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Study of the eletrochemical comportament (Platinum / Polyaniline / Palladium) modified electrode for developing hydrogen sensor permeate in mettalic structures applied in Oil Refinaries.

Lilian Machado Moya, ldemj@yahoo.com.br
Jéferson Aparecido Moreto, jeferson_moreto@yahoo.com.br
Haroldo de Araújo Ponte, hponte@ufpr.br
Universidade Federal do Paraná. Centro Politécnico, Usina Piloto A, Laboratório de Eletroquímica de Superfície e Corrosão (LESC), Bairro Jardim das Américas, Curitiba, PR, Cep. 81531-990.

Carlos Marcus Gomes da Silva Cruz, *cruz@utfpr.edu.br*
Universidade Tecnológica Federal do Paraná. Campus de Curitiba, Departamento Acadêmico de Química e Biologia, Av. Sete de Setembro, 3165, Bairro Rebouças, Curitiba, PR, Cep. 80230-901.

Abstract. *Currently one of the major problems encountered in oil processing industries is the control of deterioration in the structures of the units that compound the refining process. This deterioration is related to processes of embrittlement caused by hydrogen permeated into the metallic structure. Being thus, extremely important the continuous monitoring of these environments. In this context, this work aimed at studying the behaviour of electrochemical polyaniline (PAni) and polyaniline composed with palladium (PAni-Pd) when exposed to hydrogen seeking a possible application of these modified electrodes as sensors or indicators of hydrogen. The polyaniline, and many of its derivatives are sensitive to various types of gases, as well as palladium also sensitizes, with ease, facing the hydrogen. Thus, a set of electrodes was made, some containing only electrochemically synthesized polyaniline on the platinum and others with palladium electrodeposition on polyaniline. In order to evaluate the sensitivity of electrodes facing the times of exposure to hydrogen, tests of open circuit potential (OCP) were performed. The hydrogen chargings were made through the technique of cyclic voltammetry with determined times. After the end of each charging the electrodes were subjected to OCP measures with time set in 3600 s. The results of the potential curves versus time showed that the electrodes compound of polyaniline practically didn't change, differently of those containing palladium-polyaniline that showed high sensitivity to hydrogen, featuring a real possibility to implement them in active matrices for sensing.*

Keywords: *hydrogen permeation, Polyaniline, palladium, sensor*

1. INTRODUCTION

The presence of hydrogen in metallic structures, even in small quantities, is a critical issue that affects the equipment's integrity and how long time, in particular, of the petrochemical industry. This problem is evidenced with greater frequency by the loss of ductility, in other words, embrittlement caused by the interaction of hydrogen with the metal. This kind of interaction is usually explained through a mechanism of transport, which is composed of several stages. Initially, it is considered that the hydrogen is generated on the surface of the metal. There, in the interface, the hydrogen is adsorbed, absorbed and then it spreads itself internally by the material. In this process it may occur imprisonment of hydrogen in the metal, increasing internal pressure that may exceed the material collapse maximum tension, producing the nucleation and / or the growth of cracks (Zakroczmski et al., 2005).

In oil refineries for instance, this fact is very important, since the equipment operates in corrosive environments which leads to atomic hydrogen generation that is absorbed by the internal walls of the equipment resulting in the damage of them. As the replacement of these materials for more resistant ones is not a feasible option, one solution would be to invest in the development of more efficient methods of monitoring the corrosion, indicating the occurrence of corrosive processes in real time and allow its immediate restraint. Several types of sensors have been tested and it is expected that in the near future a definitive solution is reached (Siddiqui et al., 2005).

Conductor polymers appear as good materials to be investigated because, since its discovery, many applications have been successfully attributed to these materials. Nowadays, diodes, transistors, gas sensors, chemical and biological sensors, dosimeters, applications in biomolecular electronics, artificial muscles, light-emitting diodes, light displays and photovoltaic cells are examples of conductive polymers applications (Lindorfs and Ivasaka, 2002).

