

Short communication

## Synthesis of the ceramic-metal catalysts (PtRuNi-TiO<sub>2</sub>) by the combustion method<sup>☆</sup>

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### Abstract

Electrocatalysis on the anode side of PEM fuel cells (PEMFC) has been widely studied, however, little information has been published on cermet catalysts, probably due to the very low or negligible power density registered when a ceramic oxide is blended with Pt based powders. In spite of this, there exists an advantage in the use of oxides, such as TiO<sub>2</sub>. This type of oxide can exhibit a bifunctional catalytic effect, as a Pt protecting matrix in the hydrogen oxidation reaction (H.O.R.) which increases CO oxidation and also promotes hydroxide formation, thus improving the oxidation of hydrogen. In this work, a trimetallic composition of 50 mol% (Pt-Ru-Ni, 60:30:10)–50 mol% TiO<sub>2</sub> is investigated as anode catalyst for a PEMFC. For the preparation of this catalyst, combustion synthesis was the route selected, which allows us to achieve a powder composite with trimetallic (PtRuNi) and ceramic (TiO<sub>2</sub>) phases. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and polarisation curves (after MEA construction) are used to evaluate the catalytic activity of this type of powder. The catalyst obtained shows a single trimetallic phase with an average particle size of 8 nm. The TiO<sub>2</sub> was found mainly as anatase phase with an average particle size of 2–3 nm. No reaction was detected between the two phases. The high power density exhibited (107 mW cm<sup>-2</sup>) with this cermet may be attributable to by a bifunctional effect on the CO and hydrogen oxidation reactions which occur during the single cell operation.

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### 1. Introduction

Development of the new anode material for PEMFC and direct methanol fuel cells (DMFC) can be regarded as one of the major goals in fuel cell research. In order to achieve new catalysts with lower Pt loadings and higher CO tolerance, bimetallic [1–4] and trimetallic [5,6] compositions based on Pt have been designed. These metallic alloys have shown improved CO tolerance with significant activity towards the hydrogen oxidation reaction (H.O.R.).

In the late 1980s, White and Sammels [7] reported on ceramic materials with a perovskite structure that exhibited intrinsic catalytic activity. Although their work appeared as an alternative to the problems associated with the use of platinum as an anode

catalyst, few studies have been reported on this subject. This is probably due to the very low or negligible power density that was found when a ceramic oxide was blended with Pt-based powders. In spite of this, there is an advantage in the use of single and mixed oxides in anode catalysts, as they can exhibit a bifunctional catalytic effect which increases the oxidation of CO and promotes hydroxide formation on the catalyst surface thus improving the H.O.R. in the anode.

Therefore, the use of metal oxides for this specific application has not been rejected, but compositions have focused more on the development of composite materials: ceramic-metallic (cermets) in which the oxide behaves as a compatible protecting matrix that oxidises CO which is adsorbed on the catalyst surface. This process could also be linked to the formation of hydroxide on the metallic particle surfaces, which could contribute to the improvement of the H.O.R.

On the basis of this theory Chinarro et al. [8,9] have reported the preparation of cermets in the Al<sub>2</sub>O<sub>3</sub>-PtRu and SrTiFeO<sub>3-δ</sub>/PtRu systems, which could both exhibit an improved CO tolerance and a competitive catalytic activity. However, these catalysts showed low power density, less than

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30 mW cm<sup>-2</sup>. Nevertheless, it was found that the ceramic component also helped to obtain a better dispersion of the alloyed particles, replacing thereby partially the carbon support and reducing the total Pt content. In a recent study, Neophytides et al. [10] reported the use of TiO<sub>2</sub> as a ceramic support for the catalyst particles. It was found that the TiO<sub>2</sub> matrix plays an active role in the anode catalysis, and that anatase in particular contributes to the generation of hydroxides and intermediate phases which participate in both the CO and H<sub>2</sub> oxidation reactions. The trimetallic compound Pt-Ru-Ni (60:30:10) has been previously studied [11–13]; however, its preparation by the combustion method has not been reported before.

