New experimental set-up and procedure for analyzing the dynamics of permeation of H₂(g) across Pd-based metallic membranes.

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Abstract
Hydrogen permeation through metallic membranes is an industrial process used for purification purposes. Palladium-based alloys are generally used as permeation materials at operating temperatures above the critical value so that the metal-H system remains monophasic and that diffusion proceeds at sufficient rate. In state of the art systems, metallic membranes with typical thickness of a few tens of microns are used and rate limitation are generally attributed to atomic H transport by 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, or at least to play an increasing role. Further, when the membrane is used on the exit side of a gas reformer to directly extract hydrogen, corrosion problems are expected to occur on the upstream side of the membrane. For all these reasons, there is a need to separately measure surface and bulk (diffusion) rate contributions to the overall permeation flux. A new experimental equipment has been specifically designed for this purpose. This setup can be operated in two different modes: for sorption or permeation experiments. In a typical sorption experiment, the metallic membrane is disposed in the reaction chamber and hydrogen is allowed to react from both sides of the surface. This procedure allows the separate measurement of surface absorption and desorption resistances associated with the chemisorption step. In a typical permeation experiment, the membrane is mounted between two volume chambers, a pressurized hydrogen source reservoir and an empty sink reservoir. Initially, a difference of pressure is set between the two reservoirs. When the valve of the source tank is opened, H₂(g) flows to the membrane and permeation proceeds until pressure reaches an equilibrium value. In both experimental configurations, gas pressure transients are synchronously sampled all along the experiment. Impedances of the sorbing (permeating) membrane materials are then calculated using the theory of linear and time-invariant systems, by numerically Fourier-transforming the discretely sampled pressure signals. Using appropriate initial and boundary conditions, it is shown that the rate constants of the two major steps of the sorption (permeation) mechanisms can be separately accessed, i.e. surface resistances related to hydrogen dissociation (upstream side) and recombination (downstream side) processes, and bulk diffusion impedance. This experimental equipment and this treatment procedure therefore provide a new tool for analyzing the dynamics of hydrogen permeation across metallic membranes. This tool can be used for diagnosis purposes and for optimizing the structure and composition of permeation membranes. Results obtained with Pd and Pd₇₇Ag₂₃ foils are presented and discussed.

Keywords: metal-hydrogen system; metallic membranes; hydrogen permeation; frequency domain; Fourier analysis
1. introduction

The development of catalytic membrane reactors [1,2] for steam reforming allows the direct recovery of pure hydrogen, which in turn can feed H_2/O_2 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]. In this research project, specific composite metallic membranes are developed although results presented here were obtained with conventional massive palladium and palladium alloy membranes.

Cost considerations require significant thickness reductions for practical applications. Whereas surface processes are not playing a major kinetic role in permeation processes when thick membrane 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. Pneumatochemical 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. The technique is used in the present work to analyze the dynamics of hydrogen sorption (permeation) by (through) massive Pd and Pd_{77}Ag_{23} foils. Electrochemical activation procedures are used to reduce surface oxide layers and increase sorption kinetics.

