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# Tailoring palladium alloy membranes for hydrogen separation from sulfur contaminated gas streams



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## ABSTRACT

Lately multi-component Pd alloy membranes have garnered much interest for H<sub>2</sub> separation from coal-derived gas streams which still contain up to 40 ppm H<sub>2</sub>S after desulfurization with ZnO beds at 673–773 K. Here we report on inhibition of three PdCuAg membranes with Cu-rich, Ag-rich and nearly even Cu:Ag stoichiometry in 9:1 H<sub>2</sub>/N<sub>2</sub> mixtures with up to 35 ppm H<sub>2</sub>S at these temperatures. The comparison with a Pd<sub>81</sub>Cu<sub>19</sub> membrane shows that addition of Ag to PdCu alloys weakens the resistance towards sulfur. Still, H<sub>2</sub> flux remained at least 50% higher for a Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> membrane than for the Pd<sub>81</sub>Cu<sub>19</sub> membrane under all H<sub>2</sub>S testing conditions due to the combination of extraordinary H<sub>2</sub> permeability with relatively moderate H<sub>2</sub>S inhibition of this ternary alloy. Its H<sub>2</sub> permeation rate places the Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> membrane among the best performing, sulfur tolerant membranes reported to date. Moreover, its H<sub>2</sub> flux could be fully restored after testing with H<sub>2</sub>S through operation in H<sub>2</sub> suggesting that the employed H<sub>2</sub>S levels had no lasting detrimental effects. However, Pd<sub>4</sub>S and Ag<sub>5</sub>Pd<sub>10</sub>S<sub>5</sub> were detected on Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> but not on Pd<sub>84</sub>Cu<sub>11</sub>Ag<sub>5</sub> after exposure to 100 ppm H<sub>2</sub>S at 773 K indicating that a careful balance of alloy stoichiometry is necessary for optimum sulfur tolerance. Thus, PdCuAg membranes may provide an attractive alternative to less permeable PdCu and more expensive PdAu-based membranes for H<sub>2</sub> extraction from sulfur contaminated gas mixtures.

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## 1. Introduction

Hydrogen separation membranes made of dense Pd are an intriguing option for cost-efficient, pre-combustion CO<sub>2</sub> capture in power generation from fossil fuels [1–5]. However, Pd and most of its alloys are very sensitive to sulfur compounds even at low ppm levels [6]. Sulfur concentrations can be reduced to less than 40 ppm at usual operation temperatures of Pd-type membranes (573–773 K) using conventional ZnO beds for desulfurization [7] but application of pure Pd or e.g. highly permeable PdAg membranes in coal-fired power stations necessitates a more meticulous sulfur clean-up of the gasification products. Therefore, high-temperature sulfur sorbents are currently under development that allow H<sub>2</sub>S reduction down to 1 ppm at 623–823 K [8,9]. On the other hand, PdCu and PdAu membranes exhibit some sulfur tolerance [6] but the latter involve a noticeable raise of noble metal expenses while the former deliver significantly lower H<sub>2</sub> permeation rates with increasing Cu content. Hence, in

recent years multi-component Pd alloys have been widely researched that combine good sulfur tolerance with better H<sub>2</sub> permeability and reduced membrane costs [10–17].

In this context PdCuAg alloys and membranes have attracted a lot of attention [15,18–22] because addition of Ag is known to benefit H<sub>2</sub> permeability of Pd greatly [23,24] and this noble metal is relatively inexpensive. Yet, sulfur inhibition studies have not been reported except for a Pd<sub>85</sub>Ag<sub>11</sub>Cu<sub>4</sub> membrane at a single temperature (723 K). In that case H<sub>2</sub> permeability dropped by ca. 95% after adding 20 ppm H<sub>2</sub>S to a 9:1 H<sub>2</sub>/N<sub>2</sub> feed but H<sub>2</sub> flux recovered almost completely within 2.5 h after cutting off H<sub>2</sub>S again [15]. However, a sulfide compound was found on this Ag-rich alloy following 75 h exposure at that contaminant level which appeared to accumulate when exposure time was extended to 500 h [15]. Our current scope is to develop a more comprehensive understanding of sulfur inhibition for a wider range of PdCuAg membrane alloys. In the following we will show that ternary membranes can be obtained through careful balancing of Cu and Ag content which exhibit significantly improved H<sub>2</sub> permeation rates in the presence of practically interesting H<sub>2</sub>S concentrations while H<sub>2</sub> permeability can be fully restored after removal of the contaminant.