In this work, combustion synthesis is employed as a fast and reliable route for catalyst preparation, the method has previously been used to prepare noble metal (Pt, Pd, etc.)-based catalysts [14,15]. The composition of the cermet is based on modifications of the metal catalyst 3d orbital by the presence of the oxides, which protect the Pt. The oxidising character of the modification, brings about an enhancement of the CO conversion to CO<sub>2</sub>, thereby reducing Pt poisoning. In addition to this, the presence of TiO<sub>2</sub> could improve the catalyst surface, by the formation of intermediates which could assist the Pt in the H.O.R.

The synthesis and preparation of a novel cermet catalyst with nominal composition 50 mol% (PtRuNi, 60:30:10)–50 mol% TiO<sub>2</sub>, by combustion route, is approached in this work.

## 2. Experimental procedure

Compositions were prepared on the basis of 50 mol% (Pt<sub>0.6</sub>Ru<sub>0.3</sub>Ni<sub>0.1</sub>)–50 mol% TiO<sub>2</sub>. The reactants were all reagent grade (CH<sub>3</sub>–CO–CH=C(O–)CH<sub>3</sub>)<sub>2</sub>Pt (97%, Aldrich), (CH<sub>3</sub>–CO–CH=C(O–)CH<sub>3</sub>)<sub>2</sub>Ni (95%, Aldrich), (CH<sub>3</sub>–CO–CH=C(O–)CH<sub>3</sub>)<sub>3</sub>Ru (97%, Aldrich) and Ti(IV) isopropoxide (95% Aldrich). Urea (CO(NH<sub>2</sub>)<sub>2</sub>) (Aldrich, 98%) was used as fuel and an oxidant aid (NH<sub>4</sub>NO<sub>3</sub>) was added to achieve the stoichiometric ratio of the fuel-oxidizer mixture. The reagents were first mixed in a basin, homogenised and heated to 100–150 °C using a heating mantle, under continuous stirring. Once the solution began frothing, the temperature was then raised to 300 °C, and within seconds the ignition of the reactant mixture took place, as observed by the presence of a flame-propagation wave. The as-prepared powders were sieved through a 63 μm mesh.

The phase analysis of the combustion powders was carried out by X-ray diffraction (XRD) with a Siemens D5000 diffractometer, under work conditions of 50 kV and 30 mA, and using Cu Kα radiation (λ = 1.5404 Å). Lattice parameters were calculated using Al<sub>2</sub>O<sub>3</sub> (99.99% Fluka) as a standard. The Debye–Scherrer equation [16] was used to calculate particle size from (1 1 1) platinum XRD reflections. Transmission electron microscopy (TEM) using a Hitachi H-7000 instrument operating at 125 kV was also utilised. X-ray photoelectronic spectroscopy (XPS) analysis was performed using a Fisons ESCALAB may 200R spectrometer. Membrane-electrode assemblies (MEA) were prepared using the procedure described by Chinarro et al. [17]. Briefly, the catalytic layer was prepared from an ink with fluidificant behaviour mixing the appropriate amount of solvents, carbonaceous support (60 wt%), Nafion solution

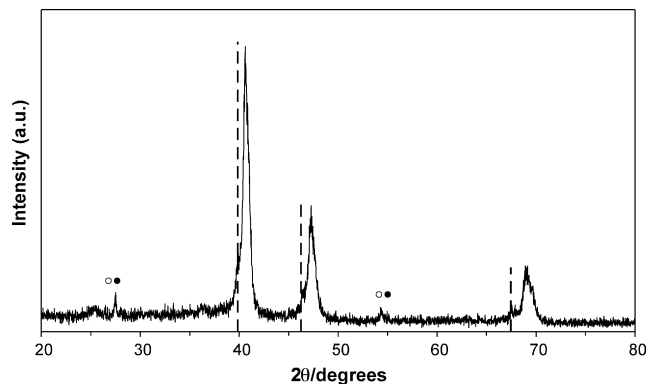


Fig. 1. XRD of the as-prepared (Pt<sub>0.6</sub>Ru<sub>0.3</sub>Ni<sub>0.1</sub>)<sub>0.5</sub>(TiO<sub>2</sub>)<sub>0.5</sub> sample, metal Pt lines (---), TiO<sub>2</sub> as rutile (●) and TiO<sub>2</sub> anatase (○).

