

Preparation of PtRu/C Electrocatalysts by Borohydride Reduction for Methanol Oxidation in Acidic and Alkaline Medium

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Received: 5 January 2017 / Accepted: 11 March 2017 / Published: 12 April 2017

PtRu/C electrocatalysts were performed according to the borohydride reduction method and characterized by X-ray diffraction (XRD), energy dispersive analysis (EDX), transmission electron microscopy, cyclic voltammetry (CV) and polarization curves in alkaline and acidic medium. The X-ray diffraction (XRD) of PtRu/C showed Pt peaks attributed to the face-centered cubic (fcc) structure and a shift in Pt(fcc) peaks indicated that Ru was incorporated into Pt lattice. TEM results showed mean particles sizes in the range of 2.0-4.0nm for all electrocatalysts prepared: therefore, the borohydride reduction process was considered effective for the preparation of PtRu/C electrocatalysts with a different atomic ratio. The activity for the methanol oxidation in acidic and alkaline media was investigated at room temperature, by cyclic voltammetry and chronoamperometry. Cyclic voltammetry and chronoamperometry studies showed that PtRu/C (50:50) had superior performance for methanol oxidation, compared with other electrocatalysts prepared considering acidic and alkaline studies. The currents values observed for alkaline media were higher than those observed for acidic media. Polarization curves, also, showed PtRu/C (50:50) with superior performance for methanol oxidation, when compared with Pt/C, and this improvement of performance could be associated with the occurrence of the bifunctional mechanism and electronic effect.

Keywords: Borohydride reduction process, PtRu/C, methanol electro-oxidation, alkaline medium, acidic media, polarization curves

1. INTRODUCTION

Liquid Fuel Cells are one of the most promising energy sources for application in portable devices, vehicles and stationary devices. Methanol has been considered a promising system for energy

conversion due to its high energy density ($702.32 \text{ kJ mol}^{-1}$), abundance combustible and low cost of production [1-2]. However, for Direct Methanol Fuel Cell, many problems still persist, such as: 1) slow methanol oxidation kinetics due to an incomplete methanol oxidation; 2) the poisoning of adsorbed intermediate species on the Pt surface; 3) the high methanol crossover through the solid state polymer Nafion membrane; 4) the high costs of the membrane and 5) the high costs of Pt electrocatalyst. [3-4].

The development of more efficient electrocatalysts for methanol oxidation is still necessary, because methanol oxidation involves the formation of several intermediates when Pt pure is utilized as electrocatalyst: usually, these products are CO_2 , formaldehyde and formic acid. Consequently, the process causes a deactivation of Pt pure electrocatalysts, so it is still necessary to modify the vicinity of Pt atoms, by adding other elements [5].

Pt electrocatalysts with some metals, such as Ru, Sn, Pd, Au has been extensively investigated to improve CO tolerance and catalytic activity for methanol oxidation [6–9]. Nevertheless, PtRu/C systems have been considered the best electrocatalysts for methanol oxidation [10] and this effect has been attributed to the bi-functional mechanism or electronic effect [11-12].

Several studies for methanol oxidation have been carried out in electrolyte acidic, but, recently, another way to improve the methanol oxidation has been proposed, consisting in the use of an alkaline electrolyte. In alkaline electrolyte, the kinetics of alcohol deprotonation is favored; consequently, the poisoning is considered smaller when compared to that in acid media. Furthermore, the oxygen reduction reaction has, also, the kinetics favored [13-16].

Kallio et al. [17] prepared PtRu catalyst for studies in acidic and alkaline electrolytes for methanol, ethanol and isopropanol oxidation and observed low conductivities of anion exchange membrane material in the direct alkaline fuel cell. However, they concluded that the development of membranes and alkaline ionomers is strongly encouraged by the promising results from electrochemical experiments. PtRu catalyst showed an increase in current and power densities for methanol, ethanol and isopropanol oxidation and a special behavior was observed with ethanol and isopropanol, due to the enhanced kinetics reaction.

In this context, the aim of this work was to prepare PtRu/C electrocatalysts by borohydride reduction process, in different Pt/Ru atomic ratios, for methanol electro-oxidation in acidic and alkaline medium. This work includes electrochemical experiments and single-cell experiments: these experiments were carried out with KOH-modified Nafion112 membrane and conventional Nafion112 membrane, as already proposed by Sun et al. [18]. These results are important because it is the first time they are presented in the literature.

2. MATERIALS AND METHODS

Pt/C and PtRu/C electrocatalysts with 20 wt% of metal loading were prepared by borohydride reduction process, where PtRu/C electrocatalysts were, also, prepared with different atomic ratios of 90:10, 70:30 and 50:50. All PtRu/C electrocatalysts were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (chloroplatinic acid, Aldrich), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (ruthenium chloride hydrate– Aldrich) as metal sources, sodium

borohydride (Aldrich), as reducing agent and Vulcan Carbon XC72, as support. In the borohydride reduction method, the Vulcan XC72 support is dispersed in an isopropyl alcohol/water solution (50/50, v/v). After that, under stirring, the metal sources were added and placed in an ultrasonic bath, for 5 minutes. Then, a solution of sodium borohydride into 0.1 mol L^{-1} KOH was added in one portion, under stirring, and the resulting solution was maintained for more 15 minutes. After this procedure, the resultant mixture was filtered and the solids washed with water and dried at $70 \text{ }^{\circ}\text{C}$, for 2 hours [19]. PtRu/C electrocatalysts were, also, characterized by XRD using a Rigaku diffractometer, model Miniflex II, with Cu $K\alpha$ radiation source (0.15406 nm); the diffractograms were recorded in the range of $2\theta = 20$ to 90° , with a step size of 0.05° and a scan time of 2seg per step. Then, these electrocatalysts were also characterized by transmission electron microscopy, using a JEOL JEM-2100 electron microscope, operated at 200 kV , where the distribution and the size of the nanoparticles in the support were determined. In this work, the histogram with nanoparticles sizes was built by 120 particles measurements, from a 10 micrograph.