Another material with special characteristics associated with hydrogen that deserves much attention is Pd. This metal, besides presenting excellent hydrogen absorption and adsorption kinetics, as well as durability and efficiency in terms of hydrogen charging and discharge, is also able to behave like a sponge accommodating quantities of hydrogen of about 900 times its volume in its crystalline lattice (Azambuja et al., 2006).

In this way, this work aimed at studying the electrochemical behaviour of electrodes composed of PAni and PAni with Pd when exposed to hydrogen, in order to evaluate the potential of such systems as active matrices in hydrogen electrochemical sensors.

2. MATERIALS AND METHODS

The electrochemical synthesis of PAni was performed using methodology found in the literature (Cruz and Ticianelli, 1997). The electrolyte solution was composed of sulphuric acid (Merck) 0.5 $molL^{-1}$, sodium sulfate (Merck) 0.5 $molL^{-1}$ and aniline (Vetec) 0.05 $molL^{-1}$ remaining stored in dark container, under nitrogen atmosphere and temperature of ± 5 ° C, thus avoiding photooxidation and degradation of the monomer present in the solution. For the experiments of Pd electrodeposition on the platinum and polyaniline surface, the reagent used was palladium chloride (Aldrich), from which a solution with concentrations of 0.2 $mmolL^{-1}$ was made (Angelo et al., 2001). All solutions were prepared with ultra-pure water obtained from a Puritech system (Permution EJ Krieger and Cia Ltda).

As a substrate for PAni electrosynthesis it was used a 0.25 cm^2 (geometric area) platinum (Pt) electrode. The applied potential reference electrode was the reversible of hydrogen (RHE) and as an auxiliary electrode, a graphite stick with 7.9 mm of diameter and 7.5 cm of length. The electrochemical cell was composed of one-compartment and three-electrode conventional system with capacity for about 100 mL of solution. The equipment used to carry out the measures was an electrochemical potentiostat / galvanostat - PAR - mod. 273A - Priceton Applied Research, interfaced to a microcomputer, through a GPIB (IEEE 488).

The aniline was electropolymerized upon the Pt electrode through the cyclic voltammetry technique. The parameters used were based on other studies found in literature (Cruz and Ticianelli, 1997) regarding the synthesis of slightly thick homogeneous films and with low formation of byproducts. So, scanning speed of 50 mVs^{-1}, interval of potentials between 0.05 V and 1.1 V and a total of 50 growth cycles were used. At the end of the growth some scans were performed in the interval between 0.05 V and 0.70 V, in which the polymer remains chemically stable and with its thickness unchanged by the action of the potential. These voltammetries were advanced to a scanning speed of 20 and 50 mVs^{-1}, in solution of 0.5 $molL^{-1}$-sulphuric acid and 0.5 $molL^{-1}$-sodium sulphate, with the objective of evaluating, at a later date, the changes caused by the action of hydrogen in the electrochemical response of the polymer.

Pd electrodeposition upon the Pt and PAni surface was held under the same conditions. The Pt electrode and the modified electrode composed of Pt-PAni were immersed in a solution of chloride of palladium ($PdCl_2$) 0.2 $mmolL^{-1}$ at a temperature of 40 ^oC and under slow agitation. The technique used for electrodeposition was the cronopotenciometric. The current density was kept in 0,002 Acm^{-2} according to literature found for palladium electrodeposition (Ito et al., 2002) and the time varied in 900 s, 1800 s and 2700 s.

OCP measures were made for a set of five electrodes, (a) metallic Pt, (b) Pt-PAni, (c) PAni-Pt-Pd, (d) Pt-Pd and (e) metallic Pd. The methodology used was the same for all electrodes. Initially there were taken measures of the potentials of balance for each electrode. Later, through the technique of cyclic voltammetry, it was imposed, to each electrode, a system disturbance through chargings of hydrogen. The chargings were of 120 s, 300 s, 600 s, 900 s and 1200 s in potentials of -0.1V. Between one and another disturbance, OCP measures were held during the time of 3600 s.

