

# Sulfur Poisoning of Metal Membranes for Hydrogen Separation

INVITED PAPER

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**Abstract** – Many industrial chemical processes attempt to produce inexpensive purified hydrogen for use in industrial applications and in fuel cell power systems. Hydrogen-permeable metal membranes made of palladium and its alloys are the most widely used for hydrogen separation due to their high hydrogen permeability and their ideally infinite hydrogen selectivity. However, sulfur poisoning has been found to have negative effects on the performance of these materials. The goal of this paper is to present experimental and theoretical information that has been published in the open literature on the mechanism of sulfur poisoning of palladium membranes. Studies based upon the reduction mechanism of transition metals have been included when relevant to the subject of this work. The collected information has been critically reviewed and conclusions drawn. Copyright © 2009 Praise Worthy Prize S.r.l. - All rights reserved.

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## I. Introduction

It is estimated that the USA has about 250 years of coal reserves at the current rate of consumption [1]. Therefore, a particular promising technology for the production of hydrogen in this country is coal gasification [2]-[4]. When heated in a controlled atmosphere, coal produces primarily synthesis gas (a mixture of H<sub>2</sub>, CO, and hydrocarbons). Synthesis gas can be further processed using a gas-shift reactor technology to produce more hydrogen. Hydrogen can then be separated from carbon dioxide and other contaminants using separation techniques based upon metal membranes [5]-[7].

Palladium and its alloys, as well as nickel, platinum, and the metals in Groups III–V of the Periodic Table, are all permeable to hydrogen. Hydrogen-permeable metal membranes made of palladium and its alloys are the most widely used due to their high hydrogen permeability, their chemical compatibility with many hydrocarbon-containing gas streams, and their ideally infinite hydrogen selectivity.

However, sulfur poisoning has been found to have negative effects on the performance of these materials [8]-[11]. It has been reported that even the presence of a small amount of sulfur compounds in the feeds can lead to deactivation of these materials after prolonged operation [12], [13]. It is well known that the catalytic activity of platinum and of most transition metals is drastically reduced when the reagents contain even very small quantities of sulfur. This poisoning of the catalyst is an important industrial problem because it reduces the catalytic activity of many reactions [13]. Catalytic poisoning by adsorbed sulfur compounds and corrosive decay produced by surface sulfidation have been reported as the two main mechanisms that reduce membrane performance [14].

Initial experiments with palladium membranes began in the middle of the 19<sup>th</sup> century [15]-[17]. Since the initial diffusion experiments, palladium has been the most widely investigated membrane material with many studies being conducted in the mid-20<sup>th</sup> century [18]-[22]. At the same time, pioneering work on palladium membrane reactors was done by Gryaznov and co-workers in the former Soviet Union. Their work has been presented by Gryaznov et al. [23], Gryaznov [24], and Shu et al. [25]. Gryaznov et al. [23], [24] have paid particular attention to the mechanical design aspects of the metal membranes and have come up with very elaborate designs.

Self-supporting, mechanically resistant palladium or palladium-alloy dense membranes must be typically a few hundred micrometers thick. The cost of these membranes is not trivial because palladium is an expensive metal. In recent years, several groups have focused their attention on the development of composite metal membranes, whereby a thin metallic film (thickness of a few micrometers) is deposited on (or in the pores) of an underlying porous support. This kind of membrane aims to have the mechanical resistance of the support and the high selectivity of a dense membrane with better permeability. Porous glass [26], ceramic [27, 28], and metal supports [29] have been utilized.

In the presence of hydrogen, palladium forms a continuous solid solution, exhibiting a face-centered-cubic (fcc) crystal structure [30]. However, at temperatures below 573 K, the phase diagram illustrates the formation of two distinctly different phases ( $\alpha$  and  $\beta$ ), a hydrogen-rich phase and a palladium-rich phase. Although the two low-temperature phases are both fcc in crystal structure, they exhibit different crystal lattice parameters.

The temperature-induced transition between the two

hydride phases significantly deteriorates the mechanical properties of the membrane. Alloying with other metals (for example, Ag, Cu, Ru, Rh) tends to lower the phase transition temperature and, under some circumstances, improve the hydrogen permeability [31].

Typically, silver is deposited on palladium films. An alloy containing 73 wt% Pd and 27 wt% Ag (Pd<sub>73</sub>Ag<sub>27</sub>) is the most commonly used commercially [32]. Sometimes an oxide layer is added between the metallic layer and the support in order to prevent intermetallic diffusion. Intermetallic diffusion between the layers leads to rapid flux decline and shortens membrane lifetime [33].

Operation of metal membranes at elevated temperatures can have deleterious effects on mechanical durability, which is linked to the thermodynamic process of the minimization in free surface energy.

The reduction in free surface energy is accomplished by crystal recovery, recrystallization, and/or crystal grain growth in which there is a strong correlation between mechanical strength and the coarseness of the crystal distribution [34].

Chemical stability of palladium-based membranes is a very important issue. Several researchers have demonstrated the influence of various chemical species such as O<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O on the performance of palladium-based membranes [35], [36]. It has been reported that oxygen exposures can highly influence surface morphology even though palladium oxides are not observed.

Oxygen exposures can vastly increase surface roughness and membrane surface area, which could cause significant technical issues with respect to thin film integrity [35]. A thorough review conducted by Gao et al. [37] indicated that all of the major gasifier effluent species exhibit adverse effects on palladium performance.

A reduction in performance in the presence of H<sub>2</sub>O and CO<sub>2</sub> was attributed to the blocking of hydrogen adsorption sites.

The influence of CO was slightly more complex, varying from competitive adsorption to decreases in permeability due to the formation of graphitic carbon within the interstitials of the palladium crystal structure [37].

Sulfur poisoning has significant negative effects on the performance of palladium-based materials [8]-[11]. It has been reported that even the presence of a small amount of sulfur compounds in the feeds can lead to deactivation of these materials after some exposure [12], [13], [38]-[40].

Poisoning of palladium-based membranes by H<sub>2</sub>S can be discussed in terms of two different processes. First, sulfur can deactivate the membrane surface by adsorbing on surface sites and diminishing the catalytic activity of the membrane surface.

Dissociative adsorption of H<sub>2</sub> is a fundamental step in the overall transport mechanism of hydrogen through dense palladium; therefore, this process negatively

impacts the membrane performance.

This process is referred to as a “catalytic poisoning” mechanism [14]. Second, the sulfur-containing gas can chemically react with the membrane to produce a corrosion product on the surface.

This corrosion product can exhibit characteristics that would limit the catalytic activity required for transport and/or reduce the overall performance by forming a layer with low permeability for hydrogen.

Depending on the growth rate of the surface scale and exposure duration, the entire membrane can potentially be converted to the corrosion product. This process is referred to as “corrosive decay” [14]. Catalytic poisoning and corrosive decay are the two main mechanisms that reduce membrane performance.

## II. Experimental Studies

### II.1. Permeation Experiments

#### II.1.1. Palladium Membranes

A brief description of hydrogen permeation through metallic layers is included here for completeness. Hydrogen permeation through metallic layers follows a solution-diffusion mechanism (Baker [31]).

The flux of hydrogen through palladium is the product of the diffusion coefficient and the concentration gradient, with the flux of hydrogen atoms being twice that of hydrogen molecules:

$$J_H = 2J_{H_2} = -D_H \Delta C_H / L_M \quad (1)$$

where  $D_H$  is the experimentally determined diffusion coefficient (mol H m / m<sup>2</sup> s Pa<sup>0.5</sup>);  $L_M$  is the membrane thickness; and  $J_H$  and  $J_{H_2}$  are the atomic and molecular hydrogen fluxes, respectively.

For thick membranes ( $L_M > 100 \mu\text{m}$ ), the limiting resistance is assumed to be the transport of hydrogen atoms through palladium.

Under these conditions, the surface reaction is considered to be very fast and the dissolved hydrogen atoms at the surface of the palladium are in equilibrium with the hydrogen gas on either side of the membrane. The concentration of hydrogen atoms in the palladium can be related to the hydrogen partial pressure by the Sieverts' equation.

The 0.5 exponent reflects the dissociation of the gaseous hydrogen molecule into two hydrogen atoms that diffuse into the metal, where an ideal solution of hydrogen atoms in palladium is formed:

$$J_H = K_S P_{H_2}^{0.5} \quad (2)$$

Combining Eqs. (1) and (2), we can derive the Richardson's equation:

$$J_H = -D_H K_S (P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5}) / (2L_M) \quad (3)$$

where  $K_S$  is the experimentally determined Sievert permeability ( $\text{mol H m} / \text{m s Pa}^{0.5}$ ) calculated by plotting hydrogen flux versus the difference of square-root pressures at both sides of the membrane [41];  $P_{\text{H}_2, \text{ret}}$  and  $P_{\text{H}_2, \text{perm}}$  are the high and low pressures on both sides of the membrane layer.

The membrane permeability ( $k$ ) is defined by:

$$k = D_H K_S / 2 \quad (4)$$

Therefore, the hydrogen flux is inversely proportional to the membrane thickness and directly proportional to the product of the hydrogen permeability and the hydrogen partial pressure gradient across the membrane. Eq. (3) can be written as:

$$J_H = k \left( P_{\text{H}_2, \text{ret}}^n - P_{\text{H}_2, \text{perm}}^n \right) / L_M \quad (5)$$

The value of the exponent “ $n$ ” in Eq. (5) is related to the transport step controlling hydrogen flux. A 0.5 value implies transport control by the diffusion step, while an  $n$  value equal to 1 implies transport control by the surface adsorption step. Table I summarizes published values for hydrogen permeability of bulk palladium membranes [42]. Deviations from the Sievert’s law behavior have been reported and attributed to various factors including surface processes, surface poisoning, and grain boundaries [25], [43]. Some researchers have concluded that diffusion-limited permeation is extended to thicknesses of less than 10  $\mu\text{m}$  [26]. Ward and Dao [43] presented a detailed transport model for hydrogen permeation through a palladium–alloy layer, which accounts for external mass transfer, surface adsorption and desorption, transitions to and from the bulk metal, and diffusion within the metal.

The authors estimated reasonable values for all rate parameters based on surface science and membrane literature. Ward and Dao reported that in the absence of external mass transfer resistance, nearly diffusion-limited permeation is expected for clean palladium for temperatures above approximately 573 K and membrane thicknesses down to 1  $\mu\text{m}$  [43]. Recently, Gabitto and Tsouris [44] used Ward and Dao’s model to simulate hydrogen permeation through composite inorganic membranes.

### II.1.2 Palladium–Alloy Membranes

Palladium has been alloyed with other materials in an effort to minimize the amount of palladium needed in membrane fabrication, increase the membrane performance, promote chemical stability, and increase mechanical resistance. Palladium has been alloyed with an array of elements including boron [38], [46], cerium [37], [38], [46], [47], nickel [37], [38], [46], [51], [52], copper [26], [38], [46], [47], [48], [49], [51], gold [38], [46], iron [37], [50], silver [26], [38], [46], [49], [52], [53], [54], yttrium [47], [55], [56], and others [57].

Binary palladium alloys with cerium, copper, gold, silver, and yttrium are unique in that these alloys can exhibit higher permeability values than each of the metals exhibit individually [38], [58], [59]. The observed change in the permeability of a metal alloy is attributed to increasing either the solubility and/or the diffusivity of hydrogen within the metal, and thus increasing permeability [58], [60], [61].

Recently, research has focused on the palladium–copper (Pd–Cu) system due to the relative high performance of the 60 wt% Pd–Cu alloy, which has exhibited flux values comparable to pure palladium in the presence of hydrogen at 350°C [38]. Hydrogen solubility studies of the Pd–Cu system indicate that the solubility of the fcc crystalline phase increases with increasing palladium content [61], [62]. The B2 composition yields significantly higher solubility values as compared to the fcc Pd–Cu alloys, with a maximum solubility at a composition of ~60 wt% Pd–Cu [63]. The B2 crystalline phase is often referred to in literature as an ordered body-centered-cubic (bcc) phase.

Additionally, studies conducted by Piper [64] and Zetkin et al. [65] revealed that the B2 phase of the Pd–Cu alloys exhibits higher diffusion coefficients as compared to fcc alloy compositions [64], [65], while dissolved hydrogen shifted the B2–fcc phase boundaries to higher palladium concentrations (but the B2 phase remained unstable at temperatures greater than 600°C) [64]. Lastly, Kuranov et al. demonstrated the enhanced mechanical properties of bcc Pd–Cu alloys as compared to fcc compositions [66].

Nam and Lee [67] prepared thin (less than 2- $\mu\text{m}$  thickness) and pinhole-free Pd–Cu alloy composite membranes with a diffusion barrier on a mesoporous stainless steel support (SUS) using a vacuum electrodeposition technique. The deposition film was fabricated by multilayer coating, and diffusion treatment and the formation of Pd–Cu alloys was achieved by annealing the membranes at 723 K in a nitrogen atmosphere. To improve the structural stability of Pd alloy/Ni–SUS composite membranes, a thin intermediate layer of silica by the sol–gel method was introduced as a diffusion barrier between the Pd–Cu active layer and a modified SUS substrate. The composition and phase structures of the alloy film were studied by energy-dispersive electronic analysis (EDS) and X-ray diffraction (XRD).

The authors reported a Pd–Cu layer with a composition of 63% Pd and 37% Cu, and the atomic inter-diffusion of palladium and copper resulted in Pd–Cu alloys having a fcc structure.

Nam and Lee [67] reported a hydrogen permeance of  $2.5 \times 10^{-2} \text{ cm}^3/\text{cm}^2 \text{ cm Hg s}$  and a hydrogen/nitrogen ( $\text{H}_2/\text{N}_2$ ) selectivity above 70,000 at 723 K. Howard et al. [68] determined the permeance of Pd–Cu alloys containing 40, 53, 60, and 80 wt% Pd over the 623–1173 K temperature range for  $\text{H}_2$  partial pressure differences as great as 2.6 MPa. The authors also evaluated pure palladium and copper membranes.