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## 2. Experimental

### 2.1 Membrane preparation

Membrane preparation was described in detail elsewhere [21] including substrate activation, electroless plating (ELP) baths [25,26], sealing with graphite and eventual high-temperature treatment. In brief, Pd, Ag and Cu were deposited in this sequence via ELP on the outside of ceramic membrane tubes (TAMI, i. d. = 10 mm, o.d. = 14 mm) provided by the Energy research Center of the Netherlands (ECN) and then alloyed under H<sub>2</sub> at 773–823 K. The membranes were stored for ca. 18 months in ambient atmosphere following initial permeation experiments in the absence of sulfur [21] and deactivated strongly during that downtime. Re-activation proved to be sluggish at 773 K under H<sub>2</sub> so that we treated the Pd<sub>84</sub>Cu<sub>11</sub>Ag<sub>5</sub> (thrice) and Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> membranes in flowing air (40–50 ml min<sup>-1</sup>) at 573 K for up to 30 min after which H<sub>2</sub> fluxes had reached previous values almost again. We abstained from additional air treatments because we did not want to diminish the already moderate ideal H<sub>2</sub>/N<sub>2</sub> selectivity  $\alpha_{H_2/N_2}$  of these membranes further (Table 1).

### 2.2 Permeation measurements

The measurements presented here were carried out in a dedicated permeation setup for testing with H<sub>2</sub>S contaminated feeds described previously [27]. The membranes were mounted into a stainless steel separation shell with an inner diameter of 25 mm. Single gases or mixtures made of H<sub>2</sub> (purity > 99%) [28], N<sub>2</sub> (99.999%) and H<sub>2</sub> containing 507 ppm H<sub>2</sub>S were supplied to the membrane outside. Permeate and retentate flows were measured with a soap bubble flow meter up to 1500 ml min<sup>-1</sup> and larger ones with a TH-ZM8 electronic soap film flow meter (Wuhan Tianhong Instrument Co. Ltd.). The molar H<sub>2</sub> fraction of retentate and permeate flows were analyzed by an online gas chromatograph (GC-8A, Shimadzu) equipped with a thermoconductivity detector. H<sub>2</sub>S content of the feed could be monitored online using a Shimadzu GC-14C gas chromatograph equipped with a flame photometric detector (FPD).

All permeation measurements were carried out at pressure difference  $\Delta P = 100$  kPa with the permeate side at atmospheric pressure and without using sweep gas. The temperature was changed at a rate of ca. 1.5 K min<sup>-1</sup>. First single gas H<sub>2</sub> and N<sub>2</sub> permeation rates  $J_{H_2}$  and  $J_{N_2}$  were determined in the range 573–773 K. Next  $J_{H_2}$  was determined for a 9:1 H<sub>2</sub>/N<sub>2</sub> mixture between 673 K and 773 K while varying the feed rate  $J_{feed}$ . Following that, sulfur inhibition was examined employing 24 h test cycles for each H<sub>2</sub>S concentration  $C_{H_2S}$  and temperature  $T$ . These cycles started with 1 h operation in the sulfur-free 9:1 mixture at high  $J_{feed}$

(3000–4000 ml min<sup>-1</sup>). Then H<sub>2</sub>S was added for 5 h during which  $J_{feed}$  was stepwise reduced to ca. 250 ml min<sup>-1</sup>. After cutting off H<sub>2</sub>S again  $J_{feed}$  was raised back to the initial maximum value and membrane recuperation was monitored for ca. 3 h. Finally the temperature was raised to 773 K and the membrane was kept under H<sub>2</sub> overnight. The next morning the single gas  $J_{H_2}$  and  $J_{N_2}$  rates were checked at 773 K before starting another test cycle at different temperature and/or H<sub>2</sub>S concentration. In this way measurements were carried out first with 7 ppm H<sub>2</sub>S at 773 K, 723 K and 673 K and then with 35 ppm H<sub>2</sub>S following the same sequence of temperatures. Note that the H<sub>2</sub> permeation data of the PdCuAg membranes was corrected for leak flow contributions and support mass transport resistance with the help of  $J_{N_2}$  as previously described [21].

