FREQUENCY-DOMAIN ANALYSIS OF HYDROGEN PERMEATION ACROSS PALLADIUM METALLIC MEMBRANES

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ABSTRACT
Hydrogen permeation (ie. hydrogen transport across metallic membranes), is an industrial process used for purification purposes. Palladium alloys are generally used as permeation materials, at operating temperatures above the critical value, to avoid the precipitation of hydride phases. In state of the art systems, a few tens of microns thick metallic membranes are used and rate limitations come from bulk atomic H diffusion. Because of cost considerations, it is necessary to reduce the thickness of these membranes. In the micron-thick range, surface contributions are expected to become rate determining, especially when the membrane is positioned on the exit side of a gas reformer used for the production of pure hydrogen from natural gas or bio-fuels. For such applications, corrosion problems are expected to appear on the upstream side of the membrane, yielding additional surface resistances. There is therefore a need to separately measure surface and bulk rate contributions during permeation processes. In this communication, a new experimental equipment and a new treatment procedure are proposed to analyze the dynamics of hydrogen permeation across metallic membranes. Permeation can be conveniently analyzed in the frequency domain, yielding information on the different steps involved in the overall mechanism. Raw kinetic data such as transient pressure signals, obtained in a typical permeation experiment, are numerically Fourier-transformed, leading to the transfer function of the membrane. It is shown that the rate parameters of the different steps involved in the permeation mechanism can be separately measured: surface resistances related to hydrogen dissociation (upstream side) and recombination (downstream side) processes, and bulk diffusion impedances. Results obtained with palladium membranes are presented and discussed.

KEYWORDS : hydrogen, palladium, permeation, transfer function.

1. Introduction
The concept of catalytic membrane reactors [1,2] used for steam reforming allows the direct production of pure hydrogen, which in turn can feed H₂/O₂ fuel cells. In these times of increasing environmental problems and oil crisis, such technologies are currently considered for the development of alternative clean means of transportation. Steam reforming, as considered here, is the endothermic reaction of bio-hydrocarbons with water. Gaseous reaction products are mixed and a purification membrane is used to selectively extract hydrogen by permeation. Different kinds of membrane materials can be used for this purpose [3-5]. For practical applications, cost considerations require significant thickness reductions. Whereas surface processes are not playing a major kinetic role in permeation processes when thick membrane (a few tens of microns) are used, they may become rate determining when thinner membranes (in the micron thick range) are used. For this reason, there is a need to separately measure surface (hydrogen dissociation and recombination) and bulk (hydrogen transport by diffusion) contributions to the overall permeation process. Pneumato-chemical impedance spectroscopy (PIS) [6] provides a powerful tool for this purpose. In PIS analysis, kinetic data is analyzed in the frequency (Fourier) domain, and the convoluted time-domain responses of individual reaction steps appear separately at different frequencies. As described in this paper, it becomes possible to separately measure surface pneumato-chemical resistances and bulk hydrogen diffusion coefficients. PIS offers the possibilities of (i) measuring each rate constant under different operating conditions, (ii) probing degradation mechanism, (iii) optimizing thicknesses and compositions for given applications, and (iv) modeling efficiently dynamic phenomena. PIS analysis is used in the present work to analyze the dynamics of hydrogen permeation through massive palladium foils. A mathematical model is proposed to account for the kinetics of permeation.
2. PIS analysis of permeation kinetics

2.1. Principles

Pneumato-chemical Impedance Spectroscopy (PIS) is a tool which was initially developed for analyzing hydriding kinetics in hydrogen absorbing materials [6]. In the present communication, PIS analysis is extended to permeation phenomena. The key feature of this technique is that polychromatic perturbations signals such as “step signals” are used instead of harmonic perturbations. The transfer function of the system is not measured on a frequency-to-frequency basis, but in a single experiment, the polychromatic perturbation and the corresponding response being synchronously sampled and decomposed into their frequency contents by the use of the Fourier transformation.

