



Study of n value and α/β palladium hydride phase transition within the ultra-thin palladium composite membrane

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ABSTRACT

The gas permeation of a 2 μm thick Pd membrane was examined between 363 K and 773 K with p_{feed} ranging from 1.4 bar to 3.8 bar and p_{perm} fixed at atmospheric pressure. The pressure exponent value ranged from 0.68 to 1.0, and it gradually decreased with increasing temperature and pressure. The transformation of rate-limiting step and enhancement of surface process were suggested to be the main reason for the fluctuation of n value, and the influence of contaminant species on the n value can be excluded in this study. The H₂ permeation flux of the membrane gave a marked change forming a peak at 413 K and 443 K with $p_{\text{feed}} = 2$ bar and 3 bar, respectively. These two peaks can be ascribed to the α/β palladium hydride phase transition. The metal membrane delaminated from the support after hydrogen embrittlement but it still maintained the nanostructure. The phase transition temperature range (20 K) for our 2 μm thick membrane was smaller than that of a 25 μm thick one (above 40 K) described in the literature.

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1. Introduction

Palladium-based membranes can be used in hydrogen separation and in membrane reactors, for example the water gas shift reaction, and methane steam reforming reaction. Recently they have received immense interest because of the prospect of a hydrogen economy. It is necessary to know the hydrogen permeation behavior of Pd membranes with thickness of several microns, which are widely used for hydrogen separation application. However, there are few reports on the pressure exponent value at different temperatures/pressures, and the α/β palladium hydride phase transition has been rarely examined as well.

1.1. Pressure exponent value

The permeation rate of hydrogen can be expressed as follows [1]:

$$J_{\text{H}_2} = \frac{P}{L} (p_{\text{feed}}^n - p_{\text{perm}}^n) \quad (1)$$

where J_{H_2} is the hydrogen flux ($\text{mol}/\text{m}^2 \text{ s}$), P is the permeability ($\text{mol m}/\text{m}^2 \text{ s Pa}^n$), L (m) is the membrane thickness, p_{feed} and p_{perm} (Pa) are the hydrogen partial pressures on the feed and permeate side, respectively and n is the pressure exponent. The permeation

rate is inversely proportional to the thickness of the membrane if bulk diffusion is the rate-limiting step. The inverse thickness dependence will change (as will the n value) if other transport steps become limiting. If n is equal to 0.5 then the hydrogen flux obeys the Sieverts' law and the bulk diffusion is the rate-determining step, which is usually valid for thick membranes. Deviation from Sieverts' law ($n > 0.5$) have often been reported for the membranes with thickness about several microns since surface processes (dissociative adsorption, absorption, recombinative desorption and bulk metal-to-surface transition) may become the rate-controlling step for permeation through the membrane [3–5] under this condition. For example, Yan et al. [6] found that for 3–5 μm thick palladium composite membranes the n value was close to 1.0 at 523 K and 0.1 MPa. Also, for 0.025–5.5 μm thick Pd alloy membranes, the pressure exponent was about unity at 548–773 K as reported in [7,8]. Recently some research indicated [2,9] that support resistance can also reduce the H₂ permeation rate and consequently n may be above 0.5 for composite membranes.

On the other hand, the n value may vary with temperature and pressure. For example, Zhang et al. [10] examined the pressure exponent value of a 2.5 μm thick Pd membrane on a 50 μm -thick Ni support, and they found that the n value decreased from 0.86 at 473 K to 0.73 at 673 K with the maximal feed pressure set at 0.166 MPa. But no reason was suggested for the decrease of n value. Morreale et al. [4] determined the n value in the 0–175 kPa, 0–775 kPa, 0–1600 kPa and 0–2600 kPa pressure ranges for a 1 mm thick bulk Pd membrane at 623–1173 K. They found that when the maximal pressure value was increased, the pressure exponent value

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increased in general from 0.5 to 0.62. The variances in the diffusion coefficient and Sieverts' constant at elevated pressures were suggested to be the main reason. However, until now it is still a challenge to understand the variation of n value at different temperatures and pressures, especially for the Pd membranes with thickness of several microns.

1.2. α/β palladium hydride phase transition

In practical applications, the pure palladium membrane is restricted since hydrogen embrittlement can be caused by the phase transition from α to β palladium hydride at temperatures below 573 K and pressures below 2 MPa [11]. Thus, in many cases the operation temperature of the Pd membrane was kept strictly above 573 K to avoid hydrogen embrittlement. But in fact the critical temperature for $\alpha \rightarrow \beta$ phase transition is contingent on the operation pressure. For example, Elkina and Meldon [12] found that for a 25 μm thick Pd foil, the α/β phase transition temperature was 478 K when the H_2 feed pressure was set at 5.1 bar, and the transition temperature decreased to 457 K when the H_2 feed pressure was decreased to 3.4 bar. It implies that the Pd membrane can be safely operated at 478 K to avoid the α/β palladium hydride phase transition if the H_2 feed pressure is always at or below 5.1 bar. Furthermore, the pure Pd membranes can be operated below 573 K through controlling the hydrogen partial pressure. Then the application of Pd membranes in the hydrogenation of pharmaceutical, and hydrogenation of fine chemicals, etc. at 473 K or even lower temperatures will be plausible [1]. Unfortunately, the experimental research about the α/β palladium hydride phase transition for Pd and its alloy membranes is limited [12–14]. On the other hand, through Monte Carlo simulations Wolf and co-workers [15,16] claimed that for nanometer-size palladium clusters no α/β palladium hydride phase transition should appear upon hydriding. This was experimentally confirmed by Pacheco Tanaka et al. [14]. They fabricated a Pd composite membrane packed with Pd nanoparticles and found it was substantially resistant to α – β phase transition. In addition, experimental data showed that nanocrystalline membranes can offer improved resistance to hydrogen embrittlement [17,18]. For example, the Pd–Fe nanoalloys did not experience the α – β phase transition when exposed to hydrogen [18]. This indicates that the hydrogen embrittlement may be greatly suppressed by nanostructured Pd or its alloy membranes, which needs to be further examined.

