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## Evaluation of gas diffusion electrodes as detectors in amperometric hydrogen sensors.

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**Abstract:** This work is directed to the study and evaluation of gas diffusion electrodes as detectors in hydrogen sensors. Electrochemical experiments were carried out with rotating disk electrodes with a thin porous coating of the catalyst as a previous step to select useful parameters for the sensor. An experimental arrangement made in the laboratory that simulates the sensor was found appropriate to detect volumetric hydrogen percentages above 0.25% in mixtures  $H_2:N_2$ . The system shows a linear response for volumetric percentages of hydrogen between 0.25 and 2 %.

**Keywords:** hydrogen sensors; amperometric sensors; gas diffusion electrodes; hydrogen oxidation; supported platinum.

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### Introduction

The control of dangerous gases such as hydrogen (flammable above of 4 % in air) in residential or industrial environments requires the development of sensitive, fast response detectors. Several commercial devices are available, like electrochemical cells, mass spectrometers and sensors with incorporated resistances of semiconductors oxides. These devices are used to control industrial environments, medicinal gases, compressed air, processes with gases under pressure, chromatographic instrumentation and research and development facilities as fuel cells operating with hydrogen. Due to the risk of explosion, it is necessary to have a sensor sensitive to low concentration levels and with a fast response.

#### *Amperometric sensors*

Amperometric sensors [1,2] are systems that

measure the concentration of a compound using as a response the electrical current generated by the electrochemical reaction of the compound which should be proportional to its concentration. Many systems use porous electrodes, called gas diffusion electrodes (GDE) similar to those used in low temperature fuel cells, made with the catalysts (in general platinum based metal nanoparticles of around 2-5 nm) supported on high surface area carbon (40-50 nm particles). A potentiostat is usually used to fix the working electrode potential.

The construction and development of an amperometric sensor requires some steps that can briefly described as follows: i) study of the electrochemical reaction on the catalytic materials, ii) study of the geometrical arrangement of the several sensor components, iii) determination of the sensitivity, linearity and speed of response, iv) determination of the stability of the sensor under continuous operation and v) determination of the influence of poisonous species .

The gas diffusion electrodes (GDE) [3,4] used in amperometric sensors are semihydrophobic and their microstructure is shown schematically in Figure 1. Usually they are composed of two layers deposited on an appropriated support. A diffusion layer is prepared with a suspension of PTFE (for example DuPont TM 30) with high surface area carbon (Cabot XC-72,  $250 \text{ m}^2 \text{ g}^{-1}$ ). The mixture is filtered on a support (a carbon cloth or a carbon paper, totally hydrophobic). Onto this layer the catalytic layer is deposited using several procedures [4-5]. The catalytic layer contains metal nanoparticles anchored on a carbon support and may incorporate Nafion® (DuPont) which is a proton exchange material, and as such, an ionic conductor. The result is a matrix which has pores, electrolyte channels, electronic pathways and electrocatalytic surfaces. The material is a good electronic conductor, porous and can conduct ions through the catalytic layer which presents a high electroactive area. The electrolyte is usually a Nafion® membrane, because it is a proton conductor with high conductivity and the interface catalyst/membrane is very stable.

#### *Hydrogen sensors*

A number of commercial instruments are under development to determine quantitatively the concentration of hydrogen in several environments. In general Pt or Pd are used as active metals in the detector electrode [6-10]. Miremadi et al. [7] built a sensor selective to  $\text{H}_2$  and inert to  $\text{CO}$ ,  $\text{CH}_4$ , propane and alcohols, using films of carbon prepared by an exfoliation technique. This sensor shows a response time of around 40 s for hydrogen concentrations between 3 and 300 ppm at  $110^\circ\text{C}$ . Tabib-Azar et al. [8] applied optic fibers in an interesting way to develop a hydrogen sensor using a Pd recovery onto the optic fiber core. When  $\text{H}_2$  is adsorbed on Pd the real and imaginary components of the refraction index change affecting the elasto-optic effect inside of the fiber. This system detects concentrations between 0.06 and 2% in the environment with a response time of around 20-30 seconds. Works which use the semiconductor properties of oxides such as  $\text{TiO}_2$  doped with Pd [9],  $\text{SnO}_2 + \text{Bi}_2\text{O}_3$  doped with Pd [10],  $\text{ZnO}$  doped with Al [11] and  $\text{V}_2\text{O}_5\text{-ZrO}_2$  [12] have been reported for applications in  $\text{H}_2$  sensors, but these systems are not very sensitive. Chaudhary et al. [13] describe a

