

Short communication

Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process

Almir Oliveira Neto^{*}, Ricardo R. Dias, Marcelo M. Tusi,
Marcelo Linardi, Estevam V. Spinacé^{*}

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes 2242, Cidade Universitária, CEP 05508-900 São Paulo, SP, Brazil

Received 6 November 2006; received in revised form 15 December 2006; accepted 15 December 2006

Available online 17 January 2007

Abstract

PtRu/C, PtSn/C and PtSnRu/C electrocatalysts were prepared by the alcohol reduction process using ethylene glycol as the solvent and reduction agent and Vulcan Carbon XC72 as the support. The electrocatalysts were characterized by EDX, XRD and cyclic voltammetry. The electrochemical oxidation of methanol and ethanol were studied by chronoamperometry using a thin porous coating technique. The PtSn/C electrocatalyst prepared by this methodology showed superior performance compared to the PtRu/C and PtSnRu/C electrocatalysts for methanol and ethanol oxidation at room temperature.

© 2007 Elsevier B.V. All rights reserved.

Keywords: PtRu/C; PtSn/C; PtSnRu/C; Alcohol-reduction process; Methanol oxidation; Ethanol oxidation; Fuel cell

1. Introduction

Fuel cells employing alcohols directly (direct alcohol fuel cell, DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage, DAFCs use a liquid fuel, thus simplifying the fuel delivery system [1–5]. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols. However, slow anode kinetics are observed. Methanol crossover through the membrane also decreases the efficiency [6–8]. Ethanol offers an attractive alternative as the direct fuel because it is produced in large quantities from biomass and it is much less toxic than methanol. However, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulties in C–C bond breaking and the formation of CO-intermediates that poison the platinum anode catalysts [9–11]. Thus, new catalyst materials and new catalyst prepara-

tion method developments have been one of the major topics studied on the electro-oxidation of methanol and ethanol [12]. Due to the low electrocatalytic activity of platinum for practical DAFC applications, elements like ruthenium and tin have been added to promote electroactivity [12–14]. However, some studies comparing the electrocatalytic activity of PtRu and PtSn catalysts for methanol electro-oxidation have shown contradictory results [15–20]. Hable and Wrighton [15] studied the oxidation of methanol on PtSn and PtRu deposited onto polyaniline by electrochemical deposition and found that the Pt–Ru catalyst was better for methanol oxidation than the PtSn catalyst. Wang et al. [16] observed an enhancement of methanol oxidation on a sputtered Pt₃Sn(1 1 0) surface. However, the magnitude was smaller than that observed on PtRu alloys. On the other hand, Napporn et al. [17] described that highly dispersed PtSn electrodes could be as active as PtRu for methanol oxidation and this fact was attributed to the preparation method of the PtSn electrodes. Similar results were observed by Morimoto and Yeager [18] for methanol electro-oxidation using ruthenium and tin electrodeposited onto smooth or platinized platinum as the catalyst. On smooth platinum, ruthenium promoted the catalytic activities steadily according to the coverage, while tin showed an enhancing effect but only for a short period of time due to

^{*} Corresponding authors. Tel.: +55 11 3816 9445; fax: +55 11 3816 9440.

E-mail addresses: aolivei@ipen.br (A.O. Neto), espinace@ipen.br (E.V. Spinacé).

the dissolution of Sn from the surface. On platinized platinum, Sn was stable and exhibited long-lasting effects as observed for Ru. Recently, Golikand et al. [19] studied the electro-oxidation of methanol using as catalyst Pb/Pt electrodes modified by a thin film of poly(*o*-phenylenediamine) where Pt, PtRu and PtSn were electrochemically deposited. It was observed that dispersed Pt–Sn prepared under precise conditions was perhaps more active than the Pt and Pt–Ru. Thus, the performance of Pt–Ru and Pt–Sn catalysts for methanol oxidation depends strongly on the catalyst preparation method.

PtSn/C electrocatalysts have been described to be more active than PtRu/C electrocatalysts for ethanol electro-oxidation. The PtSn/C electrocatalyst performance also depends greatly on preparation procedures and Pt:Sn atomic ratios [13,20].

Kobayashi and co-workers [21,22] observed that the electrocatalytic methanol oxidation over PtRuSn/C ternary alloy catalyst with a Pt:Ru:Sn atomic ratio of 50:33:17 prepared by conventional NaBH₄ reduction method and by the reverse microemulsion method was higher than that of PtRu/C and PtSn/C with a Pt:Me atomic ratio of 50:50. Recently, Rousseau et al. [23] described that the addition of a small amount of Ru to PtSn/C electrocatalyst prepared by the Bönemann method enhanced the electrical performance of the Direct Ethanol Fuel Cell.

