



Short communication

Development of Pd-based membranes as hydrogen diffusion anodes

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ARTICLE INFO

Article history:

Received 23 July 2008

Received in revised form

22 December 2008

Accepted 26 December 2008

Available online 17 January 2009

Keywords:

Pd membrane

Pd electroless

Gas diffusion electrode

Hydrogen permeable electrode

Fuel cell

HOR

ABSTRACT

Pd-based membranes have been prepared by Pd electroless deposition on porous stainless steel substrate and their structure, composition, morphology and thickness were analyzed by X-ray diffraction (XRD), EDS and scanning electronic microscopy (SEM). The performance of these membranes as hydrogen diffusion electrodes was evaluated in a three-electrode cell in alkaline medium. The activity towards hydrogen oxidation was high at the beginning of the experiment, but it significantly decreased with time. The major cause of this phenomenon has been attributed to the slow entry of hydrogen at the H₂/Pd interface. Even so, the technical feasibility of using these membranes as gas diffusion electrodes (GDE) has been proven.

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1. Introduction

The need for high purity hydrogen is one of the main requests for low and medium temperature fuel cells. CO impurity in the fuel adsorbs strongly on the anode material and decreases the cell voltage by blocking the access of H₂ to the catalyst sites. Typically, hydrogen gas is produced in reforming processes and so it must be separated from mixtures which contain other products such as CO, CO₂, N₂, H₂O, etc. Membrane separation technology has been widely used for the production of high quality hydrogen. These membranes can be fabricated from a variety of materials such as carbon, polymers, ceramics and metals. Among these, the highest purity hydrogen is achieved with dense metallic membranes and especially through Pd and its alloys.

Pd-based membranes have shown tolerance to contaminants such as CO, and have properties of high hydrogen permeability, resistance to thermal cycling, and infinite H₂ selectivity [1,2]. Taking into account these properties as well as the good activity of Pd towards hydrogen anodic oxidation [3,4], palladium and palladium alloy membranes seem to be prominent materials to be used as gas diffusion anodes in fuel cells operating with reformat streams that may contain impurities at higher concentrations than high quality hydrogen. The studies performed by Cabot et al. [5,6] and Yamaguchi et al. [7,8] have shown the applicability of hydrogen-

permeable anodes in hydrogen–air fuel cells using a commercial Pd foil. However, commercial foils are typically thick, limited by their production technique to >25 μm in thickness, the amount of costly metal being larger, and the hydrogen permeability being smaller, when the membrane thickness increases.

Usually Pd-based membranes used in the separation technology are prepared by electroless deposition of a thin film of Pd or Pd alloy (2–10 μm) on a porous substrate. This substrate provides the mechanical support of the film while preserving the gas transport across the membrane. Supporting material can be made of Vycor, glass, alumina and stainless steel. In this work Pd-based films were deposited on a porous stainless substrate (PSS) in order to preserve the conductivity of the overall membrane.

The work reported here aims to evaluate whether Pd-based membranes, prepared by electroless deposition on commercially available PSS support, will present on one hand a fully covered surface in spite of the low thickness film (1–2 μm), and on the other hand, a high catalytic activity towards the H₂ oxidation. Using typical electroless plating bath compositions described in the literature for H₂ purification/separation devices, pure Pd and Pd–P alloy films were prepared. Previously it has been shown that pure Pd, prepared at low temperature deposition, and Pd–P alloy, containing a low P content, exhibit a high catalytic activity for both hydrogen absorption and oxidation [9]. However, such studies have been carried out on films deposited on a non-permeable substrate (Cu and Ni discs) and involving atomic hydrogen generated in situ by water electroreduction.

In this work steady-state conditions in a real fuel cell are simulated by supplying H₂ continuously to the prepared gas diffusion

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Table 1
Electroless bath composition and deposition conditions.

Pd film	Reducing agent (mM)	Pd ²⁺ (mM)		NH ₃ at 25% (cm ³) ^a	EDTA (M)	T _{dep} (°C)	t _{dep} (h)	Refs.
Pd (low T)	N ₂ H ₄	27.0	28.0	30	0.11	25.0	10/15 ^b	[10]
Pd (high T)		12.0	20.0	23	0.11	50.0	2 ^c	[11]
Pd–P (low P)	H ₂ PO ₂ [−]	1.0	10.0	11.2	0.01	50.0	2 ^c	[12]
Pd–P (high P)		10.0	10.0	8.8	0.29 M NH ₄ Cl	50.0	2 ^d	[13]

^a 50.0 cm³ final volume.

^b A film with a thickness of approximately 1.0 μm is obtained.

^c A film with a thickness of approximately 0.5 μm is obtained.

