

High pressure performance of thin Pd–23%Ag/stainless steel composite membranes in water gas shift gas mixtures; influence of dilution, mass transfer and surface effects on the hydrogen flux

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Received 6 July 2007; received in revised form 31 August 2007; accepted 31 August 2007

Available online 14 September 2007

Abstract

The hydrogen permeation and stability of tubular palladium alloy (Pd–23%Ag) composite membranes have been investigated at elevated temperatures and pressures. In our analysis we differentiate between dilution of hydrogen by other gas components, hydrogen depletion along the membrane length, concentration polarization adjacent to the membrane surface, and effects due to surface adsorption, on the hydrogen flux. A maximum H₂ flux of 1223 mL cm⁻² min⁻¹ or 8.4 mol m⁻² s⁻¹ was obtained at 400 °C and 26 bar hydrogen feed pressure, corresponding to a permeance of 6.4 × 10⁻³ mol m⁻² s⁻¹ Pa^{-0.5}. A good linear relationship was found between hydrogen flux and pressure as predicted for rate controlling bulk diffusion. In a mixture of 50% H₂ + 50% N₂ a maximum H₂ flux of 230 mL cm⁻² min⁻¹ and separation factor of 1400 were achieved at 26 bar. The large reduction in hydrogen flux is mainly caused by the build-up of a hydrogen-depleted concentration polarization layer adjacent to the membrane due to insufficient mass transport in the gas phase. Substituting N₂ with CO₂ results in further reduction of flux, but not as large as for CO where adsorption prevail as the dominating flow controlling factor. In WGS conditions (57.5% H₂, 18.7% CO₂, 3.8% CO, 1.2% CH₄ and 18.7% steam), a H₂ permeance of 1.1 × 10⁻³ mol m⁻² s⁻¹ Pa^{-0.5} was found at 400 °C and 26 bar feed pressure. Operating the membrane for 500 h under various conditions (WGS and H₂ + N₂ mixtures) at 26 bars indicated no membrane failure, but a small decrease in flux. A peculiar flux inhibiting effect of long term exposure to high concentration of N₂ was observed. The membrane surface was deformed and expanded after operation, mainly following the topography of the macroporous support.

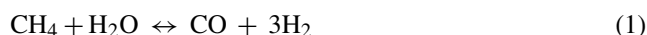
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Keywords: Palladium membrane; Hydrogen flux; Water gas shift; Concentration polarisation; CO adsorption

1. Introduction

The primary large scale industrial hydrogen production route is via methane steam reforming. The process involves two equilibrium-limited reactions: the reforming and water gas shift reaction.

1. Reforming



2. Water gas shift



Dense metal membranes based on palladium and its alloys have frequently been applied in membrane reactors for water gas shift and steam reforming reactions to simultaneously achieve a high conversion, and production of pure hydrogen [1–4]. In these extensively studied membrane reactor concepts, the compatibility of the amounts of hydrogen produced (catalytic reaction) and removed (membrane permeance) is essential [5]. Depending on the combination of Pd-membrane properties and operation conditions, different rate limiting processes may prevail. The processes commonly discussed are bulk diffusion and surface reaction. For a particular membrane the rate of bulk transport depends on membrane thickness, while the combination of surface characteristics and operation condition determines the rate of the surface reaction. Reduced hydrogen permeation rate due to surface effects is usually explained by blocking of hydrogen surface sites by strongly adsorbing species as, e.g. CO [6]. The extent of permeation reduction is therefore a function

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of the composition, temperature, pressure, and the thickness of the employed membrane [7–9]. Generally, in the presence of adsorbing gas components, the lower the temperature, and the thinner the membrane employed, the more significant the hydrogen flux is affected by surface reactions [7,10]. Reduction of hydrogen flux in reforming and WGS conditions is well known [7], however, previous studies have so far been restricted to relatively low pressure differences across the membrane, and/or relatively thick palladium membranes. In the present study, we investigate the flux behaviour for a unique combination of high pressure (up to 26 bars) and very thin Pd–23%Ag composite membranes ($\sim 2 \mu\text{m}$). The influence on the hydrogen flux by hydrogen dilution, concentration polarization due to mass transfer limitations, and adsorption effects is particularly addressed. The membranes have been prepared by the SINTEF two-stage method in which a defect free Pd–23%Ag film is first prepared by magnetron sputtering deposition onto the ‘perfect surface’ of a silicon wafer [11]. In a second step the pinhole-free film is removed from the wafer and transferred to a macroporous tubular stainless steel support to produce the composite membrane. This method allows the preparation of thin ($\sim 1\text{--}2 \mu\text{m}$) defect free membranes supported on macroporous substrates capable of operating at pressures difference of 25 bars.