In this study, PtRu/C (Pt:Ru atomic ratio of 50:50), PtSn/C (Pt:Sn atomic ratio of 50:50) and PtSnRu/C (Pt:Sn:Ru atomic ratios of 50:40:10, 50:25:25 and 50:10:40) electrocatalysts were prepared using ethylene glycol as the reducing agent [24–30] and were tested for methanol and ethanol oxidation at room temperature using the thin porous coating technique [31].

2. Experimental

PtRu/C (Pt:Ru atomic ratio 50:50), PtSn/C (Pt:Sn atomic ratio 50:50) and PtSnRu/C (Pt:Sn:Ru atomic ratios of 50:40:10, 50:25:25 and 50:10:40) electrocatalysts were prepared with metal loading of 20 wt.% using H₂PtCl₆·H₂O (Aldrich), RuCl₃·xH₂O (Aldrich) and SnCl₂·2H₂O (Aldrich) as metal sources, ethylene glycol (Merck) as the solvent and reducing agent and carbon Vulcan XC72 as the support [24–26]. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and the carbon support was added. The resulting mixtures were treated in an ultrasound bath and were refluxed for 3 h under open atmosphere. The mixtures were filtered and the solids washed with water and dried at 70 °C for 2 h.

The Pt:Ru, Pt:Sn and Pt:Sn:Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL30 with a 20 KeV electron beam and equipped with EDAX DX-4 microanalyser.

XRD analyses were performed using a Rigaku diffractometer model Multiflex with a Cu K α radiation source.

Electrochemical studies were carried out using the thin porous coating technique [31]. An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing three drops of a 6% polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min and transferred to the cavity of the working electrode. The quantity of electrocatalysts in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry and chronoamperometry experiments the current values (I) were expressed in amperes and were normalized per gram of platinum (A g_{Pt}⁻¹). The quantity of platinum was calculated considering the mass of the electrocatalysts present in the working electrode multiplied by its percentage of platinum. The working electrodes have a geometric area of 0.3 cm² with a depth of 0.3 mm. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Chronoamperometry experiments were performed at 25 °C with 1.0 mol L⁻¹ of methanol or ethanol in 0.5 mol L⁻¹ H₂SO₄ solutions saturated with N₂. using a Microquimica (model MQPG01, Brazil) potenciostat/galvanostat coupled to a personal computer with Microquimica software.

3. Results and discussion

PtRu/C, PtSn/C and PtSnRu/C electrocatalysts were prepared in a single step (co-reduction of mixed ions) using ethylene glycol as solvent and reducing agent in the presence of carbon Vulcan XC72 [24–26]. The Pt:Ru, Pt:Sn and Pt:Sn:Ru atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios used in the preparation (Table 1). The X-ray diffractograms of the electrocatalysts are shown in Fig. 1. In all diffractograms a broad peak at about 25° was associated with the Vulcan XC72 support material. The diffractogram of PtRu/C electrocatalyst showed peaks at approximately 2 θ = 40°, 47°, 67° and 82°, which are associated with the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively, of the fcc structure characteristic of platinum and platinum alloys. No peaks corresponding to a metallic ruthenium, materials rich in ruthenium with a hexagonal structure or the ruthenium oxide phase were observed [24,31]. The PtSn/C electrocatalyst also showed the peaks characteristic of the fcc structure of platinum and

Table 1
Pt:Ru, Pt:Sn, Pt:Sn:Ru atomic ratios and mean particle size of the prepared electrocatalysts

Electrocatalyst	Nominal atomic ratio			Atomic ratio, EDX			Particle size (nm)
	Pt	Sn	Ru	Pt	Sn	Ru	
PtRu/C	50	–	50	50	–	50	4.0
PtSn/C	50	50	–	50	50	–	2.7
PtSnRu/C	50	40	10	52	38	10	3.3
PtSnRu/C	50	25	25	49	29	22	3.3
PtSnRu/C	50	10	40	49	13	38	4.9

