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The effect of H_2S on the performance of Pd and Pd/Au composite membrane

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ABSTRACT

The performance of the Pd and the Pd/Au alloy (8 wt% Au) composite membrane prepared by the electroless and galvanic displacement deposition in a 54.8 ppm H_2S/H_2 mixture was investigated. Upon testing, the Pd membrane showed the permeance decline in two stages resulted from the surface site blocking and bulk sulfidation. The Pd membrane also failed to separate H_2 from other gases after the H_2S exposure due to the deterioration of the structure caused by the possible formation of bulk Pd_4S. On the other hand, the Pd/Au alloy membrane exhibited resistance to bulk sulfidation and the permeance decline during the H_2S exposure was mainly caused by the surface site blocking by the dissociative adsorption of H_2S, which was essentially reversible as evidenced by the near full restoration of the H_2 permeance in pure H_2 at 500 °C. No significant change in He leak after the H_2S tests substantiated that there was no significant structural changes of the Pd/Au alloy membrane due to the bulk sulfide formation. Higher temperatures resulted in less permeance loss during poisoning and more permeance restoration during recovery, which was due to the exothermic nature of the dissociative adsorption of H_2S on metals.

1. Introduction

Extracting H_2 from relatively abundant fossil fuels is one of the most practical and economical processes for large scale production of H_2 today. It will continue to be so until the maturity of the clean and sustainable H_2 production techniques such as the electrolysis of water has been achieved. Coal gasification, in particular, is recently considered as one of the most preferable processes since coal is the most abundant and widely dispersed fossil fuel on the globe. In addition, the H_2 concentration in the syngas produced from the coal gasification process can be further increased by a water–gas shift (WGS) reaction along with CO_2 as the main by-product.

Pd and Pd alloy membranes have been extensively studied in the above-mentioned processes due to their high H_2-selective permeability [1–4]. Higher efficiency and cost effectiveness of the H_2 production can be achieved by applying Pd-based membranes in such processes to extract high purity H_2 during the reaction. As H_2 is being extracted by Pd-based membranes, concentrated CO_2 under high pressure in the retentate side reduces the cost of the subsequent carbon sequestration process [5].

Unfortunately, a small quantity of H_2S in the syngas, as a by-product of the coal gasification, deteriorates the performance of Pd-based membranes. McKinley [6] reported a 70% permeance loss of an 1 mm thick pure Pd foil at 350 °C in the presence of 4.5 ppm H_2S/H_2 over a period of 4 days. The Pd foil lost its luster and appeared dull after the H_2S exposure. When exposed to higher H_2S concentrations, not only the performance but also the structure of Pd membranes has been degenerated. Mundschau et al. [7] observed not only the decline of H_2 permeance of the Pd foil upon feeding a 20 ppm H_2S balanced with 60% H_2–He mixture at 320 °C for over 100 h, but also the formation of numerous pinholes on the membrane after the exposure. Kulprathipanja et al. [8] reported the failure of a 4 μm Pd/ceramic composite membrane with the loss of selectivity upon exposing to a 115 ppm H_2S in a 50% H_2–N_2 mixture within 2 h at 450 °C with the formation of numerous pinholes. Edlund and Pledger [9] observed a rapid failure (within seconds) of the Pd/SiO_2/V composite membrane by a catastrophic rupture with the formation of pinholes and large cracks upon exposure to pure H_2S at 115 psia and 700 °C. Kajiwara et al. [10] also observed the rupture and cracks formation of the Pd/porous alumina composite membranes after exposure to a 6200 ppm H_2S/H_2 mixture at 400 °C within 1 h, resulting in the membrane losing its ability to separate H_2 from other gases.

The loss of permeance mainly resulted from the decrease of the H_2 adsorption caused by the adsorbed sulfur on the Pd surface. The adsorbed sulfur blocked the adsorption sites on the Pd surface and generated an energy barrier where each adsorbed sulfur effectively blocked 4–13 sites for the H_2 adsorption [11–13]. In addition, the adsorbed sulfur could incorporate with Pd to form bulk Pd_4S depending on the H_2S exposure conditions. When bulk Pd_4S formed, the Pd_4S layer acted as a mass transfer barrier with a lower H_2 permeability [8,14]. Furthermore, the formation of bulk Pd_4S generated large stress in the Pd lattices due to the large dif-

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ference in the lattice constants between pure Pd and Pd_4S, thereby causing the rupture of the Pd membranes [10].

Several approaches, such as varying the crystal structure (nanostructure or amorphous) [15], have been investigated recently to enhance the resistance to sulfur poisoning of Pd membranes [16]. However, the most promising approach to enhance the sulfur resistance was to alloy Pd with other elements, thereby altering its electronic, chemical properties and reactivity [17].

Although most efforts have been placed in Pd/Cu alloy membranes for higher sulfur resistance [8,18–20], Pd/Au alloy membranes have received increasing attention recently due to their twofold beneficial characteristics. Pd/Au alloy membranes showed higher H_2 permeability than pure Pd membranes in the Au content range below 20 wt%, which resulted from the higher solubility of H_2 in Pd/Au alloys [21–24]. Pd/Au alloys have also shown higher sulfur resistance compared to many other Pd alloys. McKinley [6] observed a flux decline of 10% on a $Pd_{60}Au_{40}$ alloy foil in the presence of 4.5 ppm H_2S at 350 °C, while a decline of 95% was observed on a $Pd_{60}Cu_{40}$ alloy foil under the same conditions. Way et al. [25] also observed a 38% permeance decline on a $Pd_{85}Au_{15}$ alloy membrane in the presence of 5 ppm H_2S at 400 °C, while a 71% permeance drop was observed on a $Pd_{94}Cu_6$ FCC phase membrane. In the literature, limited research has been done regarding the H_2S poisoning of Pd/Au alloy membranes, especially in the Au content range below 20 wt%. No systematic data were available regarding the effect of temperature and exposure time on the H_2 permeation characteristics of Pd/Au alloy membranes in the presence of H_2S. In addition, the characterization of the important phenomenon of permeance recovery of Pd/Au alloy membranes after H_2S poisoning was rarely reported.