2. Hydrogen permeation through Pd membranes

The permeation of hydrogen through Pd membranes is often described by several main steps, which include adsorption of hydrogen molecules on the membrane surface, dissociation on the surface into atomic hydrogen, transition of atomic H from the surface into the bulk metal, atomic diffusion through the bulk metal, recombinative desorption from the surface, and gas transport away from the surface to the bulk gas [12]. When the rate limiting step is hydrogen diffusion through the Pd membrane, the H_2 flux can be obtained by integration of Fick’s Law

$$J = -D \frac{dC}{dl} = \frac{D}{l} (C_{\text{H}_2,1} - C_{\text{H}_2,2}) \quad (3)$$

where J is the hydrogen flux ($\text{mol m}^{-2} \text{s}^{-1}$), D the diffusivity of hydrogen in the palladium membrane, which is assumed to be independent of the hydrogen concentration ($\text{m}^2 \text{s}^{-1}$), l the thickness of the membrane (m), and $C_{\text{H}_2,1}$ and $C_{\text{H}_2,2}$ are the hydrogen concentrations in the palladium membrane in equilibrium with the feed and permeate gas, respectively (mol m^{-3}). These concentrations can be expressed as

$$C = \kappa \eta \quad (4)$$

where κ is the hydrogen concentration constant (mol m^{-3}) and η is the atomic H/Pd ratio, which is a function of temperature and hydrogen partial pressure [13,14]. At low concentrations of hydrogen [13], η is linearly dependent on the square root of partial pressure of hydrogen giving

$$P_{\text{H}}^{0.5} = K_s \eta \quad (5)$$

where K_s is the Sieverts constant. Combining equations (3)–(5), yield

$$J = \frac{D(\kappa/K_s)}{l} (P_{\text{H}_2,1}^{0.5} - P_{\text{H}_2,2}^{0.5}) \quad (6)$$

in which the term κ/K_s represents the hydrogen solubility, S , in the palladium layer. The product of the diffusivity, D , and solubility, S , is often referred to as the hydrogen permeability, Q . Thus, if diffusion through the membrane is rate limiting, Sieverts law gives the hydrogen flux as

$$J = \frac{Q}{l} (P_{\text{H}_2,1}^{0.5} - P_{\text{H}_2,2}^{0.5}) \quad (7)$$

3. Experimental

3.1. Pd–23wt%Ag film preparation

Unsupported palladium films were prepared by the sputtering technique using a CVC 601 magnetron sputtering apparatus. The membranes were sputtered from a Pd–23%Ag target onto polished silicon single crystal substrates. The vacuum chamber was pumped down to $\sim 10^{-6}$ Torr before introducing the sputtering gas Ar into the system. Using a sputtering time of around 2 h a final membrane thickness of $2.2 \mu\text{m}$ was obtained. The membrane thicknesses were determined using scanning electron microscopy (SEM) or white light interferometry.

3.2. Composite membrane preparation

After sputtering, the palladium film was removed manually from the silicon substrate and transferred to the 4 cm long tubular macroporous stainless steel porous substrate [11]. In this study, tubular porous 316L stainless steel (PSS[®]) Accusep[™] supports (PALL Corporation, USA) have been utilized. The support diameter and wall thickness of the support were 11.85 and 0.48 mm, respectively. The effective surface area of the membrane was equal to 6.8 cm^2 . The average pore size of the support was $2 \mu\text{m}$. The surface image of the PSS[®] supports can be seen in Fig. 1.

3.3. Hydrogen permeation measurements

The tubular-supported palladium membranes were tested in a unit designed and constructed for high pressure membrane permeability testing. A supported palladium membrane was placed inside a 316L stainless steel module (inside diameter 1.9 cm) allowing the membrane to be tested with counter-current flow. Automated mass flow controllers (Bronkhorst High-Tech) were used to control the gas supply to the feed and permeate sides of the membrane. The flow of water was regulated using a liquid mass flow controller (Bronkhorst High-Tech). The tank was pressurized with N_2 to force water into an evaporator before mixing with other gases prior to entering the membrane module. At the retentate side, the steam was condensed in a water trap, before the gas was analysed by a GC (Varian Inc., CP-4900). When heating up the module, the membrane was kept in a N_2/Ar atmosphere until $300 \text{ }^\circ\text{C}$ was reached, then H_2 was introduced.

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