sensor that uses PdO with  $\text{RuO}_2$  on  $\text{SnO}_2$  in which the distribution of Ru and Pd species favors the formation of defects on the surface and this contributes to the better selectivity and sensitivity of the system. The results show a system with linear response in a concentration range between 0 and 1000 ppm.

Other  $\text{H}_2$  sensors use different materials. Varghese et al. [14] used Ti nanotubes to detect  $\text{H}_2$  with a good sensitivity in the temperature range  $180\text{-}400^\circ\text{C}$ . This sensor showed the possibility of monitoring concentrations between 100 ppm and 4 % v/v of  $\text{H}_2$  in air.

McCullen et al. [15], built a hydrogen sensor using a metal/ $\text{AlN}/\text{Si}(111)$  structure which behaves similarly to a metal-insulator-semiconductor-type capacitor. The AlN layer was deposited by plasma source molecular-beam epitaxy. The device uses alternating gates of Pd and Al and an Al black contact, all grown by magnetron sputtering. The Pd gate structures were found to be sensitive to hydrogen, down to the ppm range in the surrounding flow, while the Al gate structures showed no response to hydrogen.

Bera et al. [16] synthesized Pd nanoparticle arrays using templates (based on an Al film on a polycarbonate substrate) by assisted electrodeposition and propose this materials for a high sensitivity hydrogen detector system at room temperature.

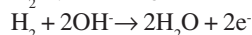
In amperometric sensors that use GDEs prepared with Pt/C the conditions to determine low  $\text{H}_2$  concentrations are favored due to the high surface area of the electrodes contributing to the determination of the currents. The detection interval with these materials is usually 0-10 % v/v of  $\text{H}_2$ .

In order to build a  $\text{H}_2$  sensor that uses Pt/C it is necessary to know the mechanism of the hydrogen electro-oxidation on Pt. It is known that the kinetics in acid media is fast [17-19]. Other metals, such as Pd [20] show high electrocatalytic activity for the hydrogen oxidation reaction (HOR). Contrary to the case of Pt and Pd, the HOR on Au surfaces [21] shows a very low activity. A brief revision on HOR studies on Pt shows that this is a very fast electrochemical reaction described by its exchange current density value in acid media ( $3.16 \text{ mA cm}^{-2}$  for low pH values) on smooth Pt electrodes [18]. Three mechanisms are accepted for  $\text{H}_2$  electrooxidation on Pt [22]:

*Direct discharge*

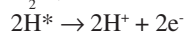
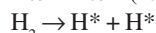