^d The thickness of the prepared film was not determined.

electrodes (GDE). Their activity towards the hydrogen anodic oxidation is evaluated in a conventional three-electrode cell, at 25 °C, using a 0.1 M NaOH solution as electrolyte. Although pure Pd membranes are inadequate for low temperature fuel cells such as alkaline fuel cells due to hydrogen embrittlement at temperatures below 293 °C, this preliminary investigation allows evaluating in situ their performance and depicting the main constraints of using them, in the future, as gas diffusion electrodes in medium temperature fuel cells.

2. Experimental

2.1. Preparation of the GDE

Electroless palladium films were deposited on stainless steel disks purchased from Mott Corporation (316L SS, 2.00 cm in diameter, 0.157 cm in thickness, 0.1 μm media grade). These porous metallic supports were cleaned in an alkaline solution containing NaOH (45 g l^{−1}), Na₂CO₃ (65 g l^{−1}) and Na₃PO₄·12H₂O (45 g l^{−1}) for grease and dirt removal, rinsed with de-ionized water and dried overnight at 120 °C. After cleaning, the supports were activated by successive dipping in SnCl₂ (1.0 g l^{−1} in 0.20 M HCl) and PdCl₂ (0.1 g l^{−1} in 0.20 M HCl) with intermediate de-ionized water rinsing. After this procedure a Pd film was deposited on one side of the disk by the electroless deposition. The deposition was performed in a 10.0 mL solution under stirring. The plating conditions for electroless deposition of palladium are given in Table 1. The deposition time (t_{dep}) accounts for the maximum time of deposition without decomposition of the plating solution (except for Pd–P (high P), which is only about 1 h, plating being performed in two steps).

On using hypophosphite ion as the reducing agent in the plating solution, phosphorous is inevitably incorporated in the metal bulk during the metal deposition process, giving rise to a Pd–P alloy. Excepting Pd–P alloy (high P), all of these films have been reported before for H₂ purification/separation devices [10–13].

The Pd/PSS membrane was then placed at the bottom of a polyvinylidene fluoride (PVDF) holder having a circular opening of 1.40 cm diameter in contact with the electrolyte solution and pressed with a screwed plug onto a stainless steel mesh (current collector). The GDE thus prepared, was continuously fed (even before the GDE immersion into the electrolyte solution) with H₂ from the backside (the non-plated side, opposite to the electrolyte) at a constant pressure of 1 atm. No gas or solution leak though the membrane pores was observed in the experimental setup. The backside of the Pd/PSS membrane remained dry during the electrochemical experiment and no bubbles were observed on the front side of the electrode.

2.2. Electrochemical and physical characterization

Electrochemical experiments were performed in a double-wall three-electrode cell using a Solartron SI 1287 electrochemical inter-

face connected to a computer and controlled by means of the electrochemical/corrosion software CorrWare version 2.6b. A saturated calomel electrode (SCE) was employed as the reference electrode, a Pt wire spiral was utilized as the counter electrode, and the GDE described above was used as the working electrode. Prior to each experiment the electrolytic solution was purged by Ar bubbling. All potentials are referred to the SCE. Cyclic voltammetry experiments were performed with Ar atmosphere or H₂ feeding in the gas side of the GDE. Unless otherwise stated the experiments were performed in 0.1 M NaOH at 25.0 ± 0.1 °C in order to compare the electrocatalytic activity of these electrodes with other Pd-based membranes reported in the literature [5,6]. The experiments were repeated several times and reliable results were obtained.

Structural analysis of the films was carried out in a Philips X'Pert diffractometer by X-ray diffraction using Cu K_α radiation. The identification of crystalline phases was done using the JCPDS database cards. A Philips-FEI Quanta 400 microscope was employed for the scanning electronic microscopy (SEM)/EDS analysis. The phosphorous atoms concentration was determined using the EDS attachment (EDAX/EDAM) with ZAF quantification without standard.

3. Results and discussion

3.1. Characterization by X-ray diffraction (XRD), SEM/EDS

SEM was used to evaluate the degree to which the micropores of the PSS substrate were filled during the electroless deposition of Pd, to characterize microstructure and morphology changes during the hydrogen charging–discharging and to estimate the thickness of the deposited Pd layer.

Fig. 1 shows that, for Pd (low T)/PSS membrane, the surface of the porous substrate is nearly fully covered by a continuous and uniform Pd film, on which the palladium particles are packed closely together. No defects are observed and few micropores are apparent in the SEM photograph. However, hydrogen absorption–desorption, at the room temperature, leads to the appearance of fissures on the Pd surface (Fig. 1e). This expectable phenomenon is due to the α → β phase transition of palladium hydride which occurs on pure palladium in the presence of hydrogen below a critical temperature (293 °C), leading to a considerable lattice expansion (about 3.5%) and internal stress and consequently to the fracture of the membrane [14]. Despite this phenomenon, no peeling from the substrate was observed, even on the membranes submitted to many (≈30) charging–discharging cycles. Except for the Pd–P (high P) film, probably because of its lower ability to absorb hydrogen and/or low usage, the other prepared films present such fissures on the surface upon hydrogen charging–discharging process. The thickness of the palladium layer was determined from electron microscopy images by observing the cross-section of the cracked film (Fig. 1f). Changing the time of electroless deposition, films ranging from approximately 0.5 μm to 2.0 μm were achieved.

