

Pd and Pd–Cu membranes: inhibition of H₂ permeation by H₂S

Ames Kulprathipanja^{a,*}, Gökhan O. Alptekin^b, John L. Falconer^a, J. Douglas Way^c

^a Department of Chemical Engineering, University of Colorado, Boulder, CO 80309, USA

^b TDA Research Inc., Wheat Ridge, CO 80033, USA

^c Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, USA

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Abstract

Low concentrations of H₂S decreased H₂ permeation through electroless-plated Pd and Pd–Cu alloy membranes by blocking H₂ dissociation sites. At high H₂S concentrations, a sulfur surface layer did not allow H₂ to even penetrate to the Pd–Cu surface. Sulfidation of Pd and Cu formed micron size pores and caused the membrane to fail. Failure depended on H₂S concentration, not time of exposure; the H₂S concentration that completely inhibited H₂ permeation was approximately 300 ppm for Pd–Cu alloys and 100 ppm for Pd surfaces. At lower H₂S concentrations, steady state permeation was obtained. Hydrogen sulfide exposure and H₂ post-treatment caused Cu segregation to the membrane feed side due to stress relaxation. For membranes with bulk Cu concentration above 60 wt%, the phase changed from body-centered cube (bcc) to face-centered cube (fcc), and this decreased H₂ permeability. Larger cracks and pores formed during H₂S exposure at 523 K than at 723 K due to a higher degree of Pd and Cu sulfidation, as predicted by thermodynamics. The presence of H₂O also increased sulfidation by aiding H₂S dissociation and blocking H₂ dissociation sites. Cast and rolled foils, which have smoother surfaces, were less prone to surface rearrangement by H₂S. Smoother surfaces have less surface area and adsorb less sulfur per unit area compared to rougher surfaces.

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1. Introduction

Palladium alloy membranes have been studied to separate H₂ from coal gasification and steam reforming product streams [1–4]. In many cases, H₂S in the process streams deactivates the metal membrane and reduces H₂ permeation and selectivity. Edlund reported a constant H₂ flux through a 50- μ m thick Pd₆₀Cu₄₀ foil membrane exposed to 1000 ppm H₂S in H₂ at 773 K and 700 kPa for 350 h [5]. However, a decrease in H₂ flux of 60% after H₂S exposure was calculated from single gas H₂ flux data previously published on the same foil membranes [6]. In an earlier study, a 25- μ m thick Pd foil failed within seconds when exposed to pure H₂S at 973 K

and 875 kPa [7]. Hydrogen sulfide corroded the membrane and formed numerous pores.

A 1967 patent by McKinley compared the effect of H₂S on pure Pd, Pd₇₃Ag₂₇, Pd₆₀Cu₄₀, and Pd₆₀Au₄₀ alloy membranes at 623 K and 520 kPa [8]. The H₂ flux through 25- μ m thick foil membranes was measured during exposure to 4–5 ppm H₂S. The H₂ flux for a pure Pd foil reduced to about 40% of its original flux after 6 h of H₂S exposure and 30% after 6 days. The H₂ flux in a Pd₇₃Ag₂₇ membrane was twice that of pure Pd, but the flux dropped to less than 1% of its original value after 6 h in 4–5 ppm H₂S. The H₂ flux through a Pd₆₀Cu₄₀ membrane decreased to 20% of its initial value after feeding H₂S, and to only 5% after 6 days. The original Pd₆₀Cu₄₀ H₂ flux was also more than twice that for pure Pd. The most resistant alloy composition to H₂S poisoning was Pd₆₀Au₄₀. The H₂ flux only dropped to 88% of its original flux after 6 h, though the original flux of the Pd–Au alloy membrane was half of the pure Pd membrane flux. Inter-

* Corresponding author. Present address: Mesoscopic Devices, LLC, 510 Compton Street, Suite 106, Broomfield, CO 80020, USA.
Tel.: +1 303 466 6968; fax: +1 303 466 6871.

E-mail address: akulprat@mesoscopic.com (A. Kulprathipanja).

estingly, when the feed was switched to 100% H₂, all the membranes recovered their original H₂ permeability. After H₂S exposure, the pure Pd and Pd–Ag membranes lost their luster and appeared dull, whereas the Pd–Au and Pd–Cu foils did not. Reversibility with H₂ exposure led McKinley to hypothesize that the decrease in H₂ flux of the Cu and Au alloy membranes was due to H₂S adsorption on the foil surface and not chemical attack or sulfide formation. However, this hypothesis is not consistent with the results reported above by Edlund or others [5,7,9,10]. At 500 K, H₂S dissociated on pure Pd to form H and S atoms [9,10].