For a solid-gas reaction, the transfer function of interest relates the pressure excitation to the resulting mass flow response. This is why the resulting transfer function is called a “pneumato-chemical” impedance, the term “pneumato” referring to gaseous hydrogen and the term “chemical” referring to the solid-state reaction which takes place inside the solid sample. Shortly, in the time-domain, the relationship between any pair \( \{i(t); o(t)\} \), where \( i(t) \) denotes an input transient signal and \( o(t) \) an output transient signal, is a convolution:

\[
o(t) = \int_{-\infty}^{\infty} i(\tau) h(t-\tau) \, d\tau = i(t) * h(t)
\]

where \( h(t) \) be the impulse response of the system when the unit impulse (Dirac) function \( \delta(t) \) is applied as input:

\[
\delta(t) \rightarrow h(t)
\]

Equation (1) can be more conveniently solved in the frequency-domain where the convolution is transformed into a simpler algebraic product:

\[
FT[i(t)*h(t)] = FT[i(t)] \cdot FT[h(t)] = FT[o(t)]
\]

where \( FT[i(t)] \) denotes the Fourier transform of \( i(t) \), etc.

More conveniently, Eq. (3) is written as:

\[
H(f) = \frac{FT[o(t)]}{FT[i(t)]}
\]

where \( H(f) \) is the transfer function of the system, \( i.e. \) the Fourier transform of the impulse response:

\[
FT[h(t)] = H(f) = \int_{-\infty}^{\infty} h(t) e^{-j2\pi f t} \, dt
\]

\( f \) is the frequency in Hz and \( \omega = 2\pi f \) is the pulsation in rad.s\(^{-1}\).

In fact, several transfer functions (such as impedances, admittances, etc.) can be defined from this very general methodology and in the present work, we will more specifically consider the pneumato-chemical impedance defined, by similarity with the electric impedance, as \( P \) denotes a pressure and \( dn/dt \) a mass flow:

\[
Z(f) = \frac{P(f)}{dn/dt(f)}
\]

Usually, \( Z(f) \) is measured by solving equation (6), using monochromatic signals. Our purpose here is to show that Eq. (6) can also be solved using polychromatic signals such as those used in permeation experiments.

2.2. Experimental setup

A new experimental setup has been specifically designed and developed to perform permeation experiments (figure 1). Basically, the system consists of four volumic chambers (316 L stainless steel capacities from Swagelok Co.) interconnected with stainless steel tubing (1/4 in. internal diameter) and VCR\textsuperscript{®} connectors (figure 2) : (i) a reservoir chamber \( Ch_0 \), (ii) a reference volume chamber \( Ch_1 \), (iii) a permeation chamber \( Ch_2 \) and (iv) a gas collection chamber \( Ch_3 \). Alphagaz grade 2 gas (H\(_2\)) is used in the experiments. Experimental results presented in this paper have been obtained using Pd foils (100 \( \mu \)m thick, 99.9% from Aldrich Chemical Co.).
For accurate mass balance calculations, the temperature is measured at different points of the setup using chromel-alumel thermocouples. The permeation chamber can be heated for high temperature operation. Different manual diaphragm valves (MVs, Swagelok Co.) are used for gas management and setting of initial gas transfer conditions. A bellows-sealed valve (Swagelok Co.) equipped with a metering stem tip is placed in the circuit. This needle valve (NV) acts as a gas flow regulator allowing non-convective and isothermal gas transfer from Ch1 to Ch2. Pressure transducers (Keller Co.) with numerical output are used to sample transient pressure signals during gas transfer experiments. This test-bench can be air-purged down to secondary vacuum (5x10⁻⁶ mbar) using a turbo-molecular pump (BOC Edwards Co.).

