;
- Atomic diffusion through the bulk metal;
- Transition from the bulk metal to the surface on the low pressure side;
- Recombinative desorption from the surface.

Each of these steps can be characterized by an element kinetic equation with their respective potential energy diagram shown in Figure 12 [18-20]. The overall observed rate of hydrogen permeation may be limited by one step, if it is the slowest one, or may be governed by a combination of steps, which is determined by their energy barriers. Although deriving a hydrogen transport equation / model is beyond the scope of this review, a more generalized relationship is provided in the following.

$$F = S \cdot D \frac{(p_{entry}^{n} - p_{exit}^{n})}{\delta}$$

Where F is hydrogen flux; S hydrogen solubility constant; D hydrogen diffusion constant; n pressure exponent; p hydrogen partial pressure upstream and downstream; δ the membrane thickness. This general picture of hydrogen transport through palladium membrane will be applied to discuss the effects of contaminants wherever necessary.

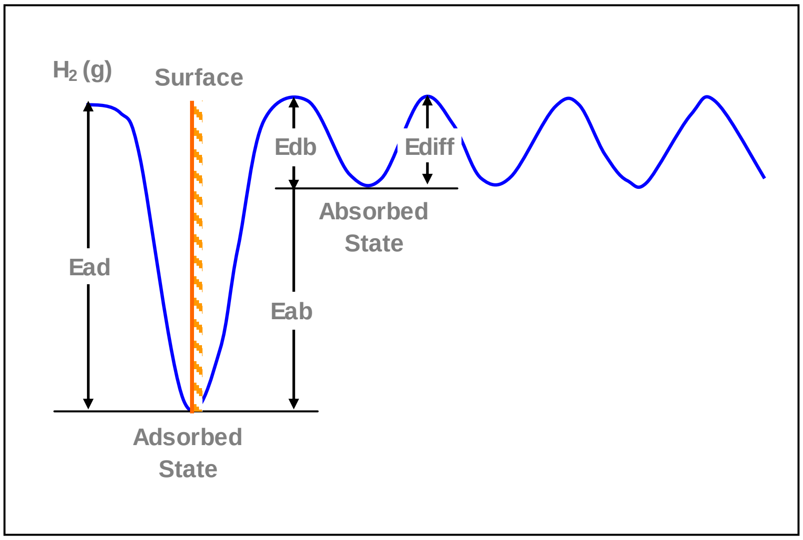

Figure 12. Potential energy diagram for hydrogen transport process steps

Effects of Syngas Components on Hydrogen Separation Membranes

An early review of the effects of contamination on palladium membranes came from R. G. Musket (1976) [21]. Purification of hydrogen by permeation through palladium and palladium alloy membranes has been the main motivation for many investigations. Such studies have provided most of the early observations about the effects of contaminants on the interaction of hydrogen with palladium. These observations were made by hydrogen permeation experiments on various palladium and palladium alloy foil samples. Hydrogen permeation results were quite divergent including hydrogen diffusion and solubility constants, the function of foil thickness, diffusion activation energy, and the pressure exponent. It was generally agreed that the contamination results from several sources:

- Segregation of bulk impurities at the surface, for instance sulfur and carbon from foil fabrication process;

- Formation of corrosion products prior to hydrogen permeation experiment as a consequence of exposure to various environmental chemicals (sulfur, carbon, chlorine, mercury, and zinc);
- Chemisorption of impurities in hydrogen gas which was used to determine hydrogen permeation and impurities include hydrogen sulfide, hydrocarbons, carbon monoxide.

In these studies, precise identification of the compounds responsible for the contamination was not possible because at that time surface compositional analysis has not been applied to this problem. And hence no detail contamination mechanisms have been established. Instead of developing alloy compositions with improved chemical resistance, early research efforts focused on general precautions, elimination of contaminants, and activation of contaminated palladium membrane surface. They are discussed as follows:

- General precautions include avoiding lubricants and volatile sealing materials, using all-metal chambers and valves, employing oil-free compressors and pumps;
- Gas pre-purification would help to remove any contaminants from raw hydrogen gas, for instance simply passing hydrogen through a solid adsorbent packed bed or a liquid nitrogen trap;
- Palladium membrane surface pre-treatment has been taken as a general practice to chemically clean the membrane surface, i.e. surface activation. Several methods were investigated to regenerate the contaminated membrane surface. The methods include vacuum argon plasma treatment, vacuum degassing-pure hydrogen treatment cycling, and oxidation-reduction procedure. Nevertheless, most commonly activation is accomplished using an oxidation-reduction procedure. Its protocol consists of air purging at 300-600^{o}C for up to usually 15 min, then vacuum out-gassing at the same temperature, and finally, a reduction in pure hydrogen also at the same temperature.

In summary, there have been numerous observations on palladium membrane contaminations which explain large discrepancies of hydrogen permeation results with palladium and palladium alloy foil samples in early days of palladium membrane diffusion technology. Contaminants were transferred primarily from membrane fabrication process and membrane system components instead of hydrogen feed gas. Simple precautions and activation procedures can be practiced to maintain high performance of an industrial hydrogen purification system. Therefore, there was little development work on sulfur or/and carbon resistant palladium alloys for hydrogen purification applications. Compared to purification applications, palladium membranes for hydrogen separation will be exposed to larger amount of various contaminants. For example, the coal gas for hydrogen separation membrane testing that the U.S. DOE-NETL (National Energy Technology Laboratory) [22] has suggested is composed of 50% H_2, 1% CO, 30% CO_2, 19% H_2O as well as other minors including H_2S, NH_3, Hg, and HCl et al. These chemical environmental conditions and contaminant concentrations pose critical challenges for the technology development and application. These technological challenges / barriers will be discussed with emphasis on contamination from sulfur and carbon species.

Effects of sulfur compounds

Impacts from sulfur compounds on palladium membranes are usually determined by hydrogen permeation experiments. Quite often, hydrogen sulfide-doped hydrogen gas is used. The advantage of this method is quantification of intrinsic effects of sulfur species. And hence it is a simple method for quick screening palladium alloys for sulfur tolerance assessment. Sometimes a specialty gas mixture with hydrogen sulfide is required to simulate a particular application. An example of gas mixture would be coal gas, which can be synthesized from pure cylinder gases or drawn from a coal gasifier. The former is employed for bench scale membrane sample testing and the latter is applied to pilot or demonstration phase membrane system testing. Depending on applications, the concentration of hydrogen sulfide ranges hundreds of ppb to a few percent. As a function of hydrogen sulfide level, two surface phenomena can take place on a palladium membrane surface, i.e. monolayer adsorption at low hydrogen sulfide level versus multilayer surface corrosion at high. Whenever possible, such difference will be taken into account to discuss relevant literature results.

H. Gao et al (2004) [23] reported a brief review of chemical stability issues about palladium-based membranes. Since then, there has been significant progress in both the understanding of the mechanism of sulfur contamination and the identification of sulfur tolerant membrane materials. In addition, we will provide a broad coverage of previous relevant literature with emphasis on well-controlled membrane samples and tests. In the early 1960's, Union Carbide [24-27] campaigned palladium alloy membrane development for large-scale hydrogen recovery from refinery processes. They systematically assessed the sulfur resistance of Pd, Pd-Cu, Pd-Ag and Pd-Au alloy foils. All the foils had a thickness of 1 mm and a diameter of 20 mm. A gas mixture of hydrogen (99%) and hydrogen sulfide was synthesized by passing hydrogen through a hot ferrous sulfide packed bed. The actual concentration of hydrogen sulfide was measured by titration with a 0.1 N cadmium chloride solution. The concentration of hydrogen sulfide was 4-20 ppmv. The sulfur tolerance test was carried at 350°C and 75 psig. The membrane samples were onstream for 2-7 days to ensure equilibrium. The results are shown in Figure 13. Their ranking in terms of sulfur tolerance is given as follows. Apparently, the PdAu(60/40) alloy had the best sulfur tolerance.

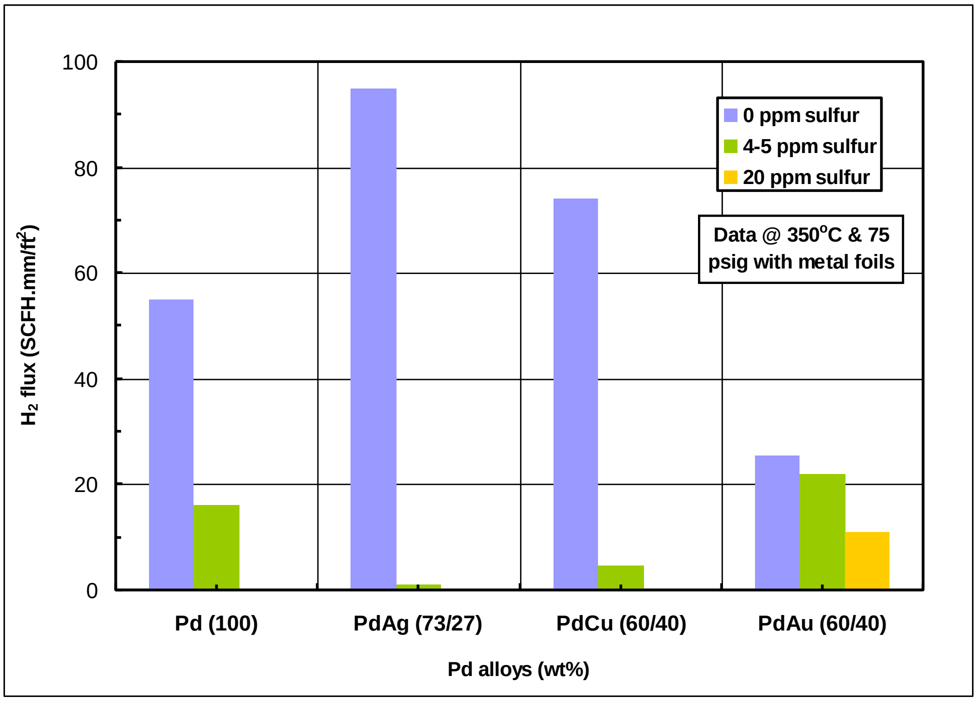

Figure 13. Comparison of the sulfur tolerance of several Pd-IB alloys

Even when the concentration of hydrogen sulfide was raised to 20 ppm in the feed gas, the PdAu foil still maintained more than 40% of its sulfur-free hydrogen flux. The authors further suggested a membrane structure with gold coated on pure Pd foil, which was then heat diffused to form Au-enriched surface. Such structure was expected to offer good sulfur tolerance and high hydrogen flux as well. The authors also noticed that both the PdAu and PdCu foils tested retained their original appearance and luster. But the pure Pd and PdAg foils were changed in appearance. The pure Pd foil lost its luster and appeared slightly dull. The PdAg foil was even more dull in appearance than the pure Pd foil and appeared slightly etched. This appearance observation is in good agreement with their respective sulfur tolerance hydrogen permeation test. M. V. Mundschau et al (2006) [28] reported their investigation of the sulfur tolerance of Pd (20 ppm H_2S), PdCu20 (20 ppm H_2S) and PdAg25 (10 ppm H_2S) at 325^{o}C. It has the following ranking. This ranking is different from the above one, but their result on PdCu20 is in agreement with what NETL reported.

PdCu20 >> Pd > PdAg25

NETL (2003-2010) [29-37] has carefully investigated Pd-Cu alloy system as potential membrane material for coal gas hydrogen separation application. They determined the sulfur resistance of Pd-Cu alloy as a function of its composition under various conditions. Their research work indicates that the PdCu40 alloy foil (BCC crystal and 25 micron thick) completely lost hydrogen permeation in presence of 1000 ppm H_2S at 350^{o}C. It is agreement with Union Carbide. Their post-test surface characterizations by XRD, SEM-EDS and XPS indicate that sulfur contamination was limited to the top surface of the PdCu40 foil and no bulk sulfides were found. In contrast, the pure Pd foil had a palladium sulfide layer of few hundred nanometers thick. Another significant development from their work is that a PdCu20 alloy with FCC structure possesses the best sulfur tolerance among its alloys. GTI (2006) [38] did a similar test with two Pd-Cu alloy foils, one PdCu20 and the other PdCu40 in presence of 100 ppm H_2S at 350^{o}C. They also observed that PdCu20 had better sulfur tolerance. It is also noted that there is discrepancy between these two tests regarding sulfur tolerance level. It may be attributed to the methods that they used to test membranes. NETL employed a transient method, i.e. pressure decay. In the GTI tests, a steady state method is applied, which allows longer time to approach to chemical equilibrium, resulting in lower sulfur tolerance level. A contradicting result came from J. Y. Yang et al (2006, 2007, 2008) [39-41]. Their membrane was made of a sandwich structure, i.e. a VNi15 alloy foil (300 microns thick) with PdCu40 (0.2 micron thick) coating on both sides. The coating was put down by sputtering and it had fcc phase structure. Such membrane showed no loss of hydrogen flux in presence of 100 ppm H_2S above 300^{o}C. We suspect that the contradiction may result from different crystal phase of PdCu40 alloy as it has two crystal phases, i.e. fcc and bcc. A conventionally cold rolled PdCu40 foil, as used by Union Carbide, NETL and GTI may have dominant phase of bcc. Sulfur tolerance test was carried out on electroless plated Pd-Cu membranes, too. However, their composition and structure are often unknown. Therefore, it is difficult to analyze those results. In summary, the sulfur tolerance of Pd-Cu alloy can be optimized as a function of its composition and crystal structure. Evidently, a FCC Pd-Cu alloy has better sulfur tolerance, but not necessary hydrogen flux.

In the above sulfur tolerance ranking of Pd-IB element alloys, PdAg27 alloy is the least resistant to sulfur contamination. L. Yang et al (2006) [42, 43] reported their sulfur tolerance test on a Pd-Ag alloy /porous ceramic composite membrane tube with 5 ppmv H_2S in H_2 gas at 500^oC and 116 psig. The membrane was prepared by electroless plating. Their SEM-EDS 2D mapping analysis showed a uniform profile of Ag across both the depth and length around 20wt%. Within 2 hours the hydrogen flux decreased to 16% of the one in pure hydrogen. This observation is similar to early Union Carbide's results. The authors also noted that the hydrogen flux was almost completely recovered at the same temperature (500^oC) within 2 hours. It indicates that sulfur adsorption is reversible. But the recovery extent is dependent on operating temperature of a membrane and likely membrane material. It should be mentioned that most of tested Pd-Ag alloy membranes were optimized, according to their hydrogen flux instead of sulfur tolerance. For example, commercial Pd-Ag alloy membranes usually have a composition of 23 wt% Ag because of high hydrogen flux. Evidently, its sulfur tolerance is low, but we suspect that it could be improved by optimizing the composition.