Palladium alloys have been made with Ni, Ag, Ru, Au, and Cu [11–13]. Palladium–copper alloy membranes have higher H₂ permeances, wider temperature operating conditions, and better mechanical properties than pure Pd membranes [8]. Alloying Pd with Cu also makes the membranes cheaper to produce. Electroless plating techniques can fabricate 1–10 μm thick Pd–Cu membranes on tubular ceramic or stainless steel supports and lower the cost of the membranes. A tubular geometry is more commercially applicable than thicker (>15 μm) flat foils, due to the higher membrane surface area to volume ratio [6,14].

Palladium–copper alloys having between 30 and 60 wt% Cu form the body-centered cubic (bcc) phase, which has higher H₂ permeability, is more resistant to sulfur compounds, and can operate at lower temperatures than the face-centered cubic (fcc) phase of pure Pd and other Pd–Cu alloy compositions [8,12,15]. Pure Pd membranes suffer from embrittlement problems at temperatures below 573 K [7,16] due to the Pd → Pd-hydride phase transition [17]. Thermal cycling, necessary when heating and cooling the separation system, also leads to membrane embrittlement. Differences in lattice parameters of the separate phases expand the lattice and form cracks. Palladium–copper alloys with either the fcc or bcc phase structure do not embrittle, even at ambient temperatures, because they do not form a hydride phase. The H atoms travel through the Pd–Cu lattice, but are not incorporated into the structure.

Hydrogen transports through Pd membranes by dissociating on the membrane surface, diffusing through the membrane as H atoms, and recombining on the permeate side. Solid-state diffusion in Pd and Pd alloy films is the rate-limiting step for most operating conditions [18], but other possible rate-limiting steps include external mass transfer resistances, reduced sticking probability due to surface contamination, and H₂ desorption for membrane thicknesses less than 1 μm [18]. Peden et al. reported the H₂ transport through Pd metal with clean surfaces was rate limited by H₂ diffusion, but sulfur impurities on the metal surface caused the H₂ transport to become limited by the dissociative chemisorption of molecular H₂ [10].

Palladium–copper alloy membranes fabricated by different techniques have different physical and separation properties. Kulprathipanja et al. reported that surfaces of Pd₆₀Cu₄₀ membranes fabricated by electroless plating were 3.5 times rougher than surfaces of foil membranes fabricated by casting

and rolling [19]. Furthermore, exposing the electroless-plated and foil membranes to CO₂ increased the height of micron-scale hillocks on the membrane surfaces by factors of 6 and 4, respectively. Increasing the hillock heights increased defect sizes and allowed gases other than H₂ to permeate through the membrane. The hillock heights increased due to stress relaxation and removal of carbon impurities from the membrane by CO₂ to form CO. The foil membranes resisted surface rearrangement better than electroless-plated membranes.

Though the Claus process and/or ZnO sorbent beds can remove much of the H₂S in a H₂ production process stream, removing the H₂S to concentrations required of a non-H₂S resistant membrane may not be economically feasible using these two processes [20–23]. The Claus process is only used for large process streams such as oil processing and has sulfur recoveries of around 96–98%. Zinc oxide based sorbents can produce a product stream with approximately 10 ppm H₂S, but their sulfur capacities and attrition resistances are too low for most commercial applications. Therefore, finding a method to separate H₂ that can resist H₂S and be mechanically stable at high temperatures and H₂S pressures is desired. The present study examined the effects of H₂S on the separation and mechanical properties of pure Pd and Pd–Cu alloy membranes prepared by electroless plating and by casting and rolling foils.

2. Experimental methods

2.1. Membrane preparation

The fabrication procedure and chemical recipe for the electroless-plated Pd and Pd–Cu alloy membranes were described in detail previously [24]. The Pd–Cu alloy membranes were prepared by successively depositing Pd and Cu onto asymmetric α-alumina tubular supports with a 20 nm pore zirconia top-layer (US Filter T1-70). The ceramic tubes were cleaned and the annulus of the tube activated by impregnating the top-layer with Pd nucleation sites using a Pd acetate solution. The activated tubes were heated in air to oxidize the organic ligand and then reduced to form dispersed Pd metal on the top-layer. The Pd film was grown to a desired thickness by nucleation and growth from the Pd metal sites. An osmotic pressure gradient was applied across the membrane by flowing an aqueous sucrose solution on the permeate side of the support during plating to reduce porosity and promote surface homogeneity [25]. After Cu was plated on top of the Pd film, intermetallic diffusion of the Pd and Cu metals was induced by annealing in a 5% H₂/He gas mixture at 623–723 K to produce a uniform alloy film. The annealing process took approximately 5 days at 673 K for membranes less than 5-μm thick. Complete annealing was determined by a steady state H₂ flux through the membrane for 2 days. The integrity of the Pd–Cu film was tested by pressurizing the membrane with N₂, immersing it in a 2-propanol/H₂O mixture, and checking it for gas leaks. A 25-μm thick Pd₆₀Cu₄₀

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