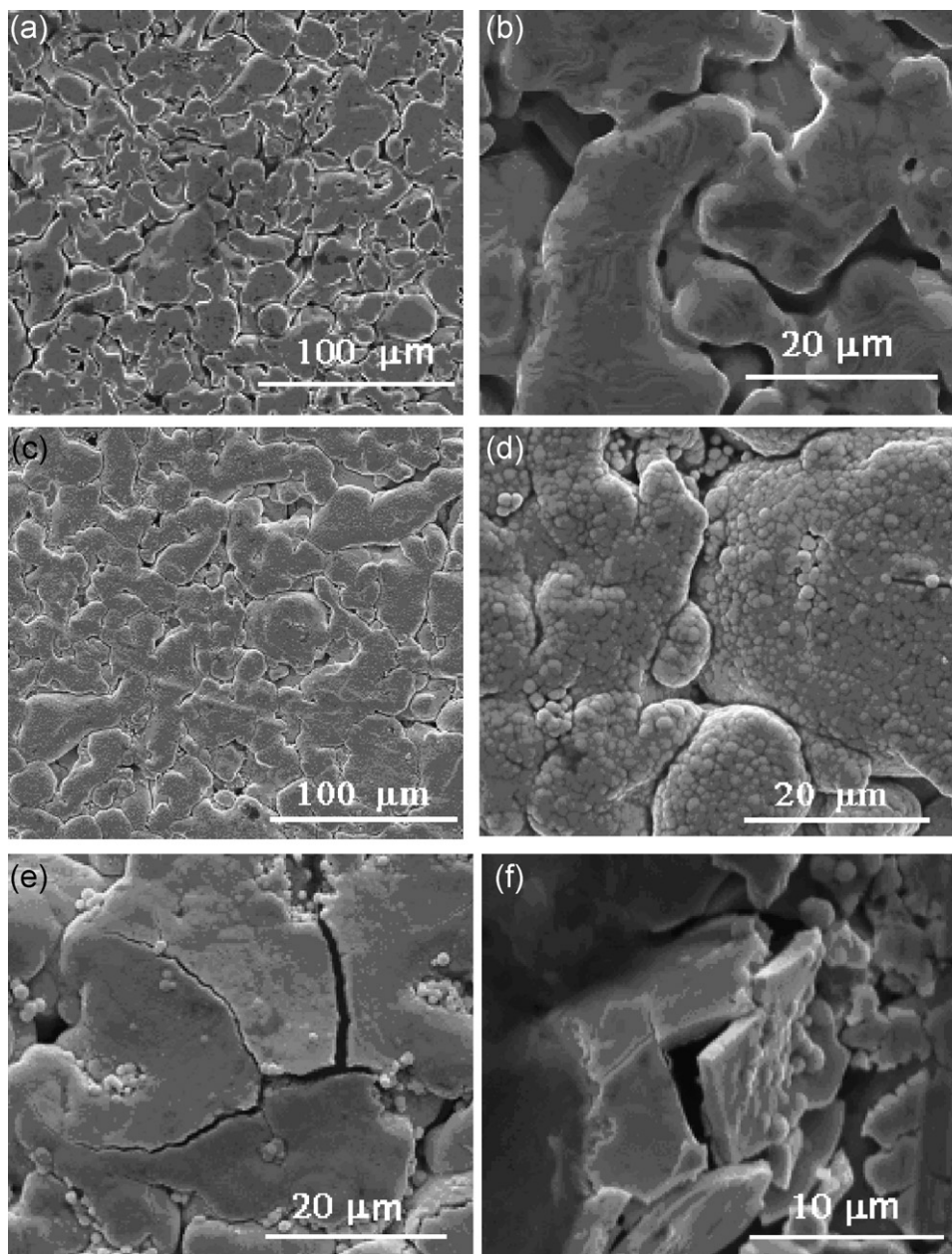


Fig. 1. SEM images: (a) and (b) original porous stainless steel substrate; (c) and (d) as-deposited Pd (low T) films; (e) Pd (low T) film after hydrogen charging–discharging; (f) cross-section of as-deposited Pd (low T) film. The thickness of the films is approximately 1.0 μm .