The objective of the present paper is to investigate the H_2 permeation of a 2 μm thick Pd membrane supported on a ceramic tube at 363–773 K with $p_{\text{feed}} = 1.4$ –3.8 bar. We investigated the pressure exponent value at different temperatures/pressures, and examined the H_2 permeation behavior crossing the α – β phase transition.

2. Experimental

2.1. Materials

The pure Pd membrane was prepared by a modified electroless-plating method [19] with an area of 20 cm^2 and a thickness of 2 μm . It is composed of a metal layer and a porous substrate- Al_2O_3 layer. By a modified electroless-plating method, little palladium was deposited into the pores of the Al_2O_3 tube [20].

2.2. Permeation measurement

The permeation apparatus has been described in [19]. In this experiment, two kinds of feeds were used, i.e. pure H_2 and N_2 gases. The purities of H_2 and N_2 were 99.995% and the flow rate was set at 6250 ml/min and 100 ml/min, respectively. The feed pressure (p_{feed})

was adjusted with a pressure controller and the permeate side was kept at atmospheric pressure. No sweep gas was used.

Before the permeation experiment the Pd membrane was treated by H_2 at 773 K for 10 h. Then the temperature was reduced in 50 K steps from 773 K to 573 K and the H_2 permeation was measured by varying p_{feed} from 1.4 bar to 3.8 bar at constant temperature. The fluxes were measured once the hydrogen permeation became stable. Afterwards two temperature cycles were carried out between 573 K and 363 K to examine the H_2 permeation behavior across the α – β phase transition. In the first cycle, the temperature was reduced in H_2 in 10 K steps from 573 K to 363 K. At each temperature, the H_2 permeation was measured after stabilization for 20–40 min. p_{feed} varied between 1.4 bar and 3.8 bar at 363 K, 473 K and 523 K while it was fixed as 2 bar at other temperatures. Following the H_2 permeation measurement at 363 K, the membrane was purged with 100 ml/min N_2 for 18 h to remove residual H_2 in the system and subsequently the temperature was increased to 573 K in N_2 at 1 K/min. Then the second cycle was carried out between 363 K and 573 K. The process for the second cycle was almost the same as the first one with only one difference: p_{feed} was set at 3 bar when the temperature was reduced from 573 K to 363 K.

Note that the pure N_2 flux was also measured at 773 K with $p_{\text{feed}} = 2$ bar and at 573 K with $p_{\text{feed}} = 1.5$ bar, 2 bar, 2.5 bar and 3 bar during the above mentioned processes. After the two temperature cycles the membrane was cooled down to room temperature in N_2 gas and then it was broken into small pieces to be characterized by X-ray diffraction (XRD), temperature-programmed oxidation (TPO) and electron dispersive spectroscopy (EDS). Membrane pieces were typically about 50 mm^2 large. XRD patterns were measured on a Philips CM-1 powder X-ray diffractometer ($\text{Cu K}\alpha$, $\lambda = 0.1543$ nm). TPO was performed by heating the membrane pieces from 323 K to 1200 K at a rate of 10 K/min in a 5% O_2/He flow (30 ml/min). The oxidation products were analyzed by a quadrupole mass spectrometer (OmniStar GSD 301). EDS analysis of the membrane was recorded with a JEOL JSM-6360LV scanning microscope.

3. Results and discussion

3.1. Pressure exponent value

The initial H_2 permeance of the membrane was 7.3×10^{-6} mol/m² s Pa with an ideal H_2/N_2 selectivity of 1300 at 773 K. Fig. 1 shows the hydrogen permeation flux for the membrane as a function of feed pressure and temperature. It can be seen

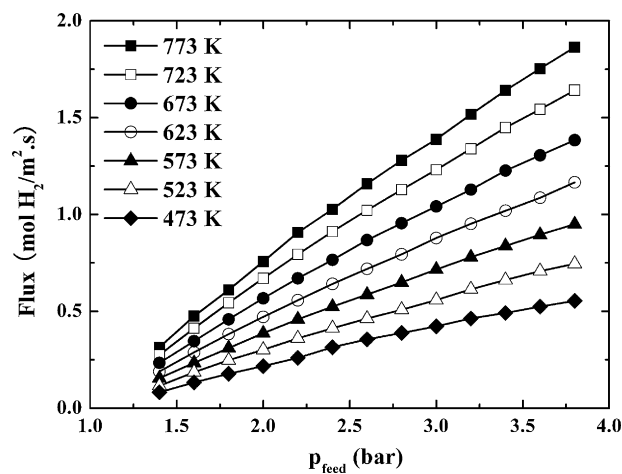


Fig. 1. Hydrogen permeation flux of the Pd membrane as a function of feed pressure and temperature.

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