



## The hydrogen permeability of Pd<sub>4</sub>S

Casey P. O'Brien<sup>a,b</sup>, Andrew J. Gellman<sup>a,b</sup>, Bryan D. Morreale<sup>a</sup>, James B. Miller<sup>a,b,\*</sup>

<sup>a</sup> National Energy Technology Laboratory, US Department of Energy, P.O. Box 10940, Pittsburgh, PA 15236, United States

<sup>b</sup> Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

### ARTICLE INFO

#### Article history:

Received 16 September 2010

Received in revised form

18 December 2010

Accepted 25 January 2011

Available online 1 February 2011

#### Keywords:

Palladium membrane

Hydrogen permeation

Sulfur corrosion

### ABSTRACT

Hydrogen permeates rapidly through pure Pd membranes, but H<sub>2</sub>S, a common minor component in hydrogen-containing streams, produces a Pd<sub>4</sub>S film on the Pd surface that severely retards hydrogen permeation. Hydrogen still permeates through the bi-layered Pd<sub>4</sub>S/Pd structure, indicating that the Pd<sub>4</sub>S surface is active for H<sub>2</sub> dissociation; the low hydrogen permeability of the Pd<sub>4</sub>S film is responsible for the decreased rate of hydrogen transport. In this work, the hydrogen permeability of Pd<sub>4</sub>S was determined experimentally in the 623–773 K temperature range. Bi-layered Pd<sub>4</sub>S/Pd foils were produced by exposing pure Pd foils to H<sub>2</sub>S. H<sub>2</sub> fluxes through the bi-layered Pd<sub>4</sub>S/Pd foils were measured during exposure to both pure H<sub>2</sub> and a 1000 ppm H<sub>2</sub>S in H<sub>2</sub> gas mixture. Our results show that H<sub>2</sub>S slows hydrogen permeation through Pd mainly by producing a Pd<sub>4</sub>S film on the Pd surface that is roughly an order-of-magnitude less permeable to hydrogen ( $k_{Pd_4S} = 10^{-7.5} \exp(-0.22 \text{ eV}/k_B T) \text{ molH}_2/\text{m}^2/\text{s}/\text{Pa}^{1/2}$ ) than pure Pd. The presence of H<sub>2</sub>S in the gas stream results in greater inhibition of hydrogen transport than can be explained by the very low permeability of Pd<sub>4</sub>S. H<sub>2</sub>S may block H<sub>2</sub> dissociation sites at the Pd<sub>4</sub>S surface.

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### 1. Introduction

Carbonaceous feeds, including coal, biomass and natural gas, can be used to produce affordable supplies of H<sub>2</sub> for use as a clean fuel or as a chemical commodity. Such supplies of H<sub>2</sub> must be separated from a gas stream composed primarily of H<sub>2</sub> and CO<sub>2</sub>. Dense Pd membranes, which dissociatively adsorb H<sub>2</sub> [1–3] and allow only atomic H to permeate through their bulk [4–8], can be used to separate very high purity H<sub>2</sub> from H<sub>2</sub>/CO<sub>2</sub> mixtures. However, coal gasification also produces H<sub>2</sub>S, a highly corrosive gas that can react with Pd to form Pd<sub>4</sub>S [9–13] via the reaction:



The H<sub>2</sub> flux across Pd membranes decreases rapidly during H<sub>2</sub>S exposure [9–11]. Morreale et al. [10] correlated the decay in H<sub>2</sub> flux during H<sub>2</sub>S exposure to the Pd<sub>4</sub>S growth kinetics measured under similar conditions. In doing so, they suggested that the decay in H<sub>2</sub> flux was due to the growth of a Pd<sub>4</sub>S film on the Pd surface which has a H<sub>2</sub> permeability more than an order-of-magnitude lower than that of Pd.