2. experimental section

A new experimental setup has been designed and developed to perform either sorption or permeation experiments. 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® connectors: (i) a reservoir chamber Ch_0 (V_{Ch0} = 996 ± 1 cm^3), (ii) a reference volume chamber Ch_1 (V_{Ch1} = 61.6 ± 0.1 cm^3), (iii) a reaction chamber Ch_2 (1 inch VCR® connectors, V_{Ch2} = 35.1 ± 0.1 cm^3) and (iv) a gas collection chamber Ch_3 (V_{Ch3} = 33.7 ± 0.1 cm^3). For accurate mass balance calculations, the temperature is measured at different points of the setup using chromel-alumel thermocouples. The reaction chamber can be introduced in a furnace for high temperature measurements. 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 Ch_1 to Ch_2. Pressure transducers (Keller Co.) 0-3000 ± 0.2 mbar with numerical output are used to sample transient pressure signals during gas transfer experiments. Numerical sampling is achieved using a RS485 serial bus connected to a personal computer, and sampling rates up to one measurement every 20 ms can be obtained. This test-bench can be air-purged down to secondary vacuum using an air-cooled diffusion pump (Alcatel Co.). In a typical sorption experiment (MV_4 is closed), Ch_1 is initially pressurized at P_1° (using gas stored in Ch_0) and Ch_2 at P_2°. Then, MV_1 and MV_2 are closed until pressure and temperature equilibrium is obtained in Ch_1 and Ch_2. Finally MV_2 is opened. Pressure equilibrium in both Ch_1 and Ch_2 is reached more or less rapidly, depending on the position of the micrometer handle of the metering valve and on the sorption ability of the sample. Alphagaz grade 2 gas (H_2) is used in the experiment. The driving force to the transfer is an initial pressure difference set between the reference and the reaction chambers, and thus, absorption and desorption kinetics are studied in separate experiments. In a typical permeation experiment, Ch_1 is initially pressurized at P_1° (using gas stored in Ch_0). Ch_2 and Ch_3 are equilibrated at P_2° = P_3° (MV_4 open). Finally MV_2 is opened. Pressure on the upstream side of the membrane increases and permeation proceeds until the pressure becomes identical in the three chambers. Experimental results presented in this paper have been obtained using Pd (100 μm thick, 99.9% from Aldrich Chemical Co., weight = 680.5 mg) and Pd_{77}Ag_{23} (20 μm thick) foils. Electrochemical characterization and activation have been done using a three electrodes cell. The reference electrode was a saturated calomel electrode and the counter electrode a platinited platinum foil. Suprapur sulfuric acid (1M) was used as electrolyte. The measurements have been made under nitrogen bubbling. A voltalab PGZ 402 (Radiometer Co.) has been used for the electrochemical impedance spectroscopy (EIS) measurements.
3. sample activation

3.1. thermodynamics

The electrochemical (this work, 291 K) and chemical (from [7], 298 K) isotherms of the PdH system, in the low concentration domain, are shown in figure 3. To avoid precipitation of the non-stoechiometric hydride phase, sorption experiments must be performed at potential (pressure) above (below) -200 mV/SCE (23 mbar).
3.2. initial sorption experiment

In an initial experiment aimed at determining whether as-received palladium membranes absorb directly hydrogen or not, the palladium foil is introduced in the reaction chamber of the SGDA. An initial pressure of 20 mbar is set in the reference chamber and a sorption experiment is performed (figure 4).

Analytical expressions for the transient pressures in the reference ($P_1$) and reaction ($P_2$) chambers when no reaction occurs have been derived elsewhere [6].

\begin{align}
P_1(t) &= \left( V_1 P_1^0 + V_2 P_2^0 \right) \left[ \frac{1 + \left( \frac{P_1^0 + P_2^0}{P_1^0 - P_2^0} \right)}{1 + \left( \frac{V_1 + V_2}{V_1 - V_2} \right) \left( \frac{P_1^0 + P_2^0}{P_1^0 - P_2^0} \right)} \right] e^{\alpha t} \tag{1}
\end{align}

\begin{align}
P_2(t) &= \frac{V_1}{V_2} \left[ P_1^0 - P_1(t) \right] \left[ 1 + \left( \frac{P_1^0 + P_2^0}{P_1^0 - P_2^0} \right) \right] \left[ \frac{1 + \left( \frac{P_1^0 + P_2^0}{P_1^0 - P_2^0} \right)}{1 + \left( \frac{V_1 + V_2}{V_1 - V_2} \right) \left( \frac{P_1^0 + P_2^0}{P_1^0 - P_2^0} \right)} \right] e^{\alpha t} + P_2^0 \tag{2}
\end{align}
Experimental data of figure 4 are fitted using these equations. No hydrogen absorption occurs and this can be ascribed to the presence of surface oxide layers.