Comparing Figs. 1 and 2, it is shown that, despite the higher thickness of Pd alloy films (2.0 μm), the degree at which the micropores of PSS were filled on these membranes is lower than in Pd (low T)/PSS membrane (1.0 μm). A higher filling of the micropores would have been achieved by increasing the thickness of Pd-based film. However such procedure would lower the hydrogen permeability and increase the membrane cost. On Pd (high T) film, a covering degree of the substrate micropores similar to the 1.0 μm -thickness Pd (low T) film is only achieved with a higher thickness film (2.0 μm). These results indicate that a lower plating temperature, and consequently a lower deposition rate, promotes the Pd deposition on the wall of the micropores. On account of these results it may be concluded that a lower expense of Pd mass is achieved on preparing the GDE with a Pd (low T) film.

In contrast with pure Pd films, Pd–P alloy films reveal the presence of spherical particles and clusters of these particles, placed on the surface, pointing out to an insufficient stability of the deposition

bath [10]. In fact, the life-time of these plating bath solutions at 50 °C was shorter (1–2 h) than Pd plating solutions at 25 °C (10–20 h).

EDS analysis of Pd–P alloys revealed that the P content is 3.5 and 15 at.%, respectively, for Pd–P (low P) and Pd–P (high P) films. The XRD pattern of the membrane shows two distinct peaks at $2\theta = 40^\circ$ and 46.5° , assigned to metallic palladium (Fig. 3). The diffraction profiles for pure Pd films indicated the crystalline character of these materials, contrasting with the clear broadness of the Pd bands observed on Pd–P alloys, which reveals an increase of amorphicity with the P content of the deposit. These results are in agreement with the XRD data obtained on the Pd-based films prepared on Cu and Ni substrates [9].

Correlation between the ratio of Pd(111) and Fe(111) peaks intensity on X-ray diffractograms and the thickness of the cracked Pd films (evaluated by electron microscopy images), was found (Fig. 4). Based on this correlation it was also possible to estimate the Pd film thickness on as-deposited films (i.e. non-cracked films).

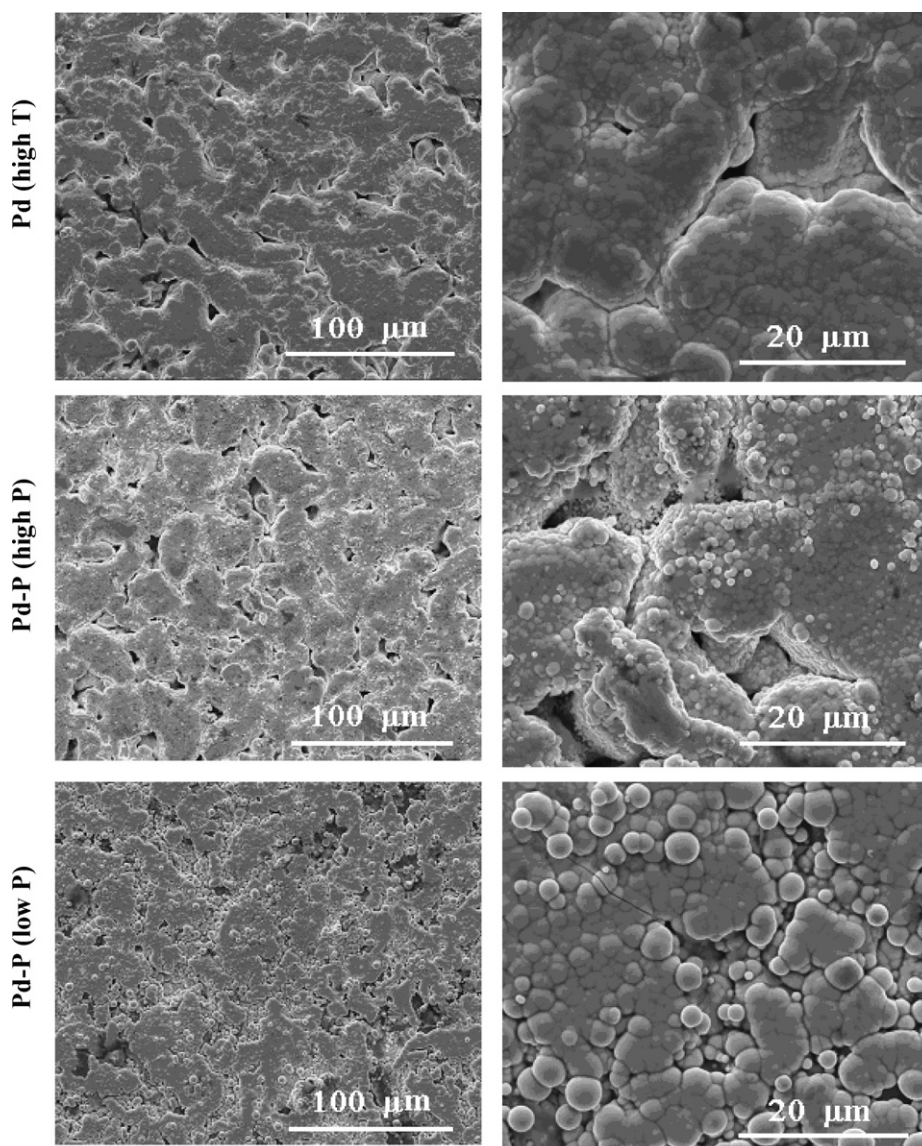


Fig. 2. SEM images of as-deposited Pd electroless films. Pd (high T) and Pd-P (low P) films present a thickness of about 2.0 μm .