3. RESULTS AND DISCUSSION

The PAni has been widely used as active matrix in different types of sensors, showing high sensitivity to various substances. Sensors to detect hydrogen gas-rich atmospheres also have been studied and those containing PAni show to be quite promising. It is recognized that the hydrogen in its atomic and/or molecular form in contact with the PAni surface can lead to the reduction of its chains oxidized parts and thereafter convert them to its insulating state, causing change in the signal that can be identified through changes in the redox properties of PAni (Lubentsov et al., 1991).

Thus, in order to examine the sensitivity of PAni and composite PAni with Pd to the hydrogen diffused by the polymer mesh; differently from other studies conducted so far, measures of open circuit potentials were made. Through these measures it was possible to verify the changes in the potential of balance according to the different times of hydrogen charging.

The first investigation conducted was with respect to the influence of the polymeric film thickness on the sensitivity of the system. Fig. 1, 2 and 3 present the results for the synthesis made up to 20, 50 and 80 cycles respectively. Yet, Fig. 4 shows the voltammetric profile for the polymer grown up to 50 cycles before and after the last time of hydrogen charging.

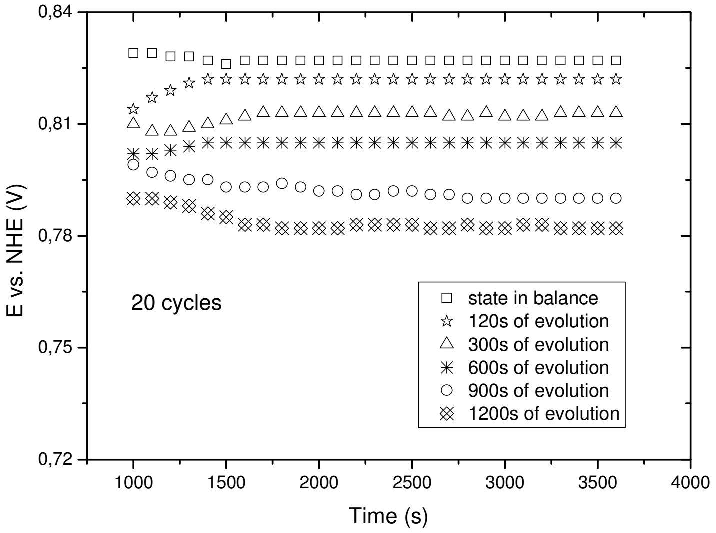

Figure 1. OCP curves for PAni deposited on Pt with duration of 3600 s.

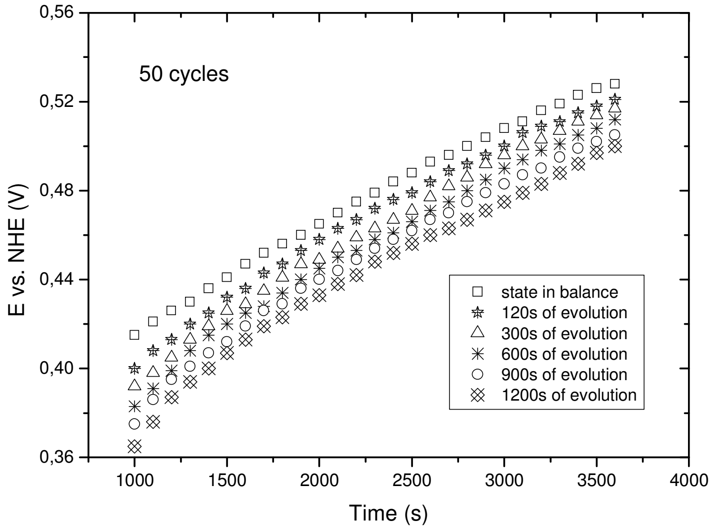

Figure 2. OCP curves for PAni deposited on Pt with duration of 3600 s.