*acid media*

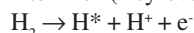


*alkaline media.*

*Atom-Atom (Tafel-Volmer)*



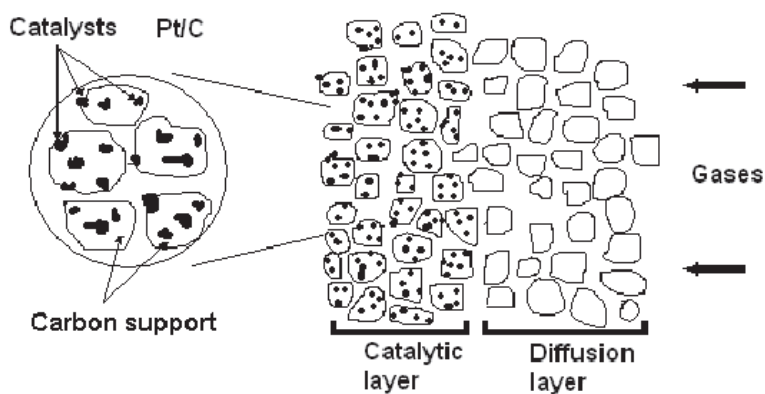
*Atom-Ion (Heyrovsky-Volmer)*



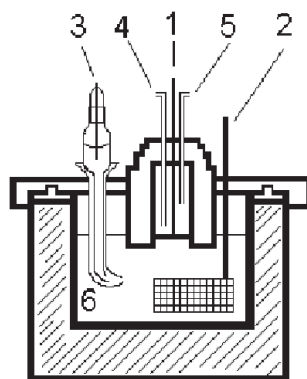
Reports by Harrison et al. [23], and Gasteiger et al. [19] show that for smooth Pt surfaces in acid media, the mechanism that operates is the reversible direct discharge (in this case, the reaction is not

limited by adsorption). With a rotating disk electrode/thin porous coating electrode (RDE/TPC) [24], it was found that for supported Pt (Pt/C), the reactions occur by the same mechanism. Inhibitory effects of the adsorption of ions [25], effects of pH [18] and impurities [26] on the HOR have been published.

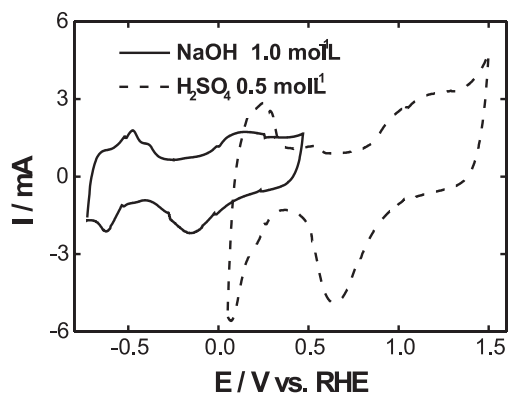
The use of GDE to build  $\text{H}_2$  sensors was described by La Conti et al. [27] in 1971 showing that a fuel cell may be used as a detector if the configuration is appropriate. At that time the Pt load in GDEs, expressed in mass of Pt per unit of geometric area, was very high ( $5 \text{ mg Pt cm}^{-2}$ ), but today the quantities used are lower than  $0.4 \text{ mg Pt cm}^{-2}$ . This work describes the construction of a  $\text{H}_2$  sensor using GDEs, prepared by the methodology used in our laboratory [4], as a detector electrode.



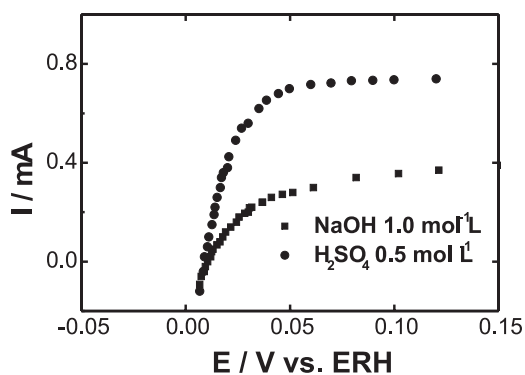
**Figure 1.** Microscopic scheme of a gas diffusion electrode.



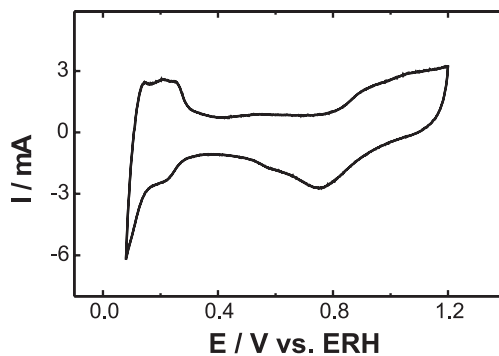
**Figure 2.** Electrolytic cell scheme used as  $\text{H}_2$  detector. 1) detector electrode (GDE) 2), counter electrode, 3) reference electrode (RHE), 4) gas inlet, 5) gas exit, 6) electrolyte.