In this work, the H<sub>2</sub> permeability of Pd<sub>4</sub>S has been determined directly, rather than by correlation to Pd<sub>4</sub>S growth, by measuring H<sub>2</sub> transport across bi-layered Pd<sub>4</sub>S/Pd foils with known Pd<sub>4</sub>S

and Pd thicknesses. To our knowledge, this work represents the first direct measurements of the hydrogen permeability of Pd<sub>4</sub>S. Our results suggest that H<sub>2</sub>S inhibits hydrogen transport across Pd membranes primarily by producing a low permeability Pd<sub>4</sub>S film on the Pd surface; however, H<sub>2</sub>S in the feed gas also appears to lower the H<sub>2</sub> flux directly, possibly by blocking H<sub>2</sub> dissociation sites on the membrane surface.

### 2. Experimental

The method for measuring H<sub>2</sub> transport through metallic foil membranes has been described in a previous publication [9]. Briefly, 25 μm thick Pd foil disks (99.9% metals purity, Alfa Aesar) with an effective membrane surface area of ~1.8 cm<sup>2</sup> were mounted in the membrane testing apparatus and heated to 623 K in inert gases. Pd<sub>4</sub>S films were produced on the surface of Pd foils by exposure to a gas mixture with a composition of 1000 ppm H<sub>2</sub>S/10% He/H<sub>2</sub> (Butler Gas Products, Inc.) at a total pressure of 269 kPa and a temperature of 623 K. The H<sub>2</sub>S exposure time varied from ~5 min for the thin (1 μm) Pd<sub>4</sub>S films to ~24 h for the thicker (>15 μm) Pd<sub>4</sub>S films. The bi-layered Pd<sub>4</sub>S/Pd membranes were then exposed to either pure H<sub>2</sub> (99.99%, Butler Gas Products, Inc.) or the 1000 ppm H<sub>2</sub>S in H<sub>2</sub> gas mixture while H<sub>2</sub> permeate flow rates were measured with a bubble flowmeter (Alltech Digital Flowmeter Model 4074) at ambient pressure. H<sub>2</sub> fluxes did not change over the course of the measurements (~30 min) and, therefore, the Pd<sub>4</sub>S thicknesses were assumed to be constant. Following membrane testing, cross-sections of the bi-layered Pd<sub>4</sub>S/Pd foils were mounted in epoxy

\* Corresponding author at: Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States. Tel.: +1 412 268 9517.

E-mail address: [jbmiller@andrew.cmu.edu](mailto:jbmiller@andrew.cmu.edu) (J.B. Miller).

and polished up to 1200 grit. The Pd<sub>4</sub>S and Pd thicknesses were measured from the cross-sections by optical microscopy (Keyence VHX-1000) and scanning electron microscopy (Aspex Personal SEM 2000, 20 keV beam energy) with sulfur energy dispersive spectroscopy mapping to highlight the Pd<sub>4</sub>S film.

### 3. Diffusion model for extraction of permeabilities

Fick's first law of diffusion governs H atom transport through dense Pd membranes according to

$$J_H = \frac{D_{Pd}(c_1 - c_2)}{x_{Pd}} \quad (1)$$

where  $J_H$  is the steady-state H atom flux,  $D_{Pd}$  is the diffusivity of H atoms in Pd,  $c_1$  and  $c_2$  are the H atom concentrations in Pd near the high-pressure (retentate) and low pressure (permeate) surfaces, respectively, and  $x_{Pd}$  is the thickness of the Pd membrane. If the H atoms dissolved in Pd are in equilibrium with gas-phase H<sub>2</sub>, then Sievert's law relates the concentrations  $c_1$  and  $c_2$  to the retentate and permeate H<sub>2</sub> partial pressures by Eqs. (2) and (3), respectively:

$$c_1 = S_{Pd}P_{H_2,ret}^{1/2} \quad (2)$$

$$c_2 = S_{Pd}P_{H_2,perm}^{1/2} \quad (3)$$

where  $S_{Pd}$  is the solubility of H atoms in Pd,  $P_{H_2,ret}$  is the retentate H<sub>2</sub> partial pressure and  $P_{H_2,perm}$  is the permeate H<sub>2</sub> partial pressure. Substitution of Eqs. (2) and (3) into Fick's first law of diffusion, Eq. (1), gives:

$$J_H = \frac{D_{Pd}S_{Pd}\Delta P_{H_2}^{1/2}}{x_{Pd}} \quad (4)$$

where

$$\Delta P_{H_2}^{1/2} = P_{H_2,ret}^{1/2} - P_{H_2,perm}^{1/2}$$

Defining the H atom permeability (2 H atom basis) of Pd,  $k_{Pd}$ , as:

$$k_{Pd} = \frac{D_{Pd}S_{Pd}}{2} \quad (5)$$

and substituting Eq. (5) into Eq. (4) gives the steady-state H<sub>2</sub> flux through Pd,  $J_{H_2}$ :

$$J_{H_2} = \frac{k_{Pd}\Delta P_{H_2}^{1/2}}{x_{Pd}} \quad (6)$$

H<sub>2</sub> transport across composite membranes has been well described in other publications [10,14–17], and the H<sub>2</sub> flux across a bi-layered Pd<sub>4</sub>S/Pd foil can be modeled by Eq. (7) if H-atom diffusion is rate-limiting [10]:

$$J_{H_2} = \frac{\Delta P_{H_2}^{1/2}}{(x_{Pd_4S}/k_{Pd_4S}) + (x_{Pd}/k_{Pd})} \quad (7)$$

where  $k_{Pd_4S}$  is the H atom permeability (2 H atom basis) of Pd<sub>4</sub>S and  $x_{Pd_4S}$  is the thickness of the Pd<sub>4</sub>S film. If H atom diffusion through a bi-layered Pd<sub>4</sub>S/Pd foil is rate-limiting, then the H<sub>2</sub> flux should be directly proportional to  $\Delta P_{H_2}^{1/2}$  with a slope that can be used to calculate the permeability of Pd<sub>4</sub>S if the permeability of Pd is known and the Pd<sub>4</sub>S and Pd thicknesses are known.

### 4. Results and discussion

H<sub>2</sub> fluxes across a pure Pd foil were measured to determine the H atom permeability of Pd. Fig. 1 shows the H<sub>2</sub> fluxes across a 25 μm thick Pd foil during exposure to pure H<sub>2</sub> in the 623–973 K temperature range. As expected, H<sub>2</sub> fluxes across the Pd foil increased with increasing pressure and temperature. Using Eq. (6) and the slopes of the fitted solid lines in Fig. 1, the H atom permeability (2 H atom

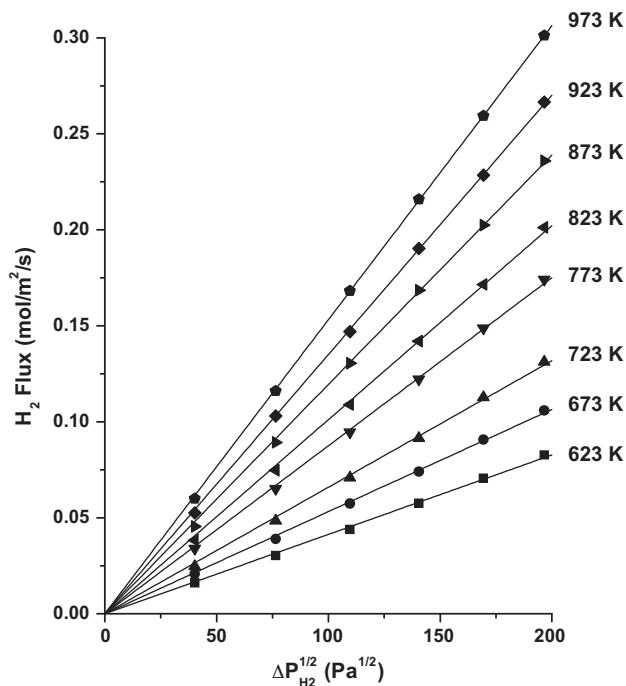


Fig. 1. H<sub>2</sub> fluxes across a 25 μm thick pure Pd foil during exposure to pure H<sub>2</sub> in the 623–973 K temperature range. The H<sub>2</sub> partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated H<sub>2</sub> was collected at ambient (101 kPa) pressure. The H<sub>2</sub> fluxes across the Pd foil increase monotonically with temperature.

