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Dynamics of hydrogen permeation across metallic membranes



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ABSTRACT

Thin and supported palladium membranes can be coupled to gas reformers to produce purified hydrogen. Such systems can potentially be used in the automotive industry to feed PEM fuel cells. However, for such applications, the membrane design must be optimized to meet some specific requirements, in particular to allow fast accelerations. The purpose of this paper is to take advantage of the possibility offered by pneumato-chemical impedance spectroscopy to analyze the dynamics of hydrogen permeation in transient conditions of flow, to determine the conditions for which shifts in rate-determining step (rds) between surface and bulk rate contributions are observed. Results reported in this paper have been obtained using a Pd₇₇Ag₂₃ metallic membrane. The gas-phase impedance of this 50 μm thick membrane has been measured. A model has been developed to evaluate separately surface and bulk rate contributions. It is shown that in a typical permeation experiment performed in transient conditions of flow, the surface step is rate-determining in the early stages of the experiment (highly transient conditions of flow) whereas the bulk diffusion step becomes rate-determining at longer time (quasi-stationary conditions of flow). The relationship between membrane characteristics, experimental conditions and the time at which the shift in rds is observed are determined, opening the way to the development of customized membranes for operation in transient conditions of flow.

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1. Introduction

Low temperature H₂/O₂ PEM fuel cells are considered by the automotive industry as promising power sources for the replacement of internal combustion engines (ICE) and for the associated reduction of carbon dioxide emissions. However, the on-board storage of hydrogen fuel remains a critical issue (pressurized vessels are potentially dangerous [1] and metal hydrides suffer from still inappropriate energy densities [2]). The widespread utilization of liquid bio-fuels such as ethanol would have a significant impact on carbon emissions, even by

direct combustion in ICEs. But liquid bio-fuels could also be used as the on-board source of hydrogen to fuel fuel-cells in hybrid electric vehicles. Compared to conventional on-board storage of hydrogen, such approach would allow a more efficient storage of fuel at atmospheric pressure [3]. To do this, the on-board catalytic reforming of liquid bio-fuels is required and a purification step is required to extract hydrogen from the gaseous reformat. Thin palladium-based metallic membranes (supported by appropriate porous substrates) could be used for that purpose. But the constraints imposed by such applications are very severe. The temperature of

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operation must extend from sub-zero values up to 400–600 °C and sub-micron thick membranes are required in order to meet acceleration and cost requirements. Basically, the gas permeation process is a two-step process including a surface (dissociative chemisorption) and a bulk (Fickian diffusion) step. Whereas bulk transport of atomic hydrogen is known to be rate-determining when thick ($>10 \mu\text{m}$) membranes are used, surface rate contributions are expected to become relatively more important in the micron- and sub-micron-thick range. In addition, membrane side in contact with the gaseous reformat is expected to experience severe surface corrosion, a situation that will gradually increase the overall membrane resistance and reduce its permeation efficiency. There is therefore a real interest at analyzing permeation processes in transient conditions of flow from both experimental and theoretical viewpoints. In the literature, surface and bulk rate contributions are usually not measured separately. In many papers [4,5], it is assumed that either the surface or the bulk step is rate-determining. In stationary conditions of flow, this is not so important. When the resistance of both steps is close, this simplifying assumption leads to the under- or over- estimation of microscopic rate parameters. But in transient conditions of flow, the situation is different. It is necessary to take into account both surface and bulk resistances because even a small surface resistance can play a critical role (e.g. control the entire permeation process) when the gas pressure is changing rapidly in the admission chamber. At the microscopic level, hydrogen permeation through metallic membranes is known to be a multi-step process and as reported elsewhere [6,7], details of the overall permeation mechanisms can be put into evidence and analyzed in the frequency domain. Thus, information on the different steps involved in the overall mechanism can be obtained and rate parameters of individual mechanism step (surface resistances related to hydrogen dissociation on the reformat side and recombination on the permeate side and bulk H diffusion coefficients) can be measured.