3.3. electrochemical activation

In order to reduce the surface oxide layer of the membrane, an electrochemical activation procedure has been used. As can be seen from figure 5 (spectrum 1), an initial impedance measurement at open circuit potential yields a 12 ohm high frequency semi-circle. The electric potential of the palladium foil is then gradually lowered down to –70 (curve 2), -150 (curve 3) and -170 (curve 4) mV/SCE. Thus doing, hydrogen is incorporated into the palladium foil and the surface oxide layer is gradually reduced. According to the isotherm of figure 3, it should be noted that in this potential region, only a solid solution \( \alpha \)-PdH is formed. The hydride phase PdH\(_{1-x}\) is prevented to precipitate in order to avoid the creation of lattice defects which could lower the value of the hydrogen diffusion coefficient and reduce the kinetics of sorption (cold working).

![Figure 5: Evolution of electrochemical impedance diagrams during the activation process; before (1) and during (2, 3, 4) the electrochemical activation procedure (frequency range: 1 mHz to 50 kHz).](image)

The main impedance characteristics obtained along the activation procedure are compiled in Table 1.

<table>
<thead>
<tr>
<th>Fixed potential for EIS</th>
<th>( R_{el} ) (( \Omega ).cm(^2))</th>
<th>( R_{ct} ) (( \Omega ).cm(^2))</th>
<th>C (( \mu F/cm^2 ))</th>
<th>Diffusion slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open potential</td>
<td>0.189</td>
<td>12.35</td>
<td>515.4</td>
<td>1.15</td>
</tr>
<tr>
<td>- 70 mV/SCE</td>
<td>0.141</td>
<td>10.48</td>
<td>540.3</td>
<td>1.306</td>
</tr>
<tr>
<td>- 150 mV/SCE</td>
<td>0.153</td>
<td>7.56</td>
<td>471.8</td>
<td>0.46</td>
</tr>
<tr>
<td>- 170 mV/SCE</td>
<td>0.157</td>
<td>3.217</td>
<td>352.2</td>
<td>0.63</td>
</tr>
</tbody>
</table>

**Tableau 1:** data extracted from the impedance diagrams of figure 5. \( R_{el} \) = electrolyte resistance, \( R_{ct} \) = charge transfer resistance; C = low frequency domain insertion capacitance.

4. pneumato-chemical sorption impedance

4.1. time domain acquisition of raw data

Once the electrochemical activation procedure is completed, the palladium foil is re-introduced in the reaction chamber for a second sorption experiment. As can be seen from figure 6, this time the palladium foil absorbs hydrogen.
At room temperature, the sorption process is rather slow but equilibrium values of pressure in reference and reaction chambers are reached within 2 hours.

4.2. experimental pneumato-chemical impedance function

Using experimental data of figure 6, it is possible to calculate the pneumato-chemical impedance of sorption $Z(f)$ of the palladium foil where $f$ denotes the frequency in hertz. The exact procedure used for this calculation has been described in detail elsewhere [6]. Briefly, the experimental impedance is obtained by taking the ratio of the Fourier transforms (FT) of the transient pressure in the reaction chamber ($P_2$) to the hydrogen mass flow ($\frac{dn}{dt}$):

$$Z(f) = \frac{FT[P_2(t)]}{FT[\frac{dn}{dt}(t)]}$$

According to Eq. (3), $Z(f)$ can be obtained in principle by taking the ratio of the FTs of any pair {P_2(t); \frac{dn}{dt}(t)}. $Z(f)$ is therefore independent of the experimental setup used for the measurements. It can be calculated as long as the denominator is non-zero at the frequencies of interest. The resulting pneumato-chemical impedance is plotted in figure 7 in Nyquist coordinates where the unit “pnohm” (= Pa.mol$^{-1}$.s) denotes “pneumatical ohm” to underline the similitude between electrochemical and gas phase impedance measurements.

