THE EFFECT OF H$_2$S ON THE LONG-TERM STABILITY OF Pd/Cu MEMBRANES AND THE CHARACTERISITICS OF H$_2$S POISONING OF ELECTROLESS DEPOSITED Pd

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Introduction

Hydrogen selective Pd and Pd alloy membranes can improve the efficiency and cost effectiveness of the coal gasification process by recovering high purity H$_2$ from the syngas. Also, the high pressure CO$_2$ in the retentate reduces the cost of carbon capture required for carbon sequestration. However, small quantities of H$_2$S present in the gas stream poison the Pd membranes and reduce the hydrogen permeance by either adsorbing on the surface or reducing the selectivity of the membrane by forming a sulfide scale. Pd/Cu membranes have been tested and shown to be more tolerant to H$_2$S than pure Pd, but bulk analysis methods such as EDS (Energy Dispersive Spectroscopy) and XRD (X-ray Diffraction) were not sufficiently surface sensitive to detect the adsorbed sulfur on poisoned membrane surfaces. Therefore, the objective of this study was to examine the interactions of H$_2$S with Pd that led to membrane poisoning with the more surface sensitive technique of XPS (X-Ray Photoelectron Spectroscopy), and to test the long-term stability of Pd/Cu membranes in the presence of H$_2$S with the purpose of designing sulfur tolerant membranes.

Experimental

All of the supports used in this study were provided by Mott Metallurgical, Inc. Coupons (1 cm x 1 cm x 0.1 cm) consisted of 316L PSS (porous stainless steel) with a 0.5 μm media grade. The tubular membrane supports (length - 6 cm, OD - 1.25 cm, thickness - 0.16 cm). consisted of a porous Inconel alloy with a 0.1 μm media grade. All supports were cleaned with an alkaline solution to remove impurities as described elsewhere [1] and oxidized at 700°C for 12 hours in order to form an oxide intermetallic diffusion barrier [2, 3] between the support metals and the H$_2$ selective Pd layer.

To block the larger pores of the support before plating the dense Pd layer, the support was attached to a vacuum and immersed in an acidic Al$_2$O$_3$ slurry for 10 seconds and dried at 140°C for 12 hours. To seal the slurry within the pores of the support, the support was activated once under vacuum and plated with Pd for 10 mintues. A Pd/Ag barrier was deposited which further bridged the larger pores of the support and also functioned as an intermetallic diffusion barrier between the support metals and the hydrogen selective layer, further details of the procedure are described elsewhere [4, 5]. The supports were activated and plated until dense, according to the procedure outlined in Mardilovich, et al. [1]. The Cu plating bath was adapted from Ma, et al. [6] and the bath composition is shown with the Pd and Ag plating bath compositions in Table 1. Cu was plated for 30 – 60 minutes, depending on the desired Cu content. After the electroless deposition of Cu, the membranes were immediately immersed in 0.01 M HCl to neutralize any residual plating solution, rinsed with DI water and then rinsed with ethanol to facilitate drying in order to prevent oxidation of the Cu layer.

The coupons were annealed in a tubular furnace and the membranes were tested in a shell and tube apparatus [1]. The He leaks of the membranes were measured at a pressure difference of 1 atm and the ideal H$_2$/He separation factors were calculated according to the ratio of H$_2$ to He fluxes through the membrane at a pressure difference of 1 atm (P$_{feed}$ = 2 atma, P$_{permeate}$ = 1 atma).

Table 1. Plating bath compositions and conditions.

Component	Pd bath	Cu bath	Ag bath
Pd(NH$_3$)$_4$Cl$_2$·H$_2$O (g/l)	4		
CuSO$_4$·5H$_2$O (g/l)		25	
AgNO$_3$ (g/l)			0.519
Na$_2$EDTA·2H$_2$O (g/l)	40.1	47.5	40.1
NH$_4$OH (28%) (ml/l)	198		198
H$_2$NNH$_2$ (1 M) (ml/l)	5.6		5.8
H$_2$CO (37%) (ml/l)		25	
EDA (ppm)		112	
K$_4$Fe(CN)$_6$·3H$_2$O (ppm)		35	
(C$_2$H$_5$)$_2$NCS$_2$Na·3H$_2$O (ppm)		5	
pH	10 - 11	12.0	10 - 11
Temperature (°C)	60	20 - 25	60