3.2. Electrochemical behavior of the GDE in 0.1 M NaOH

The cyclic voltammogram recorded on Pd (low T)/PSS membrane, in the absence of H_2 gas supply, Fig. 5, allows to establish the potential range suitable for hydrogen oxidation without interference of Pd anodic oxidation. The obtained voltammogram is representative of the electrochemical behavior of the differently prepared Pd-based/PSS membrane in 0.1 M NaOH. As can be seen from this figure, a well resolved H-oxidation peak is observed at -0.51 V and no evidence for Pd oxidation is depicted at potentials below 0 V.

In order to evaluate the performance of the prepared membranes as GDEs in 0.1 M NaOH solution, cyclic voltammograms were recorded under H_2 supply. Before starting the measurements the electrodes were fed with H_2 until a stationary open circuit potential was reached (-993 ± 2 mV). The potential was then swept from the open circuit potential (OCP) to 0.3 V. Typical cyclic voltammograms for two different thicknesses films are shown in Fig. 6. The results reveal that despite the continuous H_2 supply the current density falls after reaching a maximum. Although the same behavior was observed with the other membranes of this work, the potential

at which the maximum current is attained seems to depend on the film thickness. On the returning sweep, a small cathodic peak, only discernable on the thinner film, is indicative of Pd oxidation. In order to evaluate whether the current fall is due to hydrogen depletion on the Pd film or to Pd oxidation, further experiments were performed.

Taking into account that the time and potential effects are mixed in the potential scan experiments, potentiostatic experiments were performed, also under continuous supply of H_2 . Potentiostatic measurements were performed at -0.1 V (potential for hydrogen oxidation) after reaching a stationary OCP of -0.99 V under H_2 supply. The current response on Pd-based films of similar thickness (± 0.05 μm) is shown in Fig. 7.

Apparently, the Pd (low T) film presents a higher ability to oxidize hydrogen than Pd (high T) and Pd alloy (low P) films, but a reliable comparison is not very feasible when the real surface area of the surface films is unknown (the current density displayed relies on the geometric surface area).

Typically, the current density on Pd (low T), Pd (high T) and Pd alloy (low P) films seems to tend to a plateau (a limiting diffusion current) at the first stage of the transient, but afterwards it decays

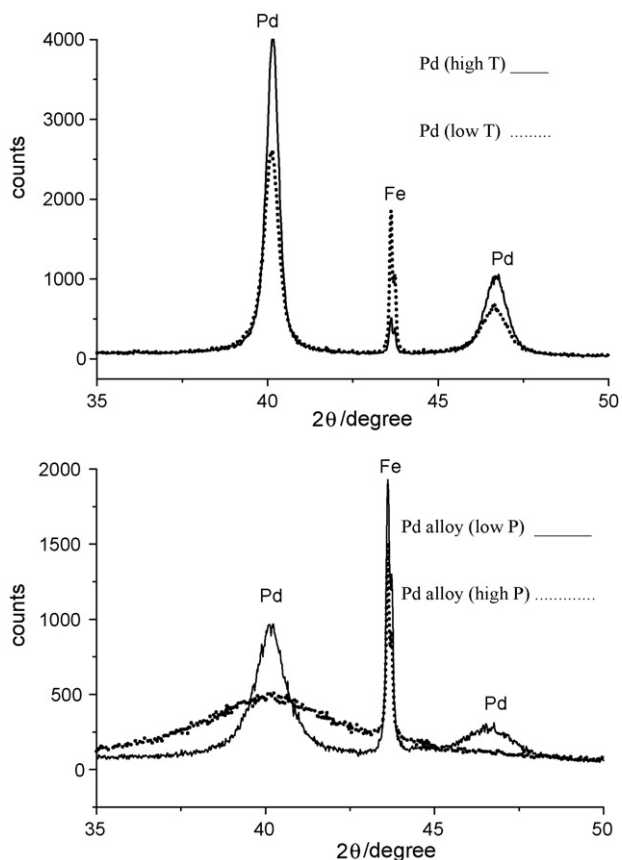


Fig. 3. XRD pattern of as-deposited Pd-electroless films.

abruptly to “residual” low values ($0.4\text{--}0.8\text{ mA cm}^{-2}$). This behavior is consistent with the current profile observed in the potentiodynamic experiments.