3. Thermodynamic and kinetic analysis of the PdH system

3.1. Thermodynamics

The electrochemical and chemical isotherms of the PdH system at room temperature are shown in figure 3. They are similar in shape, and they both exhibit a significant hysteresis in the two-phase domain. The critical temperature (Tc) of the PdH system, i.e., the temperature above which the system remains monophasic (a solid solution of H in Pd over the whole composition range), is close to 300°C. Permeation experiments should preferably be carried out above Tc, to avoid the precipitation of the hydride phase. This is not because hydrogen diffusion across the hydride phase is a slow process (in fact, in palladium, D_h is known to be slightly larger in β than in α phase) but because the precipitation of the β phase will generate many defects such as dislocations which in turn will decrease the mean D_h value and make the sample more brittle (especially in thin films). Also, modelling of the permeation process is easier in the monophasic case than in the biphasic one.

![Figure 3 - left: electrochemical (blue) and chemical (red) experimental isotherms measured on PdH at 298K; right: phase diagram of the Pd-H system.](image)
3.2. Collect of raw kinetic data

In a typical permeation experiment using pure hydrogen, Ch₁ (figure 2) is initially pressurized at P₁° (using H₂ stored in Ch₀), Ch₂ at P₂° and Ch₃ at P₃°. Then, the manual valve MV₁ is opened and transient pressure signals in chambers 1, 2 and 3 are synchronously sampled until equilibrium is reached. The hydrogen mass flow dn/dt across the membrane is calculated by derivation of P₃(t) in the collection chamber:
\[
\frac{dn}{dt}(t) = \frac{V_3}{RT} \frac{dP_3}{dt}. \]

All these transient signals provide raw kinetic data. They can be used to calculate experimental impedances in order to analyze the permeation mechanism in the frequency (Fourier) domain. They can also be used to analyze the permeation process directly in the time domain as described below.

3.3. Experimental pneumato-chemical permeation impedances

There are two different ways to model permeation processes using Eq. (6). The first one is to measure experimental permeation impedances of the membrane material and to fit them with a model equation to access microscopic rate parameters. This is done by taking the ratio of the Fourier transforms (FT) of the difference of transient pressures P₂(t) – P₃(t) to the hydrogen mass flow (dn/dt):
\[
Z(f) = \frac{FT[P_2(t) - P_3(t)]}{FT[dn/dt(t)]} \quad (7)
\]

Discrete Fourier transforms can be calculated from time-domain signals P₂(t) – P₃(t) and dn/dt(t) using a fast Fourier transform (FFT) algorithm. Z(f) can be calculated from equation (7) as long as the denominator is non-zero at the frequencies of interest [10]. The second way is to postulate a model impedance (see below) and to fit the time-domain transient pressures by using numerical inverse-Fourier transformation techniques. In this communication, we used the second method.

4. Experimental results

Data collected during typical experiments are plotted in figure 4. At low (room) temperature, the permeation process is not effective. The membrane acts as a barrier to the hydrogen flow. P₃(t) in the gas collection chamber remains close to zero while P₁(t) and P₂(t) converge on a mean pressure value, function of the ratio V₈/V₈₂ (curves 1 and 2 in figure 4). The situation is different at higher temperature where permeation takes place. Hydrogen is collected in Ch₃ (curve 5 in figure 4). All three pressures (P₁, P₂, P₃) converge on a final equilibrium value which is a function of (V₈₁) / (V₈₂ + V₈₃). It should be noted that the overall kinetics is not only a function of the characteristics of the membrane but also a function of the needle valve which can be adjusted to slow down the permeation experiments and control the hydrodynamics of gas transfer from Ch₁ to Ch₂, so as to maintain isothermal and non-convective conditions.

Figure 4 : (1,2) : transient experimental (●) and calculated (—) pressures P₁(t) and P₂(t) at room temperature (no permeation occurs).

(3,4,5) : typical experiment (■) and model (—) transient pressures P₁(t), P₂(t) and P₃(t) measured during a permeation experiments with Pd at T ≈ 300°C.
5. Modelling of the permeation process in the time-domain

5.1. Principles

Using electrical analogies, it is possible to provide an equivalent electrical circuit for the experimental setup of figure 2:

![Electric Circuit Diagram](image)

**Figure 5**: Electric circuit equivalent to the permeation setup of figure 1.

In this analogy, a pressure is equivalent to an electrical potential and a hydrogen mass flow is equivalent to a current. The needle valve behaves like a resistance, volume chambers behave like capacitances, and hydrogen like electrical charges. Initial conditions are fixed by setting initial charges \(q_1^0\), \(q_2^0\) and \(q_3^0\).