Surface characterizations were carried out with the Amray 1610 Turbo scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech Avalon energy dispersive X-ray light element detector and a RBA-1610 5MC type Robinson retractable backscattered electron detector for qualitative and quantitative analysis. The spatial resolution for SEM – EDS lies between 0.8 – 1.2 μm and the penetration depth for EDS was 1 μm for the samples investigated. Surface elemental analysis was performed with a Kratos AXIS Ultra X-ray Photoelectron Spectrometer using a monochromatized aluminum source operated at 150 W, with an analysis area of approximately 300 x 700 um and a maximum information depth of approximately 10 nm. The pass energy used for high energy resolution spectra was 20 eV. CasaXPS software [7], equipped with a Scofield-cross-section-based sensitivity factor library, was used for the peak-fitting and quantitative analysis. All spectra were calibrated using the adventitious carbon C 1s peak at 285.0 eV and a Shirley-type background was subtracted from the spectra.

Results and Discussion

Pd coupon study

In order to observe the Pd – H$_2$S interactions at membrane operating conditions, and to assess the possible effects on membrane performance, electroless deposited Pd samples were exposed to 54.8 ppm H$_2$S/H$_2$ and pure H$_2$ for 24 hours over a range of 350 - 500°C. Figure 1a shows the XPS survey spectra of three of the annealed samples. The top spectrum was a sample annealed in pure H$_2$ and exhibited no peaks characteristic of sulfur. In the case of the Pd samples annealed at 350 and 500°C in 54.8 ppm H$_2$S/H$_2$, the peaks identifying the 2s and 2p orbitals of sulfur were present, showing that sulfur had adsorbed on the Pd surface at both temperatures. Similar results were seen with the Pd samples annealed at 400 and 450°C in 54.8 ppm H$_2$S/H$_2$.
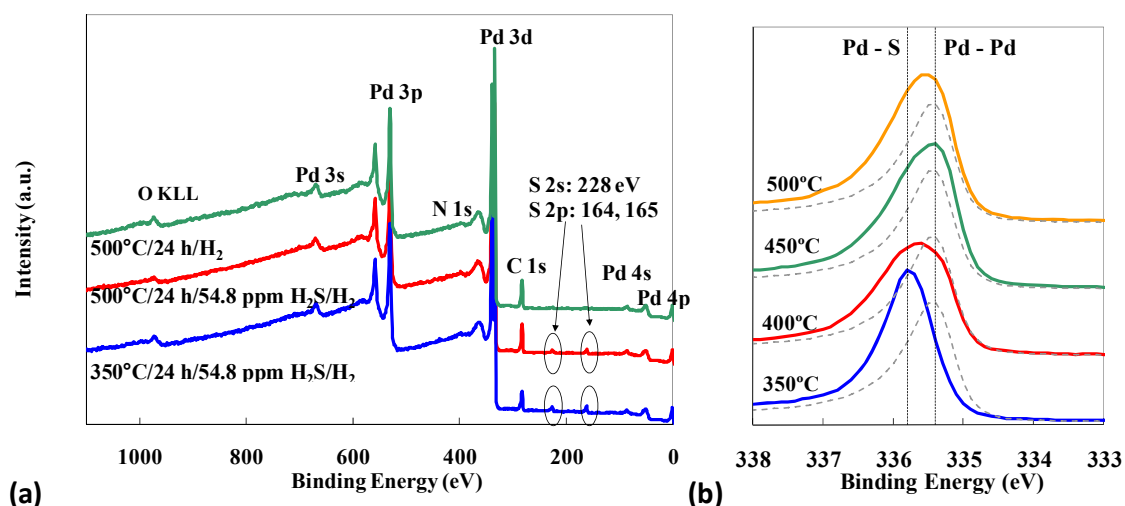
Figure 1. (a) XPS survey spectra of the annealed Pd samples and (b) High resolution XPS scan of the $3d_{5/2}$ peaks of the annealed Pd samples. The solid and dotted lines correspond to the samples annealed in 54.8 ppm H_2S/H_2 and pure H_2, respectively.