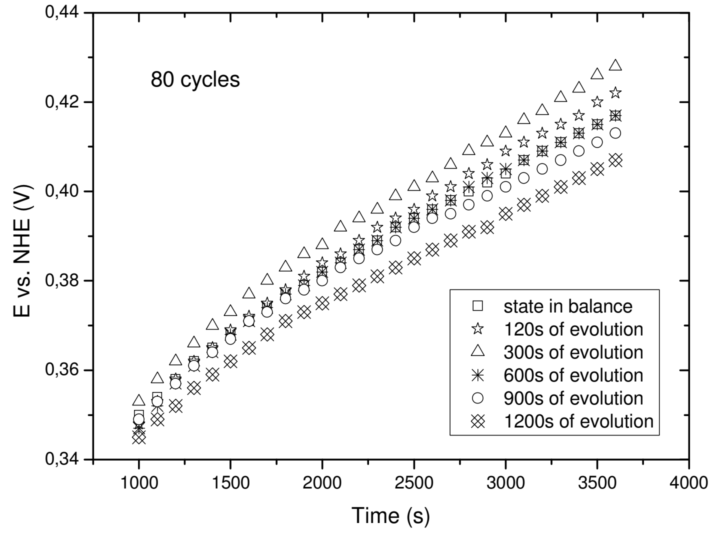

Figure 3. OCP curves for PAni deposited on Pt with duration of 3600 s.

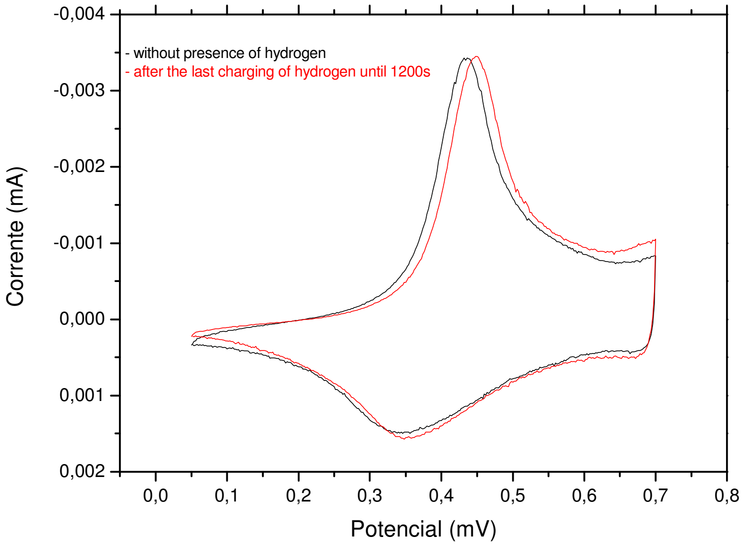

Figure 4. Voltammograms profiles with reference to the PAni electrode grown up to 50 cycles.

The analysis of previous graphs showed that the interaction between hydrogen and PAni, independently of the synthesized film thickness, was not very meaningful. This shows that the behavior of the film electrochemical potential, with the variation in the hydrogen concentration, does not suffer major changes within the zone of thickness available to be obtained for the polymerization maximum period, where a growth is proportional to time. This may be related to the formation of molecular hydrogen to the level of Pt, not having able time for the hydrogen atoms to reach the active sites of PAni. Another factor to be considered, concerns the fact of the polymer mesh to be sufficiently open, offering a small surface for interaction.

Despite the results suggest limited PAni sensitivity in view of the hydrogen, there is the possibility of this property to be improved when the polymer is associated with other materials, as it can be confirmed in literature (Li et al., 2000; Matsuguchi et al., 2002; Chabuskswar et al., 2001).