The electrochemical investigations were performed by cyclic voltammetry (CV). Chronoamperometry and polarization curves (E vs. i), cyclic voltammetry and Chronoamperometry were performed in an Autolab 302 N potentiostat, in a 0.5 mol L^{-1} H_2SO_4 solution, for acidic medium (saturated with N_2), hydrogen reference and a counter electrode of Pt wire, while alkaline experiments were performed in KOH solution, with the reference electrode of Ag/AgCl (3 mol L^{-1} KCl), a counter electrode of Pt and a Pt wire. In this paper, the work electrode was prepared in the form of thin porous coating technique [20]. Chronoamperometry (amperometric curves) was recorded in KOH electrolyte containing methanol, at -0.40 V , for 1800 s (alkaline media), while for acidic media at 0.5 V , for 1800 s , in the presence of 0.5 mol L^{-1} H_2SO_4 . The cyclic voltammetry experiments were done at a scan rate of 10 mVs^{-1} in 1.0 mol L^{-1} KOH solution or 0.5 mol L^{-1} H_2SO_4 with the presence or absence of 1.0 mol L^{-1} of methanol saturated with N_2 .

Direct alkaline or acidic methanol fuel cell tests were performed in a single cell with 5 cm^2 of area, using Pt/C and PtRu/C as anode. The anode electrode was prepared with 1 mg of Pt loading by cm^2 , while Pt/C BASF cathode, with 1 mg of Pt loading by cm^2 , was used. The MEAS were prepared with hot pressure on both sides of a Nafion 117 membrane or Nafion 117 membrane, doped with KOH, at $125 \text{ }^{\circ}\text{C}$ for 2 min , under a pressure of 225 kgf cm^{-2} . The polarization curves were obtained using a potentiostat/galvanostat, where methanol 2.0 mol L^{-1} was delivered at 1.0 mL min^{-1} and the oxygen flow was regulated at 150 mL min^{-1} [2,20].

3. RESULTS AND DISCUSSION

XRD patterns of Pt/C and PtRu/C electrocatalysts are shown in Figure 1. For all electrocatalysts prepared, peaks at approximately $2\theta \approx 40^{\circ}$, 47° , 68° , 82° and 87° were observed; are associated with the (111), (200), (220), and (311) planes, characteristic of the face-centered cubic (fcc) structure of Pt and Ru crystals. For PtRu/C electrocatalysts, shifts to 2θ values higher were observed, in comparison with Pt/C electrocatalysts; this effect could be associated to the inclusion of Ru atoms to

the fcc structure of Pt, behavior that has been related to the formation of PtRu/C alloys. The lattice parameters values for PtRu/C were near 0.390, indicating that Ru atoms are added to Pt structure [21].

Umeda et al [22] showed that the Pt (111) peak of the PtRu electrocatalyst particles was shifted to higher 2θ , compared with that of the Pt particles; these authors concluded that Pt was well alloyed with Ru, under the electrocatalyst preparation conditions used.

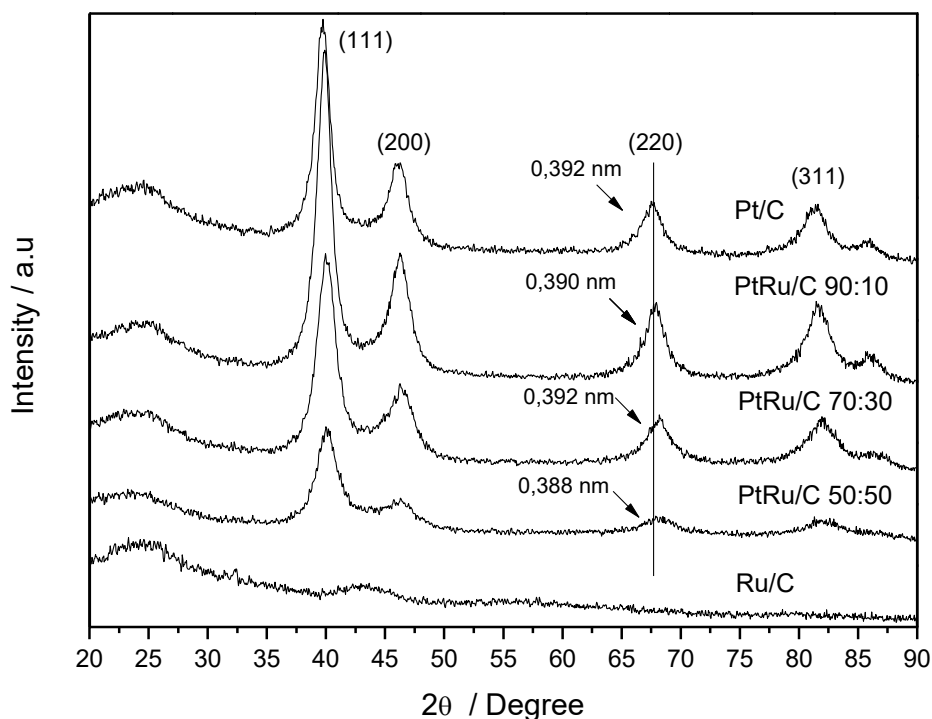


Figure 1. X-ray diffractograms of the Pt/C and PtRu/C electrocatalysts prepared by borohydride reduction process.

The micrographs and histograms of the particle size distribution, obtained by electronic microscopy transmission for Pt/C and PtRu/C electrocatalysts are illustrated in Figure 2. Pt/C and PtRu/C showed a good dispersion of the nanoparticles on the carbon support; however, the mean diameter of nanoparticles for Pt/C and PtRu/C electrocatalysts are in the range of 2.0–4.0 nm. Jung et al [23] prepared PtRu/C electrocatalysts using an aqueous co-impregnation method, with NaBH_4 as a reducing agent. In Jung work, the transmission electron microscopy (TEM) images showed spherical particles carbon blacks with 10–30 nm, and dark dots that measure, approximately, 2 nm related to PtRu metal alloys supported on the carbon blacks.

