

Characterization of sulfur resistance of Pd/Au hydrogen separation membrane prepared by galvanic displacement

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Introduction

Sulfur containing impurities are known to cause severe and irreversible poisoning of Pd membranes during the hydrogen separation application (Especially in the coal gasification) resulting in the reduction of hydrogen permeability, selectivity and structure deterioration of Pd membranes^{1,2,3}. Pd/Au alloys are found to show high sulfur resistance^{1,4} in comparison to pure Pd and other Pd based alloys (i.e., Pd/Ag, Pd/Cu, etc.) in addition to its high hydrogen permeability^{5,6}. As a result, Pd/Au alloys have recently regained great interests for membrane separation process. The preparation of Pd/Au alloys can be carried out by the galvanic displacement method^{7,8,9}, which does not require external sources of current, reducing agent and complexing agent (such as cyanide) and provides simplified plating equipment and environmentally preferable procedure. The main objectives of this study were to investigate the effect of temperature on sulfur poisoning of pure Pd and Pd/Au alloy morphologically. In addition, the hydrogen permeation characteristics of the Pd/Au membrane in the presence of H₂S and the permeance recovery after the sulfur poisoning at different temperatures were investigated.

Experimental

Porous 316 stainless steel (PSS) plates were used for the coupon preparation, while porous Inconel tubes were used for the membrane preparation. Both were media grade of 0.1 μm and purchased from Mott Metallurgical Corp. Pure Pd coupons were prepared by the electroless plating¹⁰ on the oxidized (700°C, 12 hours) PSS plates (1 cm x 1 cm), and Pd/Au alloy coupons were prepared by the Au displacement plating on the Pd plated PSS coupons (6-9 μm thick Pd) followed by annealing at 550°C for 24 hours in H₂. The prepared pure Pd and Pd/Au alloy coupons were then exposed to a 54.8 ppm (±1ppm) H₂S/ H₂ mixture for 24 hours at the temperature from 350°C to 500°C with the interval of 50°C, and characterized by SEM (including EDX) and XRD. A Pd/Au membrane, designated as C04, was prepared on the porous Inconel support (1.27 cm in O.D. and 5.08 cm in length) by the electroless plating of Pd followed by the displacement plating of Au. Prior to the plating, the support was oxidized at 700°C for 12 hours followed by the successive Pd and Ag deposition to form the inter-metallic diffusion barrier^{11,12}, and between the oxides and Pd/Ag layer, the support was graded with the Al₂O₃ slurry. The final thickness of C04 was estimated gravimetrically as 18 μm with approximately 10wt% Au. The prepared membrane was then characterized for its gas permeating characteristics in a presence of a 54.8 ppm (±1ppm) H₂S/ H₂ mixture at the temperature from 350°C to 500°C.

Results and Discussion

In order to investigate the sulfur poisoning effect morphologically, poisoning tests of pure Pd and Pd/Au alloy coupons with a 54.8 ppm (±1 ppm) H₂S/ H₂ mixture for 24 hours at the temperature from 350°C to 500°C with interval of 50 °C were performed. XRD patterns and surface morphology of pure Pd coupons after poisoning were shown in Figure 1. From the X-ray patterns, a number of new peaks appeared in addition to the pure Pd peaks in all plane indicating the formation of new phases after the poisoning. The new peaks were identified as the palladium sulfide (Pd₄S) phase. The formation of the Pd₄S indicated that the chemical reaction between Pd and H₂S and the diffusion of adsorbed sulfur

into the interior of the Pd layer forming bulk sulfide compounds. Further, the Pd₄S peak intensity was found to decrease as the poisoning temperature increased and disappeared at 500°C, indicating that the formation of palladium sulfide and the sulfur poisoning effects were temperature dependent. The less poisoning effect at higher temperatures might be resulted from the higher desorption rate of H₂S at higher temperatures. Further, the surface morphology showed the “net-like” surface structure with numerous pinholes after poisonings, which might be the result of the incorporation of sulfur into the Pd lattice, causing stress in the Pd lattice. The number of pin holes and the sulfur content detected by EDX decreased as the temperature was increased, indicating the less sulfur adsorption and poisoning at higher temperatures, which agreed with the results from the XRD analysis.