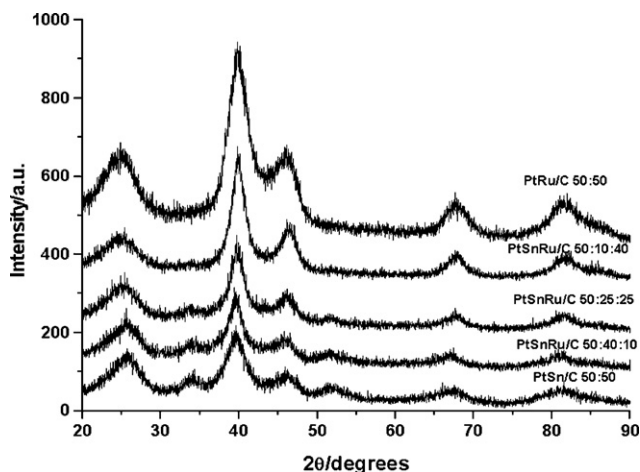


Fig. 1. X-ray diffractograms of PtRu/C, PtSn/C and PtSnRu/C electrocatalysts.

platinum alloys as observed for PtRu/C electrocatalysts. However, in this sample two additional peaks were observed at $2\theta = 34^\circ$ and 52° that were identified as a SnO_2 phase [26]. Recently, Xin and co-workers [32] described the preparation of SnO_2 nanoparticles heating ethylene glycol solutions containing SnCl_2 . The fcc lattice parameters were evaluated from the angular position of the (220) peaks and the calculated value for PtRu/C electrocatalyst (0.3886 nm) was smaller than that of Pt/C electrocatalyst (0.3916 nm), indicating a contraction of the lattice and a Pt and Ru alloy to some extent [33]. For PtSn/C electrocatalyst the fcc lattice parameter measured (0.3986 nm) was larger than the one obtained for Pt/C electrocatalyst, due to a lattice expansion after alloying [14,33], indicating that part of Sn was incorporated in the fcc structure of Pt. The fcc lattice parameters calculated for PtSnRu/C electrocatalysts were: PtSnRu/C 50:40:10 (0.3937 nm), PtSnRu/C 50:25:25 (0.3909 nm) and PtSnRu/C 50:10:40 (0.3889 nm). PtSnRu/C 50:40:10 electrocatalyst showed an increase of the fcc lattice parameter compared to Pt/C electrocatalyst while a decrease was observed for PtSnRu/C 50:10:40 electrocatalyst. The difference of lattice parameters and the shift of (220) plane indicate interactions between Pt and Sn and Ru. The peaks of the SnO_2 phase at $\theta = 34^\circ$ and 52° were clearly observed for PtSnRu/C 50:40:10 and 50:25:25, while for PtSnRu/C 50:10:40 only the peaks characteristic of the Pt fcc structure were observed. The average particle size was estimated using the Scherrer equation (Table 1) [34]. The particle sizes for PtRu/C, PtSn/C and PtSnRu/C electrocatalysts were in the range of 3–5 nm.

Fig. 2 shows the cyclic voltammetry (CV) of PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by the alcohol-reduction process, obtained in a half cell at a scan rate of 10 mV s^{-1} between 0.05 and 0.8 V in the absence of methanol and ethanol. Voltammograms of the PtRu/C, PtSn/C and PtSn/C electrocatalysts show no well-defined hydrogen adsorption–desorption region (0.05–0.4 V) as observed for Pt alloys [26]. Analysis of the cathodic scan of PtSn/C and PtSnRu/C electrocatalysts showed an increase of the peak at about 0.45 V with the increase of Sn content, which could be related to tin oxide species [26].

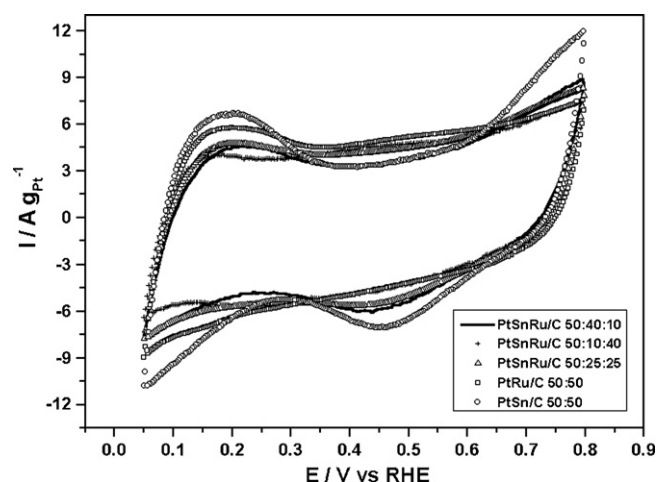


Fig. 2. Cyclic voltammograms of PtRu/C, PtSn/C and PtSnRu/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1} .