Cyclic voltammograms of Pt/C and PtRu/C electrocatalysts prepared with different ratio in acidic electrolyte and alkaline electrolyte are shown in Figure 3.

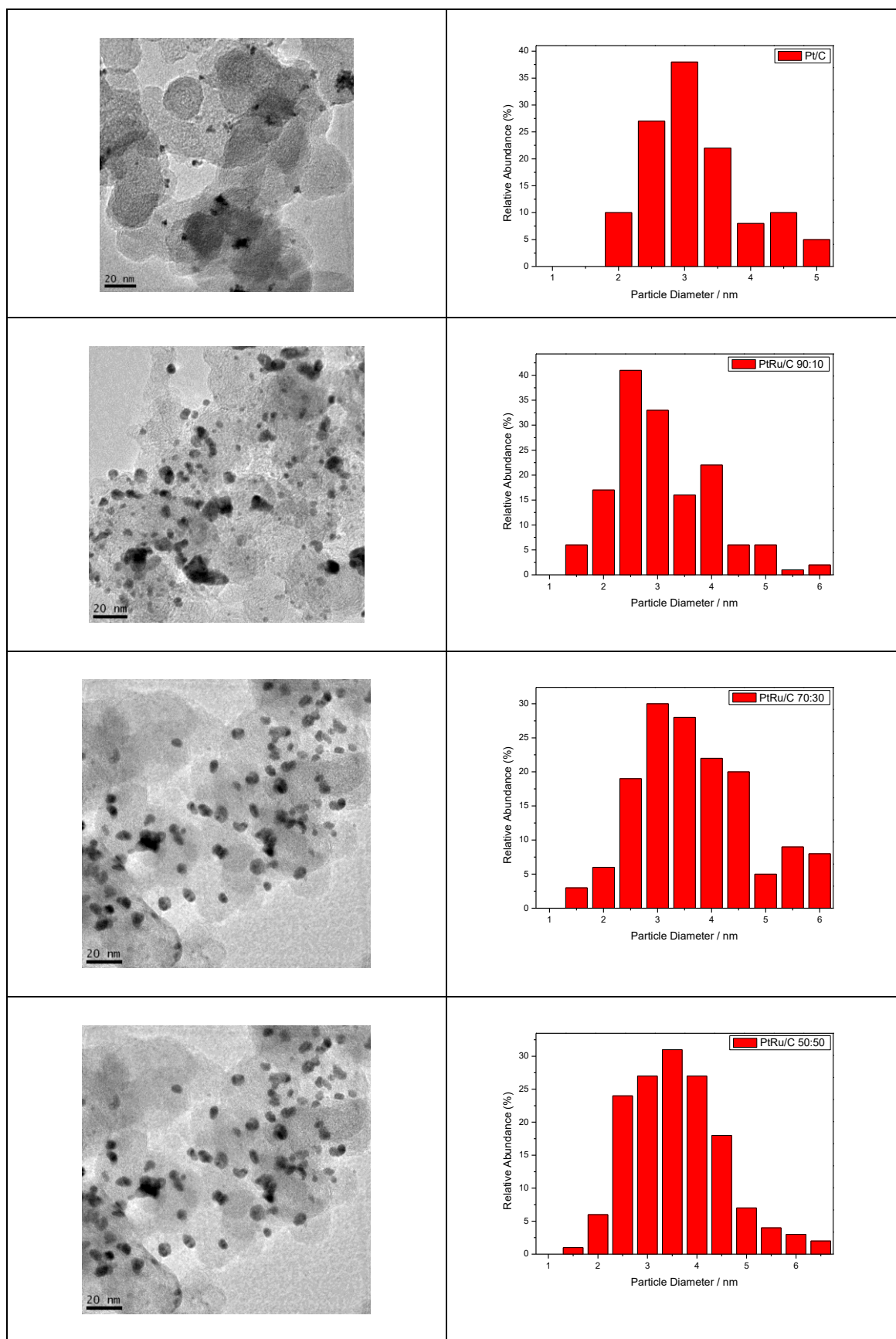


Figure 2. TEM images and histograms of the particle size distribution to Pt/C and PtRu/C electrocatalysts.