In light of the above and in order to obtain a more hydrogen-sensitive system, another set of experiments was carried out. This way, Pd was electrodeposited on the PAni surface. As it is common sense and present in the fundamental literature devoted to the science of materials, Pd absorbs, easily, appreciable quantities of hydrogen. The gas diffuses by the crystalline interstices of the metal in the atomic form, establishing a system that can be interpreted as a real solution (Tabib-Azar et al., 2005). The OCP results obtained for this new set of experiments are shown in Fig. 5. Fig. 6 presents the results for the voltammograms, before and after the last time of charging.

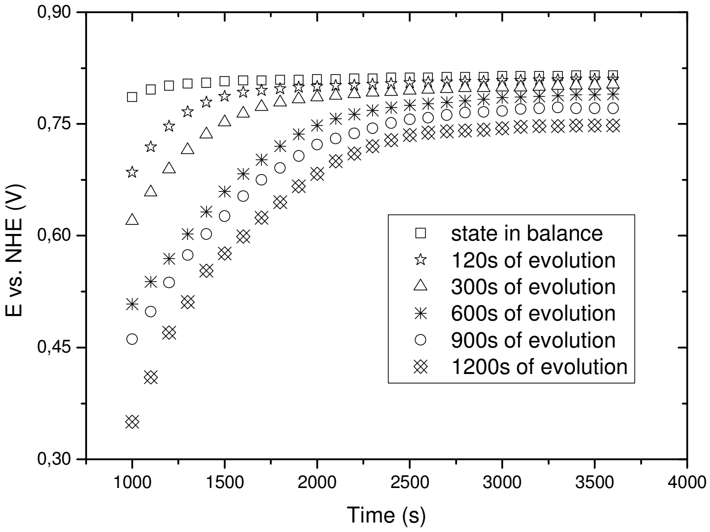

Figure 5. OCP curves for palladium electrodeposited on PAni-Pt with duration of 3600s.

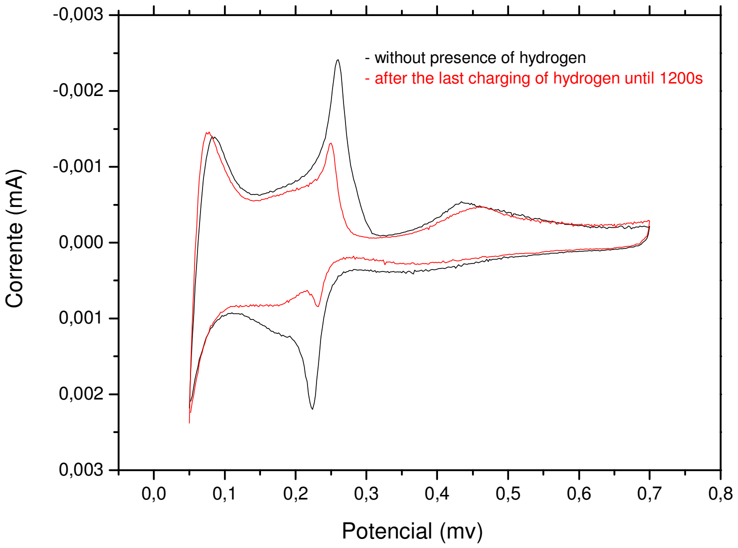

Figure 6. Voltammograms profiles with reference to the electrode containing PAni-Pd-Pt.

It is observed that the potential presented greater variation in time of hydrogen evolution for the electrodes containing Pd, showing itself more sensitive and consequently responding faster to the presence of hydrogen. This may be an indication that the Pd deposited on the PAni serves as a good hydrogen acceptor. While the difference in potential achieved by PAni, between the balance potential until the last charging of hydrogen, was of approximately 0.06 V for films grown up to 50 cycles, the PAni associated with Pd, on exposure to hydrogen during the same period of time, presented values included in 0.44 V.

Through these results it is believed that the PAni, showing great porosity, is not able to sensitize itself in the presence of hydrogen, but provides the storage of large quantities of Pd atoms for electrodeposition.

