



# Hydrogen permeation through palladium membranes and inhibition by carbon monoxide, carbon dioxide, and steam



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## ABSTRACT

Palladium membranes are being developed for the separation of hydrogen from syngas in industrial applications. However, syngas constituents carbon monoxide, carbon dioxide, and steam are known to adsorb at the membrane surface and inhibit the permeation of hydrogen. The current study combines an experimental study and modelling approach in order to investigate and quantify the inhibition effects. Experiments have been performed with a 2.8  $\mu\text{m}$  thick palladium membrane (surface area 174  $\text{cm}^2$ ) on a tubular alumina support, including systematic variation of the concentrations of carbon monoxide, carbon dioxide, and steam at 22 bar total pressure and 350–450 °C. Carbon monoxide and steam inhibit hydrogen permeation. No significant effect has been found for carbon dioxide, except indirectly by carbon monoxide produced in situ from carbon dioxide. A constriction resistance model has been derived, explicitly relating the decrease in surface coverage by adsorbed hydrogen to the ensuing decrease in transmembrane flux. Very high surface coverages by inhibiting species  $\theta_i > 0.995$  are predicted. The results highlight that inhibition effects are greatly reduced at high hydrogen partial pressures due to competitive adsorption. Due to the lateral diffusion of permeating hydrogen atoms in the metallic membrane, the thickness of the palladium membrane strongly determines the extent to which surface coverage by non-hydrogen species causes a decrease in hydrogen transmembrane flux. Depending on the operating conditions, membranes are predicted to have an optimal minimum thickness below which an increased intrinsic permeance is offset by an increased impact of inhibition.

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## 1. Introduction

Palladium has an extremely high solubility for hydrogen atoms and, provided no other species adsorb, dense palladium membranes can have an extremely high permselectivity for hydrogen. Therefore, metallic palladium membranes have received a great deal of interest from researchers worldwide since the first discovery of hydrogen permeation in the 19th century [1–4]. Palladium based membranes have been in use for the production of hydrogen in niche markets for decades and membrane separation technologies have significant economic potential in chemical industry, precombustion carbon dioxide capture, and the production of ultrapure hydrogen [1,5–7]. Different companies worldwide commercialise palladium-based membranes for hydrogen production. State of the art membranes consist of a thin (<50  $\mu\text{m}$ ) metallic palladium or palladium alloy film fixed to a porous metal

or ceramic support [8]. Palladium alloys, rather than pure palladium membranes, are used in processes where  $\alpha$ - $\beta$  palladium hydride phase transition may compromise membrane integrity (below the critical point,  $T_c = 293$  °C,  $p_c = 20$  bar [9]), to reduce surface poisoning by specific gas phase species, and to further enhance the hydrogen transmembrane flux [4]. Given the state of the art, benchmarking of membranes from different vendors is a crucial step in the introduction of hydrogen membranes to demonstrate the maturity and performance under industrially relevant conditions, i.e. about 50 vol% hydrogen at 30 bar total pressure and 400 °C (see discussion below). In previous papers [8,10], a strategy has been introduced consisting of systematic experiments and model development for the description of hydrogen permeation at high partial pressure (11–15 bar) and temperature (350–450 °C). For hydrogen–nitrogen mixtures with and without sweep, it was found that the main resistances to mass transfer are concentration polarisation in the retentate, hydrogen permeation through the metallic palladium layer, and (particularly in cases where sweep gas is used) a diffusional resistance in the support layer. The model derived has been shown to quantify, as a

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function of operating conditions, the intrinsic and external mass transfer resistances. In this paper this work is extended with dedicated experiments as well as model development to account for inhibition effects by syngas species carbon monoxide, carbon dioxide, and steam.

The term inhibition refers to the observed decrease in trans-membrane flux due to the competitive adsorption of gaseous species on the membrane surface. As such, it is fundamentally different from mass transfer resistances (e.g., concentration polarisation) and depletion. For palladium based membranes, inhibition by carbon monoxide, carbon dioxide, and steam has been reported at temperatures around 400 °C [11–20]. Barbieri et al. [21] interpreted the observed decrease in hydrogen flux through a palladium–silver membrane at 319–450 °C with inhibition by up to 2 bar carbon monoxide in terms of a Sieverts–Langmuir model, assuming a linear correlation between the decrease in hydrogen permeance and the surface coverage by carbon monoxide. Consequently, they accounted for the membrane surface fraction not available for hydrogen permeation using a Langmuir affinity constant for carbon monoxide and a temperature dependent ‘permeance reduction factor’. Mejdell et al. [22] confirmed the model for palladium–silver at 275–350 °C and 0–0.15 bar carbon monoxide, while measuring a weak effect for carbon dioxide at 350 °C. Inhibition by carbon monoxide and carbon dioxide for a palladium membrane (350–450 °C) could be described by a similar relation by Augustine et al. [16]. Building on these Langmuir isotherm based inhibition models, Israni and Harold [23] adopted a more comprehensive approach and derived a competitive adsorption model for the inhibition by methanol, steam, carbon dioxide, and carbon monoxide on the hydrogen flux through a palladium–silver membrane at 225–300 °C and pressures of 3–5 bar. Recently, Patrascu and Sheintuch [20] applied this inhibition model to a pure palladium membrane in a membrane reformer, but found significantly stronger inhibition by carbon monoxide. Abir and Sheintuch [24] developed a first principles model of adsorption, subsurface penetration, and atomic hydrogen diffusion and found that inhibition by propylene and carbon monoxide substantially reduced the hydrogen surface coverage. While these previous studies have provided better insight into the phenomenon of inhibition, they are limited in several important respects. Firstly, in terms of operating conditions, inhibition has not yet been studied in industrial syngas mixtures with systematic variations of the concentrations of hydrogen, carbon monoxide, carbon dioxide, and steam at relevant temperatures and pressures. Secondly, up until now the modelling approach has been based on a reduced, one-dimensional model for the diffusion of hydrogen atoms across the metal membrane.