**Figure 6**: experimental transient pressure signals $P_1(t)$ and $P_2(t)$ obtained during the second sorption experiment after the electrochemical activation.

**Figure 7**: experimental (•) and calculated (---) pneumato-chemical impedance diagrams obtained from the sorption experiment of figure 6 and model equations.
As can be seen from figure 7, the impedance diagram reveals an incomplete high frequency (HF) semi-circle ending in the low frequency (LF) domain by a capacitive behaviour. A better separation of the HF and LF contributions can be expected in less sloppy (pressure;composition) domains of the isotherm, as indicated in Ref. [8].

4.3. model pneumato-chemical impedance function

As discussed in Ref. [8], the formation of a solid solution from the gas phase is a multi-step mechanism:

\begin{align*}
\text{H}_2(\text{g}) \rightarrow & \text{H}_2\text{surface} \quad \text{(step 1-a, fast)} \\
\text{H}_2\text{surface} \rightarrow & 2 \text{H}_\text{ad}\text{surface} \quad \text{(step 1-b)} \\
\text{H}_\text{ad}\text{surface} \rightarrow & \text{H}_\text{ad}\text{sub-surface} \quad \text{(step 1-c)} \\
\text{H}_\text{ad}\text{sub-surface} \rightarrow & \text{H}_{\text{bulk}} \quad \text{(step 2)}
\end{align*}

Assuming first order chemical rates, the dynamics of steps 1-b and 1-c (adsorption followed by absorption) can be approached using a linear relationship between pressure and hydrogen molar flow of sorption. In other words, the surface step can be modeled using a frequency independent pneumato-chemical resistance \( R_s \). Let \( Z_D \) denotes the diffusion impedance associated with step 2. Analytical expressions of \( Z_D(s) \) have been obtained for electrochemical systems of different geometries [9,10] and adapted in the present work to chemical systems. Since the sorbing sample is massive, it is adequate to consider the case where diffusion takes place in an homogeneous foil of thickness 2\( \delta \):

\begin{equation}
Z_D^{C,\text{film}}(s) = \frac{\delta}{D_H} \frac{\partial P_H}{\partial C_H} \frac{1}{u \text{th}(u)} = R_D^{C,\text{film}} \text{coth}(u) \frac{1}{u} \tag{4}
\end{equation}

where:

\begin{equation}
R_D^{C,\text{film}} = \frac{\delta}{D_H} \frac{\partial P_H}{\partial C_H} \text{ in Pa / (mole.cm}^2.\text{s}^{-1}) \quad \text{and} \quad u = \sqrt{\frac{\delta^2}{D_H}} \tag{5}
\end{equation}

\( \frac{\partial P_H}{\partial C_H} \) is the slope of the isotherm in Pa.mol\(^{-1}\).cm\(^3\).

As discussed in Ref [8], the model impedance \( Z_T^{\text{mod}}(\omega) \) of the reaction chamber (including the sorbing sample) is obtained by considering the parallel connection of (i) the sorption impedance \( (R_s + Z_D) \) and (ii) the capacitance \( C_2 \) associated with the volume \( (V_2) \) of the reaction chamber:

\begin{equation}
Z_T^{\text{mod}}(\omega) = \left( \frac{1}{jC_2 \omega} + \frac{1}{R_s + Z_D^{C,\text{film}}} \right) \tag{6}
\end{equation}

It can be shown from Eq. (4) that \( \lim Z_D^{C,\text{film}}(\omega \rightarrow 0) \approx R_{in} - j \frac{1}{\omega C_{in}} \) \( \tag{7} \)

where:

\( R_{in} = \frac{R_D^{C,\text{film}}}{3} = \frac{\delta}{3 D_H} \frac{\partial P_H}{\partial C_H} \) and \( C_{in} = \frac{\delta^2}{D_H R_D^{C,\text{film}}} = \frac{\delta}{\frac{\partial P_H}{\partial C_H}} \)