To evaluate the influence of PAni on the system a new set of experiments was assembled, consisting only of Pd electrodeposited on Pt. The results for OCP measures can be seen in Fig. 7 and consequently the voltammograms in Fig. 8.

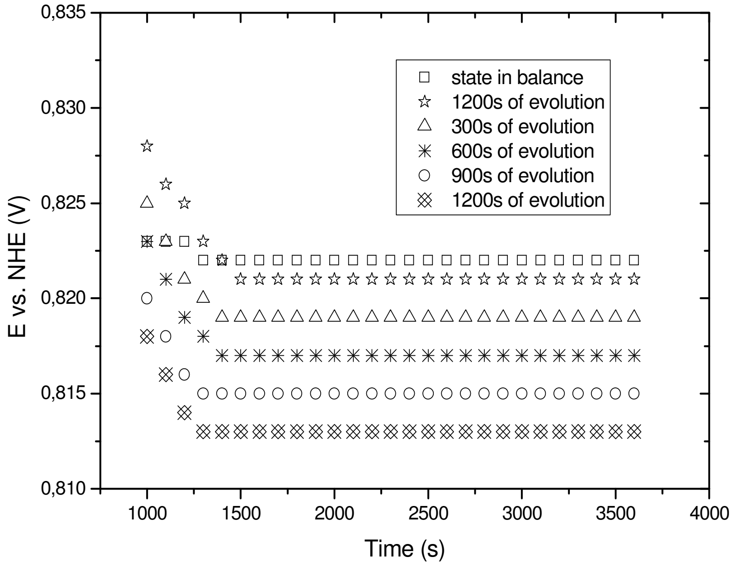

Figure 7. OCP curves for platinum with palladium electrodeposited with duration of 3600s.

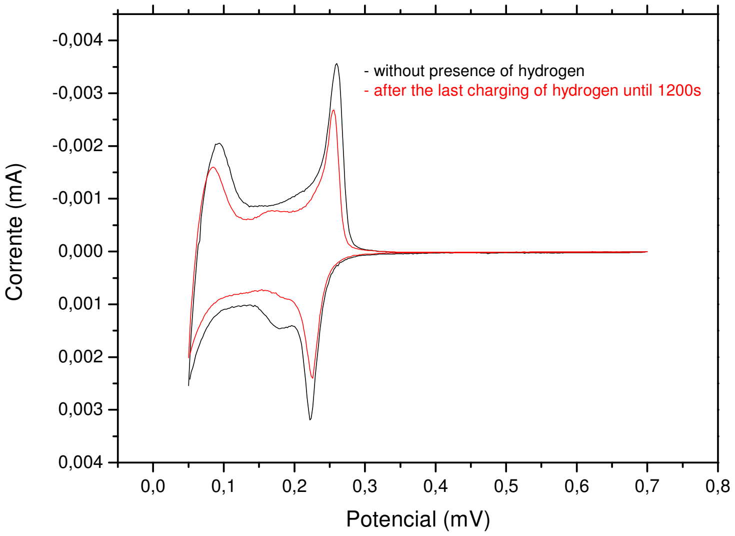

Figure 8. Voltammograms Profiles with reference to the electrode containing Pt-Pd.

Comparing the results for the electrode containing Pd electrodeposited directly on the Pt to the Pt- PAni -Pd electrode, it was observed that the variation found in the potential for the first case was much lower than that where the PAni was present. What proves the influence of the polymeric film, probably acting as a porous mesh able to accumulate higher amounts of Pd with respect to the flat surface of Pt, thus providing an area, with active sites, significant for interaction with hydrogen. Similar experimental arrangements were also conducted with pure metallic Pt and pure metallic Pd. The results are now shown in Fig. 9 and 10.

