The hydrogen permeability of Pd₄S

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Abstract

Hydrogen permeates rapidly through pure Pd membranes, but H₂S, a common minor component in hydrogen-containing streams, produces a Pd₄S film on the Pd surface that severely retards hydrogen permeation. Hydrogen still permeates through the bi-layered Pd₄S/Pd structure, indicating that the Pd₄S film is responsible for the decreased rate of hydrogen transport. In this work, the hydrogen permeability of Pd₄S was determined experimentally in the 623-773 K temperature range. Bi-layered Pd₄S/Pd foils were produced by exposing pure Pd foils to H₂S. H₂ fluxes through the bi-layered Pd₄S/Pd foils were measured during exposure to both pure H₂ and a 1000 ppm H₂S in H₂ gas mixture. Our results show that H₂S slows hydrogen permeation through Pd mainly by producing a Pd₄S film on the Pd surface that is roughly an order-of-magnitude less permeable to hydrogen (kₘ₄S ~ 10⁻¹² exp(−0.22 eV/k₅T) molH₂/m/s/Pa¹/₂) than pure Pd. The presence of H₂S in the gas stream results in greater inhibition of hydrogen transport than can be explained by the very low permeability of Pd₄S. H₂S may block H₂ dissociation sites at the Pd₄S surface.

Keywords:
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1. Introduction

Carbonaceous feeds, including coal, biomass and natural gas, can be used to produce affordable supplies of H₂ for use as a clean fuel or as a chemical commodity. Such supplies of H₂ must be separated from a gas stream composed primarily of H₂ and CO₂. Dense Pd membranes, which dissociatively adsorb H₂ [1–3] and allow only atomic H to permeate through their bulk [4–8], can be used to separate very high purity H₂ from H₂/CO₂ mixtures. However, coal gasification also produces H₂S, a highly corrosive gas that can react with Pd to form Pd₄S [9–13] via the reaction:

4Pd + H₂S ↔ Pd₄S + H₂.

The H₂ flux across Pd membranes decreases rapidly during H₂S exposure [9–11]. Morreale et al. [10] correlated the decay in H₂ flux during H₂S exposure to the Pd₄S growth kinetics measured under similar conditions. In doing so, they suggested that the decay in H₂ flux was due to the growth of a Pd₄S film on the Pd surface which has a H₂ permeability more than an order-of-magnitude lower than that of Pd.

In this work, the H₂ permeability of Pd₄S has been determined directly, rather than by correlation to Pd₄S growth, by measuring H₂ transport across bi-layered Pd₄S/Pd foils with known Pd₄S and Pd thicknesses. To our knowledge, this work represents the first direct measurements of the hydrogen permeability of Pd₄S. Our results suggest that H₂S inhibits hydrogen transport across Pd membranes primarily by producing a low permeability Pd₄S film on the Pd surface; however, H₂S in the feed gas also appears to lower the H₂ flux directly, possibly by blocking H₂ dissociation sites on the membrane surface.

2. Experimental

The method for measuring H₂ 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 cm² were mounted in the membrane testing apparatus and heated to 623 K in inert gases. Pd₄S films were produced on the surface of Pd foils by exposure to a gas mixture with a composition of 1000 ppm H₂S/10% He/H₂ (Butler Gas Products, Inc.) at a total pressure of 269 kPa and a temperature of 623 K. The H₂S exposure time varied from ~5 min for the thin (1 μm) Pd₄S films to ~24 h for the thicker (>15 μm) Pd₄S films. The bi-layered Pd₄S/Pd membranes were then exposed to either pure H₂ (99.99%, Butler Gas Products, Inc.) or the 1000 ppm H₂S in H₂ gas mixture while H₂ permeate flow rates were measured with a bubble flowmeter (Alltech Digital Flowmeter Model 4074) at ambient pressure. H₂ fluxes did not change over the course of the measurements (~30 min) and, therefore, the Pd₄S thicknesses were assumed to be constant. Following membrane testing, cross-sections of the bi-layered Pd₄S/Pd foils were mounted in epoxy...
and polished up to 1200 grit. The Pd₄S and Pd thicknesses were measured from the cross-sections by optical microscopy (Keyence VHX-1000) and scanning electron microscopy (Aspen Personal SEM 2000, 20 keV beam energy) with sulfur energy dispersive spectroscopy mapping to highlight the Pd₄S film.