and 50 mol% PtRuNi (60:30:10)/50 mol% TiO<sub>2</sub> (anode) or Pt/C (DeNora) (cathode) catalyst (40 wt%), which was automatically aerographed onto Toray carbon cloth. Nafion 112 (Dupont) was employed as solid electrolyte. The electrochemical characterisation of the MEA was carried out in an *i*-*V* test station designed and developed by the CSIC. The conditions used during the measurements were: *p*(O<sub>2</sub>) = 1 bar, *p*(H<sub>2</sub>) = 0.75 bar, cathode load = 0.77 mg Pt cm<sup>-2</sup> (commercial catalyst), anode load = 0.75 mg Pt cm<sup>-2</sup> (catalysts prepared in this work), *T*<sub>cell</sub> = 60 °C. The active surface area of the MEA was 25 cm<sup>2</sup>.

## 3. Results and discussion

The XRD pattern of the prepared sample (Fig. 1) showed pure Pt reflections which were shifted towards higher 2θ angle values, indicating the formation of a solid solution between Pt-Ru and Ni. No significant peaks associated to TiO<sub>2</sub> were indexed, although weak reflections around 25–30° were detected, which could be attributed to a mixture of anatase (○) and rutile (●) phases. Lattice parameter and particle size were calculated from the pattern obtained; results are shown in Table 1. The sample presented a particle size on the range of 8–9 nm, measured for the metallic phase of the cermet, while the ceramic phase showed a smaller particle size. The calculated lattice parameter (Table 1), is in agreement with the observations made from the analysed patterns, confirming the formation of a face-centre cubic solid solution. The value was lower than that reported for pure Pt (0.392 nm) [18], and was only slightly lower than that obtained for the metallic component (PtRuNi alloy) alone (0.389 nm) [13].

The platinum crystallite size (Table 1) is lower than that obtained for the same metallic composition [13] PtRuNi (60:30:10, ~12 nm) without TiO<sub>2</sub>, which indicates that the

Table 1  
Crystallite size calculated by Debye–Scherrer (DS) from XRD, and lattice parameter of the metal phase (PtRuNi)

Composition	Crystallite size DS (nm)	Lattice parameter (nm)
Pt <sub>0.6</sub> Ru <sub>0.3</sub> Ni <sub>0.1</sub> /50 mol% TiO <sub>2</sub>	8.8	0.384 ± 0.001

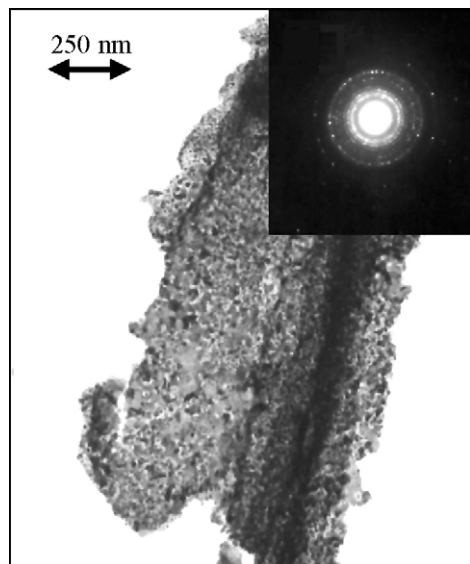


Fig. 2. TEM micrograph of the as-prepared powders and its electron diffraction.

ceramic phase brings about a decrease in the Pt-alloy particle size and, therefore, an increasing its specific surface area. The TiO<sub>2</sub> (anatase–rutile) formation in the reaction partially consumes the combustion energy thereby the inhibiting agglomeration and growth of the metallic particles.