Figure 1b shows the high resolution XPS scans of the $3d_{5/2}$ Pd orbital. The peak broadening and shift to higher binding energies than that of the Pd – Pd peak maximum (dotted lines) at 400, 450 and 500ºC showed that Pd – S bonds had formed on the surface, indicating that H_2S had undergone dissociative chemisorption and formed a surface sulfide with the Pd. Bulk sulfides had not formed as evidenced by the broad peaks between 400 - 500ºC that indicated the presence of the Pd – Pd chemistry near the surface as well as the Pd – S chemistry. However, at 350ºC the $3d_{5/2}$ peak of Pd was not as broad and the maximum was at the corresponding binding energy of the Pd – S peak maximum. The Pd – Pd chemistry was not detected at this temperature, indicating that bulk Pd sulfide had formed. The values of the Pd – Pd and Pd – S chemistries were confirmed with the literature [8 – 10].

Figure 2 shows the amount of adsorbed sulfur on the Pd surface as a function of temperature. The S/Pd atomic ratio was calculated from the survey scans shown in Figure 1a and the amount of the Pd – S and Pd – Pd chemistries were calculated from the high-resolution scans shown in Figure 1b. The amount of sulfur adsorbed and consequently, the amount of sulfur which bonded with Pd, increased with decreasing temperature. Sulfur adsorption is an exothermic reaction and higher temperatures would cause less sulfur to adsorb [11]. A similar trend was seen with bulk Pd sulfides in previous works [12, 13] indicating that bulk sulfides would only form at lower temperatures. Indeed, at 350ºC, the S/Pd atomic ratio was 0.25, which corresponded to the atomic ratio of Pd_4S. The XRD analysis further confirmed that the bulk sulfide Pd_4S phase was indeed present, in contrast to the samples annealed at 400, 450 and 500ºC which only resulted in surface sulfide formation.

Figure 3a shows the uniform granular morphology of Pd clusters annealed in H_2. Figure 3b shows that the surface sulfide formation caused a change to a more chunky morphology (encircled on the left side of the micrograph) and the formation of pores (encircled in the center of the micrograph) at the cluster boundaries. The pores and morphology change were both probably caused by the restructuring of the Pd surface atoms as they bonded with the sulfur. Figure 3c shows the Pd_4S scale which had a drastically different morphology than the annealed Pd. While Pd has a FCC lattice structure, Pd_4S has a tetragonal lattice structure and a lattice parameter almost twice that of pure Pd. The lattice reordering caused by the formation of the bulk Pd sulfide caused a coral-like scale to form on top of the Pd clusters. While the performance of a Pd membrane with adsorbed sulfur would deteriorate due to a decrease in the permeance caused by sulfur preventing the H_2 adsorption, and a decrease in the

selectivity caused by the pore formation, a Pd membrane forming a Pd$_4$S scale during operation would suffer such an irreparable damage to the selectivity that the membrane would only have Knudsen selectivity [14].
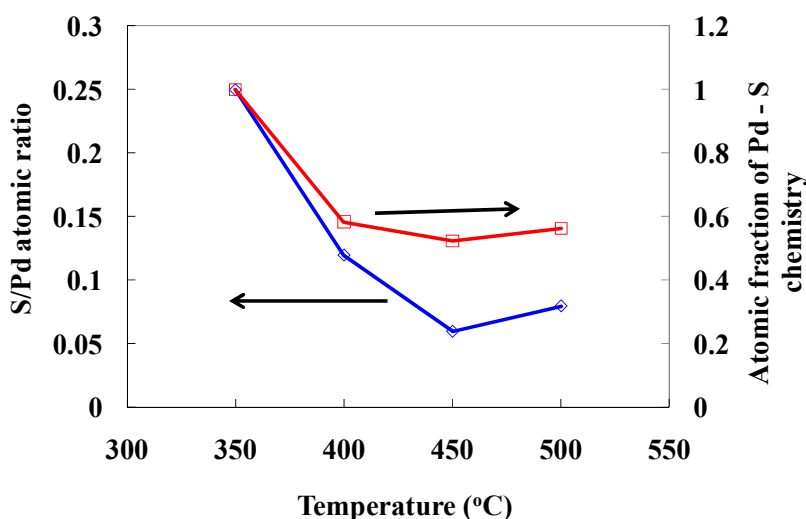