A comprehensive model of hydrogen permeation under inhibition would require a proper description of the mass transfer resistance in the membrane module, of the resistance in the membrane support, and of the permeation across the metal membrane layer, i.e. accounting for lateral diffusion in the metal. Mass transfer resistance in the membrane module becomes increasingly important with increasing transmembrane flux and it has been widely discussed in the literature [10,12,25,26]. Peters et al. [25] present a clear and comprehensive discussion of the effects of dilution, depletion, and concentration polarisation, all lowering the partial pressure of hydrogen at the membrane surface on the feed/retentate side. The same effects, *mutatis mutandis*, arise at the sweep/permeate side of the membrane. In addition, the membrane support can add friction as well as a diffusional resistance to the mass transfer resistance [10]. Kinetic modelling has shown that at industrially relevant temperatures above 300 °C and high hydrogen partial pressures, the diffusion of hydrogen atoms across the metal membrane is the rate limiting step in the absence of inhibition [27,28]. At least for membranes

with a thickness of 1 µm and over, a deviation of the pressure exponent in the flux equation from 1/2 (Sieverts’ law) in these conditions is related to the hydrogen solubility in the palladium bulk rather than due to surface limitations. With inhibiting species in the feed gas, the number of sites occupied by hydrogen atoms will decline and surface limitations become important, changing the rate limiting step. Indeed, kinetic modelling has shown that the rate of hydrogen dissociative adsorption becomes important at high coverage by carbon monoxide [15]. However, a study of the rate of adsorption and permeation of hydrogen, combined with the rates of adsorption and desorption of inhibiting syngas species, is lacking.

In the Dutch national programme CATO2, palladium-based membranes have been benchmarked for pre-combustion carbon dioxide capture in natural gas fuelled combined cycle power plants and in refineries [8,29]. Within this framework, a model is developed to describe the permeation of hydrogen in industrially relevant conditions, including the presence of inhibiting species. A systematic approach is adopted, first developing models that describe mass transfer resistance in the module and membrane support [10], then continuing to describe the kinetics of adsorption and desorption of hydrogen and the decrease in the apparent permeance by inhibiting species, and to account for diffusion of hydrogen atoms in case of inhibition. This study not only aims at further clarifying the nature of the inhibition phenomenon, but also to allow for the interpretation of membrane performance measurements in industrial syngas applications.

This paper first discusses the results of a dedicated set of experiments done with a supported palladium membrane, systematically varying the concentrations of syngas species carbon monoxide, carbon dioxide, and steam. While palladium alloys may arguably be considered state of the art, the current work benefits from having a pure palladium membrane. Apart from the fact that the operating conditions are well above the critical temperature and phase separation is impossible, the description of the adsorption and diffusion of hydrogen across pure palladium is more straightforward. Subsequently, a set of models is developed that is required for interpretation of the experiments. Firstly, the membrane flux equation is derived from pure hydrogen experiments and validated with hydrogen–nitrogen separation experiments. Secondly, a novel set of model equations is derived that describes the response of dissociative hydrogen adsorption and permeation rates to the surface coverage by inhibiting species based on the concept of constriction resistance. Finally, the complete set of models is used to quantify the observed decline in permeance in the presence of syngas species.

## 2. Material and methods

### 2.1. Experiment

Experiments have been performed on ECN’s ‘Process Development Unit’ (PDU), described in more detail elsewhere [14,30,31]. The experimental procedure has been described previously by Boon et al. [8,10].

A supported palladium membrane was obtained from Hysep (The Netherlands) [32]. It consists of a 2.8 µm thick layer of palladium on a ceramic support tube. The support is a porous alumina tube of 14 mm outer diameter and 2 mm thickness and contains three layers of different characteristics [10]. After sealing, the effective length of the membrane is 0.396 m, and the surface area 174 cm<sup>2</sup>. The membrane tube was mounted in a cylindrically shaped module (26.62 mm internal diameter), containing an insert tube (6 mm outer diameter) intended for sweep gas, creating a double annulus geometry enclosing the membrane.

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