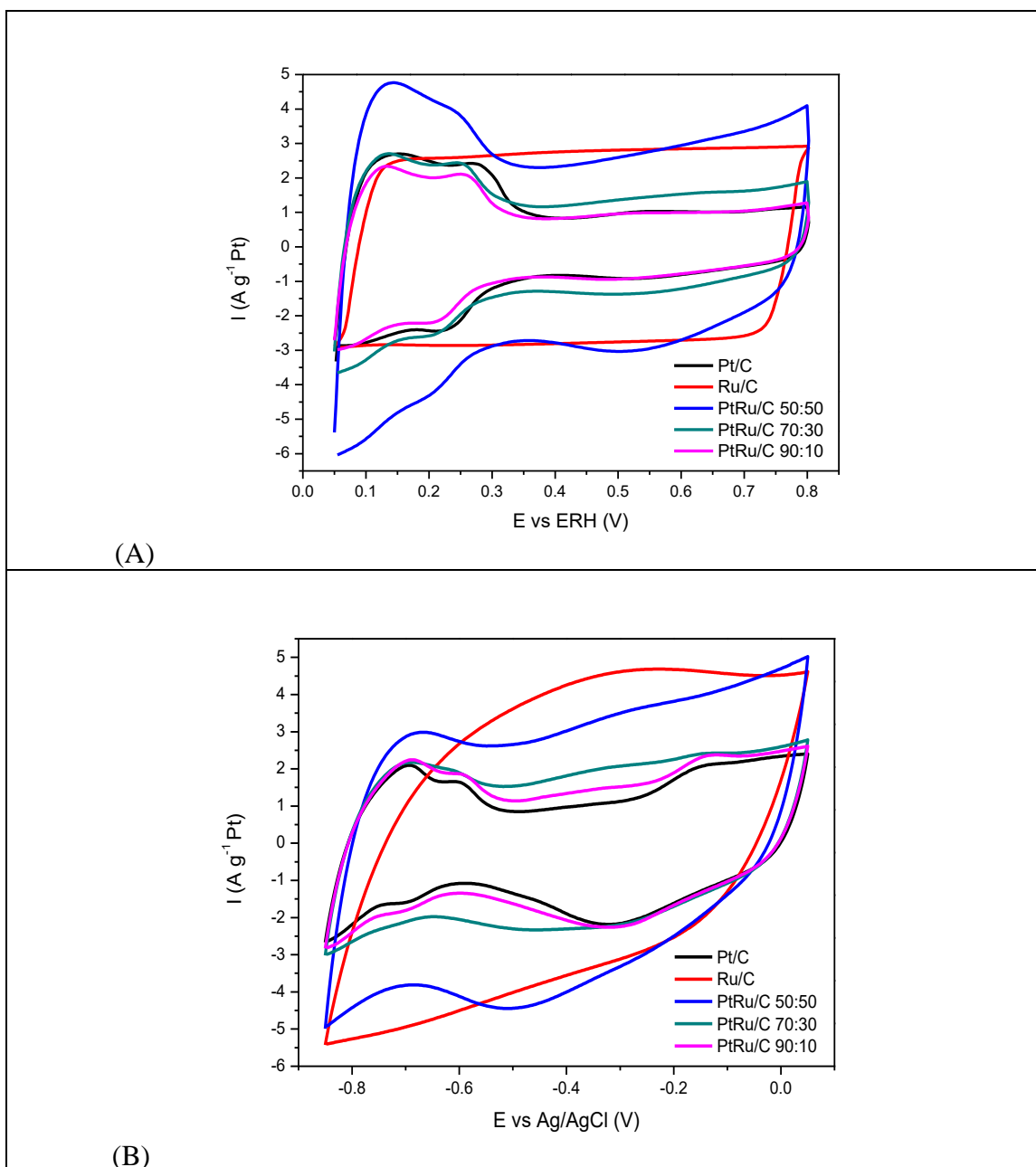


Figure 3. Cyclic voltammograms of Pt/C and PtRu/C electrocatalysts in (a) 0.5 mol L^{-1} H_2SO_4 and (b) 1 mol L^{-1} KOH solution with a scan rate of 10 $mV s^{-1}$ at 25 $^{\circ}C$.

Cyclic Voltammetry of all PtRu/C electrocatalysts, in the presence of 0.5 mol L^{-1} H_2SO_4 , showed a well-defined hydrogen adsorption–desorption region (0.05–0.4 V). The cyclic voltammograms, also, showed an increase in the currents in the double layer (0.4–0.8 V), what has been attributed to ruthenium oxide species; this effect was more pronounced with an increasing amount of ruthenium in electrocatalysts [24–26]. The Ru/C was inactive for hydrogen adsorption/desorption process; nevertheless, it was also showed an increase in the currents in the double layer, in comparison with Pt/C; this process could be related to ruthenium oxide species. Cyclic voltammetry of all PtRu/C electrocatalysts, in presence of 1.0 mol L^{-1} KOH solution, do not have a

well-defined hydrogen adsorption–desorption region (-0.85V to -0.5 V). However, it was also observed an increase in the currents in the double layer (-0.4 to -0.2V), confirming the formation of ruthenium oxide species: this effect was, also, more pronounced with an increasing amount of ruthenium in electrocatalysts.

Kallio et al [17] showed a formation of hydroxyl layer on Pt initiates at the double-layer region around 0.5 V, followed by the oxide layer formation at increased potentials for PtRu/C in electrolyte acidic, while for alkaline electrolyte there was a similar behavior to that in acidic medium, where the hydrogen adsorption region is evident and the onset current corresponding to metal oxide formation shifts to more negative potentials.