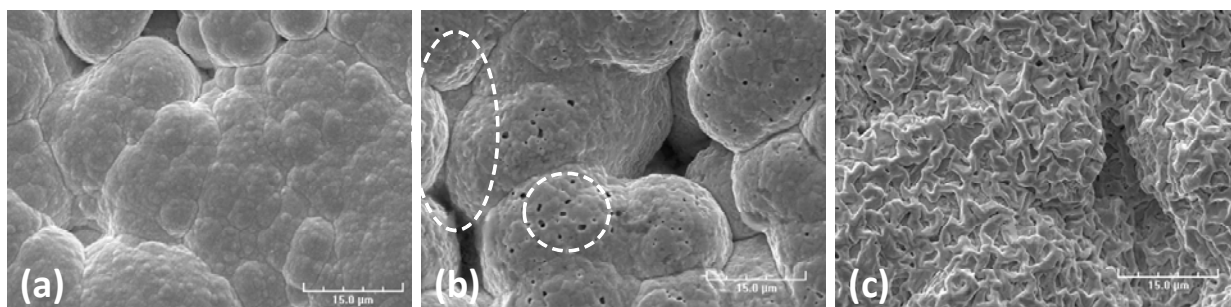**Figure 2.** Dependence of the amount of adsorbed sulfur on temperature.

Figure 3. Scanning electron micrographs of (a) deposited Pd annealed at 500ºC in H$_2$ for 24 hours, (b) deposited Pd annealed at 450ºC in 54.8 ppm H$_2$S/H$_2$ for 24 hours, (c) deposited Pd annealed at 350ºC in 54.8 ppm H$_2$S/H$_2$ for 24 hours.

Pd/Cu membrane study

The Pd/Cu membrane consisted of a 5.1 μm porous Pd/Ag barrier, a 7.6 μm Pd layer and a 3.8 μm Cu layer for a total Cu composition of 18 wt%. The membrane was characterized between the temperatures of 250 - 450ºC for over 800 hours before the sulfur testing. The permeance at 450ºC was 19.9 m^3/m^2*bar$^{0.5}$*h and the activation energy of permeation was 15 kJ/mol. The ideal H$_2$/He separation factor decreased from 1800 to 220 during the characterization. At the end of the pure H$_2$ permeationg characterization, the Pd/Cu membrane was exposed to a 54.8 ppm H$_2$S/H$_2$ mixture at 450ºC.

As seen in Figure 4a, the permeance of the membrane dropped instantaneously to 21% of the original permeance at 450ºC upon the introduction of 54.8 ppm H$_2$S/H$_2$. During the exposure to H$_2$S, the permeance remained stable for 125 hours, signifying that the cause of the permeance drop was from the surface sulfide formation since it was observed that bulk sulfide formation caused a continuous decrease in the permeance over time as the sulfide scale formed and thickened [15]. The permeance was recovered by reintroducing pure H$_2$ to the feed stream, which further substantiated the notion of the

surface sulfide formation. During the recovery, the hydrogen permeance increased at a rate of 0.017 $m^3/(m^2*bar^{0.5}*h)*h$ for roughly 300 hours until the permeance stabilized at 64% of the original permeance. The inability to completely recover the permeance was an indication that part of the sulfide poisoning was irreversible at these testing conditions. The sulfur adsorption consisting of both irreversible and reversible surface sulfides has also been observed at 500ºC with poisoned and recovered Pt/Al_2O_3 catalysts [16].