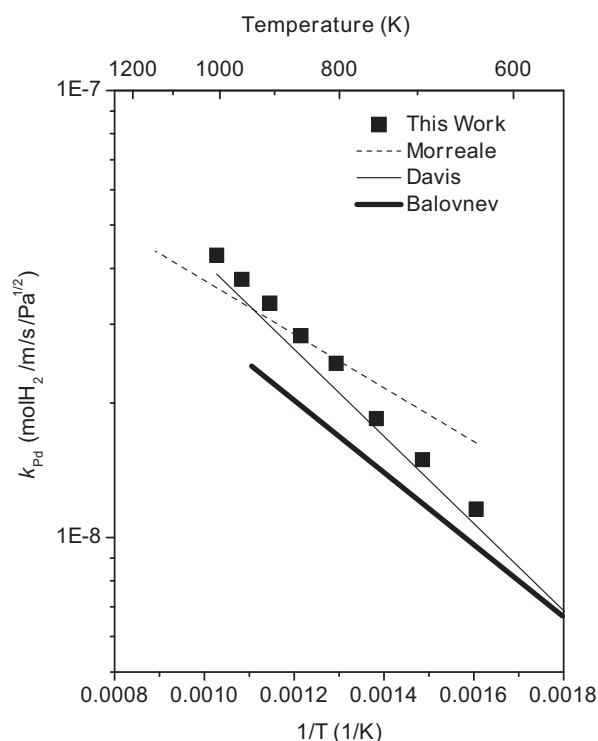
basis) of Pd ( $k_{Pd}$ ) was calculated at each temperature and was fit to an Arrhenius expression:

$$k_{Pd} = 10^{-6.33 \pm 0.03} \exp\left(\frac{(-0.199 \pm 0.004) \text{ eV}}{k_B T}\right) \text{ molH}_2 / (\text{m s Pa}^{1/2}) \quad (8)$$

where  $T$  (K) is the temperature and  $k_B$  is the Boltzmann constant. Fig. 2 illustrates that our results for the H atom permeability of Pd are consistent with previous literature reports [8,18,19].

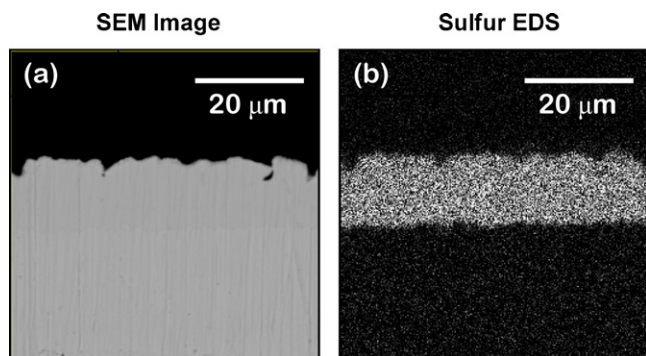
The effect of Pd<sub>4</sub>S film thickness on the H<sub>2</sub> flux across Pd<sub>4</sub>S/Pd foils was investigated by measuring H<sub>2</sub> fluxes across Pd<sub>4</sub>S/Pd foils with various Pd<sub>4</sub>S film thicknesses. Pd<sub>4</sub>S films were produced by exposing the upstream surface of pure Pd foils to a 1000 ppm H<sub>2</sub>S/10% He/H<sub>2</sub> gas mixture at a total pressure of 269 kPa and a temperature of 623 K in the membrane testing apparatus. The H<sub>2</sub>S exposure time varied from ~5 min for the thin (~1 μm) Pd<sub>4</sub>S films to ~24 h for the thicker (~14 μm) films. Fig. 3 shows a scanning electron micrograph and a S energy dispersive X-ray spectroscopy map of a cross section of a Pd<sub>4</sub>S/Pd foil with a ~14 μm thick Pd<sub>4</sub>S film. The Pd<sub>4</sub>S films were fairly uniform over the entire surface of the Pd substrates. H<sub>2</sub> fluxes were measured using pure H<sub>2</sub> to prevent Pd<sub>4</sub>S growth during measurements and to eliminate the effects of H<sub>2</sub>S on H<sub>2</sub> transport; H<sub>2</sub> fluxes did not vary over the course of the measurements (~30 min) and, therefore, the Pd<sub>4</sub>S thicknesses can be assumed to be constant throughout the experiment. Following membrane testing, the Pd<sub>4</sub>S film thicknesses were measured by cross-sectional optical microscopy of the Pd<sub>4</sub>S/Pd foils. Fig. 4 shows the H<sub>2</sub> fluxes across Pd<sub>4</sub>S/Pd foils with Pd<sub>4</sub>S thicknesses of 0 (pure Pd), 1, 2, 6, and 14 μm at 623 K. Due to the low permeability of Pd<sub>4</sub>S relative to Pd, the H<sub>2</sub> fluxes decrease as the Pd<sub>4</sub>S thickness increases.