As mentioned above, the gold-containing alloys were shown to be more resistant to contamination by sulfur. Therefore, we assessed the sulfur tolerance of a PdAu10 (10 wt% Au) alloy membrane. The tests were carried out at $300\text{-}500^oC$ and 20 psig with H_2-H_2S gas mixtures. One membrane sample was used to complete a series of sulfur level at each temperature and the concentration of H_2S gradually rose from low to high (0.1-5 ppmv). Our proprietary membrane fabrication process allows adjusting the Pd membrane to any desired composition with good uniformity of both composition and thickness. The results are shown in Figure 14. From Figure 14, we could draw several points as follows:

- As expected, the membrane lost less hydrogen flux as temperature increased from 325 to 500^{o}C. For instance, the membrane maintained about 60% of hydrogen flux with pure hydrogen as feed. Compared to 325^{o}C, it is six-time improvement. Furthermore, hydrogen permeation was less sensitive to the concentration of H_2S as temperature increased. Therefore, temperature would be an approach to improving the sulfur tolerance level of a Pd-based membrane.
- The concentration of H_2S is another dominant parameter that impacts hydrogen permeation, especially at low membrane operating temperatures. For instance, the membrane lost almost 85% of its hydrogen flux as H_2S increased to 1 ppmv.
- Taking pure Pd membrane as reference at 400^{o}C, the PdAu10 membrane showed slightly better sulfur tolerance and the improvement becomes more significant with the concentration sulfur. According to Union Carbide's results, the sulfur tolerance could be further improved with more Au in the membrane.

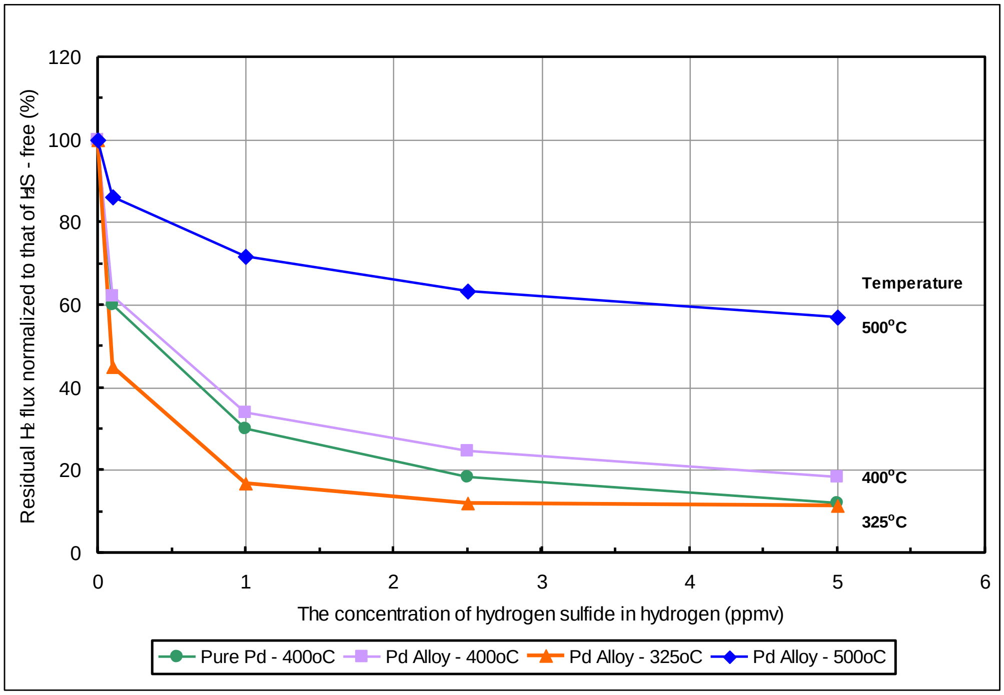

Figure 14. H2S inhibition to hydrogen permeation through a PdAu10 membrane as a function of the concentration at various temperatures (the results from Pall)

K. J. Bryden et al (1998, 2002) [44, 45] examined the effect of H_2S (52 ppmv) on hydrogen permeation through a PdFe4 alloy foil (10 micron thick) at 200^{o}C. The membrane was fabricated by pulsed electrodeposition from a binary metal bath. It appears that the membrane quickly lost hydrogen permeation ability and its hydrogen flux was about 25% of its original value. It is interestingly noted that nanostructured PdFe4 membranes displayed better sulfur tolerance than its counterpart but with coarse grain structure. However, sintering would be problem for such fine grain metal membranes if operated at high temperature. Overall, the membrane did not offer any practical advantages.

Use of other precious metals alone or as alloying components of palladium to address sulfur contamination issue is also reported in literature. D. J. Edlund et al (1993, 1994, 1995) [46-49] developed a Pt-coated vanadium foil for H_2S decomposition membrane reactor operated at 700^{o}C and 115 psia. The membrane was fabricated by laminating 30-micron vanadium foil between two 25-micron platinum with silica as diffusion barrier in between two metal foils. As the authors suggested, platinum sulfide is unstable at elevated temperatures, for instance > 225^{o}C. They reported that the membrane showed no decline in hydrogen flux even after 8 hour exposure to 100 psig H_2S at 700^{o}C. Under similar conditions, its counterpart with Pd substitution for Pt was destroyed in less than 15 seconds. It was also observed that the platinum-coated membrane remained untarnished whereas the palladium-coated membrane has experienced server corrosion resulting in holes that penetrate completely through the membrane. However, for practical purpose, the thickness of Pt needs to be reduced to increase hydrogen flux and also cut the cost. Therefore, M. Kajiwara et al (1999) [50] fabricated a thin Pt membrane supported on a porous alumina tube by a chemical vapor deposition technique (CVD) and further investigated its chemical stability with 0.62% H_2S at 400^{o}C in comparison with a pure Pd membrane. For the platinum membrane, its hydrogen flux rapidly decreased down to 5.8% of its initial hydrogen flux with pure hydrogen as feed while its inert gas leak rate remained unchanged. In contrast, the palladium membrane was quickly ruptured, which was indicated by a drastical increase in inert gas leak rate. XPS analysis indicated sulfur present on the platinum membrane surface. It should be pointed out that these two types of Pt membranes showed different behavior of responding to sulfur contamination. In other words, the Pt foil seems to more tolerate sulfur than the CVD thin Pt membrane. Kajiwara et al attributed the difference to their membrane structure and corresponding hydrogen transport mechanism. The CVD Pt membrane had a nanoporous structure and hydrogen transports through the membrane by an adsorption-surface mediated diffusion process which tends to contamination. However, its sulfur tolerance could be further improved by reducing defects.

In summary, recent studies of sulfur tolerant palladium-based alloys are still limited primarily to Pd-Cu, Pd-Ag and Pd-Au alloy systems, more often simply evaluating their sulfur chemical stability. This may be because these alloys have cost advantages and also extensively explored in history for hydrogen purification. However, of special interest to us is their sulfur tolerance ranking of Pd-IB element alloys since it would provide a systematic knowledge for us to research new sulfur tolerant palladium alloys. Therefore, we will now discuss possible mechanisms of sulfur contamination.

A quantitative understanding of the intrinsic rates and mechanisms of sulfur contamination is generally lacking [51]. Therefore, our discussion about this topic cannot be specific. What we could do is to adapt relevant knowledge from heterogeneous catalysis where palladium is employed as process catalysts for several industrially important hydrogen reactions. In addition, our discussion more focuses on monolayer surface chemistry instead of surface corrosion. This is because resistance to formation of bulk sulfides is a necessary although not sufficient criterion for resistance to contamination by sulfur. The inhibition can also occur by adsorption of a monolayer of sulfur on surfaces even if bulk sulfides do not form. However, interested readers may be referred to research work from O. Iyoha et al (2007) [34] for a topic about corrosive decay of Pd-based membranes. Wherever necessary, we will also apply the hydrogen transport theory in our discussion.

As described above, hydrogen atomically transports through palladium membrane. It implies hydrogen molecules must be adsorbed and dissociated on palladium membrane surface. Palladium possesses an excellent catalytic activity for dissociation of molecular hydrogen. In heterogeneous catalysis, sulfur is a well-established poison for palladium catalysts. A general understanding is that sulfur has very high affinity for palladium, meaning a high binding energy of sulfur to palladium. Hydrogen sulfide can dissociatively adsorb on palladium surface and approach saturation monolayer in presence of few ppm sulfur in gas phase. The adsorption is generally very rapid even at room temperature and it has low energy barrier to adsorption and dissociation until a high coverage, for instance above 0.5 ML [52-55].

Sulfur has a valence electron structure $3s^2 3p^4$ with two pairs of unshared electrons and electronegativity 2.58. Palladium's valence electron configuration is $4d^{10} 5s^0$ with electronegativity 2.20. Several studies have revealed substantial overlap of primarily sulfur p-states with the palladium surface d-band giving rise to a strong covalent bond between the adsorbate and the surface [52]. Moreover, theoretical modeling and synchrotron-based high-resolution photoemission spectroscopy showed the adsorbed sulfur withdraws charge from the surface and further reduces the density of the d-states of palladium near the Fermi level [56, 57]. LEED, STM, XPS, and AES are employed to characterize structure of adsorbed sulfur, which is important to understand how adsorbed sulfur blocks the surface sites and modify their electron configurations. In these studies, the Pd(111) surface has been used as a key model system. The finding is that the behavior of sulfur on the surface is quite varied and depends markedly on the surface coverage and temperature. For sulfur coverage 0.25 ML that is created at 27-77^{o}C by exposing the Pd(111) surface to H_2S, a ($\sqrt{3}X\sqrt{3}$) structure on the surface was identified by LEED (low-energy electron diffraction) along with other two structures ($\sqrt{7}X\sqrt{7}$) and (2X2) as minor [58]. It was observed by STM (scanning tunneling microscopy) that the adsorbed sulfur atoms coalesce into two-dimensional islands to form a simple sulfur overlayer geometry. The sulfur atoms in the ($\sqrt{3}X\sqrt{3}$) structure usually occupy threefold fcc hollow sites. At elevated temperatures 127-427^{o}C, a predominantly ($\sqrt{7}X\sqrt{7}$) structure pattern emerges [59, 60]. Moreover, with increase in the coverage (above 0.4 ML) the lattice penetration of sulfur and growth of sulfide phase occur [61]. A confirmed structure model consists of a packed arrangement of palladium triangles and pentagons on the Pd(111) surface. The sulfur atoms occupy binding sites generated by the palladium pentagons. It was suggested that the existence of a densely packed mixed S-Pd overlayer provides a major stabilizing effect for the surface [62].

There is a general agreement that sulfur inhibition to hydrogen permeation through palladium-based membranes is more catalysis issue involving chemisorption of sulfur, often called sulfur poisoning [52]. Hence it could be interpreted in terms of sulfur adsorption on the surface of the metal and its influence on some surface properties based on electronic or/and geometric effects. Accordingly, we will discuss how sulfur adsorption impacts each element steps of hydrogen permeation process as follows.

- Dissociative adsorption: hydrogen molecule dissociatively adsorbs on the surface of palladium, which requires two adjacent empty sites. This process is usually quantified by a sticking probability, the flux of hydrogen molecules impinging on the surface and surface empty sites. The sticking probability has been the subject of detailed investigations for numerous years during the 1970's in the field of hydrogen in metals. Already the early work of Langmuir and that of Roberts established that the efficiency of formation of the chemisorbed species from the collision of a reactive gas molecule such as H_2 with clean metal surface is often close to unity. These observations have been lately confirmed. It is now generally accepted that hydrogen adsorption on Pd and other transition metals is a non- or only weakly activated process, i.e. dissociation not being hampered by an energy barrier as described in Figure 1. The strong reactivity of transition metals including Pd has been correlated with the presence of unpaired d electrons in these metals and their participation in the formation of a strong chemisorption bond [63]. When the surface is covered with sulfur, the description of the interaction with H_2 is not yet so clear considering how electronic or/and geometric effects in combination act. Since one of the necessary steps in hydrogen permeation is H_2 chemisorption, investigation of the effects of adsorbed sulfur on H_2 adsorption can be crucial about sulfur contamination. Sulfur adsorption on a metal surface may alter its adsorption characteristics for H_2 adsorption, either by blocking the active surface sites and thus making them inaccessible to hydrogen molecules (geometric effects) or by structural changes caused by strong metal-sulfur interactions (electronic effects). It is also possible that sulfur will have direct chemical interaction with the adsorbed hydrogen atoms instead of having indirect interactions through substrate metal atoms [64-75]. Molecular beam studies show that the initial sticking probability of H_2 molecules scattered at Pd(100) strongly decreases with increasing coverage of preadsorbed sulfur. This is especially so for low beam energies, at which the sticking is most sensitive to the presence of non-activated reaction pathways. These results were interpreted as such that with increasing sulfur coverage the character of the dissociative adsorption process shifts towards that of an activated reaction in which the dissociation process of H_2 is governed by energy barriers in front of the Pd surface. Adsorption studies at ultralow temperature showed that the hydrogen saturation coverage decreases linearly with the amount of preadsorbed sulfur. Furthermore, the analysis of the thermal adsorption of hydrogen shows that the initial sticking probability also decreases linearly with the sulfur coverage. In contrast to the above mentioned molecular beam scattering these results were explained in terms of a blocking of surface hollow sites neighboring sulfur adatoms. The term “blocking” refers to a substantial reduction of the adatom total energy, making those sites unstable against associative desorption of hydrogen. Sulfur adatoms occupy the same surface hollow adsorption site as hydrogen and make at least one hollow site inaccessible for hydrogen adsorption; but it was suggested that the actual surface deactivation per sulfur adatom is larger, comprising about four hydrogen adsorption sites. A theoretical study of co-adsorption of hydrogen and sulfur from S. Wilke et al (1995) [66] suggested that the poisoning effect of sulfur is not caused by a strict blocking of hydrogen adsorption sites in the vicinity of sulfur adatoms. For a (2X2) sulfur adlayer (coverage 0.25 ML) hydrogen adsorption remains an exothermic process for all surface hollow sites not occupied by sulfur. The blocking of hydrogen adsorption happens only for higher sulfur coverage. Therefore, they concluded that the poisoning of Pd(100) is a combined effect of the formation of energy barriers hampering the H_2 dissociation and a modest decrease of the adsorption energy on the vicinity of the sulfur adatoms. In other words, to understand how preadsorbed sulfur prevents hydrogen adsorption, electronic effects may be important at low coverage, since one atom of sulfur can prevent hydrogen adsorption on several Pd atoms. At intermediate coverage, desorption states of H_2 are shifted to lower energies suggesting that sulfur weakens the bonds between Pd and hydrogen. Thus, at complete coverage, a simple blocking or geometrical effect is adequate to explain the poisoning, since the ensembles of Pd required for dissociation of H_2 are no longer accessible at the surface.

- Transition of atomic hydrogen from the surface into bulk metal: hydrogen atoms transfer from the surface to the bulk metal is an activation process with an energy barrier as hydrogen solution involves expansion of lattice. Its rate is usually described by the surface coverage of atomic hydrogen, the vacancies in the bulk adjacent to the surface, surface Pd atom concentration, bulk Pd atom concentration, and the activated rate constant. Evidently, sulfur adsorption blocks the surface sites for dissociatively hydrogen adsorption, leading to reduced hydrogen surface coverage. And thus it results in decrease in the transition rate of atomic hydrogen from the surface to the bulk.

