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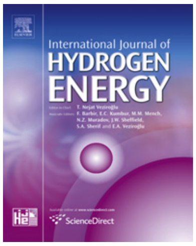

On alloying and low-temperature stability of thin, supported PdAg membranes

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ABSTRACT

Electroless plating is the technically most facile and most frequently studied method for preparation of PdAg/ceramic composite membranes. Limited high-temperature stability of such membranes requires alloying of sequentially deposited Pd and Ag layers far below their melting points, however. Here it is demonstrated that 600–800 h are needed for forming 2–4 μm thick, homogeneous alloy layers from Pd–Ag bilayers at 823 K under atmospheric H_2 pressure. This is also the time scale on which the activation energy for H_2 permeation becomes stable so that this characteristic can be employed for non-destructive, in-process monitoring of the alloying progress. High-temperature H_2 permeation rates are shown to be less well suited for this purpose because they are not sufficiently sensitive to the homogeneity of PdAg membranes. The activation energies for the well-alloyed membranes indicate that diffusion through the bulk of the PdAg layer limits H_2 permeation through these composite membranes. It is further shown that a fully alloyed $Pd_{75}Ag_{25}$ membrane tolerates temperature cycling under H_2 well down to 373 K while H_2/N_2 exchanges at that temperature trigger a rapid growth of the N_2 leak rate of that membrane. The defect formation is attributed to mechanical stress caused by the substantial expansion and shrinking of the alloy lattice during hydriding and dehydriding at low temperatures.

1. Introduction

Supported Pd and Pd alloy composite membranes are widely studied for the production of high purity H_2 and shifting the equilibrium of H_2-involving reactions [1,2]. PdAg alloy membranes continue to receive major attention [3–16] because they offer many advantages with respect to pure Pd membranes which include suppression of the α/β hydride miscibility gap toward lower temperatures, higher hydrogen permeance over a wide temperature range and cost reduction due to replacement of Pd with less expensive Ag [17]. Electroless plating routes are often employed for preparation of supported PdAg membranes [1,3–11] because they are the technically most facile methods for both co-deposition and sequential deposition of Pd and Ag. However, homogeneous alloying of separately deposited Pd and Ag layers is difficult because composite membranes on stainless steel and ceramic substrates have to be alloyed well below the Tammann temperature of Pd (913 K). This is necessary in order to prevent detrimental metal interdiffusion between stainless steel substrates and PdAg layers and to keep the thermal expansion mismatch between ceramic support and membrane within the acceptable limits.

Alloying of Pd and Ag layers on composite membranes has been studied before [5,6,10]. For example, Ayturk et al.

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demonstrated that annealing of a 15.6 μm thick Pd–Ag bilayer takes longer than 500 h at 823 K [6]. Similarly the Ag distribution remained inhomogeneous across ca. 20 μm thick PdAg layers which were annealed for 100–200 h at 773–873 K [10]. Yet it remains unclear how long it takes to form a uniform alloy membrane of only a few micron thickness from Pd–Ag bilayers. At the same time non-destructive monitoring of the progress of alloy formation in-process remains a challenge too. The stability of H_2 permeation rates is sometimes used for this assessment but it can be misleading if alloying proceeds slowly and the permeation rate varies only weakly with composition as in the case of PdAg alloys around their optimum composition [17]. This is a potentially dangerous situation if unnoticed because non-uniform membranes are much more prone to degradation processes such as hydrogen embrittlement. The permeation characteristics of alloy membranes will not be stable either until alloying has been completed. Such lack of performance consistency will complicate layout and control of membrane separation processes.

On the other hand there are surprisingly few reports about the low-temperature behavior of thin, supported PdAg membranes in H_2 atmospheres [4,11,12] considering that the superior stability of PdAg layers under such conditions is a frequent point of emphasis. Stable membrane performance under H_2 down to ambient temperature is of paramount importance for many practical applications. Obviously, propagation of hydrogen-induced defects through ultrathin PdAg membranes would occur much faster than through currently employed commercial membranes with thicknesses of at least 50 μm. Still, systematic studies are lacking on the tolerance of supported PdAg membranes to standard operations like cooling down to or atmosphere changes near room temperature. Most notably, Okazaki et al. subjected a ca. 3 μm thick $Pd_{80}Ag_{20}$/ceramic composite membrane to cycles between 373 and 573 K at $\Delta P = 200$ kPa, though heating in N_2 while cooling in H_2 [4]. The membrane withstood five of these combined temperature and H_2/N_2 exchange cycles well as evidenced by a very small N_2 leak rate even though the onset of the α/β hydride phase transition still occurred around 440 K in that alloy under the applied pressure conditions [4].