To determine whether H<sub>2</sub>S inhibits H<sub>2</sub> transport across Pd<sub>4</sub>S/Pd by factors in addition to the presence of the Pd<sub>4</sub>S film, H<sub>2</sub> fluxes across Pd<sub>4</sub>S/Pd foils were measured during exposure to a 1000 ppm H<sub>2</sub>S/10% He/H<sub>2</sub> gas mixture. Fig. 5 shows the H<sub>2</sub> fluxes across a 14 μm Pd<sub>4</sub>S/Pd foil during exposure to both pure H<sub>2</sub> and a 1000 ppm

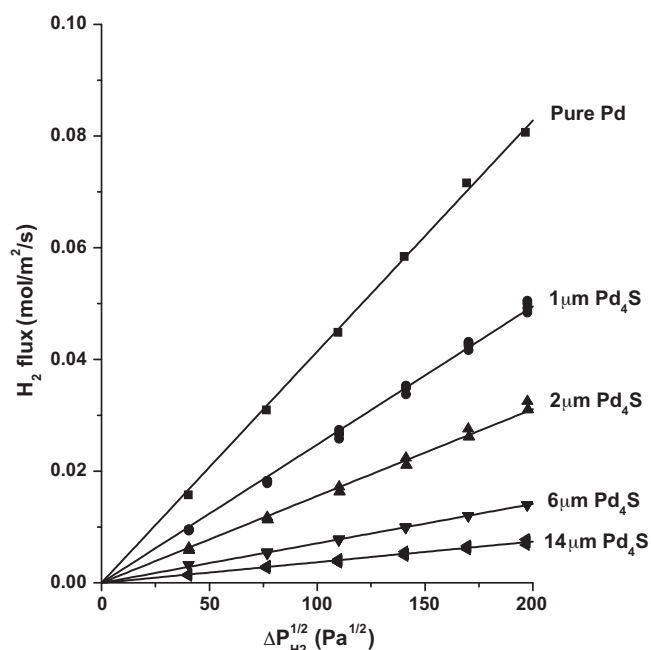


**Fig. 2.** Comparison of the H atom permeability (2 H atom basis) of Pd measured in this work (solid squares) to the work of Morreale [8], Davis [18], and Balovnev [19]. Our measurements for the H atom permeability of Pd are in good agreement with these literature reports.