Methods for improving sulfur tolerance of palladium

Pure Pd membrane can't tolerate even a very small amount of sulfur compounds; it quickly loses its mechanical integrity. To protect Pd membranes from contaminants, McBride and McKinley at Union Carbide (1965) successfully employed guard bed adsorbents. Guard beds were used to adequately remove solids, hydrocarbons, oils, compounds of sulfur and other impurities from the feed. Parallel guard beds were used. One was kept in service while the second was regenerated or replaced. Iron oxides were used to partially removed H_2S. Zeolites and other adsorbents were also employed. Nine plants based upon Pd membranes were in operation by mid-1965. The largest plant produced 9,000,000 ft^3 of hydrogen per day. Total capacity of all nine plants was 34,000,000 ft^3 per day. Recovery of hydrogen from refinery was envisioned. However, reducing sulfur to very low level is still cost challenge for coal gas hydrogen separation application although both warm and cold gas cleanup technologies are already available. In addition, uncontrollable and accidental poisoning of sulfur can be a considerable financial burden and it has been reported that millions of dollars are lost every year in the chemical industries as a result of sulfur poisoning. Therefore, the identification of sulfur tolerant membrane materials is still critical to realize full benefits that Pd membrane technology offer for the separation of hydrogen from coal gas source. To increase tolerance to sulfur, researchers have explored several material technological approaches, which could be categorized into three general strategies, i.e. materials that resist poisoning of sulfur compounds; transition metal sulfides that possess hydrogen activity; sulfur getters that are mobile on Pd membrane surface as sulfur scavenger, which are briefly discussed as follows.

- Metal alloying method: In the past decade, sulfur resistant Pd alloy development is primarily focused on Pd-IB element alloys (Pd-Cu, Pd-Ag and Pd-Au alloy systems), especially Pd-Cu alloy system. Morreale et al investigated the sulfur resistance of several Pd-Cu alloys. PdCu20 and PdCu40 alloys with FCC structure showed significant sulfur tolerance. The resistance of the FCC structure (as opposed to the BCC structure) may be attributed to geometric incompatibility to sulfur adsorption. It appears that a Pd-Cu alloy optimized for its sulfur resistance does not necessarily have optimized hydrogen flux as shown in Figure 15. The same may be true for Pd-Ag (Figure 16) and Pd-Au (Figure 17) alloys. Besides noble metals, the sulfides of Pt, Ir, Rh and Ru are much less stable than those of Pd, and hence these elements generally show better tolerance to poisoning by sulfur. Another class of interesting material is amorphous alloys that are reviewed by M. D. Dolan et al (2006) [76] and J. W. Phair et al (2006) [77]. A typical example would be Zr-based metal alloys. Although the sulfurization of zirconium is not favored, no experimental data are available to assess their sulfur resistance. Other progress in sulfur tolerance Pd alloy development is associated with theoretical modeling and computation involving thermodynamic calculation of sulfurization of transition metals and density functional method. In addition, high-throughout combinatorial method started to be used for Pd alloy development, for instance in this project in collaboration with R. B. van Dover at Cornell University [105, 106]. It is expected the combinatorial method combined with theoretical modeling will allow rapid material development.

- Transition metal sulfides: C. Ling and D. S. Sholl (2009) [78] investigated potential of metal sulfides as membrane by density functional calculation for hydrogen separation. The metal sulfides include VS, CrS, FeS, NiS, NbS, FeS_2, NiS_2 and ScS. Their calculations indicate that films of any of the sulfides have extremely low permeabilities for hydrogen although the solubility of hydrogen in some of these materials is considerable, for instance VS, CrS, FeS, and NiS (> Pd_4S). It should be also mentioned that conventional hydroprocessing catalysts $Mo(W)S_2$ have activity to adsorb and activate hydrogen. Therefore, these transition metal sulfides may be used as protective coatings and hydrogen dissociation catalyst on Pd-based membranes, a membrane structure similar to Pd-coated vanadium membranes. This could possibly sidestep the difficulties faced by Pd-based membranes.
- Mobile sulfur getters: Alkali metal additives are used in solid catalysts as promoter, for instance for improvement of sulfur resistance. They (Li, Na, K, Rb, and Cs) are strongly electropositive elements with low ionization potentials and form low melting ionic metal sulfides. Alkali metals can be adsorbed at transition metal surface in different manners ranging from sub monolayer quantities to surface or bulk compound. Therefore, these

alkali metal coatings may serve as sulfur scavengers on Pd membrane surfaces and protect Pd from sulfur poisoning.

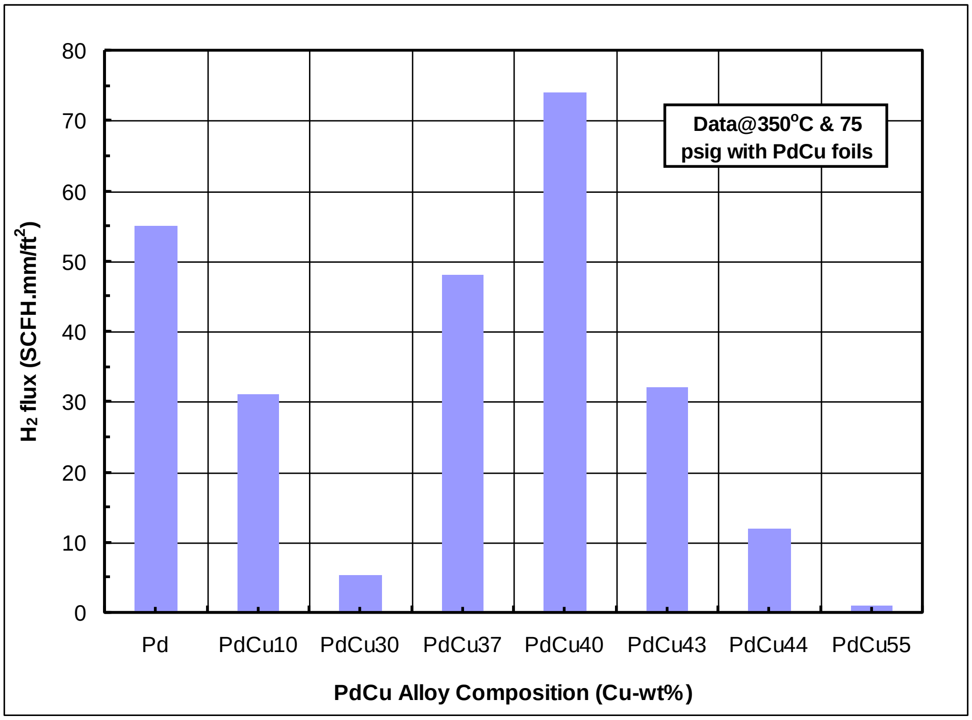

Figure 15. Hydrogen flux of Pd-Cu alloy as a function of its composition

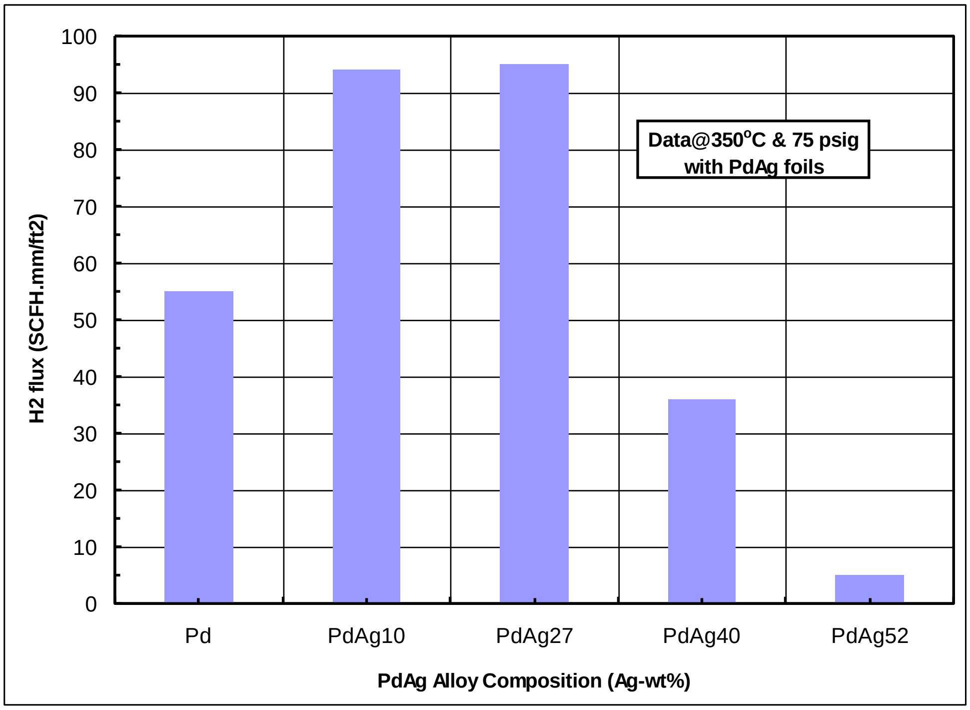

Figure 16. Hydrogen flux of Pd-Ag alloy as a function of its composition

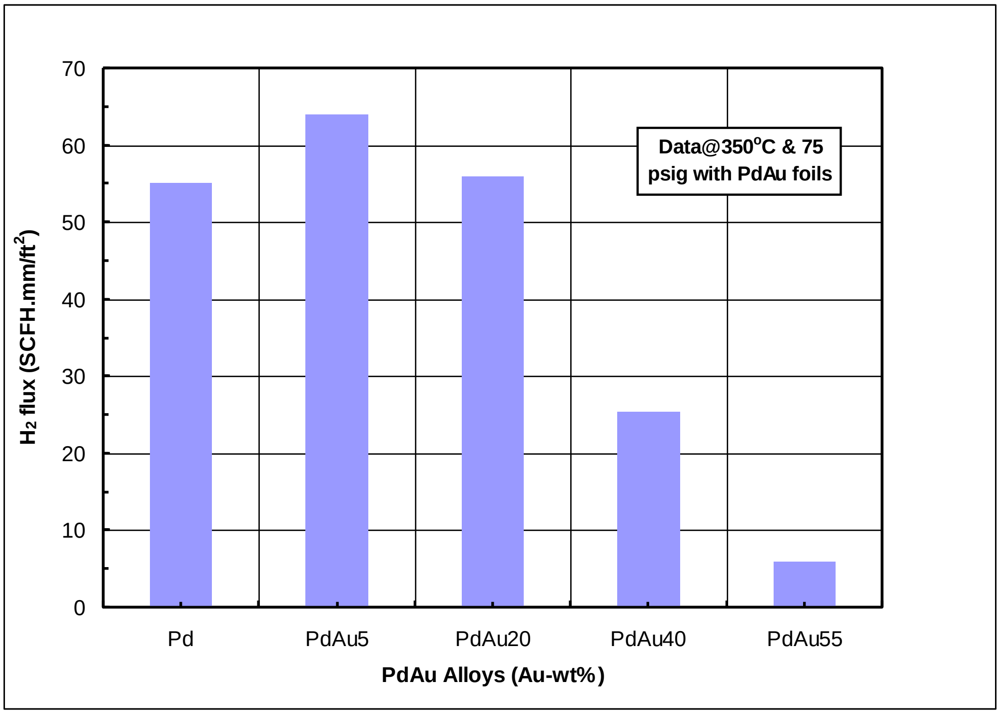

Figure 17. Hydrogen flux of Pd-Au alloy as a function of its composition

Effect of CO

CO is one of the components of coal gas (H_2, CO, CO_2, H_2O and other minors). Its amount depends on gasifier process conditions and additional downstream gas processing, typically in a range of 25-35% at a coal gasifier outlet and down to 1% after being shifted by a catalytic process. A hydrogen separation membrane test protocol recommended by the U.S. DOE- NETL suggested a coal gas composition of 50% H_2, 1% CO, 30% CO_2, 19% H_2O with total pressure 200 psia and temperature range 300-600°C [22]. The effect of CO on palladium and palladium alloy membranes has been studied by gas permeation, surface adsorption and theoretical modeling methods [79-100]. In these studies, two types of gas mixtures were used, one H_2-CO and the other simulated coal gas. In general, these gas mixtures are also called syngas. In the following, we will separately discuss the effect of CO that was investigated with these two types of syngases.

M. Amano et al (1990) [79] analyzed the effects of CO and CO_2 on hydrogen permeation through a pure palladium membrane at 150-450°C and 0.2-36.8 psia with H_2-10% CO, H_2-50% CO and H_2-50%CO_2 gas mixtures. A Pd foil had a thickness of 700 microns and 12 mm in diameter. They found that CO inhibited hydrogen permeation below 250°C and it had no inhibition above 250°C. In addition, the extent of inhibition significantly increased with the concentration of CO. Its pressure dependence was not obvious. AES (Auger electron spectroscopy) surface analysis was carried out over a foil sample that was tested using H_2-10%CO for 5 days at 200°C. Active carbon was detected and no carbide was confirmed. They also measured the hydrogen solubility coefficients of Pd foil samples with pure hydrogen, H_2-10%CO and 50%CO. They observed the same hydrogen solubility constants at each temperature. Therefore, the authors suggested that the deterioration of hydrogen permeation by CO be attributed to the decrease in effective area for H_2 dissociation by the weak adsorption of CO.

H. Amandusson et al (2000) [80] employed the Wicke–Kallenbach diffusion cell (Graham's cell) to determine the effect of CO on hydrogen permeation through a 25-micron pure Pd foil at 100-250°C and low pressure (total pressure 50 torr, 2 torr for H_2 and CO gas, respectively). The gas compositions were analyzed by a quadrupole mass spectrometer. It was observed that the effect of CO is strongly temperature-dependent. When CO and H_2 were supplied at equal partial pressure upstream, hydrogen permeation was total quenched at 100^{o}C. While at 250^{o}C there was only be a decrease in the permeation rate by approximately 10%.

F. Gallucci et al (2007) [81] investigated the effect of CO on hydrogen permeation through a pure Pd membrane tube (100 micron thick) with a wide range of CO in hydrogen using H_2-N_2 gas mixture as reference at 250-350^{o}C and feed pressure 52 psi. It was found that CO molecules remarkably inhibit hydrogen permeation at 250^{o}C, but not at 350^{o}C. This observation is agreement with what M. Amano et al (1990) reported. It is interesting noted that the inhibition of CO to hydrogen permeation is non-linear as a function of CO content in hydrogen. In other words, there exist two regions at 15% CO. Hydrogen flux rapidly decreased with CO while it was below 15%. In contrast, Hydrogen flux gradually approached to the values with H_2-N_2 gas mixtures as CO increased above 15%. As authors suggested, it was attributed to the diluting effect by CO. They further applied density functional theory to analyze CO adsorption on Pd surface. The calculations suggested that CO molecule is bonded with Pd by carbon instead of oxygen in linear mode. The bonding involves two types of Pd sites, one bridge position and the other hollow position on the (100) planes of the Pd FCC crystal, which are also activation centers for hydrogen adsorption. This explains why CO inhibits hydrogen permeation without formation of carbide. D. R. Alfonso (2006) at NETL reached similar observation about the effect of CO by density functional theory calculations. He also noted that CO dissociative adsorption can occur, depending on temperature.