TEM analysis of the as-prepared powders showed a well-dispersed, nanoparticulated catalyst. Two different phases were discerned from the micrographs (Fig. 2): the darker particles can be to the trimetallic alloy and the lighter particles to the TiO<sub>2</sub> support. The electron diffraction pattern confirmed the nanocrystalline nature of the powders.

### 3.1. Electrochemical single cell test

Cermet catalyst powders were characterised electrochemically by using single cell experiments. An electrode-membrane assembly was prepared as described in the experimental section, employing the as-prepared powder supported on carbon Vulcan as anode catalyst. The *i*–*V* and power curves (Fig. 3) showed a similar response for both tests, with a maximum power density (*dP*<sub>max</sub>) of 107 mW cm<sup>–2</sup> (Table 2). Comparing the title composition with the curves obtained for the Pt–Ru–Ni catalysts (171 mW cm<sup>–2</sup>) [13] synthesized in the same conditions, the results obtained with the cermet are promising, because the decrease in the *dP*<sub>max</sub> in the cermet is only 1.75 times lower than the power density obtained with Pt<sub>0.60</sub>Ru<sub>0.30</sub>Ni<sub>0.10</sub>. This difference, which was assumed to be even higher, can be attributed to the presence of the ceramic phase in the catalyst composition. A simple assessment using percolation theory indicated that the

Table 2  
Maximum power density (*dP*<sub>max</sub>) and maximum current density (*i*<sub>max</sub>) of the MEA tested

Test	1 (♦)	2 (▲)
<i>dP</i> <sub>max</sub> (mW cm <sup>–2</sup> )	101.3	107.5
<i>i</i> <sub>max</sub> (mA cm <sup>–2</sup> )	240.0	240.0

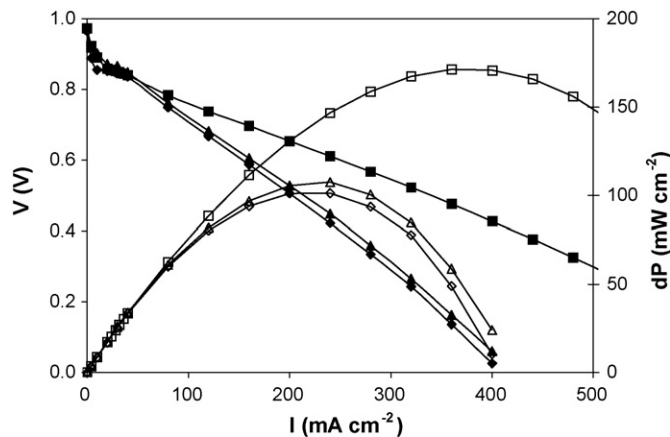
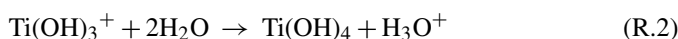


Fig. 3. Polarisation curves of the MEA prepared with the as-prepared catalysts as anode (■, □) Pt<sub>0.6</sub>Ru<sub>0.3</sub>Ni<sub>0.1</sub> (▲, △, ♦, ◇) (Pt<sub>0.6</sub>Ru<sub>0.3</sub>Ni<sub>0.1</sub>)<sub>0.5</sub>(TiO<sub>2</sub>)<sub>0.5</sub> both samples were synthesized with urea.

maximum power density achieved with TiO<sub>2</sub> concentrations as high as 50 mol% should give a value less than 50 mW cm<sup>–2</sup>; however, the value achieved in this work (107 mW cm<sup>–2</sup>) can only be explained by taking into account the assumptions of Neophytides et al. [10], who suggested an active role of the TiO<sub>2</sub> matrix in the catalytic H.O.R. process associated to oxy-hydroxide formation on the particle surface. The mechanism is described below [10]:



It is apparent that the presence of TiO<sub>2</sub> does not limit the anodic reaction by decreasing the concentration of active sites for H<sub>2</sub> adsorption. Instead there are probably less but better dispersed active sites. Moreover, the presence of oxy-hydroxides of Ti do not hinder the H.O.R. activation process, probably because a selective strong metal–support interactive (SMSI) mechanism can also operate.