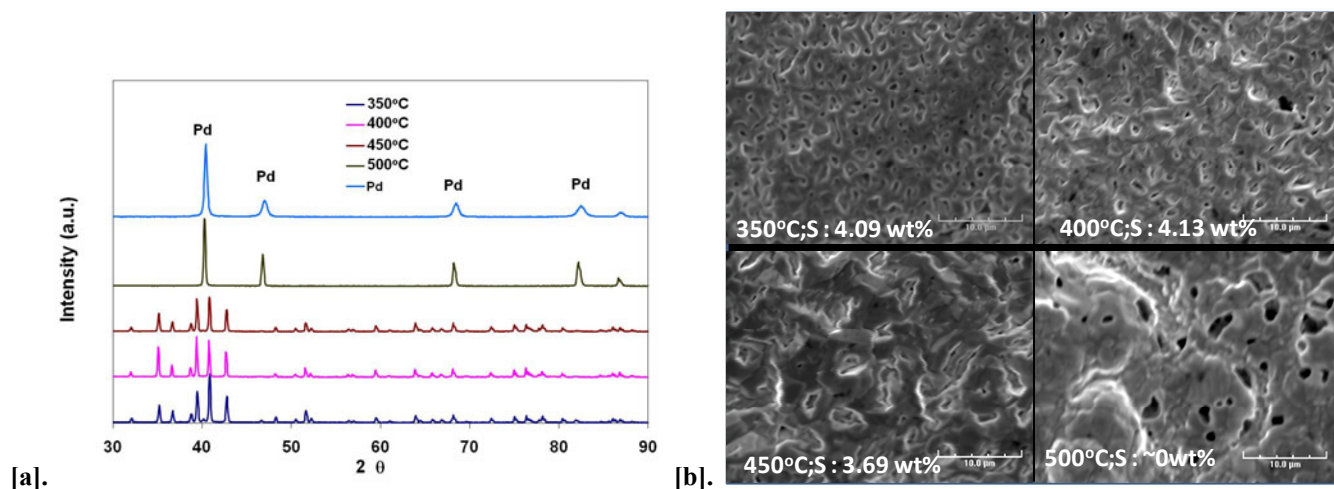


Figure 1. Temperature effect of sulfur poisoning of Pd on [a] crystalline phase, and [b] morphology.

Similar to Pd coupons, Pd/Au alloy coupons were also poisoned under the same conditions and characterized, and the resultant XRD patterns and morphology were shown in Figure 2. Unlike the pure Pd samples, the Pd/Au alloy samples showed no new peaks formation after the poisoning in the entire temperature range, and the XRD patterns of all tested temperatures remained almost identical in comparison to the one before poisoning. This indicated that the adsorption of H₂S on Pd/Au alloy was extremely small or even negligible with the same poisoning conditions as that of pure Pd coupons, suggesting the better sulfur resistance of Pd/Au alloy than pure Pd. Further, the surface morphologies of Pd/Au after poisoning at all tested temperatures showed no significant morphology changes and pin holes formation, remaining nearly identical in comparison to the one before poisoning with undetectable sulfur content by EDX. This was in agreement with the XRD results, indicating the small amount of the H₂S adsorption on the Pd/Au alloy surface. Since EDX and XRD were not able to detect the small amount of S on the very surface due to the long penetration depth of the X-ray emitted from EDX and XRD, the characterization via X-ray Photoemission Spectroscopy (XPS) (In cooperation with University of Connecticut) was further performed on the poisoned Pd/Au coupons. An average 3.4 at% S was detected on the Pd/Au sample that was poisoned at 350°C in the 54.8 ppm (± 1 ppm) H₂S/ H₂ mixture for 96 hours, indicating the small amount of S adsorbed on the Pd/Au alloy surface. More comprehensive XPS studies will continue to be performed.