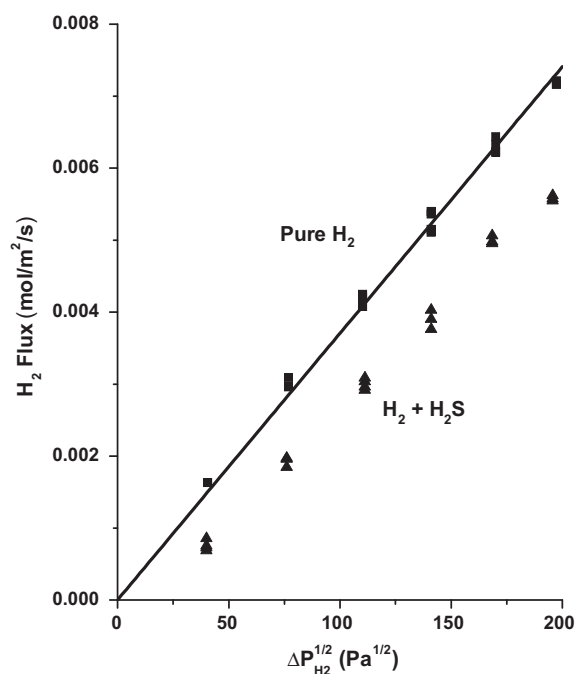
$\text{H}_2\text{S}/10\% \text{He}/\text{H}_2$  feed gas mixture at 623 K. In both pure  $\text{H}_2$  and in the  $\text{H}_2\text{S}/\text{H}_2$  gas mixture,  $\text{H}_2$  fluxes did not change significantly over the course of the measurements ( $\sim 30$  min); therefore, the  $\text{Pd}_4\text{S}$  thickness can be assumed to be constant throughout the experiment. At all  $\text{H}_2$  pressures, the  $\text{H}_2$  fluxes across the  $14 \mu\text{m}$   $\text{Pd}_4\text{S}/\text{Pd}$  foil were significantly lower in the 1000 ppm  $\text{H}_2\text{S}$  in  $\text{H}_2$  gas mixture than in pure  $\text{H}_2$ .  $\text{H}_2$  fluxes across bi-layered  $\text{Pd}_4\text{S}/\text{Pd}$  foils were also measured at 673 K with a  $\sim 14 \mu\text{m}$   $\text{Pd}_4\text{S}$  film, 723 K with a  $\sim 19 \mu\text{m}$   $\text{Pd}_4\text{S}$  film, and 773 K with a  $\sim 22 \mu\text{m}$   $\text{Pd}_4\text{S}$  film, both in pure  $\text{H}_2$  and in the 1000 ppm  $\text{H}_2\text{S}/10\% \text{He}/\text{H}_2$  feed gas mixture. At all temperatures and  $\text{Pd}_4\text{S}$  film thicknesses, the  $\text{H}_2$  fluxes across the bi-layered  $\text{Pd}_4\text{S}/\text{Pd}$  foils were lower in the  $\text{H}_2\text{S}/\text{H}_2$  gas mixture than in pure  $\text{H}_2$ . Given the relatively low  $\text{H}_2$  fluxes, the low He concentration, and



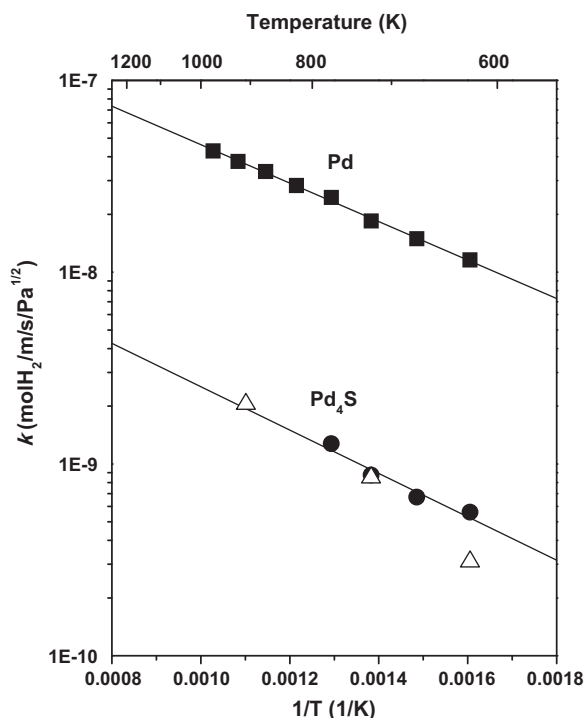
**Fig. 3.** (a) Scanning electron micrograph (SEM) and (b) sulfur energy dispersive spectroscopy (EDS) map of a cross-section of a  $\text{Pd}_4\text{S}/\text{Pd}$  foil with a  $\sim 14 \mu\text{m}$  thick  $\text{Pd}_4\text{S}$  film. The  $\text{Pd}_4\text{S}$  film was produced by exposing the upstream surface of the Pd foil to a 1000 ppm  $\text{H}_2\text{S}/10\% \text{He}/\text{balance } \text{H}_2$  gas mixture in the membrane testing apparatus at a total pressure of  $\sim 269$  kPa and a temperature of 623 K for  $\sim 24$  h. The white region in the sulfur EDS map highlights the sulfur-rich  $\text{Pd}_4\text{S}$  region in the SEM image. The  $\text{Pd}_4\text{S}$  film is fairly uniform over the entire surface area of the Pd foil.