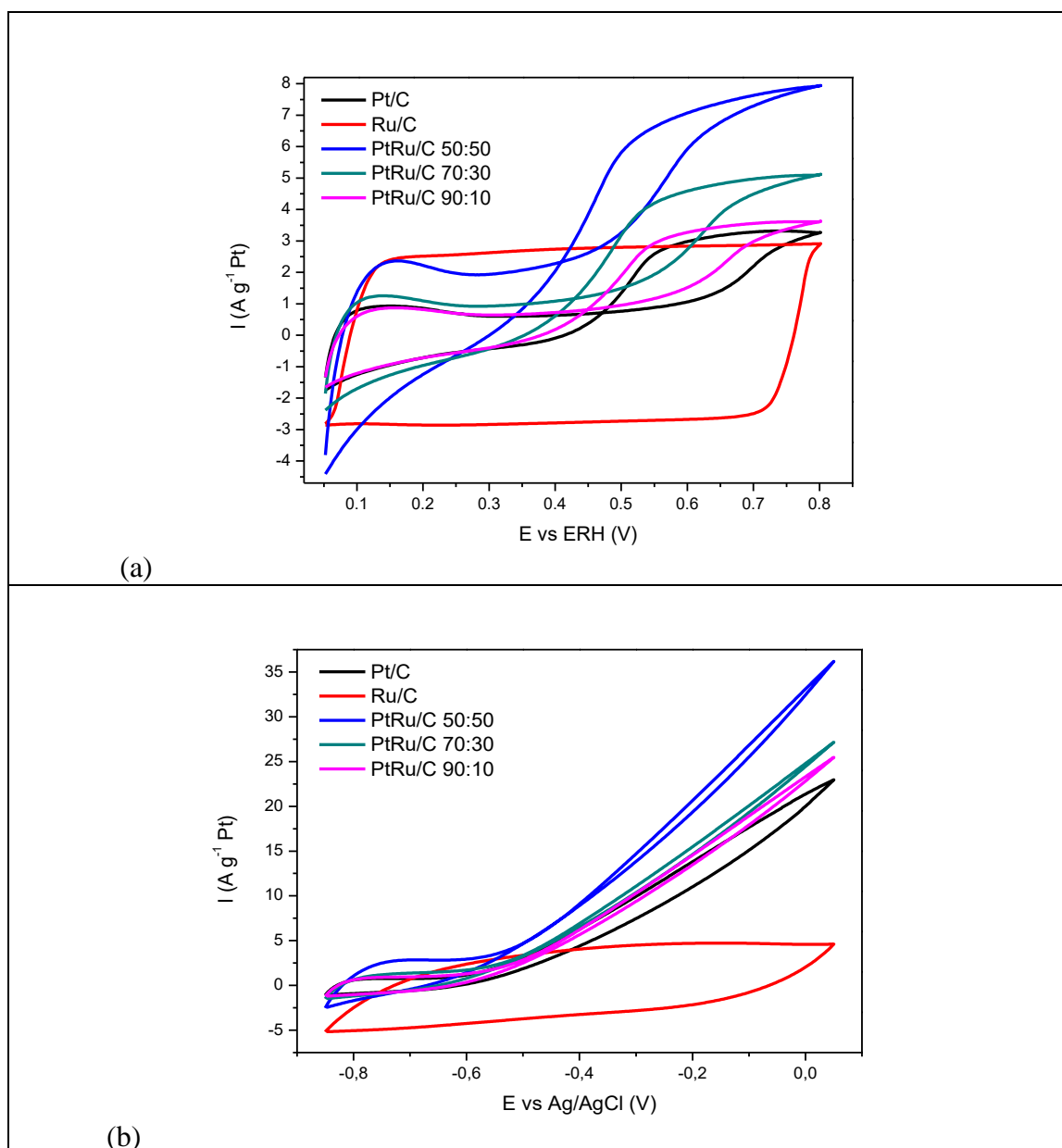
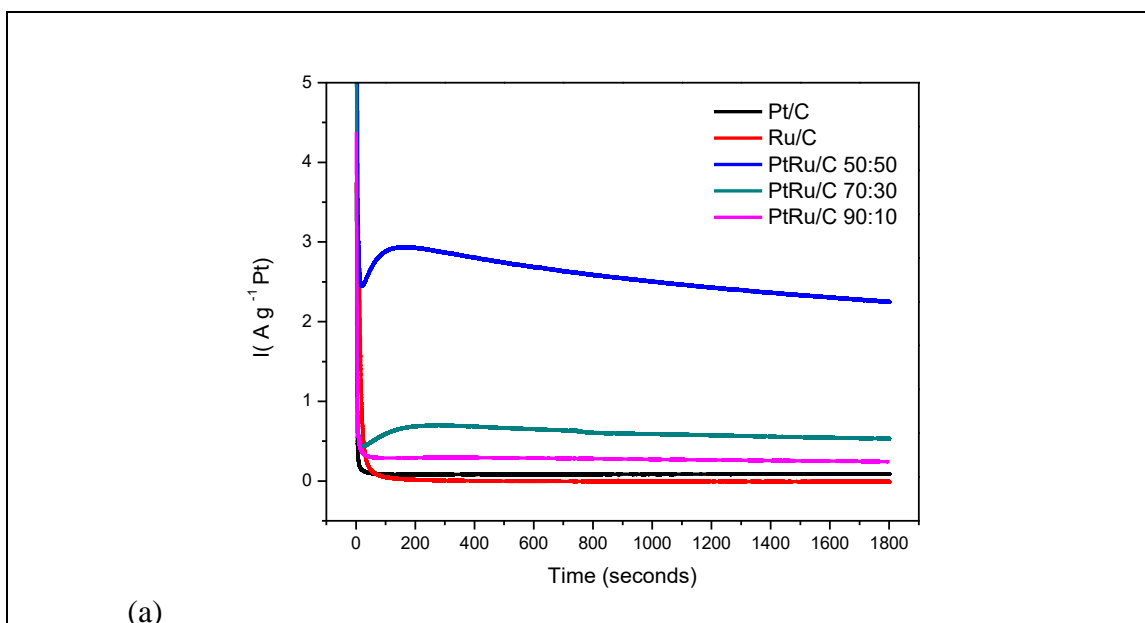


Figure 4. Cyclic Voltammograms of Pt/C and PtRu/C electrocatalysts in presence of (a) 0.5 mol L⁻¹ H₂SO₄ + 1 mol L⁻¹ methanol solution or (b) 1 mol L⁻¹ KOH + 1 mol L⁻¹ methanol with a scan rate of 10 mV s⁻¹ at 25 °C.

Figure 4 shows the CV of Pt/C and PtRu/C with different atomic ratios 90:10, 70:30, and 50:50, in the presence of methanol (1.0 mol L^{-1}) + KOH (1.0 mol L^{-1}) solutions or $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol L}^{-1}$ methanol, where the CVs were normalized by the amount of platinum in the electrocatalysts. Ru/C electrocatalysts were inactive for methanol oxidation for both media. This behavior could be associated to the fact that methanol is not adsorbed in ruthenium sites. PtRu/C electrocatalysts had more activity for methanol oxidation in comparison with Pt/C for both media: this behavior could indicate that methanol adsorption occurs on active platinum sites, while ruthenium provides oxygenated species. PtRu/C (50:50) electrocatalysts showed the best electrocatalytic activity toward methanol electro-oxidation, when compared to PRu/C (70:30), PtRu (90:10), Pt/C and Ru/C. The best performance of PtRu/C for methanol oxidation could be explained by the oxy-hydroxy interactions that occur in the catalytic layer, where the presence of oxygen species from ruthenium oxides could favor the oxidation of poisoning intermediates. However, the electronic effect associated with the formation of PtRu alloys could not be despised.

In this work, the values of currents observed in alkaline medium for PtRu/C were higher than in acidic medium: these results suggest that PtRu/C is a material appropriated to be studied in alkaline fuel cell. Qin et al [27] showed that the addition of Ru to Pt is beneficial for the methanol oxidation reaction and that the atomic ratio of Pt and Ru is crucial for optimizing catalytic performance. Silva et al [24] showed that PtRu/C electrocatalysts, with more platinum content, had superior performance for methanol electro-oxidation, at ambient temperature.

