Concentration Polarisation and Inhibition by CO in Supported Pd-based Membrane

Alessio Caravella¹, Adele Brunetti²,
Enrico Drioli¹,², Giuseppe Barbieri²

¹Dept. of Environmental and Chemical Engineering, University of Calabria (UNICAL), Via P. Bucci, Cubo 44A, Rende (CS), 87036, Italy

²Institute on Membrane Technology, National Research Council (ITM-CNR), Via P. Bucci, Cubo 17C, Rende (CS), 87036, Italy
Outline

◆ Hydrogen Permeation Model through Pd-based Membranes

◆ Non-Ideal Hydrogen Permeation

◆ Concentration Polarisation

◆ Coupled Phenomena

◆ Conclusions
Objective: Characterization of the permeation rate-determining steps

Hydrogen Permeation Model

Physical system

Membrane Sketch

Mathematical Description

Objectives:

1. Characterization of the permeation rate-determining steps
2. Identification of mass transfer mechanisms

Materials:

- Feed Side
- Pd-based layer
- Porous support
- Permeate Side
- Pd-based layer
- Multicomponent Mass Transfer
- Adsorption ($H_2$, CO)
- Surface-to-Bulk
- Bulk Diffusion
- Bulk-to-Surface
- Desorption ($H_2$)
- Layer 1
- Layer n
- Thin layer
- Porous support
- Mass transfer in the pores
- Multicomponent Mass Transfer
In ideal case, flux obeys Sieverts’ law

\[
H_2 \text{Flux} = H_2 \text{Permeance}^{(\text{Sieverts})} \times \left[ p_{H_2, \text{Feed}}^{0.5} - p_{H_2, \text{Permeate}}^{0.5} \right]
\]

Dissociative Hydrogen Adsorption

\[
0.5 \ H_2(g) \leftrightarrow H(\text{ads})
\]

The real membrane behaviour can be quite different from the ideal one

The Non-Ideality Index provides the quantitative effect of the non-ideal contribution of the hydrogen diffusion through the metal lattice [6].

The non-ideal contribution can be relevant and increases with increasing feed pressure.

This analysis allows the temperature effect to be followed more precisely avoiding the use of the n-exponent (empirical Sieverts’ law).

Concentration Polarisation in Pd-based Membranes\[11,14,19,23\]

Inert

\[\text{H}_2\] Flux “pushes” the non-permeating species towards the surface

External Resistance to Mass Transfer (in the gas phase)

Concentration Polarisation is modelled by the Multicomponent Film Theory

Bulk of the Gas Phase

Gas Film Adjacent to Membrane

Permeation Flux

Pd-based Membrane
Inhibition in Pd-based Membranes\textsuperscript{[11,14]}

Inhibition: Competitive and Reversible Physical Adsorption of some species in mixture

External Resistance to Mass Transfer (in the gas phase)

Competitive Adsorption (on membrane surface)

Inhibition ALWAYS involves Concentration Polarisation
Combined Effect of Polarisation and Inhibition \cite{11,14}

\begin{itemize}
  \item[a)] The Intrinsic Permeance is independent of the Hydrogen Concentration in absence of Inhibition
  \item[b)] The Apparent Permeance is strongly affected by Polarisation and Inhibition
\end{itemize}

An appropriate Approach is required to account for these phenomena at a macroscopic level
Concentration Polarisation Coefficient Behaviour

Calculation based on the properties of a 3 \( \mu \text{m} \)-TECNALIA Membrane
Conclusions

1. A powerful tool is already available to simulate hydrogen permeation through supported Pd-based Membranes.

2. It is shown that the non-ideality of hydrogen permeation CANNOT be neglected in high-performance Pd-based membranes.

3. A semi-empirical approach was developed to account for the deviation from ideality for a moderate pressure range.

4. It was shown also that Inhibition ALWAYS involves also Concentration Polarisation, whilst the opposite does not generally hold.

5. The presented approach allows the description of such a coupling, permitting also to evaluate these phenomena under a variety of operating conditions and geometries.
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Useful References