**Fig. 4.**  $\text{H}_2$  fluxes across bi-layered  $\text{Pd}_4\text{S}/\text{Pd}$  foils with  $\text{Pd}_4\text{S}$  thicknesses of 0 (pure Pd), 1, 2, 6, and  $14 \mu\text{m}$  during exposure to pure  $\text{H}_2$  at 623 K.  $\text{Pd}_4\text{S}$  films were produced on the surface of Pd by exposure to 1000 ppm  $\text{H}_2\text{S}/10\% \text{He}/\text{H}_2$  at 623 K and a total pressure of 269 kPa.  $\text{H}_2\text{S}$  exposure times varied from  $\sim 5$  min for the  $1 \mu\text{m}$   $\text{Pd}_4\text{S}$  film to  $\sim 24$  h for the  $14 \mu\text{m}$   $\text{Pd}_4\text{S}$  film. The  $\text{H}_2$  partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated  $\text{H}_2$  was collected at ambient (101 kPa) pressure.  $\text{H}_2$  fluxes decrease as the  $\text{Pd}_4\text{S}$  thickness increases due to the low permeability of  $\text{Pd}_4\text{S}$  relative to Pd.



**Fig. 5.**  $\text{H}_2$  fluxes across a  $14 \mu\text{m}$   $\text{Pd}_4\text{S}/\text{Pd}$  foil at 623 K during exposure to pure  $\text{H}_2$  and a 1000 ppm  $\text{H}_2\text{S}/10\% \text{He}/\text{H}_2$  gas mixture ( $\text{H}_2 + \text{H}_2\text{S}$ ). The  $\text{H}_2$  partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated  $\text{H}_2$  was collected at ambient (101 kPa) pressure.  $\text{H}_2$  fluxes across the  $14 \mu\text{m}$   $\text{Pd}_4\text{S}/\text{Pd}$  foil are significantly lower in the  $\text{H}_2 + \text{H}_2\text{S}$  gas mixture than in the pure  $\text{H}_2$  feed gas which could possibly be due to  $\text{H}_2\text{S}$  blocking  $\text{H}_2$  dissociation sites.



**Fig. 6.** Comparison of the H atom permeability (2 H atom basis) of Pd (closed squares) and the H atom permeability (2 H atom basis) of Pd<sub>4</sub>S measured in this work (closed circles) and in the work of Morreale (open triangles) [10]. The H atom permeability of Pd<sub>4</sub>S was measured using bi-layered Pd<sub>4</sub>S foils with Pd<sub>4</sub>S thicknesses of ~14 μm at 623 K, ~14 μm at 673 K, ~19 μm at 723 K, and ~22 μm at 773 K. The solid fitted lines for the H atom permeability of Pd and Pd<sub>4</sub>S are described by Eqs. (8) and (9), respectively.

the low H<sub>2</sub>S concentration, gas-phase hydrogen transport near the surface of the membranes (i.e., concentration polarization) is probably not the cause of the reduced H<sub>2</sub> flux in the 1000 ppm H<sub>2</sub>S/10% He/H<sub>2</sub> feed gas relative to that in the pure H<sub>2</sub> feed gas. Therefore, H<sub>2</sub>S probably inhibits one or more molecular processes at the Pd<sub>4</sub>S surface. H<sub>2</sub>S may inhibit the H<sub>2</sub> dissociation reaction by blocking H<sub>2</sub> adsorption sites or by increasing the barrier to H<sub>2</sub> dissociation. Alternatively, H<sub>2</sub>S may inhibit H-atom transport from the surface to the sub-surface of Pd<sub>4</sub>S.