5.2. Solutions to the model

The electric circuit of figure 5 is characterized by a set of differential equations which can be solved by using the Laplace transformation:

\[
\frac{q_1^0 - I_1(s)}{s C_1} = R_1 I_1(s) + \frac{I_2(s)}{s C_2} \tag{8}
\]

\[
\frac{I_2(s)}{s C_2} = Z_M(s) I_2(s) + \frac{I_3(s)}{s C_3} = I_3(s) \left[ Z_M(s) + \frac{1}{s C_3} \right] \tag{9}
\]

\[
I_1(s) = I_2(s) + I_3(s) \tag{10}
\]

From this set of equations, the expressions of currents \(I_1\), \(I_2\) and \(I_3\) are obtained:

\[
I_1(s) = R_1 + \frac{1}{s C_1} \left[ Z_M(s) + \frac{1}{s C_3} \right] = \frac{q_1^0}{s C_1} \tag{11}
\]

\[
I_2(s) = I_1(s) \left[ \frac{1}{s C_2} + \frac{1}{s C_3} + Z_M(s) \right] \tag{12}
\]

\[
I_3(s) = I_1(s) - I_2(s) \tag{13}
\]

Analytical expressions of the different transient voltages in the circuit of figure 5 are obtained in the time and Fourier domains:
where $Z_{C1}(t)$ is the inverse Fourier transform of the transfer function associated with the capacitance $C_1$, etc. Inverse Fourier transformation of data sets can be performed using the same FFT algorithms as for direct FFT calculation [8].

### 5.3. Permeation mechanism

The impedance $Z_m(\omega)$ associated with the metallic membrane is built from the following model permeation process:

\[
\begin{align*}
    &H_2(g) \rightarrow H_2^{\text{surface1}} \quad \text{(step 1-a)} \\
    &H_2^{\text{surface1}} \rightarrow 2 \, H_{\text{ad}}^{\text{surface1}} \quad \text{(step 1-b)} \\
    &H_{\text{ad}}^{\text{surface1}} \rightarrow H_{\text{ab}}^{\text{sub-surface1}} \quad \text{(step 1-c)} \\
    &H_{\text{ab}}^{\text{sub-surface1}} \rightarrow \text{diffusion} \rightarrow H_{\text{ab}}^{\text{sub-surface2}} \quad \text{(step 2)} \\
    &H_{\text{ad}}^{\text{sub-surface2}} \rightarrow H_{\text{ad}}^{\text{surface2}} \quad \text{(step 3-c)} \\
    &2 \, H_{\text{ad}}^{\text{surface2}} \rightarrow H_{2}^{\text{surface2}} \quad \text{(step 3-b)} \\
    &H_{2}^{\text{surface2}} \rightarrow H_2(g) \quad \text{(step 3-a)} 
\end{align*}
\]

Assuming first order chemical rates, the dynamics of steps 1-b and 1-c on one hand (adsorption followed by absorption on the upstream side of the membrane) and steps 3-c and 3-b on the other hand (adsorption followed by absorption on the downstream side of the membrane) can be approached using linear relationships between pressure and hydrogen molar flow of sorption. In other words, the surface steps can be modeled using frequency independent pneumato-chemical resistance $R_{s1}$ and $R_{s2}$. Let $Z_D(\omega)$ denotes the diffusion impedance associated with step 2, we obtain:

\[
Z_m(\omega) = R_{s1} + Z_D(\omega) + R_{s2} \quad (24)
\]

where:

- $R_{s1}$: pneumato-chemical impedance associated with the chemisorption step on the upstream side of the membrane
- $Z_D(\omega)$: diffusion-controlled hydrogen transport impedance across the bulk membrane
- $R_{s2}$: pneumato-chemical impedance associated with the chemodesorption step on the downstream side of the membrane.