The data of the *i*–*V* curve were fitted to the Tafel equation in order to study the activation overpotential of the anodic reaction. It was found that the value of the Tafel slope was 30 mV dec<sup>–1</sup>, which is in the same range as the slopes obtained both with commercial catalysts [19] and for Pt–Ru–Ni [13]. These data indicate that the activation process in the anodic reaction is limited by H<sub>2</sub> adsorption in a similar manner to that which occurs with catalysts free of ceramic phases [19]. The reactions which take place are described below ((R.3)–(R.5)):



In conclusion, the presence of TiO<sub>2</sub> in this catalyst do not interference the anodic reaction.

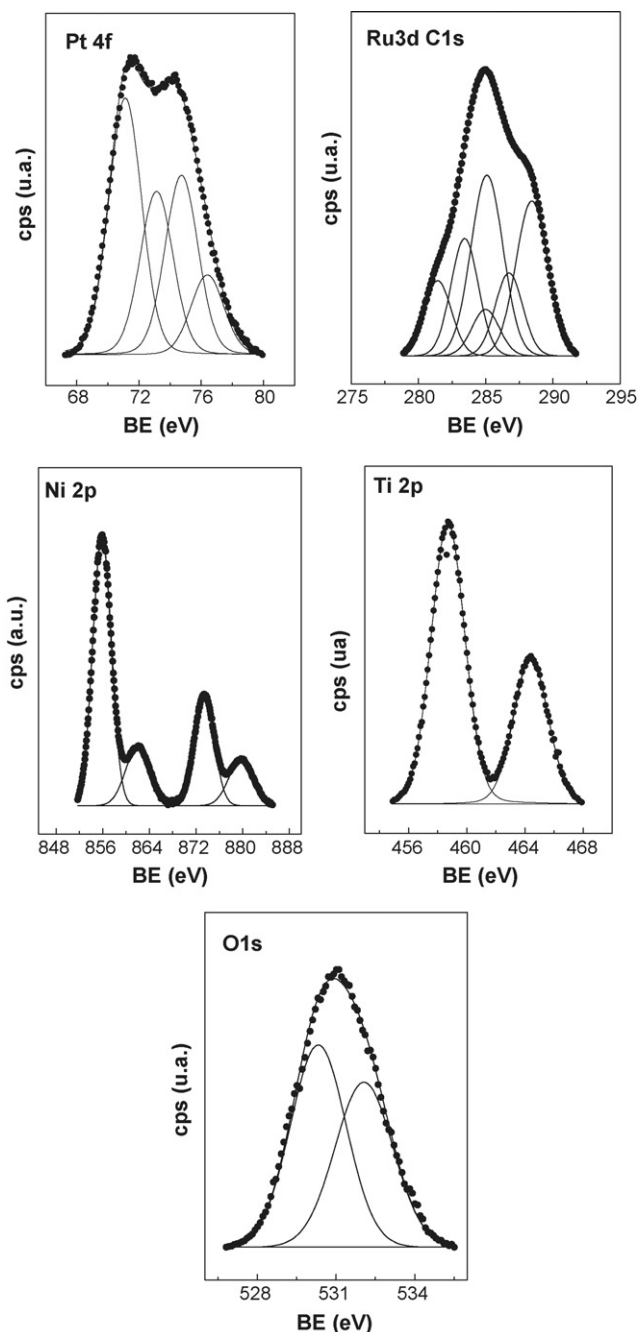


Fig. 4. XPS spectra for the elements on the surface of the sampled prepared ( $\text{Pt}_{0.6}\text{Ru}_{0.3}\text{Ni}_{0.1}\text{TiO}_2$ )<sub>0.5</sub>.

### 3.2. XPS measurements

Regarding the promising values obtained by the electrochemical tests, surface composition characterisation was carried out employing XPS. The spectra of the elements are shown in Fig. 4; the binding energy values determined by the analysis of the bands are listed in Table 3. These results have been compared with other reported data [11], and the  $\text{TiO}_2$  influence on the binding energy of the metal elements in the cermet has been studied.