The current transients reveal that hydrogen oxidation (as atomic hydrogen) in the Pd/electrolyte interface is not the slow step, since atomic hydrogen accumulated in OCP conditions appears to be rapidly oxidized (see Figs. 7–9). On the other hand, the inhibition of hydrogen oxidation on the Pd surface by the formation of an oxide layer is ruled out as the anodic oxidation of Pd is not predictable at -0.1 V . Curiously, on Pd alloy (high P) no tendency for the current plateau is observed and instead a steep current decay is recorded

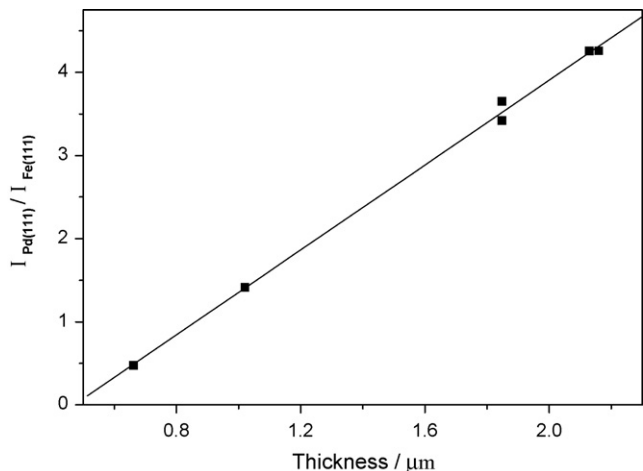


Fig. 4. Correlation between the ratio of Pd(111) and Fe(111) peak intensity on X-ray diffractograms of pure Pd/PSS membranes and the thickness of the Pd films.

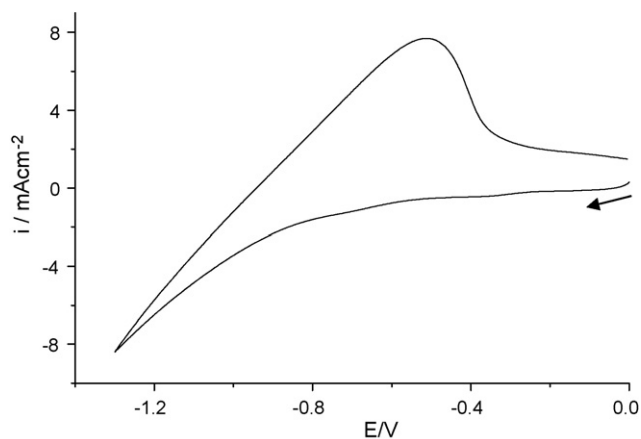


Fig. 5. Cyclic voltammograms of Pd (low T) film ($2.0\text{ }\mu\text{m}$ thickness) in 0.1 M NaOH solution. Initial potential of 0.0 V and sweep rate of 10 mV s^{-1} .

(Fig. 8). This behavior clearly points out to that this material is less suitable to be used as a GDE when compared to the others prepared in this work. On increasing the temperature to $50\text{ }^\circ\text{C}$, the same behavior was observed and only a slightly increase of the “residual” current density was attained (in the range $0.6\text{--}1.0\text{ mA cm}^{-2}$). The current decrease with time during H_2 feeding was also observed by Cabot et al. [5,6], when applying the same potential on a Pd foil (oxidized at $400\text{ }^\circ\text{C}$) used as a GDE at $50\text{ }^\circ\text{C}$. However, a quasistationary current density of about 50 mA cm^{-2} was reported in that case.

The current decrease observed during potentiostatic experiments under H_2 feeding points out that hydrogen oxidation at the Pd/electrolyte interface is drastically decreased during the electrochemical experiment. Two hypotheses are advanced in order to explain this phenomenon:

- A slow diffusion of atomic hydrogen through the Pd membrane.
- A slow entry of atomic hydrogen at the H_2/Pd interface.

In order to evaluate the first hypothesis, the effect of the Pd film thickness was analyzed in potentiostatic experiments. Fig. 9 reveals that as the thickness of the film increases, the abrupt current decrease is delayed. This behavior is not consistent with an electrode reaction controlled by the hydrogen transport through the metallic film, suggesting that diffusion of atomic hydrogen through the Pd membrane is not the slowest step. On the other hand, it is