H. Li et al (2007) [82] used a thin Pd membrane tube to examine the effect of CO on hydrogen permeation and the membrane structure at 320-500^{o}C with H_2-CO gas mixture (CO 20-33%). The membrane was prepared by electroless plating on porous alumina tube and it had a Pd coating of 3 microns thick. Their new finding is that three temperature regimes could be recognized considering the effect of CO on hydrogen permeation, 1) < 350^{o}C CO remarkably inhibited hydrogen permeation; 2) 350-450^{o}C the inhibition was moderate; 3) > 450^{o}C the inhibition seems negligible with 20-25% CO and it increased to 4-8% when CO was 30-33%. They also noticed that the inhibition gradually increased with time within 6 hours. And the higher temperature was, the more sharply the inhibition rate with time became. Other two interesting experimental observations are XRD characterization of tested membrane samples and temperature programmed surface reaction (TPR) with Pd membranes. XRD indicated formation of palladium carbide $Pd_{1-x}C_x$ above 450^{o}C. As expected, more palladium carbide phase formed at higher temperature, for instance 500^{o}C. Although palladium carbide phase is metastable under the experimental conditions, its decomposition seems kinetically rather slow. Therefore, palladium carbide phase was accumulating on/in Pd membrane with time, which is consistent with hydrogen permeation decay. Further, palladium carbide phase has litter hydrogen activity. The TPR results showed the membrane surface had catalytic activity for CO reactions (methanation and the Boudouard reactions) which are described as follows. The reactions become significant above 450^{o}C. Accordingly, they concluded that two types of CO inhibition could be distinguished, one was CO adsorption and the other carbon deposition and diffusion. The former particularly occurs below 350^{o}C and the latter became more severe above 450^{o}C. Certainly, carbon deposit can be removed by oxygen purging, but the membrane develops additional defects and loses its separation capability.

$$CO + 3H_2 = CH_4 + H_2O$$
$$2CO = C + CO_2$$

Compared to the previous observations of CO inhibition on thick Pd foil samples, it appears that the temperature threshold of CO inhibition is closely related to the membrane thickness. In other words, the temperature threshold value increases as a Pd membrane becomes thin. Another reason may be that electroless plated Pd membrane has finer grain structure than conventional cold rolled Pd foil. And hence the former may have higher surface area to adsorb CO.

Certainly, how palladium alloy membranes response to H_2+CO chemistry is a practical important topic to review. Pd-Ag alloy system has been primarily used in these studies, probably due to its commercially availability. Other alloys included Pd-25wt%(Ag-Au-Ru), Pd-7wt%Y, Pd-2wt%Al, Pd-Y(Gd)-Ag, Pd-Y-In(Sn, Pb). J. Chabot et al (1988) [83] assessed the poisoning effect of CO on a PdAg23 membrane tube with 250 microns of the wall thickness and 3 mm of the external diameter at membrane temperatures 100-450^{o}C and H_2 pressure 0.05-2 psi. The gas mixture consisted of 0.2-9.0% CO and 9.5% H_2 balanced by He. They observed that the presence of CO led to decrease in hydrogen flux in all the studied concentration range. For example, hydrogen flux dropped 75% at 250°C with CO 4.3-9.5%. Therefore, the membrane had to be operated above 250-300°C depending on CO concentration. It appears that PdAg23 alloy offered no advantage in terms of CO tolerance. It is in agreement with the finding by H. Amandusson et al (2001) [84]. They studied the role of the surface composition in CO inhibition to hydrogen through surface modified 25-micron Pd and PdAg30 foils at 100-350°C. The surface modification was made by additional silver coating. It was found that CO inhibited the permeation of hydrogen in a similar manner on all modified membranes, independent of surface silver content. F. Scura et al (2008) [85] reported their study of the CO inhibition to hydrogen permeation through two commercial PdAg alloy capillary membranes with 60 and 100 microns in thickness at 320-450°C, feed pressure 30-88 psi and 0-30% CO in hydrogen. It is noted that the CO inhibition to PdPd23 alloy membrane in this work is similar to the one with pure Pd membrane that is reported by the same research group.

A research group from SINTEF recently investigated the CO poisoning effect with a 3-micron PdAg23 alloy film at 400°C and 290 psi [86]. The membrane was fabricated by sputtering with silicon wafer as substrate. They used H_2-N_2 gas mixture as reference to quantify the intrinsic effect by CO on hydrogen permeation. Their new finding is that a large hydrogen flux reduction occurred even at very low CO concentration. The reduction approached a plateau 60% at 5% CO. It seems to be contradicting previous studies that the effect of CO on hydrogen permeation is insignificant above 300-350°C. It may be related to high-pressure CO adsorption and the membrane nanostructure. Later on, A. L. Mejdell et al (2009, 2010) [87, 88] employed a microchannel membrane configuration made of silicon wafer to study CO poisoning over the same type of PdAg23 alloy membrane. They specifically looked into how the air heat treatment of a PdAg23 alloy membrane influences CO inhibition. The heat treatment was done in static air at 300°C for 5 days. They observed that the air heat treatment remarkably improved the CO tolerance of PdAg23 alloy membrane at both 300 and 350°C. For example, hydrogen flux decreased 60% in presence of 1% CO at 350°C before the air heat treatment. And the reduction was only 15% after the air heat treatment. The latter is in agreement with the previous studies on CO poisoning. They also found that the CO coverage decreased after heat treatment in air, suggesting surface re-structuring possibly involving grain growth and segregation et al.

H. Yoshida et al (1983) [89] tested a commercial Pd-25wt%(Ag-Au-Ru) alloy membrane tube (the wall thickness 80 microns) at 372^{o}C and 87 psi with a gas mixture of 101 ppm O_2, 97.4 ppm CH_4, 90.2 ppm CO, 96.3 ppm CO_2, and 96.2 ppm N_2 balanced by H_2. As they concluded, these contaminants have no effect on the hydrogen permeation through the membrane. However, we suspect that O_2 might counteract the effect of CO on the membrane surface since catalytic activity of the membrane surface for CO conversion directly by O_2 or indirectly H_2O (O_2/H_2 reaction product).

O. Iyoha et al [90] examined the effect of CO on hydrogen permeation through a PdCu20 alloy membrane (1 mm thick) with H_2-50% CO gas mixture at 350-900^{o}C and 90-410 psi. At 350 and 465^{o}C loss of hydrogen flux is not significant, i.e. 5-7 % its original one. Hydrogen flux reduction is moderate at 765 and 900^{o}C. But a pronounced reduction occurs at 635^{o}C. SEM micrographs show surface modification and carbon deposit on the membrane surface tested at 635^{o}C. However, no notable surface modification and carbon deposit was observed on the membranes tested at 350 and 465^{o}C. The membrane tested at 765^{o}C had negligible carbon deposition, but it experienced severe surface roughening. Further GC detected 35% CO_2 and 25% CH_4 in the membrane effluent stream. In contrast, neither pitting or carbon deposition on the membrane surface at 900^{o}C was observed. These observations are in agreement with what H. Li et al (2007) reported with electroless plated pure Pd membranes. Carbon deposition is from the Boudouard reaction ($2CO = C+CO_2$). And further carbon can diffuse into the membrane to form palladium carbide which is not active for hydrogen transport. It explains the membrane at 635^{o}C had the largest hydrogen flux reduction. As temperature increases, both methanation and water gas shift reaction significantly take place and thus most of CO is converted to CH_4 and CO_2. It is why CO inhibition is low at 765^{o}C.

Another interesting research work on CO poisoning is from D. Wang et al (2004, 2005) [91, 92]. They studied influence of partially internal oxidation of Pd-Al alloys on their CO resistance. Hydrogen permeation was measured by upstream pressure decay method at 150^{o}C and upstream pressure 7.3 psi with CO 1.3 and 3.8%. The Pd-Al alloys were internally oxidized at 680^{o}C in the atmosphere for 30 min, which generally resulted in < 7% of the desired extent of internal oxidation. The interesting results are that a partially internal oxidized Pd-Al alloy offers a greater resistance to CO poisoning than pure Pd. Take 155-micron Pd membrane and 95-micron Pd-$Al_{1.2}$ as an example. Both membranes have the same hydrogen flux in pure hydrogen. Compared to Pd membrane of 15% the hydrogen flux reduction, the $PdAl_{1.2}$ membrane only lost 2.5% its hydrogen flux in presence of 1.3% at such low temperature. As reported, the authors were to extend their work to Pd-Ag-Al alloy system, which may have improved CO resistance and meantime possess high hydrogen permeation rate for practical application purpose.

Y. Sakamoto et al (1996) [93] explored several ternary palladium-based alloy systems for improvement of CO poisoning. These alloys included Pd-Y(Gd)-Ag and Pd-Y-Pb(In, Sn) with pure Pd, Pd-Ag, Pd-Y(Gd) alloys for comparison and these binary and ternary alloys all have very high hydrogen permeability. All samples in form of foil (700 micron thick and 12 mm in diameter) were tested by permeation transient method (increase in downstream pressure) with H_2-10% CO gas mixture at 250-450^oC and input gas pressure 59 / 98 psi. Here, we show a ranking in decreasing order of CO inhibition at 347^oC.

$PdGd_{6.3}Ag_5$ (reduction 62%) = $PdGd_8$ > $PdY_{6.3}Ag_5$ > PdY_8 > $PdGd_{4.7}Ag_{10}$ = PdY_3Ag_{15} = $PdGd_3Ag_{15}$ > $PdY_{1.3}Ag_{20}$ = $PdGd_{1.3}Ag_{20}$ > $PdAg_{24}$ > Pd (reduction 10%) (composition in atomic ratio)

It is noted that the above order is the same as hydrogen flux order from high to low. Therefore, we suspect that the membrane which had higher hydrogen flux was also exposed to higher CO concentration since CO was concentrated while hydrogen was permeating. It did not necessarily reflect their respective CO resistance. However, these alloys are still interesting to look into for CO resistant alloy development.

L. Peng et al (2009) [94] applied TDS (thermal desorption spectroscopy) and XPS (X-ray photoelectron spectroscopy) to study CO surface chemistry of PdY6.8 foil. The sample was conditioned with H_2-CO gas mixture at 350^oC for 1 hour. TDS profiles indicated that adsorbed CO shifted the desorption peak of hydrogen to higher temperature and also reduced the solution of hydrogen. XPD detected surface carbon and yttrium oxide species of a conditioned PdY6.8

sample. Therefore, they suggested that CO may dissociatively adsorb on yttrium. This surface chemistry may explain their TPD results. And it is also in agreement with Y. Sakamoto's results.

The influence of major coal gas components (CO, CO_2 and H_2O) on the performance of palladium-based membranes has been investigated. The consensus from these studies is that CO has the largest impact. As discussed above, temperature and CO concentration are two most important parameters. At low temperatures below 300-350^oC, CO can significantly inhibit hydrogen permeation through most of Pd-based membranes by molecular chemisorption on the membrane surface. Above 450^oC, carbon deposition and further formation of palladium carbide can result in failure of a Pd-based membrane by dissociative chemisorption. And 350-450^oC would be an optimized temperature range for operating Pd-based membranes to minimize both CO adsorption and carbon deposition. Besides temperature and CO concentration, H_2O could be utilized to minimize carbon deposition from CO reaction on the membrane surface as in water gas shift reaction. In the following, we are to discuss relevant research work in literature with emphasis on the role of H_2O in counteracting CO poisoning.

A. Li et al (2000) [95] reported their comparative study of the effect of CO and H_2O on hydrogen permeation through an electroless plated pure Pd membrane. They tested the membrane at 380^oC and 44 psi using H_2-CO, H_2-H_2O and H_2-CO-H_2O gas mixtures with H_2-N_2 gas mixture as reference. With binary gas mixtures, H_2O inhibited hydrogen permeation more strongly than did CO. And CO showed no inhibition at all. In a ternary gas mixture H_2-CO-H_2O (H_2O/CO = 2), hydrogen permeation rate was close to that in H_2O-H_2 gas mixture. K. Hou et al (2002) [96] reported a similar conclusion with PdAg alloy membranes at 275-350^oC. In addition, as expected, H_2O inhibition significantly mitigated as temperature increased. For instance, the hydrogen reduction rate is 30% at 350^oC versus 60% at 275^oC. Contradicting results about the effects of CO and H_2O came from B. Arstad et al (2006) [97]. They employed a 1.6-micron PdAg23 foil in their work. With H_2-20%CO at 255^oC, hydrogen flux reduced about 88%. In contrast, reduction in hydrogen flux was about 60% in H_2-20%H_2O at the same temperature, which is only slightly lower than in H_2-20%N_2. They suggested that the difference may be attributed to different membrane materials, microstructure and thickness. T. H. Nguyen et al (2009) [98] tried to clarify literature results on the role of CO and H_2O. They tested a PdAg25 membrane tube with H_2-CO and H_2-H_2O and H_2-CO-H_2O gas mixtures at 100-525^oC and atmospheric pressure. The membrane tube had 5-mm OD and 100-micron thickness. Their results showed the negligible effect of H_2O on hydrogen permeation through the PdAg23 alloy membrane, and the effect of CO was more remarkable especially below 350^oC. A. Unemoto et al (2007) [99] also reported that hydrogen permeation through a PdAg23 alloy foil (20 microns thick) was not affected by co-existence of H_2O up to 9.5% at 500 and 600^oC under atmospheric condition. In other three types of gas mixtures H_2-CO-H_2O, H_2-CO_2-H_2O and H_2-CH_4-H_2O, no reduction in hydrogen flux was observed by CO, CO_2 or CH_4 at 500 and 600^oC. They added steam in above gas mixtures to suppress carbon deposition. O. Iyoha et al (2008) [90] extended this research to a PdCu20 foil (1 mm thick) at higher temperature 350-900^oC and higher pressure 90-200 psi with H_2-50% H_2O. Their experiments show H_2O very modest inhibits hydrogen permeation under these conditions, i.e. no more than 7%. Their post-test SEM characterizations indicate the surface modification of the membranes exposed to H_2-50% H_2O gas mixture at 635 and 900^oC, i.e. surface roughening and pitting.

It appears that the effect of H_2O is not yet conclusive. This is because H_2O can clean the membrane surface as air purging does. Therefore, the membrane needs to be air purging before testing the membrane for study of H_2O. Thus, theoretical modeling may provide more insight into the effect of H_2O. D. R. Alfonso (2006) [100] applied density functional theory to investigate CO and H_2O interaction with Pd(111) surface. Although the bonding of CO on the surface is rather stronger that H_2O, dissociation of H_2O is a more facile process compared to CO. The dissociation of H_2O gives rise to adsorbed O which is a better poison than CO.