TABLE I  
PUBLISHED DATA FOR HYDROGEN PERMEABILITY OF BULK PALLADIUM MEMBRANES  
(DATA TAKEN FROM [42])

Author	$X_M$ ( $\mu\text{m}$ )	n	$P_{\text{H}_2,\text{ret}}$ (kPa)	$P_{\text{H}_2,\text{perm}}$ (kPa)	$k_0$ (mol/m s Pa <sup>n</sup> )	E (kJ/mol)	Ref.
Davis	130–729	0.50	0.003–101	Vacuum	$3.85 \times 10^{-7}$	18.56	18
Toda	443–973	0.50	84–85	Vacuum	$1.72 \times 10^{-7}$	13.46	22
Hurlbert and Konecny	10–150	0.68	101–710	Vacuum	$1.47 \times 10^{-8}$	11.92	75
Kofler et al.	486–762	0.50	$4.0 \times 10^{-5}$ –0.007	$1.3 \times 10^{-8}$	$2.20 \times 10^{-7}$	15.67	21
Holleck	800–2025	0.50	53–54	0.024–0.006	$1.42 \times 10^{-7}$	12.81	19
Balovnev	100–1000	0.50	1.3–10	$3.0 \times 10^{-8}$ – $7.0 \times 10^{-5}$	$1.89 \times 10^{-7}$	15.46	43
Katsuta et al.	940	0.50	101	Vacuum	$3.82 \times 10^{-7}$	20.56	20
Morreale et al.	1000	0.50	91–2480	Air sweep	$3.31 \times 10^{-7}$	13.81	42
Morreale et al.	1000	0.62	91–2480	Air sweep	$5.65 \times 10^{-7}$	13.41	42

The Pd–Cu alloys exhibited permeance values that reflected the crystalline phase structures as shown in the binary phase diagram of the material. Under conditions of fcc structure stability, the permeance increased steadily with palladium content, approaching the permeance of pure palladium membranes. The 53 and 60 wt% Pd alloys were evaluated at temperatures within the bcc stability region. For both alloys, the bcc permeance was several times greater than the fcc permeance, with the 60 wt% Pd bcc permeance at 623 K reaching about 70% of the permeance of palladium. These bcc alloys were subjected to temperature increases during testing that resulted in a transition from bcc to fcc, followed by temperature decreases that reverted the alloys to bcc. The permeances dropped abruptly during the transition from bcc to fcc. However, on cooling back to the bcc stability region, neither the 60 nor the 53 wt% Pd alloy completely regained a bcc permeance during the test period. All of the Pd–Cu alloys subjected to testing at 1173 K showed some permeance decline that was attributed to intermetallic diffusion between the membrane and support. The application of a diffusion barrier between the support and membrane foil in a 53 wt% Pd permeance test successfully blocked the intermetallic diffusion and prevented degradation of the membrane's performance [68].

Gao et al. [69] prepared two thin Pd–Cu membranes by an electroless plating technique on porous stainless steel (PSS) disks coated with a mesoporous palladium-impregnated zirconia intermediate layer. The intermediate layer provided seeds for electroless plating growth of Pd–Cu film during synthesis and served as an intermetallic diffusion barrier that improved membrane stability for practical applications. X-ray photoelectron spectroscopy (XPS) analyses showed that the average surface compositions of the two membranes were, respectively, Pd<sub>84</sub>Cu<sub>16</sub> and Pd<sub>46</sub>Cu<sub>54</sub>. X-ray diffraction (XRD) analyses indicated that the deposited Pd<sub>84</sub>Cu<sub>16</sub> alloy film contained only a  $\alpha$ -fcc phase structure, whereas the Pd<sub>46</sub>Cu<sub>54</sub> alloy film contained a mixture of  $\alpha$ -fcc and  $\beta$ -bcc phases. A 10- $\mu\text{m}$ -thick Pd<sub>46</sub>Cu<sub>54</sub>/ZrO<sub>2</sub>-PSS membrane exhibited an infinite separation factor for H<sub>2</sub> over N<sub>2</sub>, with H<sub>2</sub> permeance of  $1.1 \times 10^{-7}$  mol/m<sup>2</sup> s Pa at 753 K. The authors reported that the activation energies for hydrogen permeation and the hydrogen

pressure exponents were, respectively, 14.5 kJ/mol and 0.6 for the Pd<sub>84</sub>Cu<sub>16</sub>/ZrO<sub>2</sub>-PSS membrane and 15.4 kJ/mol and 1 for the Pd<sub>46</sub>Cu<sub>54</sub>/ZrO<sub>2</sub>-PSS composite membrane.

Zhang et al. [70] studied the hydrogen permeation performance of three thin Pd–Cu composite membranes with different thicknesses between 398 and 753 K. A hydrogen permeance up to  $2.7 \times 10^{-6}$  mol/(m<sup>2</sup> s Pa) was measured with an ideal selectivity over 1000 at 753 K. The hydrogen permeation exhibited two different activation energies over the temperature range: a low activation energy of about 9.8 kJ/mol above 548 K and a high activation energy of about 26.4 kJ/mol below 548 K.

After permeation tests, the alloy membranes were characterized by X-ray XPS, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and in situ XRD. The authors reported that according to the results of XPS, EDX, SEM, and in situ XRD analyses, it was confirmed that the turning point could be attributed to palladium segregation on the surface of alloys. Zhang et al. [70] proposed that palladium segregation would induce increasing hydrogen chemisorption on the surface of Pd–Cu alloys and change the hydrogen permeation behavior through these alloy membranes and thus, most probably, influence the activation energy. However, palladium segregation did not change the phase structure of the alloys or damage their membranes.

## II.2. Chemical Stability Experiments

### II.2.1. Catalysts

Many studies have been carried out to determine the influence of H<sub>2</sub>S on the catalytic activity of transition metals used as catalysts. These studies shed light on the poisoning mechanism of catalytic metallic surfaces.

Mathieu and Primet [71] measured the catalytic activity of Al<sub>2</sub>O<sub>3</sub>-supported platinum catalysts for benzene hydrogenation and hydrogenolysis of n-butane with and without H<sub>2</sub>S in the feed gases. The authors reported that the chemisorption of H<sub>2</sub>S on Al<sub>2</sub>O<sub>3</sub>-supported platinum is dissociative, and hydrogen was observed in the gaseous phase. Above 100°C, platinum surface atoms are fully covered by sulfur atoms.

Hydrogen treatment at 400°C partly restores the catalytic and chemisorptive properties of platinum towards benzene hydrogenation. Oxygen treatments of the poisoned catalyst, followed by hydrogen reduction under mild conditions, fully restored the properties of the starting material. Mathieu and Primet [71] added that sulfur removal from platinum occurs with the formation of sulfate groups bonded to the support. Under more severe conditions of reduction, the reduction of the sulfate groups leads again to a poisoning of the metal surface.

Chen et al. [72] studied the resistance of Pt/TiO<sub>2</sub> catalysts to hydrogen sulfide by means of pulse reactions with Pt/Al<sub>2</sub>O<sub>3</sub> as a reference. Temperature-programmed desorption (TPD) and electrical conductivity of the samples were used to elucidate the desorption, surface-reaction, and charge-transfer characteristics of the catalyst. X-ray diffraction and X-ray photoelectron spectra were measured to clarify the chemical effects resulting from sulfur contamination. Pt/TiO<sub>2</sub> was found to be much more resistant than Pt/Al<sub>2</sub>O<sub>3</sub> to H<sub>2</sub>S poisoning. The authors reported that in TiO<sub>2</sub>, there is labile oxygen that can react with H<sub>2</sub>S to form SO, or SO<sub>2</sub>, which leaves the catalyst. Therefore, in the Pt/TiO<sub>2</sub> system, a considerable part of the sulfur contamination is self-cleaned and the poisoning effect of sulfur is mitigated. However, for the Pt/Al<sub>2</sub>O<sub>3</sub> system, H<sub>2</sub>S decomposes on platinum mainly with the liberation of hydrogen and the sulfur is left bound to platinum, forming Pt<sub>x</sub>S.

L'Argentiere and Figoli [57] studied the activity and sulfur resistance of palladium-tungsten-supported catalysts having different W/Pd compositions. The maximum activity was reported for the catalyst having a W/Pd ratio equal to 6. The existence of a Pd-WO<sub>x</sub> interface that is more active and sulfur resistant was suggested by the authors. Furthermore, regeneration of the poisoned bimetallic catalysts at mild temperatures is also possible.

Deng et al. [73] investigated sulfur inhibition and poisoning of supported palladium, rhodium, and iridium catalysts for methane oxidation in air (350–600°C). All catalysts were affected substantially by the sulfur presence but differed in both reduction of activity and subsequent recovery. Above 500°C, iridium showed reduced inhibition after being partially poisoned. At low temperatures, oxidation of H<sub>2</sub>S and an accompanying oscillatory behavior were observed. Sulphate (S<sup>6+</sup>) was detected by X-ray photoelectron spectroscopy on poisoned catalysts, and amounts decreased with increasing temperature. Observed charge transfer from palladium, rhodium, and iridium were attributed to interactions with sulfate.

### II.2.2 Palladium Membranes

Antoniazzi et al. [74] studied the effect of carbon or sulfur on the permeation rate of molecular hydrogen through palladium. The authors reported that in the range

of experimental conditions used (upstream H<sub>2</sub> pressures of ~10<sup>-5</sup> to 300 Pa and temperatures in the range 355–630 K) the permeation rates varied by a factor of ~10<sup>4</sup>. An incident atomic hydrogen flux (from 10<sup>15</sup> to 3 × 10<sup>20</sup> H<sup>0</sup>/m<sup>2</sup> s) was used to probe the membrane asymmetry when the hydrogen adsorption and desorption were the rate-limiting steps in the permeation process. The hydrogen recombination coefficient, K<sub>r</sub>, derived from the permeation data, increased by a factor of ~10<sup>3</sup> when the carbon coverage was reduced from 0.36 to 0.06 at T = 600 K. A sulfur coverage decrease from 0.14 to 0.06 increased K<sub>r</sub> (T = 625 K) by approximately a factor of 4. For medium-range total impurity coverages (0.45–0.65), the reduction in the hydrogen recombination coefficient was postulated to be explainable by a mechanism whereby the impurity atoms lead to the blocking of surface adsorption sites [74].

Hurlbert and Konecny [75] studied the performance of a 25-μm palladium foil subjected to H<sub>2</sub>S poisoning. The authors reported an ~83% reduction in hydrogen flux in less than ~120 minutes at 350°C in the presence of 50 ppm H<sub>2</sub>S. The reduction in performance observed was attributed to the formation of a “dark gray” surface film and appeared to be irreversible.

McKinley [38] demonstrated the effects of H<sub>2</sub>S on the hydrogen flux through a palladium membrane at 350°C in a patent presented in 1967. Upon exposure of a 25-μm foil to 20 ppm H<sub>2</sub>S, a gradual reduction in hydrogen flux was observed in the first 4 days of exposure followed by a constant performance over the next 2 days. The total reduction observed for the palladium foil over the 6-day exposure period was ~70%. Visual inspection of the palladium membrane after the tests showed that the surface appeared dull and had lost its initial luster. Additionally, a second palladium foil was exposed to 20 ppm H<sub>2</sub>S at 350°C for approximately 4 days, in which a gradual reduction of ~70% was also observed. However, upon the removal of H<sub>2</sub>S and the introduction of hydrogen, the performance of the membrane was restored to its initial value in only 2 days. McKinley hypothesized that the reduction in performance observed in his study was due to the adsorption of H<sub>2</sub>S on the palladium surface rather than chemical attack or sulfide formation on the surface.

In an effort to enhance the reliability of a palladium-based hydrogen sensor, Lalauze et al. [76] explored the influence of surface contaminants on the hydrogen diffusion process through palladium. Temperature Programmed Desorption and Auger analysis of the palladium surface showed significant concentrations of carbon, oxygen, and sulfur, as high as 54, 5, and 18 at%, respectively. Lalauze et al. [76] concluded that the variances in performance observed for the palladium samples were attributed to the chemisorbed species on the palladium surface.

In 1993 and 1994, Edlund et al. [77], [78] explored the viability of hot-pressed composite membranes for high-temperature hydrogen separations. The composite membranes consisted of a 25-μm-thick palladium or

platinum layer on each side of a 30- $\mu\text{m}$ -thick vanadium substrate. The performance of the palladium-based composite membrane yielded considerably higher flux values in the presence of hydrogen as compared to the platinum-based membrane [77]. The palladium and platinum composite membranes were then characterized in the presence of pure  $\text{H}_2\text{S}$  at 700°C and 115 psia for an 8-hour exposure. The platinum-coated membrane showed no changes of hydrogen flux in the presence of  $\text{H}_2\text{S}$  and remained lustrous in appearance during post-test visual inspections. However, the palladium-coated membrane failed within seconds under similar conditions. Upon removal of the palladium-based composite membrane after  $\text{H}_2\text{S}$  exposure, the membrane exhibited numerous holes. This behavior was attributed to complete corrosion of the metal [78].

Kajiwara et al. [79] in 1999 explored the stability and behavior of palladium- and platinum-coated porous alumina membranes in the presence of 6200 ppm  $\text{H}_2\text{S}$  in hydrogen. Similar to the results observed by Edlund [77], [78], the palladium-based membrane ruptured within 20 minutes of operation at 400°C. Scanning Electron Microscopy (SEM) analysis of the post-test membrane sample revealed cracks in the surface of the membrane (up to several centimeters long). On the other hand, the platinum-coated membranes did not present cracks. The failure of the membrane sample was attributed to the formation of a palladium sulfide, which has a lattice constant roughly twice that of palladium, 0.39 to 0.65 nm, thus creating structural stresses which were relieved by the formation of cracks in the membranes. The lattice constant of platinum was only slightly changed by sulfidation, from 0.39 to 0.35 nm; therefore, no significant formation of cracks was observed.