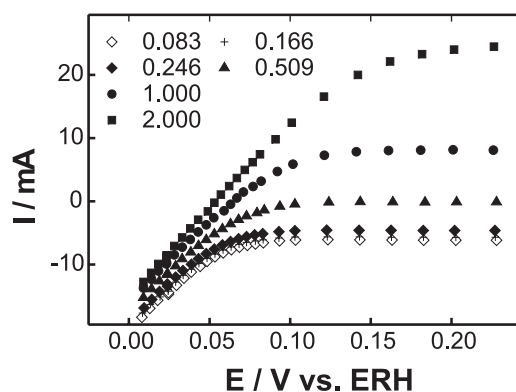
**Figure 3.** Cyclic voltammograms of thin porous coating electrodes prepared with Pt/C E-TEK in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> or 1.0 mol L<sup>-1</sup> NaOH.  $\nu = 10 \text{ mV s}^{-1}$ .



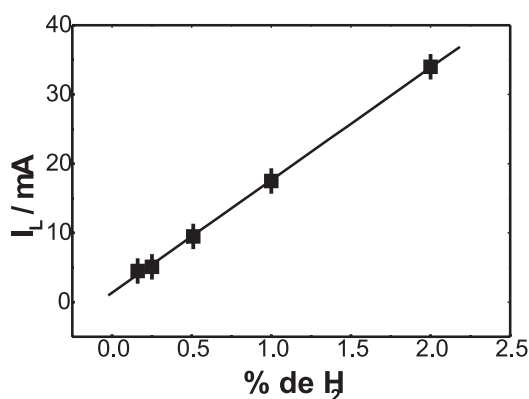
**Figure 4.** Steady state polarization curves for H<sub>2</sub> oxidation on thin porous electrodes with 20 wt. % Pt/C E-TEK in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> or 1.0 mol L<sup>-1</sup> NaOH.  $\nu = 10 \text{ mV s}^{-1}$ ;  $\omega = 1600 \text{ rpm}$ .



**Figure 5.** Cyclic voltammogram of the gas diffusion electrode containing 20 wt. % Pt/C E-TEK, 1.1 mg Nafion® cm<sup>-2</sup>, 0.4 mg Pt cm<sup>-2</sup> in the catalytic layer and 30 wt. % PTFE in the diffusion layer in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.  $\nu = 10 \text{ mV s}^{-1}$ .



**Figure 6.** Steady state potential-current density curves for  $H_2$  oxidation in the detector system using different  $H_2:N_2$  volume ratios.



**Figure 7.** Limiting current density curves vs. volumetric  $H_2$  concentration in the  $H_2:N_2$  gas mixture.

### Experimental

The study of the influence of the characteristics of Pt/C and of the electrolytic media on the HOR was made using the rotating disk/thin porous coating electrode (RDE/TPC) technique [28-29], using carbon powder (Vulcan XC-72, Cabot) catalyzed with Pt (E-TEK) containing different percentages of Pt (10, 20 e 30 w/w %). The electroactive areas were determined by the oxidation charge of hydrogen in voltammetric experiments, considering an oxidation charge for one monolayer of  $H_2$  on polycrystalline Pt as  $210 \text{ mC cm}^{-2}$  [30]. These electrodes (TPC) were prepared as described

in other reports [29,31-34] and characterized by cyclic voltammetry. Stationary state current-potential curves for the HOR were obtained with these electrodes in  $0.5 \text{ mol L}^{-1} H_2SO_4$  and  $1.0 \text{ mol L}^{-1} NaOH$  solutions. These measurements were made in an electrochemical cell where the main compartment contains the counter electrode (Pt foil,  $2 \text{ cm}^2$ ) and the working electrode (RDE/TPC), which is mounted on a graphite support with a  $0.15 \text{ mm}$  depth cavity and a geometric area of  $0.28 \text{ cm}^2$  filled with the Pt/C E-TEK catalyst. The reference electrode, a hydrogen reversible electrode (HRE), when the electrolyte was an acid solution or the calomel electrode in alkaline solutions was placed

in a small separate compartment. The reference electrode was joined to the main compartment using a Luggin-Haber capillary.