The purpose of this paper is to take advantage of the possibility offered by pneumato-chemical impedance spectroscopy to analyze the dynamics of hydrogen permeation in transient conditions of flow and to determine the conditions for which shifts in rds between surface and bulk contributions are observed. Results reported in this paper have been obtained using a commercial $\text{Pd}_{77}\text{Ag}_{23}$ metallic membrane.

2. Experimental section

2.1. Metallic membrane

A 50 μm thick $\text{Pd}_{77}\text{Ag}_{23}$ membrane (Goodfellow Co.) has been used in the experiments. The metallic membrane has been used as-received, without any preliminary (either surface or bulk) treatment. This is because our purpose was only to put into evidence shifting rds in relation with membrane structure and operating conditions. For this, there is no need to start from a reference state. At 60 °C (the maximum temperature of operation), it is not expected that changes in either the bulk microstructure or the surface roughness occur. It is therefore assumed that the impedance of the

membrane remained constant throughout the whole set of experiments.

2.2. Membrane impedance

The experimental setup used to measure gas-phase impedance diagrams is pictured in Fig. 1. It has already been used for the characterization of palladium–copper membranes as reported elsewhere [8]. Basically, this is an adaptation of the experimental setup once used by Sieverts to investigate the thermodynamics and kinetics of metal–hydrogen systems [9]. Briefly, it is made of four volumetric chambers (316L stainless steel vessels, Swagelok Co.) interconnected by a stainless steel circuitry ($\frac{1}{4}$ inch internal diameter) using VCR® (Swagelok Co.) connectors: (i) a gas reservoir Ch_0 ($V_0 \approx 1000 \text{ cm}^3$), (ii) a reference chamber Ch_1 ($V_1 \approx 50 \text{ cm}^3$), (iii) an admission chamber Ch_2 ($V_2 \approx 50 \text{ cm}^3$): this is the volume of the tubing section between the needle valve NV and the permeation reactor up to the palladium membrane (M), (iv) a gas collection chamber Ch_3 ($V_3 \approx 50 \text{ cm}^3$). A heating resistance (TC Direct Co.) is wrapped around the tubing section around the membrane and can be used to perform permeation experiments up to 600 °C. The gas temperature is measured along the gas distribution line using thermocouples (Thermocoax Co.) in order to perform accurate mass balance measurements. Several pneumatic (PV) and manual (MV) valves (Swagelok Co.) are used for the management of gases. A calibrated needle valve (NV, Swagelok Co.) is used to avoid gas convection and reduce thermal effects associated with the expansion/compression of hydrogen along the circuit (isothermal conditions of flow between Ch_1 and Ch_2). NV is also used as a mass flow meter. 0–3000 ± 0.2 mbar pressure transducers (Keller Co.) with numerical output are used to sample pressure transients during permeation experiments. A pumping station that contains a membrane primary pump and a turbomolecular pump (Boc Edwards Co.) is used to reach secondary (10^{-6} mbar) vacuum.

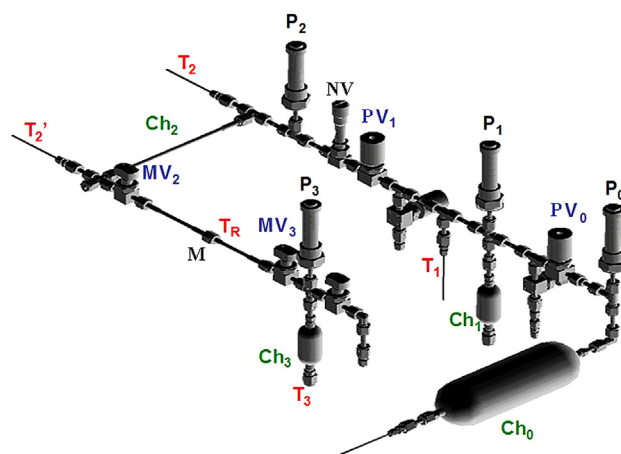


Fig. 1 – Schematic diagram of the experimental setup used to measure gas-phase impedance diagrams. PV: Pneumatic valve; MV: Manual Valve; P: Pressure transducer; T: Temperature; Ch: volume chamber; NV: Needle Valve.

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