In a recent study (2005), Kulprathipanja et al. [80] explored the inhibition by  $\text{H}_2\text{S}$  on the hydrogen permeation of an  $\sim 4\text{-}\mu\text{m}$  electroless-plated (on asymmetric  $\alpha$ -alumina tubes) palladium membrane. Several palladium membranes were exposed to  $\text{H}_2\text{S}$  concentrations ranging from 100 to 630 ppm at 450°C. SEM analysis of the palladium membranes exhibited pore and particle formation on the surfaces after  $\sim 100$  ppm  $\text{H}_2\text{S}$  exposure.

After exposure to a 20 ppm  $\text{H}_2\text{S}$  / $\text{H}_2/\text{N}_2$  gas mixture, the performance of the membrane sample decreased 33%, while a 36% decrease in the  $\text{H}_2/\text{N}_2$  selectivity was observed.

Moreover, two palladium membrane samples were tested in the presence of 100 ppm  $\text{H}_2\text{S}$ . The first membrane sample resulted in failure in less than 2 hours, while a similar test resulted in a 95% reduction in performance without failure.

Kulprathipanja et al. [80] hypothesize that the reduction in performance observed was due to "site-blocking," with complete inhibition taking place at  $\text{H}_2\text{S}$  concentrations greater than 100 ppm, while pores, cracks, and defects were a result of surface rearrangement due to metal-sulfur interactions.

### II.2.3. Palladium–Alloy Membranes

The palladium–silver (Pd–Ag) alloy membrane system was successfully commercialized in the early 1960's [81], but the reduction of palladium and addition of silver would still not be a significant cost-effective alternative for large-scale processes unless micron-scale thin films could be prepared. Successful application of these membrane alloys to the gasification process depends upon their chemical stability in the presence of the process effluent components. We will review in this section chemical stability results in the presence of  $\text{H}_2\text{S}$ . A summary of the most significant results is shown in Table II. Flux reduction refers to experimental flux values in presence of  $\text{H}_2\text{S}$  with respect to original pre- $\text{H}_2\text{S}$  values. Recovery values listed refer to hydrogen flux values measured after the original feed is replaced by a pure hydrogen mixture compared to original pre- $\text{H}_2\text{S}$  values.

Darling [82] studied the influence of pressure, temperature, and membrane thickness on the diffusion rate of the hydrogen-palladium-silver system in 1963. The author exposed a 73 wt% Pd–Ag tube with a wall thickness of  $\sim 75\text{-}\mu\text{m}$  to several  $\text{H}_2\text{S}$  concentrations. At 500°C and 200 psi, the Pd–Ag alloy exhibited negligible changes in flux in the presence of 490 and 1280 ppm  $\text{H}_2\text{S}$ , although 1600 ppm  $\text{H}_2\text{S}$  dramatically reduced its performance.

Furthermore, exposure of such an alloy to 1500 ppm  $\text{H}_2\text{S}$  for 16 hours resulted in the formation of a palladium sulfide layer on the membrane surface. Darling stated that mild poisoning (defined by <25% reduction in performance) was usually temporary and that membrane performance was regenerated by operation of the poisoned membrane in the presence of pure hydrogen for 24 hours at 500°C.

However, the author speculated that reductions in membrane performance greater than 50% are probably permanent [82].

Similar results were observed for the Pd–Ag system by Philpott and Coupland [83], where 1600 ppm  $\text{H}_2\text{S}$  reduced performance by 50% in only 16 hours at 500°C.

McKinley [38] (1967) conducted the first thorough study on the influence of  $\text{H}_2\text{S}$  on the performance of various  $\sim 25\text{-}\mu\text{m}$  palladium–alloy foils at 350°C and a feed pressure of 75 psig.  $\text{H}_2\text{S}$  concentration in the experiments conducted by McKinley [38] ranged from 3.5 to 4.7 ppm, unless otherwise noted.

The 73 wt% Pd–Ag alloy (the most commonly used alloy in commercial applications [32]) exhibited a 99% reduction in performance over a 6-day period, although the majority of the flux reduction was observed over the first 6 hours of exposure.

The Pd–Ag alloy recovered functionality when  $\text{H}_2\text{S}$  was removed from the system after 2 days of exposure. Following 1 day of exposure to hydrogen (after 2 days of  $\text{H}_2\text{S}$  exposure), the Pd–Ag alloy regained some of its original performance, exhibiting an 80% reduction in flux from the pre- $\text{H}_2\text{S}$  exposure.

TABLE II  
PUBLISHED DATA FOR HYDROGEN FLUX REDUCTION THROUGH PALLADIUM ALLOY MEMBRANES

Author	X <sub>M</sub> (□m)	Material	H <sub>2</sub> S (ppm)	Flux Reduction	Recovery (in H <sub>2</sub> atm)	Ref.
Darling	75	73 wt% Pd–Ag	490-1280	negligible	NA*	82
Darling	75	73 wt% Pd–Ag	1600	>50%	NA	82
McKinley	25	73 wt% Pd–Ag	3.5 – 4.7	99%	67%	38
McKinley	25	60 wt% Pd–Cu	3.5 – 4.7	95%	100%	38
McKinley	25	60 wt% Pd–Au	3.5 – 4.7	10-20%	120%	38
Bryden and Ying	10	Pd–Fe	59.1(for 2 temps.)	75-95%	100-100%	50
Edlung and Henry	25	75wt% Pd–Ag	50-1000	99-100%	NA	85
Edlung and Henry	25	60wt% Pd–Cu	50-1000	23-85%	NA	85
Edlung and Henry	25	Pd–Au	50	29%	NA	85
Kulprathipanja et al.	10	40wt% Pd–Cu	115	33%	NA	80
Kulprathipanja et al.	8	27wt% Pd–Cu	250	~85%	~38%	80
Morreale et al.	100	80wt% Pd–Cu	1000	0-10%	NA	86
Way and Thoen	5	85wt% Pd–Au	5	38%	NA	87
Way and Thoen	5	94wt% Pd–Cu	5	71%	NA	87
Roa et al.	7	96wt% Pd–Cu	0 to 50	~70%	100%	89
Roa et al.	6	96wt% Pd–Cu	5	~70%	100%	89
Roa et al.	7	87wt% Pd–Au	0 to 50	~0%	NA	89
Pomerantz and Ma	14	92wt% Pd–Cu	42.7	~80%	~95%	107
Cheng and Ma	10	90wt% Pd–Au	54.8	Increases with temperature	100%	108

\*NA refers to cases where no recovery experiments were done.

Over the next 3 days of exposure to hydrogen, the flux of the membrane gradually increased to a value of 67% of the pre-exposed results [38]. An alloy containing 60 wt% Pd–Cu was also studied by McKinley [38]. Likewise, the Pd–Cu alloy exhibited a significant hydrogen flux decrease in the presence of H<sub>2</sub>S.

An 82% reduction was observed immediately, shifting to a 90% reduction after 6 hours of exposure, to a limiting value yielding a 95% reduction at day 3, and then holding relatively constant for the next 5 days of exposure. The Pd–Cu foil was also tested to determine the regeneration ability of the alloy upon removal of the H<sub>2</sub>S gas mixture. After a 95% reduction in hydrogen flux was observed over the first 2 days of H<sub>2</sub>S exposure, the Pd–Cu alloy retained its performance only after 2 days of H<sub>2</sub> exposure [38].

The most sulfur-resistant alloy studied by McKinley [38] was the 60 wt% palladium–gold (Pd–Au) alloy at 350°C. Although the initial performance of this alloy was relatively low, only a 20% reduction was observed over a 6-day exposure. A second Pd–Au alloy was tested in an effort to characterize the regeneration ability of the alloy. After 2 days of exposure in the presence of H<sub>2</sub>S, a 10% reduction was observed.

However, upon the removal of the sulfur gas mixture and the introduction of H<sub>2</sub>, the membrane actually performed better, yielding a flux ~120% of the original. McKinley [38] also studied the influence of other H<sub>2</sub>S concentrations (20 ppm and 6.6%) on the performance of the Pd–Au alloy. The higher the concentration of H<sub>2</sub>S exposed to the membrane, the larger the decrease

observed in performance. However, with both concentrations, a flux of ~120% of the original was experienced after H<sub>2</sub>S was removed and pure hydrogen was reintroduced [38].

In 1994, Ali et al. [84] studied the influence of methyl-cyclohexane, toluene, sulfur, and chlorine on the performance of Pd–Ag membranes. As previously mentioned for pure palladium membranes, the authors employed an oxygen activation procedure to their Pd–Ag alloy membrane to remove surface impurities. Upon flux testing at 633°C in the presence of 0.12% dimethyl-disulfide (1630 ppm sulfur), an ~83% reduction in performance was observed. Ali et al. [84] attempted to regenerate the membrane by air cycling and increasing temperature. Air exposures at 633, 673, and 713°C resulted in flux values of 50, 75, and 108% compared to the original flux results in the presence of hydrogen at 633°C, respectively. Ali et al. [84] attributed the decrease in performance in the presence of sulfur to the blocking of dissociation sites for hydrogen adsorption on the membrane surface.

Edlund and Henry [85] (1996) studied the potential of several palladium alloys for chemical stability. The alloy foils tested were ~25 μm thick and were operated at 500°C in the presence of 1000 ppm H<sub>2</sub>S in hydrogen at ~115 psia. A 75 wt% Pd–Ag alloy, which exhibited a flux of ~97 cm<sup>3</sup>/cm<sup>2</sup>/min in the presence of pure H<sub>2</sub>, showed a flux of less than 1 cm<sup>3</sup>/cm<sup>2</sup>/min in the presence of 50 ppm H<sub>2</sub>S and no detectable flux in the presence of 1000 ppm H<sub>2</sub>S. Additionally, a gold-coated palladium membrane, which had a flux of ~18 cm<sup>3</sup>/cm<sup>2</sup>/min in pure

hydrogen, exhibited a 29% decrease in performance in the presence of 50 ppm H<sub>2</sub>S. Finally, a 60 wt% Pd–Cu alloy exhibited a hydrogen flux of ~33 cm<sup>3</sup>/cm<sup>2</sup>/min in the presence of pure hydrogen. Flux testing of the 60 wt% Pd–Cu alloy in the presence of 50 and 1000 ppm H<sub>2</sub>S resulted in a 23% and 85% reduction in performance, respectively. Edlund et al. [85] hypothesized that the observed resistance of the 60 wt% Pd–Cu alloy should increase with increasing temperatures due to increased H<sub>2</sub>S desorption [85].

Bryden and Ying [50] (2002) studied the influence of grain size on the performance of a palladium–iron (Pd–Fe) membrane fabricated by a pulsed electrodeposition technique. The authors conducted diffusion experiments in the presence of 51.9 ppm H<sub>2</sub>S at 200°C. The H<sub>2</sub>S exposure of the 10- $\mu$ m-thick 94 at% Pd–Fe alloy resulted in immediate decreases of 75 and 95% in performance for the membranes with a grain size of 28 and 100 nm, respectively. Furthermore, after 2 hours of exposure, the H<sub>2</sub>S gas mixture was removed in an effort to determine the “recovery” of the 28- and 100-nm samples. The hydrogen flux of the 28-nm sample recovered 100% of its performance in approximately 30 minutes, while over 400 minutes were needed for the 100-nm sample to achieve a similar recovery [50].

Morreale et al. [86] evaluated the hydrogen permeance of several 0.1-mm-thick Pd–Cu alloy foils (80 wt% Pd–20 wt% Cu, 60 wt% Pd–40 wt% Cu, and 53 wt% Pd–47 wt% Cu) using transient flux measurements at temperatures ranging from 603 to 1123 K and pressures up to 620 kPa with and without 1000 ppm H<sub>2</sub>S. Sulfur resistance, as evidenced by no significant change in permeance, was correlated with the temperatures associated with the fcc crystalline structure for the alloys in this study. The permeance of the bcc phase, however, was up to two orders of magnitude lower when exposed to H<sub>2</sub>S. A smooth transition from sulfur poisoning to sulfur resistance with increasing temperature was correlated with the alloy transition from a bcc structure to a fcc structure [86].

Additionally, in 2005 Kulprathipanja et al. [80] studied the influence of varying H<sub>2</sub>S concentrations on the permeability of palladium and various Pd–Cu membranes, with palladium compositions ranging from 27 to 80 wt%. The majority of the membrane samples were prepared using an electroless plating technique, while one of the samples tested was in the form of a dense foil. The membranes were exposed to various concentrations of H<sub>2</sub>S with resulting flux and surface information detailed in the manuscript. The Pd–Cu alloys studied exhibited significant surface modification after exposure to H<sub>2</sub>S, which included pore and particle formation detected by SEM as well as significant surface roughness measured by AFM measurements. Higher surface modification occurred for the electroless-plated membrane samples than for the membrane foil. Differences observed by EDS measurements of pre- and post-tested membranes indicated alloy segregation, which was evident by increases in the fcc crystalline

content in the top 1  $\mu$ m of the surface as well as the detection of sulfur in post-tested samples. However, XRD studies could not verify the formation of metal sulfides. Moreover, decreases in hydrogen flux were observed for all of the Pd–Cu alloys reported and were attributed to competitive adsorption. The authors hypothesized that total membrane inhibition would take place at a H<sub>2</sub>S concentration of only 300 ppm. At H<sub>2</sub>S concentrations greater than 300 ppm, Kulprathipanja et al. [80] predicted mechanical failure, which is attributed to the formation of palladium and copper sulfides rearranging the surface, forming large pores, and causing membrane rupture [80].

Recently, Pd–Au alloys have called the attention of several researchers [87]–[89] and [108]. This interest sprang from the work done in the 1960s by McKinley [38], [44]. The authors reported that binary alloys of palladium with gold and copper had pure hydrogen permeabilities greater than palladium and Pd–Ag alloys, were unaffected by thermal cycling, and had some resistance to sulfur poisoning by hydrogen sulfide. The 40 wt% Au–Pd alloy was the most resistant to 4 ppm H<sub>2</sub>S exposure compared to pure palladium, Pd–Ag alloy, and Pd–Cu alloy membranes.