The Pt on the catalyst surface exhibits two bands whose binding energy indicates two different oxidation states: 0 and +2 (as

Table 3

Binding energies of the XPS bands, their intensities (parentheses) and ratio of the elements in the catalysts surface

Bands	$E_{\text{bind}}$ (eV)	Atomic ratio (surface)	
Pt 4f $7/2$	71.1 (61)	Ru/Pt	0.40
	73.0 (39)		
Ru 3d $_{5/2}$	280.2 (22)	Ni/Pt	0.48
	284.4 (78)		
Ni 2p $_{3/2}$	854.6	Ti/Pt	0.54
Ti 2p $_{3/2}$	458.1		
O 1s	529.9		

PtO). These bands undergo a shift to higher energy due to a charge transfer process, observed by Park et al. [11]. The intensity of the bands (Table 3) indicate that the greatest amount of Pt in the surface is present as Pt(0).

In the case of the Ni 2p $_{3/2}$  orbital, the binding energy obtained, 854.6 eV, is consistent with NiO formation; no binding energy associated to metal Ni was found. However, in the case of the Ru 3d $_{5/2}$  orbital, the presence of metal Ru has been associated to the band located at 280.2 eV. Another band appears at a binding energy of 284.4 eV, which cannot be associated to  $\text{RuO}_2$  or  $\text{RuO}_3$ . According to Rolison et al. [20], the binding energy for Ru 3d $_{5/2}$  belonging to a hydrated oxide is shifted to higher energy in comparison with the value for the anhydrous oxide. Therefore, the above mentioned band corresponds to some hydrated Ru oxide or  $\text{Ru}(\text{OH})_x$  compound. The intensity of the bands indicate that the catalyst surface promotes the formation of hydroxide species. The presence of  $\text{Ru}(\text{OH})_x$  seems to be important in the oxidation of CO but not in the H.O.R.

The surprising result of  $107 \text{ mW cm}^{-2}$  obtained with this material as anode could be explained by a SMSI process, i.e. a strong interaction between the Pt–Ru–Ni alloy and the  $\text{TiO}_2$ . According to this theory, the process must be governed by the presence of hydroxide ions associated to  $\text{TiO}_2$ , such as reported by Neophytides et al. [10]. However, these authors do not detect the existence of hydroxide groups. Marino et al. [21] described the XPS spectrum of Ti 2p in which the band associated to Ti 2p $_{3/2}$ , can be deconvoluted in five components, which are attributed to  $\text{TiO}_2$  next to 458.8 eV while Ti–OH has a binding energy of 457.5 eV. This latter value is almost the same as that obtained for the material studied in this work.

Neophytides et al. [10] indicated that the percentage of anatase ( $\text{TiO}_2$ ) on the catalyst surface is Ti deficient, which implies that its crystal structure can contain easily transferred hydrogen atoms and hydroxide ions. In fact, the metastable anatase phase does not exist as stoichiometric  $\text{TiO}_2$ , but usually appears as  $\text{TiO}_{2-x}$ . Therefore, anatase may increase the dissolution of water molecules when M–OH groups are on the catalyst surface which may, in turn, have a positive influence on the overall catalytic process (R.O.H. and O.CO). The support (ceramic phase) has a synergic effect with respect to the main catalytic phase (alloy phase). As mentioned, this effect can be explained by the presence, of hydroxide groups associated to the alloy which help the catalysis on the cermet surface via reactions (R.1) and (R.2).

#### 4. Conclusions

1. A composite formed of two different compatible phases was prepared by combustion: a trimetallic alloy PtRuNi and a ceramic phase, TiO<sub>2</sub>, that is found as a mixture of anatase and rutile phases.
2. A bifunctional effect seems to occur when the inorganic phase, TiO<sub>2</sub>, acts as a matrix to with the metal catalyst. On the one hand, the catalysis effect is governed by the trimetallic alloy and the catalytical effect of the hydroxide groups produced, Ru(OH)<sub>x</sub> and Ti(OH)<sub>x</sub>, while the former also acts on CO oxidation (O.CO) reaction and the latter acts on both O.CO and H.O.R. processes.
3. The high power density values, 107 mW cm<sup>-2</sup>, obtained with the synthesised material as anode, may, therefore, be attributable to a SMSI process, i.e. the strong interaction between the alloy PtRuNi and the ceramic TiO<sub>2</sub>.