### 2.3 Sulfidation experiments and characterization

The end pieces of the membranes had been cut off prior to sealing of the membranes and alloyed at 1073 K in N<sub>2</sub> for 60 h for characterization of the PdCuAg layers [21]. Alloy layers from those cut-off pieces were detached from the ceramic support and exposed to 100 ppm H<sub>2</sub>S in H<sub>2</sub> at 773 K and 200 kPa for 24 h to investigate the propensity for sulfide formation on these alloys. The samples were placed in a polymer bag for analysis via X-ray diffraction (XRD) on an X'Pert PRO diffractometer (PANalytical) using Cu K $\alpha$  radiation at 40 kV and 40 mA.

## 3. Results

### 3.1 Membrane characteristics

We have reported the bulk structural characteristics of the supported PdCuAg membranes employed here already which were obtained from alloyed fragments of cut-off pieces [21]. Table 1 summarizes basic properties of these membranes including H<sub>2</sub> permeation data from our earlier study. These membranes encompass a Cu-rich and a Ag-rich stoichiometry as well as one with approximately even Cu and Ag content. Alloy stoichiometries are given in atom % throughout this paper. Table 1 contains also corresponding information of a Pd<sub>81</sub>Cu<sub>19</sub> membrane for which we tested H<sub>2</sub>S inhibition under the same conditions before [27]. In general H<sub>2</sub> permeability improved with increasing Ag and decreasing Cu content although the Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> membrane with nearly even amounts of Cu and Ag exhibited exceptionally high H<sub>2</sub> permeation rates [21]. The variation of  $J_{H_2}$  with membrane composition was the same as before deactivation (i.e. Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> > Pd<sub>76</sub>Cu<sub>5</sub>Ag<sub>19</sub> > Pd<sub>84</sub>Cu<sub>11</sub>Ag<sub>5</sub>) but the fluxes of the reactivated PdCuAg membranes remained 10–20% below the initial values at 673–773 K (Table 1).

The H<sub>2</sub> fluxes of the reactivated PdCuAg membranes have been measured in a different experimental setup than the ones reported before [21]. This appears to be the main reason for the somewhat differing permeation characteristics: We have checked single gas H<sub>2</sub> fluxes of the Pd<sub>79</sub>Cu<sub>11</sub>Ag<sub>10</sub> membrane in the originally used setup again after completion of the tests with H<sub>2</sub>S and we reached 95% of the previously reported fluxes again in the whole temperature range 573–773 K within a few days. The deviations could have been caused by differing heating characteristics of the two setups. On the other hand, the setup employed here had been used for sulfur testing before and may have had a background contamination level. This sulfur level was below the FPD detection limit but follow-up exposure experiments (vide infra) showed that especially the Ag-rich PdCuAg alloys are much more sensitive to sulfur than the Pd<sub>81</sub>Cu<sub>19</sub> membrane. Therefore, we cannot rule out that the single gas H<sub>2</sub> fluxes obtained here have been also affected

**Table 1**  
Characteristics of PdCu and PdCuAg membranes.

Membrane	$d^a$ $\mu\text{m}$	$A^b$ $\text{cm}^2$	$J_{H_2}^{c,d}$ $\text{mol m}^{-2} \text{s}^{-1}$	$J_{H_2}^{c,e}$ $\text{mol m}^{-2} \text{s}^{-1}$	$\alpha_{H_2/N_2}^{d,f}$	$\alpha_{H_2/N_2}^{c,e}$	$E_{act}^d$ $\text{kJ mol}^{-1}$	$n^d$
Pd <sub>81</sub> Cu <sub>19</sub> <sup>g</sup>	4.6	22.9	0.15	/	2369	/	22.4	0.69
Pd <sub>84</sub> Cu <sub>11</sub> Ag <sub>5</sub>	3.5	29.0	0.36	0.31	663	440	19.8	0.65
Pd <sub>79</sub> Cu <sub>11</sub> Ag <sub>10</sub>	4.6	14.1	0.48	0.44	269	288	12.5	0.63
Pd <sub>76</sub> Cu <sub>5</sub> Ag <sub>19</sub>	3.8	17.2	0.41	0.35	678	406	12.6	0.61

<sup>a</sup> Alloy layer thickness.

<sup>b</sup> Membrane area; note that PdCuAg values reported in Table 2 of Ref. [21] were incorrect.

<sup>c</sup> At 773 K and  $\Delta P = 100$  kPa.

<sup>d</sup> Before deactivation, from Ref. [21].

<sup>e</sup> After reactivation.

<sup>f</sup> At 673 K and  $\Delta P = 100$  kPa.

<sup>g</sup> All data from Ref. [27].

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