Combinatorial Methods of Alloy Development

The development of alloys must have been purely empirical in ancient times. However, from an initial understanding of physical, chemical and metallurgical processes it has become a scientific discipline that uses gained knowledge for creating alloys with desired properties. Today, this further optimization has many problems. A number of side effects such as synergistic amplification or annihilation can adversely affect the property, particularly if complex alloys with three or more elements are used. A systematic investigation of all possible combinations is no longer feasible. This has led to a renaissance of empirical alloy development, called combinatorial alloy development. Combinatorial methodology is a powerful material research technique. It involves systematically changing a process variable (i.e., material composition, film thickness, process temperature for fabrication, etc.), and fabricating a series of samples as a function of that parameter. A series of property measurements is then made in parallel, in order to (a) identify structure-property treads and (b) act as screening tool for further optimization and experimentation. A general workflow for combinatorial material development basically includes material library synthesis, characterization and data analysis [101, 102]. These phases will be briefly discussed as follows.

Combinatorial libraries

The goal of combinatorial experimentation is to recreate the diversity in the chemistry and structure, and hence the properties, of materials found in nature, called combinatorial libraries [103, 104]. Irrespective of the type of materials systems used, libraries of materials in thin-film, particulate, or bulk forms can be created. Far less work has been done on bulk materials (of particular relevance to structure/mechanical applications) than on thin films and particulates (the second is especially important in the field of solid catalysis). Regardless of the form of materials, combinatorial libraries fall into one of two broad geometrically based categories: discrete or continuous. The former category involves spatially resolved variations in chemistry that result in one-dimensional or two-dimensional arrays, very similar to the microarrays used in organic chemistry. Apart from having discrete wells or containers for each chemistry (which may be generated by a number of means, for example, robotic deposition), one can also generate a variety of discrete patterns on a substrate by lithographic techniques or by assisting self-assembly processes that result in discrete arrays. Continuous libraries effectively capture unbroken gradients in chemistry or other materials attributes (e.g., microstructure), which can be achieved in a number of ways, depending on the material, and range from thickness gradients to thermal and thermomechanical gradients. In addition, hybrid techniques include characteristics of both discrete and continuous libraries and provide some very interesting ways of generating libraries.

Continuous libraries / co-deposition [105-107] Direct control of how materials are deposited provides a means of generating controlled composition or chemical spreads. This has now become a standard approach for many applications in inorganic multicomponent alloy libraries.

The first such reported method in 1965 by Kennedy et al was developed for the rapid determination of ternary alloy phase diagrams and employed the use of three off-axis e-beam sources for deposition on a triangularly shaped substrate. The compositional spread of material, or graded profiles, were obtained by taking advantage of the natural profile of the sources which, using the right conditions, can give an uneven deposit of each element across the surface. The compositional spread of the three elements was obtained controlling the relative rate of evaporation of each element. This and subsequent approaches employing co-deposition take advantage of the deposition of off-axis PVD source for simultaneous deposition using relative deposition rate to control compositional ranges without the use of masks, either moving, fixed, or shadow masks. One of the challenges in interpretation in these libraries is to distinguish chemical gradients from the potential microstructural gradients that may form.

Continuous libraries / sequential deposition [103, 104] This technique for preparing composition spreads uses automated shutters that pass over the substrate with a fixed (or programmable) speed during the deposition, creating a gradient thickness of the deposited materials. By creating gradients in various directions for each deposition species, an overall composition spread can be prepared (e.g., a standard ternary spread is implemented by arranging three gradient vectors at 120^o intervals). As with the discrete masked approach, a high-temperature homogenizing anneal is necessary to obtain interdiffusion of the layers, yielding a uniform composition through the thickness of the film. For materials that can only be formed at a high temperature, this is usually not a server limitation. However, it should be kept in mind that reactions between adjacent layers might form binary precursors that do not then react in the same way as a film with three or more intimately mixed species.

Discrete libraries [103, 104] Arguably the most flexible approach in terms of compositions that can be explored is the discrete combinatorial approach first discussed by Xiang et al. Direct deposition or other focused processing can be used to produce discrete libraries, ranging from ink-jet-type printing to microarrays of materials deposited in wells to discrete geometric arrangements. The most serious limitation of this approach is that the compositions examined in the initial lead identification may fail to sample the properties exhibited by various compounds made up of the constituent elements.

High throughput characterization

In a typical combinatorial material development, the characterization tools are used for rapid, high-throughput and automated assessment of single or multiple properties of the large number of samples fabricated together as a combinatorial library [108]. A representative list of materials properties includes chemical, morphological, mechanical, optical, electrical, biological and thermal properties. In any typical of combinatorial experimentation, having the appropriate characterization tool is critical. Without a suitable high-efficiency screening technique, high-throughput synthesis by itself does not provide the information about material properties. For example, when a two million compound library was synthesized with only a 15 ng amount of each compound, the small amount proved to be impossible to analyze using available screening tools. To address a large number of materials-specific properties, a variety of high-throughput characterization tools are required. Ideally, a characterization system for combinatorial materials discovery should be capable of handling small samples with minimal sample preparation requirements and should have rapid turnaround using either serial or parable measurements of library elements during or after the synthesis reaction. It should also have high precision and high accuracy in measurements. In addition, data acquisition, instrument operation and communication among instruments within the discovery cycle should be automated. Data analysis should be effective in handling large amounts of data utilizing either univariate or multivaritate algorithms and should be capable of providing simple transfer functions for the property of interest. Finally, the structure of data management should be clearly laid out and well organized. Good data management schemes should lead to new opportunities in experimental designs, data mining and development of algorithms to correlate data from different characterization tools.

In advanced functional materials, the required performance of a material can become very specific depending on its application. This often means one has to design, develop and tailor screening techniques which are highly specified for individual applications. In many ways, availability of characterization tools determine the scope of one’s combinatorial materials studies. In recent decades, a large repertoire of analytic techniques has been adopted as high-throughput characterization tools. Of specific interest to us is chemical imaging methods and instrumentations including various spectroscopic, microscopic, and their combination technologies (laser-induced fluorescence detection, Fourier transform infrared, and Raman spectroscopy), mapping X-ray microdiffractometry, nuclear magnetic resonance, mass spectrometry [109-114].

Gas Separation Membrane Substrate Quality and Its Characterization

Increasing hydrogen flux and reducing cost of palladium-based membranes recently motivate developing methods to fabricate thin membrane, for instance few microns thick. As a Pd membrane becomes thin, it has to be supported on a mechanically stable substrate. In the design of supported palladium membranes, it is critical that material components are compatible each other under application conditions. The following physical and chemical properties of materials need to be taken into account. Based on these criteria, relevant results in literature are to be discussed in the following.

- Mechanical strength;
- Flow resistance to hydrogen;
- Thermal expansion;
- Thermal stability;
- Surface roughness;
- Surface wetting ability;
- Surface chemical inert;
- Sealing ability.

Because of high hydrogen permeation, vanadium, niobium, and tantalum have been used support. Pd is coated on both surfaces of these metals to promote the dissociation and re-association of hydrogen and to protect the metal surfaces from contaminants in the gas stream. G. L. Holleck (1970) [115] fabricated a PdAg23/Ta/PdAg23 membrane composite (0.52 mm and 1.08 mm thick) by laminating and rolling process. Recently, N. M. Peachey et al (1996) [116], T. S. Moss et al (1998) [117] and C. Nishimura et al (1991) [118] reported similar work. N. M. Peachey et al used an ion milling process to remove oxides on both sides of a 13-micron tantalum foil followed by palladium coating up to 1 micron by electron beam evaporation. The membrane showed higher hydrogen flux that a pure palladium membrane with the same thickness under similar conditions. C. Nishimura et al developed a VNi8 alloy for hydrogen diffusion application. Pd or Pd alloy was applied on both sides by several coating methods including electroplating, electroless plating, and vacuum sputtering. As reported, such alloy membrane can be operated as low as 200^oC and 28 psi without hydrogen embrittlement problem. Its hydrogen permeation maintained stable for two weeks at 300^oC. R. E. Buxbaum et al (1996) [119, 120] reported their work on palladium-coated V-Cr-Ti alloy, pure Nb and Ta tubes (OD 9.5 mm, the wall thickness 0.07 – 0.54 mm). Pd was coated on both ID and OD surface by electroless plating. Such configuration in tube is interesting for practical application since the membrane tubes can be built into a tube buddle as module. D. J. Edlund et al (1994) tested Pd/V/Pd membranes above 650^oC. They noticed gradual reduction in hydrogen flux due to interdiffusion at Pd/V interface. Therefore, they applied alumina paper between Pd and V foils.

The concept of the interdiffusion barrier was approved [49].Both porous ceramic and stainless steel structures have been widely used in the past as the substrates to support thin Pd or Pd alloy films [121, 122]. The main advantages of porous ceramic supports include surface chemical inert and small pore size / uniform pore size distribution. However, the major drawbacks for porous ceramic supports are fragile, susceptible to cracking and difficulty in sealing ceramic to metal parts for process integration. Recently, porous metallic substrates have received considerable attention due mainly to ease of module fabrication and process integration and their closeness of the thermal expansion coefficient to that of Pd and Pd alloys. However, contamination from the intermetallic diffusion of metal support and the large pore size / wide pore size distribution present considerable challenges for depositing thin film with good durability. Therefore, an intermetallic diffusion barrier between Pd film and the support is necessary to build. Methods used to produce the barrier layer include sputtering titanium in a nitrogen atmosphere to form a TiN layer, applying nickel powder followed by sintering combined with the application of a thin gamma-alumina layer by the sol-gel method, depositing zeolite layer by hydrothermal synthesis, and applying ceramic layer by slurry coating, in-situ forming conformal oxide coating by high temperature air treatment. K. Zhang et al (2009) [123] assessed the effectiveness of two types of interdiffusion barriers, one in-situ oxidized metal oxide and the other sol-gel derived mesoporous yttria stabilized zirconia (YSZ). It was noted that the Pd membrane with an in-situ oxidized porous stainless steel was gradually losing hydrogen permeation above 600^oC, which resulted from reduction of the oxidized layer by hydrogen. In contrast, the membrane with YSZ as intermediate layer maintained stable hydrogen flux at the same temperature. The same authors [124] also investigated the effect of metal – ceramic interface on hydrogen permeation through palladium membranes. They found that the Pd/gamma-alumina/alpha-alumina membrane had lower hydrogen permeation rate than the Pd/YSZ/alpha-alumina membrane. They suggested the formation of Pd-Al alloy. However, they have no additional chemical analysis of the membrane to support their hydrogen permeation data.

Chemical Modeling of Hydrogen Separation and Diffusion through Membranes

Metal alloys are vital materials for the fabrication of high flux, high-selectivity hydrogen separation membranes. An example would be commercial Pd-Ag alloys for small scale hydrogen diffusion purification application. Recently renewed efforts are to expand Pd-based membranes for large scale hydrogen separation applications, which have been driven by use of hydrogen as energy carrier and CO_2 capture. A major technical hurdle to recent efforts is the chemical stability issue of known Pd-based alloys. Alloying is usually an approach to modification of host metal for improvement of structure and other physiochemical properties. Therefore, alloys are widely used as catalysts, structural materials and corrosion resistant materials. However, conventional alloying element screening and optimization methods, i.e. “one at a time” is time consuming and expensive. A recent new development is combinatorial and high throughput method in material science and engineering. Its feature is “many at a time”, which remarkably accelerate material R&D cycling time. This method is being applied for sulfur/carbon resistant Pd-based alloy development through a DOE funded project. In recent years, first principles calculations based on density functional theory (DFT) have been applied to complement well with experimental methods, for instance combinatorial experimentations, for accelerating material development. Therefore, we are to review literature relevant to hydrogen alloy development.

DFT calculations have an impressive set of advantages relative to other theoretical tools: they can be applied to arbitrary configurations of atoms including all elements in the periodic table, they provide direct information on the ground state energy of these configurations, and they can be used to predict the precise mechanism of diffusion or reaction events in condensed phases. These advantages are balanced by at least two important caveats. The size of systems that can be treated by DFT is strongly limited by the considerable computational effort involved. Second, DFT calculations are not exact because they involve approximations for electron exchange-correlation effects. It is, therefore, important to establish what level of accuracy can be expected from these calculations.

D. S. Sholl's research group, [125] for a long time, has been using the DFT to study the structures and dynamics of hydrogen in metals. Their studies involved a wide range of hydrogen transport metals including binary and ternary Pd alloys (Pd-Cu, Pd-Cu-X / X: Ti, Zr, V, Nb, Ta, Ru, Rh, Pt, Ag, and Au), binary intermetallics (ZrV_2, $ZrCr_2$, $ZrMn_2$, $ZrFe_2$, and $ZrCo_2$), and amorphous alloys (Fe_3B, ZrNi and ZrNiNb). Of particular interest to this project is the work about ternary metal alloys Pd-Cu-X [126]. Their objective with screening third alloying additive was to increase hydrogen flux of FCC PdCu20 alloy and meantime retain its favorable sulfur resistant surface chemistry. Their calculations suggested Rh can enhance solubility of H. And Pt and Ru are predicted to reduce H solubility, but only lightly. Predicting the effect of additive metals on H diffusion is more difficult than examining solubility. Ru and Rh are predicted to slightly enhance diffusion. Hydrogen permeability is controlled by solubility and diffusion. Accordingly, an initial list of 10 additive metals has been screened down to two particularly promising candidates, Ru and Rh. Certainly the results provide a useful first step towards the application of first principle-based methods to screening ternary alloys for use as hydrogen purification membranes by examining hydrogen solubility and diffusivity. C. G. Sonwane et al (2006) [127, 128] reported a similar work. D. E. Nanu et al (2008) [129] reported their theoretical modeling results of two ternary Pd-based alloys (Pd-Ni-Ag and Pd-Ni-Rh) on their hydride phase diagram, which is guiding information to design hydrogen embrittlement resistant hydrogen transport alloys. It was demonstrated that the method can be employed to predict α-β hydride phase boundaries, the width of the miscibility gap and hydrogen absorption capability. O. M. Løvvik et al (2002, 2007) [130, 131] also applied density functional calculations for study of hydrogen interactions with Pd-Cu and Pd-Ag alloys for similar purpose.