The chronoamperometry curves for Pt/C and PtRu/C electrocatalysts, in presence of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mol L}^{-1}$ methanol in potential of 0.5 V , for 30 min or $1 \text{ mol L}^{-1} \text{ KOH} + 1 \text{ mol L}^{-1}$ methanol in -0.4 V , for 30 min, are illustrated in Figure 5. All PtRu/C were more active than Pt/C for methanol oxidation in both acidic and alkaline media. PtRu/C (50:50) electrocatalyst was more active than PtRu/C (70:30), followed by PtRu/C (90:10), Pt/C, and Ru/C in both media. PtRu/C (50:50) showed current values 25 times higher than those obtained with Pt/C in acidic medium, while for alkaline medium it presented a value 2.3 times higher than that obtained with Pt/C.



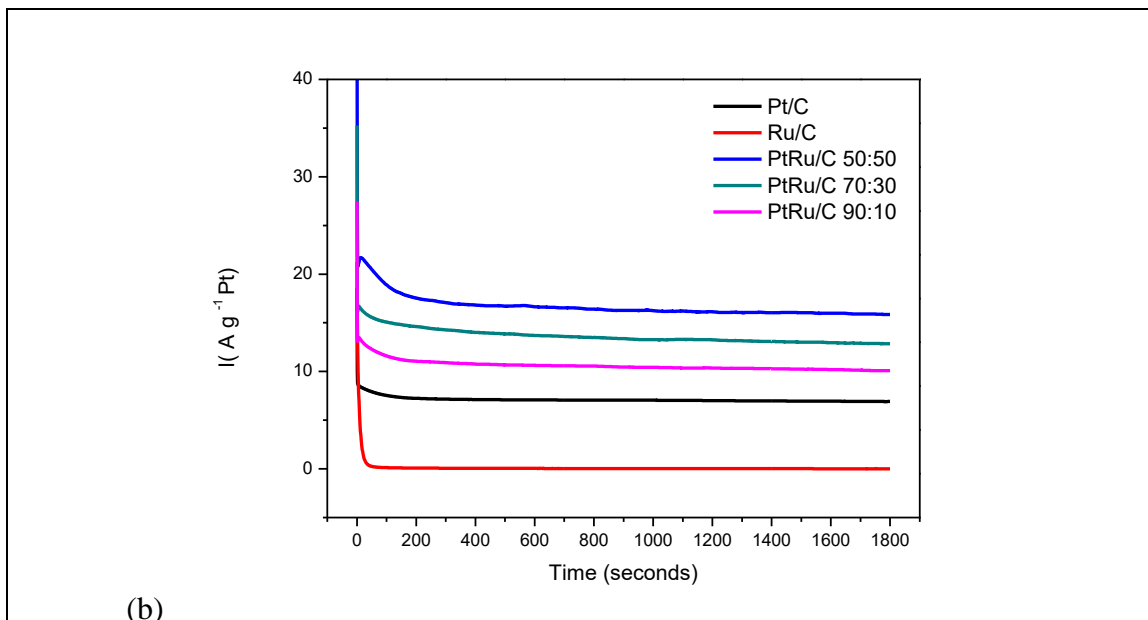
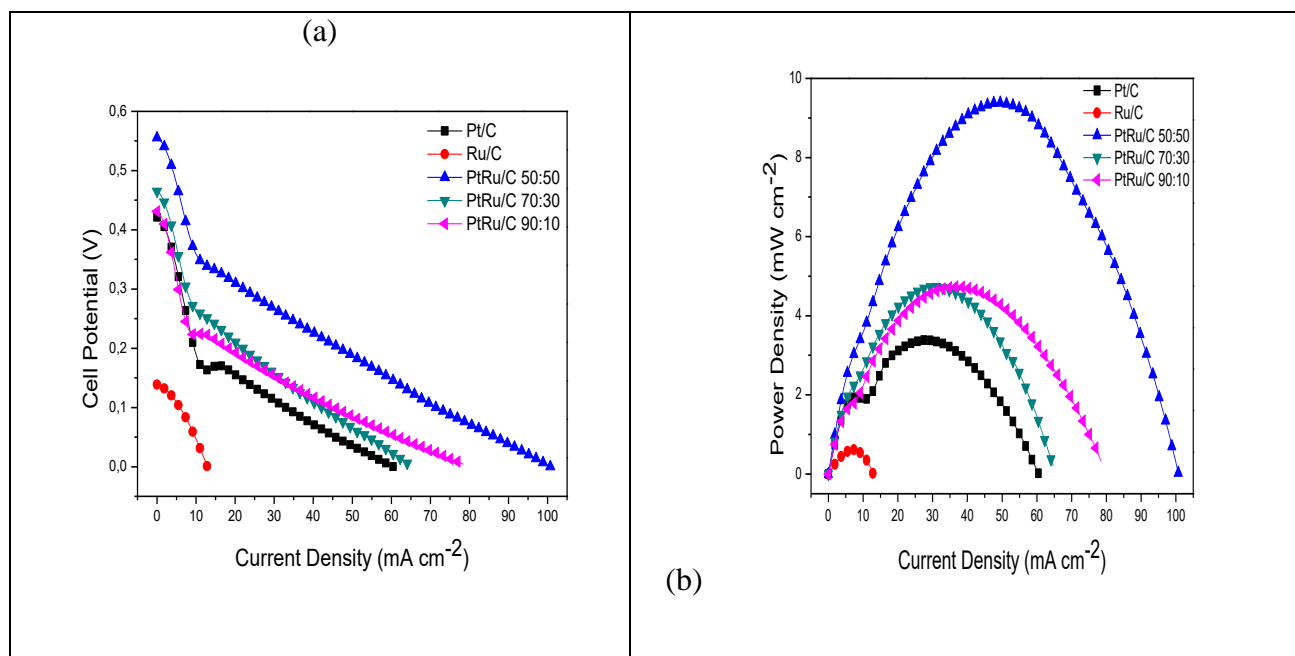


Figure 5. Chronoamperometry curves in presence of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mol L}^{-1}$ methanol at 0.5 V by 30 minutes (a) or $1 \text{ mol L}^{-1} \text{ KOH} + 1 \text{ mol L}^{-1}$ methanol at -0.4 V by 30 minutes (b) for Pt/C and PtRu/C electrocatalysts at $25 \text{ }^\circ\text{C}$.