The activation energy of permeation following the permeance recovery was 13.8 kJ/mol. The fact that the activation energy did not significantly change before and after the H_2S testing indicated that the irreversible sulfur poisoning resulted in a decrease in the effective membrane area for the H_2 adsorption, and did not change the hydrogen transport mechanism. In accordance with the XPS studies, operating the Pd/Cu membrane at a higher temperature could result in less of a permeance drop and more permeance recovered in pure H_2, due to less of the surface sulfide formation.
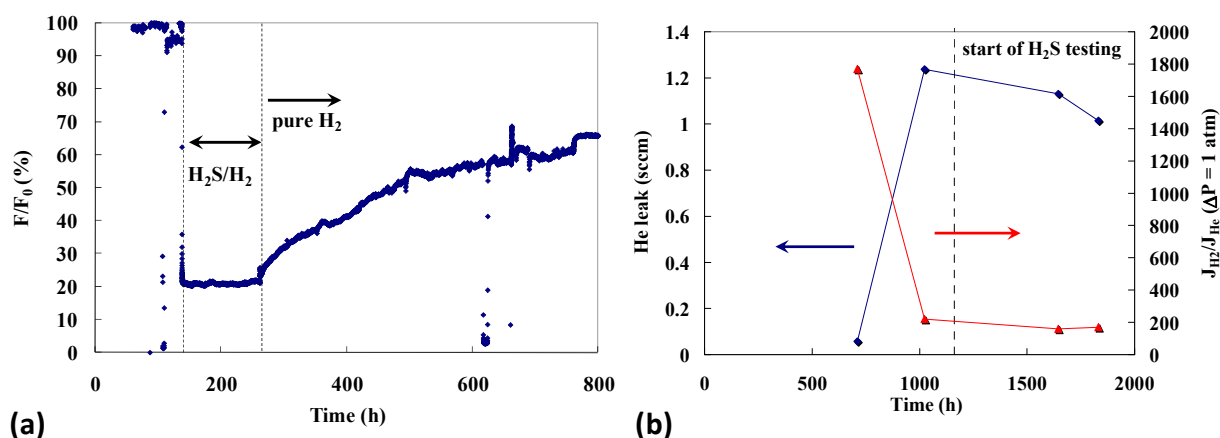

Figure 4. (a) The relative permeance of the Pd/Cu membrane as a function of time during poisoning and during recovery in pure H_2 at 450ºC. (b) The leak and ideal H_2/He separation factor as a function of time for the Pd/Cu membrane at 450ºC.

Figure 4b shows the change in leak for the duration of the Pd/Cu membrane testing. At temperatures lower than 450ºC, non-permeable gases in the permeate were undetectable, but at 450ºC a very small He leak of 0.06 sccm was detected which increased to 1.24 sccm after 300 hours, resulting in a decrease in the ideal H_2/He separation factor. The development of leaks at high temperatures over long periods of time has been documented previously [17, 18] and the cause was attributed to pinhole formation due to grain coarsening. Contrary to these results, the He leak of the Pd/Cu membrane decreased following the H_2S testing to 1.15 and then 1.01 sccm over a period of 700 hours at 450ºC. The decrease in the He leak could have been caused by sulfur segregating to the grain boundaries of the deposits, as has been previously observed [19, 20], which would reduce or block pathways for non-permeable gases. In contrast to the implications of the Pd coupons study, the Pd/Cu membrane showed leak stability in the presence of H_2S.

Conclusions

It was found that the bulk sulfide Pd_4S phase transformation did not occur at temperatures higher than 350ºC. At 400 - 500ºC, H_2S formed Pd surface sulfides, which caused slight morphology changes to the Pd surface and pore formation at the cluster boundaries. In addition, the sulfur adsorption on the Pd decreased at higher temperatures due to the exothermic nature of H_2S adsorption. While the surface

sulfide formation would reduce both the permeance and selectivity of a Pd membrane, the change in lattice parameter caused by bulk Pd$_4$S sulfide formation would render a Pd membrane useless.

During exposure to the 54.8 ppm H$_2$S/H$_2$ mixture, the Pd/Cu membrane had a reduced permeance due to the surface sulfide formation, but did not show an increase in leak that a pure Pd membrane would exhibit. Even more so, the He leak decreased during the sulfur testing, most likely due to sulfur segregating in the grain boundaries. The poisoning of the Pd/Cu membrane was found to be partly irreversible in that the full H$_2$ permeance could not be recovered. In accordance with the Pd coupon study, increasing the operating temperature should increase the tolerance of the membrane.

Acknowledgements

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