One simple and efficient way of Au deposition is the galvanic displacement method, which does not require external sources of current, reducing agent and complexing agent [26–29]. The plating technique only requires simple plating equipment and is environmental friendly. Forming Pd/Au alloy on the top layer of the membrane by the displacement plating technique (and annealing) allows the membrane to have sulfur tolerance, while overall low Au content minimizes the use of the high cost Au.

The objective of the present study was to investigate the performance of the pure Pd membrane and the Pd membrane with a thin top Pd/Au alloy layer prepared by the electroless and galvanic displacement plating techniques in a 54.8 ppm H_2S/H_2 mixture. The recovery phenomena of both the Pd and Pd/Au alloy membranes in pure H_2 after the H_2S exposure were studied. In addition, the effects of the exposure temperature and time on the H_2S poisoning and on the permeance recovery of the Pd/Au alloy membrane were also investigated.

2. Experimental

2.1. Sample preparation

Two types of samples, Pd and Pd/Au deposited coupons and membranes, were prepared. Porous 316 stainless steel (PSS) plates (dimensions: 1 cm × 1 cm × 0.1 cm) were used for the coupon preparation, while porous Inconel tubes (O.D. = 1.27 cm and length = 6 cm) were used for the membrane preparation. Both were 0.1 μm-media grade and purchased from Mott Metallurgical Corp. The electroless Pd plating procedure and chemical recipe (including activation process) reported by Mardilovich et al. [30] were adopted in this study for the Pd deposition. For the Au deposition, the galvanic displacement plating technique was used with 2–5 mM sodium tetrachloroaurate dihydrate solutions. Pure Pd coupons were prepared by the electroless plating on the pre-oxidized (700 °C/12 h/air) PSS plates, and the Pd/Au bi-layer coupons were prepared by the galvanic displacement plating of Au on the Pd-plated PSS coupons (7–10 μm thick Pd). The Pd/Au bi-layer coupons were estimated gravimetrically to have about 8–11 wt% Au (∼0.5 μm thick Au). For the pure Pd membrane preparation, the porous Inconel supports were oxidized (700 °C/12 h/air) after cleaning in the alkaline solution. The oxidized supports were then graded with the Al_2O_3 slurry to reduce the pore size and to narrow the pore size distribution, followed by the successive Pd and Ag deposition. Both the oxide and the Pd/Ag layers acted as the intermetallic diffusion barriers [31,32]. After the Pd/Ag layers were deposited on the supports, Pd was deposited by the electroless plating until gas-tight (dense). During the Pd plating, vacuum was applied inside of the supports (tube side) after the supports were impermeable to liquid to increase the homogeneity of the deposit layer and to reduce the thickness required for obtaining the gas-tight deposit layer. For the Pd/Au alloy membrane preparation, the galvanic displacement plating of Au was conducted on the gas-tight Pd membranes followed by the heat treatment at 500 °C in H_2 atmosphere for more than 48 h. The bath composition and the plating condition of Pd, Ag, and Au deposition were summarized in Table 1.

Table 1
Composition and condition of plating bath.

Composition/condition	Pd bath	Ag bath	Au bath
$Pd(NH_3)_4Cl_2{\cdot}H_2O$ (g/l)	4		–
$AgNO_3$(g/l)		0.519	
$Na_2EDTA{\cdot}2H_2O$ (g/l)	40.1	40.1	–
NH_4OH (28%) (ml/l)	198	198	–
H_2NNH_2 (1 M) (ml/l)	5.6	5.6	–
$Na{\cdot}Au(Cl)_4{\cdot}2H_2O$ (mM)	–		2–5
pH	10–11	10–11	2–4
Temperature (°C)	60	60	R.T.–60

2.2. Sample characterization

The surface characterizations were performed by using an Amray 1610 Turbo scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech Avalon energy dispersive X-ray (EDS) light-element detector and a RBA-1610 5MC type Robinson retractable backscattered electron detector for the qualitative and quantitative analysis. The spacial resolution for the SEM system was in the range of 0.8–1.2 μm, and the penetration depth of the X-ray from the EDS system was ∼1 μm for the sample investigated (consisted of primarily Pd). The crystal phase identification analysis was conducted using a Rigaku Geigerflex X-ray diffractometer (XRD) equipped with a CuKα radiation source ($\lambda = 1.54$ Å), and a curved crystal monochromator.

2.3. Membrane permeation-test

Fig. 1 shows the permeation-test apparatus used in the study for testing the performance (i.e. H_2 permeance and selectivity) of the membranes in pure H_2 or H_2S/H_2 mixtures. The permeation-test module (in the dotted line rectangle), which was a stainless steel assembly with Swagelok fittings, and the permeation-test procedure were designed and performed based on the work of Mardilovich et al. [30]. The feed gas of pure H_2, He or 54.8 ppm (±1 ppm) H_2S/H_2 mixtures flowed through the outside of the membrane (shell side) and a digital mass flow meter was used to measure the permeate flow rate at the inside of the membrane (tube side). The feed gas pressure was monitored by a pressure transducer, and controlled by either a pressure transducer (for H_2 and He feed) or a digital mass flow controller (for H_2S/H_2 mixture feed). For the characterization in pure H_2 and He, a ballast volume of 3.8 l was installed before the module and a He sweep (purge) gas at 1 atm was used