Eq. (7) is the equation of a vertical semi-line in the complex Nyquist plan. In the low frequency domain, the value of \( Z_T^{\text{mod}}(\omega) \) gives access to \( C_{in} \), the capacitance (in mole H\(_2\).Pa\(^{-1}\)) associated with the sorbing material. The experimental pneumato-chemical impedance diagram of figure 7 has been fitted using Eq. (6) and a non-linear (complex) least square procedure. The only unknown in the model were the surface resistance \( R_s \) and the diffusion coefficient \( D_H \). From this fit, the following values were obtained:
\[ R_s = 1.2 \times 10^{11} \text{ Pa.mol}^{-1}.\text{s} \]
\[ D_H = 2 \times 10^{-7} \text{ cm}^2.\text{s}^{-1} \]

Rs provides a measure of the kinetics of steps 1-b and 1-c. Its 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. Rs can be used as a probe to measure surface modifications such as those induced by poisonous impurities contained in the feed hydrogen or surface changes during activation. Dh provides an averaged measure of the diffusion process (step 2). The value of Dh can change significantly if hydride precipitation occurs during operation since hydriding/dehydriding reactions produce the formation of high strain concentrations (cold working). Therefore Dh can be used as a probe to follow internal material degradation along its lifetime. As discussed above, in favorable cases, graphs of model impedance diagrams based on Eq. (6) present three well-separated features along the frequency domain: a HF semi-circle (related to the parallel connection of C2 and Rs), followed by a medium frequency (MF) intermediate region (a 45° segment line related to H transport by diffusion) ending by a LF vertical semiline characteristic of the insertion capacitance Cin. The key factor for the separation of the two steps is the ratio C2 / Cin. In general, Cin > C2 and separation is observed when C2 / Cin < 0.1. Therefore, in solid solution domains where sloppy {pressure;composition} relationships are obtained, pseudo-capacitive behaviors such as the one of figure 3 are commonly observed. Only in low hydrogen content domains (on powdered samples) or in two-phase domains where the slope of the isotherm is much lower and hydrogen solubility higher can a clear separation of the two processes be observed. Cin can be used to measure internal degradations of the sorbing sample such as capacitance losses associated with the precipitation of non-absorbing phases.

5. pneumato-chemical permeation impedance

Permeation experiments are made using the experimental setup of figure 2. In a typical experiment, a thin Pd77Ag23 membrane is mounted on the experimental setup between Ch2 and Ch3. The operating temperature of the permeation chamber is set above the critical temperature and hydrogen is transferred from the reference chamber Ch1 to the membrane, as indicated in the experimental section. Pressure transients up to equilibrium values are collected in the reference (P1(t)), reaction (P2(t)) and gas collection (P3(t)) chambers (figure 8).

![Figure 8: permeation results obtained with a Pd77Ag23 membrane.](image)

Differently shaped curves can be obtained depending on the value of the pneumatic resistance of the needle valve, the operating pressure and temperature, and the chemical composition and thickness of the permeation membrane material. Data fitting with model equation yields similar kinetic information as for sorption experiments but measurements are made in situ, during permeation operation.
6. Conclusions and perspectives

Hydrogen purification by permeation through metallic membranes is a process of great practical interest. It is expected to play a major role in the development of H₂/O₂ fuel cell powered engines in the car industry. Whereas cost considerations require significant thickness reduction, 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 kinetic data provides a powerful tool for this purpose. As described in this paper, it is possible to separately measure surface pneumato-chemical resistance and bulk hydrogen diffusion coefficients. Therefore, it becomes possible (i) to measure each kinetic term for different operating conditions, (ii) to probe degradation mechanism, (iii) to optimize thicknesses and compositions for given applications, and (iv) to model efficiently dynamic phenomena.

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