The preparation of GDEs for the hydrogen sensor was described previously [4]. The only difference was the use of a 30 % PTFE percentage in the diffusion layer. The catalytic layer was done with 20% wt. Metal/C, 0.4 mgPtcm<sup>-2</sup> (E-TEK) and 1.1 mg Nafion® cm<sup>-2</sup>. The electrodes had a geometric area of 0.78 cm<sup>2</sup>. The system was mounted in an electrochemical cell with 50 mL volume as shown in Figure 2. The detector electrode is connected to a gold contact (inactive for the HOR). The counter electrode was a Pt mesh and the reference a reversible hydrogen electrode (RHE). The evaluation of the EDGs was done by cyclic voltammetry in the potential range between 0.05 and 1.2 V vs. RHE. The gases from commercial cylinders, the first containing a volumetric mixture H<sub>2</sub>:N<sub>2</sub> 6:94 and the second containing pure N<sub>2</sub> (both from White Martins) were flown through fluximeters and through a compartment with glass particles to mix the gases. The current density-cell potential data for the HOR were obtained in a stationary regime (point by point), using in all experiments a 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution as electrolyte in the sensor. The electrochemical measurements were done using a PAR 273 potentiostat/galvanostat and the softwares M270 and HEADSTART (EGG).

## Results and discussion

Figure 3 shows the voltamograms of Pt/C electrodes in acid and alkaline media. It is observed the typical profile for Pt in supported catalysts [35] where the hydrogen adsorption/desorption region (between 0.05 and 0.35 V vs. ERH) is not well defined due to diffusional transport and ohmic drop inside the thin porous electrode. A third anodic peak due to the oxidation of absorbed molecular hydrogen on (110) faces [36] is not observed.

The double layer region appears better defined in acid media, between 0.35 and 0.7 V, and at higher potential values, between 0.7 and 1.4 V, the formation of Pt oxides is observed.

Comparing the voltamograms with those recorded with low index single crystal faces of Pt, the low definition of the double layer in alkaline media was attributed to a higher contribution of the voltammetric profiles of (110) and (100) faces. A predominance of the (111) face may be verified by the response of the double layer, because this face is the only one that shows a defined double layer region [37]. The low current levels shown by the Pt/C electrodes in alkaline media in the hydrogen region suggest a lower activity of Pt for the HOR in that solution. The electroactive areas were determined by cyclic voltammetry and are presented in Table 1, which shows that the values are similar in the two electrolytic media.

**Table 1.** Electroactive areas of Pt/C electrodes determined by cyclic voltammetry in 1.0 mol L<sup>-1</sup> NaOH and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

Material	Area (m <sup>2</sup> g <sup>-1</sup> )		Particle size /nm*
	NaOH 1.0 mol L <sup>-1</sup>	H <sub>2</sub> SO <sub>4</sub> 0.5 mol L <sup>-1</sup>	
Pt/C			
10	36	37	2.0
20	27	28	2.5
30	25	25	3.2

\* E-TEK Catalog.

The effect of the Pt load on the HOR in acid media shows that the response with the 20 wt. % material was better than with the 10 wt. % material and similar to that of the 30 wt. % material. For the case of alkaline media, the electrocatalysts with 10 wt. % show similar performance to those with 20 and 30 wt. %. The conclusion from these results is that the most appropriate catalyst in acid media is Pt/C 20 wt. % and in alkaline media, free of CO<sub>2</sub>, is Pt 10 wt. %.

Figure 4 shows a comparison of stationary-state current density-potential curves for electrodes containing Pt/C 20 wt. % in acid and alkaline solutions. It is observed that the currents in acid media are higher than those obtained in alkaline media as a consequence of: i) higher diffusivity and solubility of H<sub>2</sub> in acid media and ii) the HOR in alkaline media is controlled by diffusion at high overpotentials. The mechanism in acid media is a direct reversible discharge, determined from the Tafel coefficient value (~30 mV/dec), calculated from mass transport corrected curves, and very close to the values obtained for the accepted mechanism for the HOR on smooth Pt [19,22]. In alkaline media the profile does not show real diffusional control for potentials up to 0.3 V but the tendency is clear. This defines the more appropriate electrolyte as the acid solution, particularly with pH between 0 and 1, to obtain larger exchange current values.