The PtRu/C, PtSn/C and PtSnRu/C electrocatalyst performances for methanol oxidation were studied by chronoamperometry in 1.0 mol L^{-1} of methanol in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at an anodic potential of 0.5 V versus RHE (Fig. 3). The current values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at room temperature [26]. The amounts of Pt in the electrocatalysts vary from 12.4–13.2 wt.%. In all current–time curves there was an initial current drop in the first 5 min followed by a slower decay, but the current values obtained for PtSn/C electrocatalysts were always higher than those obtained for PtRu/C and PtSnRu/C electrocatalysts. On the other hand, Kobayashi and co-workers [21,22] observed that the activity for methanol oxidation increased in the following sequence: PtSnRu/C (Pt:Ru:Sn atomic ratio 50:33:17) > PtRu/C (Pt:Ru atomic ratio 50:50) > PtSn/C (Pt:Sn atomic ratio 50:50), using catalysts prepared by conventional NaBH_4 reduction method and by reverse microemulsion method, using NaBH_4 as the reducing agent. For both methods only peaks of Pt (fcc) structure were observed in the XRD spectra. The superior performance of

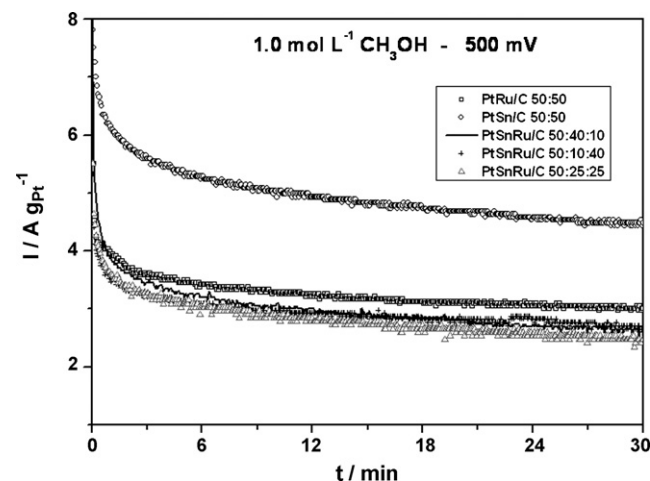


Fig. 3. Current–time curves at 0.5 V in 1.0 mol L^{-1} of methanol solution in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for PtRu/C, PtSn/C and PtSnRu/C electrocatalysts.

PtRuSn/C electrocatalyst for methanol oxidation was attributed to the alloying effect that causes a synergic effect of Ru as a water activator (bifunctional mechanism) and Sn as an electronic modifier of Pt. Thus, these results suggest that the performance of the catalysts depends strongly on the preparation method.

Mukerjee and McBreen [35] described that carbon-supported platinum (Pt/C) with an adsorbed layer of underpotential deposited Sn was a much better catalyst for methanol oxidation than carbon-supported platinum tin (PtSn/C) alloy. Studies using XRD and XAS measurements indicated that Sn alloyed with Pt causes partial filling of the Pt d band vacancies and an increase in the Pt–Pt bond, while underpotential deposited Sn does not disturb Pt structurally or electronically. It was also observed that underpotential deposited Sn on Pt/C and the surface Sn on PtSn/C were associated with oxygenated species. The differences in the activity were attributed to effects of alloying on the Pt electronic structure that inhibit the ability of the Pt to adsorb methanol and dissociate C–H bonds, which are necessary steps for methanol oxidation. Colmati et al. [36], using PtSn/C electrocatalysts prepared by reduction with formic acid, observed that catalysts exhibiting a moderate degree of alloying showed superior performance for methanol oxidation. Recently, Xin and co-workers [32] prepared PtSnO₂/C catalyst depositing Pt on SnO₂ nanoparticles observing a high-promoting catalytic activity for ethanol oxidation. Thus, the superior performance of the PtSn/C electrocatalyst, obtained in this study, for methanol oxidation could be attributed to an optimized electronic state of Pt, due to alloying with Sn and to a promoting effect of a separated SnO₂ phase.