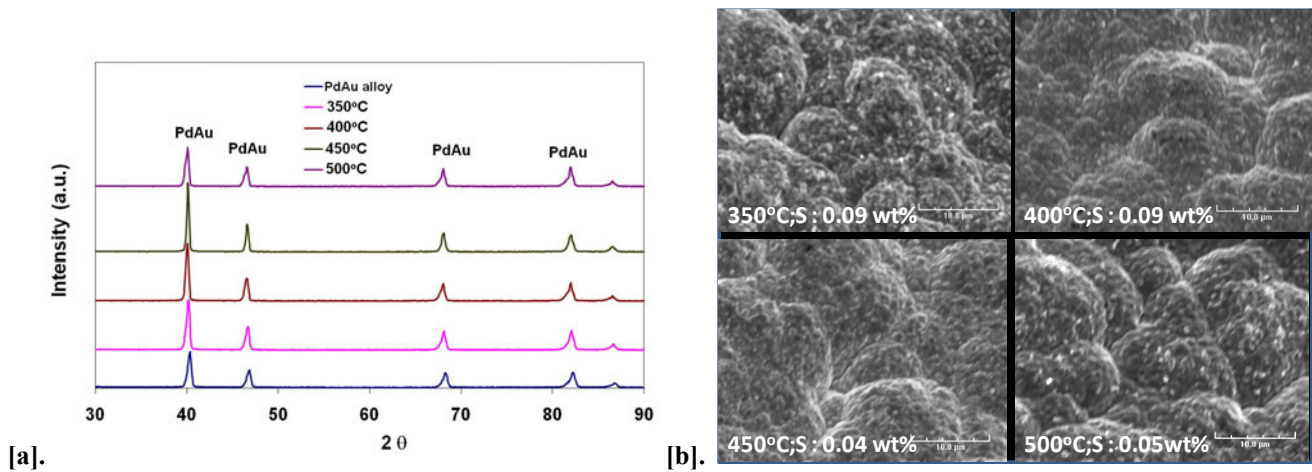


Figure 2. Temperature effect of sulfur poisoning of Pd/Au alloy on [a] crystalline phase, and [b] morphology.

In order to examine the sulfur poisoning effect on hydrogen permeating characteristics, a pure Pd membrane and the Pd/Au alloy membrane, C04, were characterized for their hydrogen permeance in the presence of a 54.8 ppm (± 1 ppm) H_2S . Firstly, the pure Pd membrane with a stable permeance of $30 \text{ m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{atm}^{0.5})$ at 400°C was characterized for its sulfur tolerance by switching the gas feed to the 54.8 ppm (± 1 ppm) H_2S/H_2 mixture, and the result is shown in Figure 3. It showed that the permeance dropped instantaneously after the 54.8 ppm (± 1 ppm) H_2S/H_2 mixture introduction at 400°C , and continued to decline for over 24 hours before it reached a steady state value. This indicated two poisoning mechanism, the instantaneous permeance drop at the beginning might be resulted from the surface adsorption which was rapid, while the slow and long decline of the permeance afterward might be resulted from the reaction between the Pd and the adsorbed sulfur which was a long process. Further, when the pure H_2 was re-introduced, the permeance remained the same value, showing no recovery, indicating the irreversible reaction occurred between Pd and H_2S during the H_2S exposure.