#### *Construction and evaluation of the hydrogen detector system*

To build a hydrogen detector system a GDE was mounted in contact with the electrolyte as shown in Figure 2. An electrical current between the diffusion layer and the circuit flows through the gold wire, a metal that for practical purposes is not active for hydrogen oxidation.

Before testing the system as H<sub>2</sub> detector the GDE was evaluated by cyclic voltammetry

maintaining the upper limit at 1.2 V vs. RHE to prevent the oxidation of the carbon. The result is presented in Figure 5 which shows that the profile is similar to that in Figure 3. A H<sub>2</sub>/N<sub>2</sub> mixture with the appropriate gas ratios was conducted up to the detector electrode and the potential vs. current density curves obtained in the stationary state for H<sub>2</sub> oxidation are shown in Figure 6. They show that for hydrogen concentrations up to 1.0 % in the N<sub>2</sub> environment the currents are diffusional for potentials above 0.1 V. For the case of hydrogen concentrations higher than 1.0 % the diffusion control appears only above 0.2 V.

The relation  $I_{\text{limit}}$  vs. H<sub>2</sub> concentration in the mixture is presented in Figure 7. As can be observed, in the range of H<sub>2</sub> concentrations between 0.25 and 2.0 % v/v, the response is linear, showing that the system is useful for applications in urban and industrial environments.

## **Conclusions**

The system used to detect H<sub>2</sub>, built with gas diffusion electrodes, shows a good performance and sensitivity for hydrogen concentrations below the critical concentration (4 % v/v), which makes it useful to be used in closed environments with relatively clean air.

## **Acknowledgement**

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W. H. Lizcano-Valbuena, J. Perez, V. A. Paganin, E. R. Gonzalez. Avaliação de eletrodos de difusão de gás como detectores em sensores amperométricos de hidrogênio.

**Resumo:** Este trabalho é dirigido ao estudo e avaliação de eletrodos de difusão de gás como detectores em sensores de hidrogênio. Os experimentos eletroquímicos foram realizados com eletrodos de disco rotatório com uma camada fina de catalisador como passo prévio para selecionar parâmetros úteis para desenhar o sensor. Um sistema experimental feito no laboratório para simular o sensor resultou adequado para detectar porcentagens volumétricas de hidrogênio acima de 0,25% em misturas  $H_2:N_2$ . O sistema mostra uma resposta linear para porcentagens volumétricas de hidrogênio entre 0,25 e 2,0%.

**Palavras-chave:** sensores de hidrogênio; sensores amperométricos; eletrodos de difusão de gás; oxidação de hidrogênio; platina suportada.

