

Mathematical modeling of high temperature and high-pressure dense membrane separation of hydrogen from gasification

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Abstract

At UTSI, Pd/Al₂O₃ membranes were prepared by a special method of laser based thermal deposition of a thin film Pd on a ceramic substrate by Nd–YAG laser irradiation of PdCl₂ coating on a γ -alumina substrate. This paper describes a mechanistic model for the hydrogen permeation process in such Pd/Al₂O₃ composite membrane developed at UTSI. The model takes into account the well-known kinetics of hydrogen adsorption/desorption in the palladium surface and hydrogen permeation in the porous alumina layer. Reasonable values for all mass transfer rate parameters were estimated based on the available surface science and membrane permeation literature. One set of experimental data (at 866.48 K) was used to determine the best values of the necessary rate parameters. These values of rate parameters were then used to predict and compare the experimental hydrogen flux data at two other temperatures (755.37 and 977.59 K). The results demonstrated that the atomic hydrogen diffusion through the palladium layer and pore diffusion in the porous alumina support both played important roles in the permeation of hydrogen through the composite Pd/Al₂O₃ membrane. A simplified resistance model was also employed to analyze the permeation behavior of hydrogen through the Pd/Al₂O₃ membrane to identify the major resistances to the mass transfer. The results indicated that the mass transfer in the Pd layer contributed about 90% of the total mass transfer resistance. Our model calculations also indicated that by reducing the thickness of the Pd layer to about 18 μ m, the DOE goal of $>5 \times 10^{-3} \text{ m}^3/\text{m}^2 \text{ s}$ (60 scfh/ft²) for hydrogen gas flux can be achieved. This can also be achieved by reducing the thickness of the Pd layer to about 20 μ m and reducing the thickness of the alumina support layer to about 2 mm or by increasing its porosity to about 50%.

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Keywords: Palladium membranes; Alumina support; Hydrogen permeation; Mass transfer resistance; Rate-limiting step/flux; Knudsen flow; Poiseuille flow; Film transfer; Dissociative adsorption; Associative desorption; Surface-to-bulk metal transition; Bulk metal-to-surface transition; Sievert's constant

1. Introduction

The extensive use of hydrogen in many industrial sectors, such as petroleum refining, petrochemical, semi-conductor, industrial material processing and in power producing devices, such as fuel cells, is expected to rise in the coming years. More so, the depletion of crude oil, natural gas and fossil fuel has led the US chemical industry to seriously consider hydrogen as one of the alternative clean energy sources. Hydrogen is mostly found bonded in chemical compounds like biomass, water, and fossil fuels. Chemical reactions are needed to break hydrogen bonds from these compounds and release hydrogen which has to be then recovered from the multi-component gas stream. Recov-

ery of high purity hydrogen can be achieved by employing the membrane separation technology. The Department of Energy (DOE) goal is to research and develop low cost, highly efficient hydrogen technologies from diverse domestic and renewable sources. Substantial advantages can be gained from fossil fuel gasification technology for the production of hydrogen and other useful gases by using membrane separation processes. The reactions involved in gasification are favored at high temperature and high pressure and are also limited by thermodynamic equilibrium. The use of a membrane for separation provides the basis for improved methods of hydrogen recovery and also reduces the cost associated with the hydrogen production at elevated temperatures and pressures. Also, combining the chemical reaction and separation steps in a single process will eliminate limitations imposed by the process thermodynamics on the yield of hydrogen. Palladium was first identified as a highly hydrogen-permeable material in the 19th century and it is used for high performance hydrogen separation applications today [1]. Dense

Abbreviations: DOE, Department of Energy; LEED, Leadership in Energy and Environmental Design; UTSI, University of Tennessee Space Institute

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palladium-based membranes have been used in recent years in the separation of hydrogen, and in catalytic membrane reactors and have been studied extensively due to their high permeability; good surface properties and high selectivity for hydrogen transport [2–5].

In this paper, a mechanistic model of the hydrogen permeation process in the Pd/Al₂O₃ composite membrane is reported. This model takes into account the well-known kinetics of H₂ adsorption/desorption at the palladium surface and H₂ permeation in the porous alumina layer. It also takes into account the mass transfer resistances associated with the viscous flow (Hagen–Poiseuille type) and Knudsen diffusion through the porous support. This mechanistic model was used to simulate the earlier hydrogen permeation experimental results obtained from the Pd/Al₂O₃ composite membrane at UTSI. Based on the data obtained from our model calculations, the optimal material and structure of a composite membrane for hydrogen separation can be effectively designed to achieve the fluxes in excess of $5 \times 10^{-3} \text{ m}^3/\text{m}^2 \text{ s}$ (60 scfh/ft²). This limit has been considered by DOE to be necessary for the commercial applications in hydrogen-fuelled fuel cells.

