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# Hydrogen permeation through Pd-based composite membranes: Effects of porous substrate, diffusion barrier and sweep gas

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ABSTRACT

Gas transport in the diffusion barrier and porous substrate layers is modeled in order to evaluate its impacts on the performance of palladium-based composite membranes for $H_2$ separation. A pseudo-2-dimensional model is created for a cylindrical membrane module with counter-current flow. It is hypothesized that displacement of proton transport paths may occur in the bulk metal membrane due to a non-permeable solid phase in direct contact with it. A flux-weighted effective membrane thickness is proposed to account for this effect, which has not been considered in previous literature. Both the dusty gas model (DGM) and binary fraction model (BFM) are used to simulate gas transport in the porous media. Predictions show that under certain circumstances, a well-designed diffusion barrier may cause a slight increase in $H_2$ flux, contrary to common belief. Two mechanisms are identified which enhance membrane performance by sweeping the permeate side. Though gases with small Schmidt number were found to be more likely to penetrate through the membrane substrate and build significant concentration at the membrane-substrate interface, the choice of sweep gas may depend on other practical considerations, especially gas separation downstream. Combinations of porosity and pore size are recommended for the membrane substrate and diffusion barrier based on modeling results.



## 1. Introduction

One of the most promising technologies for producing and separating hydrogen involves palladium-based membranes, owing to their high perm-selectivity to hydrogen. Analysis of the steps involved in hydrogen permeation leads to the Sieverts' law for relatively thick, unsupported membranes [1]. However, deviations from the theoretical power-law exponent of 0.5 are evident due to non-idealities at low temperature and high pressure, and significant contributions of other mass transfer resistances as the membrane thickness becomes smaller [2,3]. Several recent theoretical studies [4–7] highlight the renewed interest in understanding the fundamental principles underlying membrane permeation.

Most Pd-based membranes are supported or directly deposited on porous substrates to overcome mechanical integrity issues with unsupported metal films. The development of high-flux dense metal membranes, driven by the needs for both performance enhancement and cost reduction, has led to a profound change in the membrane resistance distribution under real-world conditions, with external mass transfer playing an increasingly important role [8]. Proper consideration of concentration polarization and external mass transfer resistance is essential to develop a practical membrane performance model [9,10].

Diffusion barriers have been developed to prevent undesirable atomic inter-diffusion between the membrane metal and the substrate [11–13]. One concern with the use of diffusion barriers is the potentially significant additional mass transfer resistance. However, little work has been done to understand its impact on gas transport in composite membranes.

Membranes are often swept on the permeate side with inert gases to increase the driving force for permeation. While this often makes sense in experimental studies, sweep gas operation may not be justified in applications that require high $H_2$ purity because sweeping creates a mixture that must be separated again with additional equipment and operating costs. Whether the sweep gas can effectively diffuse counter to the $H_2$ permeate flux to reduce the $H_2$ partial pressure at the membrane-substrate interface, and under what conditions it does so, are poorly understood.

To address these knowledge gaps, the present study focuses on gas transport in the porous substrate in order to answer some

*Abbreviations:* ADM, Advection diffusion model; BFM, Binary friction model; DGM, Dusty gas model; EMT, External mass transfer; ID, Inner diameter; OD, Outer diameter; PSS, Porous stainless steel; SG, Sweep gas

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fundamental questions concerning the role of the diffusion barrier, substrate and the sweep gas in composite membrane operation. The dusty-gas model (DGM) [14] and binary friction model (BFM) [15] are used to examine the transport of $H_2$ and the sweep gas in the porous substrate, and their results are compared. The modeling results provide insights into (i) the mechanism of enhanced $H_2$ permeation by sweep gas operation, (ii) the role of the diffusion barrier in optimization of composite membranes, and (iii) the primary requirements for designing the diffusion barrier and membrane substrate.

## 2. Model features

A steady-state, isothermal, pseudo-2-dimensional (i.e. one-dimensional in axial direction, multiple layers in radial direction) model was created for a cylindrical Pd/Ag composite membrane module shown in Fig. 1. The feed gas flows in an annulus between the shell and the supported membrane tube. The sweep gas, introduced from an inner tube, reverses direction at the other end to flow in the opposite direction with respect to the feed flow. The membrane is coated onto a pre-fabricated porous tube with an outer diameter (OD) of $D_0$. The figure shows one embodiment. Our model is generic, and can be readily adapted to other configurations, with different ways of introducing the feed and sweep gas.

Fig. 2 illustrates the structure of the composite membrane and hydrogen partial pressure profile, with the feed gas flowing on the left side and the permeate stream on the right. Without losing generality, the membrane support is shown to have three layers to represent a multi-layered structure.

Depending on the application, membrane modules can be planar or tubular, mostly supported on porous stainless steel (PSS), alumina or glass substrates [16–19]. With few exceptions, the feed gas mixture flows on the outside of the support tube (or high-pressure side of the plate), onto which the membrane is attached, though feeding from the inside may be preferred for unsupported membranes tubes [19].