D. R. Alfonso et al (2003) [132] employed density functional theory to comparatively study sulfur binding on pure Pd, Cu and Ag surface and Pd-Cu and Pd-Ag alloy surface as well. They observed that the binding energy on the pure metal surface show considerable variation and follow the tread: Pd(111) > Cu(111) > Ag (111). On the Pd-rich alloy surfaces, the binding energies, in general, are weaker in comparison to that on the Pd(111) surface, but the reduction in binding is not large. It was also noted that there is nearly a linear correlation between the binding energies of sulfur on similar adsorption sites and the d-band center of surface atoms. A similar research work from M. P. Hyman et al (2007) 133] but covered more palladium alloys (PdMPd, M: Cu, Ag, Au, Co, Ni, Pt, Rh, and Ir). It was suggested that three primary factors determine the binding energies of sulfur on modified Pd surface: a) the position of the d-band center relative to the Fermi level (i.e., the width of the occupied portion of the d-band), b) the density of d-states at the Fermi level, and c) the Fermi energy. The addition of metal that compress the Pd lattice will destabilize the adsorption of sulfur, as well as hydrogen since compressing the Pd lattice shifts the d-band center away from the Fermi level, lowers the Fermi energy, and reduces the density of d-states at the Fermi level. It thus increases the sulfur tolerance. Therefore, 3d transition metals such as Co and Ni may increase the sulfur tolerance of Pd. Introducing ligand effects was found to alter the distribution of the d-states and shift the Fermi level, which eliminates the correlation of the d-band center with the density of states at the Fermi level and the Fermi energy. As a result, the d-band center by itself is a poor metrics of the H_2S reaction energetics for bimetallic surface. For strained Pd(111) without ligand effects, the two metrics correlate, but d-band center shifts derived from ligand effects of an alloying metal do not correlate with the density of states at the Fermi level. The density of states at the Fermi level is an important metric as it indicates the availability of un-occupied states that reduce anti-bonding repulsion. Sulfur adsorption also is somewhat dependent on the Fermi energy because of the repulsion of S-H bonds with Pd d-band. Combining strain with ligand effects was found to lead to unpredictable alteration of the d-band. Therefore, sulfur adsorption on PdMPd surfaces do not accurately predict adsorption on Pd_3M surface. The authors further suggested that sulfur adsorption energies be correlated with lattice constants of metals. It is a simple index for selection of an alloying element for improvement of sulfur tolerance of a Pd alloy. Similar theoretical methods can be applied for study and optimization of CO adsorption on transition metals.

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APPENDIX II: HIGH THROUGHPUT SCREENING SUMMARY

In this project, a high throughput combinatorial method has been utilized to significantly accelerate novel palladium alloy development. The approach involved:

- Fabricating an alloy specimen with a continuous distribution of binary and ternary ally compositions across its surface;
- Quickly screening large number of alloy compositions and phase structures for specific properties;
- Rapidly mapping composition and structure of combinatorial specimen. It allows building a material – performance relationship in great time efficiency, which may take years by traditional 'one-by-one' method.

Method and equipment description

The unique approach of this project was to utilize a high throughput combinatorial-based strategy for sulfur/carbon resistant Pd alloy discovery and development. The typical workflow is schematically illustrated in Figure 18. It proceeds through four phases that encompass specific functional activities including composition spread fabrication, coal gas exposure, visual screening, and Raman S or/and C mapping.

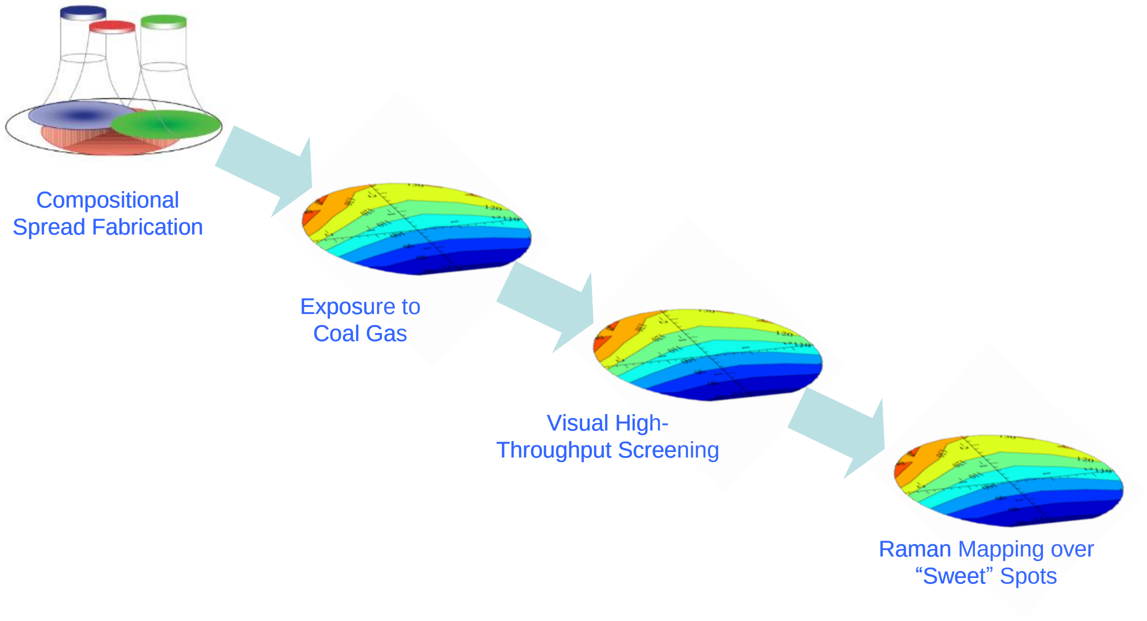


Figure 18. Combinatorial Pd alloy development workflow

A multiple target vacuum sputtering system at Cornell University[2] is used for fabrication of composition spreads as shown in Figure 19. The sputter deposition system contains three 2-inch magnetron sputter guns, a 4-inch magnetron sputter gun, and a 1-inch ion gun in the vacuum chamber. A round plate holds three substrate heaters for 3-inch silicon wafer substrate. Any of the three substrates can be brought to any of the three film processing positions, i.e. the ion gun, the 4-inch sputter gun and 2-inch sputter gun. The ion gun is used for substrate cleaning, for instance, to remove the insulating SiO_2 layer from silicon wafers. The 4-inch gun is used most commonly for depositing a tantalum or titanium adhesion layer on silicon substrates prior to the deposition of a composition spread. The three-gun assembly is used for deposition of thin film composition spreads via co-sputtering.

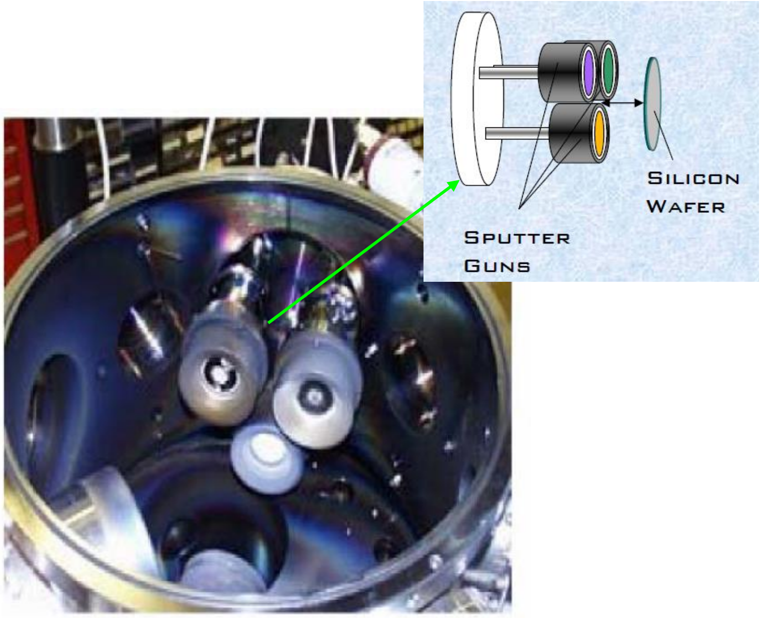


Figure 19. Schematic of a sputtering deposition system at Cornell University

A coal gas is used to condition thin film compositional spread samples for sulfur / carbon resistance screening. The gas composition was provided by National Carbon Capture Center (NCCC) at Southern Company (the project participant). It represents a product gas from air blown coal gasifier. In our experiments, a synthetic coal gas is employed and it consisted of 17.6% H_2, 17.9% CO_2, 2.6% CO, 2.6% H_2O, 59.3%N_2 and 170ppm H_2S. An experimental setup was newly built at Pall to perform coal gas exposure at elevated temperature. It included a SS process tube with quartz liner, furnace, feeding equipment and downstream exhausting system, which is shown in Figure 20.

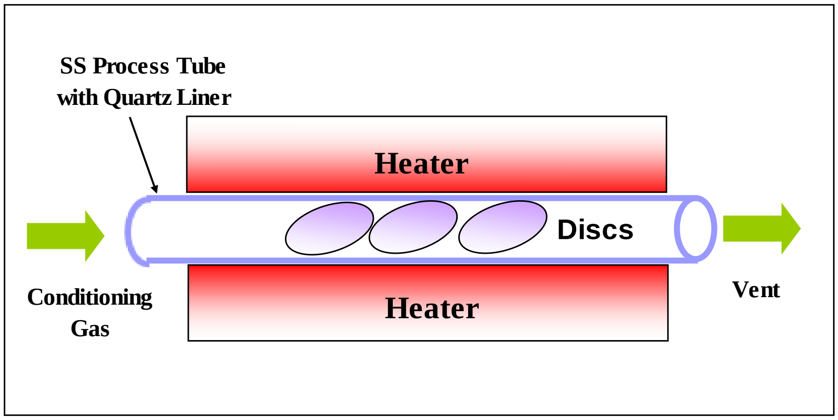


Figure 20. Schematic of an experimental setup for conditioning samples at Pall

Some transition metals, for instance silver, tarnish by sulfur and lose metallic shining color. This phenomenon was employed to initial visually survey the corrosion resistance of composition spread in coal gas in presence of hydrogen sulfide. The areas that remain still metallic shining color are identify as sweet spots for further Raman surface S / C mapping to determine their S or/and C resistance. Those spots that expel S or/and C sticking are confirmed as final candidates for membrane fabrication and hydrogen permeation test. Raman spectro-microscopy at Georgia Institute of Technology[3] is schematically shown in Figure 21.

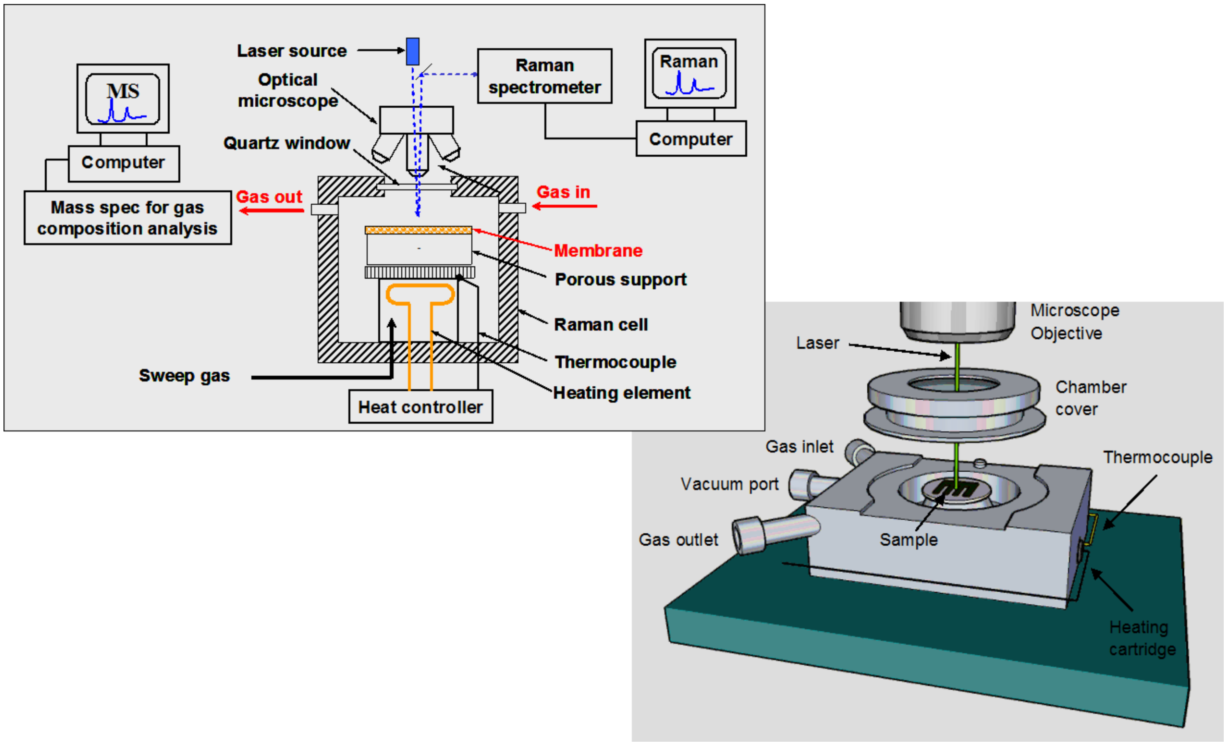


Figure 21. Schematic of Raman Spectromicroscopy at Georgia Institute of Technology

Experimental results

Eleven composition spreads were fabricated by Bruce van Dover at Cornell University. This batch of the samples focused on how to improve the sulfur / carbon resistance of traditional Pd-Cu, Pd-Ag and Pd-Au alloys by doping third element. The coal gas exposure was conducted at 350^{o}C and pressure slight above atmospheric for 24 hrs. By this report, six out of eleven composition spreads have been conditioned with coal gas. The pictures of those conditioned samples are shown in Figure 22. Sweet spots are circled. Preliminary results appear very promising. Those four disks with sweet spots will be sent to Georgia Institute of Technology for sulfur and carbon surface analysis by Raman spectromicroscopy in near future.