The PtRu/C, PtSn/C and PtSnRu/C electrocatalyst performances for ethanol oxidation were studied by chronoamperometry and are shown in Fig. 4. The superior performance of the PtSn/C electrocatalyst was also observed for ethanol oxidation. However, contrary to that observed for methanol oxidation, in this case, the PtSnRu/C electrocatalysts were more active than PtRu/C electrocatalyst. Similar results were observed by Xin and co-workers [37] for ethanol oxidation using catalysts prepared by a similar procedure using ethylene glycol as sol-

vent and reducing agent. However, the obtained materials only showed the Pt (fcc) crystalline structure. The performance of the single fuel cell operating at 90 °C with PtRuSn/C (Pt:Ru:Sn atomic ratio of 34:33:33) was higher than that of the cell with PtRu/C (Pt:Ru atomic ratio 50:50), but inferior to the performance with PtSn/C (Pt:Sn atomic ratio 50:50). On the other hand, Rousseau et al. [23] described that the addition of a small amount of Ru (PtSnRu/C catalyst with Pt:Sn:Ru molar ratio of 86:10:4) to PtSn/C (Pt:Sn atomic ratio 90:10) electrocatalyst prepared by the Bönemann method, which use a kind of borohydride as reducing agent, enhanced the electrical performance of the Direct Ethanol Fuel Cell operating at 80 °C.

4. Conclusions

The alcohol-reduction process proved to be an effective method for producing active PtSn/C, PtRu/C and PtSnRu/C electrocatalysts for methanol and ethanol oxidation. The X-ray diffractograms of the PtRu/C electrocatalyst showed a typical fcc structure of the Pt alloys. The PtSn/C and PtSnRu/C electrocatalysts showed a typical fcc structure of platinum alloys with the presence of a separated SnO₂ phase. The chronoamperometry experiments showed that the PtSn/C electrocatalyst was more active than the PtRu/C and PtSnRu/C electrocatalysts for methanol and ethanol oxidation at room temperature. The superior performance of the PtSn/C electrocatalyst for methanol and ethanol oxidation could be due to the fact that only part of the tin amount was found as a PtSn alloy, which changes the Pt electronic properties and probably “tunes” the ability of Pt to adsorb methanol or ethanol and dissociate C–H bonds, while the other part found as SnO₂ species, facilitates the oxidation of absorbed CO formed as an intermediate (bifunctional mechanism). Further work is necessary to characterize the catalysts using different surface analysis techniques and to perform experiments using these electrocatalysts in gas diffusion electrodes for tests in single direct methanol and ethanol fuel cells.

Acknowledgements

The authors thank CNPq (Processo No. 471288/2004-7) and FAPESP (03/03127-0) for financial support.

References

- [1] E.R. Gonzalez, *Quim. Nova* 23 (2000) 262.
- [2] H. Wendt, M. Gotz, M. Linardi, *Quim. Nova* 23 (2000) 538.
- [3] E.V. Spinacé, A.O. Neto, E.G. Franco, M. Linardi, E.R. Gonzalez, *Quim. Nova* 27 (2004) 648.
- [4] H. Wendt, E.V. Spinacé, A.O. Neto, M. Linardi, *Quim. Nova* 28 (2005) 1066.
- [5] C. Lamy, A. Lima, V. Lerhum, F. Delime, C. Coutanceau, J.M. Léger, *J. Power Sources* 105 (2002) 283.
- [6] E.V. Spinacé, A.O. Neto, M. Linardi, *J. Power Sources* 129 (2004) 121.
- [7] A.L.N. Pinheiro, A.O. Neto, E.C. Souza, E.A. Ticianelli, J. Perez, E.R. Gonzalez, *J. New Mater. Electrochem. Syst.* 6 (2003) 1.
- [8] T. Iwasita, *Electrochem. Acta* 47 (2002) 3663.
- [9] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, *J. Appl. Electrochem.* 34 (2004) 439.

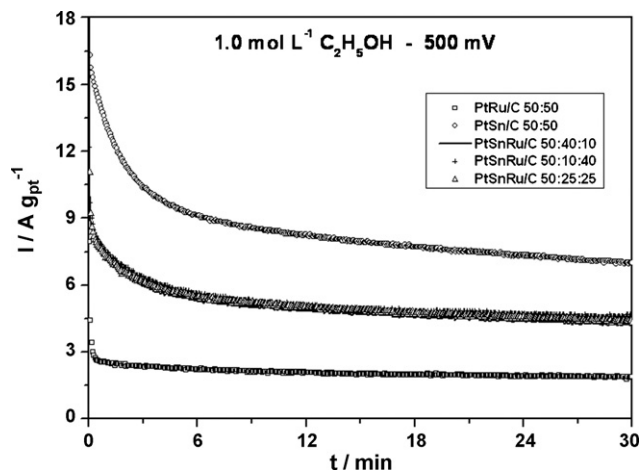


Fig. 4. Current–time curves at 0.5V in 1.0 mol L⁻¹ of ethanol solution in 0.5 mol L⁻¹ H₂SO₄, for PtRu/C, PtSn/C and PtSnRu/C electrocatalysts.