$Z_D(\omega)$ is obtained by solving Fick’s laws of diffusion, using appropriate boundary conditions. For diffusion in a plane sheet, the classical solution is [9]:

\[
Z_D(\omega) = \left( -\frac{\delta E}{\delta C} \right) \frac{1}{F} \frac{\pi}{2} \frac{\delta}{D} \left( \frac{u}{\delta} \right) \text{ in } \Omega \cdot \text{cm}^2 \quad (25)
\]

where $u = 2 \delta \sqrt{\frac{j \omega}{D}}$

The reader can check that under stationary conditions, when $\Delta P$ across the membrane of thickness $2 \delta$ is set to a constant value, $Z_D(\omega)$ takes the form of Fick’s first law of diffusion:

\[
\lim_{t \to \infty} \frac{dn}{dt}(t) = -\alpha \frac{\Delta PD}{2 \delta}
\]
The pneumatic impedances associated with steps 1-a and 3-a are either included in $R_s1$ and $R_s2$ or are a function of the hydrodynamics on each side of the membrane. When pure hydrogen is used as in the present work, and considering the fact that the pneumatic resistance of the tubing sections is small compared to the impedance of the membrane, the rate contribution of steps 1-a and 3-a can be neglected. $R_s1$ and $R_s2$ provide a measure of the kinetics of steps 1-b, 1-c, 3-c, 3-b. Their value is a function of the true surface area of the solid-gas interface which remains constant during sorption experiments when massive membranes are used. $R_s1$ and $R_s2$ can be used as a probe to measure surface modifications, especially on the upstream side of the membrane, such as those induced by poisonous impurities contained in the feed hydrogen or surface changes during activation. $D_H$ provides an averaged measure of the diffusion process (step 2). The value of $D_H$ can change significantly if hydride precipitation occurs during operation since hydriding/dehydriding reactions lead to the formation of high strain concentrations (cold working). Therefore $D_H$ can be used as a probe to follow internal material degradation along its lifetime.

5.4. Data fitting

Data points of figure 4 were fitted using an iterative procedure. First, microscopic rate parameters in Eqs. (24) and (25) were set to initial values. Then, transient pressure signals $P_1(t)$, $P_2(t)$ and $P_3(t)$ of figure 4 were fitted using equations (14), (16) and (18). The convolutions were solved numerically by inverse Fourier transformation. From the comparison of model and experimental curves, microscopic rate parameters were adjusted and a new fit was obtained. The procedure was repeated until a sufficient agreement was obtained between experimental and model transient pressures. $R_s1$ and $R_s2$ were the only adjustable parameters ($R_1$, the resistance of the needle valve, was obtained from calibration experiments and $D_H \approx 3 \times 10^{-5} \text{cm}^2\text{s}^{-1}$ was measured on thick Pd membranes). The agreement found in figure 4 with $R_s1 = R_s2 = 1 \times 10^8 \text{Pa.mol}^{-1}\text{s}$ supports the validity of the model. A more thorough report on the technique and results is under preparation [10].

6. Conclusions and perspectives

Hydrogen purification by permeation through metallic membranes is a process of great practical interest. This process is expected to play a major role in the next future in the car industry where electrical engines powered by H$_2$/O$_2$ fuel cell will be used. Whereas cost considerations require significant thickness reductions, surface processes which are not known to play a major kinetic role in permeation processes when thick membrane are used, may become rate determining. For this reason, there is a need to separately measure surface (hydrogen dissociation and recombination) and bulk (hydrogen transport by diffusion) contributions to the overall permeation process. Fourier-domain analysis of permeation data provides a powerful tool for this purpose. As described in this paper, it is possible to develop models which include surface pneumato-chemical resistances and bulk hydrogen diffusion impedances. Therefore, by fitting experimental results with model transients, it becomes possible (i) to measure microscopic rate constants ($R_s$ and $D_H$) for each kinetic step under various operating conditions, (ii) to probe degradation mechanisms, (iii) to optimize thicknesses and compositions for given applications, and (iv) to model efficiently dynamic phenomena.

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