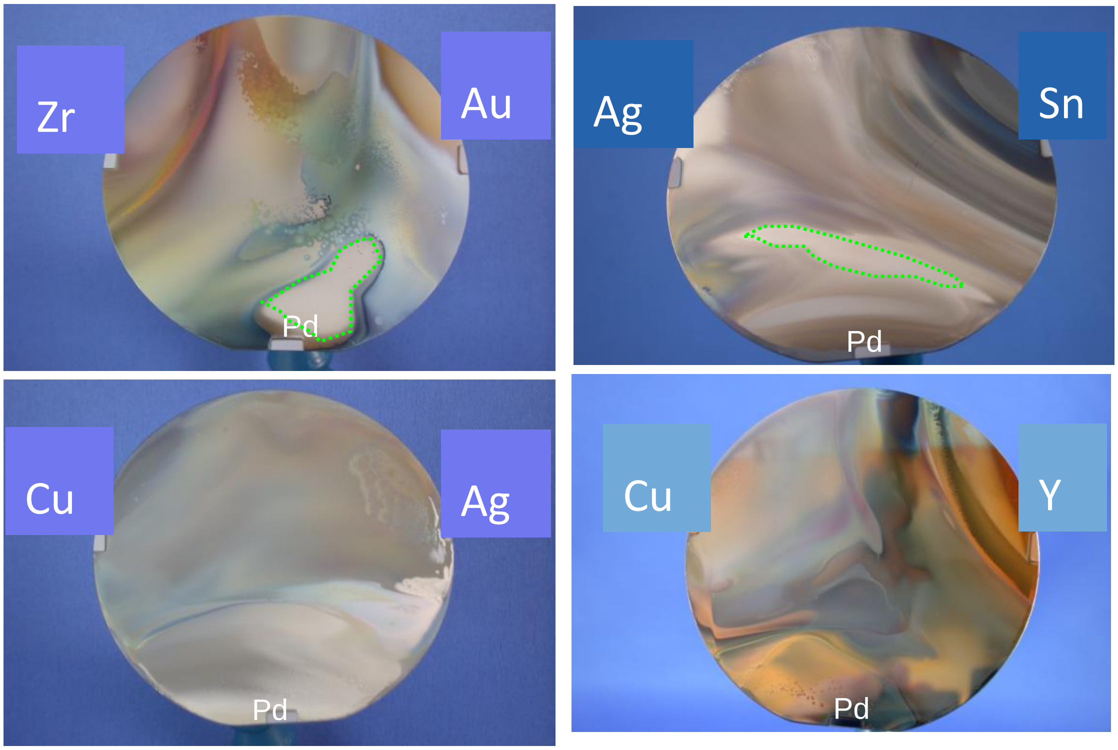


Figure 22. Pictures of 4 coal gas exposed composition spreads

In evaluating the sulfur tolerance of candidate hydrogen permeation alloys using Raman spectroscopy, the main metric is the Raman intensity of bands corresponding to sulfur-sulfur and metal-sulfur bonds. Therefore, the sensitivity of Raman spectroscopy for sulfur surface analysis was first determined at Georgia Institute of Technology. Initially a containing 10-ppm H_2S hydrogen gas was used to condition a pure Pd thin film on 3-inch silicon wafer at 350^{o}C for 3-4 hrs. Multiple Raman spectra were collected from several spots across the sample surface, which are provided in Figure 23. It has been noted that all of Raman spectra collected on thin film compositional spread disks shared a common fluorescence background (very broad modes centered at 200, 350, 540, 730 cm^{-1}) along with an "upward slope" of the spectra with increasing red shift (positive wave numbers). It made difficult to assign bands of Raman spectra of 10 ppm H_2S exposed combinatorial samples.

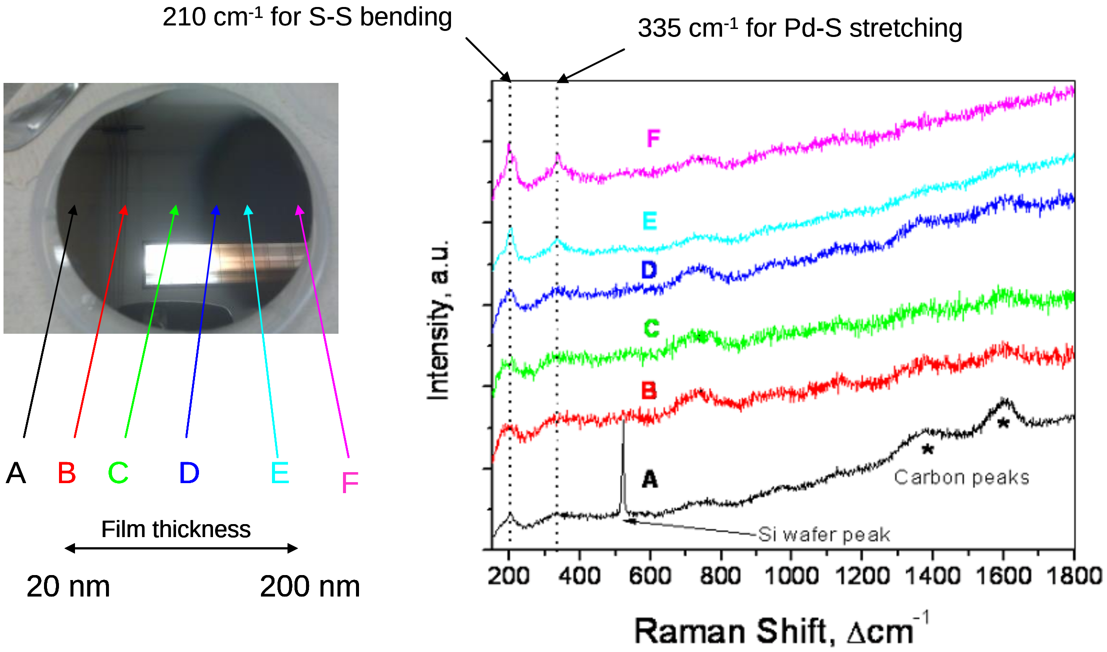


Figure 23. Raman spectra of 10 ppm H2S conditioned pure Pd film

To address this issue, our initial attempts were to create SERS effects on film surfaces by spraying 20-nm Ag colloidal particles onto the surface of thin film wafer and thus it would enhance Raman sensitivity. However, the coating process required 300^{o}C baking and it modified samples. Therefore, we were to investigate other approaches to improving Raman surface analysis:

- Theoretical modeling for de-convoluting metal fluorescence from pertinent signals;
- Stronger exposure conditions including higher concentration of H_2S and longer exposure time.

A Pd-Au binary compositional spread sample was treated with 2000 ppm H_2S in hydrogen at 350^{o}C for 24 hours. Raman spectra were collected on several spots with increasing content of Au in Pd-Au alloys. The objective was to check its space resolution. As seen in Figure 24, the intensity of the band at 335 cm-1 (Pd-S stretching) decreases as Pd-Au alloys become Au richer. Note that there is a very sharp decrease in the intensity of the 335 cm-1 between Pd70Au30 and Pd62Au38, indicating that the latter is more sulfur-tolerant. This is corroborated the S-S bending peak at 210 cm-1 that is very intense in the Pd70Au30 spectrum all but disappearing in the Pd62Au38 spectrum. This finding is in good agreement with UOP's early report that Pd60Au40 alloy had best sulfur tolerance among its alloys, which was determined by determination of hydrogen permeation. Interestingly, the 210 cm-1 peak has greater intensity in the measured compositions of higher Au content, and as Figure 11 (b) displays, is significantly more intense in the spectrum than in the Pd41Au59 composition spectra around it. Judging by the spectra from this sample, higher sulfur exposure seems to be a better route for getting information on sulfur tolerance. The Raman spectra not only seemed to show more definition with peaks at 210 and 335 cm-1, making them a bit easier to de-convolute from the metal fluorescence, but these spectra also took a much shorter time to collect. In the next, those composition spreads with sweet spots are to be sent to Georgia Institute of Technology for sulfur and carbon surface analysis by Raman spectromicroscopy. However, with 170 ppm H2S treated samples both sensitivity and space resolution are yet to be determined.

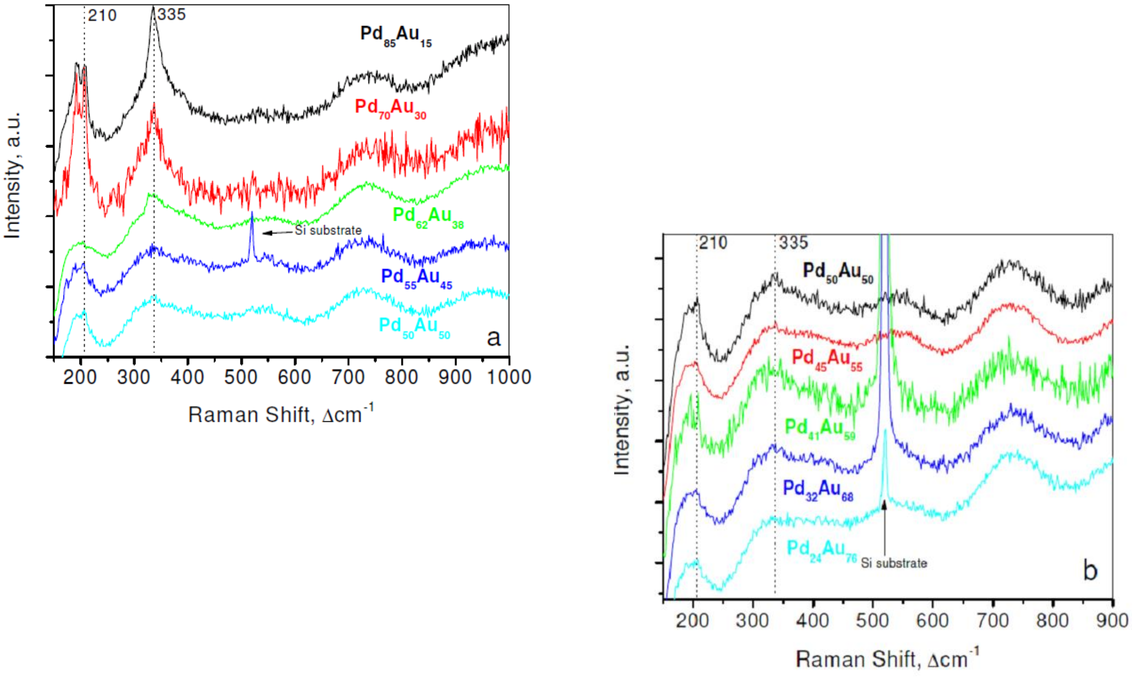


Figure 24. Raman spectra of 2000 ppm H2S exposed Pd-Au composition spread

Theoretical calculations of sulfur / carbon surface reactions on Pd-Au alloys

The projector-augmented wave (PAW) method using the Perdew-Wang (PW91) GGA functional by the VASP code was performed for the structure optimization, frequency, and PES calculations. The nudged elastic band (NEB) method was applied to the located transition states.

Binding energies of coal gas components on Pd, Au and Pd-Au alloys

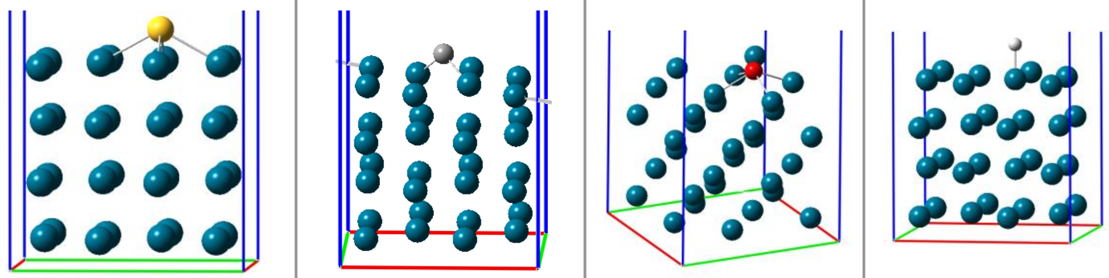
As discussed above, both sulfur and carbon especially sulfur have been found to have negative effects on the performance of palladium membrane, i.e. reduction of hydrogen flux or/and separation selectivity. Previous studies have indicated that strong adsorption of sulfur or/and carbon on palladium membrane surface are responsible for their effects. Density functional theory (DFT) has been applied for investigation of adsorption of H_2S, CO and H_2O on well-defined surfaces of pure metals and binary Pd alloys. In this project, we were to extend previous work on DFT calculation surface chemistry of palladium and palladium alloys to examine co-adsorption of coal gas components including H_2, H_2S, CO, CO_2 and H_2O and the effects of alloying the palladium surface on the co-adsorption reactions. Fundamental knowledge of the surface chemistry of binary and ternary palladium alloys in coal gas should provide a useful step towards sulfur / carbon resistant palladium alloy development, more specifically selection of palladium alloying metals. In this section, we present initial results of this work.

Binding energies for S, C and O on Pd(100) and their poisoning

Calculations were initially run on adsorption energies of elements H, S, C and O from the surface reactions of coal gas components H_2, H_2S, CO and H_2O on pure Pd surface to validate DFT model. The surface configurations of S, C and O are shown in Figure 25. Their ranking is shown in the following:

C-Pd (-141) ~ S-Pd (-130) > O-Pd (-105) >> H-Pd (-52 kcal/mole)

The values are close to what are reported in literature[4]. The binding energies of S, C and O is much higher than H. It indicates that S, C and O atoms can strongly occupy the site of four Pd atoms, which blocks H access to the membrane surface and also pull electrons away from Pd for dissociation and solution and diffusion, resulting in hydrogen flux reduction and membrane integrity degradation.



S-Pd on Pd(100) | C-Pd on Pd(100) | O-Pd on Pd(100) | H-Pd on Pd(100)

BE -130 kcal/mole | BE -141 kcal/mole | BE -105 kcal/mole | BE -52 kcal/mole

Figure 25. The surface structure of S, C and O on Pd(100)

The effect of Pd alloying on S-Pd binding energy

Pd alloying has been an approach to addressing S / C poisoning as described above. Traditional Pd-Cu, Pd-Ag and Pd-Au alloy membranes were tested with various containing hydrogen process streams in exist of H_2S. And Pd-Cu and Pd-Au were reported to show certain level of sulfur tolerance. However, experimental data are not consistent and this may be related to difference in compositions and structures of Pd alloys and conditions for membrane testing. Therefore, a first-principle based modeling has been employed in this project to quantify the effect of Pd alloys on S-Pd binding energy. And thus it provides us with fundamental understanding. A Pd-Au alloy system is selected for theoretical modeling since Pd-Au alloy membranes are being developed at Pall for reformate hydrogen separation and purification application. The results are shown in Figure 26.