Way et al. [88] patented a method to fabricate sulfur-resistant composite metal membranes. The procedure includes seeding a substrate with palladium crystallites, reducing the palladium crystallites on the substrate to the metallic form, and depositing by electroless plating alternatives films of palladium and gold metals on the substrate. These two metal films are then annealed at a temperature between about 200°C and about 1200°C to form a sulfur-resistant, composite Pd–Au alloy membrane.

Pd–Au membranes having a lower weight percent of gold in the range of Pd<sub>95</sub>Au<sub>5</sub> to Pd<sub>55</sub>Au<sub>45</sub> have a higher hydrogen flux than pure palladium and a much greater resistance to sulfide poisoning than comparable Pd–Cu or Pd–Ag membranes. For example, Way and Thoen [87] reported that a 5- $\mu$ m Pd<sub>85</sub>Au<sub>15</sub> membrane shows only a 38% drop in hydrogen flux in the presence of 5 ppm H<sub>2</sub>S compared to a 71% drop for a comparable Pd<sub>94</sub>Cu<sub>6</sub>, and the Pd<sub>85</sub>Au<sub>15</sub> membrane had a higher hydrogen flux in the presence of H<sub>2</sub>S than the Pd<sub>94</sub>Cu<sub>6</sub> membrane in the absence of H<sub>2</sub>S. A Pd<sub>80</sub>Au<sub>20</sub> membrane having a thickness of about 2.5  $\mu$ m and formed on a stainless steel substrate with a ZrO<sub>2</sub> coating has a hydrogen permeability approaching that of pure palladium and a hydrogen/nitrogen separation factor greater than the ideal value of 400 when tested at 400°C. Similarly, Way et al. [88] reported that a Pd<sub>95</sub>Au<sub>5</sub> membrane having a thickness of about 3  $\mu$ m and formed on a stainless steel substrate with a ZrO<sub>2</sub> coating had a hydrogen permeability approaching that of pure palladium and a hydrogen/nitrogen separation factor of greater than 10,000 when tested at 400°C. A Pd<sub>90</sub>Au<sub>10</sub> membrane formed on a stainless steel substrate with a ZrO<sub>2</sub> coating exposed to a water-gas-shift (WGS) mixture (51% H<sub>2</sub>, 26% CO<sub>2</sub>, 21% H<sub>2</sub>O, 2% CO) at 400°C operated at a 76%

H<sub>2</sub> recovery which is nearly the same as the hydrogen flux seen with exposure to a pure gas flux having a similar H<sub>2</sub> partial pressure, indicating a hydrogen selectivity with only minor reductions in the presence of a mixed molecular gas feed stream [88].

The authors attributed the membranes performance to the fabrication method that produces a partial Pd–Au alloy in which gold selectively segregates to the surface of the Pd–Au film, effectively forming pools of gold on the free surface of the Pd–Au film. For instance, the authors used Auger electron spectroscopy to show that a Pd<sub>70</sub>Au<sub>30</sub> alloy at 250°C actually contained 75 at% Au on its (111) surfaces and 80 at% Au on its (110) surfaces [88]. The segregation of gold to the Pd (111) surface is stronger than that of copper to the same surface [90]. For example, a 20 at% Au concentration in the bulk is predicted to give 58 at% Au on the surface, whereas a 20 at% Cu concentration in the bulk does not produce segregation on the surface [88].

Both palladium and gold form fcc structures throughout the temperature range of -73°C to 900°C. Mixtures of gold and palladium are still fcc but show a tendency to form ordered arrangements of atoms as the temperature is lowered. Within a single fcc crystal containing both gold and palladium, the order can be long range (LRO) or short range (SRO). The LRO is found near Au<sub>3</sub>–Pd, Au–Pd, and Au–Pd<sub>3</sub> stoichiometries. As the stoichiometry moves from one of these three regions, the LRO starts to deteriorate. At stoichiometries far from these values, the structure is fcc with a completely random arrangement of palladium and gold atoms. Way et al. [88] reported that experimental and *ab initio* investigations have shown that such SRO exists at stoichiometries and temperatures of interest in the commercial operation of the composite metal membranes. These data indicate that 20% Au within the bulk results in 80% Au on (111) surfaces. These experimental and computational results indicate that monolayers with roughly this fraction of gold atoms will form SRO structures that are desirable from a functionality standpoint [88].

Roa et al. [89] used an electroless plating method to fabricate Pd–Cu and Pd–Au alloy composite membranes using tubular Al<sub>2</sub>O<sub>3</sub> and stainless steel microfilters to produce high-temperature H<sub>2</sub> separation membranes. The composite membranes were annealed and tested at temperatures ranging from 350 to 400°C, at high feed pressures ( $\leq 250$  psig) using pure gases and gas mixtures containing H<sub>2</sub>, carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), H<sub>2</sub>O, and H<sub>2</sub>S, to determine the effects these parameters had on the H<sub>2</sub> permeation rate, selectivity, and recovery. No flux reduction was observed for a Pd–Au membrane for the water-gas shift (WGS) mixture compared to a pure H<sub>2</sub> feed gas at the same 25-psig partial pressure difference and 400°C. The authors reported a H<sub>2</sub> flux through a Pd–Au membrane of 0.93 mol/m<sub>2</sub>.s at a 100-psig H<sub>2</sub> feed gas pressure and 400°C. This flux value exceeds the 2010 DOE Fossil Energy pure hydrogen flux target. The H<sub>2</sub>/N<sub>2</sub> pure gas

selectivity of this Pd–Au membrane was 1000 at a partial pressure difference of 100 psi [89].

However, it was reported that inhibition of the H<sub>2</sub> flux was observed for similar experiments with Pd–Cu composite membranes. H<sub>2</sub>S caused a strong inhibition of the H<sub>2</sub> flux of the Pd–Cu composite membranes. This effect is accentuated at levels of 100 ppm or higher. Furthermore, adding 5 ppmv to the WGS feed mixture reduced the hydrogen flux by about 70%, but the inhibition due to H<sub>2</sub>S was reversible. At H<sub>2</sub>S levels above 100 ppm, the membrane suffered some physical degradation and its performance was severely affected [89].

### II.3. Hydrogen Sulfide Adsorption

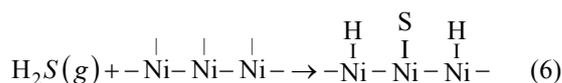
#### II.3.1. Catalysts

Fisher and Kelemen [91] studied experimentally different surface reactions on a (100) platinum surface. The surface was clean or covered with various amounts of sulfur atoms. This system was chosen for its simplicity in order to observe the mechanisms by which sulfur poisons catalytic activity. Three different poisoning mechanisms were identified: (i) When the surface is covered with one sulfur atom per two surface platinum atoms, it is chemically inert. (ii) At lower coverage, the strong chemical bond to sulfur modifies the chemical properties of the platinum surface and weakens its interaction with adsorbates. (iii) When the sulfur coverage is one sulfur atom per four platinum atoms, a regular sulfur layer is formed; molecules can adsorb on the surface but are prevented by the sulfur structure from participating in Langmuir-Hinshelwood reactions.

Rostrup-Nielsen [92] studied the chemisorption of hydrogen sulfide on nickel catalysts in the temperature range 550–645°C. The author reported that the sulfur uptake is a function of the  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  ratio. A saturation layer was observed at ratios above  $5 \times 10^{-4}$ , approximately, and at ratios above  $10^{-3}$ , bulk sulfide (Ni<sub>2</sub>S<sub>3</sub>) was formed. The sulfur content of the saturation layer was correlated with the nickel area determined by volumetric measurements of hydrogen chemisorption at -72°C. Rostrup-Nielsen [92] calculated a value of 0.54 sulfur atoms per nickel atom at 550–645°C. Other researchers questioned this value [93].

Oliphant et al. [93] calculated desorption isotherms from elution curves of H<sub>2</sub>S using a packed bed filled with unsupported nickel, alumina-supported nickel, nickel-platinum, nickel-cobalt, and ruthenium catalysts. All elution experiments were run initially at 450°C and at H<sub>2</sub>S concentrations in the exiting hydrogen stream from 30 to 0.1 ppm. Elution curves and isotherms for supported nickel-platinum were also obtained at 450 and 520°C from which an estimate of the heat of H<sub>2</sub>S chemisorption was calculated. The heat of H<sub>2</sub>S adsorption on nickel is estimated to be 30–40 kcal/mole at 450°C and high coverage (50–90%). The stoichiometry of sulfur adsorption was determined by comparing the total quantity of sulfur adsorbed at 450°C

with the corresponding quantity of hydrogen chemisorbed at 25°C for each catalyst. The data suggest that H<sub>2</sub>S chemisorption is strong and dissociative at low coverage and non-dissociative at high coverage. Ruthenium apparently has a lower capacity for sulfur adsorption than nickel or nickel alloys. The authors found that for all catalysts, except alumina and ruthenium, the slope of the linear, low-coverage portion of each Langmuir isotherm was approximately equal to one-third, which is equivalent to a value of n = 3 in the Langmuir equation. This fact suggests that upon adsorption at the lower coverage, H<sub>2</sub>S dissociates into three species covering three adsorption sites:



In the case of ruthenium and alumina, an n = 2 value suggested that partial dissociation of H<sub>2</sub>S into HS and H is the more prevalent mechanism for adsorption on these samples. Campbell and Koel [94] studied the interaction of H<sub>2</sub>S with Cu(111) using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Ion scattering spectroscopy (ISS), and low-energy electron diffraction (LEED) and measured the effects of sulfur adatoms upon the kinetics of the medium-pressure WGS reaction over Cu (111). At 120 K, H<sub>2</sub>S adsorption is partially molecular. By 200 K, some of the H<sub>2</sub>S desorbs and the rest dissociates to produce sulfur adatoms bonded on top of the Cu (111) surface. The surface saturates at room temperature in a ( $\sqrt{7} \times \sqrt{7}$ )R±19° structure ( $\theta_s = 0.43$ ) characteristic of a nearly close-packed sulfur overlayer, very similar to layers in (111)-oriented Cu<sub>2</sub>S. Sulfur adatoms are quite stable to heating in vacuum or H<sub>2</sub>, with a reaction probability for removal per H<sub>2</sub> collision with the surface of <math>10^{-9}</math> at 636 K. The rate of the forward WGS reaction decreases linearly with sulfur coverage as (1–2.6  $\theta_s$ ). Here,  $\theta_s$  is the fractional sulfur coverage. This poisoning is attributed to steric blocking by the sulfur adatoms of the sites required for dissociative water adsorption.

### II.3.2. Palladium and Palladium–Alloy Membranes

In 1990, Burke and Madix [95] studied the influence of sulfur on the hydrogen adsorption on a Pd (100) surface by temperature programmed desorption (TPD). The study indicated that the saturation coverage of adsorbed hydrogen decreases linearly with adsorbed sulfur, with hydrogen adsorption being completely blocked at a sulfur coverage of 0.28 monolayer (ML). The researchers hypothesized that this phenomenon is attributed to the direct blocking of adsorption sites on the Pd (100) surface as well as the adsorbed sulfur extending a steric influence to the four nearest adsorption sites [95].

In 1992 Forbes et al. [96] used analytical techniques including STM, LEED, and AES to characterize sulfur over-layers on a Pd (111) surface. STM images revealed

( $\sqrt{3} \times \sqrt{3}$ )R30° over-layers on the surface, while the formation of the ( $\sqrt{7} \times \sqrt{7}$ )R19.1° was more complex because the sulfur may exist in the subsurface palladium lattice. The authors speculated that the presence of sulfur in the sub-layers of the Pd–S system may indicate a high atomic mobility of the system as well as that the influence of sulfur on a membrane may be more significant than just competitive adsorption [96].

In 1992, Vazquez and co-workers [97] explored the morphological and activity influence of sulfidation on hydro-desulfurization catalysts at temperatures ranging from 400 to 450°C. TEM analysis indicated particle growth of the palladium particles on a silicon substrate, which was attributed to the sulfidation of the palladium surface and was more significant with increasing temperature. Additionally, thiophene conversion decreased over 60% at 400°C for a poisoned catalyst compared to a sulfide-free palladium catalyst [97].

In 1994, Feuerriegel et al. [98] explored the effect of H<sub>2</sub>S on the deactivation of a palladium-based catalyst during the oxidation of methane. At 240°C, H<sub>2</sub>S concentrations of 5.4, 13.3, and 21.6 ppm all resulted in complete deactivation of the commercial palladium supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst; however, higher concentrations of H<sub>2</sub>S resulted in more rapid catalyst deactivation (total deactivation was observed in as little as 14 hours and as long as 80 hours). Additionally, an H<sub>2</sub>S surface coverage of 0.08 ML completely poisoned the catalyst. XPS analysis of the post-tested catalyst exhibited metallic palladium and sulfur in a highly oxidized state (>SO<sub>2</sub>). Thus, Feuerriegel et al. [98] attributed the decrease in activity to the adsorbed sulfur species on the catalyst surface [98].

Rutkowski et al. [99] evaluated the influence of sulfur adsorbates on the stereodynamics of surface reactions for the associative desorption of D<sub>2</sub> from Pd (100). Their experimental results showed that the potential energy surface (PES) for the reaction extends spatially more into the vacuum than it does for the clean surface. A significant polar corrugation of the PES becomes evident at high  $J''$  states. The authors reported that the observed coverage dependence indicates a shift of the reaction site from the bridge to the *c*-type hollow position at a sulfur coverage of more than  $\theta_s = 0.25$  ML. Miller et al. [100] studied the effect of adsorbed sulfur on surface segregation in a Pd<sub>70</sub>Cu<sub>30</sub> alloy for sulfur coverage values from zero through saturation and for temperatures from 400 to 1000 K. X-ray photoemission spectroscopy (XPS) was used to determine the alloy composition in the near-surface region (~7 atomic layers), and low-energy ion scattering spectroscopy (LEISS) was used to probe the composition of the topmost atomic layer of the alloy. Surface segregation was observed to depend on both the presence of adsorbed sulfur and heat-treatment history. The near-surface region of the clean alloy was enriched in palladium relative to the bulk, but the topmost atomic layer was enriched in copper. Adsorbed sulfur caused a reversal of the copper enrichment of the topmost surface, resulting in a top layer that contained only palladium and

sulfur atoms. Segregation reversal may be driven by the formation of thermodynamically favored Pd–S bonds at the terminating surface of the alloy [100].