Thus, the current study has three main objectives: (1) to establish the time scale for homogeneous alloying of Pd–Ag bilayers by ex-situ X-ray diffraction (XRD) in order to form state-of-the-art membranes of less than 5 μm thickness and (2) to investigate whether the activation energy E_a for H_2 permeation is a suitable parameter for nondestructive, in-process monitoring of the membrane alloying progress; (3) in addition we probed the low-temperature stability of well alloyed membranes by subjecting them to independent temperature and H_2/N_2 exchange cycling at temperatures down to 373 K.

2. Experiments

2.1. *Preparation of PdAg/ceramic composite membranes*

Two types of 360 mm long, asymmetric Al_2O_3 membrane tubes were used as support which had a mean surface pore size of 100 nm each and inner and outer diameters of 8 and 12 mm (supplied by Nanjing University of Technology) or 7 and 10 mm (supplied by INOPOR), respectively. One end and the outer surface of each ceramic tube had been sealed gas-tight with a glaze except for 5 or 6 cm long sections, respectively, (corresponding to 18.8 cm^2 surface area in each case) near the closed tube end where the PdAg layer was to be deposited. The supports were cleaned and activated as previously described [7,8] and then connected to a vacuum pump and immersed in deionized water for 30 min before Pd electroless plating. The latter was carried out in a commercial bath (PALLA TOP, Okuno) at 318 K (250 ml, $[Pd^{2+}] = 18.9$ mM, pH = 7). After Pd plating both membrane tube sides were washed in boiling, deionized water for 1 h. The thickness of the Pd deposit layer was estimated by gravimetry. Before Ag plating the pure Pd membranes were heat treated at 823 K for several hours and then the H_2 and N_2 permeation rates were measured between 573 and 773 K. Following that they were again activated with Pd seeds. Then Ag plating was carried out in homemade baths (250 ml, $[Ag^+] = 0.3–0.85$ mM, $[N_2H_4] = 3–8$ mM, $[NH_3 \cdot H_2O] = 5$ M, $[EDTA] = 0.15$ M, pH = 12) for 180 min at 333 K. The Ag^+ and N_2H_4 concentrations were adjusted according to the targeted Ag content. After every hour of plating 10 ml NH_3 (28%) as well as 1.5 ml hydrazine (1 M) were added to the bath. All employed reagents were analytical grade. The as-prepared Pd–Ag bilayer was dried at 383 K and then heated to 823 K for alloying. Characteristic parameters of the membranes employed in this work are summarized in the Table 1. Compositions of the membranes are given in at.%. We refer to alloy layer thickness values as estimated from the weight gain in the following which agreed well with electron microscopic measurements (Table 1).

Table 1 – Characteristics of PdAg/ceramic composite membranes.

No.	Ag at.%		Thickness (μm)		Heating 823 K	Q_0 (10^{-8} mol m^{-1} s^{-1} $Pa^{-0.5}$)	E_a (kJ mol^{-1})	H_2/N_2 selectivity[c]
	XRD	EDX	ΔW[b]	SEM	(h)			
M0	24.7	25.8	3.5	3.2	800	/	/	/
M1-Pd[a]	pure Pd		2.2	–	50	8.39	10.8	29,800
M1[a]	11.4	10.8	2.5	2.3	730	5.77	7.9	3770
M2-Pd	pure Pd		2.1	–	60	9.02	11.0	34,000
M2	25.4	24.0	3.1	2.5	800	3.86	3.2	5600

a supported on INOPOR substrate.
b estimate from weight.
c at 823 K and $\Delta P_{H_2} = 100$ kPa.