The graph of Fig. 9 indicates that pure metallic Pt in contact with hydrogen practically does not suffer any kind of chemical interaction, since its balance potential presents variation less than 15 mV. This fact is in line with other discussions found in the literature where it is reported that Pt is not capable of storing hydrogen in its metal structure because of its packing degree (Dall'Antonia et al., 1999; Ciola, 1981).

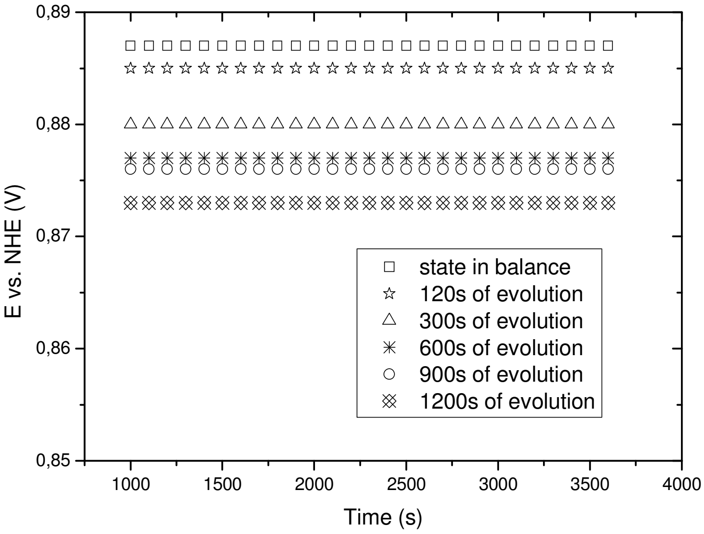

Figure 9. OCP curves for metallic platinum with duration of 3600s.

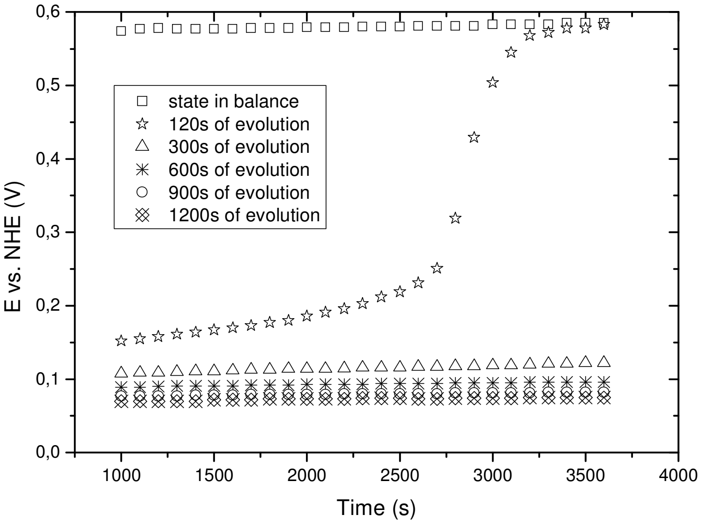

Figure 10. OCP curves for metallic palladium with duration of 3600s.

Yet, the analysis of the graph, shown in Fig. 10, shows a tendency of stabilization for the potential when the metal exposure times to the gas extends beyond 400 seconds. This effect is associated with strong absorption of hydrogen that becomes more intense as time of exposure passes, tending to a natural saturation. Once the production of gas on Pd is ceased it is verified that the open circuit potential tends to return to the pure metal values, however, the necessary time needed for it to happen is a function of the quantity of hydrogen absorbed, the mass and also the geometry of the Pd electrode. These factors determine the speed of hydrogen diffusion in Pd and consequently interfere in the distributions of the chemical potentials.

The same phenomenon is confirmed when examining the modified electrode composed of Pd-PAni-Pt; however, the time taken to reach a state of equilibrium is considerably smaller. Here, a striking consistency with the ideas set out above is found, whereas, in this case, Pd appears to be finely distributed, electrodeposited on PAni, forming a porous surface offering greater hydrogen diffusion speed, which contributes for the equilibrium to be reached more quickly.