Higher sulfur coverage in Pd (111) leads to more complex structures [101]–[103]. At room temperature Grillo et al. [101] reported that sulfur adsorption on the Pd (111) surface involves a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure, which by further exposure to H<sub>2</sub>S and heating to temperatures of approximately 450 K transforms irreversibly into a structure with  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  periodicity. There are distinct differences in the atomic structure of the high temperature and the room temperature sulfur phases. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure is two dimensional with the sulfur atoms occupying fcc, threefold hollow sites of the Pd (111) surface. At a nominal sulfur coverage of 0.33 ML, hydrogen adsorption on Pd (111) completely ceases [101]. However, the  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  structure is very complex, and different unit cells have been proposed. Bömermann et al. [102] suggested a simple model with one sulfur atom per unit cell and sulfur atoms on the fcc hollow sites, whereas Speller et al. [103] proposed a “mixed structure” with two sulfur atoms and three palladium atoms in the unit cell. Theoretical calculations suggested that one sulfur atom is located on an fcc hollow site and the other on a hexagonal close-packed (hcp) hollow site. Three palladium atoms were shifted into the adsorbate layer on the fcc hollow sites [103].

#### II.4. Surface Reaction

The interaction of potential membrane materials with an H<sub>2</sub>S-containing gas stream produces corrosion. Therefore, sulfidation is the primary corrosion mechanism of interest [34]. Corrosion-scale growth experiments are used in the experimental determination of the stability of a corrosion product [14, 34, 107, 108].

Mundschau et al. [104] investigated a variety of palladium–alloy membranes in the presence of several concentrations of H<sub>2</sub>S. Exposure of a palladium foil to 20 ppm H<sub>2</sub>S in 60% H<sub>2</sub>–He at 593 K resulted in almost a 75% loss of H<sub>2</sub> permeability in less than 2 hours. The authors reported that XRD analysis of the membrane sample after the H<sub>2</sub>S–H<sub>2</sub> exposure confirmed the formation of Pd<sub>4</sub>S on the membrane surface. Similarly, exposure of a 75 mol% Pd–Ag membrane to 10 ppm H<sub>2</sub>S in 80% H<sub>2</sub>–He at 593 K resulted in a dramatic loss of H<sub>2</sub> permeation accompanied by the formation of a ternary Ag<sub>5</sub>Pd<sub>10</sub>S<sub>5</sub> scale on the membrane surface [104].

Morreale et al. [14] used computational and experimental methods to quantify the apparent influence of a Pd<sub>4</sub>S corrosion product resulting from flux testing of 100- $\mu$ m-thick pure palladium membranes in a 0.1% H<sub>2</sub>S–10% He–H<sub>2</sub> retentate gas mixture. Sulfide growth kinetics was determined using gravimetric methods. Hydrogen permeation experiments were carried out using Pd–Cu alloys in the temperature range from 623 to 908 K. The authors determined, using experimental results and theoretical calculations, that Pd<sub>4</sub>S is the main product

of sulfur corrosion on palladium surfaces [14], [34]. Morreale et al. [14], [34] attempted to explain the decrease observed in hydrogen flux for several of the membranes in the presence of the H<sub>2</sub>S gas mixture by a sequential resistance model through a multi-layered membrane (see Fig. 1).

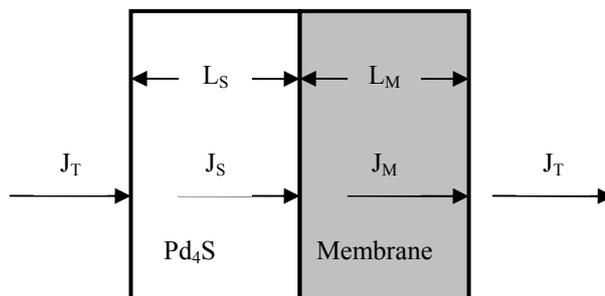


Fig. 1. Schematic of the sequential model (from reference [34])

The assumption of steady state through the system implies that the hydrogen flux through the sulfide scale must be equal to the hydrogen flux through the metal membrane, Eq. (7):

$$\begin{aligned} J_T &= J_S (\text{flux through sulfide}) = \\ &= J_M (\text{flux through metal}) \end{aligned} \quad (7)$$

Modeling of the flux decline observed during membrane testing along with the kinetics developed from the gravimetric studies resulted in the first reported value of the permeability of Pd<sub>4</sub>S. Density functional theory was used to predict the hydrogen permeability of Pd<sub>4</sub>S by examining diffusivity and solubility of hydrogen in bulk Pd<sub>4</sub>S. Morreale et al. [14] reported good agreement between the experimental results and computational predictions of the activation energy of permeation. However, only moderate agreement was reported when comparing the hydrogen permeability through Pd<sub>4</sub>S values determined theoretically and the experimental results. The permeability values obtained through experiments were approximately seven times greater than the computational predictions. Iyoha et al. [105] studied the influence of H<sub>2</sub>S-to-H<sub>2</sub> partial pressure ratio on the sulfidation of palladium and 70 mol% Pd–Cu membrane alloys using various H<sub>2</sub>S-containing gas mixtures. The authors assumed that fast adsorption of H<sub>2</sub>S on the membrane surface would produce an equilibrium situation between the gas and solid chemical species participating in the sulfidation reaction. The formation of Pd<sub>4</sub>S was determined to be a function of the  $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$  value and the solid components activity values. In the case of palladium alloys, these activity values were determined using thermodynamics calculations [106]. Iyoha et al. [105] reported that the corrosion behavior of palladium membranes exposed to various H<sub>2</sub>S mixtures was in very good agreement with their thermodynamic calculations. The membranes studied by them resisted

sulfidation when exposed to H<sub>2</sub>S-to-H<sub>2</sub> ratios below the formation equilibrium value predicted for Pd<sub>4</sub>S formation, and experienced corrosion when exposed to ratios above the equilibrium values. However, the Pd<sub>70</sub>Cu<sub>30</sub> membranes exhibited deviations from the predicted values. This phenomenon was attributed to deviations of the Pd–Cu alloy from ideality, probably due to copper segregation at the membrane surface [106]. Pomerantz et al. [107] used corrosion-scale growth experiments to study the interactions of H<sub>2</sub>S with palladium and Pd–Cu membranes in the presence of H<sub>2</sub>S. The authors used palladium-plated coupons of 316L PSS, previously oxidized to form an intermetallic diffusion barrier, by an electroless deposition method. A Pd–Cu membrane was fabricated by the electroless plating of sequential metallic layers on a porous inconel tubular support which was graded with Al<sub>2</sub>O<sub>3</sub> and plated with a Pd–Ag intermetallic diffusion barrier before the dense layer was deposited. Pomerantz et al. [107] reported that the exposure of the palladium coupons to the 50 ppm H<sub>2</sub>S/H<sub>2</sub> mixture resulted in sulfur adsorption on the palladium surface and formation of a Pd<sub>4</sub>S scale on top of the palladium layer as determined by XPS. Presence of the bulk Pd<sub>4</sub>S was verified by XRD and EDS. The permeance of the Pd–Cu membrane had an instantaneous drop to 21% of the original permeance upon exposure to 50 ppm H<sub>2</sub>S/H<sub>2</sub> at 450°C. Pomerantz et al. [107] hypothesized that the drop was due to formation of surface sulfides which decreased the effective area for H<sub>2</sub> adsorption. The Pd–Cu membrane recovered functionality after treatment in pure H<sub>2</sub> at 450°C. However, at the end of the recovery, the permeance stabilized at 64% of the permeance value before the initial H<sub>2</sub>S poisoning. The authors concluded that the inability to completely recover the permeance showed that part of the sulfide poisoning was irreversible at that temperature [107].

Cheng and Ma [108] investigated the effect of temperature on sulfur poisoning of Pd–Au alloys. In addition, the hydrogen permeation characteristics of the Pd–Au membrane in the presence of H<sub>2</sub>S and the permeance recovery after the sulfur poisoning at different temperatures were also investigated. The authors reported that SEM, EDX, and XRD analyses measured a gold surface content of about 10 wt% on the Pd–Au alloy coupons before the poisoning experiments. Their experimental results confirmed the presence of Pd<sub>4</sub>S on pure palladium surfaces. For the Pd–Au alloy coupons, no surface morphology changes were observed on the SEM micrographs and no new phase and sulfur were detected through the entire temperature range studied (350–500°C). The authors concluded that the Pd–Au alloy showed high resistance to sulfur adsorption and sulfide formation.

Cheng and Ma [108] also prepared a 10- $\mu$ m Pd<sub>90</sub>Au<sub>10</sub> membrane by sequential electroless plating and annealing. The authors reported that during the exposure to a 54.8 ppm H<sub>2</sub>S/H<sub>2</sub> mixture, the permeance declined instantaneously to a steady state value in the entire

temperature range. The percentage of permeance decline decreased as the temperature was increased. After the poisoning, permeance was recovered to a steady state value in pure H<sub>2</sub> at each poisoning temperature. The permeance, calculated as a percentage of the non-poisoned value, increased with temperature until full recovery at 500°C. Cheng and Ma [108] concluded that the higher desorption rate of the H<sub>2</sub>S molecules at higher temperatures resulted in less sulfur adsorption on the membranes surface, thereby less poisoning effect of the membrane at higher temperatures. This conclusion agrees with the observations of several researchers [14], [34], [88], [89], [107].

### III. Theoretical Studies

#### III.1. Permeation

##### III.1.1. Palladium and Palladium–Alloy Membranes

Kamakoti and Sholl [109] used plane wave density functional theory (DFT) to examine the binding and diffusion of dilute interstitial hydrogen in pure palladium, disordered fcc Cu<sub>48</sub>Pd<sub>52</sub>, and ordered bcc Cu<sub>50</sub>Pd<sub>50</sub>. Their DFT results indicated that the diffusion activation energy for interstitial hydrogen in ordered bcc Cu<sub>50</sub>Pd<sub>50</sub> is over an order of magnitude smaller than that for pure palladium. The authors also presented a detailed description of the range of diffusion activation energies available for local hops of interstitial hydrogen in disordered fcc Cu<sub>48</sub>Pd<sub>52</sub> and described how the net activation energy for long-range hydrogen diffusion in this material can be inferred from these results. In 2005, Kamakoti and Sholl [110] developed a comprehensive lattice-gas model to predict the diffusivities of dilute hydrogen in a wide range of structurally disordered fcc Cu–Pd alloys with compositions greater than 47 at.% Pd. They used density functional theory to perform detailed calculations of hydrogen binding energies, vibrational frequencies, and activation barriers to local diffusion in two representative alloys having 52 and 74 at.% Pd. Kinetic Monte Carlo (KMC) simulations of their lattice model were used to calculate hydrogen tracer diffusivities as a function of alloy composition and temperatures ranging from 400 to 1200 K. The results from these simulations were found to be in good agreement with available experimental data. Kamakoti et al. [111] studied experimentally and theoretically hydrogen permeation through binary palladium alloys. The authors used *ab initio* calculations and coarse-grained modeling to predict hydrogen fluxes through binary alloy membranes as a function of alloy composition, temperature, and pressure. Their approach only required knowledge of bulk crystal structures without any other experimental input. Kamakoti et al. [111] demonstrated their method for Pd<sub>x</sub>Cu<sub>100-x</sub> alloys, which show nontrivial behavior due to the existence of structure transitions from fcc to bcc as temperature is changed [34], [68]. The structure transitions profoundly affect the permeation behavior and the sulfur resistance

of the membranes. Their predicted results compared favorably with extensive experimental results collected by their research group [34], [68].

Ling and Sholl [112] studied the net resistance to hydrogen transport through defect-free metal membranes. The authors introduced quantitative modeling methods based on plane wave density functional theory calculations to assess the relative role of intracrystalline and surface resistances for membranes made from metal alloys. Ling and Sholl [112] demonstrated the method by studying the permeation of hydrogen through Pd<sub>75</sub>Cu<sub>25</sub> films as a function of film thickness, temperature, feed pressure, and trans-membrane pressure drop. The authors concluded that the resistances associated with surface processes are critical for thin membrane films (~1 μm) at all temperatures lower than 700 K. Recently, Semidey-Flecha and Sholl [113] used first-principles to characterize hydrogen permeance through dense metal membranes. In this study the authors used a combination of density functional theory calculations and a cluster expansion method to describe interstitial hydrogen in alloys of composition Pd<sub>96</sub>M<sub>4</sub>, where M = Ag, Cu, and Rh. They used Sieverts' law to calculate hydrogen solubility and a kinetic Monte Carlo scheme to find the diffusivity of hydrogen in Pd–Ag, Pd–Cu, and Pd–Rh alloys at a temperature range of 400 ≤ T ≤ 1200 K. Semidey-Flecha and Sholl [113] predicted that Pd–Ag permeability would be up to 1.5 times higher than that of pure palladium. For the copper alloy, the predicted permeability of hydrogen was lower than the permeability in pure palladium. Similar results were calculated for rhodium alloys.

Presently, Gabitto and Tsouris [114] are carrying out a research project to macroscopically simulate the poisoning process. The poisoning process comprises two sequential steps: sulfur adsorption/desorption and chemical reaction on the surface. Competitive adsorption between H<sub>2</sub>S and H<sub>2</sub> and surface reaction on the membrane surface are accounted for in the model. The model simulates the transport mechanism by calculation of the change in coverage of the different chemical species. The occurrence of the chemical reaction is limited by the value of the reaction rate constant [105]. Fig. 2 depicts the proposed model.