The currents values obtained for PtRu/C (50:50), in presence of methanol in alkaline medium, were 7.0 times higher than those observed for acidic medium: this result showed that studies in direct methanol alkaline fuel cell are very important and promising. Pt/C electrocatalysts showed currents values higher in alkaline medium for methanol oxidation, in comparison with acidic medium; this effect could be associated to a presence of oxygen species in solution of KOH. The presence of these species could favor the oxidation of intermediates adsorbed in Pt active sites. Ru/C was inactive for methanol oxidation in both media.



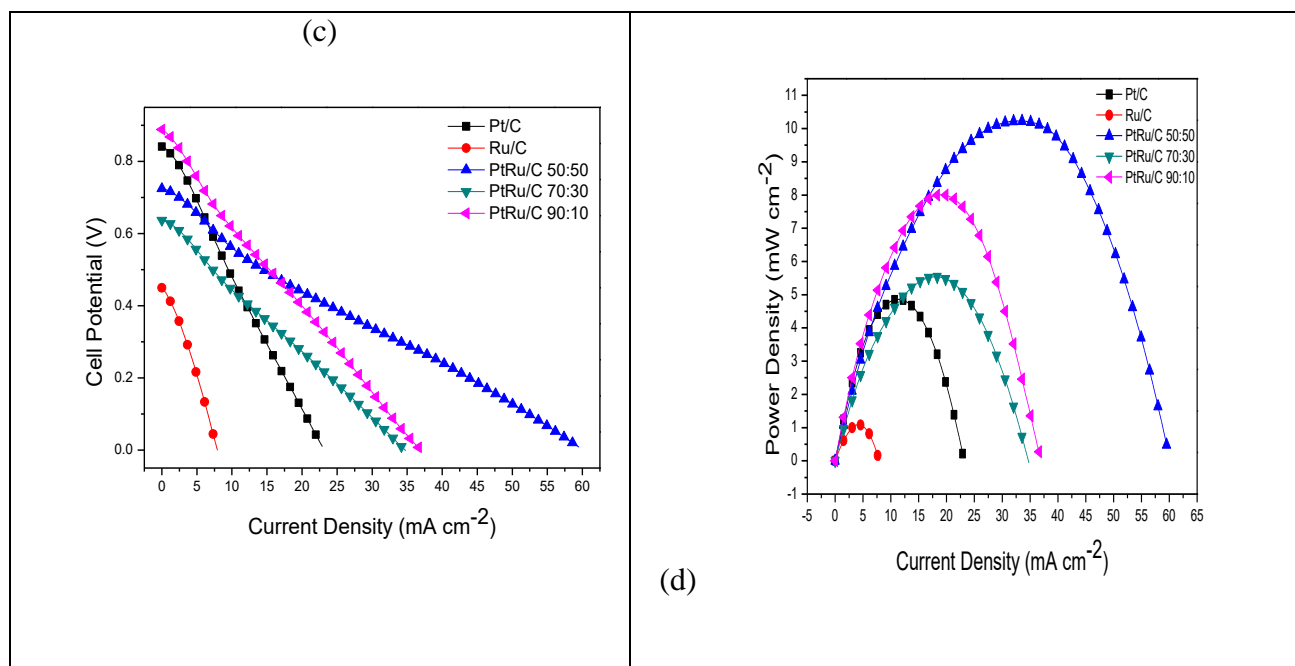


Figure 6. Polarization curves (a) and power density curves (b) in a 5 cm² DEFC at 100°C using Pt/C, Ru/C and PtRu/C electrocatalysts as anode catalysts (1 mg Pt cm⁻²) and Pt/C ETEK as the cathode catalyst (1 mg Pt cm⁻²), Nafion® 117 was used as the membrane. Methanol 2 mol L⁻¹ with 2 mL s⁻¹ flux. (c) I–V Curves and the (d) power density at 80 °C of a 5 cm² DAMFC using Pt/C, Ru/C, and PRu/C electrocatalysts anodes (1 mg metal cm⁻² catalyst loading) and Pt/C E-TEK electrocatalyst cathode (1 mgPt cm⁻² catalyst loading with 20 wt% Pt loading on carbon), Nafion_ 117 membrane KOH treated, methanol (1.0 mol L⁻¹) and oxygen pressure (2 bar).

Figure 6 shows the performances of direct methanol fuel cell or direct alkaline methanol fuel cell with Pt/C, Ru/C, and PtRu/C as anode electrocatalysts.

PtRu/C (50:50) electrocatalysts were more active than Pt/C and others PtRu/C prepared in accordance with cyclic voltammetry and chronoamperometry results. Power density values for PtRu/C were similar in both media. The results could be associated to the low conductivity of Nafion membrane material, therefore the development of new anionic membranes and alkaline ionomers are strongly encouraged by the promising results from electrochemical experiments [17]. In this context, Sun et al [13] showed that the 1,2-methylimidazolium functional group has the potential application for the AAEMs in AAEMFCs.

4. CONCLUSIONS

The borohydride reduction method was an efficient process to produce PtRu/C for methanol oxidation in alkaline and acidic media. PtRu/C electrocatalysts showed five peaks, which are associated with the face-centered cubic (fcc) structure characteristic of Pt alloys. PtRu/C electrocatalysts also showed a shift to higher 2 θ values in comparison with Pt/C electrocatalysts; this effect could be associated to the formation of PtRu alloys.

PtRu/C exhibited superior performance for methanol oxidation in both media in comparison with Pt/C, where the highest catalytic activity of PtRu/C could be related to the combination of the bifunctional mechanism and the electronic effect. The values current in alkaline medium were higher than in acidic medium, indicating that studies in alkaline fuel are appropriated and promising.