Table 1 summarizes dimensions, structural details and permeability data of the tubular membrane module being modeled, together with information of the membrane modules from which experimental data were collected for comparison with model predictions. One set of experimental data is obtained from a planar module, with a 50 µm thick Pd/25Ag membrane coated on a 1.2 mm thick PSS substrate, previously tested by the same group of authors. The other set of data reported by Peters et al. [20] is selected for comparison because of the similar cylindrical structure of the module, clarity and completeness of essential information presented in the article.

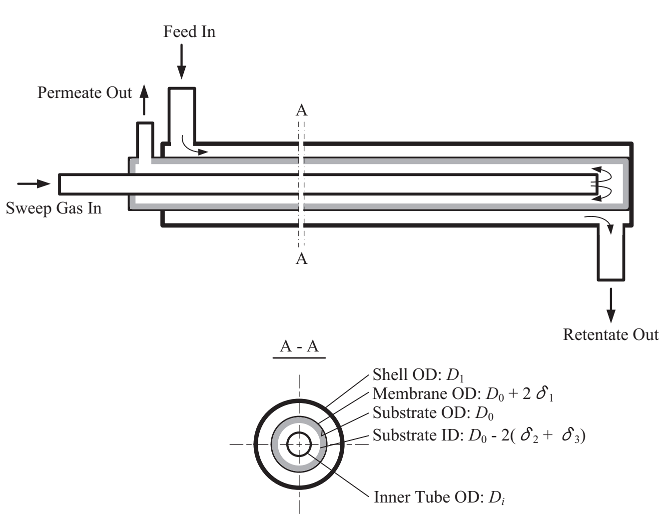


**Fig. 1.** Schematic of compact tubular membrane module.

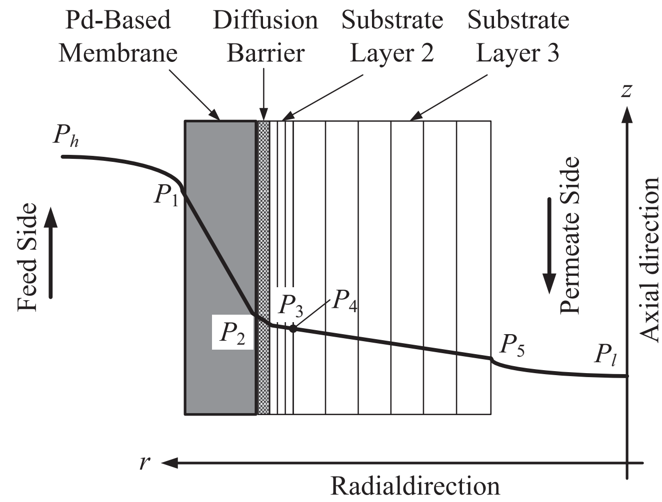


**Fig. 2.** Composite membrane with multiple support layers.

### 2.1. Transport of gases in porous membrane substrate

We examine gas transport first as the present work focuses on the effect of the porous substrate and sweeping on membrane performance, both requiring knowledge of gas transport in the porous substrate. Isothermal conditions have been assumed.

Though mathematically simple, the advection-diffusion model (ADM) is inadequate to describe gas transport in porous media [21]. The large variations in the mean pore diameter and potentially significant pressure difference make the dusty-gas model (DGM) [14,22] and the binary friction model (BFM) [15] more appealing for modeling gas transport in the porous membrane substrate, which involves molecular diffusion, Knudsen diffusion and viscous flow. Both the DGM and BFM are employed in the present study, and a brief comparison is made.

#### 2.1.1. The Dusty Gas Model (DGM)

In the DGM, the flux of component-$i$ in a gas mixture of $n$ components under isothermal condition satisfies the equation [14]:

$$\sum_{j=1, j\neq i}^{n} \frac{x_i N_j - x_j N_i}{D_{ij}^e} - \frac{N_i}{D_{K,i}^e} = \frac{P}{RT}\nabla x_i + [1 + \frac{B_v P}{D_{K,i}^e \mu}]\frac{x_i}{RT}\nabla P. \quad (1)$$

The solution of the equations is computationally-intensive for multi-component gas mixtures. Fortunately, for a binary gas mixture typically encountered in the membrane substrate, the equations can be much simplified since only one gas component, $H_2$, can permeate through a defect-free membrane. Applying the zero-flux condition to the sweep gas, we can write

$$-\frac{x_B N_A}{D_{AB}^e} - \frac{N_A}{D_{K,A}^e} = \frac{P}{RT}\nabla x_A + [1 + \frac{B_v P}{D_{K,A}^e \mu}]\frac{x_A}{RT}\nabla P; \quad (2)$$

$$\frac{x_B N_A}{D_{AB}^e} = \frac{P}{RT}\nabla x_B + [1 + \frac{B_v P}{D_{K,B}^e \mu}]\frac{x_B}{RT}\nabla P. \quad (3)$$

Here, subscripts A and B represent $H_2$ and the sweep gas, respectively. The viscosity is for the gas mixture rather than for an individual component, since viscous flow is non-separating.

It must be remembered that, although the total flux of the