## References

- [1] S. C. Chang, J. R. Stetter, *Talanta* 40 (1993) 461-477.
- [2] J. Janata, *Principles of Chemical Sensors*; Plenum Press, New York, 1989.
- [3] K. Kordesch, G. Simader, *Fuel Cells and their electrochemistry*; VCH, Weinheim, 1996.
- [4] V. A. Paganin, E. A. Ticianelli, E. R. Gonzalez, *J. Appl. Electrochem.* 26 (1996) 297-304.
- [5] X. Ren, M. S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12-L15.
- [6] B. K. Miremadi, K. Colbow, *Sensors and Actuators B* 46 (1998) 30-34.
- [7] B. K. Miremadi, S. R. Morrison, *Mater. Res. Bull.* 25 (1990) 1139-1153.
- [8] M. Tabib-Azar, B. Sutapun, R. Petrick, A. Kazemi, *Sensor Actuat. B* 56 (1999) 158-163.
- [9] N. Yamamoto, S. Tonomura, S. Matsuoka, M. Tsubumura, *Surf. Sci.* 92 (1980) 400-406.
- [10] G. S. V. Coles, G. Williams, B. Smith, *J. Phys. D: Appl. Phys.* 24 (1991) 633-641.
- [11] A. R. Raju, C. N. R. Rao, *Sensors and Actuators B* 3-4 (1991) 305-310.
- [12] A. R. Raju, C. N. R. Rao, *J. Chem. Soc. Chem. Commun.* 18 (1991) 1260-1261.
- [13] V. A. Chaudhary, I. S. Mulla, K. Vijayamohan, *Sensors and Actuators B* 50 (1998) 45-51.
- [14] O. K. Varguese, D. Gong, M. Paulose, K. G. Ong, C. A. Grimes, *Sensors and Actuators B* 93 (2003) 338-344.
- [15] E. F. McCullen, H. E. Prakasam, W. Mo, R. Naik, K. Y. S. Ng, L. Rimai, G. W. Auner, *J. Appl. Phys.* 93 (2003) 5757-5762.
- [16] D. Bera, S. C. Kuiry, S. Patil, S. Seal, *Appl. Phys. Lett.* 82 (2003) 3089-3091.
- [17] C. Hamann, A. Hamnett, W. Vielstich, *Electrochemistry*, Wiley-VCH, Weinheim, 1998.
- [18] V. S. Bagotsky, N. V. Osetrova, *J. Electroanal. Chem.* 43 (1973) 233-249.
- [19] H. A. Gasteiger, N. M. Markovic, P. N. Ross, *J. Phys. Chem.* 99 (1995) 8290-8301.
- [20] P. Stonehart, P.; *Ber. Bunsenges. Phys. Chem.* 94 (1990) 913-921.
- [21] D. T. Sawyer, E. T. Seo, *J. Electroanal. Chem.* 5 (1963) 23-34.
- [22] R. M. Q. De Mello, E. A. Ticianelli, *Electrochim. Acta* 42 (1997) 1031-1039.
- [23] J. A. Harrison, Z. A. Khan, *J. Electroanal. Chem.* 30 (1971) 327-329.
- [24] W. H. Lizcano-Valbuena, J. Perez, E. R. Gonzalez, XIII Congreso de la Sociedad Iberoamericana de Electroquímica (SIBAE), Reñaca-Chile, 1998.
- [25] V. S. Bagotsky, Y. B. Vassilyev, J. Weber, J. N. Pirtskhalava, *J. Electroanal. Chem.* 27 (1970) 31-46.
- [26] B. E. Conway, H. Angerstein-Kozłowska, W. B. Sharp, *Anal. Chem.* 45 (1973) 1331-1336.
- [27] A. B. La Conti, H. J. R. Maget, *J. Electrochem. Soc.* 118 (1971) 506-510.
- [28] A. A. Tanaka, C. Fierro, D. Scherson, E. B. Yeager, *J. Phys. Chem.* 91 (1987) 3799-3807.
- [29] J. Perez, A. A. Tanaka, E. R. Gonzalez, E. A. Ticianelli, *J. Electrochem. Soc.* 141 (1994) 431-436.
- [30] F. C. Nart, W. Vielstich, in *Handbook of Fuel Cell - Fundamentals, technology and Applications*, W. Vielstich, A. Lamm, H. A. Gasteiger, Eds., Vol. 2, Part 3, John Wiley, Chichester, 2003, pp. 302-315.
- [31] A. Oliveira-Neto, J. Perez, E. R. Gonzalez, E. A. Ticianelli, *J. New Mat. Electr. Syst.* 2 (1999) 189-195.
- [32] A. Oliveira Neto, J. Perez, W. T. Napporn, E. A. Ticianelli, E. R. Gonzalez, *J. Braz. Chem. Soc.* 11 (2000) 39-43.
- [33] S. A. M. Silva, J. Perez, R. M. Torresi, C. A. Luengo, E. A. Ticianelli, *Electrochim. Acta* 44 (1999) 3565-3574.
- [34] M. L. Calegaro, J. Perez, A. A. Tanaka, E. A. Ticianelli, E. R. Gonzalez, *Denki Kagaku* 64 (1996) 436-442.
- [35] W. H. Lizcano-Valbuena, V. A. Paganin, E. R. Gonzalez, *Electrochim. Acta* 47 (2002) 3715-3722.
- [36] T. Frelink, W. Visscher, J. A. R. van Veen, *J. Electroanal. Chem.* 382 (1995) 65-72.
- [37] N. M. Markovic, S. T. Sarraf, H. A. Gasteiger, P. N. Ross, *J. Chem. Soc. Faraday Trans.* 92 (1996) 3719-3725.