- [10] A.O. Neto, R.R. Dias, V.A. Ribeiro, E.V. Spinacé, M. Linardi, *Ecl. Quím.* 31 (2006) 81.
- [11] A.O. Neto, M.J. Giz, J. Perez, E.A. Ticianelli, E.R. Gonzalez, *J. Electrochem. Soc.* 149 (2002) A272.
- [12] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, *J. Power Sources* 155 (2006) 95.
- [13] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.-M. Léger, *Electrochim. Acta* 49 (2004) 3901.
- [14] L. Jiang, G. Sun, Z. Zhou, W. Zhou, Q. Xin, *Catal. Today* 93–95 (2004) 665.
- [15] C.T. Hable, M.S. Wrighton, *Langmuir* 9 (1993) 3284.
- [16] K. Wang, H.A. Gasteiger, N.M. Markovic, P.N. Ross Jr., *Electrochim. Acta* 41 (1996) 2587.
- [17] W.T. Napporn, H. Laborde, J.-M. Léger, C. Lamy, *J. Electroanal. Chem.* 404 (1996) 153.
- [18] Y. Morimoto, E.B. Yeager, *J. Electroanal. Chem.* 444 (1998) 95.
- [19] A.N. Golikand, S.M. Golabi, M.G. Maragheh, L. Irannejad, *J. Power Sources* 145 (2005) 116.
- [20] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, *Appl. Catal. B* 46 (2003) 273.
- [21] T. Kim, M. Takahashi, M. Nagai, K. Kobayashi, *Chem. Lett.* 33 (2004) 478.
- [22] T. Kim, K. Kobayashi, M. Takahashi, M. Nagai, *Chem. Lett.* 34 (2005) 798.
- [23] S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, *J. Power Sources* 158 (2006) 18.
- [24] E.V. Spinacé, A.O. Neto, T.R.R. Vasconcelos, M. Linardi, *J. Power Sources* 137 (2004) 17.
- [25] E.V. Spinacé, A.O. Neto, T.R.R. Vasconcelos, M. Linardi, *Brazilian Patent INPI-RJ, PI0304121-2* (2003).
- [26] E.V. Spinacé, M. Linardi, A.O. Neto, *Electrochem. Commun.* 7 (2005) 365.
- [27] W.X. Chen, J.Y. Lee, Z. Liu, *Chem. Commun.* (2002) 2588.
- [28] Z. Liu, L.M. Gan, L. Hong, W. Chen, J.Y. Lee, *J. Power Sources* 139 (2005) 73.
- [29] Z. Zhou, S. Wang, W. Zhou, G. Wang, L. Jiang, W. Li, S. Shuquin, J. Liu, G. Sun, Q. Xin, *Chem. Commun.* (2003) 394.
- [30] W.J. Zhou, B. Zhou, W.Z. Li, Z.H. Zhou, S.Q. Song, G.Q. Sun, Q. Xin, S. Douvartzides, M. Goula, P. Tsiakaras, *J. Power Sources* 126 (2004) 16.
- [31] F. Colmati, W.H. Lizacano-Valbuena, G.A. Câmara, E.A. Ticianelli, E.R. Gonzalez, *J. Braz. Chem. Soc.* 13 (2002) 474.
- [32] L. Jiang, G. Sun, Z. Zhou, S. Sun, Q. Wang, S. Yan, H. Li, J. Tian, J. Guo, B. Zhou, Q. Xin, *J. Phys. Chem. B* 109 (2005) 8774.
- [33] W.J. Zhou, S.Q. Song, W.Z. Li, G.Q. Sun, Q. Xin, S. Kontou, K. Poulianitis, P. Tsiakaras, *Solid State Ionics* 175 (2004) 797.
- [34] V. Radmilovic, H.A. Gasteiger, P.N. Ross Jr., *J. Catal.* 154 (1995) 98.
- [35] S. Mukerjee, J. McBreen, *J. Electrochem. Soc.* 146 (1999) 600.
- [36] F. Colmati, E. Antolini, E.R. Gonzalez, *Electrochim. Acta* 50 (2005) 5496.
- [37] W.J. Zhou, W.Z. Li, S.Q. Song, Z.H. Zhou, L.H. Jiang, G.Q. Sun, Q. Xin, K. Poulianitis, S. Kontou, P. Tsiakaras, *J. Power Sources* 131 (2004) 217.