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#### References

- [1] D.C. Papageorgopoulos, M. Keijzer, F.A. De Bruijn, *Electrochim. Acta* 48 (2002) 197–204.
- [2] E.M. Crabb, M.K. Ravikumar, *Electrochim. Acta* 46 (2001) 1033–1041.
- [3] M. Götz, H. Wendt, *Electrochim. Acta* 43 (1998) 3637–3644.
- [4] L. Giorgi, A. Pozio, C. Bracchini, R. Giorgi, S. Turtu, *J. Appl. Electrochem.* 31 (2001) 325–334.
- [5] A. Oliveira Neto, E.G. Franco, E. Aricó, M. Linardi, E.R. Gonzalez, *J. Eur. Ceram. Soc.* 23 (2003) 2987–2992.
- [6] K.L. Ley, R. Liu, C. Pu, Q. Fan, N. Leyarovska, C. Segre, E.S. Smotkin, *J. Electrochem. Soc.* 144 (1997) 1537–1543.
- [7] J.H. White, A.F. Sammels, *J. Electrochem. Soc.* 140 (1993) 2167–2177.
- [8] E. Chinarro, Ph.D. Thesis, Universidad Autónoma, Madrid, Spain, 2003.
- [9] E. Chinarro, J.C. Perez, B. Moreno, M. Carrasco, J.R. Jurado, in: N. Sammes, A. Smirnova, O. Vasylyev (Eds.), *NATO Science Series II: Mathematics, Physics and Chemistry*, 202, vol. XVII, 2005, ISBN 1-4020-3497-0, pp. 187–192 (429 pp., Softcover).
- [10] S.G. Neophytides, S. Zafeiratos, G.D. Papakonstantinou, J.M. Jaksic, F.E. Paulokis, M.M. Jaksic, *Intern. J. Hydrogen Energy* 30 (2005) 131–147.
- [11] K.-W. Park, J.-H. Choi, B.-K. Kwon, S.-A. Lee, Y.-E. Sung, H.-Y. Ha, S.-A. Hong, H. Kim, A. Wieckowski, *J. Phys. Chem. B* 106 (2002) 1869–1877.
- [12] Z.B. Wang, G.P. Yin, P.F. Shi, Y.C. Sun, *Electrochem. Solid State Lett.* 9 (2006) A13–A15.
- [13] B. Moreno. Ph.D. Thesis, Universidad Autónoma, Madrid, Spain, 2006.
- [14] E. Chinarro, B. Moreno, G.C. Mather, J.R. Jurado, *J. New Mat. Electr. Sys.* 7 (2004) 109–115.
- [15] M.C. Greca, C. Moraes, M.R. Morelli, A.M. Segadaes, *App. Catal. A: Gen.* 179 (1999) 87–92.
- [16] B.E. Warren, *X-ray Diffraction*, Addison-Wesley, Reading, MA, 1969, p. 251.
- [17] J.R. Jurado, E. Chinarro, M.T. Colomer, Patent No. ES 2 209 657 (2005).
- [18] T. Swanson, *Natl. Bur. Stand. (U.S.) Circ.* 0 (539) (1953) 31 (JCPDS PDF Card 4-802, CAS 7440-06-4).
- [19] N.M. Markovic, B.N. Gruger, P.N. Ross, *J. Phys. Chem. B* 101 (1997) 5405–5413.
- [20] D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, *Langmuir* 15 (1999) 774–779.
- [21] C.E.B. Marino, P.A.P. Nascente, S.R. Biaggio, R.C. Rocha-Fillo, N. Bocchi, *Thin Solid Films* 468 (2004) 109–112.