The same poisoning test was performed on C04 and the result is also shown in Figure 3. Prior to the sulfur poisoning tests, C04 was characterized in H_2 and He at the temperature from 250°C to 550°C for over 2000 hours and showed a steady state hydrogen permeance of $1.2 \text{ m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{atm}^{0.5})$ at 250°C and increased with increasing temperature reaching $6.5 \text{ m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{atm}^{0.5})$ at 500°C with a stable H_2/He selectivity of 100. The activation energy for the H_2 permeation was 13.1 kJ/mol . For the sulfur poisoning result, it showed that the permeance also dropped sharply right after the H_2S introduction (As shown in Figure 3.). However, it reached a steady state value immediately without continuing decline. Further, the permeance was found to be recovered to some extent when re-introducing the pure H_2 at the same temperature, indicating the reversible sulfur poisoning effect on Pd/Au alloy. Moreover, when increasing the temperature to 500°C during the recovery in H_2 , and permeance was found to be near fully recovered (As shown in Figure 4). The results suggested that the Pd/Au alloy membrane did show better sulfur resistance than the pure Pd membrane, and the minor and reversible sulfur poisoning effect on the Pd/Au alloy membrane was possibly due to the adsorption of H_2S on the Pd/Au surface only (i.e. No further reaction between adsorbed S and Pd/Au alloy).

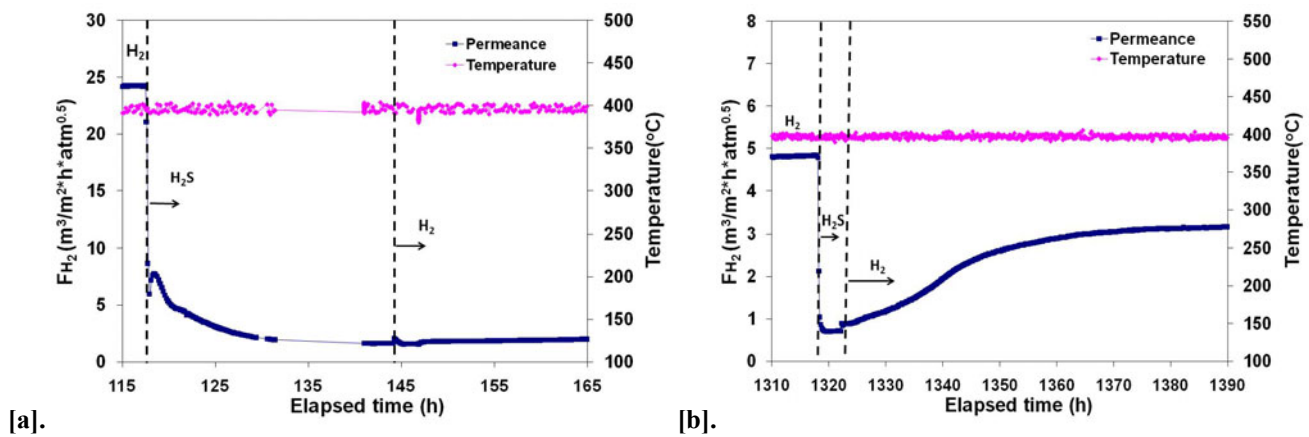


Figure 3. Effect of H₂S poisoning on hydrogen permeance at 400°C: [a] pure Pd membrane, and [b] Pd/Au alloy membrane.

Similar poisoning/recovering tests have been performed on C04 at other temperatures, and the percentage of permeance decline during the H₂S exposure was found to decrease as the temperature was increased, from 88% at 350°C, 85% at 400°C, 74% at 450°C, to 60% at 500°C (As shown in Figure 4). The recovered permeance before the full recovery at 500°C was found to increase as the temperature was increased from 43% of the original value at 350°C, 65% at 400°C, 74% at 450°C, and ~100% at 500°C (As shown in Figure 4). The results suggested that the higher desorption rate of the H₂S molecules at higher temperatures resulted in less sulfur adsorption on the membranes surface, thereby less poisoning effect of the membrane at higher temperatures. Further, from the linear recovery rate at different temperatures, the activation energy of desorption was estimated to be 71 kJ/mol by the use of Arrhenius relation, which suggested the partial physical and partial chemical adsorption of H₂S. Finally, as Figure 4 shows, the He leak flux showed no significant increase (even decreased) after the sulfur exposures over a lone testing time, indicating that the adsorbed sulfur might have segregated to the grain boundaries and defects in the Pd/Au films to block the passage-way of the non-adsorbing gas, such as He.