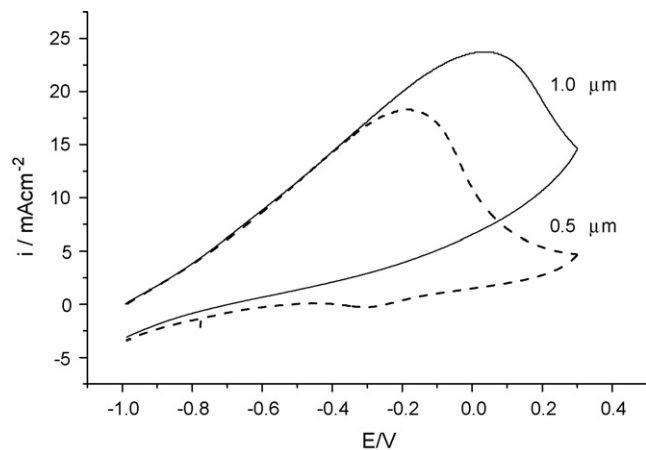


Fig. 6. Cyclic voltammograms of Pd (low T) films ($0.5\text{ }\mu\text{m}$ and $1.0\text{ }\mu\text{m}$ thickness) in 0.1 M NaOH solution under continuous H_2 supply. Sweep rate of 10 mV s^{-1} .

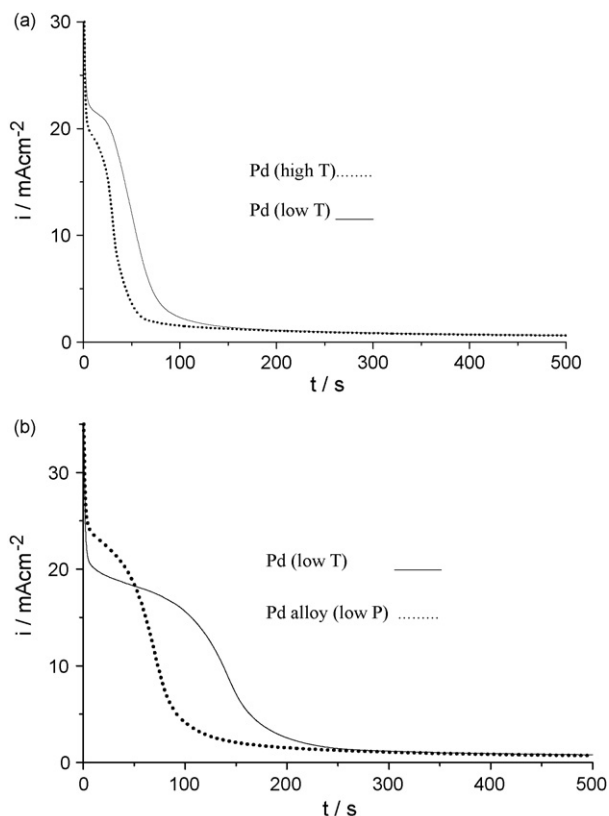


Fig. 7. Current transients for the H₂ oxidation at –0.1 V in 0.1 M NaOH solution on Pd-based films of equal thickness. (a) 0.5 μm and (b) 1.0 μm. Temperature of 25.0 °C.

also depicted that the anodic charge increases as the thickness of the membrane increases as well. This behavior seems to point out that the main contribution to the overall anodic charge comes from the hydrogen initially absorbed into the film under OCP.

Evidence about the entry of atomic hydrogen at the H₂/Pd interface as the slowest step is obtained when calculating the anodic charge needed to oxidize all the atomic hydrogen absorbed in the Pd film. A theoretical value of 10.9 C is obtained for a 1.0 μm-thickness film considering a surface roughness factor of 10 (probably underestimated because the roughness factor of a Pd electroless film deposited on a smooth Ni electrode is 5.3 [9]), Pd saturation by absorbed hydrogen (H/Pd = 0.65), with no further

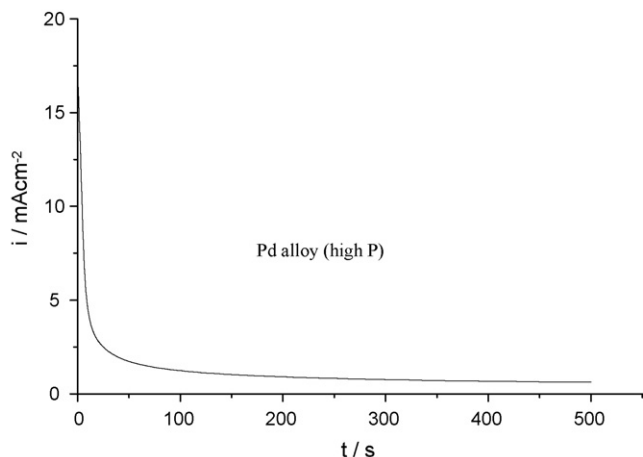


Fig. 8. Current transients for the H₂ oxidation at –0.1 V in 0.1 M NaOH on the Pd alloy (high P) film. Temperature of 25.0 °C.