During exposure to pure H<sub>2</sub> at varying pressure in the 623–773 K temperature range, the H<sub>2</sub> fluxes are directly proportional to  $\Delta P_{\text{H}_2}^{1/2}$  and intersect the origin, which indicates that H atom diffusion through the bulk of the foil is rate-limiting and that the Pd<sub>4</sub>S layer is essentially dense. Therefore, the H atom permeability of Pd<sub>4</sub>S can be calculated using Eq. (7). The temperature dependence of the H atom permeability (2 H atom basis) of Pd<sub>4</sub>S ( $k_{\text{Pd}_4\text{S}}$ ) is given by an Arrhenius expression:

$$k_{\text{Pd}_4\text{S}} = 10^{-7.5 \pm 0.2} \exp\left(\frac{(-0.22 \pm 0.03) \text{ eV}}{k_B T}\right) \text{ molH}_2 / (\text{m s Pa}^{1/2}) \quad (9)$$

where  $T$  (K) is the temperature and  $k_B$  is the Boltzmann constant. Fig. 6 is an Arrhenius plot that compares the H atom permeability (2 H atom basis) of Pd and Pd<sub>4</sub>S measured in this work and the H atom permeability of Pd<sub>4</sub>S determined by Morreale by correlation of Pd<sub>4</sub>S growth kinetics to H<sub>2</sub> permeability decay in the presence of H<sub>2</sub>S [10]. Except for the measurement made at 623 K, our results for the H atom permeability of Pd<sub>4</sub>S are in very good agreement with the experimental results reported by Morreale; the H atom permeability of Pd<sub>4</sub>S is about an order-of-magnitude lower than that of Pd. The small difference between our results and those of Morreale at 623 K may be due to the fact that the latter were determined from measurements made in the presence of H<sub>2</sub>S. As described earlier, in addition to reacting with Pd to form Pd<sub>4</sub>S, H<sub>2</sub>S may also

block H<sub>2</sub> dissociation sites on the Pd<sub>4</sub>S surface. In this work, the H atom permeability of Pd<sub>4</sub>S was determined from measurements of H<sub>2</sub> transport across bi-layered Pd<sub>4</sub>S/Pd foils during exposure to pure H<sub>2</sub>. For all of the bi-layered Pd<sub>4</sub>S/Pd foils from which the H atom permeability of Pd<sub>4</sub>S was measured, more than 90% of the total resistance to hydrogen transport was attributable to the Pd<sub>4</sub>S film and, therefore, our method for calculating the H atom permeability of Pd<sub>4</sub>S should be reasonably accurate. The good agreement between our results and the results from Morreale [10] illustrates that the decay in H<sub>2</sub> flux through a Pd foil during H<sub>2</sub>S exposure is mainly due to the growth of a low permeability Pd<sub>4</sub>S film on the Pd surface.

## 5. Conclusions

H<sub>2</sub>S degrades the performance of Pd H<sub>2</sub> separation membranes primarily by producing a Pd<sub>4</sub>S film, which has an intrinsic H atom permeability about an order-of-magnitude lower than that of Pd. In addition, H<sub>2</sub>S in the H<sub>2</sub> feed gas inhibits H<sub>2</sub> transport by a secondary mechanism that may involve blocking of H<sub>2</sub> dissociation sites. In this work, the H<sub>2</sub> permeability of Pd<sub>4</sub>S ( $k_{\text{Pd}_4\text{S}} = 10^{-7.5} \exp(-0.22 \text{ eV}/k_B T) \text{ molH}_2 / \text{m s Pa}^{1/2}$ ) was measured directly, rather than by correlation to Pd<sub>4</sub>S growth, by measuring H<sub>2</sub> transport across bi-layered Pd<sub>4</sub>S/Pd foils with known Pd<sub>4</sub>S and Pd thicknesses. To our knowledge, this work represents the first direct measurements of the hydrogen permeability of Pd<sub>4</sub>S.

## Acknowledgement

This technical effort was performed in support of the National Energy Technology Laboratory's on-going research in Computational and Basic Sciences under the RDS contract DE-AC26-04NT41817.

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