Direct Tests in methanol fuel cell showed that the power density values obtained for PtRu/C were similar in both media. This effect could be associated to the low conductivities of the Nafion membrane material, therefore the development of new anionic membranes and alkaline ionomers is strongly encouraged by the promising results from electrochemical experiments. Further research work is necessary to investigate the mechanisms of methanol oxidation using these electrocatalysts and to investigate the surface of these materials through XPS analysis.

ACKNOWLEDGMENTS

The authors thank the Laboratório de Microscopia do Centro de Ciências e Tecnologia de Materiais (CCTM) by TEM measurements and FAPESP (2014/09087-4, 2014/50279-4) for the financial support.

References

1. K.S. Lee, I.S. Park, Y.H. Cho, D.S. Jung, N. Jung, H.Y. Park, Y.E.Sung, *J Catal* 258 (2008) 143
2. M. C. L. Santos, C. A. Ottoni, R. F. B. de Souza, S. G. da Silva, M. H. M. T. Assumpção, E. V. Spinacé, A. O. Neto, *Electrocatalysis* 7 (2016) 445–450
3. J.C.M. Silva, R.F.B. De Souza, G.S. Buzzo, E.V. Spinacé, A.O.Neto, M.H.M.T. Assumpção, *Ionics* 20 (2014) 1137
4. Chun-Chen Yanga and Yan-Ting Lin. *Energy Procedia* 61 (2014) 1410–1416
5. A.S. Aricò, S. Srinivasan, V. Antonucci, *Fuel Cells* 1 (2001) 133.
6. T.Frelink, W.Visscher, J.A.R. Vanveen, *Electrochim.Acta* 39 (1994) 1871–1875
7. T.Frelink, W.Visscher, A.P.Cox, J.A.R. Vanveen, *Electrochim. Acta* 40 (1995) 1537–1543
8. B. Gurau, R. Viswanathan, R.X.Liu, T.J.Lafrenz, K.L.Ley E.S.Smotkin, E.Reddington, A.Sapienza, B.C.Chan T.E.Mallouk, S.Sarangapani, *J.Phys.Chem.B* 10 2 (1998) 9997–1000
9. Jin Xie, Qinghua Zhang, Lin Gu, Sheng Xu, Peng Wang, Jianguo Liu, Yi Ding, Ying Fang Yao, Cewen Nan, Ming Zhao, Yon You, Zhigan gZou. *Nano Energy* 21 (2016) 247–257
10. M. Watanabe, M.Uchida, S.Motoo, *J.Electroanal.Chem.*229 (1987) 395–406
11. M. Watanabe, S.Motoo, *J.Electroanal.Chem.*60 (1975) 275–283
12. B. Hammer, J.K.Norskov, Theoretical surface science and catalysis-Calculation s and concepts Impact o f Surface Science on Catalysis, in:B.C.Gates ,H.Knozinger (Eds.), *Advances in Catalysis, Vo l45*, Elsevier Academic Press Inc, San Diego,2000, pp. 71–129
13. Congrong Yang, Suli Wang, Luhua Jiang, Jinbo Hu, Wenjia Ma,Gongquan Sun. *International Journal o f Hydrogen Energy* 40 (2015) 2363-2370
14. Y. Kwon, S.C.S. Lai, P. Rodriguez, M.T.M. Koper, *J Am Chem Soc* 133 (2011) 6914
15. L. Colmenares, H.Wang, Z. Jusys, L. Jiang, S. Yan, G.Q. Sun, R.J. Behm, *Electrochim Acta* 52 (2006) 221
16. A.D. Modestov, M.R. Tarasevich, A.Y. Leykin, V.Y. Filimonov, *J Power Sources* 188 (2009) 502
17. A. Santasalo-Aarnio, S. Tuomi, K. Jalkanen, K. Kontturi, T. Kallio. *Electrochimica Acta* 87 (2013) 730– 738
18. H. Hou, S. Wang, W. Jin, Q. Jiang, L. Sun, L. Jiang, G. Sun, *Int J Hydrog Energy* 36 (2011) 5104)
19. Sirlane G. da Silva, Mônica H. M. T. Assumpção, Júlio César M. Silva, Rodrigo F. B. De Souza, Estevam V. Spinacé, Almir O. Neto, Guilherme S. Buzzo. *Int. J. Electrochem. Sci.*, 9 (2014) 5416 – 5424

20. E. G. Franco, A. Oliveira Neto, M. Linardi and E. Aricó, *J. Braz. Chem. Soc.* 13 (2002) 516-521
21. E. H. Fontes, Sirlane G. da Silva, E. V. Spinace, A. O. Neto, R. F. B. de Souza. *Electrocatalysis* 7 (2016) 297–304
22. Yoshiyuki Suda, Yoshiaki Shimizu, Masahiro Ozaki, Hideto Tanoue, Hirofumi Takikawa, Hitoshi Ueb, Kazuki Shimizu, Yoshito Umeda. *Materials Today Communications* 3 (2015) 96–103
23. Min-Soo Hyun, Sang-Kyung Kim, Byungrock Lee, Donghyun Peck, Yonggun Shul, Doohwan Jung, *Catalysis Today* 132 (2008) 138–145
24. Dionsio F. Silva, Almir Oliveira Neto, Eddy S. Pino, Marcelo Linardi, Estevam V. Spinace, *Journal of Power Sources* 170 (2007) 303–307
25. R.B. Lima, V. Paganin, T. Iwasita, W. Vielstich, *Electrochim. Acta* 49(2003) 85.
26. F. Colmati, W.H. Lizcano-Valbuena, G.A. Camara, E.A. Ticianelli, E.R.Gonzalez, *J. Braz. Chem. Soc.* 13 (2002) 474
27. Chunhui Tan, Juhui Sa, Feipeng Cai, Bo Jiang, Gai Yang, Bo Wang, Jinhua Gao, Hua Chen, Xianzhong Qin. *NANO: Brief Reports and Reviews* 11 (2016) 1650022

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