4. CONCLUSIONS

According to the characteristics of the open circuit potential curves obtained, we can conclude that the PAni showed sensitivity to hydrogen much below than that observed for PAni composed with Pd. This conclusion is supported by the fact that the balance potential of the electrode Pt-PAni practically doesn’t vary versus the different times of hydrogen evolution as opposed to what can be observed for the electrode composed of Pt-PAni-Pd that presented a considerable variation in the potential due to the times of exposure to hydrogen. These tests also led to the conclusion that synthesized films different thicknesses do not interfere in the sensitivity of PAni versus hydrogen and that the systems under study are subject to the cumulative effect related to the decrease in the electrode sensitivity to the chargings of hydrogen and necessity of a larger time to achieve stability.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Azambuja, V.M., Dos Santos, D.S., Pontonnier, L., Morales, M. and Ruchart, D., 2006, “Study of a Pd0.97Ce0.03 internally oxidized alloy“, Scripta Materialia, Vol. 54, pp. 1779-1783.

Chabuskswar, V.V., Pethkar, S. and Athawale, A.A., 2001, “Acrylic acid doped polyaniline as an ammonia sensor”, Sensors and Actuators B, Vol. 77, pp. 657-663.

Ciola, R., 1981, “Fundamentos da catálise”, Ed. Moderna, Ed. da Universidade de São Paulo, S.Paulo, Brazil, 156 p.

Cruz, C.M.G.daS. and Ticianelli, E.A., 1997, “Electrochemical and ellipsometric studies of polyaniline films grown under cycling conditions”, Journal of Electroanalytical Chemistry, Vol. 428, pp. 185-192.

Dall’Antonia, L.H., Perez, J., Tremiliosi-Filho, G. and Gonzalez, E.R., 1999, “Metodologia para crescimento de esferas monocristalinas de metais nobres”, Química Nova, Vol. 22, pp. 23-34.

Ito, H.A., Olivedira, M.F., Gomes Neto, J.A. and Stradiotto, N.R., 2002, "Eletrodo modificado em filme de paládio para determinação voltamétrica de fosfito", Eclética Química, Vol.27, pp. 22-29.

Li, D., Jiang, Y., Wu, Z., Chen, X. and Li, Y., 2000, "Self-assembly of polyaniline ultrathin films based on doping-induced deposition effect and applications for chemical sensors", Sensors and Actuators B, Vol. 66, pp. 125-127.

Lindorfs, T. and Ivasaka, A., 2002, "pH sensitive of polyaniline and its substituted derivates", Journal of Electroanalytical Chemistry, Vol. 531, pp. 43-52.

Lubentsov, B.Z., Timofeeva, O.N. and Khidekel, M.L., 1991, "Conducting polmerinteraction with gaseous substances", Synthetic Metals, Vol. 45, pp. 235-240.

Matsuguchi, M., Io, J., Sugiyama, G. and Sakai, Y., 2002, "Effect of NH_3 gas on the electrical conductivity of polyaniline blend films", Synthetic Metals, Vol.. 12, pp. 15-19.

Siddiqui, R.A., Hussein, A. and Abdulla, H., 2005, "Hydrogen embrittlemnet in 0,31% carbon Steel used for Petrochemical apllications", Journal of Materials Processing Technology , Vol. 170, pp. 430-435.

Tabib-Azar, M., Sutapum, B., Petrick, R. and Kazemi, A., 2005, "Highly sensitive hydrogen sensors using palladium coated fiber optics with exposures cores and evanescent field interactions", Sensors and Actuators B Chemical, Vol. 56, pp. 158-163.

Zakroczymski, T., Glowacka, A.and Swiatnicki, W., 2005, "Effect of hydrogen concentration on the embrittlement of a duplex stainless steel", Corrosion Science, Vol. 47, pp. 1403-1414.

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