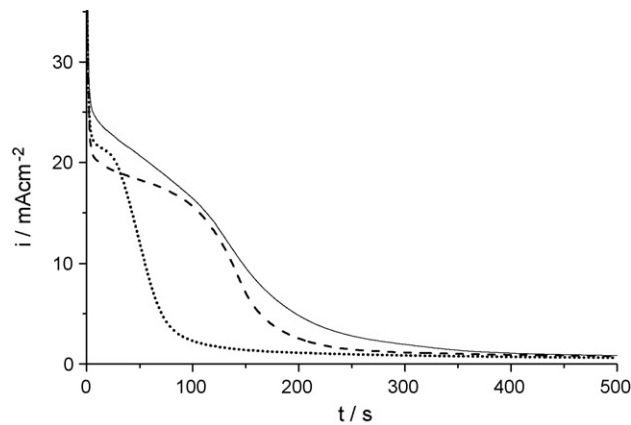


Fig. 9. Current transients for the H₂ oxidation at –0.1 V in 0.1 M NaOH solution on Pd (low T) films of different thicknesses: (···) 0.5 μm, (---) 1.0 μm and (—) 2.0 μm. Temperature of 25.0 °C.

H₂-replenishment by H₂ adsorption after electrode saturation. The experimental values for 1.0 μm-thickness films of Pd (low T) and Pd alloy (low P) are 4.6 C and 3.2 C, respectively, which are lower but of the same order of magnitude of the theoretical one. The similarity of theoretical and experimental charges suggests that the high currents at the beginning of the potentiostatic experiments are due to the hydrogen initially absorbed in the film under OCP and that the further residual current is limited by the slow entry of atomic hydrogen at the H₂/Pd interface. The slow replenishment of atomic hydrogen through the electrode/electrolyte interface is also revealed by the OCP measurements, because after the hydrogen oxidation experiments it was found that the OCP was about –0.60 V, which only slowly returned to –0.99 V (H₂ feeding was not cut off).

The important difference between the results obtained using the commercial foil [5,6] and the Pd membranes prepared herein seems to indicate that the slow entry of hydrogen at the Pd interface might be due to a non-complete isolation of the porous steel substrate from the solution electrolyte (see Figs. 1 and 2). If the substrate porosity is not completely covered and/or if cracks are formed in the Pd film, the solution electrolyte could access to the interior of the porous steel substrate, forcing the hydrogen to diffuse through the solution before reaching the Pd interface. This hypothesis is supported by comparing the OCP evolution of the Pd membrane in 0.1 M NaOH while it is fed with H₂ after its immersion in the electrolyte solution (curve a in Fig. 10), with the OCP evolution when it

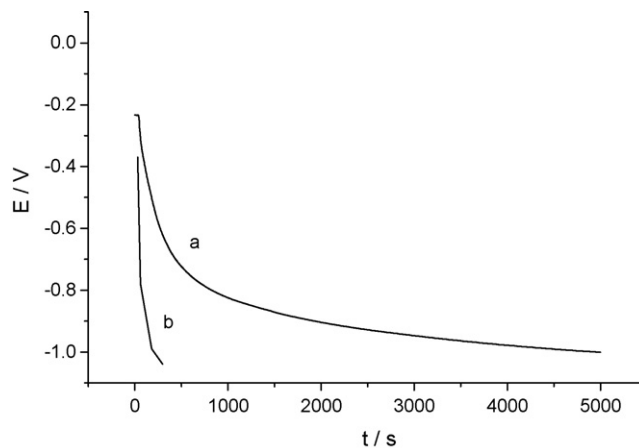


Fig. 10. OCP evolution for the Pd (low T) film in 0.1 M NaOH when the electrode is fed with H₂ (a) after its immersion and (b) before and during its immersion in the electrolyte.

is supplied before and during its immersion (curve b). The sluggish decrease of the OCP towards -1.0 V agrees with the slow entry of H_2 at the Pd interface, in particular when the membrane is immersed in the solution before H_2 supply. Further work is planned to modify the membrane in order to minimize this effect and to assure its impermeability in front of the electrolyte.

4. Conclusions

Among the different plating conditions used to prepare the Pd membranes by electroless deposition, the best recovering of PSS at a lower Pd mass expense was achieved for Pd (low T)/PSS membrane. Although microfissures have been formed on Pd films and on the Pd–P alloy after charging–discharging experiments (as expected when working at very low temperatures), they did not affect the adherence of the prepared thin films since no peeling was detected.

It was found that, independently of the composition or thickness, the activity of the prepared membranes towards the hydrogen oxidation in 0.1 M NaOH with continuous H_2 supply, was high at the beginning of the experiment, but it significantly decreased with time. This behavior was mainly attributed to a slow hydrogen entry at the H_2 /Pd interface. Evidence about electrolyte access to the interior of the porous steel substrate due to cracks and/or badly filled porous in the Pd film, forcing the H_2 diffusion through the elec-

trolyte before reaching the Pd film, is given. This work revealed that thin Pd electroless films deposited on PSS for usage as GDE is technically feasible but a good porous filling is required for liquid electrolytes.

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