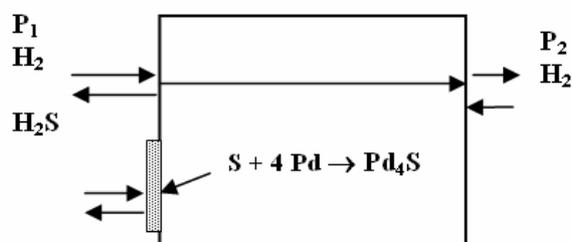


Fig. 2. Schematic of the proposed model

The equations representing the poisoning model are obtained from mass balances for hydrogen, on both sides of the membrane, and for hydrogen sulfide, on the high-

pressure side. The three mass balances lead to a system of ordinary differential equations on the fractional surface coverage values of hydrogen and sulfur. The system has been solved using numerical methods. Very good agreement has been found between model predictions and qualitative experimental observations from the literature. Preliminary results showed that hydrogen flux is strongly related to hydrogen coverage of the high-pressure side of the membrane. The increase in sulfur coverage produces a decrease in hydrogen coverage of the membrane surface. Significant work is still needed in order to assess the model accuracy. Better estimation of the transport and reaction kinetic parameters is also required.

### III.2. Adsorption

#### III.2.1. Palladium and Palladium-Alloy Membranes

In 1995, Wilke and Scheffler [115] studied the co-adsorption of hydrogen and sulfur on a Pd (100) surface using theoretical methods. The authors studied the adsorption of hydrogen on clean and sulfur-covered Pd (100) using density functional theory [116], [117]. The theoretical calculations illustrated that low-sulfur-surface coverages ( $\theta_s \leq 0.25$ ) reduce the hydrogen adsorption energy at sites close to adsorbed sulfur, while at higher surface-coverage values ( $\theta_s = 0.5$ ), strong repulsive H–S interactions strictly block the adsorption of hydrogen in the vicinity of sulfur adatoms [115].

Dong et al. [118] used an *ab initio* approach to study the dissociative adsorption of a hydrogen molecule on the palladium (111) surface. Their approach was based on the density functional theory (DFT) with a generalized gradient approximation (GGA). The wave functions were expanded in a plane-wave basis, and the electron-ion interaction was described by the use of ultra-soft pseudopotentials. The authors determined the potential energy surface (PES) for several pathways for the dissociative adsorption of hydrogen. Spontaneous dissociation paths were found to have a very small barrier of about 70 meV [118].

Wei et al. [119] studied the PES of the dissociative adsorption of H<sub>2</sub> on the sulfur-covered Pd (100) surface using density-functional theory and the full-potential linear augmented plane-wave method. The authors found that the PES was changed significantly compared to the dissociation on the clean Pd (100) surface, particularly for hydrogen close to the sulfur atoms. While the hydrogen dissociation at the clean Pd (100) surface was non-activated, for the *p*(2x2) sulfur adlayer (coverage  $\theta_s = 0.25$ ), the dissociation of H<sub>2</sub> was inhibited by energy barriers. The largest barriers were in the vicinity of the sulfur atoms due to the strong repulsion between sulfur and hydrogen. Still the hydrogen dissociation on the *p*(2x2) sulfur-covered Pd (100) surface was exothermic. Thus the poisoning effect of sulfur adatoms for H<sub>2</sub> dissociation at low-sulfur coverage ( $\theta_s < 0.25$ ) is mainly governed by the formation of energy barriers, not by blocking of the adsorption sites. For the *c*(2x2) sulfur

adlayer ( $\theta_S = 0.5$ ), the PES for hydrogen dissociation was found to be purely repulsive [119]. In 1999, Grivil and Toulhout [120] used first-principles calculations to theoretically model the interaction of sulfur and chlorine on a Pd (111) surface. The authors demonstrated that a 0.33 ML of adsorbed sulfur is sufficient to completely inhibit  $H_2$  adsorption. Additionally, Grivil and Toulhout reported that lower sulfur coverages inhibit  $H_2$  dissociation on the Pd (111) surface which is strongly dependent on the lateral separation of the adsorbed sulfur and hydrogen [120]. In the computational studies carried out by Alfonso et al. [121], [122], the interaction of several membrane materials with sulfur and  $H_2S$  has been examined. Alfonso et al. [121] demonstrated that the binding energy of sulfur on potential membrane metals shows the following trend:  $E_{Pd(111)} > E_{Cu(111)} > E_{Ag(111)}$ , while palladium alloys with copper and silver show weaker binding energies than pure palladium [121]. Additional studies conclude that although  $H_2S$  will adsorb and dissociate relatively easily on a Pd (111) surface, sulfur is the most stable adsorbed species at low surface coverage ( $\theta_S \leq 0.5$ ). While at a surface coverage of sulfur greater than 0.5 ML, adsorbed sulfur has a tendency to form S-S bonds on the palladium surface [121]. In 2005 Alfonso et al. [123] used gradient-corrected density functional theory to investigate the adsorption of  $H_2S$  on a Pd (111) surface. The authors found that molecular adsorption is stable with  $H_2S$  binding preferentially at top sites. In addition, SH and sulfur were found to preferentially bind at the bridge and fcc sites, respectively. The authors calculated the reaction pathways and energy profiles for  $H_2S$  decomposition, giving rise to adsorbed sulfur and hydrogen. Both  $H_2S(ad) \rightarrow SH(ad) + H(ad)$  and  $SH(ad) \rightarrow S(ad) + H(ad)$  reactions were found to have low barriers and high exothermicities [123]. Using density functional theory calculations, Hyman et al. [124] studied the  $H_2S$  dissociation on the (111) surfaces of Pd, Cu, Ag, Au, and various binary metallic surfaces. In modeling bimetallic surfaces, the authors used the thermodynamics of each elementary dissociation step to understand the contributions of lattice strain and electronic ligand effects. Sulfuric ( $H_2S$ , SH, and S) adsorption energies were found to correlate very well with lattice constant. The authors explained this agreement by the strong correlation of the lattice constant with d-band center, Fermi energy, and density of states at the Fermi level for strained Pd (111) surfaces [124].

Pillay and Johannes [125] investigated adsorption strengths of hydrogen and sulfur both individually and together as co-adsorbates on Pt (111), Ni (111), and  $Pt_3Ni$  (111) surfaces using density functional theory in order to determine the effect of metal alloying on sulfur tolerance. The adsorption strengths of hydrogen and sulfur singly follow the same trend:  $Ni(111) > Pt(111) > Pt_3Ni(111)$ , which correlates well with the respective d-band center positions of each surface. The authors found that the main effect of alloying is to distort both the sub-layer structure and the platinum over-layer, resulting in a

lowered d-band.

#### IV. Summary of Literature Information

In this section we will summarize the relevant facts obtained from the literature in order to propose qualitative/quantitative models of the poisoning process. We will also critically discuss the literature findings.

Binary palladium alloys with cerium, copper, gold, and silver can exhibit higher permeability values than each of the metals individually [38], [58], [59]. The alloys also exhibit improved resistance to sulfur poisoning. Relatively open crystal structures exhibit higher permeation than closer crystalline structures; however, membranes with these structures are less resistant to sulfur poisoning. The ordered bcc phase composition yields significantly higher solubility values as compared to the fcc Pd-Cu alloys, with a maximum solubility at a composition of ~60 wt% Pd-Cu [63]-[66], [68]. The resistance of the 60 wt% Pd-Cu alloy to sulfur poisoning increases with increasing temperatures [34], [85], [86], [104]. A smooth transition from sulfur poisoning to sulfur resistance with increasing temperature was correlated with the alloy transition from a bcc structure to a fcc structure [34], [86]. Palladium segregation induces increasing hydrogen chemisorption on the surface of Pd-Cu alloys and changes hydrogen permeation [70], [86], [107]. Copper segregation on the surface has also been linked to increased sulfur resistance [34], [86], [100], [107]. Pd-Au membranes show increased chemical resistance compared to similar Pd-Cu membranes [38], [87], [88], [89], [90], [108]. Comparing the binding energy between the sulfur atoms and the surface atoms of Pd, Cu, Au, Pd-Cu alloy, and Pd-Au alloy membranes, Pd-Au alloys have the lowest binding energy, while palladium metal membranes have the highest binding energy (ordered as  $Pd > Cu > Pd-Cu$  alloys  $> Au > Pd-Au$  alloys) [89]. Pd-Au membranes also show relatively high permeation flows and sulfur poisoning resistance compared to other Pd-Me (metal) membranes [88]. The improved performance of the Pd-Au membranes results from gold segregation on the surface of the Pd-Au film, effectively forming pools of gold on the free surface of the Pd-Au film [87], [88], [90], [108]. The segregation of gold to the Pd (111) surface is stronger than that of copper to the same surface [90]. In the presence of  $H_2S$ , some studies reported formation of irreversible layers on the palladium surface leading to permeation reductions up to 95% [38] compared to permeation without  $H_2S$  [38], [75], [80], [107], [108]. Other studies reported severe permeation reductions in presence of  $H_2S$ , but the permeation rate was restored upon removal of  $H_2S$  and in presence of  $H_2$  [80], [107], [108]. Some studies reported membrane failure (cracks and pinholes) in presence of relatively concentrated amount of  $H_2S$  [80]. Formation of binary and ternary sulfides on the surface of the membrane is possible [14], [34], [104], [105], [107], [108]; however, experimental results and theoretical calculations reported

that Pd<sub>4</sub>S is the main product of sulfur corrosion on palladium surfaces [14], [34], [104], [105], [107], [108]. The formation of Pd<sub>4</sub>S has been determined to be a function of the hydrogen sulfide to hydrogen partial pressures ratio and the activity values of the solid components. The value of the equilibrium constant for Pd<sub>4</sub>S formation is very high; therefore, even small amounts of hydrogen sulfide produce significant amounts of Pd<sub>4</sub>S on the surface [105]. The value of the equilibrium constant decreases with temperature; therefore, palladium sulfide formation decreases with temperature and chemical stability increases.

The poisoning process starts with the H<sub>2</sub>S adsorption on the membrane surface [14], [34], [92]-[96], [99]-[103], [115]. Numerous studies have dealt with sulfur adsorption on metallic surfaces [34], [92]-[96], [99]-[103], [115], [118]-[124]. Adsorbed sulfur atoms not only block the adsorption sites they occupy but also influence the nearest adsorption sites [92]-[95]. On Pt (111) surfaces, a surface covered with one sulfur atom per two platinum atoms is chemically inert. At lower coverage values, one sulfur atom per four platinum atoms, a regular sulfur layer is formed; molecules can adsorb on the surface but are prevented by the sulfur structure from participating in Langmuir-Hinshelwood reactions [91]. The sulfur uptake in Ni (100) is a function of the  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  ratio [92]. The sulfur content of the saturation layer presents a value of 0.54 sulfur atoms per nickel atom at 550–645°C [92]. On Cu (111) the rate of the forward WGS reaction decreases linearly with sulfur coverage as (1–2.6  $\theta_s$ ). This poisoning is attributed to blocking of adsorption sites. Hydrogen adsorption on Pd (100) is completely blocked at a sulfur coverage value of 0.28 ML. This phenomenon is attributed to adsorbed sulfur extending a steric influence to the four nearest adsorption sites [95]. The potential energy surface (PES) of the dissociative adsorption of H<sub>2</sub> on the sulfur-covered Pd (100) surface changes significantly compared to the dissociation on the clean Pd (100) surface. While the hydrogen dissociation at the clean Pd (100) surface is non-activated, for the  $p(2 \times 2)$  sulfur adlayer (coverage  $\theta_s = 0.25$ ) the dissociation of H<sub>2</sub> is inhibited by energy barriers [119]. On a Pd (111) surface, a 0.33 ML of adsorbed sulfur is sufficient to completely inhibit H<sub>2</sub> adsorption [120]. Although H<sub>2</sub>S will adsorb and dissociate relatively easily on a Pd (111) surface, sulfur is the most stable adsorbed species at low surface coverage ( $\theta_s \leq 0.5$ ) [121]. The adsorption of hydrogen sulfide on Pd (111) is a complex process involving several steps [123]. The process starts with H<sub>2</sub>S binding preferentially at top palladium sites followed by H<sub>2</sub>S dissociation into adsorbed SH and sulfur. The reaction pathways for H<sub>2</sub>S decomposition giving rise to H<sub>2</sub>S(ad) → SH(ad) + H(ad) and SH(ad) → S(ad) + H(ad) reactions have low barriers and are highly exothermic. At the same time the sulfur moieties, SH and sulfur, are found to preferentially bind at the bridge and fcc sites, respectively [123]. High sulfur coverage,  $\geq 0.33$ , on Pd (111) surfaces leads to a completely covered surface

represented by a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure at low temperatures and to more complex structures at high temperatures [101]-[103]. The formation of a sulfide scale severely decreased the hydrogen flux [14], [34], [105], [107]. Partial recovery of the membrane functionality can be achieved [107], [108]. However, the inability to completely recover hydrogen permeability suggests that part of the sulfide poisoning is irreversible [14], [34], [105], [107], [108]. Attempts to quantify the influence of a Pd<sub>4</sub>S scale on hydrogen permeation have been only partially successful [14]. Good agreement between the experimental results and computational predictions of the activation energy of permeation has been achieved, while the hydrogen permeability values through Pd<sub>4</sub>S layers obtained through experiments were approximately seven times greater than the computational predictions [14].

## V. Conclusions

Poisoning of metallic surfaces by sulfur compounds is a very serious problem affecting many industrial processes. A better understanding of the poisoning mechanism can lead to design of better materials. Several metals widely used in industry are affected by this problem, Cu, Ni, Pd, Pt, among others. Palladium and palladium-based alloys are currently the most promising for metallic membranes fabrication. Unfortunately, the operation of palladium membranes is greatly affected by sulfur compounds. Pd-Cu and Pd-Au alloys seem to be the most promising based on their relatively high hydrogen flux and sulfur resistance. Pd-Cu alloys have shown great promise; however, their potential still has not been realized. Pd-Cu membranes have good hydrogen permeation value and improved resistance compared to Pd-Ag and pure palladium membranes. The Pd<sub>60</sub>Cu<sub>40</sub> presents the best combination of permeation flux and sulfur resistance. Pd-Au membranes behave better than equivalent Pd-Cu membranes under similar operating conditions. However, the increased cost of using gold in big surface applications is an important concern. Very thin supported membranes (1–10  $\mu\text{m}$ ) are needed based upon economic considerations. Palladium-based membrane poisoning by H<sub>2</sub>S can be discussed in terms of sulfur adsorption on surface sites diminishing the catalytic activity of the membrane surface by reducing the active surface area. The process involves several dissociative steps for hydrogen separation. The adsorbed sulfur can chemically react with the membrane to produce palladium sulfide compounds on the surface. This corrosion product can produce membrane failure by distortion of the crystalline lattice. Experimental data and computational results suggest that hydrogen flux can be recovered by removal of adsorbed sulfur. The same results suggest that the formation of palladium sulfides is irreversible.