3. Diffusion model for extraction of permeabilities

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

$$J_H = \frac{D_{Pd}(c_1 - c_2)}{x_{Pd}}$$  \hspace{1cm} (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 H₂, then Sievert’s law relates the concentrations $c_1$ and $c_2$ to the retentate and permeate H₂ partial pressures by Eqs. (2) and (3), respectively:

$$c_1 = S_{Pd}P_{H2,\text{ret}}^{1/2}$$ \hspace{1cm} (2)

$$c_2 = S_{Pd}P_{H2,\text{perm}}^{1/2}$$ \hspace{1cm} (3)

where $S_{Pd}$ is the solubility of H atoms in Pd, $P_{H2,\text{ret}}$ is the retentate H₂ partial pressure and $P_{H2,\text{perm}}$ is the permeate H₂ partial pressure. Substitution of Eqs. (2) and (3) into Fick’s first law of diffusion, Eq. (1), gives:

$$J_H = \frac{D_{Pd}S_{Pd}\Delta P_{H2}^{1/2}}{x_{Pd}}$$ \hspace{1cm} (4)

where

$$\Delta P_{H2}^{1/2} = P_{H2,\text{ret}}^{1/2} - P_{H2,\text{perm}}^{1/2}.$$ 

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

$$k_{Pd} = \frac{D_{Pd}S_{Pd}}{2}$$ \hspace{1cm} (5)

and substituting Eq. (5) into Eq. (4) gives the steady-state H₂ flux through Pd, $J_{H2}$:

$$J_{H2} = \frac{k_{Pd}\Delta P_{H2}^{1/2}}{x_{Pd}}$$ \hspace{1cm} (6)

H₂ transport across composite membranes has been well described in other publications [10,14–17], and the H₂ flux across a bi-layered Pd₄S/Pd foil can be modeled by Eq. (7) if H-atom diffusion is rate-limiting [10]:

$$J_{H2} = \frac{\Delta P_{H2}^{1/2}}{(x_{PdS}/k_{PdS}) + (x_{Pd}/k_{Pd})}$$ \hspace{1cm} (7)

where $k_{PdS}$ is the H atom permeability (2 H atom basis) of Pd₄S and $x_{PdS}$ is the thickness of the Pd₄S film. If H atom diffusion through a bi-layered Pd₄S/Pd foil is rate-limiting, then the H₂ flux should be directly proportional to $\Delta P_{H2}^{1/2}$ with a slope that can be used to calculate the permeability of Pd₄S if the permeability of Pd is known and the Pd₄S and Pd thicknesses are known.

4. Results and discussion

H₂ fluxes across a pure Pd foil were measured to determine the H atom permeability of Pd. Fig. 1 shows the H₂ fluxes across a 25 μm thick Pd foil during exposure to pure H₂ in the 623–973 K temperature range. As expected, H₂ 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 basis) of Pd ($k_{Pd}$) was calculated at each temperature and was fit to an Arrhenius expression:

$$k_{Pd} = 10^{-6.33±0.03} \exp \left( \frac{-(0.199±0.004) \text{eV}}{k_B T} \right) \text{molH}_2/\text{(m s Pa}^{1/2})$$ \hspace{1cm} (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 Pd₄S film thickness on the H₂ flux across Pd₄S/Pd foils was investigated by measuring H₂ fluxes across Pd₄S/Pd foils with various Pd₄S film thicknesses. Pd₄S films were produced by exposing the upstream surface of pure Pd foils to 1000 ppm H₂S/10% He/H₂ gas mixture at a total pressure of 269 kPa and a temperature of 623 K in the membrane testing apparatus. The H₂S exposure time varied from ~5 min for the thin (~1 μm) Pd₄S 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 Pd₄S/Pd foil with a ~14 μm thick Pd₄S film. The Pd₄S films were fairly uniform over the entire surface of the Pd substrates. H₂ fluxes were measured using pure H₂ to prevent Pd₄S growth during measurements and to eliminate the effects of H₂S on H₂ transport; H₂ fluxes did not vary over the course of the measurements (~30 min) and, therefore, the Pd₄S thicknesses can be assumed to be constant throughout the experiment. Following membrane testing, the Pd₄S film thicknesses were measured by cross-sectional optical microscopy of the Pd₄S/Pd foils. Fig. 4 shows the H₂ fluxes across Pd₄S/Pd foils with Pd₄S thicknesses of 0 (pure Pd), 1, 2, 6, and 14 μm at 623 K. Due to the low permeability of Pd₄S relative to Pd, the H₂ fluxes decrease as the Pd₄S thickness increases.