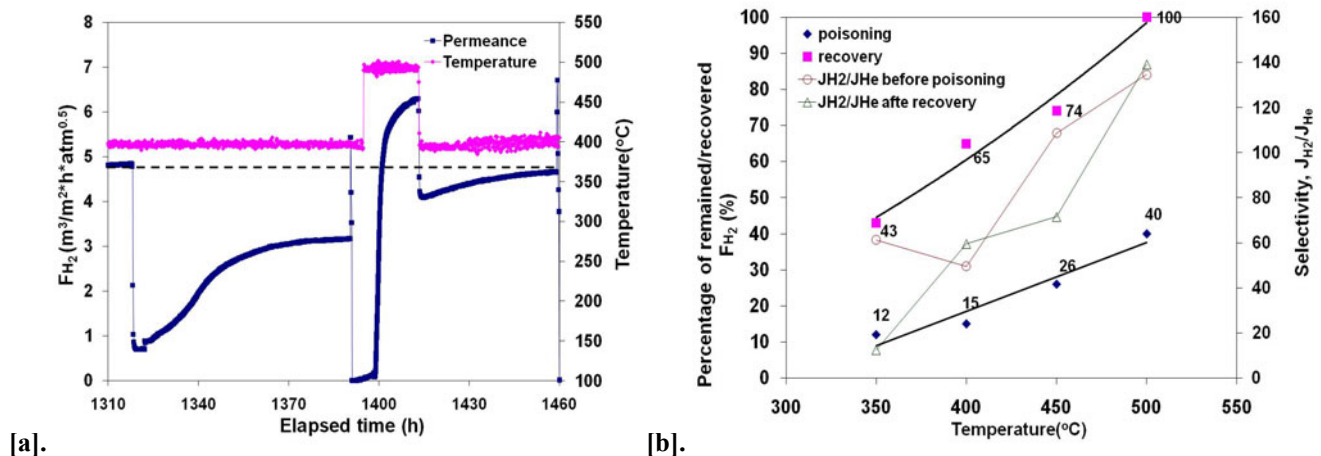


Figure 4. [a] Near full permeance recovery at 500°C, and [b] Summary of permeance remained/recovered and selectivity before/after poisoning at different temperatures.

Conclusions

H₂S was found to show severe poisoning effects on pure Pd. A 54.8 ppm (± 1 ppm) H₂S/H₂ gas mixture caused the Pd to react with, and to form Pd₄S resulting in numerous pin holes formation at the temperature of 350°C to 500°C. The formation of Pd₄S and the effect of poisoning were found to be temperature dependent and lower temperatures resulted in higher degree of poisoning. Further, the Pd membrane showed instantaneous permeance drop after the H₂S/H₂ introduction, and continued to drop over time. No permeance recovery after the re-introduction of pure H₂ has been observed, indicating the irreversible sulfur poisoning effect on pure Pd. The Pd/Au alloy, on the other hand, was found to show better sulfur resistance. No significant morphology changes and no new phase formation after the exposure of H₂S/H₂ have been observed in the entire testing temperature range. Further, although the Pd/Au membrane also showed the instantaneous permeance drop after the H₂S/H₂ introduction, the permeance reached a steady state value within a few minutes. Moreover, the permeance was able to be recovered in H₂ after the poisoning, indicating the reversible poisoning effect. The percentage of permeance recovered in H₂ after the poisoning, as well as the percentage of permeance remained during the poisoning, were found to be higher at higher temperatures, suggesting that the poisoning effect was temperature dependent, and the less poisoning effect at higher temperatures might be resulted from the higher desorption rate of H₂S.

Acknowledgements

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