Research on several aspects of membrane performance is still needed. Flow experiments will help to characterize new membranes. Accurate determination

of transport parameters is needed. Experiments especially designed to determine transport properties are required. New theoretical methods, such as the Density Functional Theory, can lead to improve estimation of transport parameters. Better understanding of the S-Pd reaction mechanism is also needed. There are few, and contradictory, thermodynamic data on Pd/Pd-alloy mixtures. Improved models using more accurate calculated transport parameters can lead to better understanding of the poisoning mechanism.

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### References

- [1] Taylor, Ch. E. "Technical Aspects of Clean Hydrogen Production," in *GCEP Energy Workshop, Stanford University, April 26 (2004)*.
- [2] Lin, S., Harada, M., Y. Suzuki, Y., Hatano, H., "Hydrogen Production from Coal by Separating Carbon Dioxide during Gasification," *Fuel* 81 (2002) 2079.
- [3] Fushimi, C., M. Goto, M., Tsutsumi, A., Hayashi, J. and Chiba, T., "Steam Gasification Characteristics of Coal with Rapid Heating," *J. Anal. Appl. Pyrolysis* 70 (2003), 185.
- [4] Czuppon, T. A., Knez, S. A., and Newsome, D. S., "Hydrogen. The Energy Technology and the environment," in: A. Bisio and S. Boots (Eds.), *Encyclopedia of Energy Technology and Environment, John Wiley & Sons, New York (1995), p. 1752*.
- [5] Buxbaum, R. E., "Membrane Reactor Advantages for Methanol Reforming and Similar Reactions." *Sep. Sci. Technol.* 34 (1999) 2113.
- [6] Lin, Y. M., Lee, G.-L., and Rei, M. H., "An integrated purification and production of hydrogen with a palladium membrane catalytic reactor." *Catal. Today*, 44 (1998), 343.
- [7] Aasberg-Petersen, K., Nielsen, C. S., and Jorgensen, S. L., "Membrane reforming for hydrogen." *Catalysis Today* 46 (1998) 193.
- [8] Grove, D. E., "Final Analysis: Catalysts - Myths and Realities." *Platinum Metals Rev.*, 47 (2003), 44.
- [9] Bucur, R. V. *J. Catal.* 70 (1981), 92.
- [10] Peden, C. H. P., Kay, B. D., and Goodman, D. W., "Kinetics of Hydrogen Absorption by Chemically modified Pd (110)." *Surf. Sci.* 175 (1986), 215.
- [11] Castro, P. J., Meyer, G., and Zampieri, G., "Effects of Sulfur poison on Hydrogen desorption from Palladium." *J. Alloy Compd.* 330-332 (2002), 612.
- [12] Lee, J. and Rhee, H., "Sulfur tolerance of zeolite beta-supported Pd-Pt catalysts for the isomerization of n-hexane." *J. Catal.* 177 (1998), 208.
- [13] Oudar, J. and Wise, H., *Deactivation and Poisoning of Catalysts* (Dekker, New York, 1991).
- [14] Morreale, B. D., Howard, B. H., Iyoha, O., Enick, R. M., Ling, Ch., and Sholl, D. S., "Experimental and Computational Prediction of the Hydrogen Transport Properties of Pd<sub>4</sub>S." *Ind. Eng. Chem. Res.* 46 (2007), 6313-6319.
- [15] Deville, H.; Troost, L., "Sur la Permeabilite du Fer a Haute Temperature." *Comptes Rendus.* 57 (1863), 965.
- [16] Deville, H., "Sur le Passage des Gaz au Travers des Corps Solides Homogenes." *Comptes Rendus.* 59 (1864), 102.
- [17] Graham, T., "Adsorption and separation of gases by colloid septa." *Phil. Trans. Roy. Soc.* 156 (1866), 399.
- [18] Davis, W. D., *Diffusion of Hydrogen through Palladium* (General Electric: Schenectady, 1954).
- [19] Holleck, G. L., "Diffusion and Solubility of Hydrogen in Palladium and Palladium-Silver Alloys." *J. Phys Chem.* 74, (1970), 503-511.
- [20] Katsuta, H.; Farraro, R. J.; McLellan, R. B., "The Diffusivity of Hydrogen in Palladium." *Acta Metallurgica.* 27 (1979) 1111.
- [21] Koffler, S. A.; Hudson, J. B.; Ansell, G. S., "Hydrogen Permeation through Alpha-Palladium." *Trans. Metallurgical Soc. AIME.* 245 (1969), 1735.
- [22] Toda, G., "Rate of Permeation and Diffusion Coefficient of Hydrogen through Palladium." *J. Res. Inst. Catalysis* 13 (1958), 1058.
- [23] Gryaznov, V. M. and Karanov, A. N. "Hydrogenation and Dehydrogenation of Organic Compounds on Membrane Catalysts (Review)," *Khim.-Farm. Zh.*, 13 (1979), 74.
- [24] Gryaznov, V. M. "Hydrogen Permeable Palladium Membrane Catalysts," *Plat. Met. Rev.*, 30 (1986), 68.
- [25] Shu, J., Grandjean, B. P. A., van Neste, A., and Kaliaguine, A. "Catalytic Palladium-Based Membrane Reactors: A Review," *Can. J. Chem. Eng.*, 69 (1991), 1036.
- [26] Uemiya, S., Sato, N., Kude, Y., Matsuda, T., and Kikuchi, K. "Separation of Hydrogen through Palladium Thin Film Supported on a Porous Glass Tube," *J. Membrane Sci.*, 56 (1991), 303-313.
- [27] Jayaram, V., Lin, Y. S., Pakal, M., and Lin, R. Y. "Fabrication of Ultrathin Metallic Membranes on Ceramic Supports by Sputter Deposition," *J. Membrane Sci.*, 99 (1995), 89-100.
- [28] Yeung, K. and Varma, A "Novel Preparation Technique for Thin Metal-Ceramic Composite Membranes," *AIChE J.*, 41 (1995), 2131-2139.
- [29] Li, A., Liang, W., and Hughes, R. "Characterization and Permeation of Palladium/Stainless Steel Composite Membranes," *J. Membrane Sci.* 149 (1998), 259-268.
- [30] Okamoto, H., "Phase Diagrams for binary alloys: A desk handbook." (ASM International, Materials Park, OH 44073-0002, USA, 2000).
- [31] Baker, R. W., "Membrane Technology and Applications" (McGraw-Hill, Chapter 3, pp. 127, 2000).
- [32] Paglieri, S. N. "Palladium Membranes," in *Nonporous Inorganic Membranes for Chemical Processing* (Sammells, A. F. and Mundschau, M. V. editors, Chapter 3, p. 77, Wiley-VCH Verlag GmbH & Co. KGaA publishers, 2006).
- [33] Edlund, D. J. "A Catalytic Membrane Reactor for Facilitating the Water-Gas Shift Reaction at High Temperature," *DOE report to contract, DE-FG03-91ER81229, 1994*.
- [34] Morreale, B. D. "The influence of hydrogen sulfide on palladium and palladium-copper alloy membranes," Ph. D. Thesis, University of Pittsburgh, Department of Chemical Engineering, 2006.
- [35] Roa, F.; Way, J. D., "The effect of air exposure on palladium-copper composite membranes." *Appl. Surface Sci.* 240 (2005). 85-104.
- [36] Collins, J. P.; Way, J. D., "Catalytic decomposition of ammonia in a membrane reactor." *J. Membrane Sci.*, 96 (1994), 259.
- [37] Gao, H.; Lin, Y. S.; Li, Y.; Zhang, B., Chemical Stability and Its Improvement of Palladium-Based Metallic Membranes." *Ind. & Eng. Chem. Res.* 43 (2004), 6920.
- [38] McKinley, D. L., "Metal Alloy for Hydrogen Separation and Purification" (USA Patent 3,350,845 1967).
- [39] Edlund, D., "A Membrane Reactor for H<sub>2</sub>S Decomposition" (US DOE, Morgantown DOE/ER/81419-97/CO749, July 16-18, 1996).
- [40] Kulprathipanja, A., Alptekin, G. O., Falconer, J. L., and Way, J. D., "Pd and Pd-Cu Membranes: Inhibition of H<sub>2</sub> Permeation by H<sub>2</sub>S," *J. Membrane Sci.*, 254 (2005), 49-62.
- [41] Beuscher, U. and Gooding, C. H. "The Permeation of Binary Gas Mixtures through Support Structures of Composite Membranes," *J. Membrane Sci.* 150 (1998), 57-73.
- [42] Morreale, B. D.; Ciocco, M. V.; Enick, R. M.; Morsi, B. I.; Howard, B. H.; Cugini, A. V.; Rothenberger, K. S. "The permeability of hydrogen in bulk palladium at elevated temperatures and pressures," *J. Membrane Sci.*, 212 (2003), 87.
- [43] Ward, T. L. and Dao, T. "Model of Hydrogen Permeation Behavior in Palladium Membranes." *J. Membrane Sci.*, 153 (1999), 211-231.