2. Literature review

There are excellent reviews on the fundamental mechanisms of gas transport through palladium membranes and on modeling of gas separation in palladium membranes. Huang et al. [2] studied the hydrogen permeation behaviors through palladium composite membranes to understand the influence of the mass transfer resistance of the Al₂O₃ support. The importance of the Pd film microstructure on the hydrogen permeation rates has been stressed by Ward and Dao [6]. A model was developed by Henis and Tripodi whereby the transport properties of each membrane layer in the composite hollow fiber membrane can be isolated and their transport resistances studied [7]. Shu et al. reviewed hydrogen permeation in pure palladium membranes, as well as the basic physico-chemical knowledge which would allow for future development [8]. The energetic, kinetic and structural properties of hydrogen chemisorbed on a Pd (100) surface were studied by Behm et al. using thermal desorption, work function and Leadership in Energy and Environmental Design (LEED) measurements [9]. More work on the fundamental surface science of hydrogen on palladium has also been reported by Conrad et al. in his work on the adsorption of hydrogen on palladium single crystal surfaces [10].

The first observation of the permeability of hydrogen through transition metals was made by Deville and Troost, whose experiments were first carried out on iron and platinum [11]. Thomas Graham carried out related measurements afterwards and observed that not only did palladium permit high throughputs of hydrogen, but that large volumes of hydrogen were also absorbed in the palladium metal. Palladium exhibits a high solubility of hydrogen when compared with other transition elements over a very wide range of temperatures and pressures of hydrogen. Palladium experiences an α to β transition at temperatures below the critical temperature (568 K) and pressures below $2.03 \times 10^6 \text{ Pa}$ (20 atm) [1,8,11], depending on the hydro-

gen concentration in the metal. This phase transition leads to lattice expansion of about 10% which then causes lattice strain and physical distortion after a few cycles. This can be possibly remedied by exposing palladium to hydrogen only at high temperatures above the critical temperature.

Gas transport through palladium-based membranes is usually rate limited by the bulk atomic diffusion and that the flux has been found to be inversely proportional to the membrane thickness with an approximate square root dependence on the hydrogen partial pressure [1,2,6,8,12,13]. This behavior is called Sievert's law behavior with the value of the exponent, n , is equal to 0.5 [14]. The exponent of 0.5 reflects the dissociation of the gaseous hydrogen molecule into two hydrogen atoms that diffuse into the metal, where an ideal solution of hydrogen atoms in palladium is formed. Collins and Way found that the value of n was significantly dependent on temperature and the n value of a palladium layer with 17 μm thickness decreased from 0.622 to 0.552 when the permeating temperatures increased from 723 to 873 K [15]. Hurlbert and Konecny [16] showed that the bulk diffusion of hydrogen was the rate-limiting step when the thickness of the palladium layer was greater than 20 μm . Uemiya et al. [17] reported that diffusion-limited permeations extended to thicknesses less than 10 μm . There has not been any agreement among experimental observations for very thin Pd films due to the complexity of the overall transport mechanism and also with difficulty in quantifying factors, such as poisoning and surface contamination. Ward and Dao [6] reported that diffusion was likely to be the rate-dominating step at moderately high temperatures ($\geq 573 \text{ K}$), even for membrane thicknesses approaching 1 μm . Ward and Dao [6] also concluded that desorption was the rate-limiting step at low temperatures and adsorption was only likely to be important at very low hydrogen partial pressure or in the presence of substantial surface contamination. The transport resistance of the support is considered to be negligible in most permeability studies, but Huang et al. [18] in their study showed that considerable transport resistance can exist in the support layer also. Burggraaf [19] in his work reported that the mass transfer resistance associated with the Knudsen diffusion or viscous flow through the porous support could be significant in a composite membrane. The purpose of our work was to develop a mechanistic model based on the literature for hydrogen permeation in the Pd/alumina composite membrane fabricated earlier at UTSI.

Hydrogen permeation measurements were carried out on the Pd/alumina composite membrane fabricated at UTSI, in a bench scale high temperature and pressure reactor system. Palladium membrane was used at UTSI due to its very high hydrogen selectivity. Palladium is permeable to hydrogen gas but impermeable to CO, CH₄ and CO₂, which are all products of gasification reaction. Alumina was used as a porous support to increase the mechanical stability of the porous membrane. Pure hydrogen and nitrogen gases were used with purity over 99.5%. Also, mixed gases containing 10 vol.% CO, 35 vol.% CH₄ and 55% CO₂ were also used [35]. Pinholes were observed in the hydrogen permeation and was corrected using the following equation: $J_{\text{H}_2(\text{metal})} = J_{\text{H}_2(\text{Total})} - J_{\text{H}_2(\text{pinhole})}$ [35]. The ratio of mole fraction of hydrogen to methane on the feed side was used

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