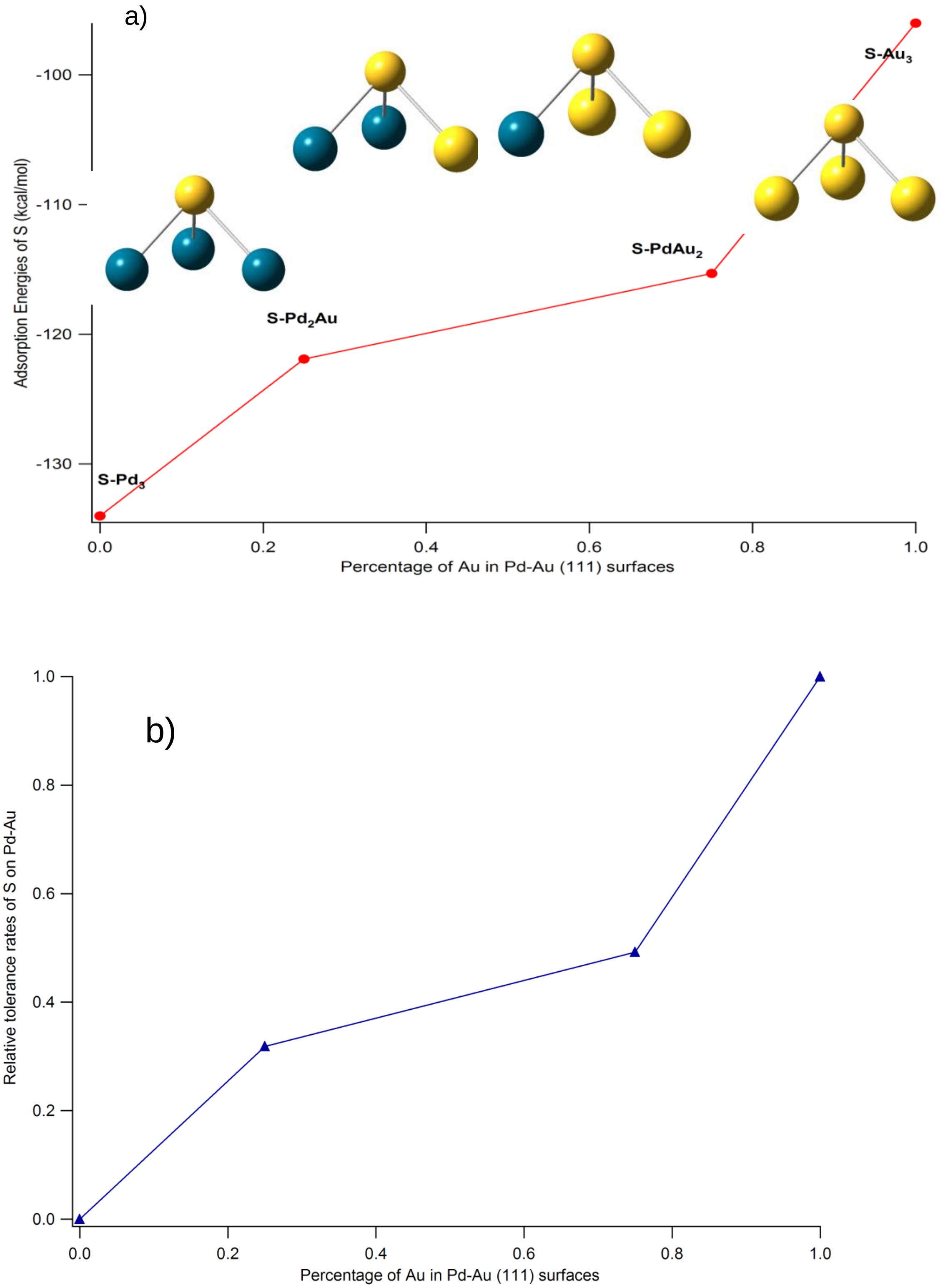


Figure 26. a) Adsorption energies of S on different Pd-Au sites (various Pd-Au alloy surfaces); b) The relative tolerance rates of Pd-Au alloys to sulfur

The data indicate that the higher the content of Au in Pd-Au alloy, the better the sulfur resistance of that Pd-Au alloy becomes, which is in good agreement with the results reported by Union Carbide Corp (1967)[1]. It is also noted that Au is much less active for the dissociation and absorption of hydrogen molecules than Pd. As a consequence, there should be an optimized hydrogen flux with the composition of Pd-Au alloy. Union Carbide Corp early (1967) reported that A $Pd_{60}Au_{40}$ (Au 40 wt%, or $Pd_{2.8}Au_1$ in mole) membrane showed best hydrogen flux in presence of 4 ppm H_2S at 350°C. Our calculations are in good agreement with this report. One question remains about the stability of alloy surfaces under application conditions. In other words, the surface of a Pd-Au alloy may experience segregation, reconstruction and phase transition in process stream at elevated temperature. Therefore, how to stabilize the surface of an alloy needs to be investigated. Another challenge is how to further improve the sulfur tolerance of Pd by alloying.

The effect of H_2O in process stream on sulfur poisoning

As shown in the following, sulfur exists in several chemical species, depending on chemical environment, i.e. SO_4^{2-} in oxidizing environment and H_2S in reducing one. The inhibition of a large variety of surface reactions that are catalyzed by noble metal catalysts with a very small amount of sulfur has been well documents. Further, the concept of toxicity of poison has been introduced long ago by Maxted[5]. It appears that H_2S has the highest toxicity, i.e. poisoning index. In hydrogen separation, hydrogen sulfide is generally considered as a poison for Pd membranes, leading to significant reduction of hydrogen flux. Taking into account the chemical species of sulfur, the poisoning index of H_2S may be lowered by its oxidation from the oxygen source of H_2O. Therefore, DFT calculations were run for adsorption of H_2O on S-covered Pd(100) and the results are shown in Figure 27. It is interestingly noted that H_2O needs to overcome over 20.1 kcal/mole to dissociate and form surface adduct HOS-Pd_4 that has lower toxicity than S-Pd_4 and thus lower inhibition to hydrogen permeation through Pd membrane. In the future, calculations will be extended to include Pd alloy surfaces.

$$SO_4^{2-}(VI) \rightarrow SO_3^{2-} or SO_2(IV) \rightarrow S_2O_3^{2-}(IV) \rightarrow S(0) \rightarrow H_2S(-II)$$

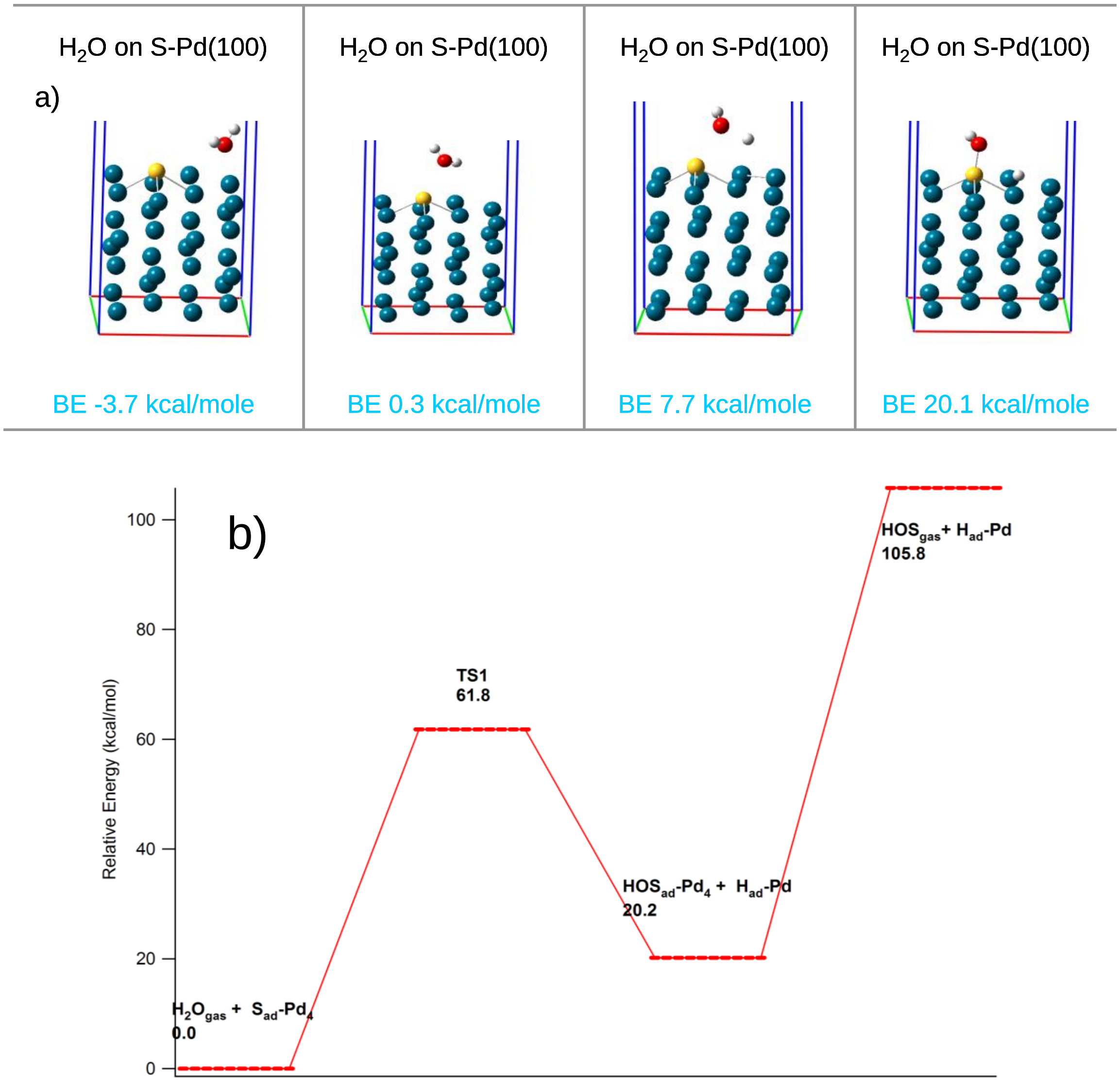


Figure 27. a) H2O adsorption on S-covered Pd(100); b) Potential energy surface for dissociative adsorption of H2O on S-covered Pd(100)

Analysis and assessment of the surface quality of ceramic-coated porous substrate

Increasing hydrogen flux and reducing cost of palladium-based membranes recently motivate developing methods to fabricate thin membranes, for instance as thin as few microns thick. As a Pd membrane becomes thin, it has to be supported on a mechanically stable substrate. At Pall, porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 400^{o}C and 400 psi were developed, scaled-up to 8 ft long and adopted as the standard substrate.

To support thin Pd / alloy film, a diffusion barrier is required to separate the Pd alloy layer from the metal substrate to prevent metallic reactions at elevated temperatures. Pall has selected ZrO_2 as the material for this diffusion barrier. The quality of the Pd alloy membranes is limited by the quality of the diffusion barrier surface. Therefore, the diffusion barrier process has been extensively optimized. The surface finish, thickness and on-porous-medium interface of the ZrO_2 layer can be controlled within a narrow range, which are characterized by bubble point test (integrity test), surface roughness and air flow measurement. The typical data are provided in the following:

- First bubble in IPA is > 30 psi
- Surface roughness ~ 329 nm Ra, 2222 nm Ry
- Air permeability @ 1000 cc/min ~ 7 psi

The surface roughness was determined by an optical method white-light interferometer. Two surface roughness parameters are provided, one arithmetical mean roughness Ra and the other maximum height Ry. A typical measurement is shown in Figure 28.

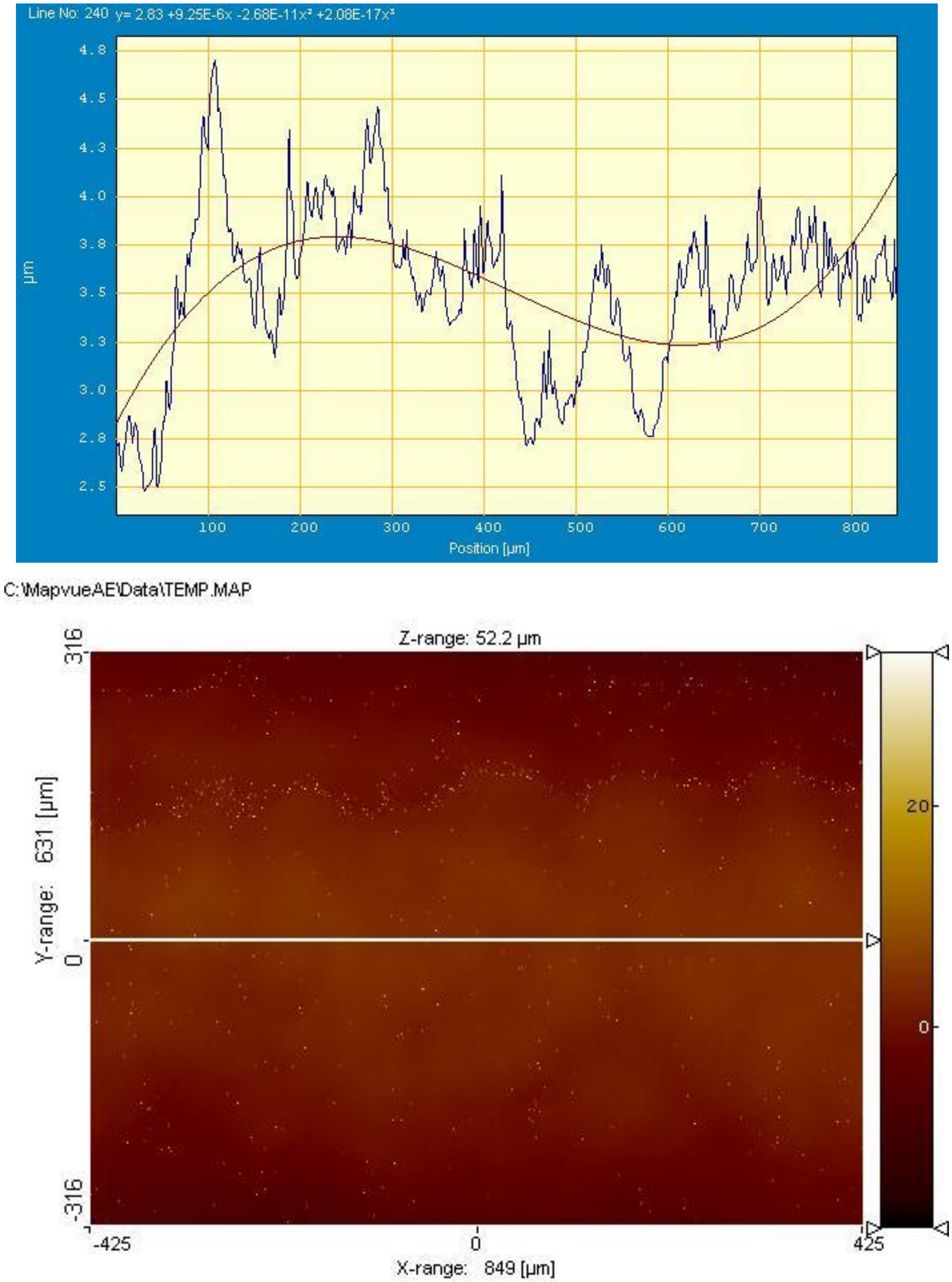


Figure 28. Surface roughness profile of ZrO2 layer

Optimization of this ZrO_2 layer enables thinner membrane formation, lowers material cost per unit area of membrane and reduces the membrane area needed. The controlled manufacturing process increased the yield and reduced the cost per tube. Commercial scale-up of the process is underway with length capabilities increased from 4 inch to 12 inch tubes. Figure 29 shows a typical ZrO_2-coated porous stainless steel tube.

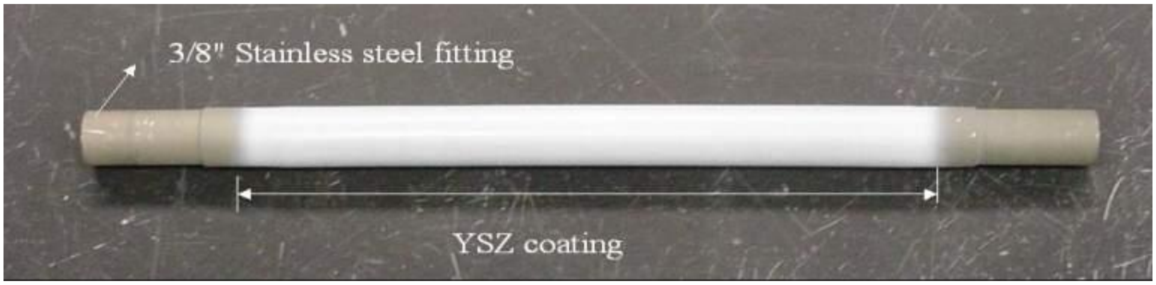


Figure 29. ZrO2-coated porous stainless steel tube

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