To determine whether H₂S inhibits H₂ transport across Pd₄S/Pd by factors in addition to the presence of the Pd₄S film, H₂ fluxes across Pd₄S/Pd foils were measured during exposure to a 1000 ppm H₂S/10% He/H₂ gas mixture. Fig. 5 shows the H₂ fluxes across a 14 μm Pd₄S/Pd foil during exposure to both pure H₂ and a 1000 ppm
H$_2$/10% He/H$_2$ feed gas mixture at 623 K. In both pure H$_2$ and in the H$_2$/H$_2$S gas mixture, H$_2$ fluxes did not change significantly over the course of the measurements (~30 min); therefore, the Pd$_4$S thickness can be assumed to be constant throughout the experiment. At all H$_2$ pressures, the H$_2$ fluxes across the 14 μm Pd$_4$S/Pd foil were significantly lower in the 1000 ppm H$_2$S in H$_2$ gas mixture than in pure H$_2$. H$_2$ fluxes across bi-layered Pd$_4$S/Pd foils were also measured at 673 K with a ~14 μm Pd$_4$S film, 723 K with a ~19 μm Pd$_4$S film, and 773 K with a ~22 μm Pd$_4$S film, both in pure H$_2$ and in the 1000 ppm H$_2$/10% He/H$_2$S feed gas mixture. At all temperatures and Pd$_4$S film thicknesses, the H$_2$ fluxes across the bi-layered Pd$_4$S/Pd foils were lower in the H$_2$/H$_2$S gas mixture than in pure H$_2$. Given the relatively low H$_2$ fluxes, the low He concentration, and

![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.](image)

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

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

![Fig. 5. H$_2$ fluxes across a 14 μm Pd$_4$S/Pd foil at 623 K during exposure to pure H$_2$ and a 1000 ppm H$_2$S/10% He/H$_2$ gas mixture (H$_2$ + H$_2$S). The H$_2$ partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated H$_2$ was collected at ambient (101 kPa) pressure. H$_2$ fluxes across the 14 μm Pd$_4$S/Pd foil are significantly lower in the H$_2$ + H$_2$S gas mixture than in the pure H$_2$ feed gas which could possibly be due to H$_2$S blocking H$_2$ dissociation sites.](image)
the low H₂S concentration, gas-phase hydrogen transport near the surface of the membranes (i.e., concentration polarization) is probably not the cause of the reduced H₂ flux in the 1000 ppm H₂S/10% He/H₂ feed gas relative to that in the pure H₂ feed gas. Therefore, H₂S probably inhibits one or more molecular processes at the Pd₄S surface. H₂S may inhibit the H₂ dissociation reaction by blocking H₂ adsorption sites or by increasing the barrier to H₂ dissociation. Alternatively, H₂S may inhibit H-atom transport from the surface to the sub-surface of Pd₄S.

During exposure to pure H₂ at varying pressure in the 623–773 K temperature range, the H₂ fluxes are directly proportional to Δp₁/₂ and intersect the origin, which indicates that H atom diffusion through the bulk of the foil is rate-limiting and that the Pd₄S layer is essentially dense. Therefore, the H atom permeability of Pd₄S can be calculated using Eq. (7). The temperature dependence of the H atom permeability (2 H atom basis) of Pd₄S (kₚ₄S) is given by an Arrhenius expression:

\[
kₚ₄S = 10^{-7.5±0.2} \exp \left(\frac{-0.22±0.03 \text{ eV}}{k_B T}\right) \text{molH}_2/(\text{msPa}^{1/2})
\]

where T(K) is the temperature and kₜ is the Boltzmann constant.

Fig. 6 is an Arrhenius plot that compares the H atom permeability (2 H atom basis) of Pd and Pd₄S measured in this work and the H atom permeability of Pd₄S determined by Morreale by correlating to Pd₄S growth, by measuring H₂ transport across bi-layered Pd₄S/Pd foils with known Pd₄S and Pd thicknesses. To our knowledge, this work represents the first direct measurements of the hydrogen permeability of Pd₄S.

5. Conclusions

H₂S degrades the performance of Pd H₂ separation membranes primarily by producing a Pd₄S film, which has an intrinsic H atom permeability about an order-of-magnitude lower than that of Pd. In addition, H₂S in the H₂ feed gas inhibits H₂ transport by a secondary mechanism that may involve blocking of H₂ dissociation sites. In this work, the H₂ permeability of Pd₄S (kₚ₄S = 10^{-7.5±0.2} \exp(-0.22±0.03 \text{ eV}/k_B T) \text{molH}_2/(\text{msPa}^{1/2}) was measured directly, rather than by correlation to Pd₄S growth, by measuring H₂ transport across bi-layered Pd₄S/Pd foils with known Pd₄S and Pd thicknesses. To our knowledge, this work represents the first direct measurements of the hydrogen permeability of Pd₄S.

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References