- [44] Gabitto, J. F. and Tsouris, C. "Hydrogen Transport in Composite Inorganic Membranes." *J. Membrane Sci.*, 312 (2008), 132-142.
- [45] Balovnev, Y. A. "Diffusion of hydrogen in palladium." *Russ. J. Phys. Chem.* 48 (1974), 409-410.
- [46] McKinley, D. L. "Method for Hydrogen Separation and Purification" (US Patent 3,439,474, 1969).
- [47] Fort, D.; Farr, J. P. G.; Harris, I. R., "A comparison of palladium silver and palladium yttrium alloys as hydrogen separation membranes." *Less-Common Met.*, 39 (1975), 293.
- [48] Juda, W.; Krueger, C. W.; Bombard, T. R., "Method of producing thin palladium copper and the like, palladium alloy membranes by solid-solid metallic interdiffusion, and improved membrane" (US Patent 6238465, 2001).
- [49] Edlund, H., "A membrane process for hot gas clean-up and decomposition of H<sub>2</sub>S to elemental sulfur" (Phase II Final Report, DE-FG03-91ER81228, 1996).
- [50] Bryden, K. J.; Ying, J. Y. "Nanostructured palladium-iron membranes for hydrogen separation and membrane hydrogenation reactions." *J. Membrane Sci.*, 203, (2002), 29.
- [51] Nam, S.-E.; Lee, S.-H.; Lee, K.-H., "Preparation of a palladium alloy composite membrane supported in a porous stainless steel by vacuum electrodeposition." *J. Membrane Sci.*, 153, (1999), 163.
- [52] Itoh, N.; Xu, W. C.; Sathe, A. M. "Capability of Permeate Hydrogen through Palladium- Based Membranes for Acetylene Hydrogenation." *Ind. & Eng. Chem. Res.* (1993), 32, 2614.
- [53] McCool, B.; Xomeritakis, G.; Lin, Y. S. "Composition control and hydrogen permeation characteristics of sputter deposited palladium-silver membranes." *J. Membrane Sci.*, 161 (1999), 67-76.
- [54] Shu, J.; Grandjean, B. P. A.; Kaliaguine, S. "Methane steam reforming in asymmetric Pd and Pd-Ag/porous SS membrane reactors." *Appl. Catalysis A: General*, 119 (1994), 305.
- [55] Fort, D.; Harris, I. R., "The physical properties of some palladium alloy hydrogen diffusion membrane materials." *Less-Common Met.*, 41 (1975), 313.
- [56] Hughes, D. T.; Harris, I. R., "A comparative study of Hydrogen permeabilities and solubilities in some Palladium solid solution alloys." *Less-Common Met.*, 61 (1978), 9.
- [57] L'Argentiere, P. C. and Figoli, N. S. "Tungsten-Palladium selective hydrogenation catalysts." *Catalysis Lett.*, 53 (1998), 149-153.
- [58] Grashoff, G. J.; Pilkington, C. E.; Corti, C. W. "The Purification of Hydrogen: A Review of the Technology Emphasizing the Current Status of Palladium Membrane Diffusion." *Platinum Met. Rev.*, 27 (1983), 157-169.
- [59] Knapton, A. G. "Palladium Alloys for Hydrogen Diffusion Membranes." *Platinum Met. Rev.*, 21 (1977), 44.
- [60] Zetkin, A. S.; Kagan, G. E.; Varaksin, A. N.; Levin, E. S., "Diffusion and penetrability of deuterium in the alloy Pd-53 at % Cu." *Soviet Physics, Solid State*, 34 (1992), 83.
- [61] Flanagan, T. B.; Chisdes, D. M. "Solubility of hydrogen (1 atm, 298 K) in some copper/palladium alloys." *Solid State Comm.*, 16, (1975), 529.
- [62] Burch, R.; Buss, R. G. "Pressure-composition isotherms in the palladium copper hydrogen system." *Solid State Comm.*, 15 (1974), 407.
- [63] Levin, E. S.; Zetkin, A. S.; Kagan, G. E. "Solubility of deuterium in Pd-Cu alloys." *Russian Journal of Physical Chemistry*, 66 (1992), 465.
- [64] Piper, J. "Diffusion of Hydrogen in Copper-Palladium Alloys." *J. Appl. Phys.*, 37 (1966), 715.
- [65] Zetkin, A. S.; Kagan, G. Y.; Levin, Y. S. "Influence of Structural Transformations on the Diffusion Parameters of Deuterium in Palladium-Copper Alloys." *Phys. Met. Metall.*, 64 (1987), 130.
- [66] Kuranov, A. A.; Berseneva, F. N.; Sasinova, R. A.; Laptevskiy, A. S. "Ordering and the Mechanical Properties of Palladium-Copper Alloys." *Phys. Met. Metall.*, 56 (1983), 167.
- [67] Nam, S-E, and Lee, K.-H. "Hydrogen separation by Pd alloy composite membranes: introduction of diffusion barrier." *J. Mem. Sci.*, 192 (2001), 177-185.
- [68] Howard, B. H.; Killmeyer, R. P.; Rothenberger, K. S.; Cugini, A. V.; Morreale, B. D.; Enick, and R. M.; Bustamante, F. "Hydrogen permeance of palladium-copper alloy membranes over a wide range of temperatures and pressures." *J. Mem. Sci.*, 241 (2004), 207.
- [69] Gao, H.; Lin, Y. S.; Li, Y.; and Zhang, B., "Electroless plating synthesis, characterization and permeation properties of Pd-Cu membranes supported on ZrO<sub>2</sub> modified porous stainless steel." *J. Mem. Sci.*, 265 (2005), 142-152.
- [70] Zhang, X., Wang, W., Liu, J., Sheng, Sh., Xiong, G., and Yang, W. "Hydrogen transport through thin palladium-copper alloy composite membranes at low temperatures." *Thin Solid Films*, 516 (2008), 1849-1856.
- [71] Mathieu, M.-V. and Primet, M. "Sulfurization and Regeneration of Platinum." *Appl. Catalysis*, 9 (1984), 361-370.
- [72] Chen, Y. Chen, Y., Li, W., and Sheng, Sh. "Sulphur-Resistant Character of Titania-Supported Platinum Catalysts," *Appl. Catalysis*, 63 (1990), 107-115.
- [73] Deng, Y., Nevell, T.G., Ewen, R. J., Honeybourne, C. L., and Jones, M. G. "Sulfur Poisoning, Recovery and Related Phenomena over Supported Palladium, Rhodium and Iridium Catalysts for Methane Oxidation," *Appl. Catalysis A: General*, 101 (1993), 51-62.
- [74] Antoniazzi, A. B.; Haasz, A. A.; and Stangeby, P. C. "The effect of adsorbed carbon and sulphur on hydrogen permeation through palladium." *J. Nuclear Materials*, 162-164 (1989), 1065-1070.
- [75] Hurlbert, R. C.; Konecny, J. O., "Diffusion of Hydrogen through Palladium." *J. Chem. Physics*, 34, (1961), 655.
- [76] Lalauze, R.; Gillard, P.; Pijolat, C., Hydrogen permeation through a thin film of palladium: influence of surface impurities. *Sensors and Actuators*, 14, (1988), 243.
- [77] Edlund, D. J. and Pledger, W. A. "Thermolysis of hydrogen sulfide in a metal-membrane reactor." *J. Mem. Sci.*, 77, (1993), 255.
- [78] Edlund, D.; Friesen, D.; Johnson, B.; and Pledger, W. "Hydrogen-permeable Metal membranes for high-temperature gas separations." *Gas Sep. & Purif.*, 8, (1994), 131.
- [79] Kajiwara, M.; Uemiyu, S.; and Kojima, T., "Stability and hydrogen permeation behavior of supported platinum membranes in presence of hydrogen sulfide," *Intern. J. Hydrogen Energy*, 24 (1999), 839.
- [80] Kulprathipanja, A.; Alptekin, G. O.; Falconer, J. L.; and Way, J. D., "Pd and Pd-Cu membranes: inhibition of H<sub>2</sub> permeation by H<sub>2</sub>S." *J. Mem.Sci.*, 254 (2005), 49-62.
- [81] Ackerman, F. J. and Koskinas, G. J., "Permeation of hydrogen and deuterium through palladium-silver alloys," *J. of Chem. & Eng. Data*, 17, (1972), 51-55.
- [82] Darling, A. S., "Hydrogen separation by diffusion through palladium alloy membranes" *Symposium on the less common means of separation. Institution of Chemical Engineers*, 1963.
- [83] Philpott, J. and Coupland, D. R. "Metal Membranes for Hydrogen Diffusion and Catalysis." *Hydrogen Effects in Catalysis*, (1988), 679.
- [84] Ali, J. K.; Newson, E. J.; and Rippin, D. W. T., "Deactivation and regeneration of Pd-Ag membranes for dehydrogenation reactions." *J. Mem. Sci.*, 89 (1994), 171.
- [85] Edlund, D. J. and Henry, H., "A membrane process for hot gas clean-up and decomposition of H<sub>2</sub>S to elemental sulfur." (Phase II Final Report, US DOE DE-FG03-91ER81228, 1996).
- [86] Morreale, B. D.; Ciocco, M. V.; Howard, B. H.; Killmeyer, R. P.; Cugini, A. V.; Enick, R. M., "Effect of hydrogen-sulfide on the hydrogen permeance of palladium-copper alloys at elevated temperatures." *J. Mem. Sci.*, 241, (2004), 219.
- [87] Way, J. D. and Thoen, P. M., "Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation" (Final Technical Report to US DOE Grant DE-FG26-03NT41792, 2006).
- [88] Way, J. D., Lusk, M., and Thoen, P. M., "Sulfur-Resistant Composite Metal Membranes" (WIPO Patent Application WO/2008/027646, 2008).
- [89] Roa, F., Thoen, P.M., Gade, S.K., Way, J.G., De Voss, S., and Alptekin, G., "Palladium-Copper and palladium-gold alloy composite membranes for hydrogen separations." A.C. Bose (ed.), *Inorganic Membranes for Energy and Environmental Applications* (DOI 10.1007/978-0-387-34526-0 12, Springer Science + Business Media, LLC 2009, Chapter 12, pp. 221, 2009).

- [90] Loboda-Cackovic, J., "Segregation Processes in a PdCu(110) and the Effects of Sulphur Impurity on Surface Composition and Microstructure from Annealing." *Vacuum*, 48 (1997), 913-923.
- [91] Fischer, T. E. and Kelemen, S. R., "Model Experiments on the Poisoning of Pt Catalysts by Sulfur," *J. Catalysis*, 53 (1978), 24-34
- [92] Rostrup-Nielsen, J. R., "Chemisorption of hydrogen Sulfide on a Supported Nickel Catalyst," *J. Catalysis* (1968), 11, 220.
- [93] Oliphant, J. L., Fowler, R. W., Pannell, R. B., and Bartholomew, C. H., "Chemisorption of hydrogen Sulfide on Nickel and Ruthenium Catalysts: I. Desorption Isotherms," *J. Catalysis*, 51 (1971), 229-242.
- [94] Campbell, Ch. T. and Koel, B. E. "H<sub>2</sub>S/Cu(111): A Model Study of Sulfur Poisoning of Water-Gas Shift Catalysts," *Surf. Sci.*, 183 (1987), 100-112.
- [95] Burke, M. L. and Madix, R. J., "Hydrogen on Pd(100)-S: the effect of sulfur on precursor mediated adsorption and desorption." *Surf. Sci.*, 237, (1990), 1-19.
- [96] Forbes, J. G.; Gellman, A. J.; Dunphy, J. C.; and Salmeron, M., "Imaging of sulfur overlayer structures on the Pd(111) surface." *Surf. Sci.*, 279 (1992), 68-78.
- [97] Vazquez, A.; Pedraza, F.; and Fuentes, S. "Influence of sulfidation on the morphology and hydrodesulfurization activity of palladium particles on silica." *J. Molec. Catalysis*, 75, (1992), 63.
- [98] Feuerriegel, U.; Klose, W.; Sloboshanin, S.; Goebel, H.; and Schaefer, J. A., "Deactivation of a Palladium-Supported Alumina Catalyst by Hydrogen Sulfide during the Oxidation of Methane." *Langmuir*, 10, (1994), 3567.
- [99] Rutkowski, M.; D. Wetzig, D.; and Zacharias, H., "Mechanism of the Poisoning Action Of Sulfur on Catalytically Active Pd(100)." *Phys. Review Let.*, 87 (2001), 246101-1 to 246101-4.
- [100] Miller, J. B.; Morreale, B. D.; and Gellman, A. J. "The Effect of Adsorbed Sulfur Segregation in a Polycrystalline Pd<sub>70</sub>Cu<sub>30</sub> Alloy." *Surf. Sci.*, 602 (2008), 1819-1825.
- [101] Grillo, M. E.; Stampfl, C.; and Berndt, W., "Low-energy electron diffraction analysis of the ( $\sqrt{7} \times \sqrt{7}$ ) R19.1°-S adsorbate structure on the Pd(111) surface." *Surf. Sci.*, 317 (1994), 84-98.
- [102] Speller, S.; Rauch, T.; Bömermann, J.; Borrmann, P.; and Heiland, W. "Surface structures of S on Pd (111)." *Surf. Sci.*, 441 (1999), 107-116.
- [103] Bömermann, J.; Huck, M.; Kuntze, J.; Rauch, T.; Speller, S.; and Heiland, W., "An STM, AES and LEED study of the segregated sulfur on Pd (111)." *Surf. Sci.*, 357/358 (1996), 849-854.
- [104] Mundschaum, M.; Xie, X.; C.R. Evenson, C. R.; and Sammells, A. F., "Dense inorganic membranes for production of hydrogen from methane and coal with carbon dioxide sequestration." *Catalysis Today*, 118, (2006) 12-23.
- [105] Iyoha, O.; Enick, R.; Killmeyer, R.; and Morreale, B. D., "The Influence of Hydrogen Sulfide-to-Hydrogen Partial Pressure Ratio on the Sulfidization of Pd and 70mol% Pd-Cu Membranes." *J. Mem. Sci.*, 305 (2007), 77-92.
- [106] Barin, I.; Sauert, F.; Schultze-Rhonhof, E.; and Sheng, W. "Thermodynamic properties of inorganic substances" (VCH: Weinheim, Germany, 1993).
- [107] Pomerantz, N.; and Ma, Y. H., "Effect of H<sub>2</sub>S on the Performance and Long-Term Stability of Pd-Cu Membranes." *Ind. Eng. Chem. Res.*, 48, 4030-4039, 2009.
- [108] Cheng, Ch.-H. and Ma, Y. H., "Characterization of Sulfur Resistance of Pd-Au Hydrogen Separation Membranes Prepared by Galvanic Displacement." *Presented at the 2008 AIChE Annual Meeting, Philadelphia, PA. November 17-21, 2008.*
- [109] Kamakoti, P. and Sholl, D. S., "A comparison of hydrogen diffusivities in Pd and Cu-Pd alloys using density functional theory." *J. Mem. Sci.*, 225 (2003), 145-154.
- [110] Kamakoti, P. and Sholl, D. S., "Ab initio lattice-gas modeling of interstitial hydrogen diffusion in Cu-Pd alloys." *Phys. Review B*, 71 (2005), 01430.
- [111] Kamakoti, P.; Morreale, B. D.; Ciocco, M. V.; Howard, B. H.; Killmeyer, R. P.; Cugini, A. V.; and Sholl, D. S., "Prediction of Hydrogen Flux Through Sulfur-Tolerant Binary Alloy Membranes." *Science*, 307, (2005), 569-573.
- [112] Ling, Ch. and Sholl, D. S., "Using First Principles Calculations to Predict Surface Resistances to H<sub>2</sub> Transport through Metal Alloy Membranes." *J. Mem. Sci.*, 303 (2007), 162-173.
- [113] Semidey-Flecha, L. and Sholl, D. S., "Combining density functional theory and cluster expansion methods to predict H<sub>2</sub> permeance through Pd-based binary alloy membranes." *J. Chem. Physics*, 128 (2008), 144701.
- [114] Gabitto, J. F. and Tsouris, C., "Sulfur Poisoning Mechanisms in Metallic Membranes." *Unpublished results*, 2009.
- [115] Wilke, M. and Scheffler, M., "Poisoning of Pd(100) for the dissociations of H<sub>2</sub>: a theoretical study of co-adsorption of hydrogen and sulphur." *Surf. Sci. Let.*, 329 (1995), L605-L610.
- [116] Dreizler, R. and Gross, E., "Density Functional Theory" (Plenum Press, New York, 1995).
- [117] Kohanoff, J., "Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods" (Cambridge University Press, 2006).
- [118] Dong, W.; Kresse, G.; and Hafner, J., "Dissociative Adsorption of H<sub>2</sub> on the Pd(111) Surface." *J. Molec. Catalysis A: Chemical*, 110 (1997), 69-76.
- [119] Wei, C. M.; Groß, A.; and Scheffler, M., "Ab initio calculation of the potential energy surface for the dissociation of H<sub>2</sub> on the sulfur-covered Pd(100) surface." *Phys. Rev. B*, 57 (1998), 15572-15584.
- [120] Gravil, P. A. and Toulhoat, H., "Hydrogen, sulphur and chlorine coadsorption on Pd(111): A theoretical study of poisoning and promotion." *Surface Science*, 430, (1999), 176.
- [121] Alfonso, D., Cugini, A., and Sholl, D., "Density functional theory studies of sulfur binding on Pd, Cu-Pd alloys." *Surf. Sci.*, 546 (2003), 12.
- [122] Alfonso, D., "First-principle study of sulfur overlayers on Pd (111) surface." *Surf. Sci.*, 596 (2005), 229-241.
- [123] Alfonso, D., Cugini, A., and Sorescu, D., "Adsorption and decomposition of H<sub>2</sub>S on Pd (111) surface: a first principle study." *Catalysis Today*, 99 (2005), 315.
- [124] Hyman, M. P.; Loveless, B. T.; and Medlin, J. W., "A Density Functional Theory study of H<sub>2</sub>S Decomposition on the (111) Surfaces of Model Pd-Alloys." *Surf. Sci.*, 601 (2007), 5382-5393.
- [125] Pillay, D. and Johannes, M. D., "Comparison of sulfur interaction with hydrogen on Pt(111), Ni(111) and Pt<sub>3</sub>Ni(111) surfaces: The effect of intermetallic bonding." *Surf. Sci.*, 603 (2008), 2752-2757.

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